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Renewable Energy Technologies for Future and Sustainable Development

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Abstract

People are relying upon oil for primary energy and this will continue for a few more decades. Other conventional sources may be more enduring, but are not without serious disadvantages. The renewable energy resources are particularly suited for the provision of rural power supplies and a major advantage is that equipment such as flat plate solar driers, wind machines, etc., can be constructed using local resources. Without the advantage results from the feasibility of local maintenance and the general encouragement such local manufacture gives to the build-up of small-scale rural based industry. This communication comprises a comprehensive review of energy sources, the environment and sustainable development. It includes the renewable energy technologies, energy efficiency systems, energy conservation scenarios, energy savings in greenhouses environment and other mitigation measures necessary to reduce climate change. This study gives some examples of small-scale energy converters, nevertheless it should be noted that small conventional, i.e., engines are currently the major source of power in rural areas and will continue to be so for a long time to come. There is a need for some further development to suit local conditions, to minimise spares holdings, to maximise the interchangeability of the engine parts, and of the engine applications. Emphasis should be placed on full local manufacture. It is concluded that renewable environmentally friendly energy must be encouraged, promoted, implemented and demonstrated by a full-scale plant (device) especially for use in remote rural areas.

Keywords: Renewable technologies, energy efficient systems, eco-systems, sustainable development

1. Introduction

The move towards a low-carbon cleaner world, driven partly by climate science and partly by the business opportunities it offers, will need the promotion of environmentally friendly alternatives, if an acceptable stabilisation level of atmospheric carbon dioxide is to be achieved. This requires the harnessing and use of natural resources that produce no air pollution or greenhouse gases and provides comfortable coexistence of human, livestock, and plants. This article presents a comprehensive review of energy sources, the development of sustainable technologies to explore these energy sources. It also includes potential renewable energy technologies, energy efficiency systems, energy savings techniques and other mitigation measures necessary to reduce climate change. The article concludes with the technical status of the GSHP technologies.

Over millions of years ago, plants have covered the earth, converting the energy of sunlight into living plants and animals, some of which was buried in the depths of the earth to produce deposits of coal, oil and natural gas [1-3]. The past few decades, however, have experienced many valuable uses for these complex chemical substances and manufacturing from them plastics, textiles, fertiliser and the various end products of the petrochemical industry. Indeed, each decade sees increasing uses for these products. Coal, oil and gas, which will certainly be of great value to future generations, as they are to the present, are however non-renewable natural resources. The rapid depletion of these non-renewable fossil resources need not continue. This is particularly true now as it is, or soon will be, technically and economically feasible to supply all of man’s needs from the most abundant energy source of all, the sun. The sunlight is not only inexhaustible, but, moreover, it is the only energy source, which is completely non-polluting [4].

Industry’s use of fossil fuels has been largely blamed for warming the climate. When coal, gas and oil are burnt, they release harmful gases, which trap heat in the atmosphere and cause global warming. However, there had been an ongoing debate on this subject, as scientists have struggled to distinguish between changes, which are human induced, and those, which could be put down to natural climate variability. Notably, human activities that emit carbon dioxide (CO$_2$), the most significant contributor to potential climate change, occur primarily
from fossil fuel production. Consequently, efforts to control CO\textsubscript{2} emissions could have serious, negative consequences for economic growth, employment, investment, trade and the standard of living of individuals everywhere.

2. Energy sources and use

Scientifically, it is difficult to predict the relationship between global temperature and greenhouse gas (GHG) concentrations. The climate system contains many processes that will change if warming occurs. Critical processes include heat transfer by winds and tides, the hydrological cycle involving evaporation, precipitation, runoff and groundwater and the formation of clouds, snow, and ice, all of which display enormous natural variability. The equipment and infrastructure for energy supply and use are designed with long lifetimes, and the premature turnover of capital stock involves significant costs. Economic benefits occur if capital stock is replaced with more efficient equipment in step with its normal replacement cycle. Likewise, if opportunities to reduce future emissions are taken in a timely manner, they should be less costly. Such a flexible approach would allow society to take account of evolving scientific and technological knowledge, while gaining experience in designing policies to address climate change [4].

The World Summit on Sustainable Development in Johannesburg in 2002 [4] committed itself to “encourage and promote the development of renewable energy sources to accelerate the shift towards sustainable consumption and production”. Accordingly, it aimed at breaking the link between resource use and productivity. This can be achieved by the following:

- Trying to ensure economic growth does not cause environmental pollution.
- Improving resource efficiency.
- Examining the whole life-cycle of a product.
- Enabling consumers to receive more information on products and services.
- Examining how taxes, voluntary agreements, subsidies, regulation and information campaigns, can best stimulate innovation and investment to provide cleaner technology.

The energy conservation scenarios include rational use of energy policies in all economy sectors and the use of combined heat and power systems, which are able to add to energy savings from the autonomous power plants. Electricity from renewable energy sources is by definition the environmental green product. Hence, a renewable energy certificate system, as recommended by the World Summit, is an essential basis for all policy systems, independent of the renewable energy support scheme. It is, therefore, important that all parties involved support the renewable energy certificate system in place if it is to work as planned. Moreover, existing renewable energy technologies (RETS) could play a significant mitigating role, but the economic and political climate will have to change first. It is now universally accepted that climate change is real. It is happening now, and GHGs produced by human activities are significantly contributing to it. The predicted global temperature increase of between 1.5 and 4.5\textdegree C could lead to potentially catastrophic environmental impacts [5]. These include sea level rise, increased frequency of extreme weather events, floods, droughts, disease migration from various places and possible stalling of the Gulf Stream. This has led scientists to argue that climate change issues are not ones that politicians can afford to ignore, and policy makers tend to agree [5]. However, reaching international agreements on climate change policies is no trivial task as the difficulty in ratifying the Kyoto Protocol and reaching agreement at Copenhagen have justified.

Therefore, the use of renewable energy sources and the rational use of energy, in general, are the fundamental inputs for any responsible energy policy. However, the energy sector is encountering difficulties because increased production and consumption levels entail higher levels of pollution and eventually climate change, with possibly disastrous consequences. At the same time, it is important to secure energy at an acceptable cost in order to avoid negative impacts on economic growth.
To date, renewable energy contributes only as much as 20% of the global energy supplies worldwide [5]. Over two thirds of this comes from biomass use, mostly in developing countries, and some of this is unsustainable. However, the potential for energy from sustainable technologies is huge. On the technological side, renewables have an obvious role to play. In general, there is no problem in terms of the technical potential of renewables to deliver energy. Moreover, there are very good opportunities for RETs to play an important role in reducing emissions of GHGs into the atmosphere, certainly far more than have been exploited so far. However, there are still some technical issues to address in order to cope with the intermittency of some renewables, particularly wind and solar. Nevertheless, the biggest problem with relying on renewables to deliver the necessary cuts in GHG emissions is more to do with politics and policy issues than with technical ones [6]. For example, the single most important step governments could take to promote and increase the use of renewables is to improve access for renewables to the energy market. This access to the market needs to be under favourable conditions and, possibly, under favourable economic rates as well.

One move that could help, or at least justify, better market access would be to acknowledge that there are environmental costs associated with other energy supply options and that these costs are not currently internalised within the market price of electricity or fuels. This could make a significant difference, particularly if appropriate subsidies were applied to renewable energy in recognition of the environmental benefits it offers. Similarly, cutting energy consumption through end-use efficiency is absolutely essential. This suggests that issues of end-use consumption of energy will have to come into the discussion in the foreseeable future [7]. The end-use consumption can be related to demand side management (DSM), which is available but yet to be applied in developing countries.

However, RETs have the benefit of being environmentally benign when developed in a sensitive and appropriate way with the full involvement of local communities. In addition, they are diverse, secure, locally based and abundant.

In spite of the enormous potential and the multiple benefits, the contribution from renewable energy still lags behind the ambitious claims for it due to the initially high development costs, concerns about local impacts, lack of research funding and poor institutional and economic arrangements [8]. Hence, an approach is needed to integrate renewable energies in a way that meets the rising demand in a cost-effective way.

3. Role of energy efficiency system

The prospects for development in power engineering are, at present, closely related to ecological problems. Power engineering has harmful effects on the environment, as it discharges toxic gases into the atmosphere and also oil-contaminated and saline waters into rivers, as well as polluting the soil with ash and slag and having adverse effects on living things on account of electromagnetic fields and so on. Thus, there is an urgent need for new approaches to provide an ecologically safe strategy. Substantial economic and ecological effects for thermal power projects (TPPs) can be achieved by improvement, upgrading the efficiency of the existing equipment, reduction of electricity loss, saving of fuel, and optimisation of its operating conditions and service life leading to improved access for rural and urban low-income areas in developing countries through energy efficiency and renewable energies.

Sustainable energy is a prerequisite for global development. Energy-based living standards in developing countries, however, are clearly below standards in developed countries.

Low levels of access to affordable and environmentally sound energy in both rural and urban low-income areas are therefore a predominant issue in developing countries. In recent years many programmes for development aid or technical assistance have been focusing on improving access to sustainable energy, many of them with impressive results. Apart from success stories, however, experience also shows that positive appraisals of many projects evaporate after completion and vanishing of the implementation expert team. Altogether, the diffusion of sustainable technologies such as energy efficiency and renewable energy for cooking, heating, lighting, electrical appliances and building insulation in developing countries has been slow.
Energy efficiency and renewable energy programmes could be more sustainable and pilot studies more effective and pulse releasing if the entire policy and implementation process was considered and redesigned from the outset [9]. New financing and implementation processes, which allow reallocating financial resources and thus enabling countries themselves to achieve a sustainable energy infrastructure, are also needed.

The links between the energy policy framework, financing and implementation of renewable energy and energy efficiency projects have to be strengthened efforts as well made to increase people’s knowledge through training.

3.1 Energy use in buildings

Buildings consume energy mainly for cooling, heating and lighting. The energy consumption was based on the assumption that the building operates within ASHRAE-thermal comfort zone during the cooling and heating periods [10]. Most of the buildings incorporate energy efficient passive cooling, solar control, photovoltaic, lighting and day lighting, and integrated energy systems. It is well known that thermal mass with night ventilation can reduce the maximum indoor temperature in buildings in summer [11]. Hence, comfort temperatures may be achieved by proper application of passive cooling systems. However, energy can also be saved if an air conditioning unit is used [12]. The reason for this is that in summer, heavy external walls delay the heat transfer from the outside into the inside spaces. Moreover, if the building has a lot of internal mass the increase in the air temperature is slow. This is because the penetrating heat raises the air temperature as well as the temperature of the heavy thermal mass. The result is a slow heating of the building in summer as the maximal inside temperature is reached only during the late hours when the outside air temperature is already low. The heat flowing from the inside heavy walls could be reduced with good ventilation in the evening and night. The capacity to store energy also helps in winter, since energy can be stored in walls from one sunny winter day to the next cloudy one. However, the admission of daylight into buildings alone does not guarantee that the design will be energy efficient in terms of lighting. In fact, the design for increased daylight can often raise concerns relating to visual comfort (glare) and thermal comfort (increased solar gain in the summer and heat losses in the winter from larger apertures). Such issues will clearly need to be addressed in the design of the window openings, blinds, shading devices, heating system, etc. In order for a building to benefit from daylight energy terms, it is a prerequisite that lights are switched off when sufficient daylight is available. The nature of the switching regime; manual or automated, centralised or local, switched, stepped or dimmed, will determine the energy performance. Simple techniques can be implemented to increase the probability that lights are switched off [13]. These include:

- Making switches conspicuous and switching banks of lights independently.
- Loading switches appropriately in relation to the lights.
- Switching banks of lights parallel to the main window wall.

There are also a number of methods, which help reduce the lighting energy use, which, in turn, relate to the type of occupancy pattern of the building [13]. The light switching options include:

- Centralised timed off (or stepped)/manual on.
- Photoelectric off (or stepped)/manual on.
- Photoelectric and on (or stepped), photoelectric dimming.
- Occupant sensor (stepped) on/off (movement or noise sensor).

Likewise, energy savings from the avoidance of air conditioning can be very substantial. Whilst day-lighting strategies need to be integrated with artificial lighting systems in order to become beneficial in terms of energy use, reductions in overall energy consumption levels by employment of a sustained programme of energy consumption strategies and measures would have considerable benefits within the buildings sector. It would perhaps be better to support a climate sensitive design approach that encompasses some elements of the pure
conservation strategy together with strategies, which work with the local ambient conditions making use of energy technology systems, such as solar energy, where feasible. In practice, low energy environments are achieved through a combination of measures that include:

- The application of environmental regulations and policy.
- The application of environmental science and best practice.
- Mathematical modelling and simulation.
- Environmental design and engineering.
- Construction and commissioning.
- Management and modifications of environments in use.

While the overriding intention of passive solar energy design of buildings is to achieve a reduction in purchased energy consumption. The non-realisation of potential energy benefits is mainly due to the neglect of the consideration of post-occupancy user and management behaviour by energy scientists and designers alike. Calculating energy inputs in agricultural production is more difficult in comparison to the industry sector due to the high number of factors affecting agricultural production, as Table 1 shows. However, considerable studies have been conducted in different countries on energy use in agriculture [14-19] in order to quantify the influence of these factors.

4. Renewable energy technologies

Sustainable energy is the energy that, in its production or consumption, has minimal negative impacts on human health and the healthy functioning of vital ecological systems, including the global environment. It is an accepted fact that renewable energy is a sustainable form of energy, which has attracted more attention during recent years. Increasing environmental interest, as well as economic consideration of fossil fuel consumption and high emphasis of sustainable development for the future helped to bring the great potential of renewable energy into focus. Nearly a fifth of all global power is generated by renewable energy sources, according to a book published by the OECD/IEA [20]. “Renewables for power generation: status and prospects” claims that, at approximately 20%, renewables are the second largest power source after coal (39%) and ahead of nuclear (17%), natural gas (17%) and oil (8%) respectively. From 1973-2000 renewables grew at 9.3% a year and it is predicted that this will increase by 10.4% a year to 2010. Wind power grew fastest at 52% and will multiply seven times by 2010, overtaking biopower and hence help reducing green house gases, GHGs, emissions to the environment.

Table 2 shows some applications of different renewable energy sources. The challenge is to match leadership in GHG reduction and production of renewable energy with developing a major research and manufacturing capacity in environmental technologies (wind, solar, fuel cells, etc.). More than 50% of the world’s area is classified as arid, representing the rural and desert part, which lack electricity and water networks. The inhabitants of such areas obtain water from borehole wells by means of water pumps, which are mostly driven by diesel engines. The diesel motors are associated with maintenance problems, high running cost, and environmental pollution. Alternative methods are pumping by photovoltaic (PV) or wind systems. At present, renewable sources of energy are regional and site specific. It has to be integrated in the regional development plans. Rasslavicius, Grzybek, and Dubrovin (2011) investigated prospects of bioenergy in Lithuania and Ukraine and put emphasis on agricultural waste-for-energy production technologies as well as on impact of bioenergy towards the improvement of the quality of life in rural communities [36]. Guilherme, Luiz, and Legey (2013) investigated energy from sugarcane bagasse in Brazil: An assessment of the productivity and cost of different technological routes [37].
Table 1 Energy equivalent of inputs and outputs [25]

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Unit</th>
<th>Equivalent energy (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Human labour</td>
<td>h</td>
<td>2.3</td>
</tr>
<tr>
<td>2. Animal labour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horse</td>
<td>h</td>
<td>10.10</td>
</tr>
<tr>
<td>Mule</td>
<td>h</td>
<td>4.04</td>
</tr>
<tr>
<td>Donkey</td>
<td>h</td>
<td>4.04</td>
</tr>
<tr>
<td>Cattle</td>
<td>h</td>
<td>5.05</td>
</tr>
<tr>
<td>Water buffalo</td>
<td>h</td>
<td>7.58</td>
</tr>
<tr>
<td>3. Electricity</td>
<td>kWh</td>
<td>11.93</td>
</tr>
<tr>
<td>4. Diesel</td>
<td>Litre</td>
<td>56.31</td>
</tr>
<tr>
<td>5. Chemicals fertilisers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>kg</td>
<td>64.4</td>
</tr>
<tr>
<td>P2O5</td>
<td>kg</td>
<td>11.96</td>
</tr>
<tr>
<td>K2O</td>
<td>kg</td>
<td>6.7</td>
</tr>
<tr>
<td>6. Seed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cereals and pulses</td>
<td>kg</td>
<td>25</td>
</tr>
<tr>
<td>Oil seed</td>
<td>kg</td>
<td>3.6</td>
</tr>
<tr>
<td>Tuber</td>
<td>kg</td>
<td>14.7</td>
</tr>
<tr>
<td>Total input</td>
<td>kg</td>
<td>43.3</td>
</tr>
<tr>
<td>Output</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Major products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cereal and pulses</td>
<td>kg</td>
<td>14.7</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>kg</td>
<td>5.04</td>
</tr>
<tr>
<td>Tobacco</td>
<td>kg</td>
<td>0.8</td>
</tr>
<tr>
<td>Cotton</td>
<td>kg</td>
<td>11.8</td>
</tr>
<tr>
<td>Oil seed</td>
<td>kg</td>
<td>25</td>
</tr>
<tr>
<td>Fruits</td>
<td>kg</td>
<td>1.9</td>
</tr>
<tr>
<td>Vegetables</td>
<td>kg</td>
<td>0.8</td>
</tr>
<tr>
<td>Water melon</td>
<td>kg</td>
<td>1.9</td>
</tr>
<tr>
<td>Onion</td>
<td>kg</td>
<td>1.6</td>
</tr>
<tr>
<td>Potatoes</td>
<td>kg</td>
<td>3.6</td>
</tr>
<tr>
<td>Olive</td>
<td>kg</td>
<td>11.8</td>
</tr>
<tr>
<td>Tea</td>
<td>kg</td>
<td>0.8</td>
</tr>
<tr>
<td>8. By products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Husk</td>
<td>kg</td>
<td>13.8</td>
</tr>
<tr>
<td>Straw</td>
<td>kg</td>
<td>12.5</td>
</tr>
<tr>
<td>Cob</td>
<td>kg</td>
<td>18.0</td>
</tr>
<tr>
<td>Seed cotton</td>
<td>kg</td>
<td>25.0</td>
</tr>
<tr>
<td>Total output</td>
<td>kg</td>
<td><strong>149.04</strong></td>
</tr>
</tbody>
</table>

Solar energy

The availability of data on solar radiation is a critical problem. Even in developed countries, very few weather stations have been recording detailed solar radiation data for a period of time long enough to have statistical significance. Solar radiation arriving on earth is the most fundamental renewable energy source in nature. It powers the bio-system, the ocean and atmospheric current system and affects the global climate. Reliable radiation information is needed to provide input data in modelling solar energy devices and a good database is required in the work of energy planners, engineers, and agricultural scientists. In general, it is not easy to design solar energy conversion systems when they have to be installed in remote locations. First, in most cases, solar radiation measurements are not available for these sites. Second, the radiation nature of solar radiation makes
the computation of the size of such systems difficult. While solar energy data are recognised as very important, their acquisition is by no means straightforward. The measurement of solar radiation requires the use of costly equipment such as pyrheliometers and pyranometers. Consequently, adequate facilities are often not available in developing countries to mount viable monitoring programmes. This is partly due to the equipment cost as well as the cost of technical manpower. Several attempts have, however, been made to estimate solar radiation through the use of meteorological and other physical parameter in order to avoid the use of expensive network of measuring instruments [21-24].

**Table 2 Sources of renewable energy**

<table>
<thead>
<tr>
<th>Energy source</th>
<th>Technology</th>
<th>Size</th>
</tr>
</thead>
</table>
| Solar energy  | • Domestic solar water heaters  
|               | • Solar water heating for large demands  
|               | • PV roofs: grid connected systems generating electric energy | Small  
|               |                                        | Medium-large  |
| Wind energy   | • Wind turbines (grid connected) | Medium-large  |
| Hydraulic energy | • Hydro plants in derivation schemes  
|               | • Hydro plants in existing water distribution networks | Medium-small  
| Biomass       | • High efficiency wood boilers  
|               | • CHP plants fed by agricultural wastes or energy crops  
|               | • Fuel alcohol by biological fermentation  
|               | • Fermentation using corn  
|               | • Fermentation using sugarcane  
|               | • Cellulose of wood and grass  
|               | • Biodiesel | Small  
|               |                                        | Medium  
| Animal manure | • CHP plants fed by biogas | Small  |
| CHP           | • High efficiency lighting  
|               | • High efficiency electric  
|               | • Householders appliances  
|               | • High efficiency boilers  
|               | • Plants coupled with refrigerating absorption machines | Wide  
|               |                                        | Wide  

Two of the most essential natural resources for all life on the earth and for man's survival are sunlight and water. Sunlight is the driving force behind many of the RETs. The worldwide potential for utilising this resource, both directly by means of the solar technologies and indirectly by means of biofuels, wind and hydro technologies, is vast. During the last decade interest has been refocused on renewable energy sources due to the increasing prices and fore-seeable exhaustion of presently used commercial energy sources. The most promising solar energy technology are related to thermal systems; industrial solar water heaters, solar cookers, solar dryers for peanut crops, solar stills, solar driven cold stores to store fruits and vegetables, solar collectors, solar water desalination, solar ovens, and solar commercial bakers.

Solar PV system: solar PV for lighting, solar refrigeration to store vaccines for human and animal use, solar PV for water pumping, solar PV for battery chargers, solar PV for communication network, microwave, receiver stations, radio systems in airports, VHF and beacon radio systems in airports, and educational solar TV posts in villages. Solar pumps are most cost effective for low power requirement (up to 5 kW) in remote places. Applications include domestic and livestock drinking water supplies, for which the demand is constant throughout the year, and irrigation. However, the suitability of solar pumping for irrigation, though possible, is uncertain because the demand may vary greatly with seasons. Solar systems may be able to provide trickle irrigation for fruit farming, but not usually the large volumes of water needed for wheat growing.
The hydraulic energy required to deliver a volume of water is given by the formula:

\[ E_w = \rho_w g V H \]  

(1)

Where \( E_w \) is the required hydraulic energy (kWh day\(^{-1}\)); \( \rho_w \) is the water density (kg m\(^{-3}\)); \( g \) is the gravitational acceleration (ms\(^{-2}\)); \( V \) is the required volume of water (m\(^3\) day\(^{-1}\)); and \( H \) is the head of water (m).

The solar array power required is given by:

\[ P_{sa} = \frac{E_w}{E_{sr} \eta F} \]  

(2)

Where: \( P_{sa} \) is the solar array power (kWp); \( E_{sr} \) is the average daily solar radiation (kWh m\(^{-2}\) day\(^{-1}\)); \( F \) is the array mismatch factor; and \( \eta \) is the daily subsystem efficiency.

Substituting Eq. (1) in Eq. (2), the following equation is obtained for the amount of water that can be pumped:

\[ V = \frac{P_{sa} E_{sr} F}{\rho_w g H} \]  

(3)

\[ P_{sa} = 1.6 \text{ kWp}, \ F = 0.85, \ \eta = 40\%. \]

A further increase of PV depends on the ability to improve the durability, performance and the local manufacturing capabilities of PV.

### 4.2 Biomass

The data required to perform the trade-off analysis simulation of bio-energy resources can be classified according to the divisions given in Table 3, namely the overall system or individual plants, and the existing situation or future development. The effective economical utilisations of these resources are shown in Table 4, but their use is hindered by many problems such as those related to harvesting, collection, and transportation, besides the photo-sanitary control regulations. Biomass energy is experiencing a surge in interest stemming from a combination of factors, e.g., greater recognition of its current role and future potential contribution as a modern fuel, global environmental benefits, its development and entrepreneurial opportunities, etc.

The use of biomass through direct combustion has long been, and still is, the most common mode of biomass utilisation (Table 5). Examples for dry (thermo-chemical) conversion processes are charcoal making from wood (slow pyrolysis), gasification of forest and agricultural residues (fast pyrolysis – this is still in demonstration phase), and of course, direct combustion in stoves, furnaces, etc. Wet processes require substantial amount of water to be mixed with the biomass. Biomass technologies include:

- Carbonisation and briquetting.
- Improved stoves.
- Biogas.
- Improved charcoal.
- Gasification.

Possible routes of biomass energy development are shown in Table 5. However, biomass usage and application can generally be divided into the following three categories:
Biomass energy for petroleum substitution driven by the following factor

<table>
<thead>
<tr>
<th>Factor</th>
<th>Requirement</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil price increase</td>
<td>Population increase</td>
<td>Electrification</td>
</tr>
<tr>
<td>Balance of payment problems, and economic crisis</td>
<td>Urbanisation</td>
<td>Irrigation and water supply</td>
</tr>
<tr>
<td>Fuel-wood plantations and residue utilisation</td>
<td>Agricultural expansion</td>
<td>Economic and social development</td>
</tr>
<tr>
<td>Wood based heat and electricity</td>
<td>Ecological crisis</td>
<td>Fuel-wood plantations</td>
</tr>
<tr>
<td>Liquid fuels from biomass</td>
<td>Fuel-wood crisis</td>
<td>Community forestry</td>
</tr>
<tr>
<td>Producer gas technology</td>
<td>Fuel-wood plantations, agro-forestry</td>
<td>Agro-forestry</td>
</tr>
<tr>
<td></td>
<td>Community forestry, and residue utilisation</td>
<td>Briquettes</td>
</tr>
<tr>
<td></td>
<td>Improved stoves, and improved charcoal production</td>
<td>Producer gas technology</td>
</tr>
</tbody>
</table>

**Table 3 Classifications of data requirements**

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Plant data</th>
<th>System data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing data</td>
<td>Size, Life, Cost (fixed and variation operation and maintenance), Forced outage, Maintenance, Efficiency, Fuel, Emissions</td>
<td>Peak load, Load shape, Capital costs, Fuel costs, Depreciation, Rate of return, Taxes</td>
</tr>
<tr>
<td>Future data</td>
<td>All of above, plus Capital costs, Construction trajectory, Date in service</td>
<td>System lead growth, Fuel price growth, Fuel import limits, Inflation</td>
</tr>
</tbody>
</table>

**Table 4 Effective biomass resource utilisation**
Briquetting is the formation of a char (an energy-dense solid fuel source) from otherwise wasted agricultural and forestry residues. One of the disadvantages of wood fuel is that it is bulky with a low energy density and therefore requires transport. Briquette formation allows for a more energy-dense fuel to be delivered, thus reducing the transportation cost and making the resource more competitive. It also adds some uniformity, which makes the fuel more compatible with systems that are sensitive to the specific fuel input. Charcoal stoves are very familiar to African societies. As for the stove technology, the present charcoal stove can be used, and can be improved upon for better efficiency. This energy term will be of particular interest to both urban and rural households and all the income groups due to its simplicity, convenience, and lower air polluting characteristics. However, the market price of the fuel together with that of its end-use technology may not enhance its early high market penetration especially in the urban low income and rural households.

Charcoal is produced by slow heating wood (carbonisation) in airtight ovens or retorts, in chambers with various gases, or in kilns supplied with limited and controlled amounts of air. The charcoal yield decreased gradually from 42.6 to 30.7% for the hazelnut shell and from 35.6 to 22.7% for the beech wood with an increase of temperature from 550 to 1,150 K while the charcoal yield from the lignin content decreases sharply from 42.5 to 21.7% until it was at 850 K during the carbonisation procedures [25]. The charcoal yield decreases as the temperature increases, while the ignition temperature of charcoal increases as the carbonisation temperature increases. The charcoal briquettes that are sold on the commercial market are typically made from a binder and filler.

4.2.2 Improved cook stoves

Traditional wood stoves are commonly used in many rural areas. These can be classified into four types: three stone, metal cylindrical shaped, metal tripod and clay type. Indeed, improvements of traditional cookers and ovens to raise the efficiency of fuel saving can secure rural energy availability, where woody fuels have become scarce. However, planting fast growing trees to provide a constant fuel supply should also be considered. The rural development is essential and economically important since it will eventually lead to a better standard of living, people's settlement, and self-sufficiency.
Table 5 Agricultural residues routes for development

<table>
<thead>
<tr>
<th>Source</th>
<th>Process</th>
<th>Product</th>
<th>End use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural residues</td>
<td>Direct</td>
<td>Combustion</td>
<td>Rural poor</td>
</tr>
<tr>
<td></td>
<td>Direct</td>
<td>Briquettes</td>
<td>Urban household</td>
</tr>
<tr>
<td></td>
<td>Processing</td>
<td></td>
<td>Industrial use</td>
</tr>
<tr>
<td></td>
<td>Processing</td>
<td>Carbonisation</td>
<td>Limited household use</td>
</tr>
<tr>
<td></td>
<td>Carbonisation</td>
<td></td>
<td>Rural household (self</td>
</tr>
<tr>
<td></td>
<td>Fermentation</td>
<td></td>
<td>sufficiency)</td>
</tr>
<tr>
<td>Agricultural residues</td>
<td>Direct</td>
<td>Biogas</td>
<td>Household, and industry</td>
</tr>
<tr>
<td></td>
<td>Direct</td>
<td></td>
<td>(Save or less efficiency as</td>
</tr>
<tr>
<td></td>
<td>Briquettes</td>
<td></td>
<td>wood)</td>
</tr>
<tr>
<td></td>
<td>Carbonisation</td>
<td></td>
<td>(Similar end use devices or</td>
</tr>
<tr>
<td></td>
<td>Carbonisation</td>
<td></td>
<td>improved)</td>
</tr>
<tr>
<td></td>
<td>Fermentation</td>
<td></td>
<td>Use</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Briquettes use</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Use</td>
</tr>
<tr>
<td>Agricultural, and</td>
<td>Direct</td>
<td>Combustion</td>
<td>Industrial use</td>
</tr>
<tr>
<td>animal residues</td>
<td>Briquettes</td>
<td></td>
<td>Limited household use</td>
</tr>
<tr>
<td></td>
<td>Carbonisation</td>
<td></td>
<td>Rural household (self</td>
</tr>
<tr>
<td></td>
<td>Carbonisation</td>
<td></td>
<td>sufficiency)</td>
</tr>
<tr>
<td></td>
<td>Fermentation</td>
<td></td>
<td>Urban fuel</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Energy services</td>
</tr>
</tbody>
</table>

4.2.3 Biogas

Biogas technology cannot only provide fuel, but is also important for comprehensive utilisation of biomass forestry, animal husbandry, fishery, agricultural economy, protecting the environment, realising agricultural recycling as well as improving the sanitary conditions, in rural areas. However, the introduction of biogas technology on a wide scale has implications for macro planning such as the allocation of government investment and effects on the balance of payments. Hence, factors that determine the rate of acceptance of biogas plants, such as credit facilities and technical backup services, are likely to have to be planned as part of general macro-policy, as do the allocation of research and development funds [25].

4.2.4 Improved charcoal

Dry cell batteries are a practical but expensive form of mobile fuel that is used by rural people when moving around at night and for powering radios and other small appliances. The high cost of dry cell batteries is financially constraining for rural households, but their popularity gives a good indication of how valuable a versatile fuel like electricity is in rural areas (Table 2.6). However, dry cell batteries can constitute an environmental hazard unless they are recycled in a proper fashion. Tables (6-7) further show that direct burning of fuel-wood and crop residues constitute the main usage of biomass, as is the case with many developing countries. In fact, biomass resources play a significant role in energy supply in all developing countries. However, the direct burning of biomass in an inefficient manner causes economic loss and adversely affects human health. In order to address the problem of inefficiency, research centres around the world, e.g., [25] have investigated the viability of converting the resource to a more useful form of improved charcoal, namely solid briquettes and
fuel gas. Accordingly, biomass resources should be divided into residues or dedicated resources, the latter including firewood and charcoal can also be produced from forest residues (Table 7). Whichever form of biomass resource used, its sustainability would primarily depend on improved forest and tree management.

### Table 6 Energy carrier and energy services in rural areas

<table>
<thead>
<tr>
<th>Energy carrier</th>
<th>Energy end-use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel-wood</td>
<td>Cooking, Water heating, Building materials, Animal fodder preparation</td>
</tr>
<tr>
<td>Kerosene</td>
<td>Lighting, Ignition fires</td>
</tr>
<tr>
<td>Dry cell batteries</td>
<td>Lighting, Small appliances</td>
</tr>
<tr>
<td>Animal power</td>
<td>Transport, Land preparation for farming, Food preparation (threshing)</td>
</tr>
<tr>
<td>Human power</td>
<td>Transport, Land preparation for farming, Food preparation (threshing)</td>
</tr>
</tbody>
</table>

#### 4.2.5 Gasification

Gasification is based on the formation of a fuel gas (mostly CO and H₂) by partially oxidising raw solid fuel at high temperatures in the presence of steam or air. The technology can use wood chips, groundnut shells, sugar cane bagasse, and other similar fuels to generate capacities from 3 kW to 100 kW. Many types of gasifier designs have been developed to make use of the diversity of fuel inputs and to meet the requirements of the product gas output (degree of cleanliness, composition, heating value, etc.) [25].

### Table 7 Biomass residues and current use

<table>
<thead>
<tr>
<th>Type of residue</th>
<th>Current use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood industry waste</td>
<td>Residues available</td>
</tr>
<tr>
<td>Vegetable crop residues</td>
<td>Animal feed</td>
</tr>
<tr>
<td>Food processing residue</td>
<td>Energy needs</td>
</tr>
<tr>
<td>Sorghum, millet, wheat residues</td>
<td>Fodder, and building materials</td>
</tr>
<tr>
<td>Groundnut shells</td>
<td>Fodder, brick making, direct fining oil mills</td>
</tr>
<tr>
<td>Cotton stalks</td>
<td>Domestic fuel considerable amounts available for short period</td>
</tr>
<tr>
<td>Sugar, bagasse, molasses</td>
<td>Fodder, energy need, ethanol production (surplus available)</td>
</tr>
<tr>
<td>Manure</td>
<td>Fertiliser, brick making, plastering</td>
</tr>
</tbody>
</table>
Application of biomass-fuel alcohol produced by biological fermentation is hugely important. There are a lot of fuel alcohol plants in USA (fermentation using corn), and Brazil (fermentation using sugarcane) [37]. Other countries use cellulose of wood and grass. Biodiesel is also a potential renewable fuel which can be extracted initially from several sorts of plant seeds in the flora of southern China. The Netherlands purchased millions of tons of used cooking oil from China for combustion of airplane engines [38].

4.2.6 Biomass and sustainability

A sustainable energy system includes energy efficiency, energy reliability, energy flexibility, fuel poverty, and environmental impacts. A sustainable biofuel has two favourable properties, which are availability from renewable raw material, and its lower negative environmental impact than that of fossil fuels. Global warming, caused by CO$_2$ and other substances, has become an international concern in recent years. To protect forestry resources, which act as major absorbers of CO$_2$, by controlling the ever-increasing deforestation and the increase in the consumption of wood fuels, such as firewood and charcoal, is therefore an urgent issue. Given this, the development of a substitute fuel for charcoal is necessary. Briquette production technology, a type of clean coal technology, can help prevent flooding and serve as a global warming countermeasure by conserving forestry resources through the provision of a stable supply of briquettes as a substitute for charcoal and firewood.

There are many emerging biomass technologies with large and immediate potential applications, e.g., biomass gasifier/gas turbine (BGST) systems for power generation with pilot plants, improved techniques for biomass harvesting, transportation and storage. Gasification of crop residues such as rice husks, groundnut shells, etc., with plants already operating in China, India, and Thailand. Treatment of cellulosic materials by steam explosion which may be followed by biological or chemical hydrolysis to produce ethanol or other fuels, cogeneration technologies, hydrogen from biomass, stirling energies capable of using biomass fuels efficiently, etc. Table 8 gives a view of the use of biomass and its projection worldwide.

However, a major gap with biomass energy is that research has usually been aimed at obtaining supply and consumption data, with insufficient attention and resources being allocated to basic research, to production, harvesting and conservation processes. Biomass has not been closely examined in terms of a substitute for fossil fuels compared to carbon sequestration and overall environmental benefits related to these different approaches. To achieve the full potential of biomass as a feedstock for energy, food, or any other use, requires the application of considerable scientific and technological inputs [25-26]. However, the aim of any modern biomass energy systems must be:

(1) To maximise yields with minimum inputs.

(2) Utilise and select adequate plant materials and processes.

(3) Optimise use of land, water, and fertiliser.

(4) Create an adequate infrastructure and strong R&D base.
### Table 8 Final energy projections including biomass (Mtoe) [27]

<table>
<thead>
<tr>
<th>Region</th>
<th>2011</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Biomass</td>
<td>Conventional Energy</td>
</tr>
<tr>
<td>Africa</td>
<td>205</td>
<td>136</td>
</tr>
<tr>
<td>China</td>
<td>206</td>
<td>649</td>
</tr>
<tr>
<td>East Asia</td>
<td>106</td>
<td>316</td>
</tr>
<tr>
<td>Latin America</td>
<td>73</td>
<td>342</td>
</tr>
<tr>
<td>South Asia</td>
<td>235</td>
<td>188</td>
</tr>
<tr>
<td>Total developing countries</td>
<td>825</td>
<td>1632</td>
</tr>
<tr>
<td>Other non-OECD countries</td>
<td>24</td>
<td>1037</td>
</tr>
<tr>
<td>Total non-OECD countries</td>
<td>849</td>
<td>2669</td>
</tr>
<tr>
<td>OECD countries</td>
<td>81</td>
<td>3044</td>
</tr>
<tr>
<td>World</td>
<td>930</td>
<td>5713</td>
</tr>
</tbody>
</table>
An afforestation programme appears an attractive option for any country to pursue in order to reduce the level of atmospheric carbon by enhancing carbon sequestration in the nation’s forests, which would consequently mitigate climate change. However, it is acknowledged that certain barriers need to be overcome if the objectives are to be fully achieved. These include the followings.

- Low level of public awareness of the economic/environmental benefits of forestry.
- The generally low levels of individuals’ income.
- Pressures from population growth.
- The land tenural system, which makes it difficult (if at all possible) for individuals to own or establish forest plantations.
- Poor pricing of forest products especially in the local market.
- Inadequate financial support on the part of governments.
- Weak institutional capabilities of the various Forestry Departments as regards technical manpower to effectively manage tree plantations.

However, social policy conditions are also critical. This is still very much lacking particularly under developing countries conditions. During the 1970s and 1980s different biomass energy technologies were perceived in sub-Saharan Africa as a panacea for solving acute problems. On the account of these expectations, a wide range of activities and projects were initiated. However, despite considerable financial and human efforts, most of these initiatives have unfortunately been a failure.

Therefore, future research efforts should concentrate on the following areas.

- Directed R and D in the most promising areas of biomass to increase energy supply and to improve the technological base.
- Formulate a policy framework to encourage entrepreneurial and integrated process.
- Pay more attention to sustainable production and use of biomass energy feedstocks, methodology of conservation and efficient energy flows.
- More research aimed at pollution abatement.
- Greater attentions to interrelated socio-economic aspects.
- Support R and D on energy efficiency in production and use.
- Improve energy management skills and take maximum advantage of existing local knowledge.
- Closely examine past successes and failures to assist policy makers with well-informed recommendations.

5. Wind Energy

Water is the most natural commodity for the existence of life in the remote desert areas. However, as a condition for settling and growing, the supply of energy is the second priority. The high cost and the difficulties of mains power line extensions, especially to a low populated region can divert attention to the utilisation of more reliable and independent sources of energy like renewable wind energy.

Accordingly, the utilisation of wind energy, as a form of energy, is becoming increasingly attractive and is being widely used for the substitution of oil-produced energy, and eventually to minimise atmospheric degradation.
Indeed, utilisation of renewables, such as wind energy, has gained considerable momentum since the oil crises of the 1970s. Wind energy is non-depleting, site-dependent, non-polluting, and a potential source of the alternative energy option. Wind power could supply 12% of global electricity demand by 2020, according to a report by European Wind Energy Association and Greenpeace. Wind energy can and will constitute a significant energy resource when converted into a usable form (see Figure 1).

As Figure 1 illustrates, information sharing is a four-stage process and effective collaboration must also provide ways in which the other three stages of the ‘renewable’ cycle: gather, convert and utilise, can be integrated. Efficiency in the renewable energy sector translates into lower gathering, conversion and utilisation (electricity) costs. A great level of installed capacity has already been achieved. Figure 2 clearly shows that the offshore wind sector is developing fast, and this indicates that wind is becoming a major factor in electricity supply with a range of significant technical, commercial and financial hurdles to be overcome.

![Fig. 1 The renewable cycle](image)

Economic projections are difficult at the best of times, when economies are relatively stable and a reference ‘business as usual’ case can be used. However, there are numerous signals that the world faces very turbulent economic conditions for a while - a credit crunch may make some project finance difficult and the shortage of raw materials could lead to supply chain difficulties.

![Fig. 2 Global prospects of wind energy utilisation by 2003-2010](image)

The offshore wind industry has the potential for a very bright future and to emerge as a new industrial sector, as Figure 3 implies. The speed of turbine development is such that more powerful models would supersede the original specification turbines in the time from concept to turbine order. Levels of activities are growing at a phenomenal rate (Figure 4), new prospects developing, new players entering, existing players growing in experience, technology evolving and political will appears to support the sector. The provision of pumped clean water is one of the best ways to improve health and increase the productive capacity of the population. Rural
access to clean water is best achieved through pumping from underground water aquifers rather than using surface water sources, which are often polluted.

6. Discussions

People rely upon oil for primary energy and this for a few more decades. Other conventional sources may be more enduring, but are not without serious disadvantages [27-38]. The renewable energy resources are particularly suited for the provision of rural power supplies and a major advantage is that equipment such as flat plate solar driers, wind machines, etc., can be constructed using local resources and without the advantage results from the feasibility of local maintenance and the general encouragement such local manufacture gives to the build up of small-scale rural based industry. This chapter comprises a comprehensive review of energy sources, the environment and sustainable development. It includes the renewable energy technologies, energy efficiency systems, energy conservation scenarios, energy savings in greenhouses environment and other mitigation measures necessary to reduce climate change. This study gives some examples of small-scale energy converters, nevertheless it should be noted that small conventional, i.e., engines are currently the major source of power in rural areas and will continue to be so for a long time to come. There is a need for some further development to suit local conditions, to minimise spares holdings, to maximise interchangeability both of engine parts and of the engine application. Emphasis should be placed on full local manufacture. It is concluded that renewable environmentally friendly energy must be encouraged, promoted, implemented and demonstrated by full-scale plant (device) especially for use in remote rural areas.
The communication reviews various options of renewable energy sources that are possibly be applied to rural based energy needs which may wholly or partly replace the conventional sources of energy. Sustainable energy is a prerequisite for development. Energy-based living standards in developing countries, however, are clearly below standards in developed countries. Low levels of access to affordable and environmentally sound energy in both rural and urban low-income areas are therefore a predominant issue in developing countries. In recent years many programmes for development aid or technical assistance have been focusing on improving access to sustainable energy, many of them with impressive results. Apart from success stories, however, experience also shows that positive appraisals of many projects evaporate after completion and vanishing of the implementation expert team. Altogether, the diffusion of sustainable technologies such as energy efficiency and renewable energy for cooking, heating, lighting, electrical appliances and building insulation in developing countries has been slow [39-31]. Energy efficiency and renewable energy programmes could be more sustainable and pilot studies more effective and pulse releasing if the entire policy and implementation process was considered and redesigned from the outset. New financing and implementation processes, which allow reallocating financial resources and thus enabling countries themselves to achieve a sustainable energy infrastructure, are also needed. The links between the energy policy framework, financing and implementation of renewable energy and energy efficiency projects have to be strengthened and as well as efforts made to
increase people's knowledge through training. Different sources of energy, which can be used for different final uses. Those sources are: wind power, solar energy, geothermal energy, the existing electricity production system and the conventional fuels with direct use (Figure 5). The main categories of final uses are: transportation, space heating, water heating and electricity for other uses.

6. Conclusions

There is strong scientific evidence that the average temperature of the earth's surface is rising. This is a result of the increased concentration of carbon dioxide and other GHGs in the atmosphere as released by burning fossil fuels. This global warming will eventually lead to substantial changes in the world’s climate, which will, in turn, have a major impact on human life and the built environment. Therefore, effort has to be made to reduce fossil energy use and to promote green energy, particularly in the building sector. Energy use reductions can be achieved by minimising the energy demand, rational energy use, recovering heat and the use of more green energy. This study was a step towards achieving this goal. The adoption of green or sustainable approaches to the way in which society is run is seen as an important strategy in finding a solution to the energy problem. The key factors to reducing and controlling CO₂, which is the major contributor to global warming, are the use of alternative approaches to energy generation and the exploration of how these alternatives are used today and may be used in the future as green energy sources. Even with modest assumptions about the availability of land, comprehensive fuel-wood farming programmes offer significant energy, economic and environmental benefits. These benefits would be dispersed in rural areas where they are greatly needed and can serve as linkages for further rural economic development. The nations as a whole would benefit from savings in foreign exchange, improved energy security, and socio-economic improvements. With a nine-fold increase in forest–plantation cover, a nation’s resource base would be greatly improved. The international community would benefit from pollution reduction, climate mitigation, and the increased trading opportunities that arise from new income sources. The non-technical issues, which have recently gained attention, include: (1) Environmental and ecological factors, e.g., carbon sequestration, reforestation and revegetation. (2) Renewables as a CO₂ neutral replacement for fossil fuels. (3) Greater recognition of the importance of renewable energy, particularly modern biomass energy carriers, at the policy and planning levels. (4) Greater recognition of the difficulties of gathering good and reliable renewable energy data, and efforts to improve it. (5) Studies on the detrimental health efforts of biomass energy particularly from traditional energy users.

7. Recommendations

● Launching of public awareness campaigns among local investors particularly small-scale entrepreneurs and end users of RETs to highlight the importance and benefits of renewable, particularly solar, wind, and biomass energies.

● Amendment of the encouragement of investment act, to include furthers concessions, facilities, tax holidays, and preferential treatment to attract national and foreign capital investment.

● Allocation of a specific percentage of soft loans and grants obtained by governments to augment budgets of (R & D) related to manufacturing and commercialisation of RETs.

● Governments should give incentives to encourage the household sector to use renewable energy instead of conventional energy.
Execute joint investments between the private sector and the financing entities to disseminate the renewable with technical support from the research and development entities.

Availing of training opportunities to personnel at different levels in donor countries and other developing countries to make use of their wide experience in application and commercialisation of RETs particularly renewable energy.

The governments should play a leading role in adopting renewable energy devices in public institutions, e.g., schools, hospitals, government departments, police stations, etc., for lighting, water pumping, water heating, communication and refrigeration.

Encouraging the private sector to assemble, install, repair and manufacture renewable energy devices via investment encouragement and more flexible licensing procedures.

References


Secondary Metabolites and Bioactivities of *Melastoma Malabathricum* (L.) Smith: An Anti-Diarrheal Plant of Bangladesh

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Abstract

*Melastoma malabathricum* (L.) Smith; a naturally growing plant of Bangladesh is investigated in the present experiment for its secondary metabolites, cytotoxic and antibacterial activities. Among the secondary metabolites alkaloid, flavonoid, sterol, tannin and glycoside found to be present while saponin is absent in its leaf. Ethanolic extract of *M. malabathricum* leaf showed significant cytotoxicity with the LC50 value of 19.38μg/ml. In the antibacterial screening, the highest zone of inhibition record was 8 mm (at 100mg/ml) and the lowest was 5 mm (at 50mg/ml). These significant cytotoxic and antibacterial activities also corroborate its ethno-medicinal practices.

Keywords. Antibacterial, cytotoxic, ethno-medicinal practices, secondary metabolites.

1. Introduction

Plants are the natural militant as they face so many obstacles in this earth [1]. During this military they produce and store versatile compounds in them [2]. The more the plant face obstacles the diverse its compounds [3]. Thus, plants become the outstanding harbor of such compounds under different conditions which are basically secondary metabolites [4]. As these are the arsenal of plants against various living and nonliving beings, these compounds adapt bioactive nature [5]. Due to this nature such compounds master healing power and apprise its reservoir as a medicinal plant. This is why; medicinal plants have various biological effects which are the prognostic of potent and powerful drugs [6].

*Melastoma malabathricum* or ‘futki’[7] is such an unexplored antidiarrhoeal plant of Bangladesh which naturally grows under versatile ecological conditions[8,9]. The appreciable medicinal properties the plant has drawn the attention of the researchers in recent times. Leaves of the plant contain phytochemical constituents strongly associated with its ethno medicinal uses[10]. It is a traditional medicine for alleviating urinary problems, leucorrhea, presence of sperm, blood or pus in urine, indigestion, rabies and diarrhea in Bangladesh as well as other countries of the world as flatulence, infection, small pox, toothache (Malaysia), leucorrhea (Java) [11].

Although a number of investigations have executed on *Melastoma malabathricum* with promising results; it is yet to be explored here in Bangladesh. Moreover, scientific investigations reveal that, similar species of different geographical and environmental conditions has significant variation in their metabolite contents as well as biological activities [12]. This impelled to investigate *Melastoma malabathricum* leaf from Bangladesh for its secondary metabolites and bioactivities.

2. Materials and methods

2.1 Collection of leaf sample:

Leaf sample was collected from *Melastoma malabathricum* plant, grown naturally in the premises of Botanical Garden, Department of Botany, University of Chittagong, Bangladesh in August, 2011. The plant was identified and a voucher specimen (accession no. 2011-110) was kept in the department. The collected leaf sample (≈ 500 g) was cleaned from undesirable materials, chopped, air dried in shade at room temperature and finally ground to a coarse powder.
2.2 Extraction

About 100 g powder was macerated with ethanol (1:5) in a sealed container for 5 days at room temperature with occasional shaking. Extract was filtered through Whatman No.1 filter paper and evaporated to dryness under vacuum below 50°C to get about 3 g blackish extract. The extract thus obtained was kept at 4°C for future use.

2.3 Assessment of secondary metabolites

Alkaloid detecting reagents were prepared following Cromwell [13] and assessed according to Aplin and Cannon[14]. Flavonoids, tannins and sterols were determined following Wall [15], Farnsworth [16] and Bhattachrjee and Das [17], respectively. Glycosides, saponins and resins in the extract were assessed qualitatively according to Ghani [18].

2.4 Bioassays

Cytotoxic activity of the extract was determined by brine shrimp nauplii lethality assay according to Meyer [19] and antimicrobial activity was determined by disc diffusion method. Each set of experiment was replicated three times and their mean values were taken.

2.5 Test Microorganisms

A total of eight human pathogenic microorganisms were used in the study. They include three Gram-positive bacteria; (Bacillus subtilis, Bacillus cereus, and Staphylococcus aureus) and five Gram-negative bacteria; (Escheretia coli, Vibrio cholerae, Shigella dysenteriae, Shigella sonnei, and Salmonella paratyphi).

3. Result and discussion

In the present work, leaf extract of M malabathricum L. was examined qualitatively for its alkaloid content using Dragendorff’s (D), Wagner’s (W), Mayer’s (M), Hager’s (H) and Tannic acid (T) reagents. The relative abundance of other secondary metabolite contents in the extract was expressed by ‘+’ ‘+’ sign in different degrees signifying the abundance. Absence of any secondary metabolite was indicated by ‘-’ sign. Results are given in Table 1. Qualitative assessment of alkaloid in the leaf extract indicated its high (3+ and 4+) presence. Among the other metabolites flavonoids, sterol, tannin and glycoside are present while saponins are absent.

| Secondary metabolite constituents of M. malabathricum L. leaf |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Secondary metabolites |
| Alkaloid | Other secondary metabolites |
| D | H | M | T | W | Flavonoids | Sterols | Tannins | Glycosides | Saponins |
| 4+ | 4+ | 3+ | 4+ | 4+ | + | + | + | + | - |

Medicinal value of a plant is associated with the bioactive compounds found within it [20]. It is proven that, medicinal plants exert antidysercentic and antidiarrhoeal properties due to their tannins, alkaloids, saponins, flavonoids, sterols and/or triterpenes and reducing sugars constituents [21, 22]. Presence of tannins in a plant is the indication of its astringent, cytotoxic or antineoplastic [23], antiviral, antibacterial activities; and capabilities to make the intestinal mucosa more resistant, reduce the secretion [24,25], aid wound healing and burns [26].
Flavonoids are renowned to exert antidiarrhoeal activity by inhibiting intestinal motility and hydro-electrolytic secretion [27]. Hence, the presence of various phytochemicals encouraged to test its cytotoxic activity which has been considered as convenient probe for the assessment of pharmacological potentialities of plant extracts and prescreening assay for antimicrobial, antitumor, antimalarial, antifungal, and insecticidal activities [28]. A number of novel natural products have been isolated using this bioassay [19, 29, 30].

Table 2. Cytotoxic effect of ethanolic extract of *M. malabathricum* L. leaf on *Artemia salina* nauplii

<table>
<thead>
<tr>
<th>Dose (µg/ml)</th>
<th>Log dose</th>
<th>Total Survived</th>
<th>Dead</th>
<th>Lethality (%)</th>
<th>Actual (%)</th>
<th>Probit</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.7</td>
<td>10</td>
<td>9</td>
<td>1</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>10</td>
<td>8</td>
<td>2</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>1.18</td>
<td>10</td>
<td>7</td>
<td>3</td>
<td>30</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>1.30</td>
<td>10</td>
<td>6</td>
<td>4</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>1.7</td>
<td>10</td>
<td>1</td>
<td>9</td>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>75</td>
<td>1.86</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>2.00</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>0.98</td>
</tr>
<tr>
<td>200</td>
<td>2.30</td>
<td>10</td>
<td>0</td>
<td>10</td>
<td>100</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The cytotoxic activity of the ethanol extract of *M. malabathricum* leaf was determined by the brine shrimp nauplii lethality bioassay using seven concentrations of the extract ranging from 5 to 100 µg/ml, each with 10 nauplii, which died progressively in greater number with the increase of the concentration of the extract and exposure time (up to 24 hours) at the rate of 0.1, 0.2, 0.3, 0.4, 0.9 and 0.98% (Table 2). In the present work, percent and probit were calculated using statistical software ‘Biostat 2009’ and the leaf extract showed LC50 value of 19.38 µg/ml (Table 3). Chi square value is insignificant at 5% i.e. the data between concentration and lethality is homogenous.

Table 3. Calculation of LC50 value, regressions equation and confidence limit.

<table>
<thead>
<tr>
<th>Log (LC50)</th>
<th>LC50 (µg/ml)</th>
<th>95% Confidence limit (µg/ml)</th>
<th>Regression equation</th>
<th>Chi square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>Tabulated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.29</td>
<td>19.38</td>
<td>14.07-26.47</td>
<td>Y=2.46+1.83</td>
<td>1.54</td>
</tr>
</tbody>
</table>

While screening cytotoxicity activity of *M. malabathricum* leaf extract; Lohezic-Le Devehat [31] found similar (<25µg/ml) cytotoxicity activity of the plant from Indonesia while Khatun [32] found a bit higher (53.84 µg/ml) from Bangladesh. The cytotoxicity of plant material would be considered as an indication of the presence of bioactive compounds in plant extract [33]. Crude extract having LC50 value less than 250µg/ml could be considered significantly active and potential for further investigation [34]. Plant extract in the present work had shown LC50 value less than 250µg/ml and presaged for its further investigation.
It has been found that antidiarrhoeal activity is associated with the antimicrobial activity[21]. Results of the ethanolic extract of *M. malabathricum* exhibited promising activity against the selected human pathogenic bacteria. These pathogens cause a variety of diseases including diarrhoea and gastroenteritis in human[35].

The antimicrobial activity (Table 4) of *M. malabathricum* determined by disc diffusion method at low concentration (2mg/ml) showed no inhibitory effect, but at increased concentrations (25mg/ml, 50mg/ml and 100mg/ml) the extract showed inhibition zone up to 8 mm. In case of Escheretia coli it was 6 mm at 25mg/ml, 7mm at 50mg/ml and 8 mm at 100mg/ml. Bacillus cereus, *Shigella dysenteriae*, *Staphylococcus aureus* and *Salmonella paratyphi* had no marked inhibition zone at 25mg/ml but they showed inhibition (5 mm to 8 mm) at 50mg/ml and 100mg/ml. However, response of five bacteria namely *E. coli*, *Vibrio cholerae*, *S.dysenteriae*, *S. sonnei* and *S.paratyphi* was highest (8 mm).

Alwash et al., [10] found similar results found in present work; whether other investigators i.e. Grosvenor [36], Wiart [37] and Thatoi [38] observed varied results during their studies regarding the antibacterial activity of the ethanolic extract of *Melastoma malabathricum* L. leaf .

<table>
<thead>
<tr>
<th>Test organisms</th>
<th>Diameter of zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mg/ml</td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>-</td>
</tr>
<tr>
<td><em>B. cereus</em></td>
<td>-</td>
</tr>
<tr>
<td><em>B. subtillis</em></td>
<td>-</td>
</tr>
<tr>
<td><em>V. cholerae</em></td>
<td>-</td>
</tr>
<tr>
<td><em>S. dysenteriae</em></td>
<td>-</td>
</tr>
<tr>
<td><em>S. sonnei</em></td>
<td>-</td>
</tr>
<tr>
<td><em>S. aureus</em></td>
<td>-</td>
</tr>
<tr>
<td><em>S. paratyphi</em></td>
<td>-</td>
</tr>
</tbody>
</table>

4. Conclusion

On the basis of the results evaluated as above, it may be concluded that, the plant *Melastoma malabathricum* have promising medicinal properties. It possesses vibrant phytochemical, cytotoxic and antibacterial properties which can be a vital source of antidiarrheal drugs in the future.

Conflict of Interests

The author declares no conflict of interests regarding the publication of this paper.
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Biosorption of Eriochrome Black T (EBT) onto Waste Tea Powder: Equilibrium and Kinetic Studies

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Abstract

Biosorption of EBT molecules from aqueous solutions onto waste Tea powder (WTP) have been examined in a batch biosorption process. The biosorption procedure was found to be dependent on biosorbent dose, pH of solution, initial dye concentration, and contact time. The experimental equilibrium biosorption data were inspected by Langmuir, Freundlich, Temkin and Dubinin–Radushkevic isotherms models. The Langmuir model gave the best fit by higher correlation coefficient ($R^2 = 0.997$, it assumes as monolayer adsorption). The maximum biosorption capacities determined from the Langmuir, isotherm models was 111.11 mg/g, at optimum circumstances. The kinetic studies showed that the biosorption operation of the EBT dye obeyed well pseudo-second-order model. According to the determined biosorption capacity, waste tea powder is considered to be as an effective, low cost, and environmentally friendly biosorbent for the removal of EBT dye from aqueous solutions.

Keywords: Biosorption, EBT, Equilibrium and Kinetic study

Subject Classification: Physical Chemistry, Adsorption, Isotherms and Kinetics

Type (Method/Approach): Removal of Dyes from waste water by adsorption

Introduction

Extended utilize of chemicals in everyday life and utmost manufacture processes have brought considerable amount of dyes and their existence produce environmental-disposal problems. Our biological system has been polluted by high levels of organic compounds produced into the environment. Modern exercises, development, urban waste treatment, and vehicle deplete are a part of the origin causing significant amounts of organic compounds tainting in environment, water, and soil [1]. Dyes are widely applied in industries such as cosmetic, rubber, textile, paper, plastic, etc. Through these several industries, textile classify first in employment of dyes for coloration of fiber. They are carcinogenic and also catalyze allergic complications. Dyes pollutions occurs in aqueous waste streams from numerous industries constitutes one of the most dangerous pollution problems and can influence the quality of water supply and cause many problems on aquatic life [2].

Various treatment techniques have been established for the elimination of dyes from waters and waste waters like precipitation, solvent extraction, filtration, ultrafiltration, membrane ion exchange, and many others [3-12]. However, these processes are not extensively used because they are expensive, and create industrial problems. Recently, adsorption techniques have been demonstrated to be the most promising choice for the removal of organic pollutants and dyes from aqueous streams [13]. Activated carbon as an adsorbent has been extensively examined for the adsorption of dyes due to their effectiveness and versatility. However, some difficulties have been reported for activate carbon in terms of engineering problems and high-cost in commercial applications [14]. Alternatively, there are various kinds of waste byproducts which have been utilized to remove dyes such as rice husk, mushroom biomass, sunflower stalks, Eucalyptus bark, wheat bran, fruit peel of orange, and Ficus religiosa leaves [15].

In our previous work, we have studied the efficiency of waste coffee and tea, orange peels, and olive leaves powders as a biosorbents for removal of some heavy metal ions from aqueous solutions [16 - 18]. In this work,
the adsorption of EBT dye onto waste tea powder has been investigated. The adsorption capacity was evaluated under various conditions of pH, contact time, initial dye concentration, and adsorbent dosage. The adsorption isotherms were also investigated to explain the probable mechanism of adsorption and to provide several information such as maximum sorption capacity, energy of sorption, homogeneity/heterogeneity, and affinity between sorbent and adsorbent.

**Materials and Methods**

**Reagents**

All chemicals used were of analytical reagent (AR) grade. 100 ppm EBT stock solution was prepared by dissolving an appropriate amount of EBT salt in deionized water. The stock solution was diluted to the required concentrations using deionized water. The solution pH was adjusted using 0.10 M HCl or 0.10 M NaOH.

**Determination of EBT Dye**

The concentration of EBT dye in the solutions before and after equilibrium was determined by Molecular Absorption Spectrophotometer 6305 from JENWAY. The pH of the solution was measured with pH Meter 3505 from JENWAY. The determination of EBT dye was carried out according to the published work [19]. The range of calibration curve concentrations of dyes prepared from stock solution varies between 5-100 ppm.

**Preparation of Adsorbents**

The tea waste powders were collected from a coffee shop, washed with double distilled water and then dried in an oven at 70°C for 24 hrs. The dried materials were sieved through 500 μm size fraction using an American Society for Testing and Materials (ASTM) standard sieve.

**Adsorption Experiments**

The adsorption experiments were carried out in a series of 250 mL Erlenmeyer flasks containing 200 ml of EBT dye solution, 0.100 g adsorbent powder and if necessary, an appropriate volume of HCl or NaOH solutions was used to adjust the pH of the solution. The solutions were shaken (175 rpm) at 25°C. Then solutions were filtered by Whatman filter paper. The removal percentage (% R) was calculated according to the following equation:

$$\% \ R = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (1)

Where: \(C_o\) and \(C_e\) are initial and final concentrations in ppm, respectively. The amount of adsorbed dye \(Q_e\) mg/g (mg dye per gram adsorbent) was calculated based on the difference between the initial \((C_o, \text{ ppm})\) and final concentration \((C_e, \text{ ppm})\) in every flask, as follows:

$$Q_e = \frac{C_o - C_e}{M} \times V$$ \hspace{1cm} (2)

Where \(Q_e\) is the dye uptake capacity (mg/g), \(V\) the volume of the dye solution in the flask (L) and \(M\) is the dry mass of biosorbent (g).

**Parameters Affecting Adsorption Experiments**

The effects of experimental parameters such as pH, biosorbent dose, contact time, and dye concentration were investigated for EBT adsorption onto tea powders. The pH dependent study was carried out in 200 ml aqueous dye solution of 90 ppm and 0.10 g powder. The investigated pH values were from 1.50 to 7.50. The effect of contact time on dye adsorption was examined for 200 ml solutions with 90 ppm concentration and containing 0.10 g powder. The effect of biosorbent doses on dye uptake was investigated with adsorbent masses of 0.2,
0.4, 0.6, 0.8, 1.0 and 1.2 g per 200 ml of 90 ppm dye solution. Finally, various concentrations of EBT dye were investigated to study the effect of dye concentration which was: 55, 65, 75, 85, 95, ppm per 200 ml solution.

Results and Discussion

![Structure of EBT](image1)

**Figure 1. Structure of EBT**

![Absorption Spectrum of EBT](image2)

**Figure 2. Absorption Spectrum of EBT**

By UV. VIS. Spectrophotometer, the concentrations of EBT dye in the solutions were determined [19]. The range of calibration curve of dye prepared from stock solution varies between 5-100 ppm as shown in Figure 3. The response of the EBT dye was found to be linear in the investigation concentration range at \(\lambda_{\text{max}} = 528\) nm and the linear regression equation was \(y = 0.009X\) with high correlation coefficient \((R^2 = 0.999)\). From the calibration curve, the concentrations of EBT in the solutions before and after equilibrium adsorption were determined.
The biosorption of EBT dye from aqueous solutions are strongly affected by the pH. The pH is considered to be as the most important parameters governing dye uptake by adsorbent substrate. The adsorption of EBT dye on (WTP) was monitored over a range of pH from 1.5 to 7.5 of individual solutions as shown in Figure 4. Low percent removal were observed at low pH values (< 5.0) and also at higher pH (above pH 7). If electrostatic interaction was the only mechanism for the dye adsorption, then the removal capacity should be at a maximum within the range pH 5 – 6. In this pH range the surface of activated tea powder is positively charged (pH > 5.0) and dyes are negatively charged (pKₐ of dyes 6.2 and 11.6). The deprotonated groups of the dye were the sulfonate (-SO₃⁻). At solution pH < 5, the removal capacity was expected to decrease, as the adsorbent was positively charged and dye molecules were either neutral or partially positively charged. At this acidic pH, the sulfonate groups of the dyes were almost protonated (-SO₃H, i.e., neutral). The large reduction in dye adsorption at highly basic conditions can be attributed to electrostatic repulsion between the negatively charged activated tea powder and the deprotonated dye molecules. Activated tea powder can also interact with dye molecules via hydrogen bonding mechanism.

**Figure 3. Calibration curve for EBT**

**Effect of pH**

**Figure 4. Effect of pH on percent removal of dye (%) by WTP**
Effect of initial concentration

The effect of different initial concentrations of dye on equilibrium of biosorption experiments onto (WTP) were investigated from 55 to 95 ppm at pH 6. The relation between equilibrium uptake $Q_m$ (mg.g$^{-1}$) with initial dye concentration is shown in Figure 5. The $Q_m$ of dye was increased gradually with an increasing the initial concentration of EBT dye as shown in Figure 5. The dye molecules adsorption is possible at lower concentrations, but as the concentration is increased, the driving force also increased, which favored the adsorption at higher concentrations. The increasing of adsorption capacity with the increasing in dye concentration is probably due to higher interaction between the EBT molecules and sequestering sites of biosorbent.

![Figure 5. Effect of initial dye concentration on dye uptake $Q_m$ onto absorbent (WTCP)](image)

Effect of contact time

The rate of biosorption is an important for designing batch biosorption experiments. Therefore, the effect of contact time of dyes biosorption on (WTP) was investigated Figure 6 shows that the biosorption of EBT molecules on (WTP) was increased considerably until the contact time reached 80 min at 25°C. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 80 min for further biosorption experiments.

![Figure 6. Effect of contact time on percent removal of dye (% R) by WTP](image)
Effect of adsorbent dose

The biosorbent dosage of (WTP) is an important parameter because this determines the maximum capacity of a biosorbent for a given dye concentration. The biosorption efficiency for EBT molecules as a function of biosorbent dosage (WTP) was investigated, Figure 7 shows that the dye uptake was decreased with the biosorbent dose up to 0.1 g/L. This result can be explained by the fact that the biosorption sites in (WTP) remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the dose of (WTP). In the further experiments, 0.1 g/L were taken as optimum biosorbent dose because a maximum capacity of the dye was attained at this value.

![Figure 7. Effect of adsorbent dose on EBT uptake Q_m by WTP](image)

Biosorption isotherms

Adsorption isotherms describe the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Biosorption of EBT onto waste tea powder (WTP) was modeled using four adsorption isotherms.

The Langmuir isotherm

It assumes as monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [20]:

$$ \frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{b Q_mC_e} $$  \hspace{1cm} (3)

![Figure 8. Langmuir adsorption isotherm for the removal of EBT dye by WTP](image)
where b is the Langmuir constant related to the energy of adsorption (Lmg\(^{-1}\)) and \(Q_m\) is the maximum biosorption capacity (the monolayer adsorption saturation capacity mg/g), \(Q_e\) (mg/g) the amount of dye molecules bound per gram of the adsorbent at equilibrium; and \(C_e\), the residual (equilibrium) dye concentration left in the solution after binding. Values of Langmuir parameters \(Q_m\) and b were calculated from the slope and intercept of the linear plot of \(1/Q_e\) versus \(1/C_e\) as shown in Figure 8. Values of \(Q_m\), b, and regression coefficient \(R^2\) are listed in Table 1. These values indicated that Langmuir model describes the biosorption phenomena favorable. The level of conformity for tea as a good sorbent is high, according to the correlation coefficients \(R^2\) of 0.997. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, \(R_L\) expressed as in the following equation:

\[
R_L = \frac{1}{1+bC_0}
\]  

(4)

The value of \(R_L\) indicated the type of Langmuir isotherm to be irreversible (\(R_L=0\)), favorable (0 <\(R_L< 1\)), linear (\(R_L=1\)) or unfavorable (\(R_L>1\)). In concentration range of 50 to 95 mg/L of EBT dye, the values \(R_L\) of biosorbed (WTP) were found to be 0.667. This is in the range of 0.0-1.0 which indicates the favorable biosorption.

The Freundlich isotherm model

It is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of Freundlich equation. Also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [21]:

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]  

(5)

Where \(K_f\) is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of \(\log Q_e\) versus \(\log C_e\), as shown in Figure 9, on the basis of the linear of Freundlich equation. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if \(n = 1\), then adsorption is linear; if \(n < 1\), then adsorption is a chemical process; if \(n > 1\), then adsorption is a physical process. The n value in Freundlich equation was found to be 0.596 (Table 1) this indicates the physical biosorption of EBT molecules onto tea adsorbate is suitable.

Figure 9. Freundlich adsorption isotherm for the removal of EBT dye by adsorption on (WTP)
Temkin isotherm

In literature [22] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin isotherm has been used in the linear form as follows:

$$Q_e = B \log A + B \log C_e$$  \hspace{1cm} (6)

![Figure 10. Temkin adsorption isotherm for the removal of EBT dye by adsorption on (WTP)](image)

The plot of $Q_e$ versus $\log C_e$ enables the determination of the isotherm constants $B$ and $A$ obtained from the slope and the intercept, Figure 10. Where $A$ (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant $B$ is related to the heat of biosorption, Table 1.

Dubinin-Radushkevich (D-R) model

This model does not assume a homogenous surface or a constant biosorption potential as the Langmuir model, and it was also used to test the experimental data [23].

$$\log Q_e = \log Q_d - \beta \varepsilon^2$$  \hspace{1cm} (7)

Where $\varepsilon$ can be correlated to $C_e$ (mg/L) by the following equation:

$$\varepsilon = RT \log \left(1 + \frac{1}{C_e}\right)$$  \hspace{1cm} (8)
Figure 11. Dubinin-Radushkevich (D-R) adsorption isotherm for the removal of EBT dye by adsorption on (WTP)

Where R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). The D-R isotherm \( \beta \) and \( Q_d \) were obtained from the slope and intercept of the plot of \( \log Q_e \) versus \( \varepsilon^2 \), Figure 11. The calculated values are listed in Table 1. The values of correlation coefficient were lower than that of other three isotherms values. In all cases, the D-R model represents the least fit to experimental data than the other isotherms models.

The mean free energy of biosorption, \( E \) defined as the free energy change when 1 mole of ion is transferred to the surface of the solid from infinity in solution and calculated from the \( \beta \) value using the following equation:

\[
E = \frac{1}{\sqrt{2}\beta}
\]  

If the magnitude of \( E \) is between 8 to 16 KJ/mol then the sorption process is supposed to proceed via chemisorption reaction, while for values of \( E \) is less than 8 kJ/mol, the sorption process is of physical nature. The value of \( E \) calculated from equation (9) for the biosorption of EBT dye by waste tea powder is 0.0.018 KJ/mol. This indicates that the biosorption process is of physical nature.

**Biosorption Kinetics**

To examine the biosorption kinetics of dye uptake onto (WTP), the two kinetic models (pseudo first-order and pseudo second-order) were fit to experimental data.

The pseudo-first order equation of Lagergren [24] is generally expressed as follows:

\[
\frac{dQ_t}{dt} = k_1 (Q_e - Q_t)
\]  

Where \( Q_e \) and \( Q_t \) are the sorption capacities at equilibrium and at time \( t \), respectively and \( k_1 \) is the rate constant of pseudo-first order sorption. The integrated form of equation (10) at boundary conditions, from \( Q_t = 0 \) to \( Q_e \), and \( t = 0 \) to \( t \), becomes:

\[
\log (Q_e - Q_t) = \log Q_e - k_1 t
\]  

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In order to fit the experimental data by integrated form of pseudo-first order equation, the equilibrium sorption capacity, $Q_e$ must be known. For this reason, and for analyze the pseudo-first order model kinetics it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity. In most cases in the literature, the amount sorbed is still significantly smaller than the equilibrium amount and the Lagergren equation does not fit well for the whole range of contact time process. The calculated values and their corresponding linear regression correlation coefficient values (which calculated from Figure 12) are listed in Table 2. $R^2$ was found to be 0.0238 which shows that this rate equation cannot be applied to predict the adsorption kinetic model.

The pseudo second-order rate expression, which has been applied for analyzing sorption kinetics rate, is expressed as [25]:

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t) \quad (12)$$

For the boundary conditions from $Q_t = 0$ to $Q_e$ and $t = 0$ to $t$; the integrated form of equation becomes:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (13)$$

Where $t$ is the contact time (min), $Q_e$ and $Q_t$ are the amount of the solute adsorbed at equilibrium and at any time $t$ (mg/g) respectively and $k_2$ is the rate constant of pseudo-second order sorption, (g/mg.min).
If pseudo-second order kinetics is applicable, the plot of $t/Q_e$ versus $t$ of the equation should give a linear relationship, from which $Q_e$ and $k_2$ can be determined from the slope and intercept of the plot, Figure 13. The pseudo-second order rate constant $k_2$, the calculated $Q_e$ value and the corresponding linear regression correlation coefficient value $R^2$ are listed in Table 2. At all initial metal concentrations, the linear regression correlation coefficient $R^2$ values was high (0.9156) which confirm that the adsorption data are better represented by pseudo-second order kinetics. The calculated $Q_e$ values agreed with the estimated experimental $Q_e$ values 90.1 (Table 1 and 2). This enhance that the adsorption of EBT dye follows pseudo-second order kinetics.

**Table 1. Langmuir, Freundlich, D-R and Temkin isotherm constants for biosorption of EBT onto WTCP**

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>$Q_m$</th>
<th>$b$</th>
<th>$R_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>111.11</td>
<td>0.0054</td>
<td>0.668</td>
<td>0.997</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$</td>
<td>$n$</td>
<td>$R^2$</td>
<td></td>
</tr>
<tr>
<td>Tea</td>
<td>17.62</td>
<td>0.596</td>
<td></td>
<td>0.997</td>
</tr>
<tr>
<td>Temkin</td>
<td>$B$</td>
<td>$A$</td>
<td>$R^2$</td>
<td></td>
</tr>
<tr>
<td>Tea</td>
<td>289.84</td>
<td>0.025</td>
<td></td>
<td>0.9809</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$Q_d$</td>
<td>$\beta$</td>
<td>$R^2$</td>
<td></td>
</tr>
<tr>
<td>Tea</td>
<td>170.37</td>
<td>0.0015</td>
<td></td>
<td>0.971</td>
</tr>
</tbody>
</table>

**Table 2. Kinetic parameters of EBT biosorption onto WTP**

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>$Q_e$</th>
<th>$k_1$ (1/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order</td>
<td>Tea</td>
<td>72.09</td>
<td>0.0004</td>
</tr>
<tr>
<td>Second Order</td>
<td>Tea</td>
<td>Graphically (90.1)</td>
<td>0.0000291</td>
</tr>
<tr>
<td></td>
<td>Estimated (111.3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Conclusions**

In our present work, we show that the waste tea powders could be used as a biosorbent for the removal of dye molecules from aqueous solutions. The removal efficiency and dye capacity were found to be dependent on pH, contact time, initial dye concentration, and biosorbent dose. Biosorption isothermal data could be well simulated by Langmuir, Freundlich, Temkin and then Dubinin-Radushkevich (D-R) models. The maximum metal capacities determined by using the Langmuir isotherm were 111.11 mg/g tea powders. The values of dye uptake capacities at equilibrium $Q_e$ calculated from equation (2) and pseudo-second-order plot were found comparable. The biosorption kinetics could be well predicted by pseudo-second-order kinetic. The results of our investigation indicate that the tea powder has a potential for use in removing EBT dye from aqueous solutions.

**Conflicts of Interest**

Submitting author is responsible for co-authors declaring their interests.

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References


Implementing Sustainable Technologies For Greener Environment

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Abstract

Over the years, all parts of a commercial refrigerator, such as the compressor, heat exchangers, refrigerant, and packaging, have been improved considerably due to the extensive research and development efforts carried out by academia and industry. However, the achieved and anticipated improvement in conventional refrigeration technology are incremental since this technology is already nearing its fundamentals limit of energy efficiency. The word ‘green’ designates more than a colour. It is a way of life, one that is becoming more and more common throughout the world. An interesting topic on ‘sustainable technologies for a greener world’ details about what each technology is and how it achieves green goals. Recently, conventional chillers using absorption technology consume energy for hot water generator but absorption chillers carry no energy saving. With the aim of providing a single point solution for this dual-purpose application, a product is launched but can provide simultaneous chilling and heating using its vapour absorption technology with 40% saving in heating energy. Using energy efficiency and managing customer energy use has become an integral and valuable exercise. The reason for this is green technology helps to sustain life on earth. This not only applies to humans but to plants, animals and the rest of the ecosystem. Energy prices and consumption will always be on an upward trajectory. In fact, energy costs have steadily risen over last decade and are expected to carry on doing so as consumption grows.

Keywords: Energy saving; energy efficiency, sustainable technologies; heat exchangers; refrigerant; future prospective

1. Introduction

This section describes the different methods and techniques for providing energy for heating and cooling systems. It also, covers the optimisation and improvement of the operation conditions of the heat cycles and the performance of the ground source heat pump systems (GSHPs).

With the improvement of people’s living standards and the development of economies, heat pumps have become widely used for air conditioning. The driver to this was that environmental problems associated with the use of refrigeration equipment, the ozone layer depletion and global warming are increasingly becoming the main concerns in developed and developing countries alike. With development and enlargement of the cities in cold regions, the conventional heating methods can severely pollute the environment. In order to clean the cities, the governments drew many measures to restrict citizen heating by burning coal and oil and encourage them to use electric or gas-burning heating. New approaches are being studied and solar-assisted reversible absorption heat pump for small power applications using water-ammonia is under development [1].

An air-source heat pump is convenient to use and so it is a better method for electric heating. The ambient temperature in winter is comparatively high in most regions, so heat pumps with high efficiency can satisfy their heating requirement. On the other hand, a conventional heat pump is unable to meet the heating requirement in severely cold regions anyway, because its heating capacity decreases rapidly when ambient temperature is below -10°C. According to the weather data in cold regions, the air-source heat pump for heating applications

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must operate for long times with high efficiency and reliability when ambient temperature is as low as \(-15^\circ C\). Hence, much research and developments have been conducted to enable heat pumps to operate steadily with high efficiency and reliability in low temperature environments [2]. For example, the burner of a room air conditioner, which uses kerosene, was developed to improve the performance in low outside temperature [3]. Similarly, the packaged heat pump with variable frequency scroll compressor was developed to realise high temperature air supply and high capacity even under the low ambient temperature of \(-10\) to \(-20^\circ C\) [4]. Such a heat pump system can be conveniently used for heating in cold regions. However, the importance of targeting the low capacity range is clear if one has in mind that the air conditioning units below 10 kW cooling account for more than 90% of the total number of units installed in the EU [5].

Conventional heating or cooling systems require energy from limited resources, e.g., electricity and natural gas, which have become increasingly more expensive and are at times subject to shortages. Much attention has been given to sources subject to sources of energy that exist as natural phenomena. Such energy includes geothermal energy, solar energy, tidal energy, and wind generated energy. While all of these energy sources have advantages and disadvantages, geothermal energy, i.e., energy derived from the earth or ground, has been considered by many as the most reliable, readily available, and most easily tapped of the natural phenomena.

Ground source based geothermal systems have been used with heat pumps or air handling units to satisfy building HVAC (heating, ventilation, and air conditioning) loads. These systems are favoured because geothermal systems are environmentally friendly and have low greenhouse emissions.

The installation and operation of a geothermal system of the present invention may be affected by various factors. These factors include, but are not limited to, the field size, the hydrology of the site the thermal conductivity and thermal diffusivity of the rock formation, the number of wells, the distribution pattern of the wells, the drilled depth of each well, and the building load profiles. Undersized field installations require higher duty cycles, which may result in more extreme water temperatures and lower HVAC performance in certain cases. Oversized field designs, on the other hand, require more wells, pumps and field plumbing and therefore will be more expensive, albeit adequate to handle almost any load circumstances. The detailed knowledge of the field rock (e.g., porosity, permeability, thermal diffusivity, heat capacity, or other aquifer parameters) may facilitate the determination of the appropriate drilling depth for each well, as well as the number and position of such wells needed at that site. Some of this information may be obtained during the drilling operation.

2. Earth-energy Systems (EESs)

The earth-energy systems, EESs, have two parts; a circuit of underground piping outside the house, and a heat pump unit inside the house. And unlike the air-source heat pump, where one heat exchanger (and frequently the compressor) is located outside, the entire GSHP unit for the EES is located inside the house.

The outdoor piping system can be either an open system or closed loop. An open system takes advantage of the heat retained in an underground body of water. The water is drawn up through a well directly to the heat exchanger, where its heat is extracted. The water is discharged either to an aboveground body of water, such as a stream or pond, or back to the underground water body through a separate well. Closed-loop systems, on the other hand, collect heat from the ground by means of a continuous loop of piping buried underground. An antifreeze solution (or refrigerant in the case of a direct expansion ‘DX’ earth-energy system), which has been chilled by the heat pump’s refrigeration system to several degrees colder than the outside soil, circulates through the piping, absorbing heat from the surrounding soil.

In some EESs, a heat exchanger, sometimes called a “desuperheater”, takes heat from the hot refrigerant after it leaves the compressor. Water from the home’s water heater is pumped through a coil ahead of the condenser coil, in order that some of the heat that would have been dissipated at the condenser is used to heat water. Excess heat is always available in the cooling mode, and is also available in the heating mode during mild weather when the heat pump is above the balance point and not working to full capacity. Other EESs heat domestic hot water (DHW) on demand: the whole machine switches to heating DHW when it is required.
Hot water heating is easy with EESs because the compressor is located inside. Because EESs have relatively constant heating capacity, they generally have many more hours of surplus heating capacity than required for space heating. In fact, there are sources of energy all around in the form of stored solar energy, which even if they have a low temperature, can provide the surroundings with enough energy to heat the soil, bedrock and ground water as a heat source for domestic dwellings as shown in Figure 1, for example. Some emphasis has recently been put on the utilisation of the ambient energy from ground source and other renewable energy sources in order to stimulate alternative energy sources for heating and cooling of buildings. Exploitation of renewable energy sources and particularly ground heat in buildings can significantly contribute towards reducing dependency on fossil fuels.

![Figure 1. Using the soil, bedrock or groundwater as the heat source [17].](image)

2.1. The Cooling Cycle

The cooling cycle is basically the reverse of the heating cycle. The reversing valve changes the direction of the refrigerant flow. The refrigerant picks up heat from the house air and transfers it directly in DX systems or to the ground water or antifreeze mixture. The heat is then pumped outside, into a water body or return well (in the case of an open system), or into the underground piping (in the case of a closed-loop system). Once again, some of this excess heat can be used to preheat domestic hot water.

Unlike air-source heat pumps, EESs do not require a defrost cycle. Underground temperatures are much more stable than air temperature, and the heat pump unit itself is located inside; therefore, problems with frost do not arise.

2.2. Function of the GSHP Circuit

The collector liquid (cooling medium) is pumped up from the borehole in tubing and passed to the heat pump. Another fluid, a refrigerant, circulates in the heat pump in a closed system with the most important characteristic of having a low boiling point. When the refrigerant reaches the evaporator, which has received energy from the borehole, and the refrigerant evaporates. The vapour is fed to a compressor where it is compressed. This results in a high increase in temperature. The warm refrigerant is fed to the condenser, which is positioned in the boiler water. Here the refrigerant gives off its energy to the boiler water, so that its temperature drops and the refrigerant changes state from gas to liquid. The refrigerant then goes via filters to an expansion valve, where the pressure and temperature are further reduced. The refrigerant has now completed its circuit and is once more fed into the evaporator where it is evaporated yet again due to the effect of the energy that the collector has carried from the energy source (Figure 2).
Efficiencies of the GSHP systems are much greater than conventional air-source heat pump systems. A higher COP (coefficient of performance) can be achieved by a GSHP because the source/sink earth temperature is relatively constant compared to air temperatures. Additionally, heat is absorbed and rejected through water, which is a more desirable heat transfer medium because of its relatively high heat capacity. The GSHP systems rely on the fact that, under normal geothermal gradients of about 0.5°F/100 ft (30°C/km), the earth temperature is roughly constant in a zone extending from about 20 ft (6.1 m) deep to about 150 ft (45.7 m) deep. This constant temperature interval within the earth is the result of a complex interaction of heat fluxes from above (the sun and the atmosphere) and from below (the earth interior). As a result, the temperature of this interval within the earth is approximately equal to the average annual air temperature [6]. Above this zone (less than about 20 feet (6.1 m) deep), the earth temperature is a damped version of the air temperature at the earth’s surface. Below this zone (greater than about 150 ft (45.7 m) deep), the earth temperature begins to rise according to the natural geothermal gradient. The storage concept is based on a modular design that will facilitate active control and optimisation of thermal input/output, and it can be adapted for simultaneous heating and cooling often needed in large service and institutional buildings [7]. Loading of the core is done by diverting warm and cold air from the heat pump through the core during periods with excess capacity compared to the current need of the building [8-10]. The cool section of the core can also be loaded directly with air during the night, especially in spring and fall when nights are cold and days may be warm.

2.3. Free Cooling

The installation can additionally be fitted with fan convectors, for example, in order to allow connections for free cooling (Figure 3). To avoid condensation, pipes and other cold surfaces must be insulated with diffusion proof material. Where the cooling demand is high, fan convectors with drip tray and drain connection are needed.

2.4. Refrigeration and Heat Pumps

The pressure (ps) is a function of how rapidly vapour can be removed through suction or formed through pressure. At equilibrium, the rate at which vapour is formed (determined by Q) equals the rate at which it is removed. Therefore, both the heat transfer rate into the liquid (Q) and the vapour removal rate (suction pump capacity) determines the pressure and hence Tsat(5) (Figure 4). This is governed by the following set of equations.
Figure 3. Diagram of cooling system.

\[ Q = m h_{fg} \]  
(1)

\[ m = \rho g V \]  
(2)

\[ Q = \rho g V h_{fg} \]  
(3)

\[ Q = V h_{fg}/v_g \]  
(4)

Both \( h_{fg} \) and \( v_g \) depend on the saturation temperature (or pressure) as assumed in Figure 5, which describes the relationship represented by eqn. 4.

The RHS of the Figure 6 is the 'converse' of the LHS, and constitutes a heat pump. Heat is 'pumped' from the LHS to the RHS. The main difference is that the vapour, after compression, will almost certainly be superheated and must cool to \( T_{sat(c)} \) before condensing will occur. The same reasoning (in converse) applies to the RHS as previously applied to LHS. Obviously, with the above system, the entire refrigerant would eventually end up on the RHS, and the heat pumping (& refrigeration) effect would cease.

Clearly, to ensure that the system can operate continuously liquid refrigerant needs to be fed from the RHS back to the LHS. This can be achieved by simply allowing it to flow back under its natural pressure difference. In this way a continuous closed-circuit refrigeration (Or heat pump) system is obtained (Figure 7).
Figure 4. Refrigeration Cycle.

Figure 5. Heat transfer rate versus volume rate.

Figure 6. Heat pumps

pc = Condenser or 'high side' pressure.

ps = Evaporator, 'low side', or suction pressure.
2.5. System Performance

The system balance requires the overall work done to be equivalent to the net energy used by the system. Hence,

\[ Q_{\text{out}} - Q_{\text{in}} = W_{\text{in}} \]  

(5)

For operation as a refrigerator, a measure of system performance is the amount of heat absorbed per unit work supplied to drive the system. This is known as the Coefficient of Performance [11].

\[ \text{COP}_{\text{ref}} = \frac{Q_{\text{in}}}{W_{\text{in}}} \]  

(6)

For operation as a heat pump, a measure of system performance is the amount of heat delivered per unit work supplied to drive the system. This is known as the Coefficient of Performance [12].

\[ \text{COP}_{\text{hp}} = \frac{Q_{\text{out}}}{W_{\text{in}}} \]  

(7)

It follows that (for the same system):

\[ \text{COP}_{\text{hp}} = \text{COP}_{\text{ref}} + 1 \]  

(8)
2.6. Vapour Compression Refrigeration

The term “vapour compression refrigeration” is somewhat of a misnomer, it would be more accurately described as ‘vapour suction refrigeration’. Vapour compression is used to reclaim the refrigerant and is more aptly applied to heat pumps. Vapour compression refrigeration exploits the fact that the boiling temperature of a liquid is intimately tied to its pressure. Generally, when the pressure on a liquid is raised its boiling (and condensing) temperature rises, and vice-versa. This is known as the saturation pressure-temperature relationship.

2.7. Refrigerant Properties

In practice, the choice of a refrigerant is a compromise, e.g., Ammonia is good but toxic and flammable while R12 is very good but detrimental to the Ozone layer. Figure 9 shows some commonly used refrigerants and their typical ranges of usability.

![Figure 9. Refrigerant chart.](image)

Ideally, a refrigerant will have the following characteristics.

- Non-toxic - for health and safety reasons.
- Non-flammable - to avoid risks of fire or explosion.
- Operate at modest positive pressures - to minimise pipe and component weights (for strength) and avoid air leakage into the system.
- Have a high vapour density – to keep the compressor capacity to a minimum and pipe diameter relatively small.
- Easily transportable - because refrigerants are normally gases at SSL conditions, they are stored in pressurised containers.
- Environmentally friendly - non-polluting & non-detrimental to the atmosphere, water or ground.
- Easily re-cycleable, and relatively inexpensive to produce.
- Compatible with the materials of the refrigeration system - non-corrosive, miscible with oil, and chemically benign.

2.8. Cooling Mode

In the cooling mode, cool vapour arrives at the compressor after absorbing heat from the air in the building. The compressor compresses the cool vapour into a smaller volume, increasing its heat density. The refrigerant exits the compressor as a hot vapour, which then goes into the earth loop field. The loops act as a condenser condensing the vapour until it is virtually all liquid. The refrigerant leaves the earth loops as a warm liquid. The flow control regulates the flow from the condenser such that only liquid refrigerant passes through the control. The refrigerant expands as it exits the flow control unit and becomes a cold liquid.

2.9. Heat Pump Antifreeze

A potential negative effect of all geothermal heat pumps is the release of antifreeze solutions to the environment. Antifreeze solutions are required in colder climates to prevent the circulating fluid from freezing. Antifreeze chemicals include methanol, ethanol, potassium acetate, propylene glycol, calcium magnesium acetate (CMA), and urea. These chemicals are generally mixed with water when used as a heat exchange fluid. These chemicals can be released to the environment via spills or corrosion of system components. Approved antifreezes include methanol, ethanol, propylene glycol, calcium chloride, or ethylene glycol. These antifreezes must be mixed with water, at concentrations of 20% or less. Geothermal heat pumps for a single-family residence and the antifreezes for these units were evaluated by Heinonen et al., (1996) [13]. These authors evaluated total energy consumption, corrosion due to the antifreeze, and the operational and environmental effects of six antifreeze solutions, namely methanol, ethanol, potassium acetate, propylene glycol, CMA, and urea. However, the excluded salt solutions, such as sodium and calcium chloride, from their study because they pose serious potential corrosion problems. The differences in total energy consumption for the studied antifreezes were considered minimal. Nevertheless, Heinonen et al., recommended that propylene glycol was a good choice based on its low health, fire, and environmental risks (Table 1). Unfortunately, these authors did not assess the leak potential of these antifreezes in the plastic pipe (e.g., HDPE & CPVC SDR-11) commonly used for the ground loop [14].

| Table 1. Cost and risk factors for heat pump antifreeze (Heinonen et al., 1996) [13] |
|---|---|---|---|---|---|---|
| Factor               | Antifreeze     |
|                     | Methanol | Ethanol | Propylene glycol | Potassium Acetate | CMA | Urea |
| Life cycle cost     | 3        | 3        | 2               | 2                             |
| Corrosion risk      | 2        | 2        | 3<sup>a</sup> | 2                             |
| Leakege risk        | 3        | 2        | 2<sup>a</sup> | 1<sup>b</sup>                 |
| Health risk         | 1        | 2        | 3               | 3                             |
| Fire risk           | 1<sup>a</sup>| 1<sup>c</sup>| 3               | 3                             |
| Environmental risk  | 2        | 2        | 3               | 2                             |
| Risk of future use  | 1        | 2        | 3               | 2                             |
Notes: Ratings- 1 means potential problems and caution required, 2 means minor potential for problems, 3 means little or no potential problems.

a) DOWFROST HD; b) GS-4; c) Pure fluid only. Diluted antifreeze (25% solution) is rated 3.

However, the bond between the grout and borehole can be compromised by desiccation of the geologic materials near the borehole, as the heat from the borehole lowers the moisture content of the geologic materials and these materials contract. In areas with thick unsaturated zones, the bentonite grout may dry out over time, compromising the seal. To improve heat exchange, some advocate the use of spacers, which moves the heat conductor pipe to the side of the borehole, putting it in contact with the geologic materials. However, the use of spacers appears to increase the environmental risk of antifreeze leaking into groundwater, by reducing or removing the bentonite between the heat conductor pipe and geologic materials.

3. Air Distribution

The air distribution system can make a big difference in both the cost and the effectiveness of geothermal heating and cooling. It also has an important effect on personal comfort and health. The air-handling component is either a separate cabinet or is part of the cabinet that houses the geothermal heat pump, and includes the blower assembly that forces air through the ductwork. The supply ductwork carries air from the air handler to the rooms. Typically, each room has at least one supply duct and larger rooms may have several. The return ductwork moves air from the room back to the air handler. Most buildings have one or more main return ducts located in a central area. The cold liquid refrigerant is circulated through the air handler where it absorbs and removes the unwanted heat from the air and vaporises the refrigerant to a gas. The gas is compressed to increase its temperature and then the underground/underwater coils act as a condenser rather than an evaporator (as in the heating cycle) (Figure 10). The heat in the refrigerant is transferred to the ground/water as the refrigerant condenses.

Refrigerants are present in the GSHP systems and so present the threat of the HCFCs and toxicity. However, new types and blends of refrigerant (some using CO₂) with minimal negative impacts are approaching the market as shown in Table 2. Because the GSHPs raise the temperature to around 40°C they are most suitable for underfloor heating systems or low-temperature radiators, which require temperatures of between 30° and 35°C. Higher outputs, such as to conventional radiators requiring higher temperatures of around 60° to 80°C can be obtained through use of the GSHP in combination with a conventional boiler or immersion heater.

![Figure 10. Heating and cooling operations.](image-url)
The GSHPs come in 15 models from 4 kW up to 30 kW (even up to 300 kW when connected in parallel). At least 65% of the heating and hot water energy consumption of a house can be saved (65–75% of heating costs with a heat pump) as a result of using such a system. However, sizing of the heat pump and the ground loops is essential for the efficient operation of the system. If sized correctly, a GSHP can be designed to meet 100% of space heating requirements. The sizing of the system is very sensitive to heat loads and should therefore be installed into properties with high-energy efficiency standards, particularly new build. It is a good and practical idea to explore ways of minimising space heating and hot water demand by incorporating energy efficiency measures (Figure 11). This is known as the saturation pressure-temperature relationship (Figure 12). The refrigerant exits the compressor as a hot vapour, which then goes into the earth loop field (Figure 13).

### Table 2. CO₂ emissions [15-16]

<table>
<thead>
<tr>
<th>System</th>
<th>Primary Energy Efficiency (%)</th>
<th>CO₂ emissions (kg CO₂/kWh heat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil fired boiler</td>
<td>60 – 65</td>
<td>0.45 – 0.48</td>
</tr>
<tr>
<td>Gas fired boiler</td>
<td>70 – 80</td>
<td>0.26 – 0.31</td>
</tr>
<tr>
<td>Condensing gas boiler + low temperature system</td>
<td>100</td>
<td>0.21</td>
</tr>
<tr>
<td>Electrical heating</td>
<td>36</td>
<td>0.9</td>
</tr>
<tr>
<td>Conventional electricity + GHSP</td>
<td>120-160</td>
<td>0.20-027</td>
</tr>
<tr>
<td>Green electricity + GHSP</td>
<td>300-400</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 11. Schematic of heat transfer through a circular tube heat exchanger.
3.1. Some Definitions

1) The word "Efficiency" is defined as the ratio of useful heat output to energy input, e.g., if an open fireplace loses half its energy up the chimney it is said to be 50% efficient.

2) The COP or "Coefficient of performance" is found by dividing the useful heat output by the energy input, e.g., a heat pump that produces 3 kWatts of heat for 1 kWatt of input power has a COP of 3. The open fireplace example with 50% efficiency would have a COP of 0.5 (1/2).

3) The heat "Source" is the outside air, river or ground, wherever the heat is being extracted from. Sometimes is referred to as an ambient source.
4) The “Sink” is the name given to the part where the heat is usefully dissipated, such as radiators in the room, underfloor heating, hot water cylinder, etc.

3.1.1. Horizontal Collector

This can be either coiled ‘Slinky’ or straight pipes that are buried 1.5 m to 2 m deep in open ground (in gardens). The pipe is usually plastic and contains a Glycol antifreeze solution.

3.1.2. Antifreeze

This is simply an additive to water that makes its freezing point lower. Common salt does the same thing, but Ethylene or Propylene Glycol is more practical for heat pump systems.

3.1.3. Refrigerant

This is the working fluid within the heat pump. It evaporates in one part and condenses in another. By doing so, heat is transferred from cold to hot. This fluid is sealed in and will not degrade within the heat pump’s life.

3.1.4. Heat Exchanger

This is a simple component that transfers heat from one fluid to another. It could be liquid-to-liquid, or liquid-to-air, or air-to-air. Two heat exchangers are housed within the heat pump, one for the hot side (the condenser), and one for the cold side (the evaporator).

3.1.5. Slinky

The name is given to the way that ground collector pipes can be coiled before buying in a trench.

3.1.6. Passive Heat Exchange

When waste hot water preheats cold input water, it is said to be ‘passive’. This costs nothing to run. A heat pump is said to be ‘active’ it can extract heat from cold waste water but requires a relatively small power input.

3.2. Some Refrigeration Characteristics

The seasonal energy efficiency ratio (SFEE) may be applied to each of the components.

Assuming that KE & PE effects are negligible, i.e., the SSFEE is applicable; vis

\[ Q + W = m \cdot h \]  \hspace{1cm} (9)

Compressor:

Compression assumed adiabatic:

\[ \cdot \cdot \cdot Q = 0 \]  \hspace{1cm} (10)

\[ W_{12} = m (h_2 - h_1) \]  \hspace{1cm} (11)

Or

\[ W_{in} = m (h_2 - h_1) \]  \hspace{1cm} (12)

Condenser:

\[ W_{23} = 0 \]  \hspace{1cm} (13)

\[ \cdot Q_{out} = m (h_2 - h_3) \]  \hspace{1cm} (14)
Expansion valve:
\[ W_{34} = 0 \text{ and } Q_{34} = 0 \]  \hspace{1cm} (15)
\[ h_3 = h_4 \]  \hspace{1cm} (16)

Evaporator:
\[ W_{41} = 0 \]  \hspace{1cm} (17)
\[ Q_{in} = m (h_1 - h_4) \]  \hspace{1cm} (18)

Refrigeration effect
It follows that:
\[ \text{COP}_{\text{ref}} = \frac{h_1 - h_3}{h_2 - h_1} \]  \hspace{1cm} (19)
\[ \text{COP}_{\text{hp}} = \frac{h_2 - h_3}{h_2 - h_1} \]  \hspace{1cm} (20)

In order to determine the above equations, the specific enthalpy values will be needed. Because refrigerants work in the liquid/vapour phases appropriate property charts or tables must be used.

![Figure 14. Refrigeration cycle.](image)

3.3. The Ideal Refrigeration Cycle
- Isentropic compression (1 ••• 2)
- Constant pressure cooling/condensation (2 ••• 3)
- Throttling (3 ••• 4)
- Constant pressure vaporisation/heating (4 ••• 1)

The ideal refrigeration cycle plotted on the p-h chart as shown in Figure 14.

3.4. Real Refrigeration Systems

Evaporator superheat
\[ g \text{ 1 given in } K \text{ above } T_{\text{sat}}(s) \]
3.4.1. Isentropic Compressor Efficiency

\[ \eta_{\text{isen}} = \frac{h_2' - h_1}{h_2 - h_1} \]  

(21)

3.4.2. Condenser Sub-cooling

NB: \( s_1 = s_2' \)

Figure 15. Evaporator superheat.

Figure 16. Isentropic compressor.

Figure 17. Condenser sub-cooling.
3.5. Refrigerant Properties (Charts and Tables)

Because refrigeration systems basically work between two pressures, and specific enthalpy is one of the most useful properties we need, refrigerant thermodynamic properties are normally presented in the form of a pressure - specific enthalpy (or p-h) chart.

This is done for convenience, and is simply an alternative way of presenting property data, instead of, e.g., p-V, or T-s, or h-s (Figures 15-17).

Other useful properties are also shown on the chart, vis: specific entropy, specific volume, temperature and quality. Regard these properties as 'contours'.

The pressure axis (y-axis) is typically logarithmic.

3.6. Pressure Drops in Evaporator and Condenser

Clearly, any or all of the above effects can be present, but the pressure drops are often small enough to be neglected (Figure 18).

3.7. Refrigeration System Performance Improvement

Liquid-Suction heat exchanger (Figure 19-20)

Assuming no losses:

\[ H_{1b} - h_{1a} = h_{3a} - h_{3b} \] (22)
Figure 19. Diagram of liquid-suction heat exchanger.

Figure 20. Liquid-suction heat exchanger cycle.
3.8. Multiple Compression Using Flash Chambers

![Diagram of multiple compressions using flash chamber.](image)

Figure 21. Cycle of multiple compressions using flash chamber.

3.9. Diagram of Multiple Compressions Using Flash Chamber

At point 3a, have a mixture of vapour and liquid, which is separated, in the flash chamber (Figure 21). The proportion of the total mass flow that is liquid (and proceeds to the evaporator) is given by:

\[ x_f = \frac{h_3(g) - h_3(l)}{h_3(g) - h_3(f)} \]  

(23)

The remaining vapour mixes with the discharge from the first stage compressor to give different inlet conditions to the second stage.

Assuming adiabatic mixing:

\[ 1^* h_{2b} = x_t h_{2a} + (1-x_t) h_3(g) \]  

(24)

A similar equation can be used to find \( s_{2b} \).

Finally, the COP is given by:

\[ \text{COP} = \frac{x_t (h_1-h_4))}{(x_t (h_{2a}-h_1) + (h_2-h_{2b}))} \]  

(25)

4. Discussions

Thermal comfort is an important aspect of human life. Buildings where people work require lighter than buildings where people live. In buildings where people live the energy is used for maintaining both the temperature and lighting. Hence, natural ventilation is rapidly becoming a significant part in the design strategy for non-domestic buildings because of its potential to reduce the environmental impact of building operation, due to lower energy demand for cooling. A traditional, naturally ventilated building can readily provide a high ventilation rate. On the other hand, the mechanical ventilation systems are very expensive. However, a comprehensive ecological concept can be developed to achieve a reduction of electrical and heating energy consumption, optimise natural air condition and ventilation, improve the use of daylight and choose environmentally adequate building materials [17]. Energy efficiency brings health, productivity, safety, comfort and savings to homeowner, as well as local and global environmental benefits. The use of renewable energy resources could play an important role
in this context, especially with regard to responsible and sustainable development. It represents an excellent opportunity to offer a higher standard of living to local people and will save local and regional resources. Implementation of greenhouses offers a chance for maintenance and repair services. It is expected that the pace of implementation will increase and the quality of work to improve in addition to building the capacity of the private and district staff in contracting procedures. The financial accountability is important and more transparent. Various passive techniques have been put in perspective, and energy saving passive strategies can be seen to reduce interior temperature and increase thermal comfort, and reducing air conditioning loads. The scheme can also be employed to analyse the marginal contribution of each specific passive measure working under realistic conditions in combination with the other housing elements. In regions where heating is important during winter months, the use of top-light solar passive strategies for spaces without an equator-facing façade can efficiently reduce energy consumption for heating, lighting and ventilation. The use of renewable energy resources could play an important role in this context, especially with regard to responsible and sustainable development. It represents an excellent opportunity to offer a higher standard of living to local people and will save local and regional resources. Implementation of greenhouses offers a chance for maintenance and repair services. Various passive techniques have been put in perspective, and energy saving passive strategies can be seen to reduce interior temperature and increase thermal comfort, and reducing air conditioning loads [18].

Renewable energy is the term to describe a wide range of naturally occurring, and replenishing energy sources. The use of renewable energy sources and the rational use of energy are the fundamental inputs for a responsible energy policy. The energy sector is encountering difficulties because increased production and consumption levels entail higher levels of pollution and eventually climate changes, with possibly disastrous consequences. Moreover, it is important to secure energy at acceptable cost to avoid negative impacts on economic growth. On the technological side, renewables have an obvious role to play. In general, there is no problem in terms of the technical potential of renewables to deliver energy and there are very good opportunities for renewable energy technologies to play an important role in reducing emissions of greenhouse gases into the atmosphere—certainly far more than have been exploited so far. But there are still technical issues to be addressed to cope with the intermittency of some renewables, particularly wind and solar. However, the biggest problem with relying on renewables to deliver the necessary cuts in greenhouse gas emissions is more to do with politics and policy issues than with technical ones. The single most important step governments could take to promote and increase the use of renewables would be to improve access for renewables to the energy market. That access to the market would need to be under favourable conditions and possibly under favourable economic rates.

One move that could help—or at least justify-better market access would be to acknowledge that there are environmental costs associated with other energy supply options, and that these costs are not currently internalised within the market price of electricity or fuels. It could make significant difference, particularly if, appropriate subsidies were applied to renewable energy in recognition of environmental benefits it offers. Cutting energy consumption through end-use efficiency is absolutely essential. And this suggests that issues of end-use consumption of energy will have to come onto the table in the foreseeable future [19].

The scientific consensus is clear—climate change is occurring. Existing renewable energy technologies could play a significant mitigating role, but the economic and political climate will have to change first. Climate change is real, it is happening now, and greenhouse gases produced by human activities are significantly contributing to it. The predicted global temperature changes of between 1.5- and 4.5-degrees C could lead to potentially catastrophic environmental impacts—including sea level rise, increased frequency of extreme weather events, floods, droughts, disease migration from various places and possible stalling of the Gulf stream. This is why scientists argue that climate change issues are not ones that politicians can afford to ignore. And policy makers tend to agree, but reaching international agreements on climate change policies is no trivial task.

The most favourable orientation, which is due north, results in diminished excessive solar gains through the windows. However, most buildings cannot be oriented at will. If the only possible orientation is due south, and no external shade is used, the index reveals extra heat gains of some 0.26 over the value of totally shaded window. Application of the model results from exploring the relative importance of the thermal inertia of walls, floor and ceiling. Heat stored in building materials, as proven in old, massive buildings, can be compensated
during high insolation hours with thermal losses at night and early morning hours, when ambient temperatures are below 25°C. Temperature variation will be lower for higher thermal capacities of building materials. However, it is known while thermal capacity increases the relative importance of individual heat flows change. For example, for lower wall temperatures, the contribution of radiative heat transfer will be reduced, and the relative importance of convective processes will increase, and thus the difficulty to calculate accurately the overall heat flows. The relevance of certain passive techniques is variable with prevailing weather [20].

Finally, the required temperature dependent air transport properties were evaluated by the following expression, which are valid between 2°C and 77°C with temperature expressed in k:

Thermal diffusivity, $\alpha = 1.534 \times 10^{-3} T – 0.2386 \ (10^{-4} \text{m}^2\text{s}^{-1})$

Kinematics viscosity, $\nu = 0.1016 T – 14.8 \ (10^{-6} \text{m}^2\text{s}^{-1})$

Thermal conductivity, $k = 7.58 \times 10^{-5} T + 3.5 \times 10^{-3} \ (\text{Wm}^{-1}\text{K}^{-1})$, and

Thermal expansion coefficient, $\beta = T^{-1} \ (\text{K}^{-1})$

In order to depict the relative contribution of each of these techniques to inside temperature, a dimensionless index is defined as follows. When interior temperature exceeds 25°C, it will be considered as a temperature discomfort condition. This reference temperature is widely elements. Then the following expression:

$$F(t) = \max (T_t – 25.25)$$  \hspace{1cm} (26)

$I$, a time function of truncated temperature and it will be able to estimate the overall discomfort by means of the integration along the day for each different scenarios $S$:

$$A(S) = \int S F(t) \ dt$$  \hspace{1cm} (27)

Then, for each passive technique, let:

$$A_{\max} = \max [A(S): \text{for all scenarios } S]$$  \hspace{1cm} (28)

Finally, the normalised temperature index for each scenario $S$ is:

$$I(S) = A(S)/A_{\max}$$  \hspace{1cm} (29)

Naturally, it would be preferred, for comfort reasons that this index would be small, preferably nil. It may be seen that the variable is directly related to temperature discomfort: the larger the value of the index, the farthest will inside conditions be from expected wellbeing. Also, the use of electricity operated air conditioning systems will be more expensive the higher this variable is. Hence, energy expenditure to offset discomfort will be higher when comparing two index values; the ratio of them is proportional to the expected energy savings [21]. When the external shade blocks the windowpane completely, the excessive heat gains belong to the lowest values in the set, and the dimensionless index will be constant with orientation. For the climate conditions of the locality, it can be seen that a naked window can produce undesirable heat gains if the orientation is especially unfavourable, when the index can have an increase of up to 0.3 with respect to the totally shaded window.

Conclusion

With increasing worldwide awareness of the serious environmental problems due to fossil fuel consumption, efforts are being made to develop energy efficient and environmentally friendly systems by utilisation of non-polluting renewable energy sources, such as solar energy, industrial waste heat or geothermal water. The GSHPs are suitable for heating and cooling of buildings and so could play a significant role in reducing CO₂ emissions. Ground source or geothermal heat pumps are a highly efficient, renewable energy technology for space heating
and cooling. This technology relies on the fact that, at depth, the Earth has a relatively constant temperature, warmer than the air in winter and cooler than the air in summer.

A geothermal heat pump can transfer heat stored in the earth into a building during the winter, and transfer heat out of the building during the summer. Furthermore, special geological conditions, such as hot springs, are not needed for successful application of geothermal heat pumps. The GSHPs are receiving increasing interest because of their potential to reduce primary energy consumption and thus reduce emissions of the GHGs. The GSHP is generally recognised to be one of the most outstanding technologies of heating and cooling in both residential and commercial buildings, because it provides high coefficient of performance (COP), up to 3-4 for an indirect heating system and 3.5-5 for a direct heating system.

The main benefit of using the GSHPs is that the temperature of the subsurface is not subject to large variations experienced by air. It is currently the most common thermal energy source for the heat pumps, and so would allow construction of more efficient systems with superior performance. The GSHPs do not need large cooling towers and their running costs are lower than conventional heating and air conditioning systems. As a result, the GSHPs have increasingly been used for building heating and cooling with annual rate of increase of 10% in recent years.

References


**Nomenclatures**

- **ACH** Air changes per hour
- **GSHP** Ground source heat pump
- **HRV** Heat recovery ventilator
- **PRT** Platinum resistance thermometer
- **1** condenser/heating
- **2** evaporators
- **a** air
- **b** brine
- **c** coil
- **cp** Specified heat at constant pressure (kJ/kg K)
- **Dp** dew point
- **e** electricity for other uses
- **f** fan
h  Enthalpy (kJ/kg)
hp  heat pump
hps  heat pump system
hpsf  hps plus fan-coil heater
g  Local acceleration of gravity (m/s²)
i  inlet
L  latent
m  means, motor
o  outlet
o/d  outdoor
R  radius
p  pump
S  sensible
tot  total
DC  Direct current
HSPF  Heating season performance factor
SEER  Seasonal energy efficiency ratio
Btu  British thermal unit
COP  Coefficient of performance (%)
N  Air change per hour (ACH) (h⁻¹)
P  Pressure (Pa) (kPa)
Q  Heat (thermal energy) (J)
Qc  Capacity (thermal power) (W)
t  Temperature (Celsius) (°C)
T  Temperature (thermodynamic) (K)
V  Volume (m³)
Vf  Volume flow (m³/s)
W  Work (mechanical or electric) (J)
Wp  Power (mechanical or electric) (W)
η  Efficiency (%)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>Relative vapour pressure (%)</td>
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<tr>
<td>λ</td>
<td>Thermal conductivity (W/m/K)</td>
</tr>
<tr>
<td>ρ</td>
<td>Density (kg/m³)</td>
</tr>
<tr>
<td>τ</td>
<td>Time (h.min.s)</td>
</tr>
<tr>
<td>GHP</td>
<td>Geothermal heat pump</td>
</tr>
<tr>
<td>GL</td>
<td>Ground loop</td>
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<tr>
<td>GSHP</td>
<td>Ground source heat pump</td>
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Synthesis, Crystal Structure and Antimicrobial Properties of 1-Diphenylmethylpiperazine-1,4-Diium Tetrachloridocuprate

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Abstract

New organic/inorganic hybrid (C17H22N2)[CuCl4] was elaborated and studied by single crystal X-ray diffraction. The compound crystallizes in the orthorhombic Pbca space group. The isolated [CuCl4]2− tetrahedra are slightly distorted building a 0-D anionic framework. The double protonation of the organic cation establish N—H···Cl interactions between organic and inorganic moieties leading to self-organized structure. Infrared, UV-Visible and photoluminescence studies were carried out. The in-vitro antibacterial and antifungal activity of the title salt against several microorganisms were studied. The purity of the material was controlled by Rietveld analysis based on structural investigations and X-ray powder diffraction.

Keywords: Crystal structure, DRX, copper, 1-diphenylmethylpiperazine, hybrid material, infrared spectroscopy, antimicrobial activity, RDA

1. Introduction

Hybrid materials are widely used in various fields [1]. The main application is as semiconductors [2] and luminescent materials [3]. This kind of materials is also seen as antimicrobial compounds [4-7]. Otherwise, copper is known for its biological activity [8]. Mixing copper behavior to the new generation of materials leads to a good candidate of copper halides that arouse great interest in diverse fields in biology as anticancer and antifungal [9]. The study of anti-ferromagnetic complexes of these low dimensional molecular magnetic lattices was widely carried out [10-12]. Copper halides are considerably studied because of the particularity of copper geometry. The choice of the organic cation plays a crucial role in the environment around anion through weak interactions as Van der Waals and hydrogen bonding. In this work, the synthesis and the crystal structure of a new tetrachloridocuprate stabilized by the 1-diphenylmethylpiperazin-1,4-diium organic cation is presented. The antimicrobial activity of the title compound is exposed using the Radial Diffusion Assay (RDA).

2. Synthesis and crystallization

The salt was prepared by reaction of 1-diphenylmethylpiperazine and Cu(NO3)2.3H2O (molar ratio 1:1) in an equal volume water-ethanol (10mL) mixed to 3 mL of hydrochloric acid 37%. The solution was stirred for one hour at 333K. After two weeks, single yellow crystals suitable for X-ray diffraction were grown by slow evaporation at room temperature.

3. X-ray structure determination

A yellow crystal has been selected for X-ray diffraction analysis. Data collection was performed on an Enraf-Nonius CAD-4 diffractometer, operating at 298 K with (Mo Kα radiation, λ= 0.71069Å). CAD4-Express program [13] was used to integrate the reflection intensities. An empirical ψ-scan absorption correction was applied [14]. The structure has been solved by direct methods using SHELXS-2014 software [15] and refined by least-square full-matrix based on F² using SHELXL-2014 software [16]. A summary of the crystallographic data and structural
determination is provided in Table 1. The final reduced atomic coordinates and the equivalent thermal factors are listed in Table 2. The hydrogen atoms were located using the riding model. The program DIAMOND version 3.0 [17] was used for molecular graphics. The complete set of the structural parameters in CIF format is available from the Cambridge Crystallographic Database Centre (CCDC 1852657). A copy can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif or deposit@ccdc.edu.

**Table 1.** Crystallographic data and refinement parameters in the crystal structure of C_{17}H_{22}N_{2}CuCl_{4}.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th></th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{17}H_{22}N_{2}CuCl_{4}</td>
</tr>
<tr>
<td>Molecular weight (g.mol^{-1})</td>
<td>459.70</td>
</tr>
<tr>
<td>Crystal System / Space Group</td>
<td>Orthorhombic / Pbc a</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298</td>
</tr>
<tr>
<td>a, b, c (Å) / V (Å^3)</td>
<td>10.8971 (10), 13.343 (2), 26.909 (3) / 3912.5 (8)</td>
</tr>
<tr>
<td>Crystal shape / color</td>
<td>Prism / Yellow</td>
</tr>
<tr>
<td>Crystal colour</td>
<td>Yellow</td>
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<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>D_\alpha (Mg m^{-3})</td>
<td>1.561</td>
</tr>
<tr>
<td>\mu (mm^{-1})</td>
<td>1.66</td>
</tr>
</tbody>
</table>

**Data collection**

| Diffractometer | Enraf Nonius CAD4 |
| Absorption correction | \psi scan |
| Monochromator | Graphite |
| Radiation type \(\lambda(\AA)\) | Mo K\(\alpha\) 0.71073 |
| Measured reflections | 6822 |
| Observed reflections | 1867 |
| Independent reflections | 4249 |
| Variation of indices hkl | h = −13 to 5  k = −1 to 17  l = −1 to 34 |

**Refinement**

| R[F^2 > 2\sigma(F^2)] | 0.062 |
| wR(F^2) | 0.219 |
| S | 0.98 |
| Parameters | 217 |
| \(\Delta\rho_{max}, \Delta\rho_{min}\) (e Å^{-3}) | 0.63, −0.50 |
Table 2. Coordinates and isotropic displacement parameters ($\AA^2$) of atoms in the crystal structure of $C_{17}H_{22}N_2CuCl_4$.

<table>
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<tr>
<th>Atom</th>
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<td>H15B</td>
<td>0.37601</td>
<td>0.17702</td>
<td>0.18829</td>
<td>0.07</td>
</tr>
<tr>
<td>C16</td>
<td>0.35190(71)</td>
<td>0.36592(62)</td>
<td>0.22416(26)</td>
<td>0.05277(195)</td>
</tr>
<tr>
<td>H16A</td>
<td>0.37305</td>
<td>0.41916</td>
<td>0.24716</td>
<td>0.064</td>
</tr>
<tr>
<td>H16B</td>
<td>0.28650</td>
<td>0.32668</td>
<td>0.23897</td>
<td>0.064</td>
</tr>
<tr>
<td>N2</td>
<td>0.46057(57)</td>
<td>0.30092(46)</td>
<td>0.21630(23)</td>
<td>0.05303(165)</td>
</tr>
<tr>
<td>H2A</td>
<td>0.47914</td>
<td>0.26992</td>
<td>0.24460</td>
<td>0.064</td>
</tr>
<tr>
<td>H2B</td>
<td>0.52446</td>
<td>0.33862</td>
<td>0.20764</td>
<td>0.064</td>
</tr>
<tr>
<td>C17</td>
<td>0.30754(66)</td>
<td>0.41064(51)</td>
<td>0.17692(23)</td>
<td>0.04143(170)</td>
</tr>
<tr>
<td>H17A</td>
<td>0.36871</td>
<td>0.45741</td>
<td>0.16476</td>
<td>0.05</td>
</tr>
<tr>
<td>H17B</td>
<td>0.23306</td>
<td>0.44818</td>
<td>0.18350</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 3. Characteristic of the hydrogen bonds in the crystal structure of C$_{17}$H$_{22}$N$_2$CuCl$_4$.

<table>
<thead>
<tr>
<th></th>
<th>D—H</th>
<th>H—A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H1A···Cl$^\text{i}$</td>
<td>0.980</td>
<td>2.249</td>
<td>3.206(6)</td>
<td>165.32</td>
</tr>
<tr>
<td>N2—H2C···Cl$^\text{iii}$</td>
<td>0.890</td>
<td>2.420</td>
<td>3.271(6)</td>
<td>160.25</td>
</tr>
<tr>
<td>N2—H2D···Cl$^\text{iii}$</td>
<td>0.890</td>
<td>2.385</td>
<td>3.154(6)</td>
<td>144.84</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x-1/2, y, -z+1/2; (ii) x-1, y+1/2, -z+1/2.

Table 4. Selected bond lengths (Å) and angles (°) in the crystal structure of C$_{17}$H$_{22}$N$_2$CuCl$_4$.

<table>
<thead>
<tr>
<th></th>
<th>Cu—Cl1</th>
<th>C8—C13</th>
<th>1.373 (9)</th>
</tr>
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<tbody>
<tr>
<td>Cu—Cl2</td>
<td>2.418 (2)</td>
<td>C8—C9</td>
<td>1.393 (9)</td>
</tr>
<tr>
<td>Cu—Cl3</td>
<td>2.204 (2)</td>
<td>C8—C1</td>
<td>1.507 (9)</td>
</tr>
<tr>
<td>Cu—Cl4</td>
<td>2.179 (2)</td>
<td>C9—C10</td>
<td>1.371 (10)</td>
</tr>
<tr>
<td>N1—C1</td>
<td>1.526 (8)</td>
<td>C2—C3</td>
<td>1.386 (9)</td>
</tr>
<tr>
<td>N1—C14</td>
<td>1.505 (8)</td>
<td>C10—C11</td>
<td>1.346 (11)</td>
</tr>
<tr>
<td>N1—C17</td>
<td>1.488 (8)</td>
<td>C2—C7</td>
<td>1.392 (10)</td>
</tr>
<tr>
<td>C2—C1</td>
<td>1.493 (9)</td>
<td>C6—C7</td>
<td>1.372 (10)</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.347 (10)</td>
<td>C12—C13</td>
<td>1.377 (10)</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.371 (11)</td>
<td>C14—C15</td>
<td>1.479 (10)</td>
</tr>
<tr>
<td>C5—C6</td>
<td>1.373 (10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl4—Cu—Cl1</td>
<td>108.85 (10)</td>
<td>C7—C6—C5</td>
<td>119.6 (7)</td>
</tr>
<tr>
<td>Cl4—Cu—Cl3</td>
<td>127.92 (9)</td>
<td>C2—C1—C8</td>
<td>111.2 (5)</td>
</tr>
<tr>
<td>Cl1—Cu—Cl3</td>
<td>105.61 (10)</td>
<td>C2—C1—N1</td>
<td>112.2 (5)</td>
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<tr>
<td>Cl4—Cu—Cl2</td>
<td>102.13 (8)</td>
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<tr>
<td>Cl1—Cu—Cl2</td>
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<td>C8—C1—N1</td>
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<tr>
<td>Cl3—Cu—Cl2</td>
<td>104.62 (8)</td>
<td>C15—C14—N1</td>
<td>112.4 (6)</td>
</tr>
<tr>
<td>C17—N1—C14</td>
<td>109.7 (5)</td>
<td>C14—C15—N2</td>
<td>111.9 (6)</td>
</tr>
<tr>
<td>C17—N1—C1</td>
<td>112.8 (5)</td>
<td>C16—C17—N1</td>
<td>113.3 (6)</td>
</tr>
<tr>
<td>C14—N1—C1</td>
<td>111.4 (5)</td>
<td>N2—C16—C17</td>
<td>111.9 (6)</td>
</tr>
<tr>
<td>C3—C2—C7</td>
<td>117.3 (7)</td>
<td>C16—N2—C15</td>
<td>111.3 (5)</td>
</tr>
<tr>
<td>C3—C2—C1</td>
<td>119.4 (6)</td>
<td>C9—C8—C1</td>
<td>115.3 (6)</td>
</tr>
<tr>
<td>C7—C2—C1</td>
<td>123.2 (6)</td>
<td>C10—C9—C8</td>
<td>120.2 (7)</td>
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<tr>
<td>C4—C3—C2</td>
<td>121.4 (7)</td>
<td>C11—C10—C9</td>
<td>120.8 (7)</td>
</tr>
<tr>
<td>C3—C4—C5</td>
<td>120.7 (8)</td>
<td>C10—C11—C12</td>
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</tr>
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<td>C4—C5—C6</td>
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<td>C13—C8—C9</td>
<td>118.0 (6)</td>
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<tr>
<td>C6—C7—C2</td>
<td>121.2 (7)</td>
<td>C13—C12—C11</td>
<td>118.7 (7)</td>
</tr>
</tbody>
</table>
4. Structural description

The asymmetric unit of the crystal structure, represented in Figure 1, is built up by one tetrahedron \([\text{CuCl}_4]^2-\) and one organic cation from diphenylmethylpiperazine doubly protonated.

Several geometries can be adopted when using copper coordinated to halogens anions. Including tetrahedral, square pyramidal, square planar and square-bipyramidal [19, 20] we can also find copper in octahedral geometry. This diversity allows copper halides to be a good candidate in the class of self-organized organic-inorganic hybrid compounds [12].

As shown in Figure 2, the environment around the anion can be described by a tetrahedron of \([\text{CuCl}_4]^2-\) surrounded by three organic ligands of diphenylmethylpiperazine linked through hydrogen bonds. The double protonation of the diphenylmethylpiperazine establish bridges between \([\text{CuCl}_4]^2-\) and the organic moieties. In agreement with the angular values of the copper-chlorine bonds summarized in the table 3, the tetrahedral copper coordination presents a slight distortion plausibly due to the hydrogen bridges N—H···Cl and particularly the result of the Jahn Teller effect.

As represented in the Figure 3, the cationic environment is revealing the protonation of organic moiety involving the couple of nitrogen’s of diphenylmethylpiperazine in hydrogen bonding with Cl1 and Cl3 vertices. Each cation of \((\text{C}_{17}\text{H}_{22}\text{N}_2)^{2+}\) is linked to three tetrahedra of \([\text{CuCl}_4]^2-\). The \((\text{C}_{17}\text{H}_{22}\text{N}_2)^{2+}\) cation adopts a chair conformation for piperazinium and a quite planar conformation for the two cyclces of phenyl characterized by a slight r.m.s deviation 0.0028(4) Å for the first cycle the maximum deviations are for C9 and -0.004(6) Å for C8. The second cycle represents almost the same r.m.s deviation with 0.004(5) Å for C17 and -0.003(6) Å for C16 as maximum deviations.

The organic chains are spread along the c axis forming parallel waved chains running along the b direction. The Figure 4, reveals that these chains are arranged parallel to a twofold screw axis parallel to a direction alternated with \([\text{CuCl}_4]^2-\) tetrahedra. The isolated \([\text{CuCl}_4]^2-\) tetrahedra classes this compound among the 0-D hybrid materials.

Along the b direction (Figure 5), the steric hindrance avoid the presence of voids in this structure even so, we can see that the shape of the organic moieties prohibits to inorganic tetrahedra to be spread away. The shape of organic moieties suggests that we can lodge small entities that may bring new behavior to this material.

In fact, hydrogen bonding and (π-π) stacking are the most important links in metal halides ensuring cohesion and stabilizing the crystal packing through bridges built between the organic and inorganic subnetworks.

For organic molecules an infrequent (π-π) mode of stacking is observed. In fact these interactions are essential for building framework and impacting on properties of metal halide materials. In the title salt, the anionic environment can be described by \([\text{CuCl}_4]^2-\) tetrahedron linked to three organic cations of 1-diphenylmethylpiperazine-1.4-dium via Cl1 and Cl3 vertices as N1—H1A···Cl3, N2—H2C···Cl3 and N2—H2D···Cl1.

Cationic environment is made up by one molecule of 1-dimethylphenylpiperazine-1.4-dium surrounded by three \([\text{CuCl}_4]^2-\) tetrahedra. The organic molecules are connected through (π-π) stacking by edge-to-face mode. The centroid distance Cg1...Cg2 is about 4.674(1) Å calculated for the two phenylic cycles in the same cation and around 4.954(1) Å measured for two independent cations.
Figure 1: ORTEP of the asymmetric unit in the crystal structure of C\textsubscript{17}H\textsubscript{22}N\textsubscript{2}CuCl\textsubscript{4}. Displacement ellipsoids at drawn with 50% probability level.

Figure 2. The hydrogen interaction around [CuCl\textsubscript{4}]\textsuperscript{2–} in the crystal structure of C\textsubscript{17}H\textsubscript{22}N\textsubscript{2}CuCl\textsubscript{4} shown as dashed lines. Displacement ellipsoids are displayed at the 50% probability level. Symmetry codes: (i) –x, y–1/2, –z+1/2; (ii) –x+1/2, y–1/2, z.

Figure 3: The environment around the (C\textsubscript{17}H\textsubscript{22}N\textsubscript{2})\textsuperscript{2+} cation showing hydrogen bridging in the crystal structure of C\textsubscript{17}H\textsubscript{22}N\textsubscript{2}CuCl\textsubscript{4}. Symmetry codes: (i) –x, y–1/2, –z+1/2; (ii) –x+1/2, y–1/2, z.
Figure 4: Self organized assembly system in the crystal structure of C$_{17}$H$_{22}$N$_{2}$CuCl$_{4}$ showing the alternate arrangement of organic-inorganic sheets.

Figure 5: Steric hindrance of organic cations in the crystal structure of C$_{17}$H$_{22}$N$_{2}$CuCl$_{4}$.

5. Spectroscopic study

Trying to explore the vibrational and the electronic transitional activities in the studied structure, three spectroscopic experimental investigations were carried out, the InfraRed (IR), the UV-visible and the Photoluminescence (PL). In addition, theoretical calculations were performed using the program CaChe [22], to identify the High Occupied Molecular Orbital and the Low Unoccupied Molecular Orbital (HOMO-LUMO) orbital’s energy and evaluate the HOMO-LUMO gap.

5.1. Infrared spectroscopy

The infrared (IR) absorption frequencies of the compound C$_{17}$H$_{22}$N$_{2}$CuCl$_{4}$ were studied using the FT–IR Bruker Tensor 27 spectrophotometer in the range of 1400–400 cm$^{-1}$ wavenumber containing the most significant solid state absorption bands. The sample was ground with 98% weight KBr and pressed into 1cm diameter discs. Calculated IR spectrum was realized using PM3 FORCE method implemented in the CAChe program [22]. Compared to the observed spectrum the calculated one exhibits a shift towards the high frequencies which can be explained by the choice of the computational method using the PM3 FORCE in our case did not rigorously apply the effect of the electronic correlation. This semi-empirical calculation method assumes that the molecules are isolated when they are actually involved in hydrogen bonds or in other electronic interactions. The calculated and observed IR spectra of this compound are presented in Figure 6a and 6b respectively.
Table 5. Observed and calculated vibration frequencies (cm\(^{-1}\)) in the crystal structure of \(\text{C}_{17}\text{H}_{22}\text{N}_2\text{CuCl}_4\) with proposed assignments.

<table>
<thead>
<tr>
<th>Observed</th>
<th>calculated</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>752</td>
<td>800</td>
<td>(\delta_{\text{C-N-C}})</td>
</tr>
<tr>
<td>1385</td>
<td>1500</td>
<td>(\nu_{\text{C-N}})</td>
</tr>
<tr>
<td>1623</td>
<td>1800</td>
<td>(\nu_{\text{C=C}/\delta_{\text{N-H}}})</td>
</tr>
<tr>
<td>3127</td>
<td>-</td>
<td>(\nu_{\text{C-H}})</td>
</tr>
<tr>
<td>3650</td>
<td>3500</td>
<td>(\nu_{\text{N-H}})</td>
</tr>
</tbody>
</table>

Figure 6. (a) Calculated and (b) Observed Infrared spectra of the crystal structure of \(\text{C}_{17}\text{H}_{22}\text{N}_2\text{CuCl}_4\).

5.2. UV-visible

Using a Perkin Elmer lambda950 spectrophotometer scanning the UV-visible spectral domain, the crystalline sample was ground in an agate mortar. A pinch of the compound was added to a water drop and kept drying at room temperature for several minutes. The absorbance registered spectrum represented in Figure 7. exhibits three particular wavelengths 321, 455 and 782 nm assigned respectively to the transition \(\pi-\pi^*\) of the organic cation \((\text{C}_{17}\text{H}_{22}\text{N}_2)^{2+}\), the ligand-metal charge transfer (LMCT) and to the d-d copper transition of the anionic inorganic cluster \(\text{CuCl}_4\).
Figure 7. UV-Visible absorption spectrum of $\text{C}_{17}\text{H}_{22}\text{N}_{2}\text{CuCl}_4$.

5.3. Photoluminescence

Using a Perkin-Elmer LS 55 luminescent spectrophotometer equipped with a 250nm exciting luminous radiation, the crystalline sample was like for the UV-visible experiment.

The emission spectrum of the studied compound represented in Figure 8. reveals three bands elucidated after a deconvolution realised by the program Origin 9.0 [24] using a Gaussian profile without considering any background. The first one (red) centred on 380 nm related to the d-d copper transition [25-26]. The second one (green) with 487 nm can be attributed to the organic cation emission [27]. The last and most intense one (533 nm) can be assigned to an electronic transition.

Figure 8. Photoluminescent emission spectrum of $\text{C}_{17}\text{H}_{22}\text{N}_{2}\text{CuCl}_4$. 
5.4. HOMO-LUMO gap calculation

The Discrete Fourier Transform DFT’s calculations were carried out by the program CaChe [22] using the semi-empirical Parameterized Model number 3 (PM3) for the title compound. The graphical representation calculated on Figure 9 is showing the orbitals frontiers in $C_{17}H_{22}N_2CuCl_4$. Located on the inorganic moiety, the HOMO exhibits the highest contribution compared to the LOMO identified on the organic cation. The gap deduced from the simulation is 1.373 eV. The studied material can be ranged among the copper based semiconductors hybrids.

![Figure 9. Photoluminescent emission spectrum of $C_{17}H_{22}N_2CuCl_4$.](image)

6. Analysis of DPMPD-TCC antimicrobial activity

The antimicrobial activity of the 1-diphenylmethylpiperazine-1, 4-diium tetrachloridocuprate DPMPD-TCC salt was determined using the Radial Diffusion Assay (RDA)[18] toward different Gram negative (Salmonella enterica and Shigella flexneri) and Gram positive (Enterococcus fecalis, Staphylococcus aureus and Bacillus cereus) bacteria, as well as, Human pathogenic fungi of Candida (C. albicans, C. parapsilosis and C. sakei). Sabouraud agar and Tryptic Soya Agar media were used for the growth of fungi and bacteria respectively.

Minimal inhibitory concentration (MIC), which corresponds to the lowest concentration exhibiting microbial growth inhibition, was evaluated by the same method using different concentration of the compound.

The bioactive compound $C_{17}H_{22}N_2CuCl_4$ exhibited growth inhibition only toward Gram positive bacteria. Enterococcus fecalis was found to be the most sensitive strain with an inhibition zone diameter of 12mm and a MIC of 0.2 mg/ml. While the MIC of Staphylococcus aureus and Bacillus cereus was 0.5 mg/ml (Table 6).

**Table 6.** Diameter of inhibition and minimal inhibitory concentration (MIC) of organisms for ($C_{17}H_{22}N_2$)$_4$[CuCl$_4$].

<table>
<thead>
<tr>
<th>Organism</th>
<th>Diameter of inhibition (mm)</th>
<th>Minimal inhibitory concentration (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candida albicans</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Candida parapsilosis</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Candida sake</td>
<td>7</td>
<td>0.2</td>
</tr>
<tr>
<td>Enterococcus fecalis</td>
<td>12</td>
<td>0.2</td>
</tr>
<tr>
<td>Bacillus cereus</td>
<td>8</td>
<td>0.5</td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
<td>8</td>
<td>0.2</td>
</tr>
<tr>
<td>Salmonella enterica</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Shigella flexneri</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>
* The mentioned diameter of the growth inhibition zones corresponds to a concentration of 1mg/ml of the compound.

The absence of inhibitory effect recorded against Gram negative bacteria may be explained by the presence of the outer membrane in the bacterial cell wall of Gram negative bacteria acting as a barrier for some antibiotics and other compounds and giving them a particular rigidity [21]

As for the human pathogenic fungi the best inhibitory activity was observed for C. sake (8mm), with a MIC of 0.2mg/ml, followed by C. albicans and C. parapsilosis with a growth inhibition zones of 6 and 4mm respectively (Figure 10)

![Evaluation of antimicrobial activity](image)

**Figure 10:** Antimicrobial activity of C\textsubscript{17}H\textsubscript{22}N\textsubscript{2}CuCl\textsubscript{4} (1mg/ml).

### 7. X-ray powder diffraction

Trying to know if the chemical synthesis is leading to pure sample the X-ray powder diffraction (XRPD) experiment was carried out using a D8 ADVANCE Bruker diffractometer equipped with Bragg-Brentano geometry and Lynxeye accelerator using Cu(K\(\alpha_1/\alpha_2\) = 1.54060/1.54439 \(\text{Å}\)) wavelength with step-scanning (\(\Delta\theta = 0.02^\circ\)), a constant time interval of 0.018 s and \(2\theta\) scanning range of [5-70] \(^\circ\).

Based on the structural data and the observed powder diffraction pattern the Rietveld study was performed using TOPAS 4.2. [23]. The calculated raw diffraction is compared to the observed one using the curve difference. The study reveals a high purity of the sample since all the Bragg pics are indexed by the crystallographic data of the studied compound confirmed by the reliability factors and the \(\chi^2\) value visible on Figure 11. Thus, the observed physical behavior of the sample can be attributed to the studied structure of C\textsubscript{17}H\textsubscript{22}N\textsubscript{2}CuCl\textsubscript{4}. Nevertheless, a consistent amorphous fraction is noted in the mixture by the presence of a diffuse and very large reflection centered around 14\(^\circ\). The thin and sharp observed reflections proof the high crystallinity of the compound.
4. Conclusion

A new salt around copper was synthesized and grown by slow evaporation. The title salt crystallizes in the orthorhombic Pbca space group. The X-ray diffraction study reveals a 0-D hybrid structure self-organized in alternating sheets of organic and inorganic moieties linked through hydrogen interactions ensuring the crystal packing cohesion. The anionic moiety \([\text{CuCl}_4]^2-\) is surrounded by three organic cations \((\text{C}_{17}\text{H}_{22}\text{N}_2)^2+\) through hydrogen bridging and \((\pi-\pi)\) stacking. Spectroscopic investigations combined to the PM3 semi-empirical simulation facilitate the assignment of the observed IR absorption bands to the vibration frequencies, the interpretation of the UV-Visible spectrum and the photoluminescence emission. The antimicrobial study results show that the salt acts only against gram positive bacteria and for antifungal. The best result was observed for the human pathogenic fungi \textit{candida sake}. The Rietveld refinements confirm the sample purity and allow the attribution of the observed behavior of the sample to the solved and refined crystal structure.

References


23. Origin 9.0. OriginLab Corporation One Roundhouse Plaza Northampton, MA 01060. USA


Adsorption Studies of Crystal Violet from Aqueous Solution Using Low Cost Material: Equilibrium and Kinetics Studies

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Abstract:
Crystal violet (CV), one of the toxic dyes which are extensively used for dyestuffs, textile, paper and plastics industries. CV does not easily biodegrades in aqueous medium and show harmful effect on aquatic as well as human life. In the present work adsorption studies of CV onto husk powder of Red gram crop (Cajanuscajan) seed was examined in aqueous solution at 27.8ºC. The effects of initial concentration, adsorbent dose, temperature, and contact time etc were determined. Highest 81.49% adsorption efficiency recorded was for 50 mg/L solution concentration onto 2.5g of husk powder of Red gram crop seed. The applicability of Langmuir and Freundlich isotherm model was investigated, and the Langmuir adsorption isotherm model exhibited the best fit than Freundlich isotherm model with the experimental data. The adsorption follows pseudo-second-order kinetics.

Keywords: Crystal Violet; Red gram crop seed husk; Isotherm; Thermodynamics; Kinetics.

Introduction:
In recent years, environmental contamination by synthetic dyes is a serious problem due to rising existence of dyes in the aqueous bodies and their negative eco-toxicological effects and bioaccumulation in wildlife[1]. Usually the industrial wastewater contains important group of chemicals and toxic substances which are harmful to fish and other aquatic life. Synthetic dyes are extensively used in paper, textile, food, leather, paint, acrylic, cosmetics, plastics, and pharmaceutical industries. About 40,000–50,000 tons of dyes are continuously entering the water systems due to improper processing and dying methods from industries [2]. It has been investigated that the decolourisation of dyes is an important aspect of wastewater treatment before discharge. The color removal was extensively studied with various techniques such as coagulation, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis, photo catalytic degradation, cation exchange membranes,

Electro-chemical degradation, integrated chemical–biological degradation, solar photo-Fenton and biological processes, and adsorption have been checked and evaluated for the treatment of dye bearing effluents. Out of these several techniques employed for dye removal, the most experimental technique was found to be the use of adsorption to adsorb the dye from waste water [3]. Several agricultural by-products have been used as adsorbents for the removal of different organic compounds. The major advantage of adsorption techniques for water pollution control is low investment for terms of cost, simple design, easy and cheap operation. Many low cost adsorbents (agricultural, domestic or plant biomass waste) have been used for removal of CV dye such from waste water BaelBark [4], rice husk [5], jackfruit leaf powder [6], ginger waste [7], black gram seed husk [8] etc. In the present work a waste material like husk powder of red gram crop seed was applied as an adsorbent for the removal of Crystal Violet (CV) dye, from aqueous solutions. The main cause of the research is to investigate the adsorption efficiency of red gram crop seed husk powder (RGSH) for Crystal Violet (CV). Red gram crop seed husk is a low cost adsorbent, easily available and biodegradable. The effects of initial solution, effect of adsorbent
dose, effect of contact time and effect of temperature on CV adsorption rate have been investigated. Adsorption kinetics, adsorption isotherms and thermodynamics were also evaluated and reported.

**Materials and methods:**

**Preparation of adsorbent:**

The mature and fresh seeds of red gram crop were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, seeds of red gram crop are soaked into distilled water up to 24 hours. Then their skin was removed and washed with distilled water. It was dried in shadow. After complete drying the seed husk was ground by grinder. The homogeneous powder was obtained by passing through mesh of desired particles size (micron) of red gram seed husk (RGSH). The dried fine powder of RGSH adsorbent was stored in an air tight glass bottle ready for further experimental process.

**Preparation of adsorbate:**

Crystal violet (CI: 4255, FW: 407.99, dye content: 88%), dye supplied by Loba Chemicals Pvt. Ltd., Mumbai (India). Crystal violet dye (Fig.1) was used as adsorbate in experimental process. The stock solution of CV dye was prepared by dissolving the desired amount of Crystal violet powder in double distilled water and suitable diluted to require initial concentrations.

![Chemical structure of crystal violet dye.](image)

**Batch Adsorption Experiments:**

Adsorption experimental techniques were carried out at room temperature (303.6 K). Stock solution of CV dye of concentration 1000 mg/L in double distilled water was used. Standard technique was followed to determine the adsorption of CV dye concentration using UV-Vis Spectrophotometer. Different initial concentrations of CV dye like 25, 50, 75 and 100 mg/L were used. To observe the effect of adsorbent dose on CV dye adsorption, adsorbent dose varies from 10 gm/L to 50 gm/L was used with 100 mg/L CV dye solution. Effect of temperature has been studied using different temperatures. The operating parameters for each set of experiment are summarized in Table: 1.

**Table 1: Variation of experimental operating parameters**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values Investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time in min.</td>
<td>5, 10, 15, 20, 25, 30, 35 and 24hrs.</td>
</tr>
<tr>
<td>Amount of RGSH adsorbent gm/50ml</td>
<td>0.5, 1.00, 1.50, 2.00, 2.50.</td>
</tr>
<tr>
<td>Initial concentration of CV dye solution (mg/L)</td>
<td>25, 50, 75, 100</td>
</tr>
<tr>
<td>Adsorption temperature (K)</td>
<td>304.2, 309.2, 314.2, 319.2, 324.2</td>
</tr>
<tr>
<td>pH</td>
<td>2, 3, 4, 5, 6, 7, 8, 9, 10, 11</td>
</tr>
</tbody>
</table>
A series of required CV dye concentrations and a fixed 50 ml. volume placed in a conical flask where they brought in to contact with RGSH powder at various temperatures. The CV dye solution corresponding to different adsorption time was then analyzed using UV-Vis. Spectrophotometer. The amount of CV dye adsorbed per unite weight of RGSH adsorbent

\[ q_t = \frac{V(C_0 - C_t)}{M} \]  

\[ \% \text{ adsorption capacity} = \frac{(C_0 - C_t)}{C_0} \times 100 \]  

Where, \( C_0 \) is the initial CV dye concentration (mg/L), \( C_t \) is the concentration of CV dye at any time \( t \), \( V \) is the volume of CV dye solution (ml) and \( M \) is the mass of red gram crop seed husk in gm.

**Results and Discussion:**

**Effect of contact time and initial concentration:**

The effect of contact time is an important parameter; the doses of adsorbent were kept constant in all bottles. The effect of contact time was studied at different initial concentration of CV dye with time. The time is varys in parameter for the adsorption of CV dye on red gram seed husk (RGSH) is shown in Fig.2. The experimental results of adsorptions of CV dye on RGSH investigates that the percentage adsorption capacity increased with increase in contact time due to availability of more number of active sites on the surface of the RGSH adsorbent. As increase the initial concentration of CV dye, increase the percentage adsorption capacity due to higher probabilities of collusion between CV dye and RGSH adsorbent. Similar observation was reported in literature [9].

![Fig.2: Effect of contact time and initial concentration of CV dye on adsorption of RGSH adsorbent.](image)

**Effect of adsorbent dose**

It is an important parameter that strongly influences the adsorption technique by affecting adsorption capacity of the adsorbent. The experiments were carried out following general procedure for adsorption studies at the various contact time for each adsorbent. The effect of dose of RGSH adsorbent the initial concentration of the dye solution in all the bottles are kept constant and the dose of adsorbent of fixed particle size was varied. The
plots of percentage adsorption of CV dye versus contact time of various dose of adsorbent. The results are shown in Fig. 3.

The influence of adsorbent dose on CV adsorption by RGSH was investigated in the range of 0.5–2.5 gm. The adsorption efficiency increased from 73.93% to 81.49% as the adsorbent dose increased from 0.5 to 2.5 gm. The increase in the percentage adsorption of the Crystal Violet dye adsorption with an adsorbent dose could be attributed to an increase in adsorbent surface area augmenting the large number of adsorbent sites available for adsorption as already reported [10].

**Effect of temperature**

It is one of the important parameters affecting separation in most of the adsorption processes. In order to examine the effect of temperature on CV dye adsorption five different temperatures were selected. Experiments were carried out at 306.2, 311.2, 316.2, 321.2, and 326.2 K. In the present work percentage removal of CV dye decreases from 87.16 % to 79.76 % by increase in temperature from 304.2 to 326.2 k. The percentage adsorption of CV dye was found to decreases with increase in temperature as shown in Fig.4. It reveals that the adsorbate-adsorbent system is exothermic in nature for which the evaluation of thermodynamic parameters was carried out. Thus, the removal of CV dyes is leading to a decrease in the residual forces on the surface of the RGSH adsorbent and hence causing a decrease in the surface energy of the adsorbent [11].

Thermodynamic study was performed to find the nature of adsorption process. Thermodynamic parameters such as Gibb’s free energy change $\Delta G^0$, enthalpy change of $\Delta H^0$ and entropy change of $\Delta S^0$ were calculated by using Van’t Hoff’s equation.
Table 2. Thermodynamic parameter values of RGSH adsorbent with CV solution at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$-(\Delta G^\circ)$ KJ/mole</th>
<th>$-(\Delta H^\circ)$ KJ/mole</th>
<th>$-(\Delta S^\circ)$ J/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>306.2</td>
<td>-4.046</td>
<td></td>
<td></td>
</tr>
<tr>
<td>311.2</td>
<td>-3.773</td>
<td>20.813</td>
<td>54.723</td>
</tr>
<tr>
<td>316.2</td>
<td>-3.499</td>
<td></td>
<td></td>
</tr>
<tr>
<td>321.2</td>
<td>-3.225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>326.2</td>
<td>-2.952</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The $\Delta G^\circ$ values obtained in this study for the CV are $< -10$ KJ/mole, it indicates that physical adsorption was the predominant mechanism in the adsorption process. The Gibb’s free energy indicates the degree of spontaneity of the adsorption process, where more negative value reflects a more energetically favourable adsorption process. The negative value of $\Delta G^\circ$ (Table 2.) indicates that the adsorption is favourable and spontaneous [12, 13]. The negative value of $\Delta S^\circ$ and $\Delta H^\circ$ suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption [14, 15].

**Adsorption isotherm:**

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence Langmuir and Freundlich isotherms were selected in the present study.

**Langmuir isotherm:** Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites. The linear form of the equation is given by,

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e}$$

Where, $C_e$ (mg/L) is the equilibrium concentration of the adsorbate, $q_e$ (mg/gm) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, $Q_0$ (mg/gm) and $b$ (L/mg) are Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption respectively. The values of $Q_0$ and $b$ are calculated from the slope and intercept of plot of $1/q_e$ against $1/C_e$ respectively. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$. Equilibrium parameter $R_L$ is a dimensionless constant referred to as separation factor.

$$R_L = \frac{1}{1+bc_0}$$

Where, $C_0$ is initial concentration in ppm and $b$ is Langmuir constant related to the energy of adsorption. $R_L$ Value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [16].

**Freundlich isotherm**

Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as

$$\frac{x}{m} = K_f C_e^{1/n}$$

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Where, \( x \) is the quantity adsorbed, \( m \) is the mass of the adsorbent, \( C_e \) is the equilibrium concentration of adsorbate (mg/L). The constants \( K_f \) and \( n \) can be obtained by taking log on both sides of equation (5) as follows,

\[
\log \frac{x}{m} = \frac{1}{n} \log C_e + \log K_f \tag{6}
\]

The constant \( K_f \) is an approximate indicator of adsorption capacity, while \( 1/n \) is a function of the strength of adsorption in the adsorption process. If \( n = 1 \) then the partition between the two phases are independent of the concentration. If value of \( 1/n \) is below one, it indicates a normal adsorption; on the other hand, \( 1/n \) being above one indicates co-operative adsorption. A plot of \( \log x/m \) against \( \log C_e \) gives a straight line with an intercept on the ordinate axis. The value of \( n \) and \( K_f \) can be obtained from the slope and the intercept of the linear plot.

### Table: 3. Isotherm parameter values of RGSH with CV dye solution.

<table>
<thead>
<tr>
<th>Concentration of CV (mg/L)</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 ) (mg/gm.)</td>
<td>( b \times 10^{-5} ) (L/gm.)</td>
</tr>
<tr>
<td>50</td>
<td>526.352</td>
<td>0.786</td>
</tr>
</tbody>
</table>

The \( K_f \) value was found to be between 0 and 1 for CV studies, it is confirm that the on-going adsorption of CV is favourable. The data reveal that the Langmuir model yields better fit than the Freundlich model. The value of \( n \) suggests that deviation from linearity, if \( n = 1 \) the adsorption is homogenous and there is no interaction between adsorbed species. The value of \( n \) is greater than unity, \((1 < n < 10)\), that means favourable adsorption [17]. If value of \( 1/n > 1 \) indicates the adsorption is favoured and new adsorption sites are generated [18-21]. The value of \( n \) presented in Table: 3, the value of \( n \) was found to be between 1 and 10, this indicates favourable adsorption.

### Kinetic model of adsorption:

Kinetic studies are significant for any kind of adsorption process. Lager Gren pseudo-first and pseudo-second order kinetic models can be suggested for an adsorption. Pseudo-first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. The Lager Gren pseudo-first order rate equation is given as,

\[
\frac{dq}{dt} = K_1(q_e - q_t) \tag{7}
\]

After definite integration by applications of the conditions \( t = 0 \) to \( t = t \) and \( q = 0 \) to \( q = q_e \) Equation (5) becomes,

\[
\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2303} \tag{8}
\]

Where, \( q_e \) (mg/gm) is the amount of adsorption at equilibrium, \( q_t \) (mg/gm) denotes the amount of adsorption at time \( t \) (min.) and \( K_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first order model. Based on experimental results, linear graphs were plotted between \( \log (q_e - q_t) \) versus \( t \), to calculate \( K_1, q_e \) and \( R^2 \).

The pseudo-second order equation can be written as

\[
\frac{dq}{dt} = K_2(q_e - q_t)^2 \tag{9}
\]
Where, $K_2$ (gm.mg⁻¹.min⁻¹) is the rate constant of the pseudo-second order.

The linear form of equation is

$$\frac{t}{q_t} = \frac{1}{K_2q_e} + \frac{1}{q_e}t$$

(10)

$K_2$ and $q_e$ can be obtained from the intercept and slope of plotting $t/q_t$ against $t$.

**Table 4. Kinetic parameter values of RGSH adsorbent with CV**

<table>
<thead>
<tr>
<th>Conc. of CV (mg/L)</th>
<th>Pseudo-First order</th>
<th>Second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (min⁻¹)</td>
<td>$q_e$ (mg/gm)</td>
</tr>
<tr>
<td>50</td>
<td>14.693 x 10⁻³</td>
<td>165.261</td>
</tr>
</tbody>
</table>

The value of $R^2$ with first order kinetics was 0.949, while for second order is 0.999 for RGSH adsorbent. The best correlation for the system provided by the pseudo second order kinetic model suggests that chemical adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate might be significant [22]. It is clear that the adsorption of CV on RGSH adsorbent was better represented by pseudo second order kinetics.

**Conclusion:**

The following conclusions can be drawn based on the investigation of CV dye adsorption by BGSH adsorbents.

1. The percentage adsorption of CV dye on RGSH increased with increasing in adsorption dose of RGSH.
2. The percentage adsorption of CV dye on RGSH adsorbent increased with increase in initial concentration of CV dye solution.
3. Higher percentage adsorption capacity of CV dye on RGSH was observed at lower temperature.
4. The negative value of $\Delta G^0$ confirms that the feasibility of the reaction and spontaneous nature of the adsorption.
5. The negative value of $\Delta S^0$ and $\Delta H^0$ suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.
6. The experimental data for the adsorption of CV dye on RGSH fits well for the Langmuir adsorption isotherm model than Freundlich isotherm model.
7. The investigation showed that RGSH adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which could be used as potential adsorbent for removal of CV dye from aqueous solution and polluted water.
References:


Structural Effects of Silicon Substitution on Hydroxyapatite Structure with High Substitution Ratio By Rietveld’s Analysis

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Abstract

The silicon-substituted hydroxyapatite (Si-HA) with three different Si-substitution levels were synthesized via aqueous precipitation method, in the absence of any surfactants and organic solvents. The composition of the Si-substituted HA phases and effect of silicon substitution on the crystal structure were investigated by Rietveld refinements from powder X-ray diffraction data. The results show that the final compounds are oxy-hydroxyapatites, a chemical formula for the Si-substituted HA phases with indication of the incorporated silicate amount is proposed.

Indexing terms/Keywords: Si-substituted hydroxyapatite, X-ray diffraction, Rietveld refinement.

Introduction

Recently, Rietveld analysis was shown to be very useful for determining the spatial coordinates of atoms within the crystal structures of polycrystallines. Rietveld analysis can precisely determine the crystal structure in one step, it’s an accurate method which can precisely determine each parameter of simulating functions fitting the integrated intensity obtained from the structural model to measured diffraction intensity. Although powder diffraction provides less information than the single crystal method, the new Rietveld analysis system Fullprof has solved this problem by development of a mathematical algorithm.

Synthetic, pure and substituted, hydroxyapatite (HA) is well established as bone replacement material in orthopedics and dentistry, due to its bioactivity and biocompatibility with the human bone [1]. Previous studies showed that the traditional HA materials lacked the ability to induce osteogenesis [2,3], while the silicon (Si) element was usually used as a functional element to improve the bioactivity of the apatite materials [4–6] and enhance the reactivity of pure hydroxyapatite [7,8]. The composition of SiHA can be described as Ca10(PO4)6-x(SiO4)x(OH)2-x [9]. Several authors have worked on this subject, assuming that Si or SiO4x-, replaces P or PO43-, respectively, at the 6 h positions, with the subsequent loss of charge equilibrium [10]. In the present study, a pure hydroxyapatite HA and a series of silicon-substituted hydroxyapatite ceramics (SixAHAs), with high substitution ratio (x=1.4; 1.6 and 1.8), were synthesized via an aqueous precipitation method. The as-obtained X-ray diffraction data were used for Rietveld refinement analysis to study the structural effect of silicon substitution ratio on hydroxyapatite structure.

Materials and Methods

A pure HA and SiHA were prepared following the aqueous precipitation method described in our previous works [11,12] using calcium hydroxide (Ca(OH)2), phosphoric acid (H3PO4) and tetraethoxysilane (Si(OCH2CH3)4) (TEOS) solutions as reagents.

The crystalline phases of powders were determined using X-ray diffraction (XRD) they were identified by means of a XPERT-PROPW3050/60 (Theta/Theta) using CuKα radiation and operating at 45 kV and 40 mA and counting
time of 0.5°/mn. Crystalline phases detected in the patterns were identified by comparison to standard patterns from the ICDD-PDF.

**Rietveld refinements**

Rietveld analysis can obtain accurate structural parameters directly from the complicated X-ray powder diffraction patterns without peak separation. For each reflection, Rietveld analysis multiplies the function, which can simulate the shape of the reflection peak to integrated intensity obtained from the structure model, and then refine the function parameters to fit the measured reflection intensity by using the least-squares method. The experimental profiles were fitted with the most suitable pseudo-Voigt analytical function. For both the Kα1 and Kα2 profiles, the line broadening function B (2θ) may be represented by the pseudo-Voigt function:

$$pV(x) = \eta L(x) + (1 - \eta) G(x).$$

(1)

The L(x) and G(x) are, respectively, the Lorentzian and Gaussian components.

The objective function to be minimized in the program is the weighted sum of squares:

$$S = \sum_{i} w_i [y_i(o) - y_i(c)]^2$$

(2)

where w_i is the weight based on counting statistics, y_i(c) consists of contributions from nearby diffraction peaks and the background, and y_i(o) is the observed intensity.

Calculating the distortion of the PO₄ tetrahedrons can do an estimation of the structure distortion. The tetrahedral distortion index was obtained from the calculated data using the relation:

$$TDI = \frac{\sum_{i=1}^{6}|OPO_i - OPO_m|}{6}$$

where OPO_i denotes the six angles between P and the four O atoms of the phosphate tetrahedron and OPO_m the average angle.

**Table 1. Lattice parameters and unit cell volume**

<table>
<thead>
<tr>
<th>Samples</th>
<th>a=b(Å)</th>
<th>c(Å)</th>
<th>V(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>9.4159</td>
<td>6.8819</td>
<td>528.4002</td>
</tr>
<tr>
<td>Si₁₄HA</td>
<td>9.4366</td>
<td>6.9111</td>
<td>532.9788</td>
</tr>
<tr>
<td>Si₁₆HA</td>
<td>9.4384</td>
<td>6.9131</td>
<td>533.3455</td>
</tr>
<tr>
<td>Si₁₈HA</td>
<td>9.4387</td>
<td>6.9132</td>
<td>533.3903</td>
</tr>
</tbody>
</table>

**Results**

The structural study was carried out by powder X-ray (XRD) and the Rietveld refinements were carried out using the program Fullprof. The refinements were performed using the atomic position set no 176 [13].

The pseudo-Voigt profile function of Thompson [14] was employed to model the peak shape of the Bragg reflections. The refinement procedure was started by refining: the scale factor, zero point of detector,
1st background parameter (polynomial function of sixth order) and lattice parameters; then gradually more parameters were opened; the peak profile (pseudo-Voigt) parameters, atomic coordinates and isotropic displacement parameters B. In the final step the individual anisotropic thermal parameters (ATPs) could be improved. Attempts to refine the ATPs of the hydrogen atom were not successful, then isotropic displacement parameter is kept fixed at the value 1.5.

The lattice parameters of HA, Si-HA samples and the unit cell volume are listed in table 1. It can be seen that the unit cell parameters and unit cell volume of Si-HA are larger than that of pure HA. This can be understood considering that the average lengths of the Si-O and P-O bonds are 1.62 and 1.51 Å, respectively. Therefore, the substitution of PO₄³⁻ by SiO₄⁴⁻ is assumed to contribute to the increase in the lattice parameters of the Si-HA materials. Both a and c parameters increase as the level of Si substitution increases. These changes also appear logical considering that the ionic radius of Si³⁺ (0.042 nm) is larger than that of P⁵⁺ (0.035 nm).

Atomic coordinates, occupancies and agreement factors for HA and Si-HA are collected in Tables 2. Tables 3 collects the anisotropic displacement parameters for HA and Si-HA. In order to study the effect of Si incorporation into the PO₄ tetrahedrons, the P–O distances and angles were calculated from the atomic coordinates. Table 4 collects distances for different atoms and Tables 5 collects bonding angles and distortions indexes (TDI) calculated from the six O–P–O angles of the PO₄ tetrahedron. No significant differences result in P–O distances due to the Si incorporation. Only a small increase of TDI can be observed.

**Discussion**

The Si or SiO₄⁴⁻; incorporation into the apatite structure at the P or PO₄³⁻; position has been studied by several authors. Gibson et al. have reported on the higher bioactivity [7], sintering behavior [15] and chemical characterization [9] of these compounds. These authors have reported on aqueous precipitated apatites and the effect of the Si is noticeable by the SiHA behavior. The main structural evidences reported so far are the decrease and increase of “a” and “c” parameters, respectively, absence of secondary phases and small tetrahedron distortion changes. The results obtained in this work agree with it, except for the behavior of the “c” parameter. In our samples, both “a” and “c” parameters increase with Si incorporation, pointing out a difference in the chemical composition respect to aqueous precipitated SiHA.

Despite of the SiO₄⁴⁻ substitution for PO₄³⁻, the P–O distances and O–P–O angles show that PO₄ tetrahedrons are significantly modified. Table 5 shows that the P–O distances do not show significant differences, and only a small increase of the tetrahedron distortion can be observed in Si-HA.

**Table 2. Atomic coordinates and occupancies for samples HA and Si-HA**

<table>
<thead>
<tr>
<th>Wyckoff</th>
<th>HA pure R_p=9.99</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Occ</th>
<th>B_iso</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>6h</td>
<td>0.32590</td>
<td>0.48244</td>
<td>¼</td>
<td>5.9154</td>
<td>2.4421</td>
</tr>
<tr>
<td>O2</td>
<td>6h</td>
<td>0.58394</td>
<td>0.46276</td>
<td>¼</td>
<td>5.8946</td>
<td>1.3273</td>
</tr>
<tr>
<td>O3</td>
<td>12i</td>
<td>0.33818</td>
<td>0.25338</td>
<td>0.06712</td>
<td>12.1170</td>
<td>1.6715</td>
</tr>
<tr>
<td>O(H)</td>
<td>4e</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.22352</td>
<td>2.0015</td>
<td>3.3422</td>
</tr>
<tr>
<td>H</td>
<td>4e</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.16450</td>
<td>1.9402</td>
<td>1.5000</td>
</tr>
<tr>
<td>Ca1</td>
<td>4f</td>
<td>1/3</td>
<td>2/3</td>
<td>0.00112</td>
<td>4.0060</td>
<td>1.8642</td>
</tr>
<tr>
<td>Ca2</td>
<td>6h</td>
<td>0.24844</td>
<td>0.99304</td>
<td>¼</td>
<td>5.9143</td>
<td>1.2372</td>
</tr>
<tr>
<td>P</td>
<td>6h</td>
<td>0.39802</td>
<td>0.36911</td>
<td>¼</td>
<td>5.9393</td>
<td>1.0943</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Si₁₋₄HA</th>
<th>R_p=25.1</th>
<th>R_τ=7.68</th>
<th>R_wp=25.4</th>
<th>R_exp=16.82</th>
<th>χ²=2.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>6h</td>
<td>0.32754</td>
<td>0.48383</td>
<td>¼</td>
<td>6.00006</td>
</tr>
<tr>
<td>O2</td>
<td>6h</td>
<td>0.58140</td>
<td>0.46124</td>
<td>¼</td>
<td>6.00079</td>
</tr>
<tr>
<td>O3</td>
<td>12i</td>
<td>0.34276</td>
<td>0.25799</td>
<td>0.06842</td>
<td>12.00482</td>
</tr>
<tr>
<td>O(H)</td>
<td>4e</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.19710</td>
<td>1.88938</td>
</tr>
<tr>
<td>H</td>
<td>4e</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.05879</td>
<td>0.52489</td>
</tr>
</tbody>
</table>
Table 3. Anisotropic displacement parameters for HA and Si,\textsubscript{HA}

<table>
<thead>
<tr>
<th></th>
<th>B\textsubscript{11}</th>
<th>B\textsubscript{22}</th>
<th>B\textsubscript{33}</th>
<th>B\textsubscript{12}</th>
<th>B\textsubscript{13}</th>
<th>B\textsubscript{23}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{HA : Ca}\textsubscript{10}(PO\textsubscript{4})\textsubscript{6} (OH)\textsubscript{2}</td>
<td>\textbf{O1}</td>
<td>0.00879</td>
<td>0.01597</td>
<td>0.00391</td>
<td>0.01477</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{O2}</td>
<td>0.01400</td>
<td>0.00991</td>
<td>0.00008</td>
<td>0.00501</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{O3}</td>
<td>0.01300</td>
<td>0.00530</td>
<td>0.00078</td>
<td>0.01042</td>
<td>0.00116</td>
</tr>
<tr>
<td></td>
<td>\textbf{O(H)}</td>
<td>0.00545</td>
<td>0.00545</td>
<td>0.03762</td>
<td>0.00273</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{Ca1}</td>
<td>0.00763</td>
<td>0.00763</td>
<td>0.00809</td>
<td>0.00381</td>
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</tr>
<tr>
<td></td>
<td>\textbf{Ca2}</td>
<td>0.00482</td>
<td>0.00151</td>
<td>0.01071</td>
<td>0.00103</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{P}</td>
<td>0.00367</td>
<td>0.00325</td>
<td>0.00762</td>
<td>0.00215</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{Si1,4HA : Ca}\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(SiO\textsubscript{4})\textsubscript{1,4}(OH)\textsubscript{0,6}</td>
<td>\textbf{O1}</td>
<td>0.00155</td>
<td>0.00291</td>
<td>0.02685</td>
<td>0.00965</td>
</tr>
<tr>
<td></td>
<td>\textbf{O2}</td>
<td>0.00743</td>
<td>0.00748</td>
<td>0.02212</td>
<td>0.00528</td>
<td>0.00000</td>
</tr>
<tr>
<td></td>
<td>\textbf{O3}</td>
<td>0.00904</td>
<td>0.01590</td>
<td>0.01997</td>
<td>0.02009</td>
<td>0.00087</td>
</tr>
</tbody>
</table>
The SiHA sample shows a similar amount of vacancies but differs in the hydroxylation degree respect to HA. From the data collected in Table 2 and following the same procedure as above, the 4e position of Si_{1.4}HA is calculated as:

\[
(\text{OH})_{0.52}\text{O}_{1.36}\text{V}_{0.11} ; (\text{OH})_{0.30}\text{O}_{1.54}\text{V}_{0.16} \text{ and } (\text{OH})_{0.16}\text{O}_{1.64}\text{V}_{0.20} \text{ for Si}_{1.4}\text{HA, Si}_{1.6}\text{HA and Si}_{1.8}\text{HA, respectively. V represent vacancies formed at this position.}
\]

In the case of HA, the fact that the sites of the O1, O2 and P atoms show some vacancies, whereas the sites of O3 maintain significantly high occupancy, undoubtedly show evidence for replacement of PO_4^{3-} by CO_3^{2-} ions in the apatite lattice [16].

### Table 4. Distance (Å) for different atoms

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>Si_{1.4}HA</th>
<th>Si_{1.6}HA</th>
<th>Si_{1.8}HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1-O1</td>
<td>2.4137</td>
<td>2.4169</td>
<td>2.4139</td>
<td>2.4207</td>
</tr>
<tr>
<td>Ca1-O2</td>
<td>2.4607</td>
<td>2.4679</td>
<td>2.4562</td>
<td>2.4473</td>
</tr>
<tr>
<td>Ca1-O3</td>
<td>2.8329</td>
<td>2.8114</td>
<td>2.8217</td>
<td>2.8130</td>
</tr>
<tr>
<td>Ca2-O1</td>
<td>2.6774</td>
<td>2.6714</td>
<td>2.7059</td>
<td>2.5880</td>
</tr>
<tr>
<td>Ca2-O2</td>
<td>2.3528</td>
<td>2.3624</td>
<td>2.3656</td>
<td>2.3670</td>
</tr>
<tr>
<td>Ca2-O3</td>
<td>2.4971</td>
<td>2.5498</td>
<td>2.5425</td>
<td>2.6177</td>
</tr>
<tr>
<td>Ca2-O3(2)</td>
<td>2.3100</td>
<td>2.3251</td>
<td>2.3404</td>
<td>2.3130</td>
</tr>
<tr>
<td>Ca2-O(H)</td>
<td>2.3797</td>
<td>2.4341</td>
<td>2.3904</td>
<td>2.4460</td>
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<tr>
<td>----------</td>
<td>--------</td>
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<tr>
<td>P-O1</td>
<td>1.5246</td>
<td>1.5198</td>
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<td>1.5227</td>
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<tr>
<td>P-O2</td>
<td>1.5161</td>
<td>1.4953</td>
<td>1.5638</td>
<td>1.5617</td>
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<tr>
<td>P-O3</td>
<td>1.5731</td>
<td>1.5551</td>
<td>1.5331</td>
<td>1.5412</td>
</tr>
<tr>
<td><strong>Average distance P-O</strong></td>
<td>1.5379</td>
<td>1.5234</td>
<td>1.5419</td>
<td>1.5418</td>
</tr>
</tbody>
</table>

Table 5. Bonding angles and distortions indexes (TDI) for PO₄ tetrahedrons

<table>
<thead>
<tr>
<th>Angles</th>
<th>Bonding angles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HA</td>
</tr>
<tr>
<td>O₁-Ca₁-O₃</td>
<td>67.77(3)</td>
</tr>
<tr>
<td>O₂-Ca₁-O₃</td>
<td>55.96(3)</td>
</tr>
<tr>
<td>O₁-Ca₂-O₃</td>
<td>71.97(4)</td>
</tr>
<tr>
<td>O₂-Ca₂-O₃</td>
<td>76.22(4)</td>
</tr>
<tr>
<td>O₁-P-O₃</td>
<td>110.74(6)</td>
</tr>
<tr>
<td>O₁-P-O₂</td>
<td>112.12(7)</td>
</tr>
<tr>
<td>O₁-P-O₃(2)</td>
<td>107.54(10)</td>
</tr>
<tr>
<td>O₃-P-O₃(2)</td>
<td>106.26(7)</td>
</tr>
<tr>
<td>O₂-P-O₃</td>
<td>108.37(5)</td>
</tr>
<tr>
<td>O₂-P-O₃(2)</td>
<td>106.15(8)</td>
</tr>
<tr>
<td><strong>Average angle O-P-O</strong></td>
<td>108.53</td>
</tr>
<tr>
<td><strong>TDI</strong></td>
<td>1.78 x 10⁻²</td>
</tr>
</tbody>
</table>

Therefore, we can estimate unit cell formulas as described in Table 6:

Table 6. Chemical formulas of the samples after refinement

<table>
<thead>
<tr>
<th>Samples</th>
<th>General chemical formulas</th>
<th>Detailed chemical formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>Ca₁₀(PO₄)₆-x(CO₃)ₓ(OH)₂yOₙ</td>
<td>Ca₁₀(PO₄)₅,₉₃(CO₃)₀,₀₇(OH)₁,₉₄O₀,₀₀₆</td>
</tr>
<tr>
<td>Si₁,₄-HA</td>
<td>Ca₁₀(PO₄)₄,₆₆(SiO₄)₁,₃₄(OH)₀,₅₂O₁,₃₄V₀,₁₁</td>
<td></td>
</tr>
<tr>
<td>Si₁,₆-HA</td>
<td>Ca₁₀(PO₄)₄,₄₁(SiO₄)₁,₅₈(OH)₀,₃O₁,₅₃V₀,₁₆</td>
<td></td>
</tr>
<tr>
<td>Si₁,₈-HA</td>
<td>Ca₁₀(PO₄)₆-x(SiO₄)ₓ(OH)₂-yzOₙV₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca₁₀(PO₄)₄,₂₂(SiO₄)₁,₇(OH)₀,₁₆O₁,₆₄V₀,₂</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

In the present study, a pure hydroxyapatite HA and a series of silicon-substituted hydroxyapatite ceramics (SiₓHA), with x = 1.4; 1.6 and 1.8, were synthesized by an aqueous precipitation method. The Rietveld analysis for different samples shows a slight disruption of hydroxyapatite structure without deformation. The insertion of silicon atoms into HA matrix lead to an increase in unit cell parameters (a and c) suggesting the substitution...
of phosphates by silicates. The calculation of tetrahedral distortion index TDI confirms that the HA structure is slightly affected by the substitution phenomena.

Finally, the Rietveld refinement revealed that the as-prepared samples are not hydroxyapatite and silicon-hydroxyapatite as expected, but rather carbonated oxy-hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_{5.93}(\text{CO}_3)_{0.07}(\text{OH})_{1.94}\text{O}_{0.06}$ and silicated oxy-hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_{x}(\text{OH})_{2-y-z}\text{O}_y\text{V}_z$ respectively.

References

Synthesis and Characterization of Methacrylate Based Polymeric Additives for Crude Petroleum Oil

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Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling-734013, India

pizy12@yahoo.com

Abstract:

Wax deposition in crude oil especially at low temperature causes serious problem during its storage and transportation since this deposited wax gradually immobilizes the oil. Thus, waxy crude oils have high pour point resulting lots of handling problems. To solve this problem, a number of flow improvers (FI) or pour point depressants (PPD) have been prepared. But still it is a challenging aspect of this research area to find out the perfect chemistry with an improved efficiency and cost-effective additives over the conventional one. In this context and in continuation of our effort for the development of additive systems for lube and crude oils, homo polymer of decyl methacrylate and its copolymers with styrene and vinyl acetate at different percentage composition in the presence of benzoyl peroxide (BPO) as initiator have been prepared. All the prepared polymers are characterised by FT-IR, NMR and Gel Permeation Chromatography (GPC). The prepared additives showed excellent performance as flow improver (FI) or pour point depressant (PPD) in crude oil.

Keywords: Crude oil, additives, flow improver, wax crystal network, homopolymer, copolymer.

Introduction

Crude oil is a complex mixture of hydrocarbons containing non-polar n-paraffins and polar components such as asphaltenes and resins (Huang et al., 2011). When the temperature decreases paraffin precipitates out from the crude oil and forms wax crystals network. Their presence causes many problems (Guo et al., 2006) during storage and transportation mainly because of the crystallization and deposition of paraffin wax crystals in the flow line causing a number of handling problems as well in regions where the service temperatures (Xu et al., 2011; Frohlich et al., 2005; Atta et al., 2011; Al-Shafey et al., 2011) are or become seasonally very low (Song et al., 2005; Huiyang et al., 1991).

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. When wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures with each other that inhibited the flow property.

Some commercially available properly designed polymeric flow improvers are poly (ethylene-co-vinyl acetate) (EVA) (Machado et al., 2001), poly(ethylene-butene) (PEB) (Schwahn et al., 2002), polymethacrylates (Soldi et al., 2007; Jung et al., 2011), and modified maleic anhydride copolymers (Wu et al, 2012; Xu et al., 2011; Deshmukh and Bharamde, 2011). Basically, these polymeric wax inhibitors consist of a non-polar long hydrocarbon chain of 14 to 25 carbon atoms in addition with a polar segment typically acrylates or acetates. The hydrocarbon part is responsible for the interaction between the additive and paraffin of the oil while the polar part limits the degree of co-crystallization and thus inhibits the aggregation stage. Recently Chen et al. investigated the interaction of crude oil waxes with polyacrylate pour point depressants (PPDs) bearing different structures and reported that polyacrylate polymers with polar building blocks interacted more easily with the paraffin content which would effectively inhibit wax-crystal precipitation and improve crude oil low-temperature fluidity (Chen et al., 2014). Another study supports that an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer having pendant hydrocarbon chain groups (Kumar, 1989). Again, some investigations indicated that molecular weight (MW) and molecular weight distribution (MWD) should also play an important
role in the performance as a flow improver for crude oil (Borthakur et al., 1996; Castro et al., 2011). For example, polybehenyl acrylate with a lower MW exhibited better efficacy as a flow improver for asphaltene-rich crude oil (Chanda et al., 1998) and acrylate/methacrylate polymer additives with a lower range of MWs achieved the optimum effectiveness for waxy crude oils (El-Gamal et al., 1994). According to Kuzmic et al., polymeric additives of alkyl acrylate with styrene, acrylic acid, and 1-vinyl-2-pyrrolidone with MWS below 20000 were not efficient for crude oils from Croatian oil fields (Ercegkuzmic et al., 2008) while in another study by Taraneh et al., it was reported that ethylene vinyl acetate copolymer with a higher MW was the better additive for crude oils with low asphaltene contents (Taraneh et al., 2008). T. J. Behbahani had investigated the influence of different concentrations of polymeric flow improver such as dodecylpolymermethacrylate and tetradodecylpolymermethacrylate on pour point of waxy oils and found that the higher molecular weight flow improver (tetradodecylpolymermethacrylate) had better efficiency on pour point of waxy oils (Behbahani, 2014). Moreover, the performance of a flow improver is also related to the wax and asphaltene composition in the crude oil (Kumar, 1989; Borthakur et al., 1996; Ercegkuzmic et al., 2008; Castro et al., 2011). Hence it can be summarized that the performance of a polymeric flow improver is dependent upon both the structure of the flow improver and the oil composition (El-Gamal et al., 1992).

Vinyl acetate copolymer, acrylate copolymer and their derivatives (Qian et al., 1996; Jordan et al., 1978) are broadly applicable to improve the flow ability of very waxy crude oil, diesel fuel and other base oils at low temperature. Vinyl acetate copolymers satisfy most of the properties which a good additive must possess. On the other hand, methacrylate polymers, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today due to the molecular structure of the polymers and the tremendous flexibility in chemical structure. In the present context, we have prepared homopolymer of decyl methacrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions and evaluated them as flow improver for crude oil collected from Oil India Ltd, Duliajan, Assam (India). The properties of the crude oil are listed in table 1.

**Experimental Section**

**Materials**

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), Styrene (99%, Sigma-Aldrich), Vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), Decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H\(_2\)SO\(_4\) (98%, Merck Specialties Pvt. Ltd.) was used as received. Crude oil was collected from Oil India Ltd, Duliajan, Assam (India). Before experiment the crude oil was tested for pour point and was found 24 °C.

**Preparation of the monomer and its purification**

The monomer (decel methacrylate, DMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of decyl alcohol in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication (Ghosh et al., 2011).

**Preparation of polymers:**

The polymers (homo and copolymers) were prepared by free radical polymerization (scheme1) at different percentage composition of monomers (table 2) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in our earlier publication (Ghosh et al., 2011). (Please insert scheme 1 here)
Measurements

Molecular weight determination

The number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 308K temperature at a flow rate of 1mL/min.

Spectroscopic Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range (400 to 4000) cm$^{-1}$. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl$_3$ was used as solvent and tetramethylsilane (TMS) as reference material.

Performance evaluation as pour point depressants/flow improvers in crude oil

The effect of additive concentration on pour point of the crude oil was tested by using different doping concentrations ranging from 1% to 6% (w/w) for each of the prepared polymer. According to the ASTM D 97-09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India).

Results and Discussion

Molecular Weight Analysis:

The experimental values of $M_n$, $M_w$ and PDI (polydispersity index) of the prepared polymers are tabulated in table 2. From table 2, it can be stated that on increasing the percentage of styrene or vinyl acetate both the number average molecular weight and weight average molecular weight gradually increases. But the copolymers of vinyl acetate are less polydispersed than those of styrene-based copolymers. (Please insert table 2 here)

Spectroscopic analysis:

The homopolymer of decyl methacrylate shows IR absorption band at 1735.8 cm$^{-1}$ corresponds to the ester carbonyl group and those at 1064.6, 710 and 690 cm$^{-1}$ are due the bending of C–H bond. Due to the presence of –CH$_2$CH$_3$ group the peak at 2854.5 cm$^{-1}$ and 2924 cm$^{-1}$ appeared and for the CO stretching vibration the peaks at 1465.8, 1404, 1229, 1211 and 1149.5 cm$^{-1}$ appeared. The IR spectrum of copolymers of decyl methacrylate with styrene (P-2 to P-5) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1735.8 cm$^{-1}$ shifted to 1728.1 cm$^{-1}$ in the copolymer and the peaks at 748.3 cm$^{-1}$ and 702 cm$^{-1}$ were due to the C–H bond of the phenyl group of styrene. For the copolymers of decyl methacrylate and vinyl acetate (P-6 to P-9) the IR spectrum are similar and showed the following results: Peaks at 1456.2 cm$^{-1}$, 1377.1 cm$^{-1}$, 1368.4 cm$^{-1}$, 1321.1 cm$^{-1}$, 1296.1 cm$^{-1}$, 1238.2 cm$^{-1}$, 1163.0 cm$^{-1}$, 1065.5 cm$^{-1}$ and 1011.6 cm$^{-1}$ were due to CO stretching vibration and absorption bands at 814.9 and 721.3 cm$^{-1}$ were for bending of C–H bond.

In the $^1$H NMR data of the homopolymer, the methyl and methylene protons appeared in the range of 0.890 to 1.934 ppm for all alkyl groups and a broad peak at 3.928 ppm for the protons of –OCH$_2$ group. Absence of any peak in the range of 5-6 ppm corresponds to sp$^2$ carbon confirms the polymerisation. In the $^1$H NMR of the copolymers of styrene, a broad peak at 7.014–7.329 ppm appeared for the protons of phenyl group. The peaks appeared in the range of 3.933–4.15 ppm indicated the presence of –OCH$_2$ protons. All the sp$^3$ protons appeared in the range of 0.9–1.942 ppm. Here again the absence of peaks in the range of 5-6 ppm indicated total
polymerisation. In the $^1$H NMR of copolymers of vinyl acetate a broad peak at 3.926-4.158 ppm indicated the protons of $\text{--OCH}_2$ and $\text{--OCH}_3$ groups. The hydrogen atoms attached to sp$^3$ carbons appeared in the range of 0.858 ppm to 2.637 ppm. Absence of any peak in the range of 5-6 ppm confirmed the polymerisation successfully.

In $^{13}$C NMR of the homopolymer, the peaks at 177.54 ppm indicated the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirmed the presence of $\text{--OCH}_2$ carbon and peaks in the range of 14.16-45.12 ppm accounted for all sp$^3$ carbon atoms of alkyl groups. Absence of sp$^2$ carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In the $^{13}$C NMR of the copolymers of styrene, the peaks in the range of 176.8-177.79 ppm indicated the ester carbons. The phenyl carbons appeared in the range of 125.04-128.56 ppm. Peaks appearing at 64.86 ppm and 65.02 ppm indicated the $\text{--OCH}_2$ carbon whereas peaks in the range of 14.12-54.41 ppm corresponded to all the sp$^3$ carbons.

In $^{13}$C NMR of the copolymers of vinyl acetate the peaks at $\delta$ 176.60-176.70 ppm were due to the presence of ester carbonyl group. The peaks at 64.66 - 65.06 ppm corresponded to the $\text{--COCH}_3$ methyl carbon and $\text{--OCH}_2$ carbons, peaks ranging from 14.08-45.09 ppm for all other sp$^3$ carbons. Again, no peak in the range of 120-150 ppm indicated the absence of sp$^2$ carbons and confirmed the polymerization.

### Analysis of pour point values

The experimental values of pour point are given in table 3. The values suggest that all the prepared polymers (P-1 to P-9) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for Duliajan crude oil. The copolymers (P-2 to P-9) are better than the homopolymer (P-1) as FI. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of decylmethacrylate and styrene (P-2 to P-5), P-2 copolymer with the lowest percentage of styrene (2.5%) acts as the better FI than the others and using 5% (w/w) solution of this polymer we get the lowest pour point of 8.1°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that P-3 to P-5 copolymers with higher percentage of styrene gradually showed higher pour point and at 6% (w/w) solution P-5 copolymer with highest percentage of styrene (10%, w/w) shows highest pour point of 16.1°C. The vinyl acetate copolymers (P-6 to P-9) showed better results than the copolymers of styrene. These polymers are better FI and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals (Abdel-Azim et al., 2006) that happened in case of styrene copolymers. The P-7 copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4.2 °C. Polymers with higher molecular weights especially P-5 and P-9 showed comparatively poor results. It may be because of their low solubility in the crude oil. (Please insert table 3 here)

### Conclusion

From the above study it is found that homopolymer of decyl methacrylate and its copolymer with styrene and vinyl acetate are effective as flow improver for the crude oil. The vinyl acetate-based copolymers are better as flow improver than styrene based copolymers. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight and the chemistry of polymer chain have a significant role in relation to the performance of the additives as flow improvers for crude oil.

### Acknowledgement

The authors thank Oil India Ltd., Duliajan, Assam (India) for providing crude oil and UGC, New Delhi for providing financial support.
References


Scheme 1

Preparation of ester:

\[
\text{H}_2\text{C} = \text{C} \quad \text{COOH} + \text{C}_{10}\text{H}_{21}\text{OH} \xrightarrow{\text{HQ/H}^+ 120 \degree \text{C}} \text{H}_2\text{C} \quad \text{C} \quad \text{COOC}_{10}\text{H}_{21} + \text{H}_2\text{O}
\]

Homopolymerisation:

\[
\begin{align*}
\text{n H}_2\text{C} = \text{C} & \quad \text{COOC}_{10}\text{H}_{21} \xrightarrow{\text{BZP 85 \degree C}} \text{CH}_2 \quad \text{C} \quad \text{COOC}_{10}\text{H}_{21} \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2
\end{align*}
\]

Copolymerisation:

\[
\begin{align*}
\text{n H}_2\text{C} = \text{C} \quad \text{COOC}_{10}\text{H}_{21} + \text{n H}_2\text{C} & \quad \text{CH} \quad \text{C}_2\text{H}_5 \xrightarrow{\text{BZP 85 \degree C}} \text{CH}_2 \quad \text{C} \quad \text{COOC}_{10}\text{H}_{21} \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2
\end{align*}
\]

\[
\begin{align*}
\text{n H}_2\text{C} = \text{C} \quad \text{COOC}_{10}\text{H}_{21} + \text{n H}_2\text{C} & \quad \text{CH} \quad \text{OCOCH}_3 \xrightarrow{\text{BZP 85 \degree C}} \text{CH}_2 \quad \text{C} \quad \text{COOC}_{10}\text{H}_{21} \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2 \\
& \quad \text{CH}_2
\end{align*}
\]
Table 1: Specification of the crude oil

<table>
<thead>
<tr>
<th>Source</th>
<th>Duliajan, Assam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pour point</td>
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</tr>
<tr>
<td>Density</td>
<td>900 Kg/m³</td>
</tr>
<tr>
<td>Plastic viscosity</td>
<td>5.2 mPa.s at 27°C</td>
</tr>
<tr>
<td>Yield value</td>
<td>10 dy/cm² at 30°C</td>
</tr>
<tr>
<td>Wax content</td>
<td>&gt;10%</td>
</tr>
</tbody>
</table>

Table 2: Percentage composition, Mₙ, Mₜ and PDI values of polymers (P-1 to P-9)

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>% of DMA</th>
<th>% of Sty.</th>
<th>% of VA</th>
<th>Mₙ</th>
<th>Mₜ</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
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<td>100</td>
<td>-</td>
<td>-</td>
<td>20482</td>
<td>49682</td>
<td>2.4256</td>
</tr>
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<td>P-2</td>
<td>97.5</td>
<td>2.5</td>
<td>-</td>
<td>21592</td>
<td>58982</td>
<td>2.7316</td>
</tr>
<tr>
<td>P-3</td>
<td>95</td>
<td>5</td>
<td>-</td>
<td>27457</td>
<td>77688</td>
<td>2.8294</td>
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<tr>
<td>P-4</td>
<td>92.5</td>
<td>7.5</td>
<td>-</td>
<td>28946</td>
<td>81556</td>
<td>2.8175</td>
</tr>
<tr>
<td>P-5</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>30345</td>
<td>93842</td>
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<td>21575</td>
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<td>-</td>
<td>7.5</td>
<td>56866</td>
<td>66210</td>
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<tr>
<td>P-9</td>
<td>90</td>
<td>-</td>
<td>10</td>
<td>61990</td>
<td>81219</td>
<td>1.3100</td>
</tr>
</tbody>
</table>

DMA = Decyl methacrylate, Sty. = Styrene, VA = Vinyl acetate, Mₙ = Number average molecular weight, Mₜ = Weight average molecular weight, PDI = Polydispersity index

Table 3: Pour point data with respect to the different concentrations of the additives in crude oil

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Pour point (°C) of additives doped crude oil (% in w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>P-1</td>
<td>24</td>
</tr>
<tr>
<td>P-2</td>
<td>24</td>
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<td>P-3</td>
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<tr>
<td>P-8</td>
<td>24</td>
</tr>
<tr>
<td>P-9</td>
<td>24</td>
</tr>
</tbody>
</table>
Interaction of EDNA with Proton-A DFT Treatment

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Abstract.

A composite of EDNA, with proton in vacuum have been considered within the constraints of density functional theory at the levels of B3LYP/6-31++G(d,p) (restricted and unrestricted) and ωB97X-D/6-311+G(d,p). The results of structure optimization indicated that unexpectedly hydrogen molecule production occurs by the interaction of proton and a methylenic hydrogen of EDNA resulting a carbocation formation on the explosive molecule. The remnant of the nitramine molecule is stabilized partly by the nearby nitro oxygen atoms through space. The calculated IR and UV-VIS spectra of the species were obtained and discussed.

Key words: EDNA, Haleite, Explosives, Proton, Nitramine, DFT.

1. Introduction

EDNA is also named as Haleite, N,N’-dinitroethylene diamine, 1,2-dinitrodiaminoethane (C\textsubscript{2}H\textsubscript{6}N\textsubscript{4}O\textsubscript{4}). It has energy of formation and enthalpy of formation values of -576 kJ/kg and -691.6 kJ/kg, respectively [1]. Its oxygen balance is -32% so it is mostly used together with some oxidizing agents. It is characterized with 37.33 % nitrogen content, crystallizes as white orthorhombic crystals (d:1.71 g/cm\textsuperscript{3})[1]. EDNA is an explosive that combines the properties of a high explosive like TNT [2]. Indeed, it is more powerful than TNT and slightly less powerful than RDX [3]. It has high brisance and comparatively low sensitivity to impact (8 Nm) [1,2] and at the same time so readily explodes by heat. Its explosion temperature is relatively low (melts with decomposition at 177.30 °C) approaching that of mercury fulminate or nitroglycerine [2]. It possesses detonation velocity (confined) value of 7570 m/s [1]. EDNA acts as a dibasic acid and forms various neutral salts which also have some explosive properties [1].

Heat sensitization of EDNA (beside some other explosives) was investigated along time ago [4]. Thermochemical data including EDNA (Haleite) relative to the constituents of propellants were reported [5]. Its decomposition mechanism depending on the properties of the medium was studied [6]. Its crystallographic data were published By McCrone [7]. The use of co-crystallizations is emerging as a new avenue for modifying the solid-state properties of a wide range of high-value chemicals. Co-crystals of ethylenedinitramine (EDNA) has been prepared by crystal engineering [8]. Insensitive EDNA/DAT Co-crystal was investigated by Zeman and coworkers [9]. Spaeth and Winning managed to produce ethylene dinitramine pellets by using some additives to obtain ameliorated performance [10]. The general use of EDNA is restricted due to its relatively high chemical reactivity, caused by the presence of two highly acidic protons. Thus, EDNA is corrosive and can, over time, react with metals and metal salts which may in turn produce brand new and unknown materials with completely unpredictable properties [8]. Theoretical calculations of hot-spot initiation in explosives, including EDNA, was performed by Bruckman and Guillet [11].

On the other hand, cosmic rays have great penetrating power. The intensity of them varies with latitude. Cosmic rays consist largely of the nuclei of elements of low atomic weight, protons being the most abundant type [12]. The hard component of cosmic rays is μ-mesons produced in flight by π-meson decay. The soft component which is not very penetrating consists of photons, electrons and positrons [12-16].
In the present study, EDNA+proton composite (EDNA+p) system has been considered in vacuum conditions within the constraints of density functional theory (DFT).

2. Method of calculation

Structure optimizations of all the species, leading to energy minima were initially achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [17,18] (at the restricted level [19,20]. The subsequent optimizations have been achieved at Hartree-Fock level using various basis sets hierarchically. Then, the structure optimizations were managed within the framework of density functional theory [21,22], finally at the levels of both B3LYP /6-31++G(d,p) [19] and ωB97X-D/6-311+G(d,p) [23,34]. For the open-shell systems or for special purposes unrestricted DFT calculations were performed. The exchange term of B3LYP consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke’s gradient correlation to LSD exchange [22,25]. Note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [26] and Lee, Yang, Parr (LYP) correlation correction functional [27].

The vibrational analyses were also done. The total electronic energies are corrected for the zero-point vibrational energy (ZPE). The stationary points to energy minima were proved in all the cases by calculation of the second derivatives of energy with respect to the atom coordinates. The normal mode analysis for each structure yielded no imaginary frequencies for the 3N–6 vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each system corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [28].

3. Results and discussion

EDNA is a nitramine type explosive. Mesomerically electron withdrawing nitro group and adjacent electron donating amino group dictate most of the characteristic behavior of EDNA. The following mesomorphic structures are to be considered for the nitramine group.

Two adjacent positively charged nitrogen atoms in structure II, may initiate a 1,3 tautomerism if it is structure allows.

On the other hand, when a charged particle approaches a molecule, the electric field generated by its presence disturbs the electric field around the neutral molecule. This is a time-dependent dynamic process. As the charged particle gets slower and slower its ionization density (ionization along the particle’s path, the Bragg’s curve) increases [29]. However, prior to or just after the spark breakdown (very small Δt seconds earlier or later) the whole picture can be simplified as the molecule and a charged-particle (composite system) at the equilibrium geometry. Obviously, due to the polarization effects, bond lengths and angles of the molecule adapt themselves to minimize the energy of the composite system. It is known that any form of nuclear radiation (charged particles, neutrons or electromagnetic radiation) directly or indirectly produces ionization and certain chemical
changes in its passage through matter [15,29]. Positively charged particles, engender rather strong electric field around them to initiate ionization of nearby molecules.

### 3.1. Bond lengths and distances

Figure 1 shows the optimized structures and the resultant bond lengths/distances calculated at two different DFT levels and the direction of dipole moment vector. Note that the levels of calculations have two different basis sets and functionals in order to visualize whether the bond lengths/ distances are independent from the method of calculations or not. The results reveal that in each case, one of the methylenic hydrogen-carbon bonds is highly elongated implying its cleavage. The distance between the originally proton and originally methylenic hydrogen is 0.745 Å (B3LYP/ 6-31++G(d,p)) and 0.747 Å (ωB97X-D/ 6-311+G(d,p)) suggesting some strong interaction (bond formation) between them.

![Figure 1](image.png)

**Figure 1.** Optimized structure and bond lengths for EDNA+p system.
3.2. Charges

The ESP charges on EDNA+p system is shown in Figure 2. The ESP charges are obtained by the program based on a numerical method (CHELP algorithm) that generates charges that reproduce the electrostatic potential field from the entire wavefunction [28]. In this algorithm the charges at the atoms are chosen to best describe the external field surrounding the molecule. Ideally this area should include everything outside of the Van der Waal radii. In practice, a shell surrounding the atoms having a thickness of 5.5 au is chosen for ESP calculations.

The hydrogen originally in protonic form, and similarly the methylenic hydrogen have very minute charges or nil. The affected methylenic carbon has quite big partial positive charge (see Figure 2).

![Figure 2. The ESP charges (esu) on atoms of EDNA+p system.](image)

3.3. IR spectra

Figure 3 displays the IR spectra of EDNA as well as the composite, EDNA+p system. At the B3LYP/6-31++G(d, p) level, the peak at 1665 cm\(^{-1}\) is the nitramine N-H bending coupled with asymmetric N-O stretching of EDNA which occurs at 1718 cm\(^{-1}\) and 1771 cm\(^{-1}\) in EDNA+p composite system. These peaks at \(\omega B97X-D/6-311+G(d,p)\) level of calculations are very closely spaced at 1797 cm\(^{-1}\). Also, the N-H stretching peaks are not well resolved in this level of calculations as compared to B3LYP/6-31++G (d, p) level. The nitramine N-H stretching occurs in the region of ca. 3554-3571 cm\(^{-1}\).
Figure 3. IR spectrum of EDNA and EDNA+p system.

3.4. Molecular orbital energies and UV-VIS spectra

Figure 4 shows some of the molecular orbital energy levels of EDNA and the composite system EDNA+p. As seen in the figure and Table 1, the presence of proton in the composite system lowers both the HOMO and LUMO energy levels. The effect of this energy lowering on the interfrontier molecular orbital energy gap ($\Delta\varepsilon$, $\varepsilon_{\text{LUMO}}$-$\varepsilon_{\text{HOMO}}$) is narrowing of the gap. Consequently, the UV-VIS spectrum of the composite system is expected to exhibit a bathochromic shift to visible region of the spectrum.
**Figure 4.** Some of the molecular orbital energy level of EDNA and EDNA+p system.

**Table 1.** The HOMO, LUMO energies and FMO gaps for the systems considered.

<table>
<thead>
<tr>
<th>System</th>
<th>$\varepsilon_{\text{HOMO}}$</th>
<th>$\varepsilon_{\text{LUMO}}$</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDNA</td>
<td>-806.42</td>
<td>-215.27</td>
<td>591.15</td>
</tr>
<tr>
<td></td>
<td>(-1016.31)</td>
<td>(-10.50)</td>
<td>(1005.81)</td>
</tr>
<tr>
<td>EDNA+p</td>
<td>-1279.26</td>
<td>-792.63</td>
<td>486.63</td>
</tr>
<tr>
<td></td>
<td>(-1478.88)</td>
<td>(-599.28)</td>
<td>(879.6)</td>
</tr>
</tbody>
</table>

Energies in kJ/mol. B3LYP/6-31++G(d,p) and B97X-D/6-311+G(d,p) (in parenthesis) levels.
Figure 5. The HOMO and LUMO patterns for the systems considered (B3LYP/6-31++G(d,p)).

Figure 6 shows the UV-VIS spectra (time dependent) of EDNA and EDNA+p composite system. It is to be noted that B3LYP/6-31++G(d,p) level of calculations yield a spectrum closer to visible region as compared to ωB97X-D/6-311+G(d,p) level. Note that, as mentioned above, the UV-VIS spectrum of the composite system is expected to exhibit a bathochromic shift to visible region of the spectrum from the direct consequence of narrowing of the FMO gap (see Table 1). However, the calculated UV-VIS spectra at the level of ωB97X-D/6-311+G(d,p) is insensitive to the presence of proton compared to EDNA system. This might be because of the limited number of molecular orbitals considered in spectral calculations for the sake of minimizing the calculation expenses.

Figure 6 contd.
3.5. The mechanism of interaction

For the mechanism studies, the proton and the methylenic hydrogen affected by the proton are removed from the optimized structure of EDNA+p system. Then, calculations were performed by adopting the unrestricted formalism (UB3LYP/6-311++G(d,p)). These types of structures are indicated as EDNA-H₂.

Although, proton is positively charged and EDNA has NO₂ groups which have negatively charged oxygen atoms, the proton nearby EDNA seems to prefer the covalently bound methylenic hydrogen of EDNA. Figure 7 shows the optimized structures of the systems considered for the mechanism of interaction. All the optimizations in this section were carried out at the unrestricted level, irrespective of closed or open shell systems have been considered. Note that the main skeleton and the direction of dipole moments in the cases of EDNA+p and EDNA cation are quite similar.
**Figure 7.** Optimized structures for the species considered (UB3LYP/6-31++G(d,p)).

Table 2 shows various energies of the systems considered obtained either restricted or unrestricted manner.

<table>
<thead>
<tr>
<th>Specie</th>
<th>$E$</th>
<th>ZPE</th>
<th>$E_c$</th>
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<tr>
<td>EDNA*</td>
<td>-1574071.20</td>
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<td>-1573765.47</td>
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<tr>
<td>EDNA+p*</td>
<td>-1574775.12</td>
<td>308.83</td>
<td>-1574466.29</td>
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<tr>
<td>EDNA+p**</td>
<td>-1574775.12</td>
<td>308.81</td>
<td>-1574466.31</td>
</tr>
<tr>
<td>EDNA-H$_2$ cation**</td>
<td>-1571677.29</td>
<td>279.20</td>
<td>-1571398.09</td>
</tr>
<tr>
<td>EDNA-H$_2$ radical**</td>
<td>-1572366.70</td>
<td>273.75</td>
<td>-1572092.95</td>
</tr>
</tbody>
</table>

Energies in kJ/mol. * B3LYP/6-31++G(d,p), ** UB3LYP/6-31++G(d,p)

Figure 8 shows the bond lengths of EDNA+p and cation and radical obtained after the removal of H$_2$ from RDNA+p system.

![Figure 8](image1.png)

**Figure 8.** Bond lengths in the species considered (UB3LYP/6-31++G(d,p) level, hydrogens are omitted).

Figure 9 displays the IR spectra of various species considered in this section. Note the high similarity between the spectrums of EDNA+p and EDNA-H$_2$ cation. In these systems, the peaks at 1771 cm$^{-1}$ and 1718 cm$^{-1}$ are the nitramine N-H bending coupled with asymmetric N-O stretching of nitramine groups present in EDNA.
Figure 9. IR spectra of the species considered (UB3LYP/6-31++G(d,p)).

Figure 10 shows the calculated (time dependent, TDDFT) UV-VIS spectra (UB3LYP/6-31++G(d,p)) of the species considered. A high similarity between the UV-VIS spectrums of EDNA+p and EDNA-H₂ cation are observed. It shows that in the composite system, methylenic hydrogen of EDNA leaves of the molecule in pro-hydride form to combine with the proton nearby and EDNA remnant is left in the cationic form.

Figure 10 contd.
Figure 10. UV-VIS spectra of the species considered (UB3LYP/6-31++G(d,p)).

Figure 11 shows some of the molecular orbital energy spectra of the species considered (UB3LYP/6-31++G(d,p)) in this section. Note that the calculations are unrestricted thus for open shell systems α- and β-type orbitals arise.
Conclusion

According to the present level of DFT calculations, exposure of EDNA to cosmic protons from the primary cosmic rays result in H₂ formation in which one of the H atoms originates from the methylene moiety present in the structure of EDNA. The present study shows that in space (vacuum), chemistry (at least for EDNA) could be quite unexpected and different from aqueous or solution chemistry. Presently, only the effect of a static proton nearby EDNA molecule has been modeled. Note that cosmic protons have high speed and the electric field generated by them has dynamic features as well. Anyhow, the present study focuses attention to the stability of energetic materials to be used in space conditions.

References


5. Tavernier P, Thermochemical data relative to the constituents of propellants, Memorial des Poudres, 38 (1956) 301-36.


FIGURE CAPTIONS

Figure 1. Optimized structure and bond lengths for EDNA+p system.

Figure 2. The ESP charges (esu) on atoms of EDNA+p system.

Figure 3. IR spectrum of EDNA and EDNA+p system.

Figure 4. Some of the molecular orbital energy level of of EDNA and EDNA+p system.

Figure 5. The HOMO and LUMO patterns for the systems considered (B3LYP/6-31++G(d,p)).

Figure 6. UV-VIS spectrum of systems presently considered.

Figure 7. Optimized structures for the species considered (UB3LYP/6-31++G(d,p)).

Figure 8. Bond lengths in the species considered (UB3LYP/6-31++G(d,p) level, hydrogens are omitted).

Figure 9. IR spectra of the species considered (UB3LYP/6-31++G(d,p)).

Figure 10. UV-VIS spectra of the species considered (UB3LYP/6-31++G(d,p)).

Figure 11. Some of the molecular orbital energy spectra of the species considered (UB3LYP/6-31++G(d,p)).
An Organo-Catalyst Mediated Synthesis of Chalcones of Dehydroacetic Acid And Determination of Their Anti-Oxidant Activity.

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Abstract:

A diverse series of chalcones of dehydroacetic acid were synthesized and subjected to antioxidant activity. Highest DPPH scavenging effect was observed in case of HR 4 displaying IC\textsubscript{50} of 4.18 mg/ml in comparison to the standard ascorbic acid (IC\textsubscript{50} of 4.04 mg/ml). However the highest hydroxyl radical scavenging effect was displayed by HR 25 exhibiting (IC\textsubscript{50} 10.21). Keeping in view the very low cytotoxicity issues of most of the chalcone derivatives of dehydroacetic acid, this study provides an important aspect with regard to the use of dehydroacetic acid based derivatives as antioxidants.

Keywords: Dehydroacetic acid, Chalcone, Anti-Oxidant, Cytotoxicity, DPPH.

Introduction:

4-Hydroxy-2-pyrones are the most abundant and biologically most significant class of 2-pyrones [1-3] e.g., Fusapyrone and Deoxyfusapyrone (Figure 1), isolated from the rice cultures of \textit{Fusarium semitectum} [4]. They show considerable anti-fungal activity with high selectivity and low toxicity [5]. 4-Hydroxy-2pyrone represents the active component of naturally isolated anti-TB agents like Pseudo pyronine B [6,7] and Myxopyronin [8,9] and clinically approved anti-HIV agent like Tipranavir [10,11] (Figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Some biologically significant 4-hydroxy-2-pyrones}
\end{figure}

Chalcones of dehydroacetic acid are well known for their anti-TB [12], anti-cancer[13,14], and anti-microbial [15] and anti-HIV [16] activities. Because of the above mentioned biological properties, it is envisaged that the chalcone derivatives of dehydroacetic acid could be further investigated to explore its additional biological properties. A thorough literature survey revealed that anti-oxidant properties of chalcones of dehydroacetic acid were yet to be investigated. Keeping this fact in mind as well as our previous work on 2-pyrones [17-20], we
directed our studies towards the synthesis of a diverse series of chalcones of dehydroacetic acid of biological interest. All the synthesized analogs were subjected to DPPH and hydroxyl radical scavenging assay to check their anti-oxidant potential. This work provides a report on SAR of chalcones of dehydroacetic acid to come up with analogs having better activity, and improved selectivity.

**Results and discussion**

Chalcones of 3-Acetyl-4-hydroxy-6-methyl-2-pyrene (1) were synthesized by classical Clasen Schmidt condensation in good to excellent yields by treating 1 equivalent of (1) with aromatic aldehydes (1.1 equiv.) in ethanol in presence of catalytic amount of piperidine. The reaction mixture was heated at 60 °C for 1-4 hours (Figure 2).

![General reaction for the synthesis of chalcones](image)

Completion of the reaction was monitored by TLC. After the completion, the desired product was purified by column chromatography technique using Hexane:Ethylacetate as eluent. A library of 25 chalcones (HR1-HR25) enlisted in (Table 1) were synthesized for biological screening. The products formed were easily confirmed by **1**H and **13**CNMR spectra.

Table 1: Library of synthesized chalcones of 3-Acetyl-4-hydroxy-6-methyl-2-pyrene.

All the synthesized derivatives were subjected to antioxidant activity using DPPH scavenging assay and Hydroxy radical scavenging assay. To evaluate their DPPH scavenging effect, the derivatives were screened at different concentrations to obtain their IC50 values, as shown (Table 2).

Ascorbic acid was used as positive control in this assay. Amongst the synthesized derivatives, a notable difference in DPPH scavenging was observed which may be attributed to the type of the aldehyde and position and the type of substituent in the aldehyde used. Amongst the derivatives HR 4 (4-Hydroxy aldehyde analog) was found to be most active with an IC50 of 4.58 although less than the control used but still very comparative. The ortho-hydroxy benzaldehyde derivate HR 19 and meta-hydroxy benzaldehyde derivative HR 20 were less active displaying IC50 values of 5.1 mg/ml and 6.9 mg/ml respectively. The next active analog of the series was found to be HR 25 with an IC50 value of 4.69. The effect of substituents had hardly any effect on the antioxidant activity. However, the hydroxyl benzaldehyde derivatives were found to comparatively more active than other analogs of aromatic aldehydes. The results have been summed up in table 2.

Table 2. DPPH and OH radical scavenging potential of derivatives of dehydro acetic acid

These derivatives were further subjected to hydroxyl scavenging effect at different concentrations, the IC50 values are shown in (Table 2). Again ascorbic acid was taken as control in this assay. 4-Hydroxy 3-methoxy benzaldehyde derivate HR 25 of dehydroacetic acid displayed the highest hydroxyl radical scavenging activity with an IC50 of 10.21 which is in comparative to the OH radical scavenging value of ascorbic acid. From the table it is clear that the hydroxyl radical scavenging capacity is independent of the nature and position of the substituents. However, it is clear that the hydroxy benzaldehyde substituents have displayed better ability of hydroxyl radical scavenging. All the results have been summed in Table 2 above.
<table>
<thead>
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<th>Compound</th>
<th>Yield (%)</th>
<th>Structure</th>
<th>Compound</th>
<th>Yield (%)</th>
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<tbody>
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<td>77</td>
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<tr>
<td>HR 2</td>
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<td>HR 22</td>
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<td>HR 10</td>
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Chalcones of 4-Hydroxy pyrones (HR1-HR25)
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Conclusion:

In conclusion, a diverse series of chalcones of dehydroacetic acid (DHA) has been developed using piperidine as catalyst. Among all the derivatives, (E)-4-hydroxy-3-(4-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 4) showed the highest DPPH scavenging ($IC_{50}$ of 4.58), while as (E)-4-hydroxy-3-(3-(4-hydroxy-3-methoxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 25) displayed the best OH radical scavenging with $IC_{50}$ of 10.21 which is very close to the $IC_{50}$ values of ascorbic acid used as standard. Owing to the fact that these chalcones exhibit very low cytotoxicity, they show a promising potential in getting explored in food industry.

Supporting Information:

Experimental section including synthesis and antioxidant activity of chalcones of dehydroacetic acid, $^1$H and $^{13}$CNMR spectra of the synthesised compounds can be found associated with this article as supplementary data.

References:

Supporting Information

General experimental procedures

All the solvents and reagents for the preparation of the extracts, chemical synthesis and biological assays were purchased from Sigma Aldrich. The chemical reactions were monitored using F254 silica gel TLC plates (E. Merck) with ceric ammonium sulphate as charring agent and UV chamber (366 and 254 nm) for the detection of spots. The synthesized products were purified using column chromatography on silica gel (60 – 120 mesh). 1H NMR and 13C NMR spectra (chemical shifts expressed in ppm and coupling constants in Hertz) were recorded on Bruker DPX 400 instrument using MeOD as the solvent with TMS as the internal standard. IR was recorded on Cary 630 FT-IR Spectrometer and Mass spectra were carried out on LC–MS 8030 tandem mass spectrometer manufactured by Shimadzu Corporation, Kyoto, Japan. All the compounds were analysed in full scan mode with nitrogen serving as interface gas. Detection was done in ESI mode having probe voltage of 180.0 V, with probe temperature of 400 °C.

Chemicals used: 2, 2-diphenyl-1-picrylhydrazyl (DPPH), ascorbic acid, dry ferric chloride, ferric nitrate, Potassium ferricyanide (1% w/v), phosphate buffer (0.2 M, pH 6.6), TCA, trichloro acetic acid (10%), ferric chloride (0.1%).

General procedure for the synthesis of pyrone based chalcone derivatives:

To a mixture of 3-acetyl-6-methypyron-2-one (1 equiv) and aromatic aldehyde (1 equiv) in ethanol (2 mL), catalytic amount of piperidine was added. The reaction mixture was allowed to stir at 60 °C for 1 to 4 hrs. The progress of the reaction was monitored using TLC. After the completion of the reaction as monitored by TLC, ethanol was evaporated and the crude mixture was subjected to column chromatography (petroleum ether/EtOAc) to obtain the desired product.

Spectral analysis:

3-cinnamoyl-4-hydroxy-6-methyl-2H-pyrone-2-one (HR 1):

1H NMR (400 MHz, CDCl3) δ 8.30 (d, J = 15.7 Hz, 1H), 7.94 (d, J = 15.8 Hz, 1H), 7.67 (dd, J=6.5, 2.8 Hz, 2H), 7.39 (dd, J = 11.3, 7.7 Hz, 3H), 5.94 (s, 1H), 2.26 (s, 3H).

13C NMR (101 MHz,CDCl3) δ 193.04, 183.40, 168.90, 161.44, 146.56, 134.97, 131.33, 129.42 (2 x C), 129.18 (2 xC), 123.25, 102.62, 99.70, 20.87. ESI MS (m/z): 256 [M+Na]+. Anal. Calc. for C15H12O4: C,70.31; H, 4.72; Found C,70.38; H, 4.68.

(E)-4-hydroxy-6-methyl-3-(3-(p-tolyl)acryloyl)-2H-pyrane-2-one (HR 2):

1H NMR (400 MHz, CDCl3) δ 8.30 (d, J = 15.7 Hz, 1H), 7.98 (d, J = 15.7 Hz, 1H), 7.61 (d, J=7.8 Hz, 2H), 7.32 – 7.22 (m, 2H), 5.97 (s, 1H), 2.42 (s, 3H), 2.30 (s, 3H).

13C NMR (101 MHz,CDCl3) δ 192.96, 183.50, 168.70, 161.49, 146.83, 142.12, 132.30, 129.95 (2 x C), 129.52 (2 xC), 122.10, 102.71, 99.64, 77.55, 77.23, 76.92, 21.84, 20.84. ESI MS (m/z): 270 [M+Na]+. Anal.Calc. for C16H14O5: C, 71.10; H, 5.22; Found C,71.17; H, 5.27.

(E)-3-(3-(4-ethoxyphenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyrane-2-one (HR 3):

1H NMR (400 MHz, CDCl3) δ 8.18 (d, J = 15.6 Hz, 1H), 7.94 (d, J = 15.7 Hz, 1H), 7.63 (t, J = 7.8 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 5.91 (d, J = 2.6 Hz, 1H), 4.11 – 4.02 (m, 2H), 2.25 (s, 3H),1.45 – 1.37 (m, 3H).

(E)-4-hydroxy-3-(3-(4-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 4):

1H NMR (400 MHz, DMSO) δ 10.29 (s, 1H, -OH), 8.03 (d, J = 15.7 Hz, 1H), 7.90 (d, J = 15.7Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.27 (s, 1H), 2.26 (s, 3H). 13C NMR (101 MHz, DMSO) δ 191.58, 182.76, 169.51, 161.10, 160.59, 146.54, 131.39 (2 x C), 125.41, 118.69, 116.23 (2 x C), 102.03, 98.69, 20.01. ESI MS (m/z): 272 [M+Na]+. Anal. Calc. for C15H12O5: C, 66.17; H, 4.44; Found C,66.12; H, 4.40.

(E)-3-(3-(furan-2-yl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 5):

1H NMR (400 MHz, CDCl3) δ 8.11 (d, J = 15.4 Hz, 1H), 7.70 (d, J = 15.4 Hz, 1H), 7.56 (s, 1H), 6.78 (d, J = 2.3 Hz, 1H), 6.50 (s, 1H), 5.92 (s, 1H), 2.25 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.35, 183.41, 168.71, 161.32, 152.07, 146.30, 132.17, 120.68, 117.70, 113.13, 102.68, 99.0, 77.55, 77.23, 76.91, 20.84. C13H10O5 246. ESI MS (m/z): 246 [M+Na]+. Anal. Calc. for C13H10O5: C, 63.42; H, 4.09; Found C,63.47; H, 4.03.

(E)-4-hydroxy-6-methyl-3-(3-(thiophen-3-yl)acryloyl)-2H-pyran-2-one (HR 6):

1H NMR (400 MHz, CDCl3) δ 8.09 (d, J = 15.6 Hz, 1H), 7.93 (d, J = 15.6 Hz, 1H), 7.65 (s, 1H), 7.46 (d, J = 4.2 Hz, 1H), 7.34 (s, 1H), 5.92 (s, 1H), 2.25 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 193.10, 183.40, 168.73, 161.44, 139.82, 138.61, 130.69, 127.27, 126.19, 122.90, 99.61, 20.83. C13H10O4S 262. ESI MS (m/z): 262 [M+Na]+. Anal. Calc. for C13H10O4S: C, 59.53; H, 3.84; Found C,59.58; H, 3.88.

(E)-4-hydroxy-6-methyl-3-(3-(2-methoxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 7):

1H NMR (400 MHz, CDCl3) δ 8.35 (s, 2H), 7.71 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 5.92 (s, 1H), 3.91 (s, 3H), 2.25 (s, 3H). 13CNMR (101 MHz, CDCl3) δ 193.20, 183.59, 168.55, 161.49, 161.34, 141.96, 132.79, 129.79, 124.01, 123.22, 121.04, 111.42, 102.76, 101.66, 55.78, 20.81. ESI MS (m/z): 268 [M+Na]+. Anal. Calc. for C16H14O4: C, 57.13; H, 4.93; Found C,67.17; H, 4.90.

(E)-4-hydroxy-6-methyl-3-(3-(2-(trifluoromethyl)phenyl)acryloyl)-2H-pyran-2-one (HR 8):

1H NMR (400 MHz, CDCl3) δ 8.27 (bs, 2H), 7.93 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.3 Hz, 1H), 7.59 (t, J = 7.0 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 5.96 (s, 1H), 2.27 (s, 3H). 13CNMR (101 MHz, CDCl3) δ 192.79, 183.15, 169.35, 161.45, 141.05, 132.39, 130.33 (2 x C), 128.84 (2 x C), 127.29, 126.45, 126.39, 102.44, 99.87, 20.92. ESI MS (m/z): 324 [M+Na]+. Anal. Calc. for C16H11F3O4: C, 59.27; H, 3.42; Found C,59.21; H, 3.48.

(E)-4-hydroxy-6-methyl-3-(3-(3-(trifluoromethyl)phenyl)acryloyl)-2H-pyran-2-one (HR 9):

1H NMR (400 MHz, CDCl3) δ 8.32 (d, J = 15.8 Hz, 1H), 7.91 (d, J = 15.0 Hz, 1H), 7.85 (d, J = 7.1 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 5.96 (s, 1H), 2.27 (s, 3H). 13CNMR (101 MHz, CDCl3) δ 192.85, 183.17, 169.34, 161.40, 144.15, 135.77, 131.86, 129.70, 127.48, 127.44, 126.10, 126.06, 125.20, 102.44, 99.81, 20.91. ESI MS (m/z): 324 [M+Na]+. Anal. Calc. for C16H11F3O4: C, 59.27; H, 3.42; Found C,59.22; H, 3.46.

(E)-4-hydroxy-6-methyl-3-(3-(4-(trifluoromethyl)phenyl)acryloyl)-2H-pyran-2-one (HR 10):

1H NMR (400 MHz, CDCl3) δ 8.34 (d, J = 15.7 Hz, 1H), 7.89 (d, J = 15.7 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.1 Hz, 2H), 5.96 (s, 1H), 2.27 (s, 3H). 13CNMR (101 MHz, CDCl3) δ 192.87, 183.17, 169.41, 161.39, 143.98, 138.31, 129.34 (2 x C), 126.15, 126.12, 126.08, 126.04, 125.85, 102.43, 99.86, 20.92. ESI MS (m/z): 324 [M+Na]+. Anal. Calc. for C16H11F3O4: C, 59.27; H, 3.42; Found C,59.30; H, 3.44.

(E)-4-hydroxy-3-(3-(2-methoxy-4-(trifluoromethyl)phenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 11):

1H NMR (400 MHz, CDCl3) δ 8.39 (d, J = 15.9 Hz, 1H), 8.24 (d, J = 16.0 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.23 (d, J = 7.4 Hz, 2H), 7.11 (s, 1H), 5.95 (s, 1H), 3.95 (s, 3H), 2.27 (s, 3H). 13CNMR (101 MHz, CDCl3) δ 193.17, 183.33,
169.08, 161.44, 158.97, 139.69, 129.88 (2 x C), 127.34, 125.76 (2 x C), 117.72, 108.23, 102.56, 99.86, 56.12, 20.89. ESI MS (m/z): 354 [M+Na]+. Anal. Calc. for C17H13F3O5: C, 70.3157.63; H, 3.70; Found C,57.67; H, 3.75.

(E)-3-(3-(4-bromothiophen-2-yl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 12):

1H NMR (400 MHz, CDC13) δ 7.95 (q, J = 15.4 Hz, 2H), 7.13 (d, J = 3.6 Hz, 1H), 7.04 (d, J = 3.7 Hz, 1H), 5.93 (s, 1H), 2.26 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.09, 183.27, 168.94, 161.36, 142.36, 137.68, 133.13, 131.72, 122.27, 118.57, 102.59, 99.87, 20.89. ESI MS (m/z): 341 [M+Na]+. Anal. Calc. for C17H9BrO4S: C, 47.56; H, 2.66; Found C,45.79; H, 2.60.

(E)-3-(3-(3-bromophenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 13):

1H NMR (400 MHz, CDC13) δ 8.25 (d, J = 15.7 Hz, 1H), 7.88 – 7.74 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.32 – 7.20 (m, 1H), 5.95 (s, 1H), 2.26 (s, 3H). 13C NMR (101 MHz, CD1C3) δ 192.83, 183.22, 169.22, 161.38, 144.42, 137.07, 133.94, 131.94, 130.64, 127.79, 124.71, 123.31, 102.48, 99.78, 20.91. ESI MS (m/z): 335 [M+Na]+. Anal. Calc. for C15H11BrO4: C, 53.76; H, 3.31; Found C,53.70; H, 3.30.

(E)-3-(3-(4-bromophenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 14):

1H NMR (400 MHz, CDC13) δ 8.27 (d, J = 15.7 Hz, 1H), 7.84 (d, J = 15.7 Hz, 1H), 7.52 (s, 4H), 5.94 (s, 1H), 2.26 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 192.84, 183.27, 169.08, 161.41, 144.86, 133.88 (2 x C), 132.44, 130.65 (2 x C), 125.70, 123.90, 102.53, 99.72, 20.88. ESI MS (m/z): 329 [M+Na]+. Anal. Calc. for C15H11BrO4: C, 53.72; H, 3.30; Found C,53.72; H, 3.30.

(E)-4-hydroxy-3-(3-(3-methoxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 15):

1H NMR (400 MHz, CDC13) δ 8.28 (t, J = 15.5 Hz, 1H), 7.89 (d, J = 15.7 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.14 (d, J = 16.7 Hz, 1H), 6.92 (dd, J = 20.2, 8.0 Hz, 1H), 5.93 (s, 1H), 3.82 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.93, 183.32, 168.90, 161.37, 160.12, 146.39, 136.29, 130.11, 123.48, 122.11, 117.37, 113.94, 102.55, 99.67, 55.53, 20.81. ESI MS (m/z): 286 [M+Na]+. Anal. Calc. for C16H14O5: C, 67.13; H, 4.93; Found C,67.16; H, 4.90.

(E)-4-hydroxy-3-(3-(4-methoxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 16):

1H NMR (400 MHz, CDC13) δ 8.18 (d, J = 15.6 Hz, 1H), 7.93 (d, J = 15.7 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 5.92 (s, 1H), 3.84 (s, 3H), 2.25 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.65, 183.61, 168.47, 162.54, 161.56, 146.72, 131.43, 127.82, 120.56, 114.70, 102.83, 99.51, 55.66, 29.90, 20.80. ESI MS (m/z): 286 [M+Na]+. Anal. Calc. for C16H14O5: C, 67.13; H, 4.93; Found C,67.15; H, 4.96.

(E)-4-hydroxy-6-methyl-3-(3-(m-tolyl)acryloyl)-2H-pyran-2-one (HR 17):

1H NMR (400 MHz, CDCl3) δ 8.31 (d, J = 15.7 Hz, 1H), 7.95 (d, J = 15.7 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.29 (dt, J = 16.7, 7.5 Hz, 2H), 5.97 (s, 1H), 2.41 (s, 3H), 2.29 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.94, 183.38, 168.78, 161.40, 146.81, 138.83, 134.86, 132.21, 129.81, 129.01, 126.78, 122.90, 102.60, 99.63, 21.46, 20.79. ESI MS (m/z): 270 [M+Na]+. Anal. Calc. for C16H14O4: C, 71.10; H, 5.22; Found C,71.14; H, 5.27.

(E)-3-(3-(2-chlorophenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 18):

1H NMR (400 MHz, CDCl3) δ 8.29 (d, J = 15.8 Hz, 1H), 8.20 (d, J = 15.7 Hz, 1H), 7.77 (dd, J = 7.2, 2.0 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.29 – 7.17 (m, 2H), 5.89 (s, 1H), 2.20 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 192.83, 183.20, 169.12, 161.37, 141.65, 136.10, 133.09, 131.88, 130.37, 128.62, 127.36, 125.56, 102.47, 99.77, 20.85. ESI MS (m/z): 290 [M+Na]+. Anal. Calc. for C15H11ClO4: C, 61.98; H, 3.81; Found C,61.92; H, 3.86.
(E)-4-hydroxy-3-(3-(2-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 19):

$^1$H NMR (400 MHz, DMSO) δ 10.49 (s, 1H, -OH), 8.29 (d, J = 15.9 Hz, 1H), 8.18 (d, J = 15.9 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.02 – 6.85 (m, 2H), 6.29 (s, 1H, -OH), 3.32 (s, 1H, -OH), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 192.24, 182.70, 169.73, 160.47, 157.86, 141.67, 132.90, 129.36, 121.90, 121.12, 119.66, 116.45, 101.94, 98.91, 20.04. ESI MS (m/z): 272 [M+Na$^+$]. Anal. Calc. for C15H12O5: C, 66.20; H, 4.44; Found C, 66.20; H, 4.41.

(E)-4-hydroxy-3-(3-(3-hydroxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 20):

$^1$H NMR (400 MHz, DMSO) δ 9.73 (s, 1H, -OH), 8.13 (d, J = 15.8 Hz, 1H), 7.83 (d, J = 15.8 Hz, 1H), 7.34 – 7.23 (m, 1H), 7.14 (d, J = 6.6 Hz, 2H), 6.95 – 6.87 (m, 1H), 6.31 (s, 1H), 2.28 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 192.03, 182.46, 170.08, 160.62, 157.86, 145.66, 135.53, 130.28, 122.67, 120.62, 118.79, 114.27, 101.85, 99.10, 20.09. ESI MS (m/z): 272 [M+Na$^+$]. Anal. Calc. for C15H12O5: C, 66.20; H, 4.44; Found C, 66.20; H, 4.41.

(E)-3-(3-(ethoxyxyphenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 21):

$^1$H NMR (400 MHz, CDCl3) δ 8.26 (t, J = 16.0 Hz, 1H), 7.87 (d, J = 15.7 Hz, 1H), 7.26 (dt, J = 7.4, 5.8 Hz, 2H), 7.15 (s, 1H), 6.93 (d, J = 7.8 Hz, 1H), 5.92 (s, 1H), 4.06 (p, J = 7.0 Hz, 2H), 2.24 (s, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 192.92, 183.59, 168.68, 161.59, 159.53, 146.37, 136.32, 130.10, 123.59, 122.08, 117.89, 114.54, 102.79, 99.82, 63.83, 20.83, 14.98. ESI MS (m/z): 300[M+Na$^+$]. Anal. Calc. for C17H16O5: C, 67.99; H, 5.37; Found C, 67.92; H, 5.31.

(E)-3-(3-(2,5-dimethoxyphenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one (HR 22):

$^1$H NMR (400 MHz, CDCl3) δ 8.37 – 8.25 (m, 2H), 7.29 – 7.18 (m, 1H), 6.94 (dd, J = 9.0, 3.0 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 5.92 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 193.11, 183.54, 168.60, 161.49, 153.99, 153.79, 141.69, 124.50, 123.41, 119.00, 113.57, 112.76, 102.74, 99.70, 56.36, 56.07, 20.81. ESI MS (m/z): 316 [M+Na$^+$]. Anal. Calc. for C17H16O5: C, 64.55; H, 5.10; Found C, 64.51; H, 5.14.

(E)-4-hydroxy-6-methyl-3-(3-(2,4,5-trimethoxoxyphenyl)acryloyl)-2H-pyran-2-one (HR 23):

$^1$H NMR (400 MHz, CDCl3) δ 8.41 (d, J = 15.8 Hz, 1H), 8.26 (d, J = 15.7 Hz, 1H), 7.24 (s, 1H), 6.54 (s, 1H), 5.97 (s, 1H), 3.99 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 192.52, 183.85, 168.09, 161.75, 155.68, 153.87, 143.74, 141.97, 119.98, 115.83, 111.39, 103.09, 99.48, 96.76, 56.72, 56.60, 56.33, 20.78. ESI MS (m/z): 346 [M+Na$^+$]. Anal. Calc. for C18H18O7: C, 62.42; H, 5.25; Found C, 62.47; H, 5.20.

(E)-4-hydroxy-6-methyl-3-(3-(3,4,5-trimethoxoxyphenyl)acryloyl)-2H-pyran-2-one (HR 24):

$^1$H NMR (400 MHz, CDCl3) δ 8.19 (d, J = 15.6 Hz, 1H), 7.86 (d, J = 15.6 Hz, 1H), 7.25 (d, J = 4.3 Hz, 1H), 6.88 (s, 2H), 5.94 (s, 1H), 3.87 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 2.26 (s, 1H). $^{13}$C NMR (101 MHz, CDCl3) δ 192.69, 183.43, 168.78, 161.58, 153.67, 146.69, 141.34, 130.45, 122.36, 106.65, 102.71, 99.64, 61.23, 56.46, 20.85. ESI MS (m/z): 346 [M+Na$^+$]. Anal. Calc. for C18H18O7: C, 62.42; H, 5.25; Found C, 62.45; H, 5.22.

(E)-4-hydroxy-3-(3-(4-hydroxy-3-methoxoxyphenyl)acryloyl)-6-methyl-2H-pyran-2-one (HR 25):

$^1$H NMR (400 MHz, CDCl3) δ 8.16 (d, J = 15.6 Hz, 1H), 7.88 (d, J = 15.6 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H), 7.20 (dd, J = 8.4, 1.8 Hz, 1H), 5.92 (s, 1H), 5.62 (s, 1H, -OH), 3.93 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 192.71, 183.60, 168.58, 161.51, 149.64, 146.84, 146.17, 128.79, 123.53, 121.28, 114.52, 110.81, 102.80, 99.59, 56.30, 20.85. ESI MS (m/z): 302 [M+Na$^+$]. Anal. Calc. for C16H14O6: C, 63.57; H, 4.67; Found C, 63.52; H, 4.61.
Representative Spectra

$^1$HNMR and $^{13}$CNMR of 3-cinnamoyl-4-hydroxy-6-methyl-2H-pyran-2-one

$^1$HNMR of

$^{13}$CNMR

$^1$HNMR and $^{13}$CNMR of (E)-3-(3-(furan-2-yl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one

$^1$HNMR
$^{13}$C-NMR and $^{1}H$-NMR of (E)-4-hydroxy-6-methyl-3-(3-(2-(trifluoromethyl)phenyl)acryloyl)-2H-pyran-2-one
$^{13}$CNMR

$^1$HNMR and $^{13}$CNMR of (E)-3-(3-(4-bromothiophen-2-yl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one
HNMR and CNMR of (E)-3-(3-(3-bromophenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one ¹H NMR
$^{1}$HNMR and $^{13}$CNMR of (E)-3-((3-ethoxyphenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one

$^{1}$HNMR
$^1$HNMR and $^{13}$CNMR of (E)-3-(3-(2,5-dimethoxyphenyl)acryloyl)-4-hydroxy-6-methyl-2H-pyran-2-one

$^1$HNMR
Dehydroacetic acid + Aldehyde → Chalcones of hydroxy-2-pyrene (2a-y, 70-85%)

- Easy to synthesize and scale up
- IC₅₀ ranging from 4.5-25 mg/mL
- Non-toxic to human kidney cell line
Staircase Voltammetry using Rotating Disk Electrode

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Abstract

A theory of staircase voltammetry on the rotating disk electrode is developed. The simulation is based on the method of variable diffusion layer thickness. Critical parameters that define the form of responses are calculated.

Keywords: Staircase voltammetry, Rotating disk electrode, Theory

1. Introduction

Staircase voltammetry is replacing linear scan voltammetry in the new instrumentation [1 - 5]. In this technique the response depends on three variables: the potential step amplitude, the step duration and the current sampling parameter [6 - 12]. Here, we present the theory of staircase voltammetry as applied to the rotating disk electrode. These electrodes are frequently used for the investigation of electrochemical mechanisms [13 - 16]. They are characterized by the mass transport that is controlled by the rotational velocity and by the establishment of steady-state conditions [17 - 20]. Theoretical analysis of linear scan and cyclic voltammetry on the rotating disk electrodes is performed using digital simulation [21] and the so-called “bound – unbound” limitary diffusion approximation [22 - 25]. In this paper we are using the variable diffusion layer thickness approximation [26 - 28]. It was applied to the linear scan voltammetry [28], the pseudo polarography [29] and electro-catalytic reactions [30].

2. Model

A simple, reversible electrode reaction of soluble reactant and product is considered:

\[ \text{Red}^{m+} \leftrightarrow \text{Ox}^{(m+n)^+} + ne^- \]  

(1)

On the rotating disk electrode, the mass transport is defined by the following equation:

\[ \frac{\partial c_R}{\partial t} = D \frac{\partial^2 c_R}{\partial x^2} + v_x \frac{\partial c_R}{\partial x} \]  

(2)

where \( v_x = \kappa \omega^2 \) and \( \kappa = 0.51 \omega^{3/2} \nu^{-1/2} \). The symbols \( \omega \) and \( \nu \) stay for the rotation rate and kinematic viscosity, respectively, and \( c_R \) is the reactant concentration. In the applied approximation it is assumed that the concentration depends linearly on the distance from the electrode surface within the diffusion layer and that it is equal to the bulk value \( c^*_R \) outside this layer:

\[ c_R = c_{R,x=0} + (c_{R}^* - c_{R,x=0}) \frac{x}{\delta} \quad \text{for} \quad 0 \leq x \leq \delta \]  

(3)

\[ c_R = c_R^* \quad \text{for} \quad x > \delta \]  

(4)

The diffusion layer thickness \( \delta \) depends on time and the purpose of calculation is to resolve this dependence. Firstly, the differential equation (2) is integrated from \( x = 0 \) to \( x \to \infty \) and transformed into the following form:

\[ d\delta/dt = \frac{2D}{\delta} - 2\kappa \omega^2 /3 + \delta (c_R^* - c_{R,x=0}) \]  

(5)
Under the steady-state conditions \( (d\delta/dt = 0 \text{ and } dc_{R,x=0}/dt = 0) \) the diffusion layer thickness approaches the limiting value: \( \delta_{ss}^2 = 3D/\kappa \). The differential equation (5) can be further transformed by the substitution \( u = \delta^2/D \). In this form it can be solved numerically.

\[
du/dt = 4 - 4ku^{3/2}/3 + 2u(c_R^{0} - c_{R,x=0})^{-1}dc_{R,x=0}/dt
\] (6)

where \( k = \kappa \sqrt{D} \). Electrode reaction (1) satisfies Nernst equation and the reactant concentration at the electrode surface depends on the potential:

\[
c_{R,x=0} = c_{R}^{0}[1 + \exp(nF(E - E^0)/RT)]^{-1}
\] (7)

In the staircase voltammetry the potential is changed for the discrete value \( \Delta E \) at the beginning of each step and remains constant during the step. So, the reactant concentration at the electrode surface is changed only when the potential is changed:

\[
 dc_{R,x=0}/dt = c_{R}^{0} \{[1 + \exp(nF(E + \Delta E - E^0)/RT)]^{-1} - [1 + \exp(nF(E - E^0)/RT)]^{-1}\}
\] (8)

The formal scan rate is defined as \( \nu = \Delta E/\tau \), where \( \tau \) is the step duration. The current depends on the concentration gradient at the electrode surface:

\[
i = nFSD(c_{R}^{0} - c_{R,x=0})/\delta
\] (9)

Under steady-state conditions the limiting current appears:

\[
i_{lim} = nFSDc_{R}^{0}/\delta_{ss}
\] (10)

3. Results and discussion

Staircase voltammogram on the rotating disk electrode is either the wave or the curve with the maximum and the limiting current. This is shown in figures 1 and 2. The maximum increases with the scan rate and decreases with the rotation rate. Note that \( k = 0.51\omega^{3/2}(D/\nu)^{1/2} \). If the scan rate is low and the rotation rate is high, the maximum disappears, and the response acquires the form of the wave, as in d.c. polarography. At high potentials all responses tend to the limiting current that is defined by eq.(10).

![Staircase voltammograms on the rotating disk electrode](image)

Fig. 1 Staircase voltammograms on the rotating disk electrode, \( \Delta E = 1 \text{ mV}, n = 1, k = 1 \text{ s}^{-3/2} \text{ and } \nu/(\text{V/s}) = 0.1 \) (1), 0.5 (2), 0.8 (3) and 1 (4).
Fig. 2 Staircase voltammograms on the rotating disk electrode, \( \Delta E = 1 \text{ mV} \), \( n = 1 \), \( v = 1 \text{ V/s} \) and \( k / s^{3/2} = 1 \) (1), 2 (2), 4 (3) and 20 (4).

The current maxima and peak potentials depend on the dimensionless scan rate \( \sigma = nFv \delta_{ss}^2 / DRT \). This variable embrace both the scan rate and the rotation rate because the steady-state diffusion layer thickness is defined by the following equation: \( \delta_{ss} = 1.61D^{1/3}v^{1/6} \omega^{-1/2} \). These relationships are shown in figures 3 and 4. The dependence of the ratio of maximum and limiting currents on the square root of the variable \( \sigma \) is a curve with two asymptotes: \( i_{max} = i_{lim} \) for \( \sqrt{\sigma} < 3.50 \), and \( i_{max} / i_{lim} = 0.42\sqrt{\sigma} - 2.48 \) for \( \sqrt{\sigma} > 12 \). If the potential increment is 2 mV, the slope of the second asymptote is 0.40 and applies for \( \sqrt{\sigma} > 12 \). The first asymptote corresponds to the responses that resemble polarographic wave and exhibit no maxima. The second asymptote defines the conditions under which the current maximum increases linearly with the square root of scan rate and the slope of this relationship is independent of the rotation rate: \( \Delta i_{max} / \Delta \sqrt{\sigma} = 0.42nFSc_R^2 \sqrt{DF/RT} \). The factor 0.42 is the consequence of the assumption that the current is sampled at the end of each step.
Fig. 3 Dependence of current maxima (A) and peak potentials (B) of staircase voltammograms on the square root of the dimensionless scan rate ($\sigma = nFv\delta_{2,1}^{2}/DRT$) for $n = 1$ and $\Delta E = 1$ mV.

The peak potentials are inversely proportional to the variable $\sigma$, as can be seen in Fig. 3B. If $\sqrt{\sigma} < 6$ the peak potential is higher than $0.1$ V vs. $E^0$ and apparently tends to infinity as $\sqrt{\sigma} \rightarrow 3.50$. These are the characteristics of the responses with very small maxima, as can be seen in Fig. 3A. The potentials of significant maxima are lower than $0.075$ V if $\sqrt{\sigma} > 10$.

Fig. 4 Relationship between current maxima of staircase voltammograms and the dimensionless scan rate for $n = 1$ and $\Delta E = 2$ mV.
These calculations have shown two critical parameters that determine the form of responses: $\sqrt{\sigma_{\text{crit}}} = 3.50$ and $\sqrt{\sigma_{\text{crit}}} = 12$. The voltammogram appears in the form of polarographic wave if the ratio of scan rate and the rate of rotation satisfies the following inequality: $\nu/\omega < 4.726(D/\nu)^{1/3}RT/nF$. If $n = 1$, $D = 10^{-5}$ cm$^2$/s and $\nu = 10^{-2}$ cm$^2$/s, this condition is $\nu/\omega < 0.012$ V/rad. The second critical parameter defines the condition for voltammograms with well developed maximum: $\nu/\omega > 55.55(D/\nu)^{1/3}RT/nF$. In the particular case as above, this condition is $\nu/\omega > 0.143$ V/rad.

4. Conclusion

Staircase voltammetry on rotating disk electrode depends on the ratio of scan rate and the rate of rotation. The critical values of this parameter, that are determined in the presented calculations, can serve for the optimization of experimental procedure.

References


Experiments on The Effects of Reagents and Electricity on Seed Germination Growth and Viability

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Abstract:
Most plants develop from seeds. Dry seeds under dormant condition show no sign of life. Only on the availability of stimulants like water, an adequate temperature etc., do seeds undergo biochemical reactions and develop into plants. Generally the first and most important thing for seeds to germinate is the availability of an optimum quantity of water. Under all circumstances seeds are soaked in ‘plain’ water before germination. They swell up, their surfaces become smooth and slowly radicles protrude. Various chemical changes occur within a seed during germination. Now these reactions may be altered by use of reagents. If the chemical natures of the constituents of seed layers are known, it may be possible to change the chemicals by suitable reactions. For E.g. if aldehydic group be present, it may either be oxidized or reduced. But if this occurs the entire process of germination and plant growth 'should' be affected. In this paper chemical effects on seed germination have been expounded in detail.

Keywords: Seed; Germination; Radicle; Oxidation

Introduction:
Germination of seeds is a natural phenomenon which prevents extinction of plant species. From the agricultural point of view germination is important because it is the basis of crop production. Use of disease resistant varieties along with the extensive use of chemical fertilizers have enhanced yield in the recent years. Before plantation seeds are either soaked in water for a predetermined time or they may be scattered directly on wet soil to facilitate germination. The process to be chosen depends on the nature of the seed. Dry seeds contain 10-15% water. Low levels of respiration have been reported in dry seeds. During imbibitions in 15 minutes is the reformation of keto acids from amino acids by deamination and transamination. Whatsoever the case may be the prerequisite of seed germination is water. The source of water is either soil moisture or it may be supplied from ponds, lakes etc. Though the water may contain dissolved minerals in it, the germination process is unaffected due to their quantity being minute. Now if chemicals are present in considerable amounts, would the seeds still germinate? The following questions are self-assertive:-

- The chemical may induce side reactions within the seed. So in a way the chemical may be harmful.
- The excess addition of electrolytes may render the solution hypertonic so there may be a chance of plasmolysis.

If the germinated seeds are planted in soils with excess of salts would the plants still flourish? What would be the effects on plant growth?

Before proceeding further a general idea regarding the composition of a seed is essential.

Seed Coat. It is easily permeable and in no way delays germination. It consists of four layers viz.

I. The outer portion of the pericarp, consisting of one or more layers of cells whose walls contain some pectic substance. Glucose is present in the pericarp.

II. The inner epidermis of the pericarp in which lignification has occurred.

III. The lignified testa.
IV. The suberized remnant of the nucellar tissue.

**Endosperm**: Contains large amount of starch (carbohydrates), proteins like glutenin and gliadin minute quantities of fats and some minerals.

**Embryo**: Contains carbohydrates like sucrose, enzymes like peroxidase, and catalase minerals like potassium and magnesium.

Generally the seed coat is permeable. This is evident from the fact that large quantities of water are imbibed by the seed resulting in its swelling. Many chemicals are encountered in seeds like glucose, starch, cellulose, sugars enzymes etc. Their percentage varies according to the nature of the seed.

Various compounds are present within the seed among which number cellulose, glucose, starch, proteins, enzymes, sugars etc. Now looking into these compounds one by one:

i. **Cellulose**: Bearing a formula \((C_6H_{10}O_5)_n\), it is a poly saccharide consisting of a linear chain of several hundred to many thousands of \(\beta (1\rightarrow 4)\) linked D-glucose units. \(\text{CH}_2\text{OH}\) group is susceptible to attack by oxidizing agents.

ii. **Glucose**: Contains one \(-\text{CHO}\) and one \(\text{CH}_2\text{OH}\) group. These are easily oxidizable using agents like \(\text{HIO}_4\), \(\text{HNO}_3\) etc. While on oxidation using periodic acid, it yield a mixture of formic acid and formaldehyde, on using nitric acid it gives glucaric acid (saccharic acid).

iii. **Starch**: Contains 20% water soluble amylase along with 80% insoluble amylopectin. Amylose contains \(-\text{CH}_2\text{OH}\) group which may get oxidized, though the reactions may be slow due to its long chain structure and presence of neighboring groups.

iv. **Sugars**: May be in the form of fructose, sucrose etc. These may exhibit characteristic reactions of sugars.

v. **Proteins and amino acids**: These are viable to attack in the \(\text{COO}^-\) and \(\text{NH}_3^+\) groups. Strong conditions may alter the structure of protein.

vi. **Enzymes**: Presence of external chemicals can retard or accelerate their activity, the determination of which requires careful observation.

**Chemicals and Apparatus required:**

1. Pea, Mung, Lentil and Gram (purchased from a grocer)
2. Oxalic acid crystals
3. Ammonium sulfate
4. Sodium Chloride
5. Sucrose (Ordinary table sugar)
6. Monosodium glutamate
7. Potassium Permanganate
8. Dilute sulfuric acid.
9. Muriatic acid
10. Hydrogen peroxide (6% solution)
11. Iron, Aluminum, Zinc, Copper
12. 5V D.C source
13. 4W LED lamp operating from 230V source
14. 100W incandescent lamp
15. Merbromin 2% solution
16. Methylene blue stain solution
17. Tea leaves extract
18. Flour
19. Sodium hydroxide .1N solution
20. Kerosene oil
21. Acetone
22. Absolute alcohol
23. Mustard oil
24. Boric acid I.P

**Experimental:**

The choice of seeds was crucial because germination time and availability were important factors. For the experiments Pea (*Pisum Sativum*), Mung bean (*Vigna Radiata*), Gram (*Cicer Aritinum*) and Lentil (*Lens Culinaris*) were chosen. The reason behind choosing the above were:

I. Short time required for germination (≤24 hours).
II. Rapid growth
III. Large availability and low cost.

The above seeds (in dry condition) when soaked in tap water for 8-10 hours swell up by imbibing water and the surface becomes smooth. The water is then removed and the wet seeds are covered and kept in the dark. After about a day radicles are observed. When planted in soil, they develop into plants. Under favorable conditions the plants bear fruit. This is the commonest method practiced for the production of plants. When large scale production is required, the dry seeds are often scattered on wet soil by broadcasting method. The moisture which is the prerequisite of germination comes from the soil itself. However under any circumstance if the seeds are soaked in water beforehand, the entire process gets accelerated.

To start with a simple experiment similar to the one adopted by farmers for the cultivation of crops was tested. Ten pieces each of pea, gram, mung bean, and lentil were soaked in 100ml. water for 8 hours. The period chosen was exactly half of the 16 hour soaking period by which imbibition is supposed to reach completion. After completion of 8 hours, the water was thoroughly rinsed and the seeds were covered. After another 10 hours emergence of radicles was observed. These were allowed to grow for another 10 hours and were planted in untreated soil sprinkled with water. Very quickly all the 40 seeds (10 from each sample) developed into healthy plants. It was also observed that mung beans display the fastest rate of germination and a few germinated during the soaking period itself. So the entire process of germination was complete within 12 hours for mung and 28 hours for the remaining samples. The plants were kept under diffused sunlight not enough to scorch them.

The effect of salinity on the germination and growth has already been studied. It has been found that high salinity is harmful for the development of plants in terms of height, length of root, no. of leaves, leaf dry mass and root dry mass.

Previously it has been stated that the seed coat is permeable. A simple experiment was performed to test it.
Five seeds of each sample were soaked in turn in kerosene oil, mustard oil, acetone and absolute alcohol for 24 hours. Apparently no absorption occurred. The seeds retained their crooked structure as is expected when they are dry. The surfaces of the seeds soaked in kerosene oil mustard oil became oily but those immersed in acetone and absolute alcohol remained normal. After the completion of 24 hours, the seeds were immersed in water for 10 hours, the water was removed and the seeds were covered to induce germination. Within the next 30 hours they germinated. They were planted and developed into healthy plants. So it may be inferred that nonionic liquids like mustard oil, alcohol etc have no apparent effect on seed germination and viability.

**Experiment no. 1**

Pea seeds were soaked in a solution of KMnO₄ acidified with a few drops of dilute H₂SO₄ for 8 hours. The solution gradually faded in color indicating oxidation in some form. After 8 hours the seeds were properly washed with cold water and left in the air for half an hour. These were then covered and kept in the dark to allow germination. After about 15 hours emergence of radicles was observed. These were planted in moist soil. The cotyledons showed rapid growth. From after two days potassium permanganate solution was added to the soil in doses of 5-10 drops at a time and this was done 3 times a day. The plants were not kept under sunlight. They were irradiated by a 4W LED instead for 4 hours a day. The plants showed very rapid growth. Within four hours shoot length increased by 2.5 mm under constant irradiation.

Pea seeds were ground into powder using a mortar and pestle. The powder was treated with acidified potassium permanganate. It slowly turned colorless indicating oxidation of the powder. The same must have occurred when the seeds were soaked in acidified potassium permanganate solution.

**Experiment no. 2**

Concentrated tea leaf extract was used to soak pea and gram seeds in separate beakers for 10 hours. They were washed with cold water and covered. They germinated and were planted in soil enriched with the same tea leaf extract. The plants were irradiated in turn by a 4W LED and a 25W GLS lamp. The plants showed very rapid growth. Doses of tea leaf extract were added to the soil instead of water to keep it moist.

A sample of the same tea leaf extract that was used for soaking the seeds was treated with acidified KMnO₄ which turned colorless indicating oxidation of the extract.

**Experiment no. 3**

Pea seeds were soaked in a solution of strong sodium carbonate for 10 hours. The seeds imbibed and swelled up as usual. They were washed and kept in air for half an hour. After this they were covered and allowed to germinate. After 20 hours it was found that the seeds had shrunked and only 50% seeds had germinated. When planted in soil they showed retarded growth. The shoots were lean and the plants unsteady. They did not survive long.

**Experiment no. 4**

Gram seeds were soaked in a solution of .1N NaOH for 10 hours. They were washed with cold water and kept covered for 20 hours. The seeds shrunked and did not germinate. After 1 day black particles were observed on the surfaces of the seeds. So clearly NaOH had damaged the cells and allowed the growth of microbes.

**Experiment no. 5**

Pea seeds were soaked in a strong sucrose solution and allowed to rot. The principle behind this was that sugar and pea being both biodegradable should be acted upon by microbes and broken down in to simpler substances. As expected the solution rotted within two days. It was allowed to stand for another 5 days till black scummy mass floated on the surface of the solution. This solution has been referred to as the ‘extract’. Pea, gram and
mung were soaked in 80ml water ‘poisoned’ with 10 drops of the extract. The soaking period was 10 hours. They were then allowed to germinate. Emergence of radicles was observed 15 hours except for mung where this period was only 6 hours. The same experiment was repeated, this time with 20 drops of extract. Every seed germinated. They were planted in soil enriched with the extract. They developed in to very healthy plants.

**Experiment no. 6**

Pea, gram and mung were soaked in a solution of 1% boric acid for 10 hours. The seeds swelled up and the surfaces became smooth. The seeds were rinsed and left in the open for half an hour. After this they were covered to induce germination. After another 10 hours emergence of radicles was observed. These were planted in soil moistened with the same 1% boric acid solution that was used for soaking the seeds. They rapidly developed in to healthy plants. The soil was kept moist by periodic addition of 1% boric acid solution in drops. The plants were irradiated using a 4W LED emitting 350 lumens for 4 hours a day.

**Experiment no. 7**

Mung was soaked in a solution of 2% NaCl along with a few drops of methylene blue so as to render the solution blue for 8 hours. The seeds developed a blue hue. They were covered after rinsing the solution. Very healthy radicles emerged. They were planted in soil enriched with the same solution. Very rapidly they developed in to healthy plants. The same experiment was repeated using pea. They yielded similar observations and results.

**Experiment no. 8**

Mung was soaked in 6% hydrogen peroxide to a depth such that the top of the seeds were in the peroxide air interface. A lot of bubbling was observed. The green color of the seeds faded and they seemed bleached. This was certainly due to oxidation by nascent oxygen. After 8 hours even before the removal of the solution, tiny radicles were observed. They were allowed to grow and were planted in soil. They developed in to very healthy plants. But gram treated by the same method showed contradictory results and showed no germination. The surfaces of the seeds were hued black and they shriveled.

**Experiment no. 9**

Mung was soaked in pure lemon juice for 10 hours. The seeds did not swell up indicating no absorption. When left in the open air after the post soaking period, no change in physical appearance of the seeds was noticed. They were now dipped in water. Still no absorption occurred. The seeds were scattered over wet soil. Slowly they dried up and shrinked. So clearly lemon juice having 6% citric acid by composition had destroyed the imbibing capacity of the seeds.

**Experiment no. 10**

Pea was soaked in M/50 solution of oxalic acid for 12 hours. The seeds swelled up indicating absorption. They were washed with water and kept covered to allow germination. But no germination occurred. Instead white particles were observed on the surfaces of the seeds. The seeds became ‘sticky’. Mung treated by a similar method germinated and developed in to plants.

**Experiment no. 11**

Strong ammonium sulfate solution was used to soak pea seeds for 14 hours. The seeds imbibed as usual. These were washed with water and covered. No germination occurred. White sticky mass formed on the seed surfaces instead.

Besides conducting these experiments for studying seeds germination and growth, several ‘generations’ of plants were grown to study the overall effect of soil chemicals and electric current on plant growth and
development. The use of the word generation here is improper because no study was made on the offspring. Moreover the same species of plant was not grown for two successive generations.

For these experiments two separate pots of maximum diameter 7cm and minimum diameter 4.5cm were filled with equal quantities of soil. One was labeled ‘SET UP A’ while the other ‘SET UP B’. Consequently the first generation of ‘SET UP A’ was named ‘Generation 1A’ and so on.

**Generation 1A**

Pea seeds were soaked in plain water for 10 hours and were covered. After germination they were planted in soil. The soil was kept moist by periodic addition of small doses of water. The plants were irradiated using a 4W LED emitting 350 lumens at an average of 90 minutes a day. The light was connected in series with the soil and the soil was used as a conducting medium so as to pass 30mA A.C current through the soil. After 3 days 5 ml of 6% H$_2$O$_2$ was added to the soil and a lot of bubbling was observed. 24 hours hence M/20 solution of potassium permanganate was added in doses of 3ml at a time thrice a day. The current was increased to 100mA by replacing the LED with an incandescent lamp. The leaves started yellowing and drooping. They lasted for a total of 10 days.

**Generation 2A**

Gram seeds were soaked in a solution of monosodium glutamate prepared by dissolving 5g of the solute in 100ml water along with a few drops of methylene blue. The idea behind this was to test whether the compound would poison the seeds in any way. The seeds shriveled up but germinated, nevertheless. They were planted in the soil. The plants were irradiated using a 4W LED emitting 350 lumens. 4.5-6mA D.C was passed through the soil using iron electrodes. The anode gradually corroded and a brown scar mark was observed around the anode. So iron was slowly dissolved in the soil. The plants were quite healthy and showed rapid growth. 20 ml of M/20 potassium permanganate was added to the soil. After 2 days 20 ml water with 5 drops of methylene blue was added. 20 ml strong tea leaf extract was also added to the soil. The plants were very healthy. They lasted for 20 days.

**Generation 3A**

Mung was soaked in strong sucrose solution energized from the output of electronic ballast (used in fluorescent tubes). The solution became hot and the temperature increased to 60°C. The solution developed a yellow hue. The seeds dried up once the solution was removed. On stimulating by a few drops of water they germinated and were planted. Very healthy plants developed. The soil was energized using 230V-50Hz A.C using a 2.5µF capacitor in series. The plants developed very rapidly. Their life span was 20 days.

**Generation 4A**

Mung was soaked in a solution prepared by dissolving .2g KMnO$_4$ and 5g ammonium sulfate in 100ml water. Only 50% seeds germinated. They were planted in soil and M/20 potassium permanganate (20ml) was added to the soil. Very healthy plants were obtained. They were irradiated by a 4W LED. The plants lived for 15 days.

**Generation 1B**

50ml. M/20 KMnO$_4$ solution was added to soil. Dry mung was scattered over this wet soil. The soil was energized from a 230V-50 Hz A.C source with a 2.5µF capacitor in series. An additional earth electrode was also buried in the soil. All the electrodes were made of copper having a crossection of 1.5mm$^2$. Emergence of radicles was observed in less than 48 hours. The plants were irradiated using a 4W LED emitting 350 lumens. 40 ml of M/20 potassium permanganate was added to the soil in doses of 10 ml at a time 4 times a day. Strong tea leaf extract was also added. Plants flourished. They lasted for 20 days.

**Generation 2B**

10 drops of lemon juice was diluted to 25ml and was added to the soil. Zinc and iron electrodes were buried in the soil. Pea seeds were soaked in M/20 potassium permanganate for 12 hours and in water for another 45
minutes. These were allowed to germinate and were planted in soil. They developed into very healthy plants. As usual they were irradiated from a 4W LED. The plants survived for 25 days.

**Generation 3B**

Pea seeds were soaked in water for 12 hours and allowed to germinate. 50ml M/20 KMnO₄ was added to the soil and the germinated seeds were planted in this soil. 5V D.C was applied to the soil using Al electrodes at an average of 4 hours /day. Concentrated sugar solution (50ml) was added to the soil after 5 days. 25ml water, sucrose and flour were allowed to rot. The rotten solution was added to soil. Ammonium sulfate solution was added to the soil. The plants lasted for 20 days.

**Generation 4B**

Pea seeds were soaked in solution of 100 ml water and 5 drops of 2% merbromin \((C_{20}H_{8}Br_2HgNa_2O_6)\) for 9 hours. This is an organomercuric compound and a fluorescein. Mercury being toxic might affect germination and retard plant growth. During the soaking period the solution was supplied with 5V D.C using aluminum electrodes which caused electrolysis of the solution. The seeds were stained red. They were planted in the soil. Pre-germinated gram seeds were also scattered over the soil and the plants were irradiated by a 4W LED. The seeds germinated in their due course. Apparently Hg had no effect.

**Observations:** The results of the experiments have been tabulated below, the parameters of comparison being time required for radicle emergence, germination percentage, and nature of the radicles (healthy or unhealthy) and maximum height attained.
Table no. 1

<table>
<thead>
<tr>
<th>Seed used</th>
<th>Solution used</th>
<th>Time of immersion in hours</th>
<th>Time required for emergence of radicles in hours</th>
<th>% of germination</th>
<th>Nature of radicles</th>
<th>Max. height in cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pea</td>
<td>M/20 KMnO₄ acidified with dilute H₂SO₄</td>
<td>8</td>
<td>15</td>
<td>100</td>
<td>Very healthy</td>
<td>29</td>
</tr>
<tr>
<td>Gram</td>
<td>Conc. Tea leaf extract</td>
<td>10</td>
<td>15</td>
<td>100</td>
<td>Very healthy</td>
<td>29</td>
</tr>
<tr>
<td>Pea</td>
<td>Conc. Na₂CO₃</td>
<td>10</td>
<td>20</td>
<td>&lt;50</td>
<td>Unhealthy</td>
<td>10</td>
</tr>
<tr>
<td>Gram</td>
<td>.1N NaOH</td>
<td>10</td>
<td>20</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pea, gram and mung</td>
<td>Water poisoned with extract</td>
<td>10</td>
<td>15-20 hours for pea and gram, 6 hours for mung</td>
<td>100</td>
<td>Very healthy</td>
<td>27.5</td>
</tr>
<tr>
<td>Pea, gram and mung</td>
<td>1% boric acid</td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>Very healthy</td>
<td>29.5</td>
</tr>
<tr>
<td>Mung and pea</td>
<td>2% NaCl with few drops of methylene blue</td>
<td>8</td>
<td>10</td>
<td>100</td>
<td>Very healthy</td>
<td>28</td>
</tr>
<tr>
<td>Mung and Gram</td>
<td>6% H₂O₂</td>
<td>8</td>
<td>0 for mung, no germination for gram</td>
<td>100</td>
<td>Very healthy for mung</td>
<td>26 (for mung)</td>
</tr>
<tr>
<td>Mung</td>
<td>Pure lemon juice</td>
<td>10</td>
<td>No germination</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pea and Mung</td>
<td>M/50 oxalic acid</td>
<td>12</td>
<td>No germination</td>
<td>70 for mung, 0 for pea</td>
<td>Healthy for mung</td>
<td>26 (for mung)</td>
</tr>
<tr>
<td>Pea</td>
<td>Strong ammonium sulfate</td>
<td>14</td>
<td>No germination</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pea</td>
<td>Merbromin solution excited by passage of 5V D.C</td>
<td>9</td>
<td>15</td>
<td>100</td>
<td>Healthy</td>
<td>24</td>
</tr>
</tbody>
</table>

It has been observed that irradiation by LED cool daylight/6500K caused very rapid growth. Addition of KMnO₄ drop wise to the soil proves to be highly beneficial for the growth of pea. Dissolution of aluminum slowly in to the soil by electrolysis also increased growth and helped plants flourish rapidly. Constant excitation from a 230V-50Hz source using a capacitor in series is also beneficial.
Results and Discussions:

Seeds germinate as a result of complex biochemical reactions occurring within the seeds stimulated by the availability of water and a prerequisite temperature. Chemicals affect the reactions in various ways. Only a few have dealt with in this paper. The following important results have been summarized:

I. Acidified M/20 solution of KMnO₄ leads to excellent germination rates in legumes (in peas, gram and mung). Its addition in regulated doses to the soil leads to rapid growth of plants.

II. If the plants (as mentioned above) are irradiated by LED lamps, the growth is accelerated. This prevents the risk of the plants from getting scorched in direct sunlight.

III. Ammonium sulfate though an excellent fertilizer totally retards seed germination. The percentage of germination decreases significantly. The few seeds that germinate display weak and lean radicles that do not show growth.

IV. Oxalic acid allows ‘preferential’ germination. While mung germinates in a solution of oxalic acid others do not.

V. Alkaline solutions like sodium hydroxide and sodium carbonate totally retard germination. They assist in the growth of fungi instead.

VI. Hydrogen peroxide allows the germination of mung but retards the germination of other legumes (pea and gram).

VII. Pure lemon juice having 6% citric acid disallows germination. The seeds don’t absorb. However, lemon juice diluted with water causes germination and rapid growth.

VIII. No absorption of organic solvents like acetone, absolute alcohol and kerosene is noticed. But soaking in these solvents does not damage the seeds either. On soaking the seeds back in water, the seeds absorb water and germinate.

IX. Application of electricity to the solution during the soaking period causes electrolysis of the solution but has no apparent effect on the germination process. However, if copper or iron electrodes are used insoluble metal hydroxides on the seeds surfaces hinders absorption and consequently retards germination.

X. Application of low voltage D.C at 5-12V and 5-10mA to the soil using aluminum electrodes leads to slow dissolution of electrodes in the form of Al³⁺ in to the soil. It proves highly beneficial for the growth of plants.

XI. Compound of boric acid, merbromin and methylene blue have no significant effect on the germination.

XII. Best results are obtained if the soaking period is ≈8hours and the seeds are soaked in plain water for 15 to 20 minutes during the post soaking period.

XIII. Solutions of strong acid like HCl just like strong bases (discussed earlier) have a detrimental effect on seed germination. Concentrations of ≥.01M may be harmful.
XIV. High voltage A.C (230V-50Hz) in ‘short pulses’ to the soil renders the soil hot and assists in destroying harmful bacteria and helps in plant growth.

Compounds like potassium permanganate are inexpensive and easily available in the market. Careful application can significantly increase the yield of legumes. Also, the legumes do not require sunlight and a low power LED serves the purpose. Hence the plants may be cultivated under LED without compromising with growth and yield. However, GLS lamps consume more power and produce more heat resulting in yellowing and consequent drying up of the leaves and are not useful for growth. It has been observed that tea leaf extract is highly beneficial for germination and growth. The extract is 80-90% more effective as compared to ordinary leaves used as manure. Occasional addition of boric acid proves helpful. Zinc, iron and aluminum electrodes buried in soil causes their slow leaching in to the respective ions increasing growth.

Conclusion:

Addition of chemicals e.g. potassium permanganate in predetermined doses can significantly affect the germination rate and growth of leguminous plants like pea, mung and the like. These may also prevent the growth of harmful microbes and hence enhance productivity. KMnO₄ works best under these situations owing to its oxidizing nature. Irradiation from a LED placed at a short distance about 1 inch horizontally from the plant causes very rapid growth and eliminates the dependence on sunlight. Slow dissolution of zinc and aluminum ions in to the soil also increases yield to a great extent. For this electrolysis at low voltage and 5-10mA current is highly useful. However current should not exceed 20mA as it would lead to very fast dissolution of ions and increase their concentration in the vicinity of the roots causing plasmolysis. The voltage should be maintained at 5-10V.

Acknowledgements:

This work has been financed and encouraged by Mr. P.B Nandi and Mrs. Krishna Nandi.

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Effect of Oxidant 1, 3-Dichloro-5,5-Dimethylhydantoin and 5, 5-Dimethylhydantoin with Different Substrates: The Kinetic Measurements

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Abstract:

The kinetic measurement with different concentration of oxidant 1,3-dichloro-5,5-dimethylhydantoin and 5,5-dimethylhydantoin with ℓ-alanine, ℓ-glycine and ℓ-valine. The catalytic effect of acid in the reaction rate reveal an interaction between oxidants species H2O+Cl and substrates. The observed order of reactivity of ℓ-amino acids (ℓ-glycine > ℓ–alanine > ℓ-valine) was explained on the basis of hydrolysis of reacting species.

Keywords: Kinetic measurement, concentration, catalytic effect, hydrolysis, reveal.

1. Introduction

N-chlorinated hydantoin are important and versatile chlorinating agents. That have found use in a range of synthetic operations. The prototypical example, 1,3-dichloro-5, 5-dimethylhydantoin (DCDMH) has been employed as a chlorine source for the α-chlorination of acetophenones1 and 1-aryl-2-pyrazolin-5-ones,2 for the preparation chlorohydrin derivatives of corticosteroids3 for the benzylic chlorination of 2-methylpyrazine,4 and for the selective chlorination of a heavily functionalized quinoline derivative in route to the antibiotic ABT-492.5 In the latter DCDMH6-8 was employed to trap an enolate resulting from the attack of dimethyl zinc on to an α,β-unsaturated ketone, DCDMH has been employed as a number of transformation including the halodeboration of aryl boronic acids,9 the oxidation to triazolinediones,10 the microwave-assisted cleavage of oximes11, the preparation of dialky chlorophosphatges,12 and as a terminal oxidant in the sharpless asymmetric amino hydroxylation reaction.13,14 DCDMH has emerged as leading of silyl linkers for solid-phase organic synthesis.15-18

1. Experimental

All the reagents and solvents used were of analytical grade (B.D.H., C.D.H. and Acros). The solution of DCDMH is standardized iodometrically. The solution of sodium thiosulphate was prepared by taking a B.D.H. grade simple in a doubly distilled water and was standardized against copper sulphate solution using KI and starch as an indicator iodometrically. Other solutions of NaCl, KCI, DMH were prepared by dissolving. Their requisite amount of AnalAr sample in distilled water. The reaction kinetics was studied by using thermostat maintained at constant temperature.

2. Results And Discussion

The kinetic data have been collected for five-fold concentrations of the oxidant [DCDMH] (1.25 – 5.0 × 10⁻³ mol dm⁻³) and at fixed concentration of ℓ-alanine at 303 K temperature (Table: 1 and Fig. 1). The unit slope of plot of log [DCDMH] vs. time was found to be linear indicating first-order dependency on the reaction rate. The effect of [5,5-dimethylhydantoin] (DHM) on the rate of oxidation of was investigated by taking its varying five-fold concentration of (0.50 – 5.00 × 10⁻² mol dm⁻³) maintaining. The concentration of ℓ-glycine and ℓ-valine constant at fixed temperature (Table: 2 and Fig. 2). The inverse plot of k⁻¹ vs. [DMH] was obtained linear in each substrate.
Mechanism

1,3-dihloro-5,5-dimethylhydantoin (DCDMH) on hydrolysis yields finally dimethyl hydantoin (DMH) in aqueous solution. The following equilibrium exists.

\[
\text{HOCl} + \text{H}^+ \xrightleftharpoons[K_1]{K_3} \text{HOCI}^+ \\
\text{(Protonated)}
\]

\[
\text{\text{(S)}} + \text{RCH(OH)COO}^- \xrightarrow{\text{fast}} \left[ \begin{array}{c} \text{R} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \right] - \text{Cl} + \text{NH}_4^+ \\
\text{(Zwitter ion)}
\]

\[
\text{[S]} + \text{H}^+ + \text{Cl}^- \xrightarrow{\text{fast}} \text{NH}_4^+ \text{Cl} \\
\text{(S)}
\]

\[
\text{[DCDMH]} \xrightarrow{\text{slow}} \left[ \begin{array}{c} \text{R} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \right] - \text{Cl} + \text{H}_2\text{O} \\
\text{(Oxonium ion)}
\]

\[
\text{[DMH]} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{NH}_4^+ \text{Cl} \\
\text{(Reacting species)}
\]

where, \( R = \text{CH}_3, -\text{CH}-(\text{CH}_3)_2 \) for corresponding aldehydes.

The final rate law derived based on mechanism using steady state approximation is represented by equation (8).

\[
\frac{-d}{dt} [\text{DCDMH}] = \frac{k K_1 K_2 K_3 [S] [H^+]}{[\text{DMH}] + K_2} \\
\text{(8)}
\]

The observed order of reactivity was found in sequence

\( \ell\text{-glycine} > \ell\text{-alanine} > \ell\text{-valine} \)
The similar mechanism has also been earlier reported by authors\textsuperscript{19-22} for the study of $\ell$-AA-DCDMH system. The reaction yielded acetaldehyde, formaldehyde and butyraldehyde end-products which is characterized by the spot test and other modern physical methods.

4. CONCLUSION

1,3-dichloro-5,5-dimethylhydantoin has been in route to the antibiotic ABT-492. DCDMH was employed to trap an enolate resulting from the attack of dimethylzinc on to an $\alpha$$\beta$-unsaturated ketone thus generating an $\alpha$-chloro-$\beta$-methyl ketone functionally in route to a building block of Amphotericin B.

**Table 1 : Effect of concentration of DCDMH on rate of reaction**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[DCDMH] ×10$^3$ (mol dm$^{-3}$)</th>
<th>$k_1$ ×10$^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.25</td>
<td>4.56</td>
</tr>
<tr>
<td>2.</td>
<td>2.00</td>
<td>4.65</td>
</tr>
<tr>
<td>3.</td>
<td>2.50</td>
<td>4.63</td>
</tr>
<tr>
<td>4.</td>
<td>3.33</td>
<td>4.58</td>
</tr>
<tr>
<td>5.</td>
<td>4.00</td>
<td>4.66</td>
</tr>
<tr>
<td>6.</td>
<td>5.00</td>
<td>4.64</td>
</tr>
</tbody>
</table>

$\ell$-alanine (CH$_3$CHNH$_2$COOH)

**Table 2 : Effect of variation of [5,5-dimethylhydantoin] (DMH) on reaction rate**

$10^3$ × [DCDMH] (mol dm$^{-3}$) = 2.50 (1, 2) ;

$[\text{H}^+]$ (mol dm$^{-3}$) = 0.50 (1), 0.80 (2) ;

CH$_3$COOH- H$_2$O % (v/v) = 20 (1), 50 (2) ;

Temp. K = 308 (1), 303 (2)
<table>
<thead>
<tr>
<th>S. No.</th>
<th>[5,5-dimethylhydantoil]×10³ (mol dm⁻³)</th>
<th>$k_1 × 10^4$ (s⁻¹)</th>
<th>$\ell$-glycine (NH₂CH₂COOH)</th>
<th>$\ell$-valine (CH₃CHCHNH₂COOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>4.75</td>
<td>3.82</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>0.50</td>
<td>4.56</td>
<td>3.63</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>1.00</td>
<td>4.49</td>
<td>3.34</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>1.25</td>
<td>4.10</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2.00</td>
<td>3.77</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>2.50</td>
<td>3.42</td>
<td>2.39</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1**

Influence of concentrations of DCDMH on reaction velocity

1. [DCDMH] = 1.25 × 10⁻³ (mol dm⁻³)
2. [DCDMH] = 2.00 × 10⁻³ (mol dm⁻³)
3. [DCDMH] = 2.50 × 10⁻³ (mol dm⁻³)
4. [DCDMH] = 3.33 × 10⁻³ (mol dm⁻³)
5. [DCDMH] = 4.00 × 10⁻³ (mol dm⁻³)
6. [DCDMH] = 5.00 × 10⁻³ (mol dm⁻³)

Plot of log (a-x) Vs. TIME
5. References


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