ADVANCED OXIDATION IN COMBINATION WITH CARBONACEOUS MATERIALS FOR THE TREATMENT OF WASTE WATER

Submitted by
SARIFUL SARDAR
M.E in Chemical Engineering
University Roll No.: 002010302010
Registration No.: M4CHE22010

Under the guidance of
Professor PRASANTA KUMAR BANERJEE &
Professor PAPITA DAS
Department of Chemical Engineering
JADAVPUR UNIVERSITY
Kolkata - 700032

CERTIFICATE

This is to certify that the thesis entitled "**Advanced oxidation process in combination with carbonaceous materials for the treatment of wastewater**" has been carried out by **Sariful sardar** in the fulfilment of the requirements for the degree of the Master of Chemical Engineering from JadavpurUniversity, Kolkata is recorded as bona fide work that has been conducted under the supervision of **Professor Prasanta Kumar Banerjee and Professor Dr. Papita Das**. The contents embodied in thethesis have not been submitted to any other university for the award of any degreeor diploma.

Prof. Prasanta Kumar Banerjee
Thesis Supervisor
Chemical Engineering Dept.Jadavpur
University

Prof. Papita Das
Thesis Co-Supervisor
Chemical Engineering Department
Jadavpur University

Prof. Rajat Chakraborty
HOD
Chemical Engineering Dept.
Jadavpur university

Prof. Chandan Mazumdar
Dean of FET

Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Chemical Engineering studies. All information in this document have been obtained and presented in accordance withacademic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Thesis Title: Advanced oxidation process in combination with carbonaceous materials for the treatment of wastewater.

SARIFUL SARDAR

M.E. in Chemical Engineering

Roll No.-002010302010

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Abstract

Water is considered to be a fundamental part for our entire and sole presence. However, the source is further getting limited due to extreme water pollution, which is caused by the human activities and rapid growth of industrialization. Although, industrialization is making our life better but on the other hand generating tremendous amounts of wastes, adulterating nearby water bodies. These toxic and carcinogenic wastes are easily not recoverable.

In this study Fenton's process was discussed and investigated as an Advanced oxidation process (AOP) using Fenton's reagent for decontamination of cationic dye from wastewater. Cationic dye used in this process are malachite green. Different parameters which affect the reaction such as the initial Fe^{2+} concentration, solution pH, initial H_2O_2 concentration, reaction temperature and concentration of target dye had been studied.

For eliminating MG from aqueous solutions, the experimental Fenton's reaction has shown to be highly effective. For the Fenton oxidation of MG, the variations of parameters for $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[MG]_0$, pH, and temperature were 0.1 ml/L to 0.2 ml/L, 25 ppm to 100 ppm, 10 mg/L to 50 mg/L, 2 to 10, and 25°C to 40°C respectively. The optimal conditions for oxidative degradation of malachite green were found to be pH at 4, hydrogen peroxide (H_2O_2) concentration at 0.2 ml/L, initial ferrous concentration at 50 ppm for 10 ppm of malachite green dye concentration at 30°C. Under these optimal reaction conditions, removal of malachite green dye was experimentally found to be 99% after completion of 90 minute of reaction.

Methodology involved in the treatment of raw rice husk, activated rice husk and chemically treated activated rice husk as an efficient adsorbent to remove cationic and anionic dyes from contaminated water were investigated. Parameters such as solution pH, concentration of target organic pollutants, reaction time, adsorbent dose and reaction temperature were also studied to improve adsorption process.

The adsorption kinetics and thermodynamic studies were calculated of all the adsorbents to find out the nature of the reaction. Data obtained from kinetics study were fitted in pseudo second order model and data obtained from thermodynamics study indicates the reaction was exothermic in nature. For the Adsorption process of MG, the variations of parameters for adsorbent dose, $[MG]_0$, pH, and temperature were 0.5 g/L to 2 g/L, 10 mg/L to 50 mg/L, 2 to 10, and 25°C to 40°C respectively. Under all these parameters which affect the reaction rate, 99% removal of malachite green dye was removed in this study.

Comparative study on the removal of dye using thermally synthesized biochar and Fenton's process and its Batch and Optimization studies were done to determine the suitable and novel techniques for decontamination of emerging organic pollutants from wastewater.

Keywords: Fenton's reagent, Malachite green, Advanced oxidation, Hydrogen peroxide, Batch study, Adsorption process, Kinetic study, Thermodynamic study.

Chapter 1

1.1. General Introduction

Water is considered to be a fundamental part for our entire and sole presence. Earth being a blue planet, it has an abundance of water. However, most of the water covers up water bodies. Out of which only a small percentage of water gets trapped in the glaciers or in rivers and it becomes our primary source of potable water. However, the source is further getting limited due to extreme water pollution, which is caused by the human activities and rapid growth of industrialization. Although, industrialization is making our life better but on the other hand generating tremendous amounts of wastes, adulterating nearby water bodies. These toxic and carcinogenic wastes are easily not recoverable. As the world is progressing, we are putting ourselves in the face of immediate danger. The rapid industrialization is very alarming since it is not considering the balance of the environment which is detrimental towards mankind. Despite various regulations, the industry sector is discharging pollutants in water causing water borne disease which consequently is leading to water crisis on a global scale. Water pollution is a major global problem and one of the leading causes of worldwide deaths and diseases. More than 14 thousand people die on a daily basis and the same in India is estimated to be 580 deaths daily.

Wastewater purification and reclamation is the need of the hour to deal with the increasing water crises all over the world. Conventional methods used in municipal wastewater treatment plants find it difficult to remove pharmaceutical chemicals, and other heavy toxic metals from wastewater.

- It is high time that the research community develops efficient methods for treating the wastewater effluents from the pollutants that are present in trace levels and are not removed by conventional treatment techniques. Wastewater treatment is now becoming a major concerning area of research where scientists are trying to invent various novel techniques, combination of existing techniques. Water is the most valuable necessity of mankind, is getting polluted by the addition of organic and inorganic contaminants, it may be heavy metals also. Various different technologies are used for the treatment of wastewater by industry before contaminating the water as well as the ecosystem. A major number of new and novel techniques are discovered rapidly in replacement of various traditional techniques.

For the last 10 years, environmentalism has gained the attention of the world to a great extent. Quality standards rules and regulations have come into action in many countries. Conventional technologies used for this purpose include stripping techniques, adsorption process and other methods in the case of which contaminants are destroyed.

Industrial development raises environmental health concerns. Starting from sustainable raw material procurement to safe waste disposal is a crucial challenge for modern factories. It is not only important to accurately abide by the EIA protocols but also to increase profitability. In doing so, waste disposal is a rising problem for mining, smelting, foundry, battery, plastic, wood, preservation, paper processing, textile and dye related industries. These are the prime sources of sewage water containing dyes and heavy metals such as Arsenic, Cadmium, Chromium, Lead, Mercury etc.

In Japan rapid industrialization during the period of-post World War II cause severe pollution primarily to air and fresh water sources. Indiscriminate release of untreated toxic waste caused contamination of food chain. Large number of people suffered from mercury poisoning due to consumption of fish that were contaminated with industrial wastewater. This incident was followed by Japan’s formulation of world’s first overarching pollution control policy in 1967.

In the Tirupur city of South Indian state of Tamil Nadu was adversely affected due to its blooming textiles industry during 1970s. In an article by The Hindu in 2015 also mentioned that the Tirupur textile park has only worsen the situation, as the total dissolved solid (TDS) in the Noyyal river was found to be between 7000 ppm (parts per million) and 11000 ppm which was way above the maximum permitted limit 2100 ppm. This city caters nearly 733 dyeing units and is ranked top in terms of generating hazardous waste.

In India rice husk charcoal (RHC) has been used traditionally to clean teeth before toothpaste replaced it. The basic reason behind this was high adsorption capacity of RHC. It has high surface area that makes it a highly efficient adsorbent. Adsorbent prepared from rice husk charcoal was successfully tested for purifying biodiesel from used frying oil. Therefore, preliminary it can be assumed that RHC has the potential to remove broad spectrum pollutants from contaminated solution.

In an article published by M. Shahbendeh on Rice-Statistics & Facts mentioned that the global average rice cultivated area across the world was 167.25 hectares. According to USDA in 2016 China topped the rank with 144,560,000 Mt followed by India 104,800,000 Mt, Indonesia 35,560,000 Mt and Bangladesh with 34,500,000 Mt among the top producers of rice. Similarly, during the FY 2018-2019 China again topped the rice production with 148.5 million Mt followed by India 116.42 million Mt, Indonesia 36.7 million Mt and Bangladesh 34.91 million Mt.

Moreover, according to FCI West Bengal tops the rank with 14.68 million tones of rice produced followed by Uttar Pradesh 12.17 million tones and Punjab 11.11 million tones as of 2015-2016. On the alternative hand all through milling of paddy 78% of the load is acquired as rice and bran; the ultimate 22% is hull. This is approximately 3.23 million ton per year of rice husk in West Bengal alone.

Rice husk is composed of 28%, 28.6%, 24.4% and 18.4% cellulose, hemicellulose, lignin and extractive matter such as silica respectively. Research attempts have been made to produce Xylitol, Furfural, Ethanol, Acetic acid, Ligno-sulphonic acid, Bioethanol and silica from rice husk.

In a ground survey from 10 rice mills across West Bengal it was realized that a greater portion of this rice husk produced are used as a fuel to heat the par boiler. The rice husk obtained can also be used in brick kilns, boilers, furnaces and power plants. The heating value of RHC normally ranges from 12.6 MJ/Kg to 17.0 MJ/Kg of which 18.8%, 62.8% and 9.3% is carbon, volatile material and moisture content respectively.

The transformation of waste products into useful yet harmless substances or mineralised contaminants to CO_2, H_2O and inorganics are Chemical oxidation aims. Surely the chemical destruction based on methods after complete development give rise to complete solutions to problems of pollution abatement differently from those only a phase separation is realized as a consequent problem of the final treatment. Advanced Oxidation Processes (AOP) at or near ambient pressure and temperature has come out as a special oxidation technique in the last decade.

Advanced oxidation processes (AOPs) are extremely efficient and novel techniques for decontamination of a wide range of toxic and hazardous pollutants by its rapid oxidation power. In this method, organic and toxic pollutants are degraded into inorganic and non-toxic materials. The most common and useful AOPs are Fenton, Fenton-like, photo-Fenton, Photodegradation, Ultrasonication using sound waves, and Ozonation. During the advanced oxidation process, produced highly reactive with an oxidation potential of 2.33 V hydroxyl radicals (•OH) which can easily degrade major sections of organic and hazardous materials that are present in the wastewater. AOPs, unlike traditional physicochemical methods, have a faster reaction rate while also being successful at removing various bio-refractory organics from water and wastewater.

Advanced oxidation processes (AOPs) use strong hydroxyl radicals as a strong oxidizing agent. It was first proposed in the 1980s for potable water treatment. In this study, reviews on the fundamentals of the Advanced Oxidation Processes for wastewater treatment and its recent advancements are discussed.

AOP technologies can be classified broadly into two categories. UV with other chemical additives, such as: UV/O_3, UV/H_2O_2, UV/TiO_2, UV/Fenton. Three AOPs developed have gathered the most research and have been used industrially: UV/H_2O_2, Ionization and Photocatalysis that utilizes UV (Ultraviolet) or solar irradiation with titanium dioxide (TiO_2).

1.2. Literature Review

1.2.1. Water Pollution

Recycling of wastewater is a process that can ensure a sustainable supply of water to urban and rural communities. Due to rapid industrialisation and urbanization in India, there is a growing scarcity of freshwater. Recycling used water is necessary to obtain alternative water supply as well as to meet the increasing demand. Water contamination is a great problem in India. Untreated water is India's most significant source of water contamination. Currently, untreated toxic waters and effluents are considered to be major sources of water pollution. It is estimated that nearly 70 to 80% of illness in developing countries is a result of such water contamination. Coloured pigments stand out among other Contaminants because they are visible to the human eye as well as being hazardous.

The central pollution control board has assisted river pollution based on monitoring results. According to a CPCB report published in September 2018, 323 rivers had 351 polluted sketches. The report shows that 323 rivers have experienced 351 polluted stretches due to Biological Oxygen Demand, which is an indicator of organic pollution. Industrial wastes and effluents polluted the majority of rivers and all other sources of freshwater. All the living organisms in this wasted aquatic life are affected and for that natural treatment processes are getting difficult.

In addition, India's growing urbanisation has created environmental challenges such as water supply, wastewater generation, collection, treatment, and disposal in India, heavy metal residues are not eliminated from municipal water treatment plants. Apart from the fact that polluted rivers are the principal source of municipal water for most towns and cities along their pathways, every consumer is assumed to have been exposed to an unknown amount of a range of pollutants. Furthermore, Indian cities have evolved in an unplanned way as a result of rapid population increase. There is currently flowing water in several Indian cities and towns, but many more do not. As a result, flush toilets are being used more frequently, and households are using more water for bathing and laundry, utensils and other purposes. As a result, large amounts of domestic wastewater are generated.

The water quality monitoring carried out by the Central Pollution Control Board (CPCB) shows that the quality of water has gradually decreased. For example, during 1995-2009, more than 57% of samples contained BOD levels below 3 mg/L, in 2007 this number was 69% had BOD values ranging from 3-6 mg/L, with the highest proportion of samples falling into this group in 1998 (Murty & Kumar, 2011). The number of observations remained constant, while the fraction of observations with BOD between 3 and 6 mg/1 followed a static trend. Between 1995 and 2009, the number of observed BOD levels greater than 6 mg/L range from 13 to 19 percent, with the greatest percentage of 19 percent occurring in 2001, 2002, and 2009. The highest percentage (19%) of sampling sites with unacceptable levels of BOD is concerning, since it could indicate that discharge sources are not complying with the criteria, or that even if they are, their high volume of discharge adds to increased levels of pollutants (Rajaram & Das, 2008). In order to prevent pollution and preserve rivers, proper sewage treatment is necessary. This needs to be given higher priority by the central and state governments. The current situation of sewage treatment plants shows that the maintenance of these plants is not a high priority for local governments. Unless this issue is addressed, the problem will likely worsen (Bhawan & Nagar, 2007).

1.2.2. Commonly found contaminants

There are several types of water pollutants. Pathogenic organisms, oxygen-demanding wastes, plant nutrients, synthetic organic chemicals, inorganic chemicals, microplastics, sediments and radioactive substances are all types of water pollutants. Sewage from farms and industrial facilities is the primary source for most of these pollutants. Untreated sewage disposal causes eutrophication, an influx of nutrients that promotes water blooms. Algal blooms can deplete oxygen levels in the water, resulting in a lack of oxygen. When algae make oxygen through photosynthesis during the day, they use dissolved oxygen in the water at night. Water blooms are frequently accompanied by the mortality of a huge number of aquatic organisms. Sulphur, asbestos, toxic solvents, polychlorinated biphenyls, lead, mercury, nitrates, phosphates, acids, alkali, dyes, pesticides, benzene, chlorobenzene, carbon tetrachloride, toluene, and volatile organic compounds such as sulphur are all common industrial pollutants that cause water contamination (Maulin P. 2017).

Industrial wastewater can be very variable in quality, depending on what type of industry is producing it. Organic and synthetic substances, along with heavy metals, are the main concerns with industrial wastewater. Industry discharges a mix of contaminants into the environment every day.

During this study a few emerging pollutants were selected to identify the decontamination potential of various water treatment pathways. The selected pollutants are such as: Methylene Blue, Malachite Green and Tartrazine dye.

1.2.3. Source of pollution

The element chromium is utilised in a variety of applications. They are mostly employed as an anticorrosive and in the formulation of pigments, as well as in the refractories industry. Standard procedures for determining organic matter in soils, chemical oxygen demand (COD) in water quality investigations. Because of their wide range of applications, chromium compounds are significant sources of Cr (VI) contamination in the environment. The maximum chromium concentrations allowed in wastewater for hexavalent [Cr (VI)] and trivalent [Cr

(III)] are 0.1 and 0.5 mg L^{-1}, respectively, according to the Environmental Protection Agency (EPA) and the European Environment Agency (EEA) (Gromboni et al., 2010).

Dyes are used to colour items in a variety of industries, including paper, plastics, cosmetics, textiles, and food. These companies' effluents contain enormous amounts of dyes, which not only degrade the aesthetics of receiving water bodies but may also be hazardous to aquatic life. Methylene blue (MB) is a methylthioninium chloride, and Malachite green (MG) is an N-methylated diaminotri-phenyl methane, and they are two of the most extensively used dyes in their category for colouring. Both of these cationic dyes have a wide range of uses, including paper colouring, cotton, wool, silk, leather, jute dyeing, and paper stock coating. (Bulut et al., 2008; Yi & Zhang, 2008).

Both of these dyes are also extensively used in agriculture worldwide for treatment of parasitic and fungal infections in fish and shellfish along with external infections in ornamental fish (Plakas et al., 1999).

PAHs (also known as polycyclic organic matter or POM) are highly toxic hazardous pollutants and strong carcinogens that can induce tumours in same creatures. They are well-known toxic hazardous pollutants and highly potent carcinogens that have two to six fused benzene rings (Anbia & Moradi, 2009). PAHs can be found in both natural and man-made environments. Anthropogenic sources include engine exhaust, industrial processes, crude oil, urban run-off, household heating systems, and smoke. Natural sources include terrestrial coal deposits, volcanic eruptions, and forest fires. The major sources of PAHs in surface water are atmospheric condensation, run-off from degraded soils, and sewage discharges (Ehrampoush et al., 2012).

1.2.4. Diseases caused

According to the WHO in 2007, India loses 0.4 million lives per year due to the lack of water sanitation, and hygiene, while air pollution kills 0.52 million people. Environmental causes cause 60 years of sickness per 1,000 persons in India, compared to 54 years in Russia, 61 years in Brazil, and 34 years in China. Water pollution has extraordinarily high socioeconomic costs: 1.5 million children under the age of five die each year from water-related ailments. 200million person days of work are lost year, and the country loses around Rs 366 billion per year (Lead et al., 2004). Water contamination had similar impacts; however, the size of the effect was small (McKenzie & Mookherjee, 2003). According to the study, water-borne diseases cause India to lose 90 million days per year, costing the country Rs 6 billion in lost output and treatment costs. India has lost 30.5 million disabled adjusted life years (DALY) due to poor water quality, sanitation, and hygiene.

Some industrial wastes, along with sewage from private residences, are classified as common waste. Such waste can be easily treated by municipal infrastructure. On the other hand, heavy metals, volatile compounds, and fats and oils require special attention (Maulin P. 2017).

Malachite Green is also employed as a medicinal agent (fungicide, ectoparasiticide) and as an antiseptic, but only for external wounds and ulcers; nevertheless, due to the presence of nitrogen, oral ingestion of Malachite Green is toxic, dangerous, and carcinogenic (Bulut et al., 2008; Kushwaha et al., 2014). Malachite green produces inflammation, redness, and pain when it comes into contact with the skin and eyes. As a result of the negative effects on receiving waterways, the treatment of effluents containing such dyes is of major interest.

1.3. Conventional Treatment methods of Pollutants

In nations like India, the rapid development in industrialization and urbanisation necessitates the availability of alternate water sources as well as the recycling of wasted water in order to satisfy the growing scarcity of fresh water. Untreated toxic wastes and effluents are currently regarded the primary sources of freshwater pollution, with untreated toxic wastes and effluents accounting for about 70-80 percent of all illnesses in poor nations.

Some sectors continue to rely on antiquated and outmoded technology that pollute the environment more than new technologies. Industries primarily use outdate technologies to avoid the expensive expense of current or complex technologies, despite the fact that they are known to be less efficient than modem technologies. Industrial water is not properly treated in many countries before being released into rivers or lakes. This is particularly true for small businesses that lack the financial resources to invest in pollution control technology. Water contamination is a result of unplanned industrial expansion (Maulin P. 2017: Rajaram & Das, 2008).

Methods such as ion-exchange (Li et al., 2017), membrane separation (Kozlowski & Walkowiak, 2002), coagulation (ADHOUM et al., 2004), chemical precipitation (Golbaz et al., 2014), extraction (Dupont & Guillon, 2003), dialysis (Peng et al., 2005), and electrochemical separation (Kongsricharoern & Polprasert, 1996) have proved to be capable of removing contaminants such as hexavalent chromium, fluoride, dyes and polyaromatic hydrocarbon such as naphthalene from wastewater. Adsorption is undoubtedly the most successful, economically viable, environmentally sustainable, and technologically promising of these various approaches (T. Chen et al., 2015).

To meet severe laws and restore a clean environment. it's become critical to develop wastewater treatment technologies that are low-cost, versatile, and long-lasting. Various approaches for removing pollutants from contaminated media have been developed in recent decades, including coagulation. chemical oxidation, solvent extraction, membrane separation proco73 s. catalytic degradation, and biodegradation (electrochemical, aerobic, and anaerobic), among others (Han et al. 2009: Yagub et al., 2015). Physical, chemical, and biological approaches to wastewater treatment have all been widely characterised. However, because of their high operating costs, large amounts of sludge produced, and time-consuming processes, these systems are usually unappealing (Ali et al., 2020).

Majority water sources are getting polluted due to the growing population and industrialization. In consequence of that, wastewater treatment becomes a more important issue for the whole mankind. Scientists from each corner of the world are focusing on the treatment of wastewater to discover efficient, cheap and novel technology. And the effective use of existing water resources. The Sewage treatment plants are needed for three reasons; These are water source reduction, WWT and recycling.

Wastewater treatment and recycling technologies have been classified and are carried out in three stages.

They are:

Primary Treatment Methods: Primary treatment includes preliminary physical and chemical cleaning procedures.

Secondary Treatment Processes: Secondary treatment depends on the biochemical decomposition of organic solids into inorganic or stable organic solids.

Tertiary treatment methods: Through tertiary treatment methods, wastewater is converted into water of good quality and can be used as drinking water or medical supplies.

At the end of these three steps, almost all pollutants (up to 99%) can be removed from the water. In order to produce high quality and safe water, all these three processes should be combined.

In the treatment of wastewater, the removal of heavy metals has become the most important. Of all the pollutants, heavy metals have received the most attention from environmental chemists due to their toxic nature. Heavy metals are usually present in trace amounts in natural waters, but many of them are toxic even at very low concentrations. Metals such as arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium are highly toxic even in small amounts. The increasing amounts of heavy metal in our resources is currently a cause for major concern, particularly since a large number of heavy metals industries are discharging their metal-bearing effluents into freshwater without proper treatment. Heavy metals become toxic when not metabolized by the body and build up in soft tissues. They can enter the human body through food, water, air, or absorption through the skin when in contact with people in agricultural, manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure is a common route of exposure for adults. Ingestion is the most common route of exposure in children. Natural and human activities contaminate the environment and its resources, discharging more than the environment can handle.

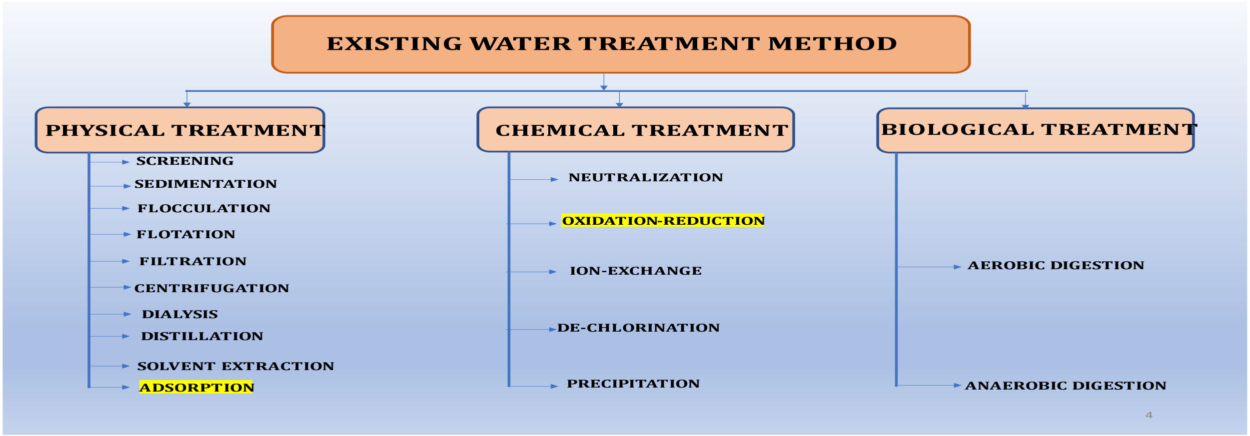


Figure 1: Existing water treatment method.

These techniques are classified as follows:

Physio-Chemical Techniques

1.3.1. Adsorption

The absorption process is a relatively inexpensive process. Adsorption has certain advantages over conventional methods, such as minimization of chemical and biological sludge, low cost, high efficiency, regeneration of adsorbents, and the possibility of metal recovery. Adsorbents that have already been used for heavy metal removal are activated carbon, zeolite, manganese oxides, agricultural waste products such as water hyacinth, hazelnut shell, orange peel pulp, sunflower, coconut pulp, bacterial bio-sorbent, fungal bio-sorbent, seaweed, microbial and plant-derived biomass.

1.3.2. Oxidation

Oxidation can be applied for contaminant destruction to reduce the contaminant concentrations in contaminated groundwater. During the chemical oxidation processes, oxidants are used for pollutants oxidation (destruction) and oxidize chemicals to less hazardous by-products or end products (e.g., carbon dioxide, water). Many types of chemicals (e.g., fuels, solvents, pesticides) can be destroyed by the chemical oxidation processes.

When in situ chemical oxidation (ISCO) is applied for site remediation, polluted soils are not exacavated and groundwater is not extracted. Instead, oxidants are injected into the subsurface via the remediation wells or injection wells around the hot zone or polluted area for contaminants oxidation. The injected oxidants react with the target chemicals and result in the breakdown of the chemicals (Ameta and Ameta, 2018).

To accelerate the site remediation via the ISCO process, groundwater circulation can be used to improve the oxidants mixing with the contaminants in the subsurface. During the circulation stage, oxidants are pumped in via the upgradient wells and extracted from downgradient wells. The extracted groundwater is then pumped back (recirculated) down the upgradient injection wells. The injection, pumping, and mixing processes help the oxidation of the contaminants and accelerate the site cleaning up. Detailed contaminant plume delineation and site investigation are required to effectively determine the right spots in the ground for remediation wells installation.

1.3.2.1. Advanced Oxidation Process

Advanced oxidation processes (AOPs) generate highly reactive species including HO, HO_2, and O_2 radicals in the aqueous phase. These radicals are generated by chemical oxidizing agents such as H_2O_2, O_3 in combination with catalysts or radiation (γ-rays or UV radiation). The high reactivity of these free radicals makes AOPs suitable for oxidizing many inorganic and organic pollutants. AOPs include UV/ H_2O_2, O_3/UV, O_3/ H_2O_2, Fe^{2+}/ H_2O_2, photo-Fenton oxidation, and heterogeneous photocatalysis. Zero-valent iron (ZVI), titanium dioxide used in this process.

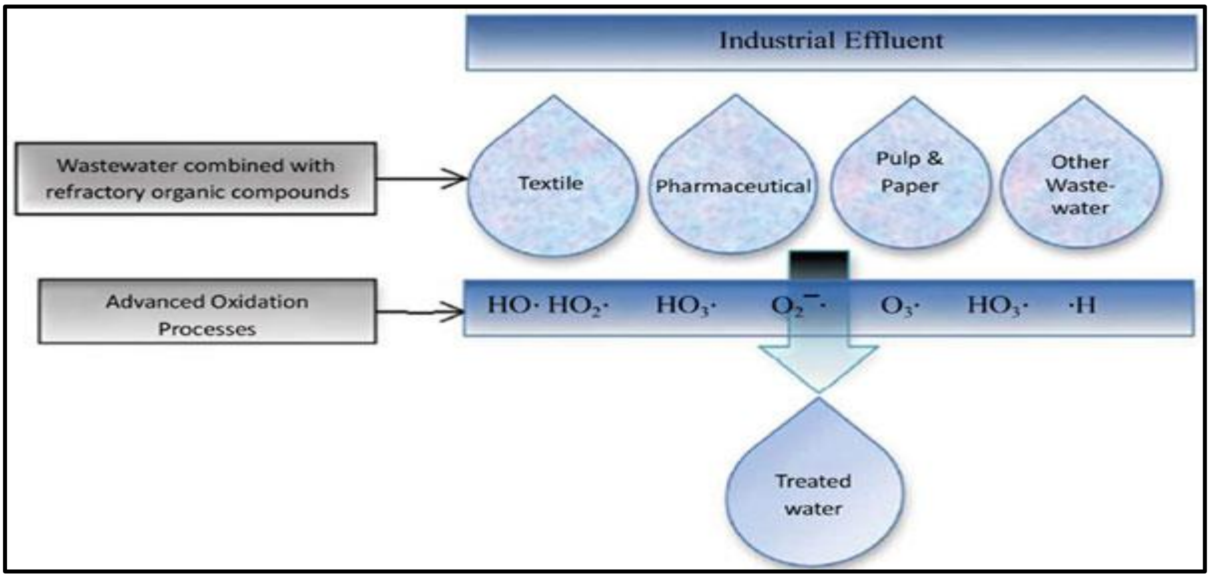


Figure 2: A graphic representation of advanced oxidation process.

1.3.3. Ion exchange

Ion exchange resins have been used successfully to remove arsenic from drinking water. Custom made anion exchangers are available that can reduce the arsenic concentration to 10 μg/L. Synthetic ion exchange resins generally have quaternary ammonium groups and a polystyrene cross linked divinylbenzene (as the polymer matrix). These resins are particularly efficient for dye adsorption.

1.3.4. Precipitation-Coagulation

Coagulation is a simple method of treating large volumes of arsenic-contaminated water. Coagulants destabilize colloidal particles through particle charge neutralization, causing them to aggregate followed by precipitation. During coagulant precipitation, soluble arsenic species are converted to flocs by the coagulants and can be easily removed by filtration. These processes combine coagulation, adsorption and sedimentation using inexpensive chemicals and low installation costs. Thus, coagulation and filtration have enormous application potential for low-cost savings. To remove arsenic, arsenic is converted to arsenate, followed by its removal by adsorption on coagulated floc, followed by filtration. Chemical precipitation filtration is used to remove arsenic and fluoride in municipal water treatment plants. Aluminium polychloride, aluminium sulphate, alum, and anionic polymer flocculants are commonly used coagulants for as removal. Coagulation-based arsenic removal systems are economical and very effective. Electrocoagulation is a newer alternative to aqueous arsenic removal. Electrocoagulation offers many advantages. flower mud volume; It is quite compact and operates smoothly even at high flow rates and requires no additional chemicals.

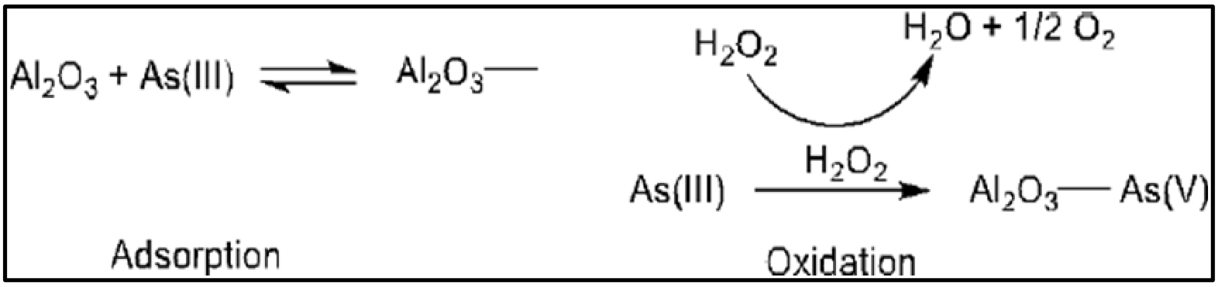


Figure 3: Reactions of precipitation-coagulation.

1.3.5. Membrane filtration

It offers a high separation performance, does not require a phase change, saves energy, is easily scalable and is environmentally friendly. The technique used to remove heavy metals is ultrafiltration (UF), reverse osmosis (RO) and nanofiltration. One of the key advantages of membrane processes over adsorption is that removal efficiency is relatively less affected by feedstock chemistry and pH. This is especially true for RO and NF systems. However, it has been observed that different toxic element removal increases (by about 20%) for pH values increasing indicating the need to find optimal operating pH values even for membrane treatments. RO is the most suitable option for treating high salinity water.

1.3.6. Limescale softening

Hard water contaminated with arsenic can be efficiently disposed of with lime softening, especially at pH N 10.5. In addition, the dye removal mechanism with lime precipitation may also involve the precipitation of salts.

Biological Techniques

1.3.7. Photochemical Oxidation

Photochemical oxidation, or solar oxidation and arsenic removal (SORAS), is a very simple, inexpensive, and popular technology that involves the oxidation and precipitation of arsenic. SORAS has been successfully deployed at household level in developing countries such as Bangladesh and India.

1.3.8. Biological treatment with live microbes

Aerobic Separation Process: In biological treatment processes, organic matter can be biodegradable by aerobic and facultative bacteria. Along with BOD and COD, aerobic treatment techniques are the most effective method for removing suspended, volatile and dissolved organics, nitrates and phosphates.

Anaerobic Separation Method: Anaerobic decomposition, called putrefaction, occurs when there is no free dissolved oxygen in the wastewater, and this process is known as the anaerobic treatment technique. In this treatment technique, organic matter is converted into other organic matter, including sulphur and carbon, by anaerobic and facultative bacteria.

1.4. Methods used in my Study

1.4.1. Advanced Oxidation Process

Advanced oxidation technologies (AOTs) consist of strong oxidizing intermediates (such as the hydroxyl radical •OH) that can degrade the toxic organic contaminants from polluted air and wastewater. AOTs are capable of degrading a wide range of emerging pollutants, even those that are difficult to degrade with other upcoming new technologies such as filtration, reverse osmosis, activated carbon etc. To create •OH radicals which are most commercially feasible advanced oxidation processes are Fenton's Process, oxidation using ozone or different photochemical processes. Ozone treatment is not regarded as an AOTs, despite the factors that lie on oxidation.

Treatment with AOTs results in the complete mineralization of the pollutants and their by-products (i.e., the only products are CO_2, H_2O, and mineral acids [e.g., HCl, HNO_3, H_2SO_4, etc.] for any Cl, N, S, etc. present in the pollutants), as well as the destruction of the target pollutants susceptible to oxidation. Treatment to complete mineralization is neither essential or cost-effective in most circumstances because the intermediate products of AOT reactions are generally harmless and/or rapidly biodegradable with biological treatment.

1.4.1.1. Possible Applications

AOTs could be used to oxidize pollutants in a variety of source waters. However, when compared to other treatment technologies, there are three main areas where AOTs provide effective treatment and are cost-efficient (e.g., granular activated carbon, membranes, etc).

Micropollutant Treatment

Micropollutants are pollutants found in water at concentrations of a few micrograms per Litre (g/L) or less. VOCs, pesticides, herbicides, endocrine-disrupting substances, personal care items, medications, and other chemicals fall under this category. Most micropollutants are difficult to eliminate in traditional water treatment techniques, and their possible health impacts are a worry. Endocrine-disrupting substances, for example, are known to disrupt the hormone system of mammals at certain levels and can result in malignant birth abnormalities, or developmental diseases. 1,4-dioxane, a solvent stabilizer, is an example of a micropollutant that is difficult to remove or oxidize using other treatment methods.

Treatment of Taste-and-Odour Compounds

Algal blooms produce taste-and-odour chemicals like geo-min and 2-methylisoborneol in some drinking water sources throughout the summer months (MIB). Although these compounds do not pose a health risk, customers can notice them at concentrations in the nanogram-per-Litre (ng/L) range because they provide a disagreeable taste and odour to drinking water. Algal blooms may also be accompanied with algal toxins (e.g., microcystin) that have been linked to health problems.

Recycled Water Treatment

There is a growing interest in wastewater reuse and recycling. Membranes can remove most wastewater contaminants from secondary effluents; nevertheless, many micropollutants [e.g., 1,4-dioxane or N-nitroso-dimethylamine (NDMA)] cannot be entirely eliminated. AOTs can provide a broad treatment barrier for contaminants present in recycled water applications that are not normally found in most drinking water applications, especially if the water is supplementing potable water supplies indirectly or directly.

1.4.1.2. Types of Advanced Oxidation Processes (AOPs)

Types of different Advanced oxidation Processes are shown in a diagram below:

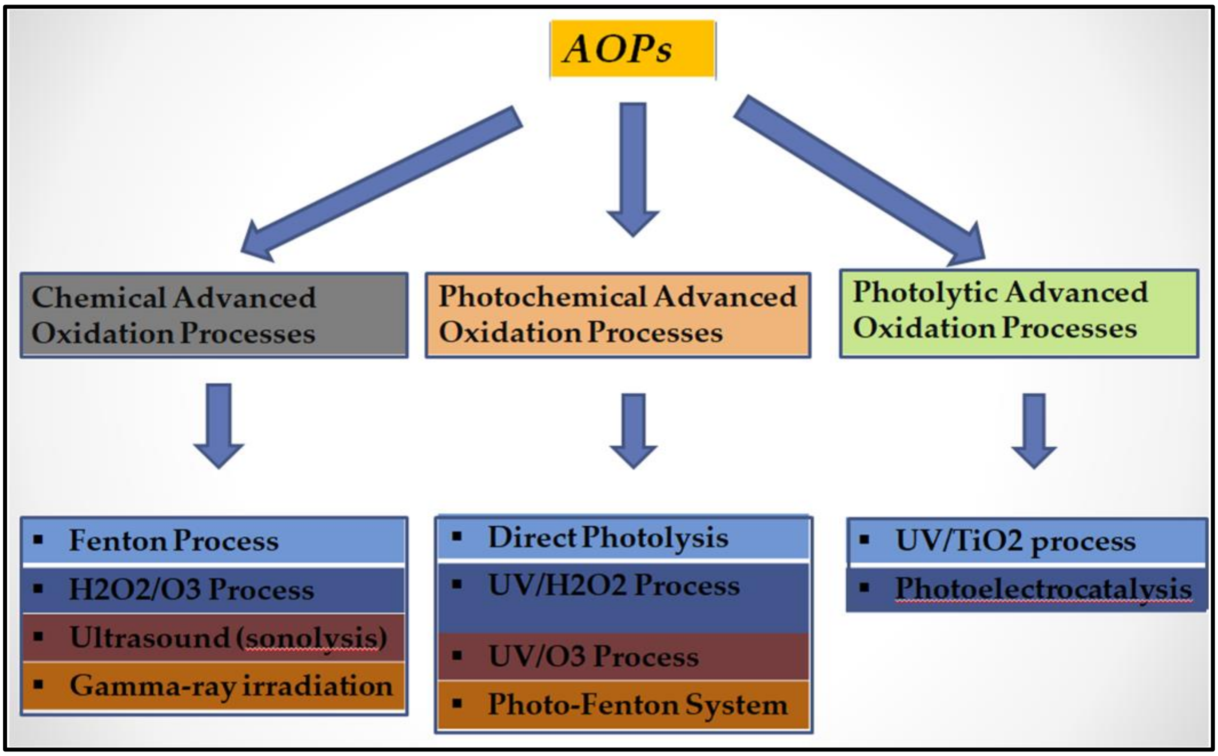


Figure 4: Types of Advanced oxidation process based on Chemical reaction.

Chemical Advanced Oxidation Processes

1.4.1.3. Fenton Process

Oxidation processes already exist in nature and it degrades contaminants from waste but these natural processes take time for decontamination of emerging organic and inorganic pollutants. The term ‘Advanced’ is used in the oxidation process to improve the natural oxidation processes in a proper and efficient way by changing its various factors which affect oxidation. Under this paragraph we will discuss the Fenton Process as an advanced oxidation process. Fenton Process is assigned to a combination of hydrogen peroxide (H_2O_2) and ferrous/ferric ions, called Fenton’s reagent. In 1894, scientist Henry John Horstman Fenton discovered that tartaric acid oxidized and degraded by hydrogen peroxide in the presence of ferrous ions, in continuation with that this process is named as Fenton Process. Later on, the combination of Hydrogen peroxide and Ferrous ions was used as an oxidizing agent of a large domain of organic contaminants. In 1934, scientist Haber and Weiss were added that the oxidation occurs with the presence of highly reactive Hydroxyl radicals •OH which can degrade a large section of organic pollutants and this •OH radical is generated during the combination of hydrogen peroxide and ferrous ions.

Generation of highly reactive •OH radicals have opened the door for a major area of research for the treatment of wastewater to convert contaminants into carbon dioxide, water and harmless inorganic compounds. In subsequent years, several researches were found for practical applications of this Fenton process to a great extent. Many review papers, novel studies have been published frequently. Much literature shows that the Fenton process is best and efficient to remove any target pollutant from wastewater due to generation of more reactive radicals. Fenton's process is efficient in acidic pH conditions (at pH 3-4). In acidic medium, ferric ions Fe3+ is produced from ferrous ions and it can easily oxidize to ferrous ions by accepting one electron species by producing hydro peroxide radicals which can also produce •OH radicals. And regeneration of Fe^{2+} ions will take place for further treatment. Hydroperoxide ion itself, a one electron species and highly reactive, can break the organic compounds. All the reactions given below are occurring during the reaction and to produce more radicals for the reaction.

The favourable reactions of Fenton's process are given below:

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(III)} + \cdot\mathrm{OH} + \mathrm{OH^-}$$

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(II)} + \mathrm{HO_2}\cdot + \mathrm{H^+}$$

$$\mathrm{HO}\cdot + \mathrm{H_2O_2} \longrightarrow \mathrm{HO_2}\cdot + \mathrm{H_2O}$$

$$\mathrm{HO}\cdot + \mathrm{Fe(II)} \longrightarrow \mathrm{Fe(III)} + \mathrm{OH^-}$$

$$\mathrm{Fe(III)} + \mathrm{HO_2}\cdot \longrightarrow \mathrm{Fe(II)} + \mathrm{O_2H^+}$$

$$\mathrm{Fe(II)} + \mathrm{HO_2}\cdot + \mathrm{H^+} \longrightarrow \mathrm{Fe(III)} + \mathrm{H_2O_2}$$

$$\mathrm{HO_2}\cdot + \mathrm{HO_2}\cdot \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2}$$

Figure 5: Chemical reactions of Fenton's process and it's loop reaction.

The controlling factors in Fenton's process are

(i). pH,

(ii). Temperature,

(iii). Concentration Of target pollutants,

(iv) Concentration of H_2O_2, and

(v). Concentration of Fe^{2+}.

(i). Effect of pH on Fenton's process: Fenton's process is efficient in acidic medium. So, acidification of media has to be made before contamination of organic compounds. With increasing the pH value, precipitation of $Fe(OH)_3$ will occur which slows the oxidation process. So, the oxidation rate decreases. That's why we have to carry the contamination process in acidic medium.

(ii). Effect of Temperature on Fenton's process: In this process, hydroxyl radical •OH breaks the organic pollutants into water and inorganic nontoxic compounds. Degradation of contaminants will increase if the generation of hydroxyl radical •OH increases during the reaction. Higher temperature enhanced the reaction to produce more •OH radicals by increasing the reaction rate between Fe^{2+}/Fe^{3+} ion and H_2O_2. But after 20 minutes of reaction time, it will increase the degradation efficiency of pollutants, so the reaction time will decrease with increasing temperature.

(iii). Effect of concentration of target pollutants: Concentration of target pollutants depend on other factors like solution pH, concentration of ferrous ion used, concentration of hydrogen peroxide and also the reaction temperature. With the constant value of other factors, the reaction rate decreases with increasing concentration of target pollutants. Different literature shows that the reaction time decreases with increasing initial concentration of the contaminants. It takes time to degrade pollutants completely. After a few minutes degradation efficiency will be lowered due to higher concentration of the organic contaminant even in longer reaction time. This implies that the generation of hydroxyl radical with constant concentration of hydrogen peroxide and ferrous ion will be minimum for higher concentration of pollutants used in the Fenton process. Gradually the generation of hydrogen peroxide reduces and thus, MG degradation slows down to a great extent.

(iv). Effect of initial concentration of Fe^{2+}: This also depends on other factors such as concentration of target pollutants which have been discussed earlier. We have to optimize the concentration of Fe^{2+} also. We found in many of the literatures that higher concentration of Fe^{2+} could be the cause of self-scavenging of •OH radical by Fe^{2+} and could lead to a decrease in the rate of degradation of pollutants:

$$\boxed{\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-}$$

(v). Effect of initial concentration of H_2O_2: Increasing H_2O_2 dose, the removal will be higher at the beginning of the reaction. But after that, the reaction rate decreases due to less available •OH. And this phenomena is described below:

When used in high dosage, H2O2 becomes a strong •OH scavenger:

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O$$

$$H_2O_2 + OH_2\bullet \rightarrow OH\bullet + O_2 + H_2O$$

$$HO_2\bullet + OH\bullet \rightarrow H_2O + O_2$$

In this way, degradation does not improve with higher concentration of H2O2. Due to the excess H_2O_2, hydroperoxyl radicals ($HO_2\bullet$) was generated. $HO_2\bullet$ is a strong oxidant itself and it promotes radical chain reactions, it still has much lower oxidation potential than •OH has. Oxidative degradation of organic compounds occurs only due to the reaction with hydroperoxyl radicals.

1.4.1.4. Advantages of Fenton's Process

The advantages are given below

1. Simple and more flexible procedure.
1. No energy will be required to carry out the process.
2. Don't need any special instrument throughout the whole process, and
3. Operation is easy to handle.

1.4.1.5. The disadvantages of Fenton's Process

The disadvantages are

1. Comparatively high risk to use hydrogen peroxide and high cost,

2. Creation of acidic medium to make pH at 4.0 before treatment,
3. After treatment we have to neutralize the solution,
4. Difficult to remove iron sludge and needs for further treatment,

1.4.1.6. Alternative methods to overcome the disadvantages

1. After knowing the actual concentration, we can decrease the additional amount of H_2O_2 used as a reagent in the reaction.
2. Iron sludge could be minimized or removed by processes like filtration, membrane separation and also could be separated using alumina, iron-coating catalysts, iron-modified clays etc.
3. In practical cases, Fenton's process is a combination of several methods for efficient removal of emerging organic contaminants such as filtration, biodegradation, and coagulation. So, the process could be effective by changing variables of several methods.
4. Fenton's process can be done in the presence of lamps which emit UV radiation for improvement. This process is well known as Photo-Fenton.

1.4.2. Adsorption process

Adsorption involves the interaction of substances with two phases. Mass transfer occurs in this process at the interface of liquid-gas, liquid-solid or liquid-liquid. The substance that absorbs the other is called an adsorbent, and the other which is adsorbed is termed as adsorbate. The properties of both substances depend on their components and are substance-specific.

Adsorption can be performed in any system by different forces and types of interactions. The process between adsorbate and adsorbent is a physical process known as physisorption. In this type of interaction, the van der Waals force plays an important role. Because they have comparatively weak power, the end result of this process is reversible. In this process, entropy and free energy decreases accordingly. Thus, this process is exothermic.

If, on the other hand, adsorption occurs due to chemical bonds between two substances, this is called chemisorption. In contrast to physisorption, this process only takes place as a monolayer. In addition, the chemisorbed adsorbates are difficult to remove from the solid surface, since chemical bonds are involved in this process. In any system of interest, both processes can occur simultaneously under favourable conditions.

The following adsorbents were used to degrade toxic metals and pollutants by adsorption processes:

Activated Carbon Adsorbent

Activated carbon is one of the well-recognized adsorbents for removing toxic metals and inorganic pollutants. This substance has a large internal surface and well-developed pores. Any substance with a high carbon content can be converted into activated charcoal. This substance is used to remove lead, copper and chromium. It was also found that the adsorption capacity decreases when Pb (II) > Hg (II) > Cu (II).

Carbon Nano-Tube (CNT) adsorbent

CNT is a well-known and widely used substance for adsorption. Due to its stability, large specific area, mechanical and electrical properties, it has excellent adsorption efficiency. CNTs are developed by chemical vapor deposition technique over activated alumina doped with Ni and Fe.

Clay, Minerals and Other Geological materials

Pentavalent arsenic is adsorbed to naturally occurring clay in the oxidative state. This is an important immobilization mechanism in an aquatic environment.

Bio-sorbents: Bio-sorbents are also able to remove arsenic. Many macrophytes are widespread and efficient for removing arsenic, copper, zinc, iron, etc. However, this method is limited due to its lack of sensitivity and non-specific iron exchange.

Synthetic Adsorbents

Aluminium, iron and magnesium oxides are some synthetic adsorbents. You can efficiently remove arsenic. Arsenate and Arsenic are significantly removed by binary oxides. These include Fe/Al, Fe/Mn, Zr/Mn, cerium-doped iron oxide, ZrO2-Fe3O4 magnetic nanoparticles, and bismuth-impregnated al-oxide. Mixed metal oxide is also used for arsenic removal. This process occurs in different ways depending on the type of solution and the nature of the oxide species. Processes involved in adsorption are co-precipitation, ligand exchange, acid-base interactions and electrostatic interactions.

1.4.2.1. Factor affecting Adsorption Process

Controlling factors which affect the adsorption process are:

(i) surface area, (ii) nature and initial concentration of adsorbate, (iii) pH of the solution, (iv) temperature, (v) interfering substances and (vi) nature and dose of adsorbent.

(i). **Surface area:** Adsorption process is a surface phenomena activity and adsorbent absorb adsorbate from solution. Therefore, the specific surface area is a major factor that affects the rate of adsorption. specific surface area is the surface area available for adsorption. so, more finely divided and more porous adsorbent cause greater amounts of adsorption. Pores at molecular dimension contribute to the adsorption process.

(ii). **Nature and initial concentration of adsorbate:** The physical nature, chemical properties of adsorbent and its initial concentration affect drastically on adsorption. Adsorption mainly depends on the solubility, molecular size, charge, surface topology and concentration of adsorbents.

(iii). **pH of the solution:** The pH of the solution shows an effect on the degree of adsorption. As the pH of the solution changes, different functional groups adsorb accordingly.

(iv). Temperature: As adsorption reactions are usually exothermic, temperature is an important factor. Generally, as temperature increases, adsorption efficiency decreases.

(v). **Interfering substances:** Another important factor of adsorption is the presence of different substances in water. A mixture of different adsorbates can affect the adsorption capacity of other compounds or act independently. It was found that in most cases natural organic factors (NOM) have a negative impact on the adsorption of newly formed compounds.

(vi). **Adsorbent type and dose:** It was found that as the dose of catalyst increases, the removal percentage also increases. Though after a certain increase of removal percentage there is no significant change with the increasing concentration of catalyst.

1.4.2.2. Adsorption as a green technology

Adsorption can be considered as an efficient wastewater treatment process. It was found that a good percentage of removal can be achieved by this process. Also, being a physical process no bi-product formed in this process. The adsorption process can be integrated in any wastewater treatment system of treatment plants.

The most widely used adsorbent is activated carbon for wastewater treatment. But one problem in this method is cost efficiency. Scientists are searching for a more cost-efficient way for adsorption.

1.4.2.3. Advantages of Adsorption Process

The advantages of adsorption process include:

1. In spite of adsorbents preparation the whole process is simple in equipment and several treatments related to adsorption process are adaptable,

2. Adsorbents can be prepared from agro-waste using annealing or chemical treatment such as sawdust, rice husk. rice straw etc. So, we can produce a wide range for commercial purposes.

3. Adsorption can remove a wide variety of contaminants

4. The Adsorption process is an effective and efficient method with first kinetics to treat effluent in an excellent quality.

1.4.2.4. Disadvantages of Adsorption Process

The disadvantages of adsorption process include:

1. Investment in this process is too high,

2. Processes involved are non-destructive and non-selective,

3. Efficiency in the adsorption process depends on the nature of the adsorbents used for several steps. Chemical treatment will require to activate the adsorbents to increase the adsorption capacity and clogging will occur.

4. Adsorption process is not efficient for certain contaminants and metals elimination is difficult for some adsorbents, regeneration or replacement will be required for that.

5. Replacement or regeneration is very expensive for adsorbents, more materials will be lost and also it is non-viable for many companies such as paper and pulp, textile etc.

Chapter 2

Objective of this Study

2.1. Objectives of my Study

Based upon this review of existing literature discussed in Chapter 2 and from the above discussed wastewater treatment methods following objectives were selected for the present study.

(i). Detailed discussion about Advanced Oxidation Processes and other treatment methods have been done for removal of toxic and emerging pollutants from wastewater. Now, the aim is to develop efficient methods for treating the waste water effluents from the pollutants that are present in trace levels and are not removed by conventional treatment techniques.

(ii). To evaluate the performance efficiency and underlying mechanisms of advanced oxidation processes like Fenton, Fenton-like, photo Fenton, electro-Fenton and also to increase degradation efficiency using various combination of parameters which effect on the reaction to remove cationic and anionic azo dyes from their aqueous solutions.

(iii). Synthesis of novel carbonaceous materials using annealing and chemical treatment from agro-waste. Improvement of adsorption process using synthesized carbonaceous materials. Particle analysis of synthesized materials has to be studied to understand the relation of surface area in adsorption process and to enhance the adsorption process.

(iv). Wastewater treatment is now becoming a major area of research where scientists are trying to invent various novel techniques, combinations of existing techniques. In my present study I am trying to incorporate carbonaceous materials in advanced oxidation processes where adsorption as well as oxidation will occur together. In that way cost will be optimized in wastewater treatment methods.

The ultimate goal of this study was to maximize the practical use of the combined advantages of advanced oxidation processes and advantages of all components of charcoal as active materials for improving their adsorption performance and potential. The primary focus of this study was to evaluate efficient advanced oxidation processes and the preparation, characterization, potential application of activated charcoal for removal of dye present in simulated effluents and elucidation of underlying mechanisms via analysis of process isotherms, kinetics and thermodynamics. Adsorption processes were also optimized for best results in terms of significant experimental parameters and investigated for effect of inter parameter interactions on efficiency of adsorbents studied.

And finally incorporating synthesized carbonaceous materials with advanced oxidation processes to find out novel techniques for the treatment of wastewater.

2.2. Work done

Wastewater treatment using advanced oxidation processes in combination with various carbonaceous materials like activated charcoal, reduced graphene, graphene oxide, carbon nanotubes, biochar etc. Degradation and decolorization of Malachite green, Methylene blue, Tartrazine dye from wastewater employing the Fenton and Fenton like process and also tried to combine different adsorbents with this process. In this process, we have used ferrous/ferric ions as a catalyst to activate hydrogen peroxide into hydroxyl radical (•OH) and super hydroxide ion ($\bullet O_2$-) but after that iron remains in the treated water, itself a harmful compound for the human body. Now we are tiring to remove it from that treated water using adsorbents, filtration processes in batch and column study.

Comparative study on the removal of dye using thermally synthesized biochar, carbon nanotubes and graphene oxide and its Batch and Optimization Study. Decolorization of malachite green and methylene blue dye using O_3, O_3/ H_2O_2 and ozonation with carbonaceous materials. Charring of raw rice husk and sugar straw using annealing & Chemical treatment, characterization and its application to remove pollutants from wastewater. Processes familiar with Fenton, Fenton-like, photo Fenton, electro-Fenton, ozone(O_3), ozone/hydrogen peroxide (O_3/H_2O_2), ozonation with synthesized carbonaceous materials, charring of agro-waste, chemical treatment of char ("Modified Hummer's Method") to produce r-GO, NaOH treatment of rice husk and its char, silica extraction from solution which remains after NaOH treatment, Response Surface Methodology (RSM) etc.

2.3. Novelty of this Study

Wastewater treatment is now becoming a major area of research where scientists are trying to invent various novel techniques, combinations of existing techniques. Water, the most valuable necessity of mankind, is getting polluted by the addition of organic and inorganic contaminants, it may be heavy metals also. Various different technologies are used for the treatment of wastewater by industry before contaminating the water as well as the ecosystem. A major number of new and novel techniques are discovered rapidly in replacement of various traditional techniques.

The present research proposal brings forth a noble combination of adsorption and some certain advanced oxidation processes as mentioned previously such as Fenton, electro Fenton and ozonation. The adsorption process will be combined to each of these processes. Since Fenton based processes require oxidants such as H_2O_2, $Na_2S_2O_8$ it makes the process expensive. Combining them with adsorption will make the entire process easy to initiate, it shall increase the removal and separation efficiency. The need for using oxidants will be reduced making the process cost effective. It will be an efficient method to incorporate different adsorbents with advanced oxidation processes in such a way that regeneration and reuse of synthesized biochar can easily be done in many techniques. These eco-friendly adsorbents can be prepared in laboratory scale as well as industrially due to availability in nature.

Therefore, in my study I am trying to determine the optimized data for all the chemicals and adsorbents used in the reaction in various combinations and discovered an efficient and novel technique to remove hazardous materials from fresh water which are not easily removed by conventional treatment methods.

Chapter 3

Materials and Methods

3.1. Chemicals and Reagents

Malachite Green (MG), Methylene Blue (MB), Tartrazine Dye, Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), Hydrogen peroxide (H_2O_2), Hydrochloric acid (HCl), Potassium dichromate ($K_2Cr_2O_7$), Sodium Hydroxide (NaOH), Sulfuric acid (H_2SO_4), O_3, Acetone. Sodium hydroxide was used to remove silica present in raw rice husk. The chemicals used during the study were of analytical grade and glassware used were thoroughly washed to remove any impurities if present.

3.2. Preparation of Malachite Green Solution

Synthetic wastewater was mimicked by dissolving 0.15g MG in 1000 ml distilled water to obtain 150 mg/L concentration as a stock solution. Required aliquots were homogeneously mixed with distilled water to obtain various concentrations of dye solutions.

3.3. Preparation of Tartrazine Dye Solution

Synthetic wastewater was mimicked by dissolving 0.15g MG in 1000 ml distilled water to obtain 150 mg/L concentration as a stock solution. Required aliquots were homogeneously mixed with distilled water to obtain various concentrations of dye solutions.

3.4. Preparation of Fenton Reagent

Fenton reagent was prepared by addition of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) and hydrogen peroxide (H_2O_2). This reagent was used to malachite green solution in different proportion for the batch study treatment. In my study I have used 25, 50, 75, 100 ppm of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) and 0.1, 0.2, 0.3, 0.4 ml/L of hydrogen peroxide (H_2O_2) respectively.

3.5. Adsorbents

Raw rice husk was collected from the Burdwan district, West Bengal, India. The collected rice husk was first washed using distilled water to get rid of any unwanted debris. The washing was done 7-10 times. Cleaned Rice Husk was then dried at 80^0C for 24 hours. As an alternative method it can also be done using sunlight in case of bulk quantity to reduce drying cost. The dried rice husk was grinded using an electrical kitchen grinder provided by Havells ASPRO, such that the particle size remains above 250 microns. The powdered rice husk was further dried and stored in an airlock bottle.

3.5.1. Preparation of Rice Husk Charcoal (RHC)

Powdered rice husk was then carbonized within a ceramic crucible placed in an airtight muffle furnace at a 500^0C for 2 hours. Rice husk charcoal was collected after the muffle furnace has cooled to at ambient temperature. The obtained RHC was further washed using distilled water to remove the fine particles by straining the mixture with a strainer of 100 mesh size so that the particles were above 150 microns. RHC was found to certain markable amount of silica, therefore RHC was stored in airtight bottle within a decreasing chamber in order to maintain low moisture content.

3.5.2. Preparation of r-GO

Reduced Graphene oxide was prepared by Modified Hummer’s Method. Herein, GODs were prepared by modifying Hummers and Offeman’s method of GO preparation from graphite powder. In this reaction, 2 g of graphite, 2 g of sodium nitrate ($NaNO_3$), and 92 mL of sulfuric acid (H_2SO_4) were stirred together in an ice bath for 45 minutes at 5-7 °C with a magnetic stirrer at 400rpm. Next, 12 g of potassium permanganate ($KMnO_4$) was slowly added to the mixture. Once mixed, the solution was transferred to a 35 ±5 °C water bath and stirred for 1 h, and a thick paste was formed. Next, 160 mL of deionized water was added, and the solution was stirred for 30 min while the temperature was raised to 190 ±5 °C. Finally, 400 mL of deionized water was added, followed by the slow addition of 20 mL of hydrogen peroxide (H_2O_2) (30%), turning the color of the solution from dark brown to yellow. The warm solution was then centrifuged at 2000 rpm for 5min (Centrifuge REMI PR-24, India). The supernatant was decanted cautiously into a separate container and again centrifuged at 20000 rpm for 15 min. The pellet was scraped using micro-spatula and dispersed again in deionized water by using sonication for 15 minutes using an ultrasonic cleaner (LABMAN Scientific Instruments, India, Model-LMUC-4 with a frequency of 40KHz) and then centrifuged at 20000 rpm for 15 minutes using REMI PR-24 centrifuge (India). This cycle, re-suspension and centrifugation at 20000 rpm for 15 minutes, was done until the pH change to neutral (pH 7±0.05). The final sediment collected was then dried for 1 h at 120 °C under a hot air oven.

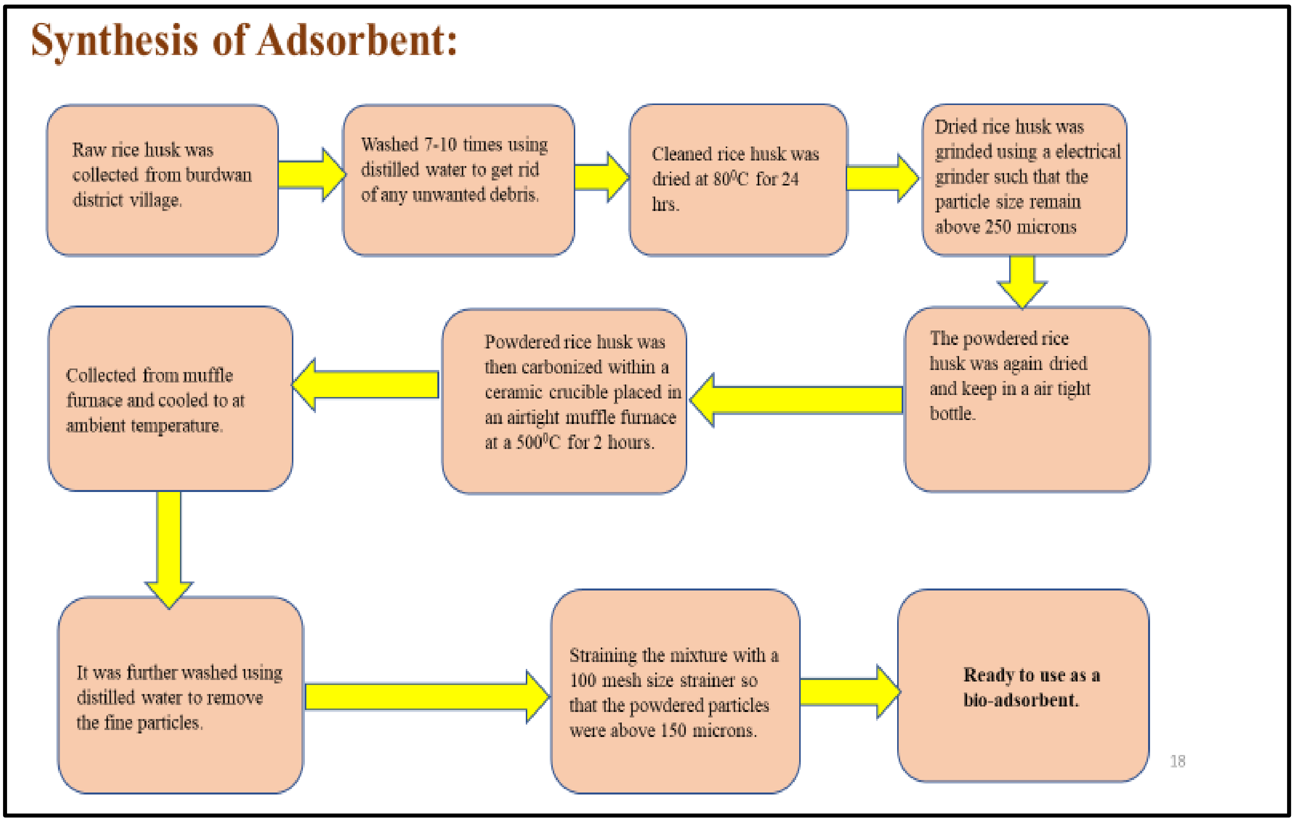


Figure 6: A pictorial representation of the synthesis of bio-adsorbent from raw rice husk.

3.6. Characterization of adsorbents

Rice husk (RH), Rice Husk Charcoal (RHC), Reduced-Graphene Oxide (r-GO) surface methodology and elemental analysis were studied using a Scanning Electron Microscope (SEM Zeiss EVO MA/10 FEI INSPECT F50) facilitated with EDX (Brucker EDS X-Flash 630). The crystallography was analysed through X-ray diffraction analysis (XRD Brucker D8 Advance). Fourier transform infrared spectroscopy (FTIR) was used to identify the surface functional groups present in the adsorbent in FTIR Perkin Elmer Spectrum Two.

3.7. Batch Oxidation Experiments

A 50-ml stoppered glass (Erlenmeyer flask) was used as a batch reactor. Batch experiments of MG degradation were performed by adding H_2O_2 to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either 0.1N H_2SO_4 or 0.1N NaOH. Following the pH adjustment, the Fe^{2+} ions were quickly added to the dye solution. The flask was then placed in a thermos-stated water-bath shaker and agitation were provided at 150 rpm. The samples were taken out from the conical flask periodically using a 1-ml syringe and were analysed immediately. The effect of initial MG concentration $[MG]_0$ in the oxidation of MG was studied by varying the amount of $[MG]_0$ used for the experiment (10, 20, 30, 40 and 50 mg/L), while maintaining pH, agitation speed, initial ferrous concentration $[Fe^{2+}]_0$, initial hydrogen peroxide concentration $[H_2O_2]_0$ and temperature constant at 4, 150 rpm, 50 ppm, 0.2 ml/L and 30°C, respectively. The solutions were agitated in a thermostatic water-bath shaker for a period of 70–100 min. The effect of pH on MG degradation was studied using 250mL of 10 mg/L dye solution taken in a stoppered conical flask containing 50 ppm and 0.2 ml/L of $[Fe^{2+}]_0$ and $[H_2O_2]_0$, respectively. The pH of the solution was varied from 2 to 10 using 0.1N H2SO4 and 0.1N NaOH. The solution at the respective pH was agitated in a thermostatic water-bath shaker (150 rpm) for a period of 60 min at 30°C.

The effect of the $[Fe^{2+}]_0$ dosage on the MG degradation was also studied. To 250 mL of 10 mg/L MG solution, different $[Fe^{2+}]_0$ concentrations (25, 50, 75 and 100 ppm) were added along with 0.2 ml/L of $[H_2O_2]_0$. The flasks were agitated in a thermostatic water-bath shaker for a period of 60 min at 30°C. Samples were taken out from the conical flask periodically for analysis purposes. The effect of H_2O_2 in the oxidation of MG was studied by varying the amount of H_2O_2 used for the experiment (0.1, 0.2, 0.3, and 0.4 ml/L) with $[Fe^{2+}]_0$ of 50 ppm. The solutions were agitated in a thermostatic water-bath shaker for a period of 60 min at 30°C. To study the effect of reaction temperature, 250 mL of 10 mg/L MG solution was agitated with 50 ppm of $[Fe^{2+}]0$ and 0.2 ml/L $[H_2O_2]_0$ at pH 4 for a period 60 min at various temperatures (25, 30, 35 and 40°C).

3.8. Batch Adsorption Experiment

Comparative analysis of batch adsorption capacity to remove various pollutants such as hexavalent chromium, Fluoride, Malachite green, Methylene Blue, Tartrazine was performed using raw rice husk, rice husk charcoal, reduced-graphene oxide. Experiments were performed in 100 ml glass conical flask with 50 ml sample volume; agitated in rotary shaker at 150 rpm. The batch adsorption experiments were performed at multiple combination of parameters such as initial target pollutants concentrations (mg/L), adsorbent dose (g/L), pH of the solution and temperature of the reaction (K) with respect to time until it reached equilibrium. Remaining concentration of target pollutants were analyzed by UV-Vis Spectrophotometer (Shimadzu UV-1800) at respective maximum wavelength (λ_{max}). After that using Beer-Lambart law we can analyse concentration difference in that particular solution.

3.9. Optimization using Response Surface Methodology

Design expert 7.0 software was used to optimize the best combination of parameters to obtain maximum efficiency. Three important variable parameters like pH of the solution, adsorbent dosage and time required to treat the effluent and various combination of parameters were experimented to find the optimized condition. RSM chart were prepare and batch experiment were performed according to the RSM chart. Hence, obtained responses that is removal percentage were feed to the software to provide an idea about the resemblance between predicted and actual removal efficiency.

Calculations

3.10. Batch adsorption experiments

Equilibrium adsorption of the solute using raw rice husk (RH) and rice husk charcoal (RHC) were carried out in a set of 100 mL Erlenmeyer flasks at an agitation speed of 120rpm, at varying temperature ranges (25 to 40° C), adsorbent dose (2 to 10g/L) based on the dry weight of adsorbent, initial dye concentrations of (5 to 20 mg/l), and fixed pH of 7. Samples were collected at 15 mins intervals until equilibrium was established. Experimental samples needed to be centrifuged at 15000 rpm for 15 mins. The collected supernatant had been analysed by UV-Vis Spectrophotometer for dye contents at 617.70 nm. Each experiment was conducted thrice and was expressed as the mean value of the obtained results. The adsorption behaviours the samples were studied by evaluating the adsorption capacity from the following relations where qt (mg g-1) and qe (mg/g) were denoted as adsorption capacity at time(t) and at equilibrium conditions respectively, (Das et al., 2020a, 2021; Khan et al., 2018):

$$q_t = (C_0 - C_t) \times \frac{V}{W}$$

$$q_e = (C_0 - C_t) \times \frac{V}{W}$$

Where V (L) signifies the volume of the experimental solution and W (g) denotes the weights of the adsorbent utilised. The initial dye concentration (C0) and the removing dye concentration (Ct) (mg/L) are the initial and remaining dye concentrations, respectively. Ce, is the abbreviation for "equilibrium concentration."

The dye adsorption efficiency was determined by the following formula in terms of dye removal percentage (Chakraborty et al., 2021).

$$Removal = (C_0 - C_t) \times \frac{100}{C_0}$$

3.11. Adsorption isotherm

To detect adsorption behaviour, the batch adsorption data was analysed using Langmuir and Freundlich equations. The Langmuir isotherm model is expressed as (Das et al., 2020a)

$$\frac{C_u}{q_t} = \frac{1}{k_l q_m} + \frac{C_u}{q_m}$$

Where Ce is the adsorbate concentration at the time of equilibrium and qe is the adsorption capacity (mg/g). qm stands for maximum monolayer adsorption capacity (mg/g) and kL, stands for Langmuir rate constant.

Freundlich isotherm is another popular model that is expressed as (Das et al., 2020a)

$$Logq_e = Logk_f + \frac{1}{n}logC_e$$

Where k_f Freundlich isotherm rate constant and n is empirical constant.

Temkin isotherm model can be best explained by the equation,

$$q_e = \frac{RT}{b_\tau}LnC_e + \frac{RT}{b_\tau}Lnk_\tau$$

R is the ideal gas constant. T is the temperature in kelvin, bt, is the Temkin isotherm constant, kt, is the Temkin isotherm equilibrium binding constant (L/g), and B is the heat of sorption constant (J/mol) where B = RT/bt.

3.12. Adsorption kinetics

Pseudo 1st order and 2nd order kinetic models were fitted with the obtained adsorption data. Following are the representation of both the kinetic model (Das et al., 2021)

$$Log(q_e - q_t) = Logq_e - \frac{k_1 t}{2.303}$$

Where k, is the 1st order rate constant.

Pseudo 2nd order can be expressed in linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Here, k, is the 2nd order rate constant with the unit g mg-1 min-1.

3.13. Thermodynamic experiments

All the thermodynamic parameters and the characteristics of the adsorption system were derived by the following empirical formula: (Banerjee et al., 2016)

$$K_c = \frac{C_a}{C_e}$$

$$Lnk_c = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Where Kc, denotes the adsorption distribution coefficient, ΔG is the Gibbs free energy difference, and ΔS denotes entropy fluctuations. Similarly, Enthalpy variation, ideal gas constant, and absolute temperature are represented by ΔH, R, and T respectively. The amount of dye adsorbed per unit mass of adsorbent is denoted by Ca.

Characterization of adsorbents

3.14. FTIR:

Due to C-O and C-C-O stretching, the Fourier Transform Infrared (FTIR) characterisation analysis RHC in the below figure was concentrated at a common point between 1060 and 1083 cm-1. While the peak 1615 cm-1 corresponds to C=C, the typical C-H stretching vibrations around 2916 cm-1 and 3425 cm-1 correspond to the presence of the OH group in the form of moisture and silica, respectively.

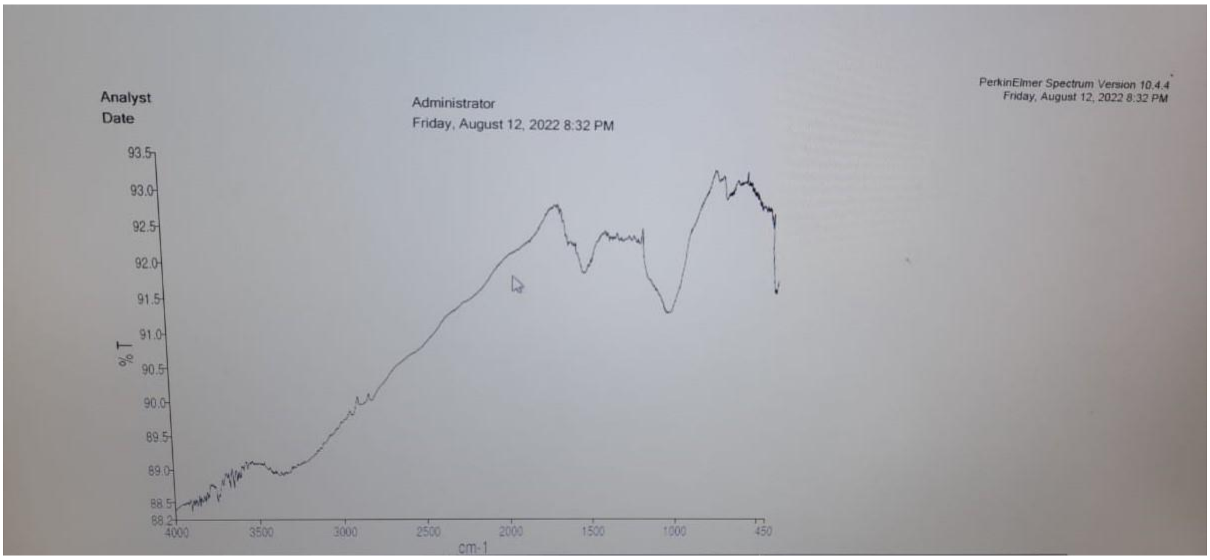


Figure 7: FTIR graphical representation of rice husk charcoal before use.

3.15. XRD

Figure (8) shows the XRD patterns of rice husk charcoal (RHC) before use. The hump formation noticed between 20° to 25° represents the excitation of amorphous carbon due to X-ray. Silica present in RHC was found to remain in its organic form until solubilized with NaOH as sodium silicate, Sodium silicate was further precipitated as crystalline SiO_2.

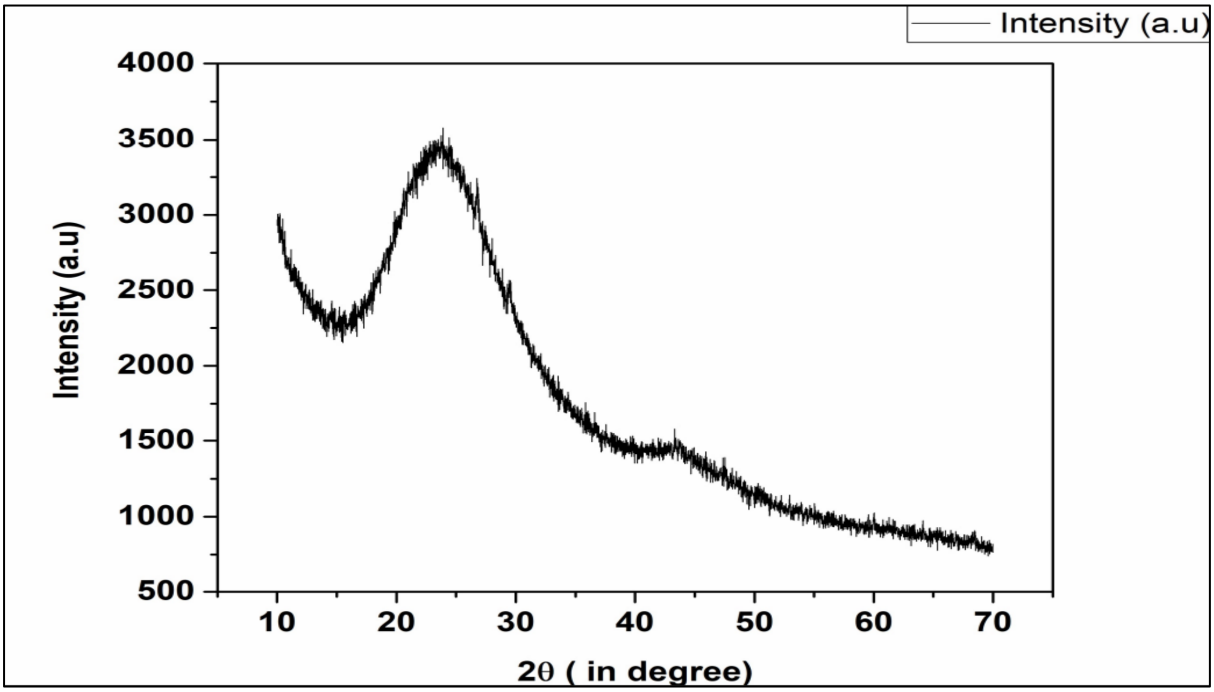


Figure 8: Graphical representation of XRD of rice husk charcoal before use.

3.16. SEM

The below figure is the representation of SEM image of rice husk charcoal.

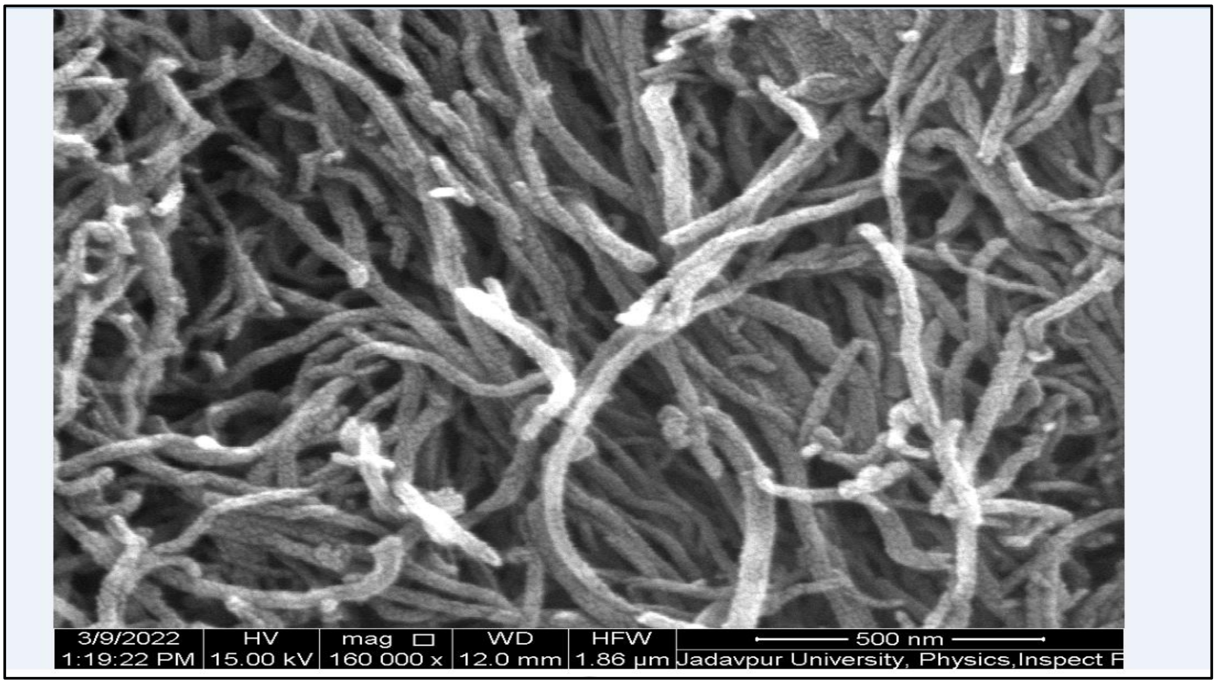


Figure 9: SEM image on rice husk charcoal.

Chapter 4

4.1. Fenton Process for Malachite Green (MG) dye Removal

4.1.1. Abstract

In this study Fenton's process was discussed and investigated as an Advanced oxidation process (AOP) using Fenton's reagent for decontamination of cationic dye from wastewater. Cationic dye used in this process are malachite green. Different parameters which affect the reaction such as the initial Fe^{2+} concentration, solution pH, initial H_2O_2 concentration, reaction temperature and concentration of target dye had been studied.

The optimal conditions for oxidative degradation of malachite green were found to be pH at 4, hydrogen peroxide (H_2O_2) concentration at 0.2 ml/L, initial ferrous concentration at 50 ppm for 10 ppm of malachite green dye concentration at 30°C. Under these optimal reaction conditions, removal of malachite green dye was experimentally found to be 99% after completion of 90 minute of reaction.

4.1.2. Introduction

In order to colour the product in the textile, paper production, lather, and food technology, the synthetic dyes have proved useful in the modern era, which also includes more different industries for making the product more colourful. The malachite green colour has been considered for the printing inks and paints, which also includes the process to colour the paper, silk, cotton and many other manufacturing products. One of the important properties that has been considered for the respective dye colour has included the water proof property that can be hard to remove. The malachite green dye has proved helpful for producing the spirits, along with the process that can be helpful for having a proper colouring process to the distillers. Aquatic life is adversely affected when malachite green is discharged into receiving streams;

as a result, the pituitary gonadotropic cells, liver, gonads, kidneys, and gills suffer. For the sake of the ecology, it is therefore imperative to eliminate coloured synthetic organic dyes from waste effluents. As effective pre-treatment methods for wastewater that isn't as biodegradable, Fenton's reagent (H_2O_2 and ferrous ion), titanium dioxide (TiO_2), ultraviolet (UV), and other complex oxidation processes have recently attracted a lot of interest. Due to its accessibility, simplicity, compatibility with organic molecules, and absence of production of hazardous by-products during oxidation, Fenton's reagent has been utilised extensively among them. The Fenton reaction, which uses Fe^{2+} as a catalyst to form hydroxyl radicals from H_2O_2 that oxidatively degrade the contaminants, is one of the most effective ways to oxidise organic pollutants.

$$\boxed{\mathbf{Fe^{2+} + H_2O_2 \rightarrow OH\bullet + OH^-}}$$

When ferrous salts are utilised, hydrogen peroxide and ferrous ions quickly interact, leading to the rapid formation of the hydroxyl radical. In a two-step process, the ferric ion and hydrogen peroxide first react slowly before quickly reacting with additional hydrogen peroxide to produce the hydroxyl radical seen in ferric salts.

$$\boxed{\mathbf{Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+}}$$

The efficiency of Fenton's technique depends on the concentrations of H_2O_2, Fe^{2+}, and reaction pH. Recent academic research determined that the pH level should be between 3-5. Using Fenton's reagent, it has been shown that the decolorization of C.I., the removal of COD and colour from animal effluent, and the removal of colour from industrial wastewater are all extremely effective treatments for a range of industrial wastewater components. Treatment of wastewater including high quantities of organic material from textiles, alkyd resin, acid yellow 23 and dye, and acid yellow 23 and dye. reactive black b dye oxidation Since then, Fenton's reagent has been used to eliminate a variety of contaminants, including those produced by the chemical and textile industries. The major objective of this experiment was to evaluate the efficiency of MG removal from an aqueous solution using the Fenton reaction. The Fenton system is influenced by the pH, iron content, and hydrogen peroxide concentrations. Experiments were conducted to determine how various operational conditions affected the treatment system's performance.

Many different types of products, including those in the textile, leather, paper, food technology, etc. industries, are coloured using synthetic dyes. Malachite green (MG), a common colouring agent, is also used in paints and printing inks and imparts a characteristic appearance to cotton, silk, paper, and leather. Due to its characteristics, malachite green is difficult to remove from aqueous solutions. Malachite green is a common colouring agent used in distilleries. When malachite green is released into receiving streams, it damages aquatic life as well as the organs and tissues of the liver, gills, kidney, stomach, gonads, and pituitary gonadotropic cells. Waste effluents must be free of artificial organic colourants in order to protect the environment. For less biodegradable wastewater, sophisticated oxidation treatments like ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton's reagent (H_2O_2 and ferrous ion) have recently gained a lot of interest. Fenton's reagent has been one of the most popular because to its availability, ease of use, favourable interactions with organic molecules, and lack of production of harmful chemicals when it is oxidised. When organic contaminants are subjected to Fenton's reaction, which employs Fe^{2+} as a catalyst, they are oxidatively removed by hydroxyl radicals produced by H_2O_2.

4.1.3. Materials and Methods

4.1.3.1 Reagents

The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42,000, chemical formula = C52H54N4O12, MW= 927.00, λ max = 617.70 nm (measured value). The chemical structure of malachite green oxalate is shown in Fig. 1. The Fe^{2+} ions were provided from solutions of ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and the hydrogen peroxide (H_2O_2) was from stock of 30% (w/w). All chemicals were of analytical grade and were used without any further purification. Distilled water was used throughout this study.

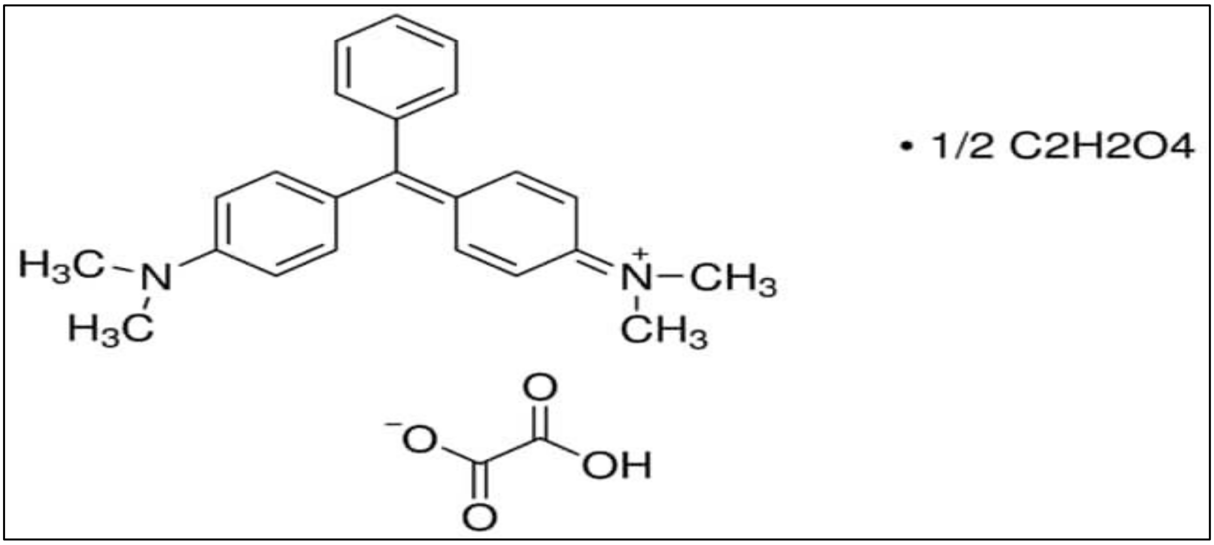


Figure 10: The chemical structure of Malachite green.

4.1.3.2. Preparation of synthetic dye solution

The dye solution was prepared by dissolving the MG dye in distilled water to produce a stock solution of 500 mg/L. This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

4.1.3.3. Experimental procedures

A 50-ml stoppered glass (Erlenmeyer flask) was used as a batch reactor. Batch experiments of MG degradation were performed by adding H_2O_2 to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either 0.1N H_2SO_4 or 0.1N NaOH. Following the pH adjustment, the Fe^{2+} ions were quickly added to the dye solution. The flask was then placed in a thermos-stated water-bath shaker and agitation were provided at 150 rpm. The samples were taken out from the conical flask periodically using a 1-ml syringe and were analysed immediately. The effect of initial MG concentration $[MG]_0$ in the oxidation of MG was studied by varying the amount of $[MG]_0$ used for the experiment (10, 20, 30, 40 and 50 mg/L), while maintaining pH, agitation speed, initial ferrous concentration $[Fe^{2+}]_0$, initial hydrogen peroxide concentration $[H_2O_2]_0$ and temperature constant at 4, 150 rpm, 50 ppm, 0.2 ml/L and 30°C, respectively. The solutions were agitated in a thermostatic water-bath shaker for a period of 70–100 min. The effect of pH on MG degradation was studied using 250mL of 10 mg/L dye solution taken in a stoppered conical flask containing 50 ppm and 0.2 ml/L of $[Fe^{2+}]_0$ and $[H_2O_2]_0$, respectively. The pH of the solution was varied from 2 to 10 using 0.1N H2SO4 and 0.1N NaOH. The solution at the respective pH was agitated in a thermostatic water-bath shaker (150 rpm) for a period of 60 min at 30°C.

The effect of the $[Fe^{2+}]_0$ dosage on the MG degradation was also studied. To 250 mL of 10 mg/L MG solution, different $[Fe^{2+}]_0$ concentrations (25, 50, 75 and 100 ppm) were added along with 0.2 ml/L of $[H_2O_2]_0$. The flasks were agitated in a thermostatic water-bath shaker for a period of 60 min at 30°C. Samples were taken out from the conical flask periodically for analysis purposes. The effect of H_2O_2 in the oxidation of MG was studied by varying the amount of H_2O_2 used for the experiment (0.1, 0.2, 0.3, and 0.4 ml/L) with $[Fe^{2+}]_0$ of 50 ppm. The solutions were agitated in a thermostatic water-bath shaker for a period of 60 min at 30°C. To study the effect of reaction temperature, 250 mL of 10 mg/L MG solution was agitated with

50 ppm of $[Fe^{2+}]_0$ and 0.2 ml/L $[H_2O_2]_0$ at pH 4 for a period 60 min at various temperatures (25, 30, 35 and 40°C).

4.1.3.4. Analytical methods

The efficiency of the proposed process was evaluated by monitoring MG degradation by measuring absorbance at 617.70 nm using a double beam UV/vis spectrophotometer (Shimadzu). Therefore, the concentration of the MG in the reaction mixture at different reaction times was determined by measuring the absorption intensity at max 617.70 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard MG solution with known concentrations. Because the reaction continued after sampling, the measurement. The absorbance of the reaction solution was done within 1 min. The degradation efficiency of MG was defined as follows:

$$\boxed{\mathbf{\%\ removal = (1 - C_t/C_0) \times 100\ \%}}$$

where C_0 (mg/L) is the initial concentration of MG, and C_t (mg/L) is the concentration of MG at reaction time t (min).

4.1.4. Batch Study

4.1.4.1. Effect of the initial MG concentration in Fenton's process

All experiments employed the same pH, agitation rate, amount of ferrous solution, and temperature (50 ppm, 0.2 ml/L, and 30°C). Between 10 and 50 mg/L of $[MG]_0$ was present at the beginning. The effect of the Fenton oxidation by $[MG]_0$ on the compound's oxidative degradation is shown in Figure 2. It is obvious that as initial attention wanes, reaction times shorten. The degradation efficiency at 10 mg/L is 98% and 100%, respectively, after 45 and 60 minutes. Even with longer reaction times, lower degradation efficiencies were seen at higher starting concentrations. For example, the clearance efficiencies were 97.8, 93.79, and 83.52%

for starting MG concentrations of 10, 20, and 50 mg/L, respectively. This reveals that within the first 30 minutes, there were greater $[H_2O_2]_0$, $[Fe^{2+}]_0$, and MG concentrations. After 30 minutes, the hydrogen peroxide level in the system dramatically dropped, which considerably slowed the MG's fall.

time	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
0	0	0	0	0	0
15	54.1	70.9	77.1	80.35	81.52
30	97.8	93.79	91.86	90.59	83.52
45	98.94	99	95.16666667	93.79	86.488
60	99.57	99.225	99.16666667	98.9425	87.986
75	99.73	99.37	99.51666667	99.33	90.798
90	99.98	99.59	99.63666667	99.525	93.1

Table 1: Effect of the initial MG concentration in Fenton's process for MG removal.

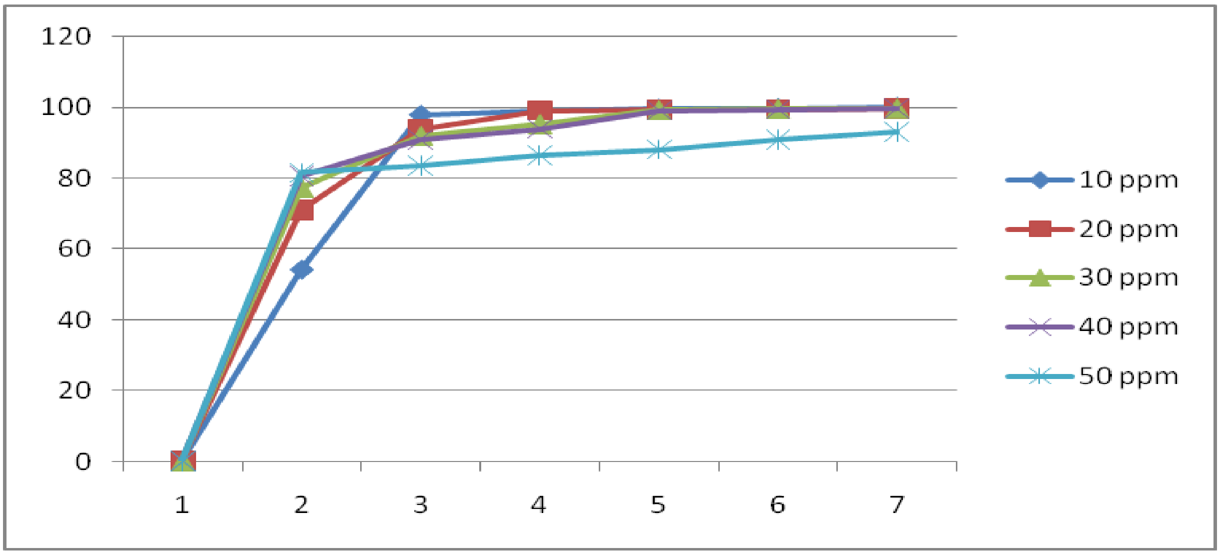


Figure 11: Comparison graph of %removal vs. Concentration of Malachite green dye.

4.1.4.2. Effect of pH in Fenton's process

Throughout multiple trials, the concentrations of Fenton solution, $[H_2O_2]_0$, and $[MG]_0$ were kept at 10 mg/L, 50 ppm, and 0.2 ml/L, respectively. We investigated the impact of pH on MG oxidation by Fenton. Additionally, the reaction mixture's optimal pH was established. The outcomes showed that the solution's pH had a substantial impact on how quickly MG broke down, with pH 4 being the optimal level. The precipitation of Fe $(OH)_3$ may be the cause of the efficiency drop at high pH levels. In this case, iron breaks down H_2O_2 into oxygen and water to halt the oxidation of hydroxyl radicals.

time	pH 2	pH 4	pH 6	pH 8	pH 10
0	0	0	0	0	0
15	23.59	12.19	31.08	31.3	48
30	92.05	89.52	69.25	55.64	69.49
45	98.17	93.47	81.64	66.98	82.91
60	98.59	95.93	92.3	80.16	90.93
75	98.76	96.56	95.72	83.98	93.58
90	98.81	97.94	96.31	85.53	94.22

Table 2: Effect of pH in Fenton's process for MG removal.

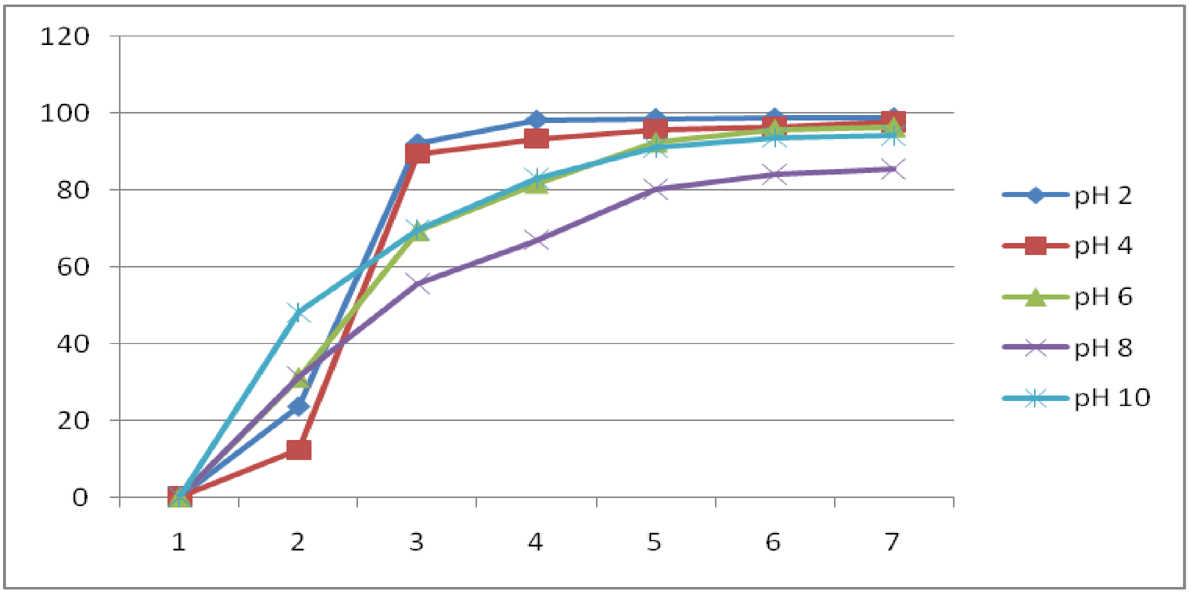


Figure 12: Comparison graph of %removal vs. pH of the solution.

4.1.4.3. Effect of ferrous ion (Fe^{2+}) concentration in Fenton's process are shown below:

Several tests were conducted with $[Fe^{2+}]_0$ varying from 25 to 100 ppm to investigate the impact of the starting Fe^{2+} concentration on the oxidation of MG. The outcomes are displayed in Fig. 4. The degrading efficiency of MG varied significantly in the $[Fe^{2+}]0$ range of 25 to 100 ppm. The highest degrading efficiency was observed during a 60-minute reaction at a concentration of 100 ppm ferrous solution, while the lowest (32.1%) was observed at a concentration of 25 ppm ferrous solution.

By stimulating Fe^{2+} to self-scavenge •OH radicals, certain experiments that have been reported in the literature show that using a significantly higher concentration of Fe^{2+} may slow down the rate of contaminant breakdown.

$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$$

time	**25 ppm Fe2+**	**50 ppm Fe2+**	**75 ppm Fe2+**	**100 ppm Fe2+**
0	0	0	0	0
15	1	98.8	97.22	95.83
30	11	98.92	98.93	96.12
45	20.6	99	99.04	97.28
60	32.1	99.02	99.36	97.36
75	33	99.16	99.46	98.92
90	40.6	99.58	99.5	99.77

Table 3: Effect of ferrous ion (Fe^{2+}) concentration in Fenton's process for MG removal.

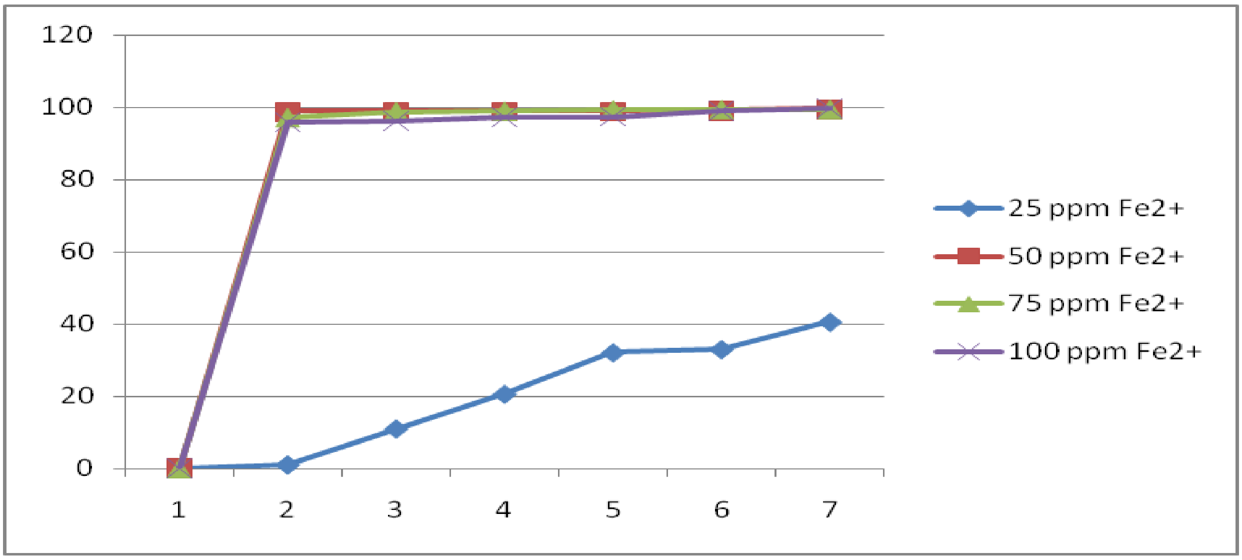


Figure 13: Comparison graph of %removal vs. Concentration of Fe^{2+}.

4.1.4.4. Effect of Hydrogen peroxide (H_2O_2) concentration in Fenton's process

Tests were conducted at 30 °C with an initial MG concentration of 10 ppm and a ferrous solution concentration of 50 ppm to evaluate how $[H_2O_2]_0$ effects MG degradation. The effect of $[H_2O_2]_0$ was examined between 0.1 and 0.4 ml/L, as shown in Fig. 5. The early dye decolorization of the process was accelerated by the rise in $[H_2O_2]_0$ as anticipated. The decolorization efficiency climbed from 85.59 to 87.72% when the H_2O_2 dosage was elevated from 0.5 to 4.0mM at 10 min. This may be explained by the impact of extra OH• radicals being produced. The figure, however, demonstrates that raising $[H_2O_2]_0$ had little to no effect on the declining efficiency% after 35 minutes. Degradation percentages of 99.66, 99.51, and 95.69 were obtained after 50 minutes of reaction time with 0.50, 2.00, and 4.00 mM of H_2O_2. H_2O_2 is known to hasten the degradation of dyes by raising the quantum yield of hydroxyl radical generation, according to Aravindhan et al explanation of this occurrence. This is expected to increase the rate of decline. However, H_2O_2 is a powerful OH• scavenger at high doses:

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O$$

$$H_2O_2 + OH_2\bullet \rightarrow OH\bullet + O_2 + H_2O$$

$$HO_2\bullet + OH\bullet \rightarrow H_2O + O_2$$

Deionized water was used to dissolve the MG dye, creating a stock solution with a 500 mg/L concentration. The dye solution was prepared using this technique. This stock solution was precisely diluted to provide solutions with different starting concentrations. As a result, adding the additional H_2O_2 concentration was not required to make things better. Hydroperoxyl radicals ($HO_2\bullet$), which are created when there is an excess of H_2O_2, may be to blame for this. Even though it is a powerful oxidant on its own and encourages radical chain reactions, $HO_2\bullet$ has a far lower oxidation potential than OH•. Because hydroperoxyl radicals are far less reactive than OH•, they do not participate in the oxidative destruction of organic substrates.

time	**0.1ml/L**	**0.2ml/L**	**0.3ml/L**	**0.4ml/L**
0	0	0	0	0
15	98.02	98.8	97.86	79.2
30	98.1	98.92	97.92	98.91
45	98.39	99	98.82	99.04
60	98.78	99.02	99.11	99.06
75	98.89	99.16	99.21	99.2
90	98.94	99.58	99.36	99.64

Table 4: Effect of Hydrogen peroxide (H_2O_2) concentration in Fenton's process for MG removal.

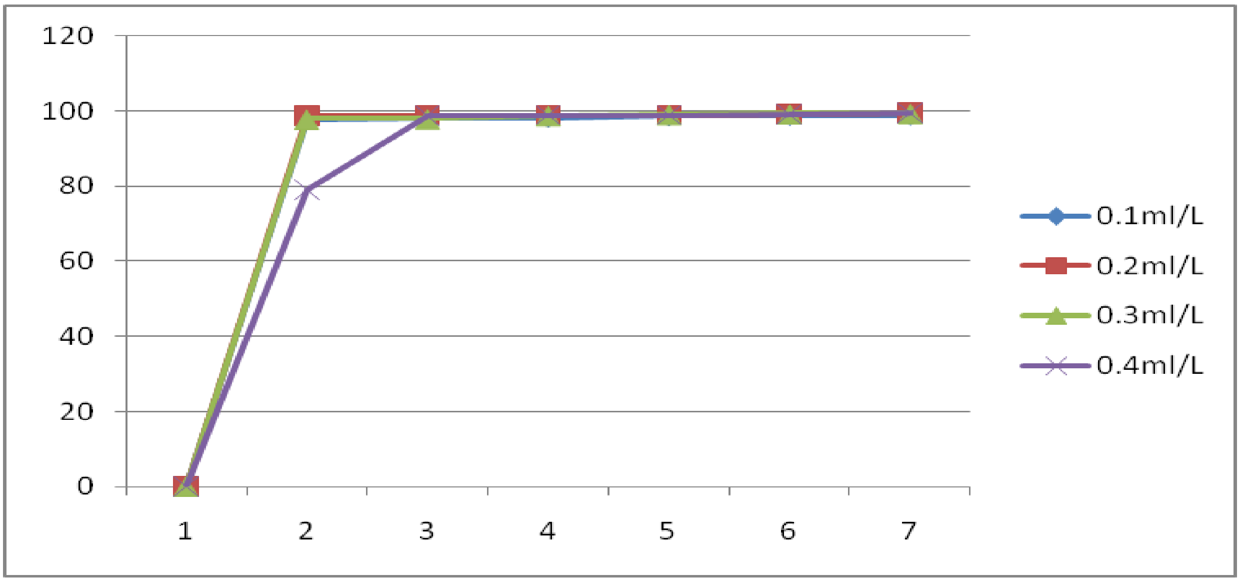


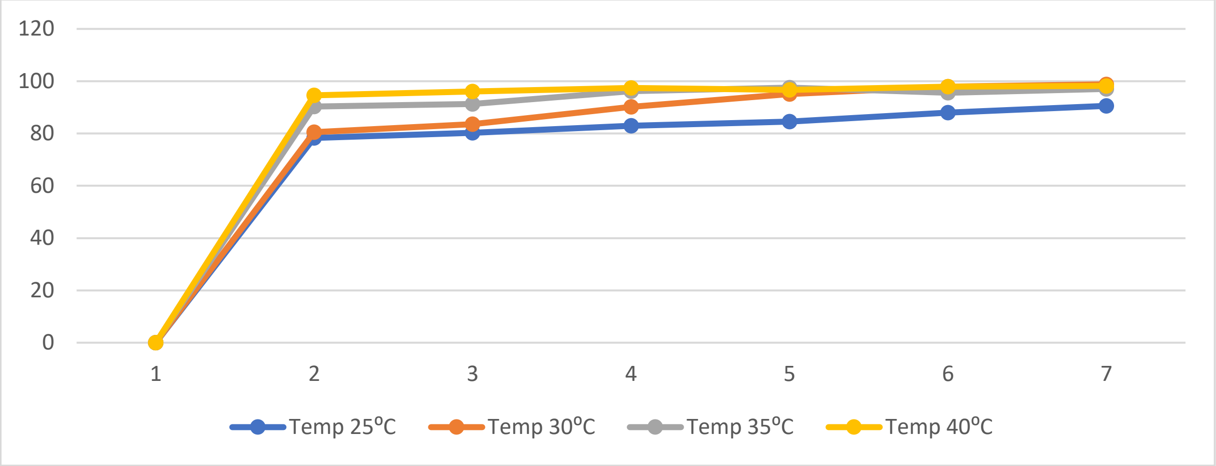
Figure 14: Comparison graph of %removal of MG vs. H_2O_2 concentration.

4.1.4.5. Effect of temperature in Fenton's process

Numerous investigations looked at how reaction temperature affected the rate of MG breakdown at 30, 40, and 50 C. The outcomes are displayed in Fig. 6. The decreasing efficiency of the MG improved from 85.59 to 98.14% when the temperature was raised from 30 to 50 C during the first 10 minutes of the oxidation process, as shown in Fig. 6. Higher temperatures hasten the generation of highly oxidising species like the •OH radical or high-valence iron species by accelerating the interaction between hydrogen peroxide and any ferrous or ferric iron, chelated or not. After a reaction period of 20 minutes, the temperature-dependent MG degradation is essentially non-existent.

Comparison time	Temp 25^oC	Temp 30^oC	Temp 35^oC	Temp 40^oC
0	0	0	0	0
15	78.32	80.56	90.25	94.64
30	80.23	83.54	91.32	96.08
45	82.97	90.21	96.23	97.42
60	84.56	95.12	97.54	96.74
75	88	97.87	95.63	97.88
90	90.56	98.82	97.02	98.2

Table 5: Effect of temperature in Fenton's process for MG removal.



<u>Figure 15: Comparison graph of %removal of MG vs. Temperature of the reaction.</u>

4.1.5. Conclusion

For eliminating MG from aqueous solutions, the experimental Fenton's reaction has shown to be highly effective. For the Fenton oxidation of MG, the optimal values for $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[MG]_0$, and pH were 0.2 ml/L, 50 ppm, 10 mg/L, 4, and 30°C. After 60 minutes of reaction time, 99% of the MG in aqueous solution under these circumstances was destroyed. By encouraging the production of less reactive radicals, increased hydrogen peroxide may reduce the rate at which MG discolours.

4.2. Activation of Raw Rice Husk and its application in removing pollutants from wastewater

4.2.1. Abstract

Methodology involved in the treatment of raw rice husk, activated rice husk and chemically treated activated rice husk as an efficient adsorbent to remove cationic and anionic dyes from contaminated water were investigated. Parameters such as solution pH, concentration of target organic pollutants, reaction time, adsorbent dose and reaction temperature were also studied to improve adsorption process. Fourier transform infrared spectroscopy (FTIR) and Dynamic light scattering (DLS) particle size analyser was used to determine the bond breaking during the reaction, indication of intermediates and the relation between particle size and adsorption process.

Adsorption capacity was calculated from the data obtained in this process at equilibrium stage by fitting to Freundlich isotherm model and it was found that maximum adsorption capacity was 1000 mg/g at temperature 303 K. The adsorption kinetics and thermodynamic studies were calculated of all the adsorbents to find out the nature of the reaction. Data obtained from kinetics study were fitted in pseudo second order model and data obtained from thermodynamics study indicates the reaction was exothermic in nature. Under all these parameters which affect the reaction rate, 99% removal of malachite green dye was removed in this study.

4.2.2. Batch Study

4.2.2.1. Effect of the initial MG concentration in Adsorption process

The concentration of dye solution was varied between 10 mg/L to 50 mg/L or 10-50 ppm. Studies were performed by adding 1 g/L adsorbent at 120 rpm, 303K or 30°C and pH 6. It was observed that the removal efficiency gradually decreases at higher dye concentration. The MG removal efficiency drastically improved for RHC with decrease in initial dye concentration. This proves high density active adsorption sites are available on RHC. NaOH treatment of pyrolyzed rice husk created more mesopores by removal of SiO_2, in the form of Sodium Silicate. However better adsorption was observed at lower dye concentration for all three adsorbents. This indicates that at higher dye concentration the rate of pore saturation increases. The equilibrium conditions were reached within 1 hour. The maximum adsorption efficiency obtained by RHC 50 mg/L was 98.83%.

time	**10 ppm**	**20 ppm**	**30 ppm**	**40 ppm**	**50 ppm**
0	0	0	0	0	0
15	87.99	75.96	56.88	41.06	15.1
30	97.37	85.51	67.63	52.12	27.4
45	97.57	85.71	74.32	54.7	37.7
60	98.44	86.19	78.3	56.91	41.23
75	98.51	87.92	79.8	57.79	47.2
90	98.83	88.9	80.3	61.75	51.86

***Table 6:** Effect of the initial MG concentration in Adsorption process.*

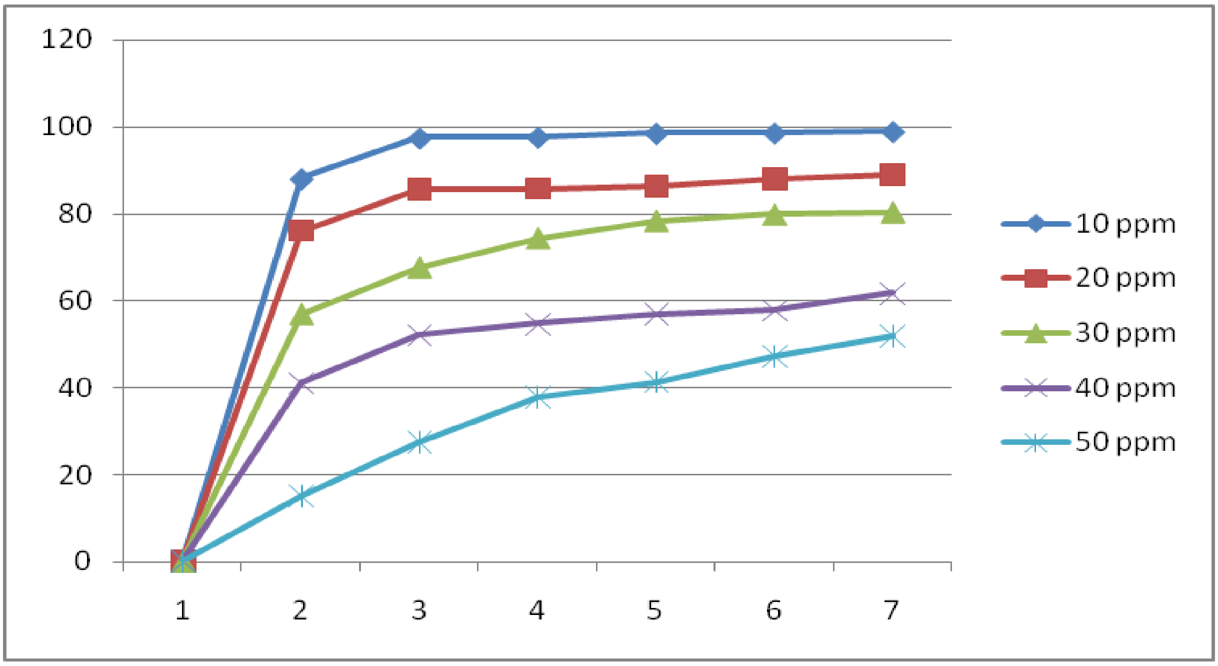


Figure 16: Comparison graph of %removal of MG vs. concentration of Malachite green in adsorption process.

4.2.2.2. Effect of the adsorbent dose (g/L) in Adsorption process

Time dependent adsorption process is also driven by the amount of adsorbent used or also termed as adsorption dosage. Effect of variable dosage on adsorption efficiency was studied using fixed feed concentration of 10 mg/L. Adsorbent dosage was varied between 0.5, 1.0, 1.5 and 2 g/L at 303K or 30°C, 120 rpm and pH 6 for 120 min. The experiment displayed an increase in removal efficiency at higher dose of adsorbent. However, the adsorption efficiency widely varied among three adsorbents at any given dosage. It was observed that the remaining dye concentration reduced with the increase in the dosage from 0.25 g/L. to 1 g/L. The rate of adsorption increased with increase in adsorbent dosage. Either way, dosage of over 1g/L didn't display any remarkable increase in adsorption efficiency, as over clouding of adsorbent leads to agglomeration. Clumping of adsorbent reduces the concentration of active site. We therefore decided to work with 1 g/L dosage for further study to avoid wastage of adsorbents.

The maximum adsorption efficiency obtained by RHC 50 mg/L was 98.83%.

Comparison				
time	0.5g/L dose	1g/L dose	1.5g/L Dose	2g/L Dose
0	0	0	0	0
15	78.42	87.99	85.77	91.79
30	83.28	97.37	92.73	98.27
45	83.91	97.57	93.52	99.14
60	84.21	98.44	94.13	99.3
75	84.76	98.51	94.73	99.52
90	86	98.83	95.12	99.98

Table 7: Effect of the adsorbent dose (g/L) in Adsorption process.

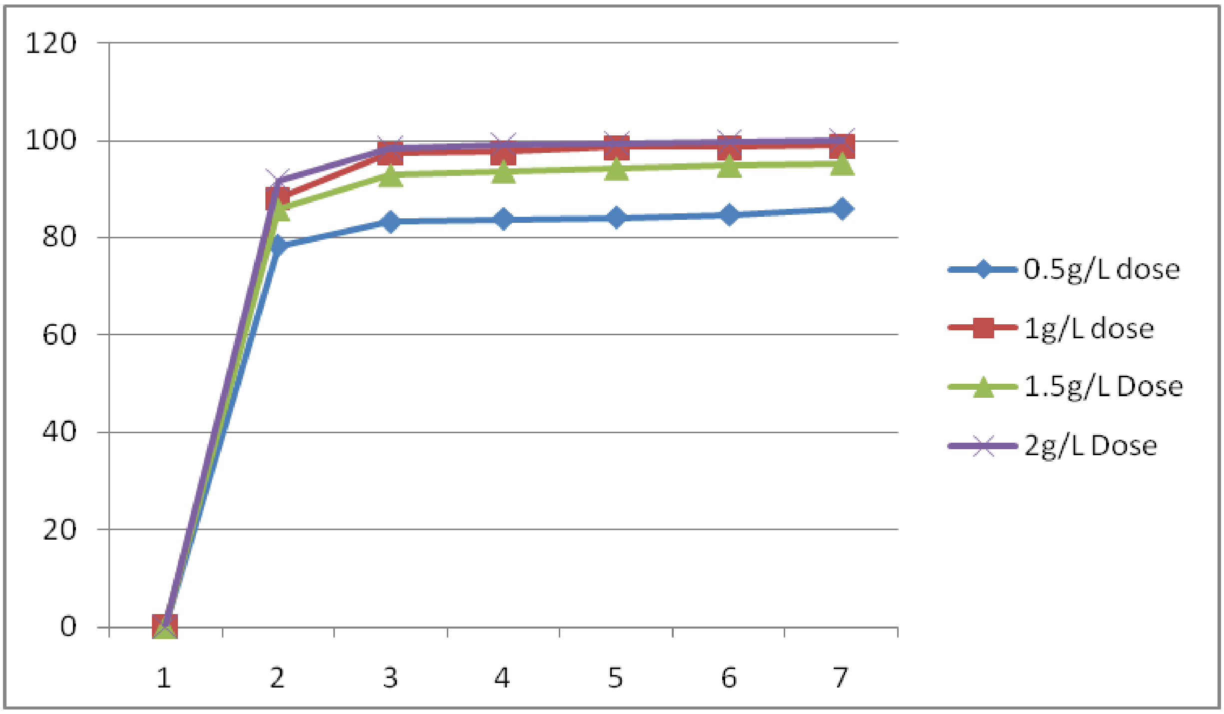


Figure 17: Comparison graph of %removal of MG vs. adsorbent dose in adsorption process.

4.2.2.3. Effect of pH in Adsorption process

The pH value of the adsorption system was found to be the most important limiting factor as pH of the solution modifies adsorption surface characteristics. Studies were performed at various pH conditions at a constant dye concentration of 10 mg/L, 120 rpm and 30°C. Acidic condition was not favoured as adsorption capacity was found to be reduced for all three adsorbents. At acidic conditions such as pH 2, availability of excess H^+ ions neutralize the negatively charged active sites which were crucial for adsorption of the cationic dye (Chowdhury & Saha, 2010: Das et al., 2021). It was also observed that adsorption efficiency improves at higher pH condition such as pH 8. However, it was found that the cationic MG dye automatically decolorizes at basic without the adsorbent. Due to which at basic pH condition it is difficult to distinguish between the amount of dye removed and the amount of dye decolorized. Malachite green solution has a neutral pH when dissolved in demineralised water. Therefore, all further studies were performed at pH 6.

The maximum adsorption efficiency obtained by RHC 50 mg/L was 98.11%.

Comparison					
time	**pH 2**	**pH 4**	**pH 6**	**pH 8**	**pH 10**
0	0	0	0	0	0
15	45.1	78.18	93.21	96.81	97.9
30	67.23	87.56	97.81	97.99	98.58
45	72.08	89.78	97.99	98.16	98.77
60	78.18	91.74	98.11	98.46	98.89
75	79.88	92.9	98.32	98.65	99.11
90	80.97	93.52	98.66	98.85	99.25

Table 8: Effect of pH in Adsorption process.

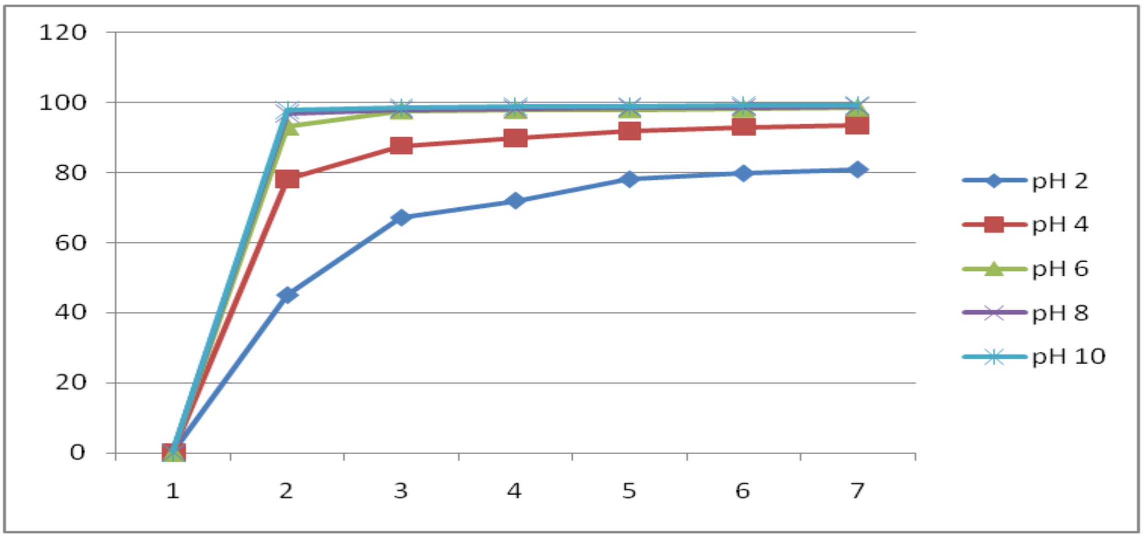


Figure 18: Comparison graph of %removal of MG vs. pH of the solution in adsorption process.

4.2.2.4. Effect of temperature in Adsorption process

Temperature parameters were varied between 298K or 25°C to 323K or 40°C at 10 ppm MG, 120 rpm and dosage of 1 g/L. The adsorption efficiency was studied by determining the remaining dye concentration. It was observed that adsorption efficiency reduced with increase in temperature. Compared to other adsorbents raw RH displayed the least adsorption efficiency of 48.46% at 323K and maximum equilibrium time of 70 min. Increase in system temperature aggravates molecular vibrations which further reduces availability of active sites (Das et al., 2021). In addition to that increasing the temperature may also increase rate of desorption due to high molecular mobility. In case of raw RH may also lead to swelling effect (Bao & Zhang. 2012). Therefore, 303K or 30°C was considered to be the most feasible temperature for further studies.

The maximum adsorption efficiency obtained by RHC 50 mg/L was 98.82%.

Comparison time	Temp 25°C	Temp 30°C	Temp 35°C	Temp 40°C
0	0	0	0	0
15	87.6	91.88	93.79	97.02
30	96.76	97.06	98.04	99.21
45	96.99	97.81	98.38	99.2
60	97.48	98.57	98.75	99.45
75	97.6	98.73	98.89	99.83
90	97.68	98.82	98.97	99.92

Table 9: Effect of temperature in Adsorption process.

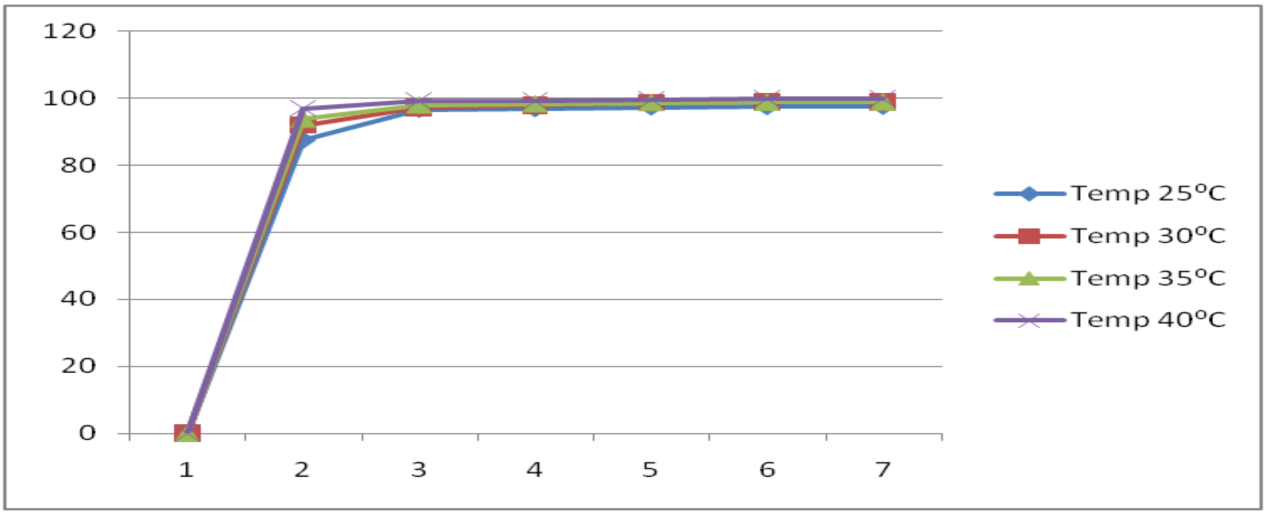


Figure 19: Comparison graph of %removal of MG vs. Temperature of the reaction in adsorption process.

4.2.2.5 Effect of time

Contact period plays an important role in adsorption process. During the contact period the system is agitated to increase the interaction between the total sorption surface area and the soluble dye molecules. In such a system the batch equilibrium studies were performed at 1 g/L of adsorbent dosage to 10 ml of 50 mg/L dye solution at 6 pH and 30°C temperature for duration until it attained equilibrium. The flasks were agitated in shaker at 120 rpm. Samples were collected at 15 min intervals up to 120 min and concentration was analysed.

The adsorption efficiency at best suited combination of parameters, we see that with increase in time adsorption efficiency reduces as the remaining dye concentration reduces up to certain time, also termed as equilibrium time and then become stable. The equilibrium time for Raw RH and RHC were found at 75 min. and 60 min respectively. After equilibrium time no significant adsorption takes place as sorption sites are already occupied and no further sites are available for adsorption (Shrivastava et al., 2011). Moreover, on prolonged agitation the system demonstrated desorption.

4.2.3. Evaluation of isotherm models

The estimated values of Langmuir isotherm model were obtained by plotting $1/q_e$ vs $1/C_e$ whereas log q_e vs log C_e plot was used to obtain Freundlich constants. The values are represented in table 10.

It was observed that Raw RH and RHC was best fitted to Freundlich model as R value were better than that of Langmuir model. Untreated Raw RH exhibited heterogeny (V. K. Gupta, Suhas, et al., 2004).

Models	Parameters	Description	Unit	Adsorbent Dosage (mg/gm)		
				0.5 g/L	1 g/L	1.5 g/L
Langmuir $\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0}$	C_e	Equilibrium pharmaceutical concentration in solution	mg L^{1}	1.4	0.117	0.53
	q_e	Theoretical maximum adsorption capacity	mg g^{-1}	17.2	9.88	6.31
	Q_0	Maximum monolayer coverage capacity	mg g^{-1}	13.39	8.66	5.31
	b	Langmuir coefficient of energy of adsorption	L mg^{-1}	3.11	46.2	10.53
	R^2	Correlation coefficient		0.999	0.999	0.999
Freundlich $\ln q_e = \frac{1}{n_f} \ln C_e + \ln K_f$	n_f	Adsorption intensity calculated from slope of $\ln q_e$ vs. $\ln C_e$ plot		4.6	19.27	9.21
	K_f	Freundlich coefficient of adsorption capacity calculated from intercept of $\ln q_e$ vs. $\ln C_e$ plot	mg g^{-1}	18.57	8.95	5.94
	R^2	Correlation coefficient		0.994	0.94	0.98
Temkin $q_e = B_T \ln C_e + B_T \ln K_T$	B_T	Coefficients of heat of adsorption calculated from slope of q_e vs. $\ln C_e$ plot at operational temperature T	J mol^{-1}	3.56	0.4838	0.647
	K_T	Temkin equilibrium binding constant calculated from intercept of q_e vs. $\ln C_e$ plot at operational temperature T	L g^{-1}	178.1	110669208.3	9733.051
	R^2	Correlation coefficient		0.995	0.94	0.983
Dubinin-Radushkevich $\ln q_e = \ln Q_s - B\varepsilon^2$	B	Dubinin–Radushkevich constant calculated from slope of $\ln q_e$ vs. ε^2 plot.	mole ^{2} KJ^{-2}	0.0000001	0.00000004	0.00000002
	Q_s	Theoretical isotherm saturation capacity calculated from intercept of $\ln q_e$ vs. ε^2 plot.	mg g^{-1}	14.35	8.95	4.3
	E	Polanyi potential	kJ mole^{-1}	2236.1	3535.53	5000
	R^2	Correlation coefficient		0.969	0.77	0.9

Table 10: Evaluation of isotherm models for MG removal using biochar.

4.2.4. Adsorption kinetics for MG dye

Kinetic parameters were calculated by plotting log (q_e-q_t) vs time (t) and t/q_t vs time (t) for pseudo 1st and 2nd order respectively. Equilibrium adsorption capacity q_e and constant K were determined from the slope and intercept. As represented in the table (2) it was observed that 2nd order fits better than 1st order for all three adsorbents with a better R value. It is also reflected by the disparity between the experimental value $q_{e(exp)}$ and the calculated value $q_{el(cal)}$ of 1st order model. On the other hand, for 2nd order model displayed minimum difference between the experimental and calculated value of equilibrium adsorption capacity

Models	**Parameters**	**Description**	**Units**	**Temperatures (K)**		
				298 K	303 K	308 K
Pseudo first order $\log(q_e - q_t) = [\log q_e - \frac{k_1}{2.303}t]$	k_1	Pseudo-1^{st}order rate constant	min^{-1}	0.088	0.058	0.063
	q_e (cal)	Quantity of Carbamazepine adsorbed at equilibrium	mg g^{-1}	15.82	1.36	1.02
	R^2	Correlation coefficient		0.93	0.99	0.98
Pseudo second order $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2	Pseudo-2^{nd} order rate constant	mg g^{-1} min^{-1}	0.07	0.088	0.131
	q_e	Quantity of Carbamazepine adsorbed at equilibrium	mg g^{-1}	9.95	10.02	9.99
	R^2	Correlation coefficient		0.99	1	1
Intraparticle diffusion $q_t = K_{diff} t^{1/2} + C$	K_{diff}	Intra-particle diffusion rate constant	mg g^{-1} min$^{-1/2}$	0.151	0.1119	0.0804
	C	Constant calculated from the intercept of regression plot of $q_t$vs. $t^{1/2}$ where t is time (min).	mg g^{-1}	8.5125	8.9321	9.2181
	R^2	Correlation coefficient		0.63	0.76	0.7
Elovich Istherm $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	α	Initial adsorption rate	mg g^{-1} min	774.41	1705.88	3423.38
	β	Initial desorption rate	mg g^{-1}	1.94	2.68	3.69
	R^2	Correlation coefficient		0.74	0.86	0.81
Liquid film diffusion model	R	Liquid film diffusion constant		0.0743	0.0585	0.0498
	R^2	Correlation coefficient		0.96	0.99	0.76

Table 11: Adsorption kinetics for MG dye.

4.2.5. Thermodynamic study

Thermodynamic parameters like spontaneity (ΔG), enthalpy (ΔH) and entropy (ΔS) were obtained from the batch adsorption experiments where adsorption behaviour of three different adsorbents such as Raw RH and RHC were studied at four different temperature conditions. As represented in table………; we see that for Raw RH ΔG is positive at higher temperature which makes the reaction extremely impractical. Thus, we have obtained very poor adsorption efficiency for Raw RH at higher temperature. For all other combinations the reaction was extremely feasible. However, it was also observed that for all three adsorbents ΔG increases with increase in temperature. This indicates the adsorption efficiency is better at lower temperature of 303K. Moreover, negative ΔH suggests that the adsorption process was exothermic (Chowdhury et al., 2013) and positive ΔS indicates increase in system randomness with time (Chowdhury et al., 2013; Chowdhury & Saha, 2010; Das et al., 2021; Nekouei et al., 2015).

Temperature (K)	**ΔG (kJ/mole)**	**Δ H (kJ/mole)**	**Δ S (joule/mole/kelvin)**	**E a (kJ/mole)**
298 K	-9.27	62.19	243.85	28.69
303 K	-11.15			
308 K	-11.69			

Table 12: Thermodynamic study for MG dye.

4.2.6. RSM

Data from a dye removal trial was evaluated and interpreted using Design-Expert software. The experiment's findings revealed that the simulated values were quite close to the experimental values In terms of actual factors, the final equation is as follows:

$$\boxed{\begin{aligned}&\%\ \text{Removal} = 84.68051 + 26.61394 * \text{Dose} + 1.23118 * \text{pH} + 0.028892 * \text{Time} - 0.58625 * \\ &\text{dose} * \text{pH} - 9.75000\text{E-}003 * \text{Dose} * \text{Time} + 2.56250\text{E-}004\ \text{pH} \times \text{Time} - 25.03685 * \text{Dose2} - \\ &0.040451 * \text{pH2} - 1.21346\text{E-}004 * \text{Time2}\end{aligned}}$$

The model was very significant, with a F statistic of 50.01 (p0.0001) and a high R2 value, according to the results of a regression study (0.9783). With a low CV, the Adj R-Squared value was 0.9587, while the Pred R-Squared value was 0.8351. (0.34) (Chowdhury & Saha, 2012).

4.3. Advanced Oxidation Process in combination with synthesized carbonaceous materials for pollutants removal:

Charing of raw rice husk and sugar straw using annealing & Chemical treatment, characterization and its application to remove pollutants from wastewater were done experimentally. Comparative study on the removal of dye using thermally synthesized biochar, carbon nanotubes (CNT) and reduced graphene oxide (r-GO) and its Batch and Optimization studies were done to determine the suitable and novel techniques for decontamination of emerging organic pollutants from wastewater. Wastewater treatment using advanced oxidation processes in combination with various carbonaceous materials like activated charcoal, reduced graphene, graphene oxide, carbon nanotubes, biochar etc. Degradation and decolorization of Malachite green, Methylene blue, Tartrazine dye from wastewater employing the Fenton and Fenton like process and also tried to combine different adsorbents with this process. In this process, we have used ferrous/ferric ions as a catalyst to activate hydrogen peroxide into hydroxyl radical (•OH) and super hydroxide ion ($\bullet O_2^-$) but after that iron remains in the treated water, itself a harmful compound for the human body. Now we are tiring to remove it from that treated water using adsorbents, filtration processes in batch and column study.

Different combinations of existing Advanced oxidation processes (AOPs) incorporating carbonaceous materials studies are doing to find out novel, economically suitable and eco-friendly techniques for complete decomposition of emerging organic and inorganic pollutants from wastewater.

The below tables are attached because of various combination of different parameters were studied.

Fenton Followed by Biochar:		
	Time (min)	**% Removal**
	15	54.1
	30	99.73
	45	99.6
	60	99.57
After adding Biochar	75	95.68
	90	96.23
	105	96.54
	120	96.73
		0
		0
		0
Fenton Followed by Gr O:	15	98.57
	30	99.28
	45	99.59
	60	99.94
After adding GrO	75	93.11
	90	95.7
	105	96.19
	120	98.38
		0
Fenton Followed by CNT:	15	98.81
	30	99.76
	45	99.94
	60	99.98
After adding CNT	75	97.24
	90	98.85
	105	99.55
	120	99.71

Table 13: Batch study of MG using method Fenton's process followed by biochar.

Fenton + Bio-char:			
		Time (min)	**% Removal**
		15	92.97
Optimized Dose Used		30	93.78
[MG] = 20 ppm		45	94.88
$[H_2O_2]$ = 0.2 ml/L		60	95.67
$[Fe^{2+}]$ = 50 ppm		75	95.7
Adsorbent Dose = 1g/L		90	95.72
		105	96.44
		120	97.2
			0

Fenton + GrO:		15	96.73
		30	96.75
		45	97.27
		60	97.7
		75	97.85
		90	99.05
		105	98.26
		120	98.29
			0
Fenton + CNT:		15	90.19
		30	92.92
		45	93.24
		60	96.2
		75	97.38
		90	95.44
		105	94.79
		120	96.47

Table 14: Batch study of MG removal using incorporation of biochar in Fenton's process.

Fe2+ + Biochar:			
		Time (min)	**% Removal**
Optimized Dose Used		15	89.67
[MG] = 20 ppm		30	90.06
[H2O2] = 0.2 ml/L		45	94.41
[Fe2+] = 50 ppm		60	95.13
Adsorbent Dose = 1g/L		75	94.1
		90	95.14
		105	96.7
		120	97.2
			0
Fe2+ + GrO :		15	92.7
		30	96.42
		45	96.72
		60	97.09
		75	97.34
		90	97.94
		105	98.64
		120	97.39
			0

Fe2+ + CNT :		15	92.61
		30	95.49
		45	95.76
		60	97.33
		75	98.32
		90	96.7
		105	96.1
		120	96

Table 15: Batch study for MG removal using Fe^{2+} with addition of biochar.

Biochar Followed by Fenton :		
	Time (min)	**% Removal**
	15	95.26
	30	96.11
	45	96.16
	60	96.37
After adding Fenton	75	96.74
	90	96.8
	105	96.96
	120	97.12
		0
GrO Followed by Fenton :	15	90.66
	30	92.18
	45	94.59
	60	94.62
After adding Fenton	75	95.12
	90	97.67
	105	94.99
	120	94.27
		0
CNT Followed by Fenton :	15	95.6
	30	96.48
	45	98.21
	60	98.6
After adding Fenton	75	97.34
	90	96.76
	105	95.85
	120	95.58

Table 16: Batch study of MG using method biochar followed by Fenton’s process.

Conclusion

For eliminating MG from aqueous solutions, the experimental Fenton's reaction has shown to be highly effective. For the Fenton oxidation of MG, the optimal values for $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[MG]_0$, and pH were 0.2 ml/L, 50 ppm, 10 mg/L, 4, and 30°C. After 60 minutes of reaction time, 99% of the MG in aqueous solution under these circumstances was destroyed. By encouraging the production of less reactive radicals, increased hydrogen peroxide may reduce the rate at which MG discolours.

Adsorption capacity was calculated from the data obtained in this process at equilibrium stage by fitting to Freundlich isotherm model and it was found that maximum adsorption capacity was 1000 mg/g at temperature 303 K. The adsorption kinetics and thermodynamic studies were calculated of all the adsorbents to find out the nature of the reaction. Data obtained from kinetics study were fitted in pseudo second order model and data obtained from thermodynamics study indicates the reaction was exothermic in nature. Under all these parameters which affect the reaction rate, 99% removal of malachite green dye was removed in this study.

Future Scope

Evaluation of the performance efficiency and underlying mechanisms of Fenton's process were investigated. Fenton's process itself a better process to remove dye from wastewater.

Adsorption process was also used in my study and saw that dye was removed above than 90% in respect to initial concentration using synthesized carbonaceous materials.

Now, here we used the combined study to reduce the cost which we have used in Fenton's process as Fenton's reagent and also to find more efficient process for decontamination of organic and inorganic pollutants from wastewater.

During the study, we have used ferrous/ferric ions as a catalyst to activate hydrogen peroxide into hydroxyl radical (•OH) and super hydroxide ion ($\bullet O_2$-) but after that iron remains in the treated water, itself a harmful compound for the human body. Therefore, we can remove it from that treated water using adsorbents, filtration processes in batch and column study.

In my study, I can't complete my study due to shortage of time, I will do that if I get a chance to research or I can share my all data if anyone want to continue my study.

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