ADSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING BIOCHAR

Project report submitted to the

MAHATMA GANDHI UNIVERSITY, KOTTAYAM

In partial fulfillment of the requirement

For the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

BY

STEFY MARIA JOSE

Reg.No. 190011010516

POST GRADUATE DEPARTMENT OF CHEMISTRY

PAVANATMA COLLEGE, MURICKASSERY

2019-2021

PAVANATMA COLLEGE
MURICKASSERY, IDUKKI 685604
NAAC Re-Accredited with A Grade

CERTIFICATE

This is to certify that the project entitled "**Adsorption of Methylene bkue using activated charcoal**" is a bonafide work carried out by Miss **STEFY MARIA JOSE** (Reg.NO: **190011010516**) under guidance of Dr.ANEESH MATHEW, PG Department of Chemistry, Pavanatma College, Murickassery, for partial fulfillment of therequirement for the award of Degree of Master of Science in Chemistry ofMahatma Gandhi University during the year 2019-2021.

Dr. ANEESH MATHEW,
Assistant Professor on contract,
PG Department of Chemistry,
Pavanatma College,
Murickassery.

Murickassery
09/08/2021

DECLARATION

I, STEFY MARIA JOSE**,** do hereby declare that this dissertation entitled "**ADSORPTION USING BIOCHAR"** is a bona-fide work carried out by me during **2019-2021** at Pavanatma College, Murickassery under the supervision and guidance of **Prof. Dr. Surendran Parambadath** and **Dr. Aneesh Mathew,** and no part therefore has been submitted for the award of any degree, diploma or recognition of university.

STEFY MARIA JOSE

Reg. No. 190011010516

Murickassery

Date:09/08/2021

ACKNOWLEDGEMENT

I wish to express my deep gratitude to the Principal, Pavanatma College, Murickassery for providing me the necessary facilities for doing this project work.

I am grateful to Prof. **Dr. Saji K. Jose** (Head of Department) for his valuable guidance and support.

I would like to thank **Prof. Dr. Surendran Parambadath,** PG and Research Department of Chemistry, Sree Neelakanta Government Sanskrit College, Pattambi, Palakkad for his valuable suggestions in completing this work.

I am greatly indebted to **Dr. Aneesh Mathew** for his valuable suggestions and support as the supervising guide.

I extend my deep gratitude to all teachers and non-teaching staffs of our department for their valuable support to this project.

I would like to thank my parents for their help and prayers for completing this project.

I am also greatly indebted to my friends for their valuable co-operation.

Above all, I thank Almighty God for all the grace he has bestowed upon during this work

STEFY MARIA JOSE

INDEX

1. INTRODUCTION

2. OBJECTIVES

3. LITERATURE SURVEY

4. MATERIALS AND METHODS

5. INSTRUMENTATION

6. RESULTS AND DISCUSSIONS

7. CONCLUSION

8. REFERENCE

ADSORPTION USING BIOCHAR

1. INTRODUCTION

Bio char is the char co product from the thermo chemical processing of biomass utilized as a soil amendment and/or carbon sequestration agent. Processes that produce bio char include pyrolysis (heating without oxygen) and gasification; other co products include heat, electricity, bio-oil, and syngas. Interest in bio char soil applications originally stemmed from the long-term fertility of anthropogenic soils in the Brazilian Amazon. More recently, the recalcitrance of biochar carbon has attracted international attention as an inexpensive and effective way to sequester atmospheric carbon for centuries to millennia while simultaneously producing carbon-negative energy and improving soil quality. Current research focuses on relationships between feedstocks, reaction conditions, biochar properties, soil and crop responses to biochar applications, and economics

Biochar has drawn remarkable consideration for soil improvements due to their enhanced soil fertility, nutrient immobilization and slow-release, carbon storage, which are some of the handful of benefits for soil amendments made with biochar. These enhanced properties are a result of the cumulative effects arising from the changes in the microbial activities in soils along with the agrochemical application. The community structure of the soil biota alters, nutrients transformation rates changes, and so is the release of nutrients from the applied agrochemicals. This chapter reviews the linkages between the biochar applications in soils and the available nutrients for plant growth arising from the agrochemical applications to soils. Furthermore, the alteration in mechanisms of nutrient uptake for food crops growth has also been reviewed upon biochar amendments in soils. Biochar significantly affects the soil conditions and plant growth, which needs further understanding. The chapter gives insights to future directions with regard to the implications, drawbacks of using biochar as soil amendments for an effective biochar plant nutrient interaction.

Biochar is defined as a carbon-rich material produced during pyrolysis process that is a thermo chemical decomposition of biomass with a temperature about ≤ 700°C in the absence or limited supply of oxygen .Biochar is usually produced as a cost-effective and environmentally friendly sorbent. The ability of biochar in stabilizing organic and mineral compounds is due to its physicochemical properties such as porous structure, expanded specific surface area, high organic carbon content, active functional groups, and also high cation exchange capacity (CEC). Pyrolysis is usually the method of choice to produce biochar, though biomass gasification produces a smaller char yield compared with pyrolysis. The production of biochar using pyrolysis process is influenced by the source of biomass, the properties (particle size and moisture content) and composition (contents of cellulose, lignin, and ash) of biomass, and also the process parameters (temperature, heating rate, pressure, and residence time). In order to produce a high char yield, a low-temperature and low-heating-rate process is more preferred. The characteristics of biochar are mainly determined by the type of biomass used and the parameters of pyrolysis process. By knowing the effect of each parameter on the biochar properties, the production of biochar with a desired performance can be tailored. The type of biomass chosen to undergo pyrolysis process plays an important role in determining the status of biochar. Biomass chemical compositions and its size, shape, and structure can significantly affect the sorption capacity of biochar. Agricultural wastes that are locally available can be considered as a low-cost and renewable pyrolysis feedstock. By converting this biomass into the biochar, the residues are able to be utilized in a sustainable way.

Biochar is a super charcoal made by heating any biomass for example, corncob, husk or stalk, potato or soy hay, rice or wheat straw – without oxygen. All of the cellulose, lignin and other, non-carbon materials gasify and are burned away. What remains is pure carbon 40% of the carbon originally contained in the biomass. Biochar production is a simple process that anyone can do. Warm Heart has designed cheap and easy methods for converting biomass waste into biochar. The simplest and cheapest method is to dig a hole in the ground. You can also build a cheap biochar oven using an old oil drum, or build a trough. Whichever method is used, the process is the same, and biomass is burned with a lack of oxygen, turning the biomass in biochar, smoke free.

1.1 BENEFITS OF MAKING BIOCHAR

They also produce large quantities of smog precursors such as ammonia that react with sunlight to form smog. Finally, that smoke that blocks the sun is PM2.5 particulate matter so small that it passes through the walls of the lungs into the bloodstream to wreak havoc throughout the body. Crop waste eliminated through the process of making biochar produces no smoke. Every year farmers in the developing world burn more than 10 billion tones of crop wastes in their fields. This releases 16.6 billion tones of CO_2, 11.2 billion tones of CO_2, 1.1 billion tones of smog precursors and 65.7 million tons of PM2.5 into the atmosphere. The combined annual CO_2 and CO_2 emissions from crop waste burning are equivalent to the annual emissions of 714 coal fired power plants. The alternative – converting the waste into biochar instead of burning it removes three tons CO_2 from the atmosphere for every ton produced; when added to fields as a soil amendment, that carbon is permanently sequestered. The long term benefits of making biochar are a huge reduction of greenhouse gases that contribute to global warming.

1.2 THE MANY USES OF BIOCHAR

Biochar is recognized as offering a number of soil health benefits. The extremely porous nature of biochar is found to be effective at retaining both water and water-soluble nutrients. Soil biologist Elaine Ingham indicates the extreme suitability of biochar as a habitat for many beneficial soil micro organisms. She points out that when pre-charged with these beneficial organisms biochar becomes an extremely effective soil amendment promoting good soil and, in turn, plant health. Biochar has also been shown to reduce leaching of E-coli through sandy soils depending on application rate, feedstock, pyrolysis temperature, soil moisture content, soil texture, and surface properties of the bacteria.

For plants that require high potash and elevated pH, biochar can be used as a soil amendment to improve yield. Biochar can improve water quality, reduce soil emissions of greenhouse gases, reduce nutrient leaching, reduce soil acidity, and reduce irrigation and fertilizer requirements. Biochar was also found under certain circumstances to induce plant systemic responses to foliar fungal diseases and to improve plant responses to diseases caused by soil borne pathogens. The various impacts of biochar can be dependent on the properties of the biochar, as well as the amount applied, and there is still a lack of knowledge about the important mechanisms and properties. Biochar impact may depend on regional conditions including soil type, soil condition (depleted or healthy), temperature, and humidity. Modest additions of biochar to soil reduce nitrous oxide N_2O emissions by up to 80% and eliminate methane emissions, which are both more potent greenhouse gases than CO2.

1.3 CATION EXCHANGE

Biochar can exchange its own cations (Example: H^+, K^+, Na^+, $Ca2^+$) metals and therefore form a chemical bond to retain the heavy metals on its surface. The exchangeable cations of biochar come from two fractions: H^+ from its acidic functional groups such as carboxyl and phenol groups and alkaline minerals (example: K_2CO_3/K_2O) in biochar, which is formed during production. The heavy metals adsorbed on biochar through cation exchange are regarded as a readily bio available fraction, which can be easily up taken by plants. They may also desorb from biochar and pose environmental risks when pH significantly changes. This adsorption mechanism has the potential to be applied in water treatment due to reusability, as with physical adsorption. Adsorption of heavy metals on biochar through cation exchange may not be suitable for immobilizing heavy metals in contaminated soils in the long term.

1.4 BIOCHAR FROM WOOD

Charcoal is a lightweight black carbon residue produced by strongly heating wood (or other animal and plant materials) in minimal oxygen to remove all water and volatile constituents. In the traditional version of this pyrolysis process, called charcoal burning, the heat is supplied by burning part of the starting material itself, with a limited supply of oxygen. The material can also be heated in a closed retort. This process happens naturally when combustion is incomplete, and is sometimes used in radiocarbon dating. It also happens inadvertently while burning wood, as in a fireplace or wood stove. The visible flame in these is due to combustion of the volatile gases exuded as the wood turns into charcoal. The soot and smoke commonly given off by wood fires result from incomplete combustion of those volatile. Charcoal burns at a higher temperature than wood, with hardly a visible flame, and releases almost nothing except carbon dioxide (typically 2.5 to 3 kilograms for every kilogram of charcoal burnt, depending on the carbon content) and heat.

1.5 PRODUCTION METHODS

Charcoal has been made by various methods. The traditional method in Britain used a clamp. This is essentially a pile of wooden logs (e.g. seasoned oak) leaning in a circle against a chimney. The chimney consists of 4 wooden stakes held up by some rope. The logs are completely covered with soil and straw allowing no air to enter. It must be lit by introducing some burning fuel into the chimney; the logs burn very slowly and transform into charcoal in a period of 5 days' burning. If the soil covering gets torn or cracked by the fire, additional soil is placed on the cracks. Once the burn is complete, the chimney is plugged to prevent air from entering. The true art of this production method is in managing the sufficient generation of heat, by combusting part of the wood material, and its transfer to wood parts in the process of being carbonized. A strong disadvantage of this production method is the huge amount of emissions that are harmful to human health and the environment (emissions of unburned methane). As a result of the partial combustion of wood material, the efficiency of the traditional method is low. Modern methods employ retorting technology, in which process heat is recovered from, and solely provided by, the combustion of gas released during carbonization. Yields of retorting are considerably higher than those of kilning, and may reach 35%-40%.

The properties of the charcoal produced depend on the material charred. The charring temperature is also important. Charcoal contains varying amounts of hydrogen and oxygen as well as ash and other impurities that, together with the structure, determine the properties. The approximate composition of charcoal for gun powders is sometimes empirically described as C_7H_4O.

Figure-1-Charcoal

1.6 USES

Charcoal has been used since earliest times for a large range of purposes including art and medicine, but by far its most important use has been as a metallurgical fuel. Charcoal is the traditional fuel of a blacksmith's forge and other applications where an intense heat is required. Charcoal was also used historically as a source of black pigment by grinding it up. In this form charcoal was important to early chemists and was a constituent of formulas for mixtures such as black powder. Due to its high surface area charcoal can be used as a filter, and as a catalyst or as an adsorbent.

1.7 WOOD CHARCOAL

The process of making charcoal is ancient, with archaeological evidence of charcoal production going back about 30,000 years. Wood charcoal has been used since earliest times for a large range of purposes including cooking, medicine, art, metallurgy, industry etc. The raw material for wood charcoal could be wood chips, branches, saw dust, agricultural wastes etc. Wood charcoal is mostly pure carbon, called char (the first syllable of charcoal), made by heating wood above 400° C in a low oxygen environment. The process, called pyrolysis, can take days and burns off volatile compounds such as water, methane, hydrogen, and tar. There are some methods that burn the volatile gasses to prevent them from escaping as pollution and producing surplus heat, other methods collect them for later use as bio fuels.

PROCEDURE IN MAKING WOOD CHARCOAL

The manufacturing of charcoal is a multi-step process that requires control of the various factors that could affect the process: the wood used, heating temperature, air availability, and time of processing. In commercial processing, the burning takes place in large concrete or steel kiln, which is almost three meters in diameter and a little over a meter in height. Once the dry wood is split into smaller pieces and stacked loosely almost to the top of the charcoal chamber, the kiln is closed and covered with an insulation layer. A small fire is started in the combustion chamber and soon the chimney begins to produce very wet, low temperature steam. The purpose of maintaining this fire is twofold, to create heat for driving out water and impurities, and to use up the oxygen coming into the kiln. Depending on the size of the wood inside, after a while the smoke changes to bluish and almost clear, what means that the water is gone and the wood should be mostly converted to charcoal. The process leaves black lumps and powder, about 25% of the original weight. It takes about 14-16 hours and produces ready-to-use lump charcoal. It should be noted that if the kiln is opened while the charcoal is still hot, it will burst into flame and all of the charcoal will turn to ash.

1.8 DYE

A **dye** is a colored substance that chemically bonds to the substrate to which it is being applied. This distinguishes dyes from pigments which do not chemically bind to the material they color. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments are colored, because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble. Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment. The color of a dye is dependent upon the ability of the substance to absorb light within the visible region of the electromagnetic spectrum (380-750 nm). An earlier theory known as Witt theory stated that a colored dye had two components, chromospheres which impart color by absorbing light in the visible region which serves to deepen the color. This theory has been superseded by modern electronic structure theory which states that the color in dyes is due to excitation of valence π-electrons by visible light.

1.9 METHYLENE BLUE

Methylene blue, also known as methylthioninium chloride, is a salt used as a medication and dye. As a medication, it is mainly used to treat methemoglobinemia[4,2]. Specifically, it is used to treat methemoglobin levels that are greater than 30% or in which there are symptoms despite oxygen therapy. It has previously been used for cyanide poisoning and urinary tract infections, but this use is no longer recommended. It is typically given by injection into a vein. Common side effects include headache, vomiting, confusion, shortness of breath, and high blood pressure. Other side effects include serotonin syndrome, red blood cell breakdown, and allergic reactions. Use often turns the urine, sweat, and stool blue to green in color. While use during pregnancy may harm the baby, not using it in methemoglobinemia is likely more dangerous. Methylene blue is a thiazine dye. It works by converting the ferric iron in hemoglobin to ferrous iron. Methylene blue was first prepared in 1876, by Heinrich Caro. It is on the World Health Organization's List of Essential Medicines.

Formula: $C_{16}H_{18}ClN_3S$

Molar mass: 319.85 g/mol

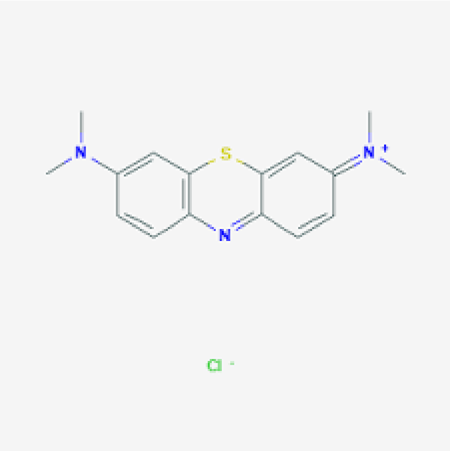

Figure-2- Structure of methylene blue

USES

Methemoglobinemia

Methylene blue is employed as a medication for the treatment of methemoglobinemia, which can arise from ingestion of certain pharmaceuticals, toxins, or broad beans. Normally, through the NADH or NADPH dependent methemoglobin reductive enzymes, methemoglobin is reduced back to hemoglobin. When large amounts of methemoglobin arise secondary to toxins, methemoglobin reductive is overwhelmed. Methylene blue, when injected intravenously as an antidote, is itself first reduced to leucomethylene blue, which then reduces the heme group from methemoglobin to hemoglobin. Methylene blue can reduce the half life of methemoglobin from hours to minutes. At high doses, however, methylene blue actually induces methemoglobinemia, reversing this pathway.

Methylphen

Hyoscyamine/hexamethylenetetramine/phenyl salicylate/methylene blue/benzoic acid are a drug combination. It is not safe or effective for any medical purpose. This medication is used to relieve the discomfort, pain and cramps caused by an infection or a medical procedure .It also help to prevent the growth of bacteria in the urine.

Cyanide poisoning

Since its reduction potential is similar to that of oxygen and can be reduced by components of the electron transport chain, large doses of methylene blue are sometimes used as an antidote to potassium cyanide poisoning, a method first successfully tested in 1933 by Dr. Matilda Moldenhauer Brooks in San Francisco, although first demonstrated by Bo Sahlin of Lund University, in 1926.

1.10 ADSORPTION

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid is dissolved by or permeates a liquid or solid (the absorbent). Adsorption is a surface phenomenon, while absorption involves the whole volume of the material, although adsorption does often precede absorption. The term sorption encompasses both processes, while desorption is the reverse of it.Like surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are fulfilled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increasing storage capacity of carbide-derived carbons and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorbents are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Pharmaceutical industry applications, which use adsorption as a means to prolong neurological exposure to specific drugs or parts thereof are lesser known. Adsorption is applied in the preparation of gas masks using activated charcoal to avoid poisonous gases likes CO. froth floatation method used for concentration of sulphide ores is based on adsorption.

PHYSISORPTION

Physical adsorption results from interactions between subcritical fluid species and nearly any solid surface. The measurements are made by a variety of well-developed techniques and interpreted by using ever more sophisticated models. Physical adsorption experiments probe thermodynamic phase equilibrium between bulk fluid phases and adsorbed phases, which progress from single, isolated molecules to a single layer of molecules on the surface (a monolayer) to multi layers to condensation (or sublimation). Analyses of equilibrium data characterizing the adsorption of gases are commonly employed to estimate the morphology of the sample, including the total surface area, the distribution of the dimensions of any pores (ranging in diameter from about 0.1 to 50 nm), and the total pore volume/void fraction. These analyses are employed to guide understanding of the influence of morphology on sorption, separations, and catalysis. Considerable progress has been made in the last several decades in investigations of physical adsorption on high-surface-area solids, both experimentally and theoretically (*1–8*), such that we now understand the phenomena associated with sorption far better than we ever have. Furthermore, materials synthesis has developed to such an extent that we can now produce materials possessing very high surface areas (> 1000 m^2 g^{-1} of solid) or with uniform pores in the range 1–20 nm, or even solids with multi scale porosity comprising a network of pores of one size embedded within a network of pores of another dimension and/or connectivity. Physical adsorption is then employed to characterize, design, and optimize the morphology of the material for specific applications.

CHEMISORPTION

Chemisorptions are a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbent surface. Examples include macroscopic phenomena that can be very obvious, like corrosion, and subtler effects associated with heterogeneous catalysis, where the catalyst and reactants are in different phases. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds. In contrast with chemisorptions is physisorptions, which leaves the chemical species of the adsorbate and surface intact. It is conventionally accepted that the energetic threshold separating the binding energy of "physisorption" from that of "chemisorption" is about 0.5 eV per adsorbed species. Due to specificity, the nature of chemisorption can greatly differ, depending on the chemical identity and the surface structural properties. The bond between the adsorbate and adsorbent in chemisorptions is either ionic or covalent.

1.11 FACTORS AFFECTING ADSORPTION

Adsorption occurs on the surface of almost all solids. However, the extent of adsorption of a gas on the surface of a solid depends upon the following factors:

(i) Nature and surface area of the adsorbent

(ii)Nature of the adsorbed gas

(iii)Temperature

(iv)Pressure of the gas

Let us now discuss these factors briefly.

(i)Nature and Surface Area of the Adsorbent

Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents. Greater the surface area more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance. A cube of each side equal to 1cm has six faces. Each of them is a square with surface area of 1cm^2. Thus, the total surface area of this cube is 6 cm^2. If its each side is divided into two equal halves, ½ cm long, and the cube is divided into two equal halves, ½ cm long, and the cube is cut along the lines indicated in the cube would be divided into 8 smaller cubes with each side 0.5 cm long.

(ii) The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquefiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO_2 or NH_3 adsorbed by charcoal is much more than that of H_2 or O_2 gases. It is because the intermolecular forces are stronger in more easily liquefiable gases; therefore, they get adsorbed more strongly.

(iii) Temperature

The extent of adsorption decreases with rise in temperature. For example, less than one atmosphere pressure, one gram of charcoal adsorbs about 10 cm^3 of N_2 gas at 272 K, 20 cm^3 at 248 K and 45 cm^3 at 195 K. Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed is called enthalpy of adsorption. The adsorption process is similar to the condensation process. The reverse process is called desorption and is endothermic in nature. It is similar to the evaporation process. When a gas is kept in contact with a solid adsorbent in a closed container, a dynamic equilibrium is established in due course of time.

Gas adsorbate + solid adsorbent ↔ gas adsorbed on the solid + heat

Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favored at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature.

(iv) Pressure of the gas

At a constant temperature the extent of adsorption increases with increase in the pressure of the gas. We shall study the relation between the two in detail a little later.

1.12 Mechanism of Adsorption

- Adsorption occurs because the particle on the surface and the particle in the bulk of the adsorbent are not in the same environment. That is, the net force acting on them is not the same.
- The particle on the surface has unbalanced forces acting on it which are also called residual attractive forces

- Due to these forces, the surface particles of the adsorbent attract the adsorbate particles

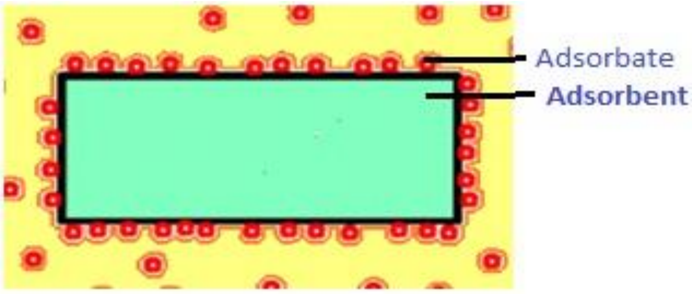

Figure-3- Mechanism of Adsorption

- During adsorption, there is always a decrease in the residual attractive forces of the surface. That is, the energy of the surface decreases and this appears as heat. This is called the heat of adsorption
- The amount of heat evolved when one mole of adsorbate is adsorbed on the adsorbent surface is called enthalpy of adsorption
- Adsorption is always exothermic and the enthalpy change, ΔH is always negative
- When the adsorbate molecules are adsorbed on the surface of the adsorbent, their freedom of movement becomes restricted and hence ΔS the entropy decreases
- We know that Gibbs free energy, $\mathbf{\Delta G = \Delta H - T\Delta S}$. For adsorption to be spontaneous, ΔG must be negative. This can happen if ΔH has a significantly high negative value as $-T\Delta S$ is positive.
- As the adsorption continues, ΔH becomes less and less negative till it becomes equal to $T\Delta S$ and ΔG becomes zero. At this point, equilibrium is attained.

1.13 Applications of Adsorption

1. for production of high vacuum.

2. Gas masks containing activated charcoal is used for breathing in coalmines. They adsorb poisonous gases.

3. Silica and aluminum gels are used as adsorbents for controlling humidity.

4. Removal of coloring matter from solutions.

5. It is used in heterogeneous catalysis.

6. in separation of inert gas.

7. as adsorption indicators.

8. in chromatographic analysis.

9. Qualitative analysis, e.g., Lake Test for Al^3+.

2. OBJECTIVE OF THE STUDY

- To study the dependence of variable parameters on the adsorption of Methylene blue, on biochar.
- To confirm the activity of adsorbant.

3. LITERATURE REVIEW

Adsorption is a process that occur when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or aromatic film (the adsorbate). Adsorption is operative in most natural physical, biological and chemical system, and is used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for waste water treatment because of its simplicity and cost effectiveness. Synthetic dyestuffs have been an important class of pollutants, which are extensively utilized in many fields such as textiles, paper, plastic, leather, cosmetics, and food processing, wool and printing. The residual dyes in the waste waters have posed a serious threat to the environment due to their high visibility, recalcitrance, and adverse efforts on both the aquatic biota and human health.

Dyes are an important group of chemicals that are widely used in industries such as textiles, paper, rubber, plastics, cosmetics, etc., to color their products. They are invariably left in the industrial wastes and consequently discharged mostly in surface water resources and are visually detected even at low concentrations. As per various surveys around the globe, 8000 tons of dyes annually are used by food, textile, and cosmetic industries out of which 10 to 15% are discarded to environment. Commercially there are around 10,000 verities of dyes available and production rate are 7 x 10^5 tons per year. Basically dyes are use due to its characteristic like long term durability, solubility, rapid binding action and effective even in less concentration. These are also main characteristic which makes it pollutant, when it interacts with environment. They also affect the aquatic life and food web. Aesthetic pollution, perturbation in aquatic life is basically due to colored water. The contamination of water bodies by synthetic dyes has created a serious environmental problem worldwide. A considerable amount of dyes is released into the aquatic ecosystems through the wastewater streams of industries such as textile, carpet, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic, pesticide etc. Dye residues affect photosynthetic activity by preventing light penetration in aquatic life and produce toxic chemicals of aromatics, metals, amines and chlorides, having a detrimental effect on flora, fauna and human beings. Some physicochemical methods, such as advanced oxidation and biological process, coagulation, membrane filtration, electrochemical, and adsorption techniques have been proposed to satisfy the above requirements. For both environmental and health reasons, it is essential to remove these dyes completely before they reach the effluent stream to the discharge water supply. Among the different dye removal strategies, adsorption has attracted considerable attention owing to its low cost and high efficiency. Recently, modified porous materials were introduced for the adsorption study.

4. MAERIALS AND METHOD

4.1CHEMICALS REQUIRED

Methylene blue

Figure-4-Methylene blue

CHARCOAL FROM VENGA TREE

Charcoal is a lightweight black carbon residue produced by strongly heating wood (or other animal and plant materials) in minimal oxygen to remove all water and volatile constituents. Here we have used the charcoal obtained by burning the wood of venga tree. In the traditional version of this pyrolysis process, called charcoal burning, the heat is supplied by burning part of the starting material itself, with a limited supply of oxygen. The material can also be heated in a closed retort. This process happens naturally when combustion is incomplete, and is sometimes used in radiocarbon dating. It also happens inadvertently while burning wood, as in a fireplace or wood stove. The visible flame in these is due to combustion of the volatile gases exuded as the wood turns into charcoal. The soot and smoke commonly given off by wood fires result from incomplete combustion of those volatile. Charcoal burns at a higher temperature than wood, with hardly a visible flame, and releases almost nothing except carbon dioxide (typically 2.5 to 3 kilograms for every kilogram of charcoal burnt, depending on the carbon content) and heat.

Figure-5-Venga Tree

Figure-6-Charcoal

4.2 PREPARATION OF THE ADSORBENT

Dye adsorption behaviour of Methylene blue

The adsorption experiment was performed using a 0.02M solution of the dye material. The effects of important parameters, such as amount of adsorbent, volume of dye solution, time were also studied on the adsorption using methylene blue dye solution.

Effect of initial adsorbent amount

The experiments were carried out using 20ml of 0.02M concentrated dye solutions and different amounts of adsorbent (10,20,30mg), and the amount adsorbed was calculated by analyzing the initial and final concentrations of dye solution using a colorimetric analysis. The dyes adsorptions were linearly increased on raising the amount of adsorbent. The increase in the number of active site causes the rise in adsorption amount.

Effect of time

The experiments were carried out using 30mg of wood charcoal and 20 ml of methylene blue solutions in different 5 test tubes. Then we shake these 5 mixtures (6, 12,24hrs) and the amount adsorbed was calculated by analyzing the initial and final concentrations of the dye solutions using a colorimetric analysis. The dyes adsorptions were linearly increased by raising the amount of adsorbent. The increasing number of active sites causes the rise in adsorption amount.

Effect of concentration of dye

The experiments were carried out using 30g of wood charcoal and different concentrations of dye solutions (0.02, 0.04, 0.06, 0.08M) and the amount adsorbed was calculated by analyzing the initial and final concentrations of dye solution using a colorimetric analysis. The dyes adsorptions were linearly increased by raising the amount of adsorbent. The increase in the number of active site causes the rise in adsorption amount.

5. INSTRUMENTATION

The instruments used for making the biochar and batch adsorption include,

5.1 HOT AIR OVEN

Figure-7-Hot Air Oven

Hot air ovens are electrical devices which use dry heat to sterilize. They were originally developed by Pasteur. Generally, they use a thermostat to control the temperature. Their double walled insulation keeps the heat in and conserves energy, the inner layer being a poor conductor and outer layer being metallic. There is also an air filled space in between to aid insulation. An air circulating fan helps in uniform distribution of the heat. These are fitted with the adjustable wire mesh plated trays or aluminum trays and may have an on/off rocker switch, as well as indicators and controls for temperature and holding time. The capacities of these ovens vary. Power supply needs vary from country to country, depending on the voltage and frequency (hertz) used. Temperature sensitive tapes or biological indicators using bacterial spores can be used as controls, to test for the efficacy of the device during use.

5.2 HEAVY ROTARY SHAKER

Figure-8- Heavy rotary shaker

These Shakers are ideal for mixing and development of cultures, chemicals, solvents, and assays etc. in Microbiological, Cell Culture & Life Science laboratories. The Unit has base assembly fabricated from heavy mild steel sections. Brushless Induction drive motor with frequency drive makes the unit suitable for continuous non-stop operation. Step less electronic frequency control ensures gentle start and maintains preset speed. Compact counter balanced drive mechanism ensures high stability and reliability even in continuous operation & uneven load distribution.

5.3 WEIGHING MACHINE

Figure-9-Weighing Machine

A scale or balance is a device to measure weight or mass. These are also known as mass scales, weight scales, mass balances, and weight balances. The traditional scale consists of two plates or bowls suspended at equal distances from a fulcrum. One plate holds an object of unknown mass (or weight), while known masses are added to the other plate until static equilibrium is achieved and the plates level off, which happens when the masses on the two plates are equal. The perfect scale rests at neutral. A spring scale will make use of a spring of known stiffness to determine mass (or weight). Suspending a certain mass will extend the spring by a certain amount depending on the spring's stiffness (or spring constant). The heavier the object, the more the spring stretches, as described in Hooke's law. Other types of scales making use of different physical principles also exist.

6. RESULT AND DISCUSSION

About 0.014g of Methylene blue is weighed and transferred into 250 ML beaker, and it is diluted to 250 ML using distilled water. About 20 ML of made up solution is transferred into 3 different conical flask and then 0.30gm of charcoal is added to each of the conical flask. It is then placed on heavy rotary shaker for 5hrs.It is then taken out and filtered using Whatmann filter paper and then the absorbance is measured using calorimeter. This method is repeated for 6, 12, 24 hrs respectively.

1) Methylene blue is added to a 250 ml beaker and stirred

Figure-10- Methylene blue solution

2)20 ml of the prepared solution is pipette out into each of the 3 conical flasks.30 mg of charcoal is added.

Figure-11- Conical flasks containing methylene blue and charcoal

3) Conical flasks are placed in a heavy rotary shaken and shaken well for a fixed duration.

Figure-12-Conical flasks in heavy rotary shaker

4) Conical flasks were taken out after 4,5 and 6 hours one by one and filtered using a whatmann no:41 filter paper.

Figure-13-Filtration of the sample

5) The filtered solution is placed in a colorimeter and the absorbance was measured.

Figure-14-Coulorimeter

TIME (Minutes)	TRANSMITTANCE (%)

	Before adsorption	**After adsorption**
10	**36**	**58**
20	**36**	**70**
30	**36**	**82**
40	**36**	**92**
50	**36**	**92**
60	**36**	**93**

7. CONCLUSION

The project dealt with study of determination of adsorption of methylene blue on biochar**.** Absorbance was analyzed by using colorimetry**.** Initially calibrated the concentration of dye solution and observed the minimum amount as 0.02M for getting reliable result. The different adsorption experiment with this concentration of methylene blue and varying adsorbent amount resulted 30mg is a minimum amount for getting a consistent result. Kinetics of this adsorption abridged the fast adsorption capacity of the activated charcoal. All the adsorption parameters discussed above has been supported the efficiency of activated charcoal towards methylene blue adsorption from aqueous solution.

8. REFERENCES

1. Atkins, P. W.; De Paula, Julio; Keeler, James (2018). Atkins' Physical chemistry , Oxford, United Kingdom. ISBN 978-0-19-876986-6. OCLC 1020028162.
2. Glossary of atmospheric chemistry terms (Recommendations 1990). Pure and Applied Chemistry. **62**. 1990. p. 2167.
3. Ferrari, L.; Kaufmann, J.; Winnefeld, F.; Plank, J. (2010). "Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements". J. Colloid Interface Sci.**347** (1): 15–24. Bibcode:2010JCIS..347...15F.
4. Czelej, K.; Cwieka, K.; Kurzydlowski, K.J. (May 2016). "CO_2 stability on the Ni low-index surfaces: Van der Waals corrected DFT analysis". Catalysis Communications. **80** (5): 33–38.

5. Czelej, K.; Cwieka, K.; Colmenares, J.C.; Kurzydlowski, K.J. (2016). "Insight on the Interaction of Methanol-Selective Oxidation Intermediates with Au- or/and Pd-Containing Monometallic and Bimetallic Core@Shell Catalysts". Langmuir. **32** (30): 7493–7502.
6. Kayser, Heinrich (1881). "Über die Verdichtung von Gasen an Oberflächen in ihrer Abhängigkeit von Druck und Temperatur". Annalen der Physik und Chemie. **248** (4): 526–537. Bibcode:1881AnP...248..526K. In this study of the adsorption of gases by charcoal, the first use of the word "adsorption" appears on page 527:
7. Foo, K. Y.; Hameed, B. H. (2010). "Insights into the modeling of adsorption isotherm systems". Chemical Engineering Journal. **156** (1): 2–10
8. Czepirski, L.; Balys, M. R.; Komorowska-Czepirska, E. (2000). "Some generalization of Langmuir adsorption isotherm". Internet Journal of Chemistry. **3** (14). ISSN 1099-8292.
9. Burke GM, Wurster DE, Buraphacheep V, Berg MJ, Veng-Pedersen P, Schottelius DD. Model selection for the adsorption of phenobarbital by activated charcoal. Pharm Res. 1991;8(2):228-231.
10. Physical Chemistry of Surfaces. Arthur W. Adamson. Interscience (Wiley), New York 6th ed