# ADSORPTION OF ERICHROME BLACK T FROM AQUEOUS SOLUTION USING BIOCHAR

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# CERTIFICATE

This is to certify that the project entitled “**Adsorption of erichrome black t from aqueous solution using biochar**” is a bonafide work carried out by Miss **BESTY JOHNY** (Reg.No: **190011010501**) under guidance of Dr. ANEESH MATHEW, PG Department of Chemistry, Pavanatma College, Murickassery, for partial fulfillment of the requirement for the award of Degree of Master of Science in Chemistry of Mahatma Gandhi University during the year 2019-2021.

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# DECLARATION

I, **BESTY JOHNY,** do hereby declare that this dissertation entitled “**ADSORPTION USING BIOCHAR”** is a bonafide 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.

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**BESTY JOHNY**

# CONTENTS

# CHAPTER I

## INTRODUCTION

Biochar is the char coproduct from the thermochemical processing of biomass utilized as a soil amendment and/or carbon sequestration agent. Processes that produce biochar include pyrolysis (heating without oxygen) and gasification; other coproducts include heat, electricity, bio-oil, and syngas. Interest in biochar soil applications originally stemmed from the long-term fertility of terra preta 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 biochar 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 thermochemical 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 adsorbent. 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. As reported by Angin, temperature is the only pyrolysis parameter that can control the elemental compositions of biochar and their atomic ratios. This 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, biomass is burned with a lack of oxygen, turning the biomass in biochar, smoke free.

## BENEFITS OF MAKING BIOCHAR

They also produce large quantities of smog precursors such as ammonia and the SOx (sulphur oxides) 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 tonnes of crop wastes in their fields. This releases 16.6 billion tonnes of $CO_2$, 11.2 billion tonnes of $CO_2$, 1.1 billion tonnes of smog precursors and 65.7 million tonnes 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 is a huge reduction of greenhouse gases that contribute to global warming.

## THE MANY USES OF BIOCHAR

While it may be invaluable for farmers, it has many other practical uses too. The absorption qualities of biochar make it a perfect solution for odor control, useful for eliminating unwanted odors: in cars, homes, compost piles, pet odors, closets, bathrooms, even in stinky old sneakers. The powerful moisture adsorption quality makes it extremely helpful in cutting down mildew in damp areas. Look for ways to enrich your life with biochar, and help build a market to encourage widespread manufacturing of this simple, yet amazing natural product. It could help save the world!

## CATION EXCHANGE

Biochar can exchange its own cations (e.g., $H^+$, $K^+$, $Na^+$, and $Ca^{2+)}$ with heavy 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 phenolic groups; and alkaline minerals (e.g., $K_2CO_3/K_2O$) in biochar, which is formed during production.

The heavy metals adsorbed on biochar through cation exchange are regarded as a readily bioavailable fraction, which can be easily uptaken by plants (Filgueiras et al., 2002). They may also desorb from biochar and pose environmental risks when pH significantly changes. Therefore, the adsorption of heavy metals on biochar through cation exchange may not be suitable for immobilizing heavy metals in contaminated soils in the long term. However, as the exchangeable heavy metals on biochar are relatively easily desorbed by changing pH or compulsive exchange (Gillman and Sumpter, 1986), this adsorption mechanism has the potential to be applied in water treatment due to reusability, as with physical adsorption.

## 1.1 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 volatiles. Charcoal burns at a higher temperature than wood, with hardly a visible flame, and releases almost nothing except heat.

## 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 carbonised. A strong disadvantage of this production method is the huge amount of emissions that are harmful to human health and the environment (emissions of unburnt 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 carbonisation. 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 gunpowders is sometimes empirically described as $C_7H_4O$.

**Figure1. Charcoal**

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.

## 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 biofuels.

**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

## 1.2 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, a chromophore which imparts color by absorbing light in the visible region (some examples are nitro, azo, quinoid groups) and an auxochrome 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.

## ERIOCHROME BLACK T

Eriochrome Black T is a complexometric indicator that is used in complexometric titrations, e.g. in the water hardness determination process. It is an azo dye. Eriochrome is a trademark of Huntsman Petrochemical, LLC. In its deprotonated form, Eriochrome Black T is blue. It turns red when it forms a complex with calcium, magnesium, or other metal ions.

**FORMULA**: $C_{20}H_{12}N_3O_7SNa$

**MOLAR MASS**: 461.381 g/mol

**APPEARANCE:** dark red/brown powder

**ABBREVIATIONS**: EBT

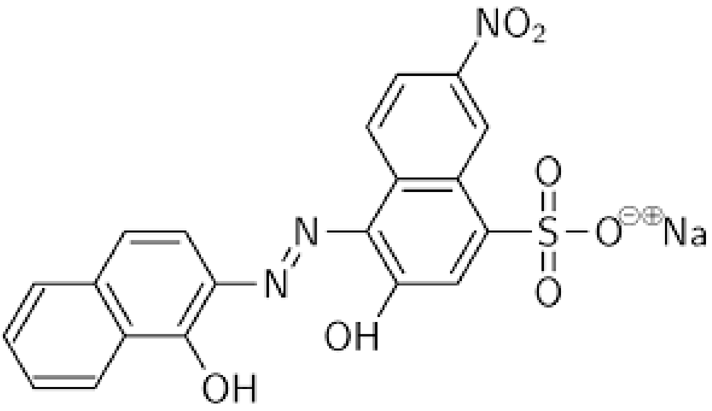

**Figure 2. Structure of Eriochrome Black T**

**APPLICATIONS**

When used as an indicator in an EDTA titration, the characteristic blue end-point is reached when sufficient EDTA is added and the metal ions bound to the indicator are chelated by EDTA, leaving the free indicator molecule. Eriochrome Black T has also been used to detect the presence of rare earth metals.

## 1.3 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 (the absorbate) 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 (characteristic of weak van der Waals forces) 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 adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

## 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 equilibria 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 multilayers to condensation (or sublimation). Analyses of equilibrium data characterizing the adsorption of physisorbing 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 m2 g− 1 of solid) or with uniform pores in the range 1–20 nm, or even solids with multiscale porosity comprising a network of pores of one size embedded within a network of pores of another dimension and/or connectivity. Physical adsorption (physisorption) is then employed to characterize, design, and optimize the morphology of the material for specific applications.

**CHEMISORPTION**

Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbant 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 chemisorption is physisorption, 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 chemisorption is either ionic or covalent.

## 1.4 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. The extent of adsorption also depends upon the surface area of the solid. 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 $1 cm^2$. 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, the cube would be divided into 8 smaller cubes with each side 0.5 cm long Surface area of each small cube would be $(6 \times 0.5 \times 0.5) = 1.5 cm^2$ and the total surface area of all the 8 smaller cubes would be $12 cm^2$ which is double the surface area of the original cube. If it is subdivided into smaller cubes, each of side equal to $1 \times 10^6$ cm the surface area will increase to $6 \times 10^6 cm^2$ or $600 m^2$. The increase in surface area would result in greater adsorption.

### (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 liquifiable 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 liquifiablegases, therefore, they get adsorbed more strongly.

### (III) TEMPERATURE

The extent of adsorption decreases with rise in temperature. For example, under 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.

gasadsorbate + 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 favoured 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 (adsorbate). We shall study the relation between the two in detail a little later.

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## 1.5 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

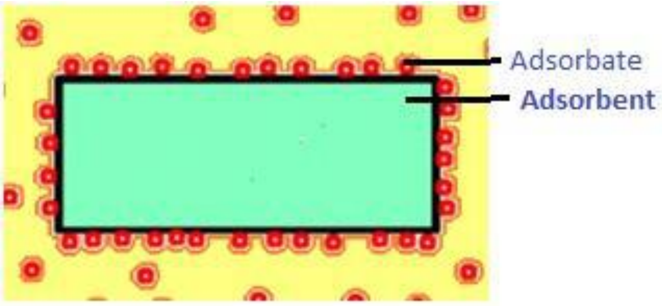

**Figure 3. Mechanism of adsorption**

- 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, $\Delta G = \Delta H - T\Delta S$. 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 TΔS and ΔG becomes zero. At this point, equilibrium is attained.

## 1.6 APPLICATIONS OF ADSORPTION

1) For production of high vacuum
2) Gas masks containing activated charcoal are used for breathing in coalmines. They adsorb poisonous gases.
3) Silica and aluminium gels are used as adsorbents for controlling humidity.
4) Removal of colouring 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 $Al^{3+.}$

# CHAPTER II

# OBJECTIVES

- To study the dependence of variable parameters on the adsorption of eriochrome black t onbiochar
- To confirm the activity of adsorbant.

# CHAPTER III

# LITERATURE REVIEW

Nowadays, contamination of dyes becomes one of focuses to be concerned in liquid waste treatment activities. Source of dyestuff waste originates from various industrial processes such as in the textile, paints, polymers and many other industries. The textile industry plays a role as the largest sources of the presence of dyestuffs in the environment, in which most of the dyes have toxic, mutagenic and carcinogenic properties.

Methylene blue (MB) and Eriochrome black T (EBT) are included in azo dye compounds which represents more than half of the global dye production. These reactive azo dyes contain one or more azo bonds (–N=N–) that act as chromophore in the molecular structure. These dyes have been identified as the most problematic dyes in effluents due to its resistance to be degraded by the exposure of light, water and chemicals as it has a complex chemical structure. Several methods in processing dyestuff waste continue to be developed in order to minimize the adverse effects prior its disposal in the environment. Adsorption is one method that is widely used in wastewater treatment processes because it is affordable, effective and easy to be operated. Some materials that potentially applied as adsorbents are activated carbon, fly ash, resin, metal oxides, clay materials, and composite magnetic particles. Activated carbon is the most commonly adsorbent applied for the adsorption of organic pollutants because of its large availability, low cost and effectiveness. After adsorption process, separation between activated carbon and the treated solution is usually done by filtration or centrifugation which considerably time consuming, therefore, previous research fabricates it with the magnetic properties in order to be more efficient in practical. However, the fabrication brings consequences such as in its physical properties and adsorption ability to certain organic pollutants. In order to access the adsorption ability, it is important to evaluate how much adsorbate can be adsorbed by the adsorbent which can be analyzed using Langmuir and Freundlich isotherm. The Langmuir model is based on the assumption that monolayer adsorption occurs on a homogeneous surface with a finite number of adsorption sites and negligible mutual interactions between the adsorbed molecules.

The Freundlich model assumes that molecules are adsorbed on the heterogeneous surface of adsorbent based on different sites with different adsorption energies. This model takes into account the mutual interaction between adsorbed molecules. The application of the Freundlich equation also suggests that adsorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent. From the previous research, adsorption study of EBT using activated carbon (AC) has been conducted however, its study using magnetite carbon composite (MCC) has not been done. Therefore, in this research, determination of adsorption capacity of EBT as well as MB (as model compound) on the MC was studied in comparison with the adsorption on the AC to observe the adsorption abilities of both adsorbents; the characteristic of the adsorbents, effect of the contact time variation and effect of dye concentration on the adsorption processes. Analysis of adsorption kinetics data from the contact time variations was tested by pseudo first-order and pseudo second-order equations. Furthermore, the equilibrium data was also analyzed based on the Langmuir and Freundlich equations. Synthetic dyes are common pollutants in industrial wastewater. They are stable, highly soluble and when enter in the water bodies present environmental hazards and potential threats to health. Some of the azo dyes have been found to be carcinogenic, sensitizing and reproductive to humans; some of the triarylmethane dyes are also carcinogenic and have long-term adverse effects in the aquatic environment; some of the anthraquinone dyes are chemically stable and refractory to biodegradable. Hence, Acid Orange II (azo dye), Reactive Blue (anthraquinone dye) and Acid Fuchsin (triarylmethane dye) were employed in this study to investigate the various kinds of dye. The treatment methods for dye-bearing wastewater include physical methods, chemical methods and biological methods. Among them, adsorption decolorization is the most effective method. According to the different interaction forces between the adsorbate and the adsorbent, the adsorption can be divided into physical adsorption and chemical adsorption. The physical adsorption is caused by the intermolecular force (Van der Waals force). Chemical adsorption was caused by the formation of chemical bonds or surface coordination compounds by adsorbate molecules and adsorbents by means of ion exchange, electron transfer and electron pair sharing. Sepiolite is a hydrous magnesium silicate with a fibrous cross-section. The merits of sepiolite were low thermal conductivity, high salt resistance, non-polluting, environmentally friendly. It has been widely used in various fields due to the special structural properties and low cost. In China, the sepiolite was presented with two types, hydrothermal type and clay type. The clay type is mainly distributed in Hunan province. The water in sepiolite mainly exists with three forms, adsorbing water, coordinating water and hydroxyl water, in which the adsorption water enters the sepiolite a pore, the coordinating water is mainly bound by Mg2+ and the hydroxyl water exists as OH group. The structure of sepiolite was greatly impacted by the bound water, especially after heated. The three forms of water are gradually lost and the structure of sepiolite will change differently at various temperatures. Serna et al found that the adsorbed water in the sepiolite pores was mainly lost and the specific surface area of the pores was increased at 25~250 ◦C, but the structure of the sepiolite is folded when the temperature was higher than 300 ◦C. The adsorbent generally has the following characteristics, large specific surface area, suitable pore structure and surface structure, high adsorption capacity, no chemically react with the medium, good mechanical strength, etc. The sepiolite, a fibrous hydrous magnesium silicate, has been widely explored as an adsorbent by two reasons: suitable specific surface area; low price, only 20–30 dollars per ton in China. There are three kinds of adsorption active sites from sepiolite: oxygen atom in silicon tetrahedron, water molecules coordinated with magnesium ions, which can form hydrogen bonds with adsorbate and Si-OH combination, formed after the destruction of Si-O-Si. In order to further improve the adsorption performance of sepiolite, modifications such as thermal acid treatment, surfactant organic and inorganic modifications have been employed. Mahir Alkan et al found thermally modification at 200, the highest adsorption amount was obtained. A wider temperature range of the sepiolite modification was reported by Jiquan Wang et al. The surfactant modification also attracts researcher's attention. Bulent Armagan et al used an organic modification method of natural sepiolite with cetyltrimethylammonium bromide to investigate its adsorption property for anionic dyes (active black, reactive red, active yellow). In this study, to improve the adsorption property of sepiolite, a combination of heat and surfactant modification method was applied. To confirm the success of this combined method, unmodified and modified forms of sepiolite were characterized by BET, XRD, XPS, FT-IR and SEM. On the other hand, this study also focused on the adsorption performance and mechanism of mixed dye system with modified sepiolite since the kinetics and thermodynamics of two-component and three-component solution were much more complicated. Hence, the three dyes, Acid Orange II, Reactive Blue and Acid Fuchsin were employed as target adsorbate with single, two-component and three-component solution type.

# CHAPTER IV

# MATERIALS AND METHOD

## MATERIALS REQUIRED

All chemical in this world were of analytical grade without any further treatment.

## CHEMICALS REQUIRED

### Eriochrome Black T

**Figure 4 Eriochrome Black T**

**Vengai collected from Nedumkandam**:

Vengai is also known as "Merbau", "Kwila", and in Karnataka, it is known as "Honne". In Tamil Nadu, people consider it as "God's Tree". Vengai is a dense hardwood with yellow-brownish in color and can contain a "Gold" fleck that runs through the grain, considered to be attractive by some. The grains are straight and can be painted. Vengai contains "Natural Oil" in it that protects the wood from termite or any other insect attacks. People in Southern India use this wood to build the main door for their home. Being a "Holy Wood", it is used for building Temple Doors and Temple Chariots with this wood. The only constraint with this wood is that, it should be protected from moisture and water logging as it leaves a stain when water logged. Vengai is mostly used for door frames, window frames, door shutters & window shutters as there are lesser chances for bending and cracks.

**Figure 5. A mature specimen in Hong Kong**

**Figure 6. Pterocarpus indicus**

# 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 volatiles. 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 7. Vengai Tree**

Figure 8. Charcoal

## INSTRUMENTS REQUIRED

Colorimeter, Weighing machine, Heavy rotary shaker, Hot air oven.

## PREPARATION OF THE ADSORBENT

### Dye adsorption behaviour of eriochrome black t

The adsorption experiment was performed using a 0.02 mM 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 eriochrome black t dye solution.

### Effect of initial adsorbent amount

The experiments were carried out using 20 ml of 0.02 mM concentrated dye solutions and different amounts of adsorbent (10, 20, 30 mg), and the amount adsorbed was calculated by analysing the initial and final concentrations of dye solution using a colorimetric analysis. The dyes adsorptions were linearly increased in progressing 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 30 mg of wood charcoal and 20 ml of eriochrome black t solutions in different 5 test tubes. Then we shake these 5 mixtures (6, 12, 24 hrs) and the amount adsorbed was calculated by analysing the initial and final concentrations of the dye solutions using a colorimetric analysis. The dyes adsorptions were linearly increased in progressing 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 30 g of wood charcoal and different concentrations of dye solutions (0.02, 0.04, 0.06, 0.08 mm) and the amount adsorbed was calculated by analysing the initial and final concentrations of dye solution using a colorimetric analysis. The dyes adsorptions were linearly increased in progressing the amount of adsorbent. The increase in the number of active site causes the rise in adsorption amount.

# CHAPTER V

# EXPERIMENTAL ANALYSIS

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

## 1) HOT AIR OVEN

**Figure 9. 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 aluminium 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.

### 2) HEAVY ROTARY SHAKE

Figure 10. HEAVY ROTARY SHAKE

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.

### 3) WEIGING MACHINE

Figure 11. 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.

# CHAPTER VI

## RESULT AND DISCUSSION

About 0.023g of Eriochrome Black T 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 6,12,24hrs respectively.

**1) Eriochrome Black T is added to a 250 ml beaker and stirred**

**Figure 12. Beaker containing Eriochrome Black T and charcoal**

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

**Figure 13. Three conical flask with charcoal and Eriochrome Black T**

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

**Figure 14. Shaking for 40 min in a mechanical 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. The filtered solution is placed in a coulorimeter and the absorbance was measured.**

**Figure 13. coulorimeter**

**Table 1. Colorimetric transmittance vale of Eriochrome Black T aqueous solution before and after adsorption by coconut shell biochar.**

| **TIME IN MINUTES** | **TRANSMITTANCE (%)** | |
|---|---|---|
| | Before adsorption | After adsorption |
| **0** | 26 | 26 |
| **10** | 26 | 45 |
| **20** | 26 | 57 |
| **30** | 26 | 75 |
| **40** | 26 | 83 |
| **60** | 26 | 85 |
| **80** | 26 | 84 |

# CHAPTER VII

# CONCLUSION

The project dealt with study of determination of adsorption of biochars on Eriochrome Black T. Absorbance were analysed by using colorimetry. Initially caliberated the concentration of dye solution and observed the minimum amount as 0.02 Mm for getting reliable result. The different adsorption experiment with this concentration of Eriochrome Black T and varying adsorbent amount resulted 30mg is aminimum amount for getting a consistant result. Kinetics of this adsorption abridged the fast Eriochrome Black T adsorption capacity of the activated charcoal. All the adsorption parameters discussed above have been supported the efficieny of activated charcoal towards Eriochrome Black T adsorption from aqueous solution.

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