ADSORPTION OF METHYLENE BLUE USING BIOCHAR

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CERTIFICATE

This is to certify that the project entitled "**Adsorption of methylene Blue using biochar**" is a bonafide work carried out by Miss **JISNA JOSEPH** (Reg.NO: **190011010505**) 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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09/12/2020

DECLARATION

I, **JISNA JOSEPH,** do hereby declare that this dissertation entitled "**ADSORPTION OF METHYLENE BLUE 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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JISNA JOSEPH

CONTENT

1. INTRODUCTION

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 adsorption which a fluid (the adsorbate) is dissolved by or permeates liquid or solid (the adsorbent), respectively. Adsorption is a surface phenomenon, while absorption involves the whole volume of the material. The term sorption encompasses both processes.

Increase in the concentration of a substance at the interface of a condensed and a liquid or a gaseous layer owing to the operation of surface forces.

Adsorbed molecules are those that are resistant to washing with the same solvent medium in the case of adsorption from solutions. The washings conditions can thus modify the measurement results, particularly when the interaction energy is low.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the boding requirements of the constituent atoms of the materials are filled by other and in the materials. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atom 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. It may also occur due to electrostatic attraction.

Adsorption is present in many natural, physical, biological and chemical system and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal, other process requirements, synthetic resins, increasing storage capacity or carbide – derived carbons and water purification.

1.1 Biochar

Coconut Shell Activated Charcoal: Coconut shell activated charcoal is made from coconut husk. It is a vapor-activated material, so it does not contain chemical agents that can contaminate or react with the medium where it is used. They are characterized by having a large amount of micro to mesopores (5nm-50 nm) suitable for the removal of small molecules; contains a neutral PH, can be manufactured in any particle size. Coconut shell charcoal is super stiff, hard and resistant. Most manufacturers base the quality of activated coconut charcoal on the adsorption capacity that is directly related to the contact area, and they generally perform adsorption tests with an iodine solution.

By rule: greater iodine number = better quality of activated carbon = greater adsorption = greater duration and useful life of the activated carbon. The key is in the activation process used (by steam or chemical reaction), in addition to the residence time, temperature, pressure, in general, the operating conditions. Therefore, activated coconut shell charcoal can be used in air purification, eliminating odors and a good number of organic gases or solvents. It helps in the purification of natural gas, adsorbing highly toxic hydrogen sulfide.

Coconut Shell Activated Charcoal Coconut is a fruit, obtained from the coconut palm, the most cultivated palm in the world. The leading producers are The Philippines, Indonesia and India. In its growing stage, it can reach a height of approximately 25 meters. Activated carbon is obtained from the coconut shell, in which it goes through physical or chemical activation processes. Coconut shell activated charcoal tends to be microporous and adsorbs more efficiently the low molecular weight organic pollutants that are most present in well water all activated carbon of vegetable or mineral origin contains inorganic salts and elements, some of which are soluble in water.

Coconut shell charcoal is prepared from coconut shells. It is ecological since the husks of the small coconut are used that would otherwise go to waste. To activate it, the coconut shell is heated to more

than 1000 degree Celsius without presence of oxygen. Activated means that it has its 100% adsorption characteristics and maximum porosity.

Activated carbon works by using the adsorption process. Do not confuse absorption with adsorption. Adsorption is a process whereby atoms, ions, gas molecules, liquid or dissolved solids are trapped or retained on the surface while absorption is a phenomenon of volume.

Composition: coconut activated carbon is composed of 70 to 80% carbon, is practically pure, and the ash content varies between 5 to 10%.

1.2 Dyes and Classification

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.

Acid dyes are anionic, soluble in water and are essentially applied from acidic bath. These dyes possess acidic groups, such as SO_3H and COOH and are applied on wool, silk and nylon when ionic bond is established between protonated –NH2 group of fiber and acid group of dye.

Basic dye, also known as basic group dyes, is the salt generated by aromatic bases reacting with acids (organic and inorganic acids), videlicet that is colored organic base salts whose basic group is generally amino, which becomes -NH2 • HCl salt groups when the salt occurs.

Acid dyes stain acidophilic structures (e.g. cytoplasm, basic tissue proteins). Examples of acid dyes are Indian ink, Congo red, Nigrosoine.

Methylene blue, also known as methylthioninium chloride, is a medication and dye. As a medication, it is mainly used to treat methemoglobinemia. 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. The maximum adsorption of light is near 670nm. The specifies of adsorption depends on a number of factors, including protonation, adsorption to other materials and metachromasy the formation of dimers and high-order aggregates depending on concentration and other interactions.

Figure 1: Methylene blue

1.3. Adsorption

The term adsorption was first coined in 1881 by a German physicist named Heinrich Kayser. Adsorption is often described as a surface phenomenon where particles are attached to the top layer of material. It normally involves the molecules, atoms or even ions of a gas, liquid or a solid in a dissolved state that is attached to the surface.

Adsorption is mainly a consequence of surface energy. Generally, the surface particles which can be exposed partially tend to attract other particles to their site. Interestingly, adsorption is present in many physical, natural, biological and chemical systems and finds its use in many industrial applications.

For the adsorption process, two components are required, Adsorbate: Substance that is deposited on the surface of another substance. For example, H2, N2 and O2 gases. Adsorbent: Surface of a substance on which adsorbate adsorbs. For example, Charcoal, Silica gel, Alumina

Types of Adsorption On the basis of interaction forces between adsorbate and adsorbent, adsorption is of two types.

1.Physical adsorption:

This type of adsorption is also known as physisorption. It is due to weak Van der Waals forces between adsorbate and adsorbent. For example, H2 and N2 gases adsorb on coconut charcoal.

Characteristics of physical adsorption:

1.This type of adsorption is caused by physical forces.

2.Physisorption is a weak phenomenon.

3.This adsorption is a multi-layered process.

4.Physical adsorption is not specific and takes place all over the adsorbent.

5.Surface area, temperature, pressure, nature of adsorbate effects physisorption.

6.Energy for activation is low (20 – 40 kg/mol).

2.Chemical adsorption: This type of adsorption is also known as chemisorption. It is due to strong chemical forces of bonding type between adsorbate and adsorbent. We can take the example involving the formation of iron nitride on the surface when iron is heated in N2 gas at 623 K. Adsorption of gas on a solid is a spontaneous exothermic reaction. The amount of heat liberated when a unit mass of a gas is adsorbed on the surface is called heat of adsorption.

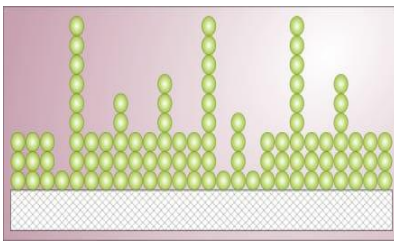

Figure 2 : Adsorption of molecules on the material surface

Characteristics of chemical adsorption:

1. This type of adsorption is caused by chemical forces.

2. It is a very strong process.

3. This type of adsorption is almost a single-layered phenomenon.

4. Chemisorption is highly specific and takes place at reaction centers on the adsorbent.

5. Surface area, temperature, nature of adsorbate effects chemisorption.

6. Energy of activation is very high 40 – 400 kJ/mol.

1.4. Factors affecting adsorption

Factors Affecting 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

1.5. Mechanism of adsorption.

It is an exothermic process which means that energy is liberated during this process. The amount of heat that gets evolved when one mole of the adsorbate is adsorbed on adsorbent is known as enthalpy. The change in enthalpy is denote to be negative. The reason behind this is that when adsorbate molecules are adsorbed on the surface, freedom of movement of molecules become restricted and this results in a decrease in entropy. At constant temperature and pressure, adsorption occurs spontaneously.

1.6. Application

- Air pollution masks
- Separation of noble gases by Dewar's flask process
- Purification of water

- Removal of moisture and humidity
- Adsorption chromatography
- Ion exchange method
- In metallurgy

OBJECTIVE OF STUDY

In this project the main objective of study is to remove the dye from the solution by adsorption technique using eco-friendly coconut shell bio-char and also discuss about,

i) Effect of amount of biochar on adsorption.

ii) Effect of time on adsorption.

2. LITERATURE REVIEW

Adsorption is defined as the deposition of molecular species onto the surface. The molecular species that gets adsorbed on the surface is known as adsorbate and the surface on which adsorption occurs is known as adsorbent. Common examples of adsorbents are clay, silica gel, colloids, metals etc. Adsorption is a surface phenomenon. The process of removal of adsorbent from the surface of adsorbate is known as desorption. The amount of heat evolved when one mole of the adsorbate is adsorbed on adsorbent is called enthalpy of adsorption. Adsorption is an exothermic process and enthalpy change is always negative. When adsorbate molecules are adsorbed on the surface, freedom of movement of molecules become restricted and this results in decrease in entropy. Adsorption is a spontaneous process at constant pressure and temperature, thus Gibb's free energy is also decreased.

Adsorption is defined as the adhesion of a chemical species onto the surface of particles. German physicist Heinrich Kayser coined the term "adsorption" in 1881. Adsorption is a different process from absorption, in which a substance diffuses into a liquid or solid to form a solution. In adsorption, the gas or liquid particles bind to the solid or liquid surface that is termed the adsorbent. The particles form an atomic or molecular adsorbate film. Isotherms are used to describe adsorption because the temperature has a significant effect on the process. The quantity of adsorbate bound to the adsorbent is expressed as a function of the pressure of concentration at a constant temperature**.**

A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Synthetic dyes are man-made. These dyes are made from synthetic resources such as petroleum by-products and earth minerals. Dyes are used primarily to impart color in textile, leather, paints, cosmetic, and food industries. Many natural dyes (animal, mineral, or vegetal extracts)

have been largely replaced by synthetic dyes that were developed at the end of the nineteenth century. Dyes should be safe, with no toxicity, carcinogenicity, or allergenicity. However, the most frequently reported causes of unexpected side effects of garments are textile dyes, and some dyes formerly used for food like Butter Yellow are known to be carcinogenic. It is actually arduous to routinely detect the exact composition of dyes, because the chemicals used are generally not declared in textiles, contrary to the case with cosmetics or foods. Unlike most organic compounds, dyes possess color because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (color-bearing group), 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds.

Coconut shell activated charcoal is made from coconut husk. It is a vapor-activated material, so it does not contain chemical agents that can contaminate or react with the medium where it is used. They are characterized by having a large amount of micro to mesopores (5nm-50 nm) suitable for the removal of small molecules; contains a neutral PH, can be manufactured in any particle size. Coconut shell charcoal is super stiff, hard and resistant. Most manufacturers base the quality of activated coconut charcoal on the adsorption capacity that is directly related to the contact area, and they generally perform adsorption tests with an iodine solution.

3. MATERIALS AND METHODS

Materials required:

Biochar – coconut shell charcoal

Methylene Blue – Nice Chemicals Pvt. ltd

Apparatus required:

Beaker, conical flask, funnel, measuring jar, glass rod, filter paper – Whatman no –41

Instruments required:

Colorimeter - Systronics colorimeter

Heavy rotary shaker

Analytical balance

Methods:

Experiment 1 Effects of amount biochar on adsorption

About 0.015g of methylene Blue is accurately weighed out using an analytical balancer into a 250 ml beaker containing distilled water. The transmittance value of the colored solution were recorded. The 20 ml of the above solution is transferred into different conical flasks. Add 0.15g, 0.25g, 0.35g, 0.45g, 0.5g, of adsorbent added to the conical flasks. Mixed well with a mechanical shaker for a constant time. After shaking the conical flasks are taken out and filtered using whatman no - 41 filter paper. The transmittance values of the filtrate solutions are recorded.

Experiment 2 : Effect of time on adsorption

About 0.015g of Methylene Blue is accurately weighed out using an analytical balancer into a 250 ml beaker containing distilled water. The transmittance value of the colored solution were recorded. The 20 ml of the above solution is transferred into different conical flasks. 0.35g of adsorbent added to each of the conical flask. Mixed well with a mechanical shaker for a constant time interval. After shaking the conical flasks are taken out and filtered using whatman no - 41 filter paper. The transmittance values of the filtrate solutions are recorded.

Figure 3 : Filtration process

4. INSTRUMENTATION

The instruments used for the experiment:

1. Heavy rotary shaker
2. Colorimeter
3. Analytical balance

1. **Heavy rotary shaker**

A shaker is a piece of laboratory equipment used to mix, blend, or agitate substances in a tube or flask by shaking them. It is mainly used in the fields of chemistry and biology a shaker contains an oscillating board that is used to place the flasks, beakers or test tubes. A platform shaker has a table board that oscillates horizontally. The liquid to be stirred are held in beaker, jars, or Erlenmeyer flaks that are placed over the table, or sometimes, in test tubes or vials that are nested into holes in the plate

.

Figure 4 : Heavy rotary shaker

2. Colorimeter

A colorimeter is a device used in colorimetry. In scientific fields the word generally refers to the device that measures the absorbance of particular wave lengths of light by a specific solution. This device is used to determine the concentration of a known solute in a given solution by the application of the Beer-Lambert Law, which states that the concentration of a solute is proportional to the absorbance.

Cuvettes: In a manual colorimeter the cuvettes are inserted and removed by hand. An automated colorimeter is fitted with a flow cell through which solutions flows continuously.

Output: the output from a colorimeter may be displayed by an analogue or digital meter and may be shown as transmittance (a linear scale from 0 to 100%) or as absorbance (a logarithmic scale from 0 to infinity). The useful range of the absorbance scale from 0 to 2 but it is desirable to keep within the range 0 to 1, because above 1, the results become unreliable due to scattering of light. In addition, the output may be sent to a chat recorder, data logger or computer.

Figure 5 : Colorimeter

3. Analytical Balancer

Analytical Balances are highly sensitive lab instruments designed to accurately measure mass. Their readability has a range between 0.1mg – 0.01mg.

Analytical balances have a draft shield or weighing chamber to prevent the very small samples from being affected by air currents.

Figure 6 : Analytical Balancer

5. RESULTS AND DISCUSSION

Experiment 1

Time (min)	**Amount of charcoal(g)**	**Transmittance**
30	0.15	45.5
30	0.25	68.7
30	0.35	78.9
30	0.45	88.1
30	0.5	89

Table 1. Effect of adsorption of charcoal at constant time.

Figure 7 : experimental result of adsorption of charcoal

Experiment 2

Time (min)	Amount of charcoal(g)	Transmittance
0.5	0.3	58.2
1	0.3	78.4
1.5	0.3	85.4
2	0.3	90.2
2.5	0.3	98.4

Table 2 Effect of time on adsorption

Figure 8 : experimental results of adsorption on time

From experimental observations it is that, the color of the dye got decreased with increasing amount of adsorbent and with that of increasing time of shaking. This is because, as the amount of adsorbent increases, rate of adsorption also increases. As a result of more amount of dye get adsorbed, its concentration decreases and it seemed to be more lighted in color than the mother solution taken. Likewise, increase in time of shaking also increases rate of adsorption.

6. CONCLUSION

Activated carbon is also called activated charcoal is a form of carbon processed to have small, low volume pores that increases the surface area available for adsorption or chemical reaction. The adsorption effectiveness of dyes on coconut shell charcoal depends on the type of dye. The effectiveness of adsorption on the tested adsorbent characterizing the cationic dyes is many times higher than that of anionic dyes.

The main purpose of the work was to check the possibility of using coconut shell to remove the dyes from aqueous solutions. From experimental observations it is concluded that, the color of the dye got decreased with increasing amount of adsorbent and with that of increasing time of shaking. This is because, as the amount of adsorbent increases, rate of adsorption also increases. As a result of more amount of dye get adsorbed, its concentration decreases and it seemed to be more lighted in color than the mother solution taken. Likewise, increase in time of shaking also increases rate of adsorption.

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