Preparation of Activated Carbon using Almond Shell for Removal of Thymol Blue Dye from Waste Water Sample

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***Abstract** - The present study was designed to model the adsorption of geosmin from water under laboratory conditions using the freundlich isotherm model. This model was used to compare the efficiency of sugarcane bagasse and almond shell based powdered activated carbon to the efficiency of coal based commercial activated carbon when data were generated from freundlich isotherms pore structure characterization and sorption capacities of activated carbons prepared from shells of almond and treatment with sulfuric acid and increased the total surface area. Activated carbons from almond shell, using physical activation by CO_2 is reported in this work. The used method has produced activated carbons with apparent BET surface areas. By FTIR analysis it was possible to identity, in the surface of the activated carbons, several functional groups, by the analysis of XRD patterns is was possible to calculate the micro crystallites dimensions .The XRD it was also possible to identify the presence of traces of inorganic hetroatoms.*

***Key Words**: Activated Carbon, Almond Shells, Freundlich model, Thymol blue indicator, Muffle Furnace, X- Ray, Spectrophotometer.

1. INTRODUCTION

Adsorption is the adhesion of a chemical substance (adsorbate) onto the surface of a solid (adsorbent). An adsorbent is a solid substance used to collect solute molecules from a liquid or gas, and an adsorbate is any substance that has undergone adsorption on the surface. Adsorbate and adsorbent are the important parts of adsorption phenomenon. Adsorption isotherm is an empirical relationship used to predict how much solute can be adsorbed. Adsorption isotherm is defined as a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations. The three well known isotherms are (a) Freundlich, (b) Langmuir, and (c) BET adsorption isotherm [1]. It maps the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations. The adsorption isotherm is based on data that are specific for each system, and the isotherm must be determined for every application.

The most widely used adsorbent is activated carbon. The adsorption process is being widely used by various researchers for the removal of dyes from waste streams, and activated carbon has been frequently used as an adsorbent. Providing a information of the course taken by the system under study, indicates how efficiently a carbon will adsorb and allows an estimate of the economic feasibility of the carbon's for specified applications.

The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. The most popular adsorption model for a single solute system, the Freundlich model, is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium .The basic Freundlich equation is:

Where, x is amount of adsorbant adsorbed,

m is weight of carbon,

x/m is concentration of adsorbed substance,

Ce is equilibrium constant,

k and n are empirical constants.

Generally, activated carbons have isotherms that obey the Freundlich model in the middle range of pressure, with less agreement at high pressures and low temperatures . Adsorption isotherms expressed as Freundlich isotherm constants are better measures of the adsorptive properties of activated carbons. [2] Adsorption is a most versatile and convenient method for the removal of dyes without the production of any hazardous products. Adsorption has also gained favaour due to its proven efficiency in the removal of pollutants from effluents compared to other methods.[3] Specific surface area of the material is the amount of the surface area per unit volume or unit mass. Interface is the boundary between solid and its surrounding environment: liquid, gas, or another solid .It is one of the important parameters used in evaluating many capabilities of powders and porous materials, such as activity, adsorptive performance, catalytic performance and so on. As important adsorbent and catalyst support, activated carbon has been widely used, and specific surface area is one of the important parameters characterized its physical properties. It has very important significance to measure specific surface area of materical accurately.[4]Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications .Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibilitand simplicity of design,ease of operation and insensitivity to toxic pollutants [5a-d].

2. Characterization techniques

2.1. Spectrophotometer

Lambert Beer's law: The light transmitted through a solution changes as an inverse logarithmic relationship to the sample concentration and path length.

Transmitance, T = (It / Io)

Optical density (O.D) = log (Io / It)

Where, It = Intensity of light passing through the sample

Io = Intensity of light falling on the sample

Absorbance, A = a b c

Where , a = absorbity constant of the specimen

b = light path length

c = concentration

The visible spectrophotometer is single – beam ratio-indicating instrument with a wavelength range of 340-600nm (Nanometer). The basic wavelength range may be converted to 340-950 nm by using accessory phototube and filters.

INSTRUMENTATION :-

Main components:- Visible spectrophotometer essentially consists of following basic components as shown,

1. Radiation Source (Light)
2. Optical System (Monochromatic)
3. Sample Section
4. Detector
5. Filters

Applications :-

Spectrometry is the quantitative measurement of the reflection or transmission properties of material as a function of wavelength.

Important features of spectrophotometers are spectral bandwidth (the range of colors it can transmit through the test sample), the percentage of sample-transmission, the logarithmic range of sample-absorption, and sometimes a percentage of reflectance measurement.

A spectrophotometer is commonly used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, such as polished glass, or gases. Although many biochemicals are colored, as in, they absorb visible light and therefore can be measured by colorimetric procedures, even colorless biochemicals can often be converted to colored compounds suitable for chromogenic color-forming reactions to yield compounds suitable for colorimetric analysis.

2.2. FT-IR SPECTROPHOTOMETER

Principle:-

The different regions of the electromagnetic spectrum will be used in this section to learn about the structure and reactions of organic molecules. For each spectroscopic method, it is helpful to understand how much energy corresponds to each wavelength and how this relates to the physical process after absorption of radiation. Organic molecules can absorb IR radiation between 4000 cm^{-1} and 400 cm^{-1} which corresponds to an absorption of energy between 11 kcal/mole and 1 kcal/mole. This amount of energy initiates transitions between vibrational states of bonds contained within the molecule. IR spectroscopy is a very powerful method for the identification of functional groups. The most important regions of the IR spectrum are >1650 cm^{-1}, whereas the fingerprint region (600 -1500 cm^{-1}) of the spectrum cannot easily be used for identification of unknown compounds. Many references exist which tabulate the IR frequencies for various functional groups and organic compounds.

FT-IR INSTRUMENT:-

Applications:-

Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long term unattended measurement of CO_2 concentrations in greenhouses and growth chambers by infrared gas analyzers.

2.2 What is X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

Fundamental Principles of X-ray Powder Diffraction (XRD)

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. All diffraction methods are based ongeneration of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

Applications:

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

Characterization of crystalline materials identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically determination of unit cell dimensions measurement of sample purity.

With specialized techniques, XRD can be used to:

Determine of modal amounts of minerals (quantitative analysis)

Characterize thin films samples by:

Determining lattice mismatch between film and substrate and to inferring stress and strain determining dislocation density and quality of the film by rocking curve measurements measuring superlattices in multilayered epitaxial structures determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements. Make textural measurements, such as the orientation of grains, in a polycrystalline sample.

3. Experimental

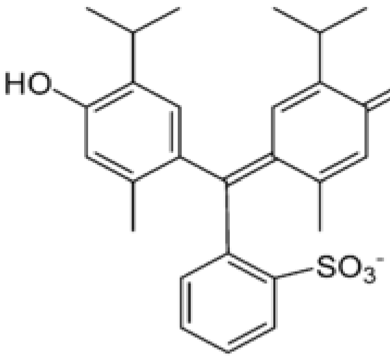
3.1. Introduction

Dyes are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc. to colour their products, which generates wastewater, characteristically high in colour and organic content[6] Organic dyes are used for textile dyeing and other purposes. Wastewaters emanating from these activities are discharged into aquatic environment as industrial wastes. These industrial effluents form part of the major environmental pollutants which in turn affect the survival of living organisms in the ecosystem. Therefore, wastewaters from dyeing activities have to be treated for the protection of life and remediation of environmental pollution[6]

Activated carbon is a known adsorbent of widely applied in the purification of polluted environment, treatment of gaseous effluents discharged from industry, and has additionally been effective for the removal of coloured substances in wastewater [7]. To improve the effluent quality before discharging into the environment, physical and/or chemical treatments comprising adsorption, photocatalytic degradation, electrochemical methods or reverse osmosis are necessary. Adsorption using activated charcoal is simple, cost effective, and efficient in removing organic and inorganic contaminants [8]. Here activated carbon can be prepared from almond shell.

The almond (*Prunus dulcis*, syn. *Prunus amygdalus*) is a species of tree native to Mediterranean climate regions of the Middle East, but widely cultivated elsewhere. The almond is also the name of the edible and widely cultivated seed of this tree. The fruit of the almond is a drupe, consisting of an outer hull and a hard shell with the seed, which is not a true nut inside. Shelling almonds refers to removing the shell to reveal the seed. Almonds are sold shelled or unshelled.

Characterized by FT-IR, XRD and used for the removal of Thymol blue dye from wastewater. **Thymol blue** (thymolsulphonephthalein) is a brownish-green or reddish-brown crystalline powder that is used as a pH indicator. It is insoluble in water but soluble in alcohol and dilute alkali solutions.



Stucture of Thymol blue

3.2. Equipments

The pH measurements were made using a pH meter (Digital pH meter model EQ 610, India).X-ray measurements were performed using a Philips X-ray diffractometer employing nickel-filtered Cu Kα radiation. The infrared spectrum of the adsorbent was recorded in the range of 600-4000 cm^{-1} using a FT/IR-4600 Jasco, Japan. Absorbance measurements were made on a UV-visible spectrophotometer model Lab-India 3600^{+}. The spectrophotometer response time was 0.1 s, and the instrument had a resolution of 0.1 nm. The concentration of dyes was measured with a 1-cm-light path cell, with an absorbance accuracy of ±0.004 at the maximum wavelength of the dye. The absorbance was found to vary linearly with concentration

3.3. Adsorbent preparation

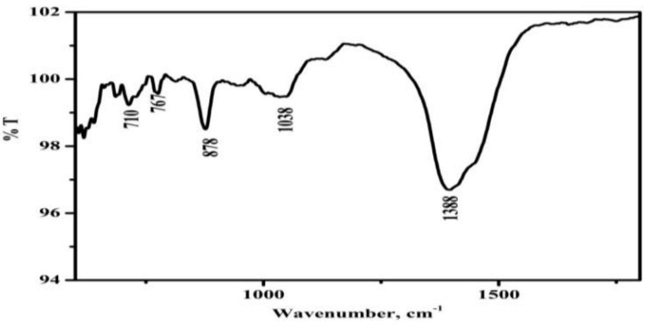
The shells of the almond were collected from --- and dried in sun light for some days. These shells were cut into small pieces and crushed to get a powder. The activated carbon was prepared by treating this powder with concentrated sulfuric acid[9].

The fine 1-2 mm mesh outer shell of almond was activated by soaking it in100 ml conc. Sulfuric acid for 24 h at room temperature. The direct carbonization process was carried out using Muffle furnace at 200-400 ^{0}C for 1-4 hours. The carbon was washed with of double distilled water to remove excess of acid until the pH of that water becomes 6.08 and dried again in a muffle furnace at $200^{0}C$ until it was completely dried. The dried activated carbon was stored in an airtight container for further study.

4. Result and discussion

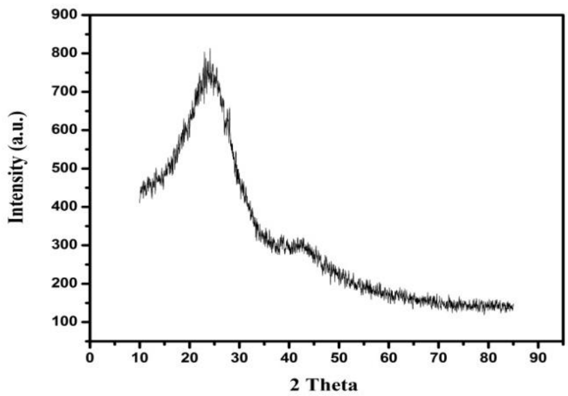
4.1. FT-IR analysis of activated carbon

FT-IR analysis was done using FT-IR (model- 4600 Jasco, Japan.) in the range of 600-4000 cm^{-1} at the spectral resolution of ----cm^{-1}. FT-IR spectra of almond activated carbon is shown in Figure



Peaks occurring at 1388 cm^{-1} are decribed to oxygen functionalities such as highly conjugated C–O stretching in carboxylic groups, and carboxylate moieties [50]. The relatively intense band at 1038 cm^{-1} can be assigned to alcohol groups (R-OH). The peaks below 878 cm^{-1} shows alkanes

4.2. PXRD analysis activated carbon



For this activated carbon prepared under optimized condition, the X-ray diffraction patterns shown in Fig. exhibit broad peaks and absence of a sharp peak that revealed predominantly amorphous structure, However, the occurrence of broad peaks around 25^0 and 42^0 showed signs of formation of a crystalline carbonaceous structure,

5. Applications:

5.1. Effect of contact time

The effect of contact time plays an important role in the adsorption process. The adsorption of dye by A.C. occurs with good results, corresponding to 82.13 % removal at an 60 min. Rate of adsorption goes on increases with increase in contact time of adsorption process.

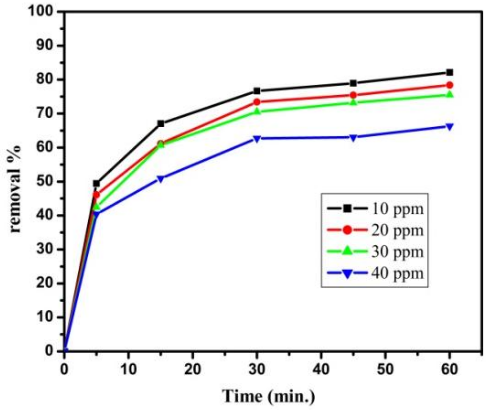
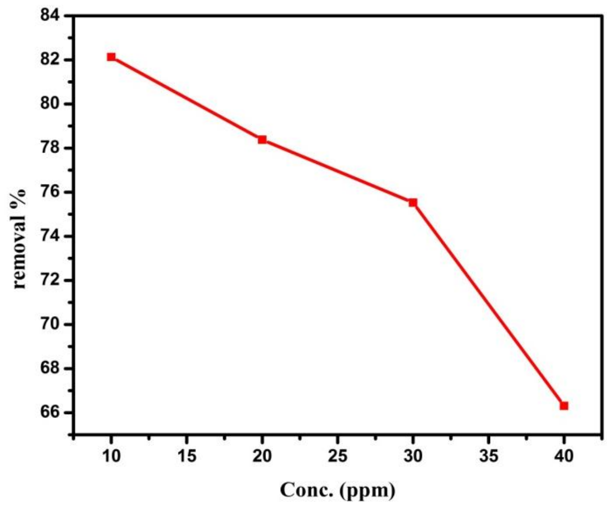


Table: Adsorption study of Thymol blue dye at pH 6.08 with stirring time 60 min.

Sr.No.	Conc.of Thymol blue dye (ppm)	Amount of A.C (g)	Total volume (ml)	% of removal
1	10	0.025	50	82.13
2	20	0.025	50	78.38
3	30	0.025	50	75.53
4	40	0.025	50	66.31

5.2. Effect of Initial Concentration

The dye removal percentage was achieved using 0.025 g of adsorbent with different initial dye concentration in the range (10, 20, 30 and 40 mg/L) at room temperature. The quantity of thymol blue adsorbed on activated carbon decreasesd with increase in initial concentration of dye until saturation is reached.



6. Conclusions:-

From our work we have to cover a wide range of non-conventional low cost adsorbent so that we can get an idea about various types of low cost adsorbent used for removal of thymol blue from the aqueous solution of dye.Inexpensive locally available activated carbon prepared from almond shell used in place of commercial activated carbon from the removal of thymol blue from aqueous solution.This activated carbon is low cost adsorbent perform very well in adsorption of thymol blue from aqueous solution .The studies shows the activated carbon prepared from almond shell can be effectively used in treatment of dye solution.The most suitable PH for adsorption of thymol blue is 6.08.

The overall batch experiment performed in 1hrs.The thymo blue removal percentage was achived using 0.025 g adsorbent. The percentage of removal of thymol blue from aqueous solution goes on decreases on increasing concentration at room temperature. As time passes the percentage of removal increases. The low cost activated carbon prepared from almond shell is successfully used for removal of thymol blue from aqueous solution.

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