

Solvent Based Synthesis of Charcoal, Characterisation and Adsorption Studies on Methylene Blue

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Abstract

Activated carbon (AC) is an industrially important adsorbent as it is an efficient adsorbent for dyes and metal salts. It can be used for water purification. Water remediation is very important as it may be easily contaminated with various industrial wastes. A major contaminant of water body is the dye chemicals from coir industry. A lot of studies have been conducted to separate the dye chemicals from the effluent of different industries. Activated carbon can be effectively used for the effluent treatment and other such water bodies. Adsorption properties of AC encourage researchers to use AC in almost every field of chemistry, basically due to its simplicity of design and operation. In this particular study a sol-gel based synthesis of AC from a carbon source is done using ethylene glycol as solvent. Con. Sulphuric acid is used as dehydrating agent. Four different samples are prepared in different condition and methylene blue adsorption is done and analyzed by spectroscopic method. Characterization and morphology of the sample is done by XRD, and SEM. Chemical activation is also done by treating with calcium chloride solution and verified.

Keywords: *Water pollution, Adsorption, Activated charcoal, Methylene blue*

INTRODUCTION

Water is of major importance to living bodies. Uncontrolled release of waste materials to water bodies results in high amount of water pollution which results in serious problem in aquatic environment.[1][2][3][4][5] Important sources of water pollution are the waste discharge of textile industries, cosmetics, printing, dying, food processing, paper-making and coir industries [6][7][8]. Water is contaminated with dye chemical from these industrial wastes. So removal of dye from industrial waste water became an important challenge. Several studies are being carried out and reported for the effective treatment of waste water. Some important methods for the purpose include photochemical degradation, electrochemical degradation, bioremediation, adsorption, flocculation-coagulation and ion exchange [9][10][11][12][13]. Among all these available methods, adsorptions are one of the best methods because of its feasibility, availability of adsorbents and low cost. Moreover, water remediation through adsorption is very easy to design and is a highly efficient method with less unhazardous byproducts. Adsorption is a process by which the adsorbent attaches the soluble matter from aqueous phase to its surface. Adsorption can be physical or

chemical in nature depending on the nature of adsorbent. Several factors such as morphology, porosity and surface area can influence the extent of adsorption. Surface modification is another way by which adsorption potential can be improved [14]. Activated charcoal is a unique adsorbent for removal of both inorganic and organic pollutants especially dyes from waste water. Several studies are reported in the literature for the synthesis of activated charcoal from natural or synthetic sources. Activated carbon can be synthesized from waste biomaterials through physical and chemical activation methods. The utilization of activated carbon obtained from agricultural wastes is a mostly adopted method for water purification as it provides both low cost adsorbent and solve agricultural waste problem altogether. Adsorption capacity of charcoal varies with the carbonaceous source and method of preparation. E Misran et. al prepared activated charcoal using waste banana stem as a precursor and studied methylene blue (MB) adsorption and influence of pH of the solution on results. In another study activated carbon is prepared by from Pea Shells and used for MB adsorption studies as reported by ÜnalGeçge et.al. A number of similar studies are reported in the literature [15]. In this particular study a sol-gel based synthesis is adopted for the

synthesis of charcoal from the carbon source honey [16]. As honey is a carbohydrate it can be easily charred to get charcoal which can be activated by surface modification. Here ethylene glycol a common solvent for sol-gel synthesis is used as a medium for the synthesis [17]. No special chemical method is adopted for surface modification except the dehydration is done with concentrated sulphuric acid which may itself serves as a modifier. Water samples containing methylene blue is treated with the prepared samples and the results are analyzed.

MATERIALS AND METHODS

A branded sample of honey is used for the synthesis of charcoal. All other chemicals used are of analytical grade.

Synthesis of samples

About 10gm of honey is mixed with 5 ml of ethylene glycol (EG) stirred well using a magnetic stirrer for 15 minutes and solution is placed in an electric heating mantle at 100°C with continuous stirring for charring. After 30 minutes it is taken out and crushed into fine powder using mechanical mortar. Washed with deionized water to remove unreacted carbohydrate and other chemicals and dried in a hot air oven for 30 min at 100°C. This sample is designated as C1. The

above experiment is repeated with addition of H₂SO₄ as dehydrating agent to the solution of honey in ethylene glycol. Charcoal obtained by this process is designated as C2.

Sample preparation for Spectrophotometric analysis

An aqueous solution of methylene blue of about 10 ppm concentration is prepared by taking 0.1 gm of MB in 100ml standard flask and made up the solution. 10 ml of this solution is pipetted out in a 1000 ml standard flask and made up to volume using distilled water and kept as the stock solution. About 0.1, 0.2, 0.3 gm of charcoal is weighed into three different conical flasks marked as A, B and C. From the stock solution of MB, 30 ml is pipetted into conical flasks A, B, C and subjected to shaking in a mechanical stirrer for 5 minutes. The solutions are centrifuged well and the clear solution is used for spectrophotometric analysis.

X-ray diffraction technique

X Ray crystallography is an imperative tool in solid state chemistry. This technique will accurately ascertain the amorphous nature of crystal. XRD pattern is known as finger print of a crystalline material because it gives information on the crystal structure, phase and purity of

material. In the present study, the phase analysis of the samples was carried out using Rigaku D/max-B model X-ray diffractometer using $\text{CuK}\alpha$ radiations. The wavelength of $\text{CuK}\alpha$ radiation is $1.5406\text{\AA}$ and the scan rate used was $5^\circ/\text{minute}$. The results were recorded in the 2θ range from 3° to 70° .

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a useful tool to get idea of topography, morphology, and microstructural information of materials. It shows the layered structure of crystals. The image is formed by scanning a probe of focused electron beam across specimen. The electron beam interacts with surface of specimen resulting in back scattering of electrons of high energy, generation of secondary electrons of low energy and X Ray's. These signals are monitored by detectors and magnified. The images are collected and analyzed. SEM analysis of the samples is done with the SEM make TESCAN Model-Vega3SBH, at Maharaja's College, Ernakulam. The images are collected at different magnifications and are analyzed.

UV – Visible spectroscopy

Absorption of methylene blue in the UV-Visible region is recorded using Shimadzu

UV – VIS spectrophotometer (UV 2600). Comparison of the absorption intensity after treating with charcoal gives the idea about the extent of adsorption of MB by charcoal.

RESULTS AND DISCUSSIONS

XRD analysis

To know about the crystalline/ amorphous nature of the samples XRD is taken and the X-ray diffractogram is shown in figure 1.

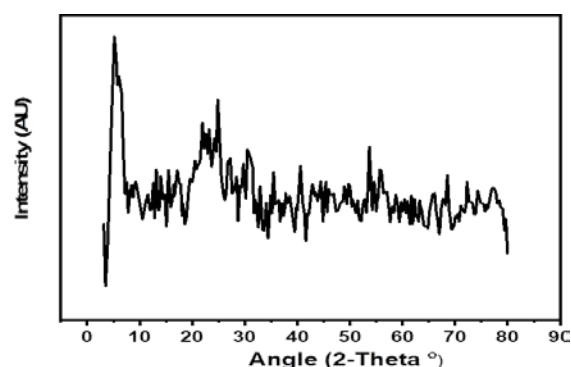


Figure 1 X-Ray diffractogram of charcoal

XRD pattern as shown in figure 1 indicates amorphous nature of the samples. No sharp intense peak is observed in the spectrum which shows that sample doesn't have any crystalline characteristics.

A peak observed in the 2θ value of 24° indicates the possibility for the formation of graphite like structure.

SEM analysis

SEM images at different magnification are given figure 2. Flake like structure is observed as seen in the images. This particular structure results from the charring of the carbonaceous source honey in presence of ethylene glycol. Ethylene

glycol is a solvent used for the sol-gel synthesis as it can easily form a gel like structure due to dehydration and polymerization of simple molecules of EG. Addition of sulphuric acid can enhance the dehydration process which may result in a flake like structure.

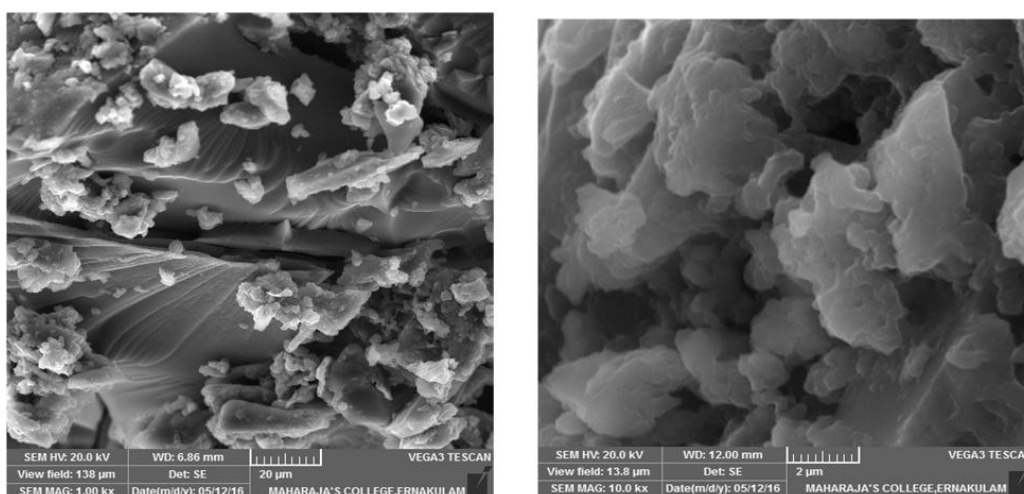


Figure 2 SEM images at different magnification

3.3 Spectrophotometric studies

UV-visible spectrum is recorded in the wavelength range of 200-800 nm. The absorption spectrum of MB before treating with charcoal is shown in figure 3. Characteristic absorption peak of MB is observed at 664 nm.

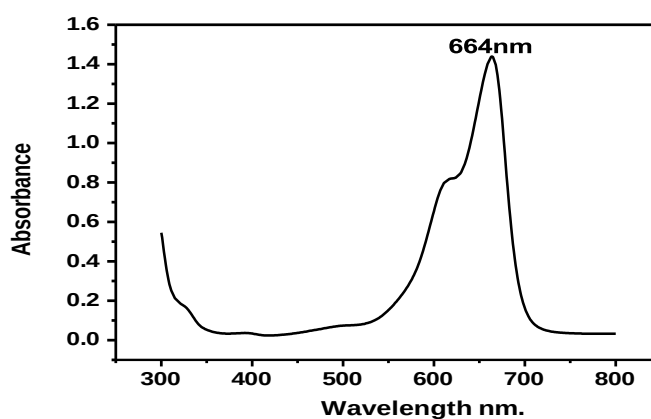


Figure 3 UV-Vis Spectrum of Methylene Blue

UV spectra of MB treated with different amount of sample C1 is shown in figure 4. Comparing with figure 3 it can be seen that intensity of absorption is decreased when the MB solution is treated with charcoal. Intensity of absorption is directly proportional to the concentration of MB. So the decrease in intensity of treated MB solution indicates the adsorption of MB by CI. From figure 4, it is clear that as the amount of C1 increases from 0.1g to 0.3g intensity of absorption decreases which is directly proportional to the amount of MB.

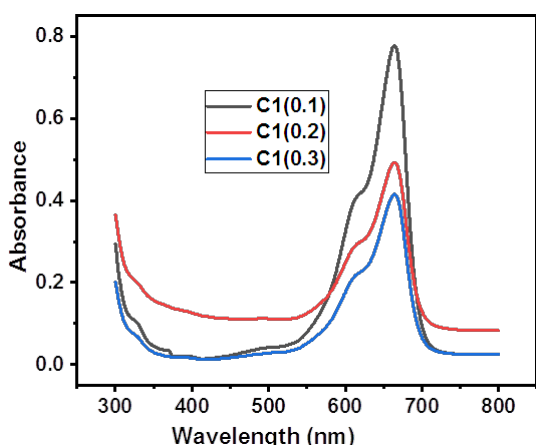


Figure 4 UV-Vis Spectrum of MB after treatment with Charcoal (C1)

Figure 5 shows the UV-Visible spectra of MB treated with different amount of C2. Absorption of MB is enhanced after treating with sample C2 as the intensity is found to be less than that for the untreated MB solution. Absorption peak intensity is found to decrease with increase in the amount of adsorbent.

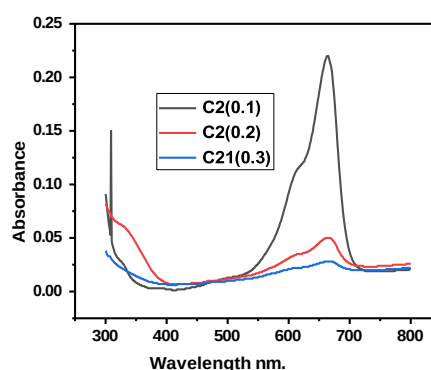


Figure 5 UV-Vis Spectrum of MB after treatment with Charcoal (C2)

Absorption intensity of MB after treating with C1 is in the range 0.76, 0.49 and 0.40 for 0.1g, 0.2g and 0.3g respectively. In the case of C2 these values are 0.22, 0.05 and 0.030. Higher peak intensity indicates lesser amount of adsorption. So C2 is a better adsorbent than C1

Sample C2 is prepared using H_2SO_4 as a dehydrating agent. This results in self-modification of surface that may cause enhanced adsorption capacity of sample C2. In order to compare the adsorption capacity of sample 1 and 2 adsorption efficiency is calculated using the equation

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 and C_e are the initial and final concentrations which can be taken as the intensity of MB absorption peak with and without the adsorbent respectively. Absorption efficiency calculated using above equation for samples C1(0.1) and

C2(0.1) is 46 and 86 respectively. In the case of C2(0.3) it is 98. That is almost all MB is absorbed by C2 at higher amount.

CONCLUSION

Activated charcoal can be prepared by several methods from different sources. In this particular study a solvent based preparation of charcoal is reported. Ethylene glycol is a commonly used solvent in sol-gel synthesis of nano particles. Two different samples of charcoal is prepared using this solvent and in one of the method H_2SO_4 is used as dehydrating agent. To ascertain the physical nature XRD is taken and the samples are found to be amorphous nature. Morphology is analysed from SEM image and found to have a layer like structure. Methylene Blue adsorption of these samples is studied by taking UV-Vis spectrum of MB before and after treating with the samples. Results show that both the samples are good adsorbents for MB. There is no shift in the characteristic absorption peak of MB, which indicates that no chemical interaction occurs between the MB and AC. Adsorption efficiency calculation shows that sample C2 is a better adsorbent than C1. This method can be effectively used for the synthesis of charcoal without any additional surface modification and can be

used as an adsorbent for synthetic dyes. Thus the samples can be used for industrial waste water treatment.

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Abbreviations

AC: Activated Carbon

MB: Methylen Blue

EG: Ethylene Glucol

XRD: Xray Diffraction

SEM: Scanning Electron Microscopy