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RESEARCH ARTICLE

IR, XRD AND SEM STUDIES ON THE ADSORPTION OF METHYLENE BLUE DYE ONTO MICROWAVE ASSISTED $ZnCl_2$ ACTIVATED CARBON PREPARED FROM *Delonix regia* PODS

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Abstract

The activated carbon from *Delonix regia* (Flame tree) pods was prepared using orthogonal array experimental design method with the parameters such as microwave radiation power, radiation time, concentration of $ZnCl_2$ solution and impregnation time. Optimized conditions were found to be radiation power 850 W, radiation time 12 min, 60 % of $ZnCl_2$ and impregnation time 24 hours. Carbon prepared was designated as MWZAC (Microwave assisted Zinc chloride Activated Carbon). Adsorption interactions of methylene blue dye onto MWZAC from aqueous solution using FT-IR spectra, Fe-SEM and XRD techniques. IR studies revealed that the possibility of partial chemisorption though maximum adsorption is physical in nature. Fe-SEM showed the morphological observations of loaded and unloaded adsorbents. XRD studies exhibited the crystalline nature of unloaded adsorbent compared with loaded adsorbent.
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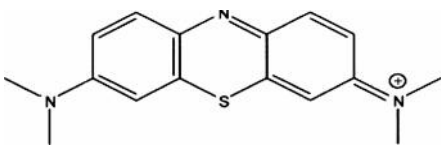
Keywords: Adsorption, $ZnCl_2$ activated microwave carbon, methylene blue dye

Introduction

The textile manufacturing process is characterized by the high consumption of resources like water, fuel and a variety of chemicals in a long process sequence that generates a significant amount of waste. The common practices of low process efficiency result in substantial wastage of resources and a severe damage to the environment. Many treatment methods have been used to remove the dyes from wastewater. Among the various methods, adsorption is an effective separation process which is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewater (Moreno-Castilla 2004; Abechi et al., 2011). Activated carbon is the most common adsorbent for the removal of many organic contaminants. The adsorption process of activated carbon, however, is prohibitively expensive, which limits its application. Therefore, there is a need to produce activated carbon from cheaper and readily available materials. In the past years, several investigations have been reported the removal of dyes using activated carbons developed from industrial or agricultural wastes (Salleh et al., 2011).

Structure of MB



In this present study, pods of *Delonix regia* (flame tree) have been used to prepare activated carbon. *Delonix regia* belongs to royal Poinciana or flamboyant, a member of the bean family which produces brown woody seed pods merely a waste material (Yuh-Shan Ho et al., 2009).

Recently, microwave energy has been widely used in research and industrial processes (Yagmur et al., 2008). Compared with conventional heating techniques, microwave heating has the following additional advantages as follows: interior heating, higher heating rates, selective heating, greater control of the heating process, no direct contact between the heating source and heated materials, and reduced equipment size and waste (Bykov et al., 2001; Foo Keng Yuen and Hameed, 2009). Hence microwave radiation is used to prepare carbon from the plant material instead of conventional heating methods.

Materials and Methods

Preparation of Adsorbents

The air dried pods were cut into small pieces and powdered in a pulveriser. Taguchi experimental design method was used to prepare and to determine optimal parameters to prepare efficient carbon (Yuh-Shan Ho et al., 2009; Makeswari and Santhi, 2012).

20 g of the powdered pods was mixed with 75 mL of $ZnCl_2$ solution of desired concentration (20, 40 and 60 %). The slurry was kept at room temperature for 24 hours, to ensure the access of the $ZnCl_2$ to the *Delonix Regia* pods. Then the slurry was subjected to microwave heating of pre- determined power (450, 600, 850 watts) for pre- determined duration (8, 10, 12 minutes).Thus the carbonized samples were washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reach 7. Then the carbon was filtered and dried at 423 K. Totally 27 number of carbons were prepared by varying preparation parameters such as concentration of $ZnCl_2$ solution, Microwave heating watts power and radiation times which are given in the Table 1 (Namasivayam and Sangeetha, 2004).

Instrumental Studies

FTIR Spectroscopy

Characterization of unloaded MWZAC

IR analysis permits spectrophotometric observation of the adsorbent surface in the range 400–4000 cm^{-1}, and serves as a direct means for the identification of the organic functional groups on the surface (Mohan et al., 2001). An examination of the adsorbent surface before and after adsorption reaction possibly provides information regarding the surface groups that might have participated in the adsorption reaction and also indicates the surface site(s) on which adsorption has taken place. IR studies indicate the participation of the specific functional groups in adsorption interaction. IR spectrum of the carbon showed (Fig. 4) peaks at 3851.57 and 3742.23 cm^{-1} which can be assigned to the O–H stretching vibration mode of hydroxyl functional groups including hydrogen bonding. The presence of the band at 3398.95 cm^{-1} denotes the presence of C=O stretching. The band between 2927.80 and 2851.74 cm^{-1} may be due to the presence of the alkanes. The presence of the band at 2298.39 cm^{-1} denotes the presence of phosphine and peaks in the range of 1543.68, 1375.44 and 1112.99 cm^{-1} indicate the presence of nitro, alkanes and alkyl halide groups. The bands in the region of 830–617 cm^{-1} may be due to presence of alkene groups (Namasivayam and Kavitha, 2006).

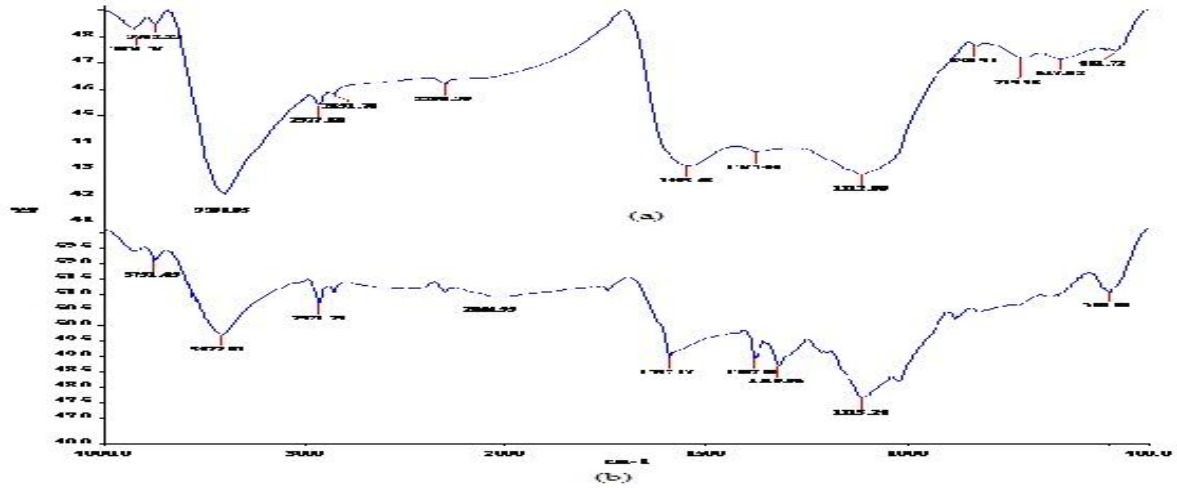
Characterization of MB dye loaded MWZAC

Adsorption of adsorbate over carbon studied has resulted in some spectral changes such as disappearance of some bands, broadening of some bands and spectral shifts. It could be seen from the spectrum that almost there is no change in the spectral pattern before and after adsorption however there is a slight reduction of absorption bands. The peak at 2298.39 cm^{-1} of the carbon also disappeared and a new peak appeared around 2066.55 cm^{-1} showed that there is a formation of N=C in R-N=C=S bond between carbon and dye. The peak around 830.91 – 617.82 cm^{-1} for alkene groups present in the carbon disappeared for all the adsorbate loaded carbons. This clearly indicates that the possibility of partial chemisorption though maximum of adsorption of MB onto MWZAC adsorbent is by physical forces. (Namasivayam and Kavitha, 2006).

SEM studies

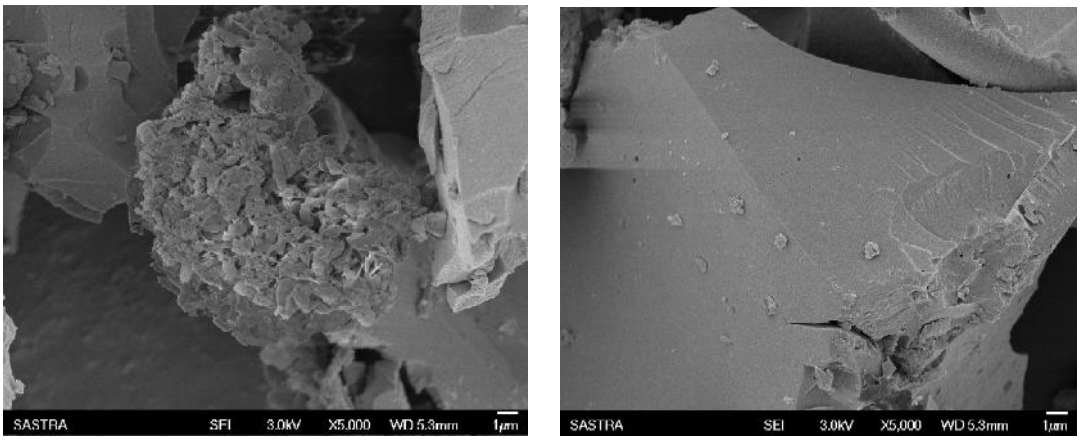
SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM is used to assess morphological changes in the carbon surfaces following adsorption of MB dye.

Figure 1. FTIR spectra of MWZAC



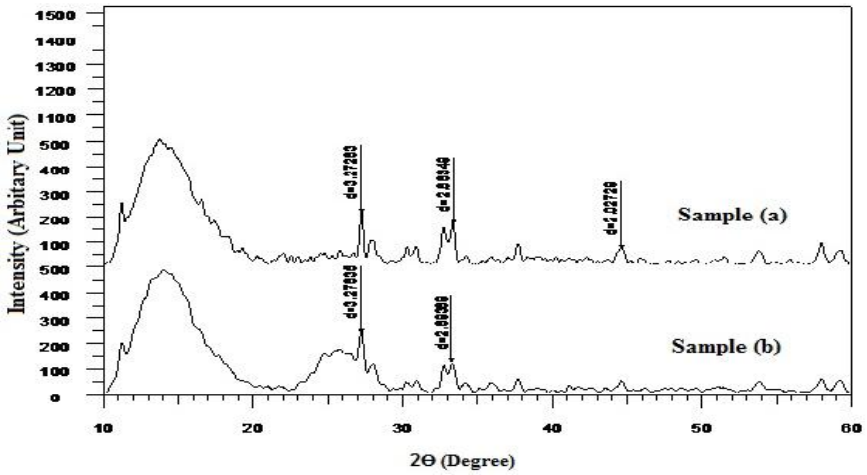
(a). Before MB adsorption (b). After MB adsorption

Figure 2. Scanning electron micrographs of MWZAC



(a). Before MB adsorption (b). After MB adsorption

Figure 3. XRD pattern of MWZAC



(a). Before MB adsorption (b). After MB adsorption

Morphology of unloaded MWZAC

The morphology of prepared MWZAC was examined before adsorption is shown in the Fig. 5 a. SEM micrographs of MWZAC particles showed cavities, pores and more rough surfaces on the carbon samples. This shows that $ZnCl_2$ was effective to create well developed pores with uniform distribution leading to large surface area and porous structure (Namasivayam and Kavitha, 2006).

Morphology of MB loaded MWZAC

The morphology of the loaded adsorbent showed some important observations. Coverage of the surface of the adsorbent due to adsorption of MB dye is shown in the Fig. 5 b. The white layer (molecular cloud) indicates the uniform coverage of MB dye over the MWZAC surface.

X ray diffraction studies

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. If the material under investigation is crystalline, well-defined peaks are observed while non-crystalline or amorphous systems show a hallow instead of well-defined peak (Cullity, 1978).

XRD pattern of unloaded adsorbent

The XRD pattern of unloaded MWZAC carbon is crystalline in nature and shows sharp peaks corresponding to 2Θ=27.00, 33.5 and 44.5 were shown in the Fig. 6 a (Namasivayam and Kavitha, 2006).

XRD pattern of MB loaded adsorbent

The XRD pattern of MWZAC adsorbent loaded with MB dye have slightly changed peaks when compared to unloaded MWZAC. This suggests that the MB dye molecules diffuse into micropores and macropores and adsorb mostly by physisorption and partially by chemisorption with altering the structure of the carbon. Studies on the effect of pH and desorption indicated the physisorption and small amount of chemisorption. (Namasivayam and Kavitha, 2002, 2003 and 2004). XRD studies show changes in the crystallinity of the adsorbent due to the adsorption reaction.

Conclusions

Microwave assisted zinc chloride activated carbon (MWZAC) was prepared from *Delonix regia* (Flame tree) pods found to have good capacity of adsorption. FTIR, SEM, XRD studies and enthalpy of adsorption values lead to conclude that the adsorption was mostly physical in nature with small amount of chemisorptions.

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