Adsorption of Methylen Blue (MB) by Pistachio in Presence of $CuFe_2O_4$ Nanocomposite

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Abstract- In this work, adsorption of methylen blue (MB) onto nutshells of pistachio, $CuFe_2O_4$ and pistachio/ $CuFe_2O_4$ composite has been investigated. The adsorption kinetics of MB on pistachio and $CuFe_2O_4$/pistachio powder composite was similar. The adsorption kinetics of MB onto $CuFe_2O_4$/pistachio composites was pseudo-second order. The results suggest adsorption capacity of the pistachio/ $CuFe_2O_4$ composite was more than that of natural pistachio. In order to optimize the adsorption process, effect of pH and contact time were studied.

Keywords: Adsorption, kinetic, Methylen blue, Nanocomposite, Pistachio

1. Introduction

Dyes are widely used in the textile industry to color products. One of the major problems concerning textile wastewaters is colored effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms [3]. Methyl Violet is a triphenylmethane dye soluble in water, ethanol, methanol, diethylene glycol and dipropylene glycol, it has molecular formula $C_{24}H_{28}ClN_3$. it is used to obtain shades of deep colors that can be applied for dyeing of cotton, silk, paper, bamboo, weed, straw and leather[1]. The dye Methyl Violet is widely used in analytical chemistry laboratories as a pH indicator to test pH ranges from 0 to 1. From the chemical structure of the dye it is observed that there are three aromatic rings attached to a central carbon atom.

The toxic nature of the dye can be explained by considering the fact that on decomposition it gives out hazardous products. These products are toxic and may cause several health problems to mankind as well as animals, thus MB attracts noteworthy attention to innovate effective techniques for its removal. Adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional method [2, 5, 6].

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2. Materials and Method

Soft pistachio shells were used as starting materials. The pistachio shells were preheated in an oven at 100 °C for about 48 h to reduce the moisture content. They were then crushed with a high speed mill and sieved on a sieve mechanical shaker, and the size fraction of lower than 180 μm that has been passed through US standard sieve number 80, was used in this study. Analytical grade copper (II) chloride dehydrates and ferric chlorides were obtained from Merck. $CuFe_2O_4$ was prepared using a co-precipitation method [4]. $CuFe_2O_4$/pistachio composites were prepared using a co precipitation method. The pistachio was added into a 400 ml solution containing copper (II) chloride (0.02mol) and ferric chloride (0.04mol) at room temperature. The amount of pistachio was adjust to obtain $CuFe_2O_4$/pistachio mass ratio of 1:10 under vigorous magnetic-stirring, slowly raised the pH by adding NaOH (5mol l^{-}) solution to around 10 and stirring was continued for 30 min, and the stopped stirring. The suspension was heated to 95-100 ºC for 2h. After cooling, the prepared composite was repeatedly washed with distilled water. By a simple magnetic procedure, the obtained materials was separated from water and dried in an oven at 105 ºC. MB was purchased from Merck and used without further purification. The stock solution of MB was prepared with distilled water (100 mg l^{-1}). MB was analyzed by shimadzu 160A UV-Vis spectrophotometer. The crystalline structure of $CuFe_2O_4$ was determined using the X-ray powder diffraction method with a Philips PW1840 diffractometer using Ni-filtered Cu k_α radiation and wavelength 1.54˚A. Scanning electron microscopy was carried out using a Hitachi S-3500 Scanning Electron Microscope.

3. Results and discussion

The morphologies of pistachio, the prepared $CuFe_2O_4$ ferrite and $CuFe_2O_4$/ pistachio were studied by SEM. Fig 1a-c show the views of pistachio, $CuFe_2O_4$ and $CuFe_2O_4$/ pistachio composite, respectively. It can be showed the agglomeration of many micro fine particles, which led to a rough surface and the presence of pores structure.

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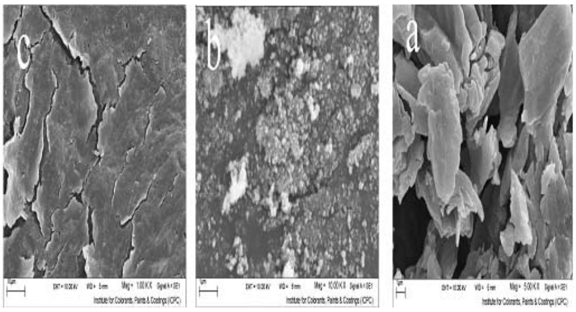

Fig 1a-c SEM image of a-pistachio, b-$CuFe_2O_4$ and c-$CuFe_2O_4$/ pistachio composite

3. 1. Catalytic effect of $CuFe_2O_4$

The experiments were carried out with 50 ml of MB dye solutions on 0.1 g of pistachio, $CuFe_2O_4$ and $CuFe_2O_4$/pistachio composite. Fig. 2 shows the effects of agitation time. The plots show that the adsorption of MB increases with an increase in agitation time and attains equilibrium earlier of adsorption (30 min) for $CuFe_2O_4$/pistachio composite and more than 90%. In the equilibrium time of 60 min was needed for $CuFe_2O_4$/pistachio and $CuFe_2O_4$. The higher adsorption capacity of $CuFe_2O_4$/pistachio composite than that pistachio attributed to the presence of $CuFe_2O_4$ catalyst.

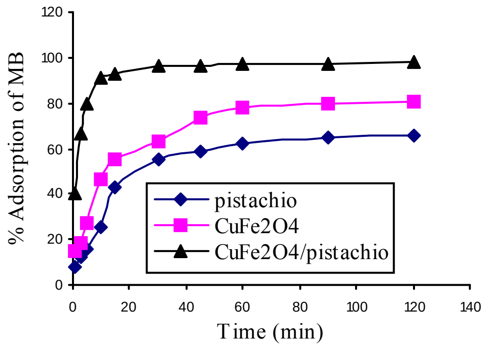

Fig. 2. Effect of time for adsorption of MB onto pistachio, $CuFe_2O_4$ and $CuFe_2O_4$/pistachio composite.

3. 2. Effect of pH

Fig. 3 shows the effect of pH on the adsorption of MB onto $CuFe_2O_4$/pistachio. The adsorption capacity increased with increasing pH of the solution. The maximum adsorption capacity of MB on

$CuFe_2O_4$/pistachio was observed at pH 10. The effect of pH on MB removal from $CuFe_2O_4$ and pistachio were similar. This could be explained by the fact that at low pH, more protons will be available to protonate hydroxyl groups, reducing the number of binding sites for the adsorption of MB. The adsorption behavior showed that adsorption of MB onto nanoparticle composite is governed by electrostatic interactions. The influence of pH on the adsorption capacity showed decreasing affinity with increasing electrostatic repulsion between MB and the adsorbent with a maximum value at pH 10.

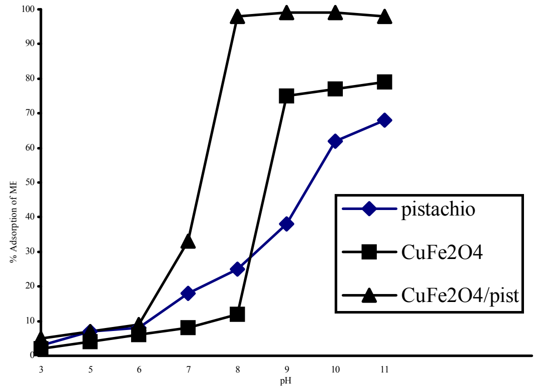

Fig. 3. Effect of pH for adsorption of MB onto pistachio, $CuFe_2O_4$ and $CuFe_2O_4$/pistachio composite for 50 ml MB 100 ppm and 0.1 g sorbent

3. 3. Adsorption kinetics

The two adsorption kinetic modes used in this study are pseudo-first order and pseudo-second order equations.

The pseudo-second order model is based on adsorption equilibrium capacity. (Fig. 4.)

$$t/q = t/q_e + 1/(k_2 q_e^2)$$

Where q_e and q represent the amount of dye adsorbed (mg g^{-1}) at equilibrium at any time. k_2 in the rate constant of the pseudo-second order equation (g mg^{-1} min^{-1}) [7]. A plot of t/q versus time (t) would yield a line with a slope of 1/ q_e and an intercept of $1/(k_2 q_e^2)$, if the second order model is a suitable expression.

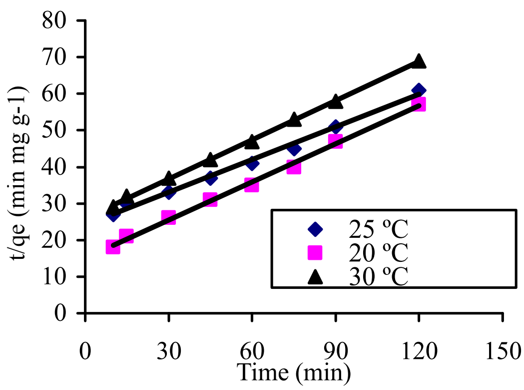

Fig. 4. Kinetics of MB adsorption onto $CuFe_2O_4$/pistachio composite for 50 ml of an initial concentration of 100 mg/l MG , pH 10, 0.1 g adsorbent for pseudo-second-order model

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4. Conclusions

$CuFe_2O_4$/pistachio can be used as a cost effective adsorbent for removal of MB from water and wastewater. Alkaline pH is found to be better than acidic pH. The adsorption follows pseudo-second order kinetics.

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