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ORIGINAL PAPER

Removal of methylene blue dye from aqueous solutions by a new wood/plastic composite based on HDPE and wood particles

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ABSTRACT

In the present work, the ability of wood-plastic composite containing high density polyethylene and wood powder as a recycled material to remove methylene blue cation pigment was studied. The effect of some important parameters such as pH, adsorbent amount and contact time was investigated. Adsorption efficiencies for methylene blue were maximized at alkaline pH. Adsorption capacity increased with increasing adsorbent amount and contact time. The value of R^2 in Langmuir model was equal to 1 and the separation factor for 0.5 and 1 g of adsorbent was 0.09 and 0.1, respectively. Given that the methylene blue adsorption data were more consistent with the Langmuir isotherm model, it can be stated that the wood-plastic composite probably has uniform adsorption surfaces and the adsorption process occurred in a homogeneous system on the adsorbent surface. Based on the results of this study, it was observed that this composite is a suitable adsorbent for removing methylene blue from aqueous solutions and used as a purifying agent in the decolorization of effluents containing pigments. This adsorbent is recyclable and cost-effective for dye removal from textile industry wastewater. **Polyolefins J (2023) 10: 27-33**

Keywords: Wood plastic composite; adsorption; methylene blue; Langmuir isotherm.

INTRODUCTION

In recent years, the development of industry has increased the production of industrial wastewater and sometimes environmental pollution. Dyes are one of the most important pollutants in industrial wastewater, which are generally used in the textile, paper, cosmetics, food, pharmaceutical and leather industries [1]. Due to their complex structure, dye molecules are very resistant to biodegradation and will cause many health problems including skin allergies, allergies, cancer, mutations, etc., [2,3]. Colored water is not only aesthetically unpleasant, but also reduces the penetration of light into the water and thus reduces the photosynthetic efficiency of aquatic plants [4-7]. Methylene blue, also known as methylthioninium chloride, is a cationic chemical dye that is a dark green, odorless, and solid powder at room temperature that gives a blue solution

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when dissolved in water. This cationic pigment is one of the most common dyes used in the textile industry and has been used in human and veterinary pharmacopoeia for a long time [8-10]. Due to the characteristics and problems caused by paints, it is necessary to remove artificial colors from wastewater before discharging them into the environment in order to protect the environment. Various methods to remove dye from wastewater including physical, chemical and biological methods such as coagulation and flocculation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation have been used in the past years [11-13]. Due to the low biodegradability of dyes, conventional biological wastewater treatment processes are not effective in the treatment of colored wastewater, so colored wastewater is usually treated by physical or chemical methods [14-20]. The adsorption process is one of the physicochemical processes that has been developed over the past years due to its low initial cost, easy operation, flexibility and simplicity for wastewater treatment to remove dyes, organic matter and metals [21]. An ideal adsorbent suitable for wastewater treatment should have features such as environmentally friendly, high adsorption capacity and recyclability, and also the adsorbed contaminants should be easily removed from its surface [22]. Wood-plastic composites are composed of thermoplastic polymers and wood particles, which are generally melted and mixed above the melting point of polymers and are used in the manufacture of various wood products such as street protection, floors, facades, billboards, park tables, benches, sidewalks, etc., [23]. Wood is a natural absorber that is available in large quantities and low prices. Also, polymers as adsorbents have been considered by different researchers due to their wide surface area, high mechanical stability and ability to remove environmental contaminants in the adsorption process [24-26]. The low-cost sorbent used in this research is a wood-plastic composite, which was previously prepared and characterized by our group [27]. This sorbent contains 55% by weight of wood particles and 29.5% by weight of high-density polyethylene. The effect of important parameters on adsorption experiments such as contact time, adsorbent dosage and pH has been investigated. Also, the equilibrium data have been analyzed using the Langmuir and Freundlich isotherm model and the adsorption thermodynamics has been evaluated. Moreover, the reuse of wood-plastic composite after MB desorption has been assessed in order to minimize the economic cost of the method.

EXPERIMENTAL

Materials

High density polyethylene (HDPE), 62N07 with melt flow index (MFI) value of 7 g/10 min (2.16 kg at 190°C) was purchased from Lorestan Petrochemical Co., Iran. Commercial Irganox 1010 (powder with molecular weight of 1178 g/mol) and Chinox 168 (powder with molecular weight of 646.94 g/mol) antioxidants were provided from BASF Co., USA and Double Bond Chemical (DBC) Co., Taiwan, respectively. Anti-flame powder (Sb_2O_3) with melting point of 656°C was supplied from Satrbetter Co., China. Calcium stearate powder (melting point of 150°C) and paraffin wax (CH36WAX, melting point of 105°C) were provided from Chimiaran Co., Iran. Maleic anhydride grafted polyethylene 1040 (MAPE) was obtained by ExxonMobil Co., USA, with MFI of 1g/10 min. Waste poplar flour (PF) was supplied from a local sawmill in Tehran, Iran. The sawdust was milled down to particle size of 60 mesh and then dried at 100°C for 24 h to less than 2% moisture content. Methylene blue (molecular weight of 319.85 g/mol), hydrochloric acid (molecular weight of 6.46 g/mol) and sodium hydroxide (molecular weight of 39.997 g/mol) were purchased from Merck and double distilled water was used for the experiments.

Wood-plastic composite preparation

The wood-plastic composite used was prepared and characterized according to our previous work [27]. Appropriate amount of HDPE was mixed with MAPE for 1 minute in a 60 mL internal mixer (Brabender, GmbH & Co., Germany) with the rotor speed of 60 rpm at 180°C as processing temperature. Then, other additives including antioxidants (2.5 wt%, 2:1 w/w ratio of Chinox 168 to Irganox 1010), anti-flame (4 wt%), calcium stearate (1.5 wt%) and paraffin wax (3 wt%) were added and the mixing continued for another minute. PF (55 wt%) was added and mixing continued for the appropriate time. The resulting wood-plastic composite was used for the removal of methylene blue.

Drawing of calibration curves

500 ml of 500 ppm methylene blue stock solution was prepared with double distilled water and different solution concentrations of 10, 20 and 30, 50, 100 ppm were prepared from the stock solution. The resulting solution was analyzed with a UV-vis spectrophotometer at 665 nm to obtain the calibration curve.

Absorption experiment

For the absorption studies different parameters including pH (4, 7 and 9), contact time (10, 30, 60 and 90 minutes) and the amount of adsorbent (0.5 and 1 g) were investigated using a shaker at a speed of 150 rpm at room temperature. After certain shaking times, the solutions were filtered through filter paper and their adsorption was measured using a UV-Visible spectrophotometer at 665 nm. Dye adsorption capacity (Q_t, mg/g) and dye removal percentage (% R) by adsorbent at any time were calculated using the following equations, respectively [28]:

$$Q_t = \frac{(C_0 - C_t)v}{m}$$

(♣♣)♣♣♣=♣♣ $\frac{(C_0 - C_t)}{C_0} \times$

In the above equations, C_0 and Ct are the initial concentration and the concentration at equilibrium (mg /L), ʋ is the volume of solution (L), and m is the adsorbent weight (g).

RESULTS AND DISCUSSION

Factors affecting the adsorption of methylene blue pigment using wood-plastic composite as adsorbent

pH effect

For the evaluation of methylene blue adsorption experiment at different pHs, 25 ml of different concentrations of methylene blue including 10, 20 and 30 ppm was poured into three separate Erlenmeyer flask and pH of solutions was adjusted at 4, 7 and 9 with HCl (0.1N) and NaOH (0.1N), and the adsorption of the resulting solution was analyzed with using a UV-vis spectrophotometer at 665 nm. Then 1 gr of the wood-plastic composite was added to each Erlenmeyer flask and shacked at 150 rpm at room temperature for 90 minutes. After a specific period of time, the mixture was filtered and the adsorption of the filtrate was measured by a UV-vis spectrophotometer at 665 nm [29]. The result is shown in Figure 1.

The results demonstrate that the efficiency of MB adsorption increases more significantly as pH raises from 4 to 9. This behavior can be explained by the reactions on the wood-plastic composite surface in aqueous media. Due to the presence of OH group in the surface of adsorbent, in basic media the surface gets a negative charge that promotes adsorption of MB cations. So, for studies of subsequent effects, pH 9 was selected as the optimal pH [29].

Contact time effect

The adsorption dynamics of the methylene blue solution/wood-plastic composite system strongly depend on the contact time. The extent of MB removal by wood-plastic composite at optimal pH was examined at different shaking times up to 90 min. According to Figure 2, at concentrations of 10, 20 and 30 ppm the absorption of MB dye increases by the time.

The adsorption mechanism on a heterogeneous adsorbent is surface adsorption and the contact time has a direct effect on the increase of absorption [30].

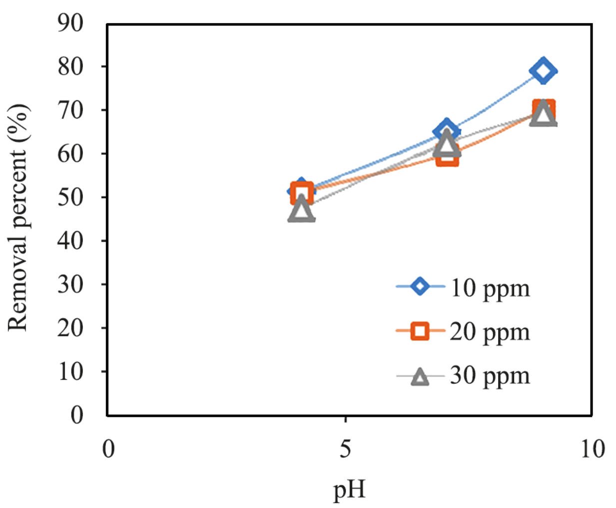

Figure 1. Effect of pH on the adsorption of methylene blue.

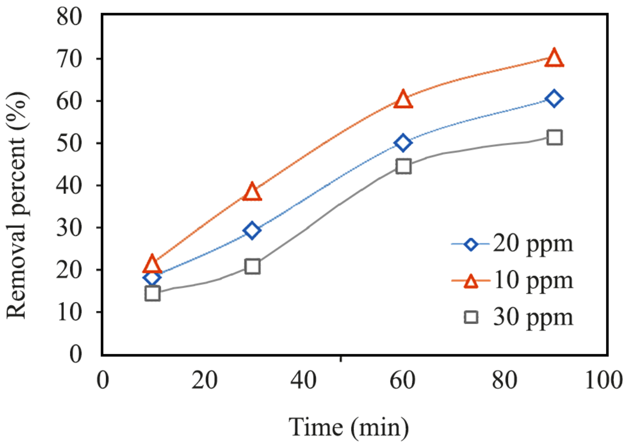

Figure 2. Effect of contact time on the absorption of methylene blue.

Adsorbent amount effect

To evaluate the effect of adsorbent dosage, 0.5 g and 1 g of adsorbent were added to three different concentrations of MB solution and shacked for 90 minutes. According to Figure 3, it can be seen that with increasing the amount of adsorbent, the removal efficiency of methylene blue increases. The increase in adsorption with an increase in adsorbent quantity can be attributed to the greater surface area and the availability of more adsorption sites [30].

Adsorption isotherms

The relationship between the amount of adsorbed substance (Q) and the concentration of that substance in the fluid (C) at temperature T is called the adsorption isotherm at temperature T. Adsorption isotherm has certain constant values that determine the surface

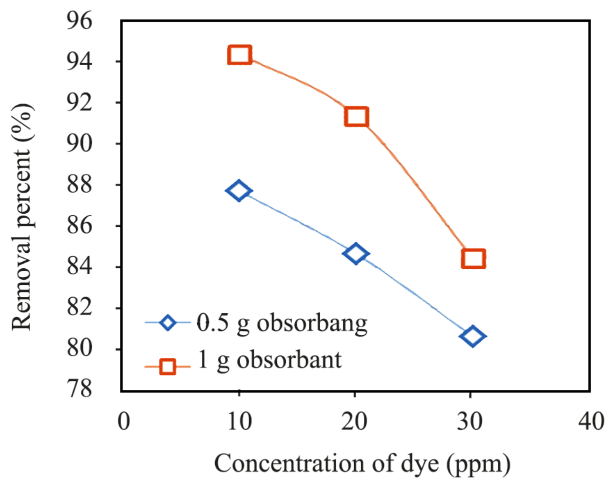

Figure 3. Effect of adsorbent dosage on methylene blue adsorption.

characteristics, adsorption dependence and adsorption capacity of different contaminants. Therefore, the adsorption isotherm can provide information about the maximum adsorbents for the adsorption of pollutants, which in turn, is useful for designing adsorption processes. In this study, Langmuir and Freundlich isotherm models were used to obtain the adsorption mechanism. The Langmuir model is based on the assumption that adsorption is monolayer without reaction between adsorbed molecules. The Langmuir equation is as follows:

$$\frac{1}{q_e} = \frac{1}{Q_{\max,KL}} + \frac{1}{Q_{\max}} C_e$$

In the above equation, C_e is the equilibrium concentration of dye in solution (mg/L), q_e is the adsorption value (mg/g), Q_{max} is the maximum adsorption capacity (mg/g) and KL is the Langmuir constant. In Langmuir equation, the dimensionless parameter of separation factor (R_L) is used to describe information from the following equation:

$$R_L = \frac{1}{1 + KL\ C_e}$$

The value of R_L determines the type of isotherm, that is reversible ($R_L = 0$), suitable ($0 < R_L < 1$), linear ($R_L = 1$) or unsuitable ($R_L > 1$).

The Freundlich isotherm model is an experimental equation used to describe heterogeneous systems. The Freundlich linear shape is the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

In this equation, 1/n indicates the suitability of the adsorption process and the values of K_f and n are obtained from the y-intercept and the slope of the line, which are both Freundlich constants and determine its adsorption capacity and intensity. The magnitude of n is a measure of desirable adsorption. Values of n between 1 and 10 indicate optimal adsorption [29]. The data obtained from the effect of amount of adsorbent were used to calculate the equilibrium parameters such as maximum adsorption capacity and to evaluate the accuracy of each of the Langmuir and Freundlich isotherms. The results are shown in Figures 4 and 5. The calculated

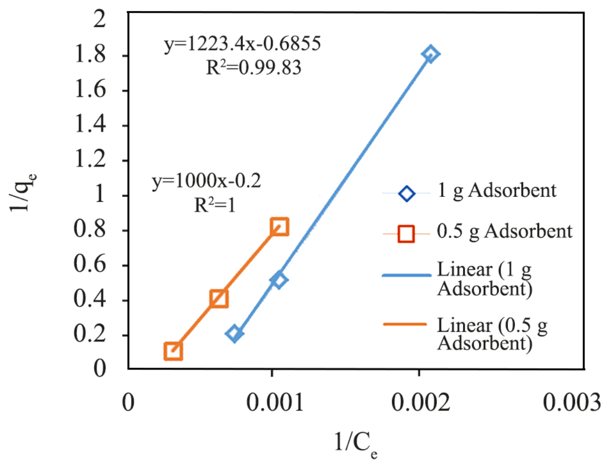

Figure 4. Langmuir isotherm curve.

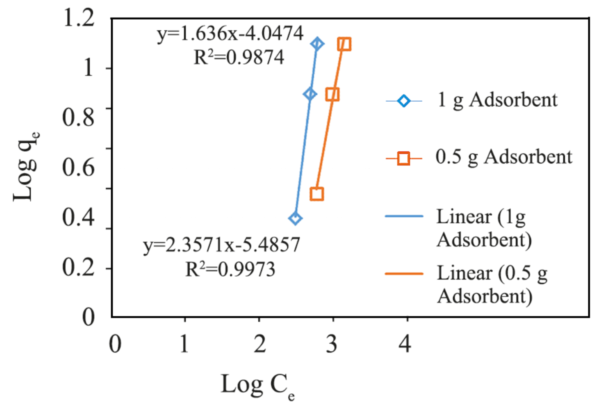

Figure 5. Freundlich isotherm curve.

Table 1. Langmuir and Freundlich constants.

Adsorbent	Langmuir constants				Freundlich constants		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F	n	R^2
0.5 g	1000	0.2	0.09	1	5.4857	2.3571	0.9973
1 g	1223.4	0.6855	0.1	0.9983	4.0474	1.63	0.9874

data are also given in Tables 1-3.

According to Figures 4 and 5, we find that the adsorption data of methylene blue by wood-plastic composite are better described by Langmuir isotherm with R^2 value of 1. This fact that the experiment data is more consistent with the Langmuir equation is due to the homogeneous distribution of active sites on the wood-plastic composite surface, because the Langmuir isotherm is based on the fact that the adsorption surfaces are uniform and methylene blue molecules are adsorbed on the adsorbent surface. There is also a good agreement between the obtained results with the Freundlich isotherm model, but the value of R^2 was higher in the Langmuir model. According to the separation factor (RL) values of 0.09 and 0.1 obtained for 0.5 and 1 g of adsorbent, it can be concluded that the Langmuir isotherm is suitable for the absorption of methylene blue [26, 30].

CONCLUSION

Wood-plastic composites containing high density polyethylene and wood particles were used as adsorbent for the adsorption of methylene blue cation dye from aqueous samples in the batch system. The effect of different parameters including pH, contact time and adsorbent dosage was studied. Based on the results, it was found that with increasing pH, the efficiency of dye adsorption increases. By increasing the contact time, the removal efficiency increases and also, with increasing the amount of adsorbent, the removal efficiency of methylene blue increases. Langmuir and Freundlich isotherm models were used to investigate the adsorption mechanism. According to the results, the methylene blue pigment adsorption mechanism follows the Langmuir monolayer isotherm model and the results of Freundlich isotherm confirm the suitability of the adsorption process. This study will be helpful for further applications in designing adsorbers for the treatment of dye-containing waste discharged by the textile industry.

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