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Removal of Methylene Blue from Waste Stream by Fly Ash-clay-sand Adsorbent

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Abstract: Methylene Blue (MB) adsorption from aqueous solution was investigated. Solid adsorbents were fabricated from charcoal fly ash, clay and fine sand with the proportion of 50, 25 and 25 percent, respectively. Experiments were conducted in a packed column to remove MB from the synthetic wastewater. The generated wastewater contained 4 *mg/l* of MB. The wastewater with flow rates of 18, 35 and 50 *ml/min* was continuously pumped through the column. The effluent samples were collected at a time interval of 2 *min*. It was observed that the amount of adsorption was enhanced as the flow rates were gradually decreased. Langmuir and Freundlich isotherm models of adsorption were investigated to interpret the experimental data. The obtained results revealed that the sorption data were well projected by the Freundlich model. Adsorption model represented by Langmuir isotherm also depicts similar results. Maximum adsorption of 3.88 *mg/g* at the contact time of 8.8 *min* was obtained.

Key words: Adsorption · Methylene blue · Fly ash · Clay · Packed bed

INTRODUCTION

Dyes are organic compounds used as coloring agents in chemical, textile, pulp and paper, printing, cosmetics, leather and food industries [1, 2]. In process of washing and finishing colored products, wastewater contaminated with dyes is generated. The contaminated wastewaters are hazardous which is a great threat to environment [2, 3]. Discharge of hazardous wastewater without further treatment can seriously damage the environment. The colored discharged effluents inhibit penetration of sunlight and oxygen which are crucial requirements of aquatic life [4]. Biodegradation of dyes is not an easy process due to their toxic and complex aromatic structure [5, 6].

Removal of dyes from industrial effluents using physical, chemical or biological processes is considered as basic engineering solution to the related problems [7, 8]. Trickling filter, activated sludge, chemical coagulation and flocculation, oxidation or ozonation, membrane separation, photodegradation and adsorption processes are the most conventional waste treatment technologies [5, 9-11]. However, these processes have their own disadvantages and limitations. They may be costly processes, generate secondary pollutants, unable to treat large quantities of wastes or have poor removal efficiency [12, 13]. Physical adsorption has received considerable attention as an effective method for lowering the concentration of dissolved dyes in waste streams [2, 14]. Adsorption is a suitable physical process for the removal of low concentration of organic colors such as methylene blue (MB). The organic dye accumulates on the surface and texture of solid adsorbents. The system is easily regenerated and desorption may take place with modification of physical and chemical conditions. Porous structure of the adsorbent, chemical nature of the surface and pH of the aqueous solution act as major parameters in adsorption and desorption processes [15, 16].

Numerous approaches have been found in the literature regarding the adsorption of chemical dyes on various adsorbents such as activated carbon [5, 15, 17], clay [18], silica [2, 19, 20], metal hydroxides [21], polymers [22], carbonic matter from agricultural wastes [23-26], alumina [27] and zeolites bed [13, 28]. Among all these potential adsorbents, fly ash and clay have received considerable interest. Fly ash is a waste material originated in great amounts in combustion process and clay is a natural scavenger of water pollutants. They are locally available and also practically in low cost [29].

The objective of the present research was to investigate the adsorption of MB from aqueous phase using a novel adsorbent. The adsorbent was fabricated from charcoal fly ash, clay and fine sand. The new

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adsorbent was experimented in a packed bed column. The ability of the adsorbent to remove dye from the synthetic wastewater was evaluated. Various adsorption isotherm models were investigated to interpret the experimental data. The effect of wastewater flow rate on the color removal efficiency of the adsorption column was also examined. The breakthrough curve for the absorption column was obtained.

MATERIAL AND METHODS

Fly ash was locally obtained from Tonekabon, Iran. It was supplied from burning waste woods. Clay was provided from a ceramic industry, Sophal Tabarestan, Neka, Iran. Fine sand with particle size of 150±50 μm used in the preparation of adsorbents was supplied from Firoozkooh, Iran. A solid mixture of fly ash, clay and sand with proportion of 50, 25 and 25 weight percent was prepared. The mixture was blended thoroughly and uniformly. In preparation of the granulated adsorbents, 10 *ml* of distillated water and 10 *ml* of 5 weight percent poly vinyl alcohol (Merck, Germany) were added to 8 *g* of uniformly mixed solid adsorbent. The paste material was pelletized in a stainless steel cast and compacted in hydraulic press. The pelletized adsorbents were in cylindrical shape. The air dried pellets were placed in furnace (Nobertherm, Germany) and heated to 600°C for 2 hours. Figure 1 shows the fabricated cylindrical pellets applied in the experiments. A scheme of the cast used to form the pellets is shown in Figure 2. The porous and calcined solid cylindrical pellets were packed in a Plexiglas column with internal diameter of 25 *mm* and height of 80 *cm*.

MB (Merck, Germany) with concentration of 4 *mg/l* was used as synthetic wastewater. The generated wastewater was pumped through the column using peristaltic pump (B series peristaltic pump, Italy). Figure 3 shows the bench scale experimental set up used in the adsorption process.

To investigate the effect of flow rates on dye removal efficiency of the adsorption column, several flow rates of 18, 35 and 50 *ml/min* were selected. To adjust the flow rate, a suitable flow meter was used. The effluent samples were collected with respect to time at a time interval of 2 *min*. Standard calibration curve was prepared. The dye concentration was determined using spectrophotometer (Unico, 2100 series, USA) at wavelength of 664 *nm*.

To examine the effect of operation time on adsorption of MB, the system was continuously run for 600 *min*, at flow rate of 18 *ml/min*. Then the system was temporary shut down for 10 hours and after

Fig. 1: The fabricated cylindrical pellets

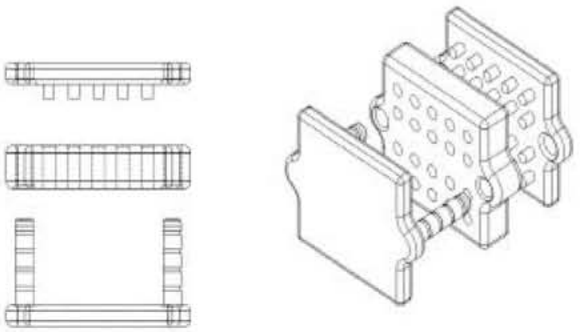

Fig. 2: A scheme of the cast used to shape the adsorbent

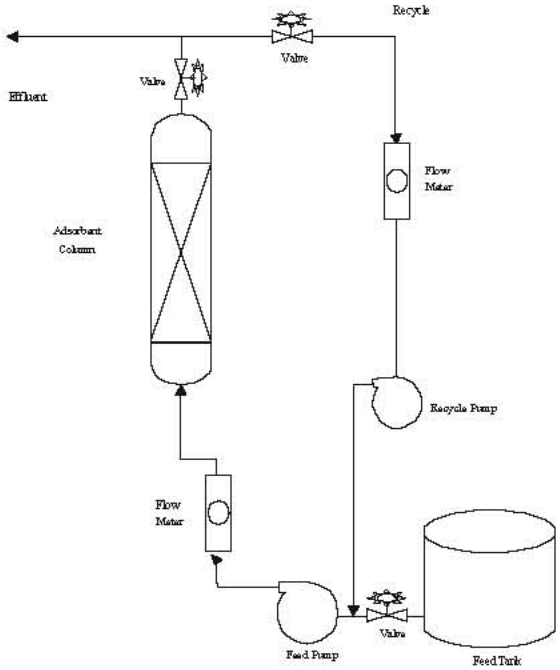

Fig. 3: Schematic diagram of experimental set up in adsorption process

that, the system was run for the second round (600 *min*). Samples were taken from the effluent at a time interval of 15 *min*. The breakthrough curve was obtained. The experimental data were collected and fitted with the adsorption models.

RESULT AND DISCUSSION

Adsorption Isotherms: Adsorption isotherms are used to evaluate the performance of the adsorption process. The adsorption models represent the surface properties and affinity of the adsorbent. Several adsorption isotherms are used to describe the interaction between the adsorbates and adsorbents [4, 5, 26]. In cases where the interaction between the adsorbed solute particles is negligible, Langmuir isotherm is used. This model is valid for monolayer adsorption on a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The linearized equation is given as follows [4, 5]:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Kq_{max}} + \frac{C_{eq}}{q_{max}} \quad (1)$$

where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/l), q_{eq} is the amount of adsorbate adsorbed per mass of adsorbent at equilibrium (mg/g), q_{max} is the maximum adsorption capacity and K is the adsorption equilibrium constant related to the sorption energy between the adsorbate and adsorbent (l/mg).

A plot of C_{eq}/q_{eq} vs C_{eq} leads to a straight line with the slope of $1/q_{max}$ and an intercept of $1/Kq_{max}$.

Freundlich isotherm is another well known adsorption model which represents repulsive interactions between adsorbed solute particles. This empirical model is based on adsorption on a heterogeneous surface representing that binding sites are not equivalent and/or independent. The logarithmic form of Freundlich equation is stated as follows [5, 26]:

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq} \quad (2)$$

where K_f is the adsorption capacity and n is the adsorption intensity. The coefficients of K_f and n are easily obtained by plot of $ln\ q_{eq}$ vs $ln\ C_{eq}$.

The amount of MB adsorbed on the adsorbent at equilibrium was calculated based on following equation:

$$q_{eq} = \frac{(C_0 - C_{eq}).V}{W} \quad (3)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of MB in the solution (mg/l), V is the volume of MB solution (l), W is the weight of the adsorbents (g) and q_{eq} is the amount of adsorbate per mass of the adsorbent (mg/g).

Table 1: Langmuir and Freundlich isotherm parameters for MB adsorption

Langmuir			Freundlich		
q_{max} (mg/g)	K_l (l/mg)	R^2	K_f (mg/g)(l/mg)$^{1/n}$	n	R^2
3.88	0.53	0.9567	1.19	1.41	0.9997

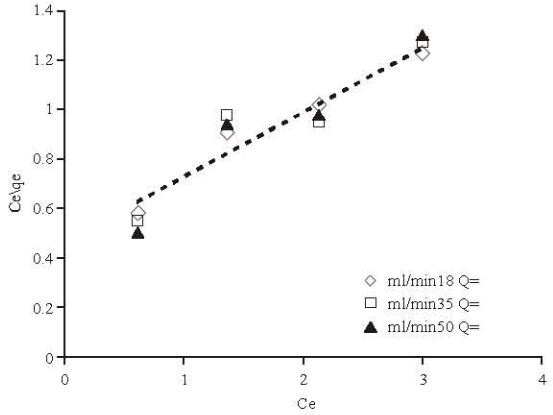

Fig. 4: Langmuir isotherms for MB adsorption

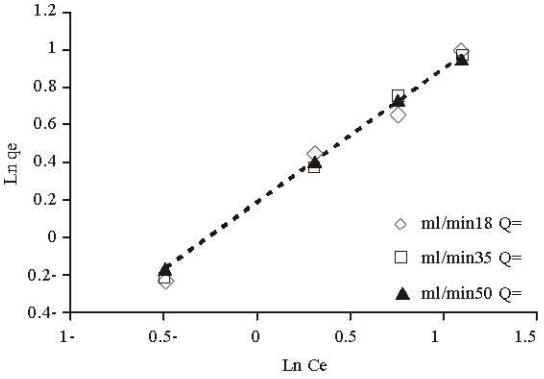

Fig. 5: Freundlich isotherms for MB adsorption

Figures 4 and 5 show Langmuir and Freundlich linearized models applied for the obtained experimental data. The collected data fitted well with the adsorption models. Freundlich model was fitted to the adsorption data slightly better than the Langmuir model with R^2 of 0.99 which represents a heterogeneous surface for adsorption. The constants of the isotherms and the maximum adsorption capacity of the adsorbent are tabulated in Table1. Maximum adsorption capacity of 3.88 mg/g was obtained at the flow rate of 18 ml/min.

Effect of Flow Rate on Adsorption of MB: The effect of flow rate on adsorption of MB from the aqueous solution is shown in Figure 6. It was observed that the adsorption capacity increased as the flow rate was decreased. While the flow rate of the waste stream decreased from 50 to 18 ml/min, the contact time of MB solution with the

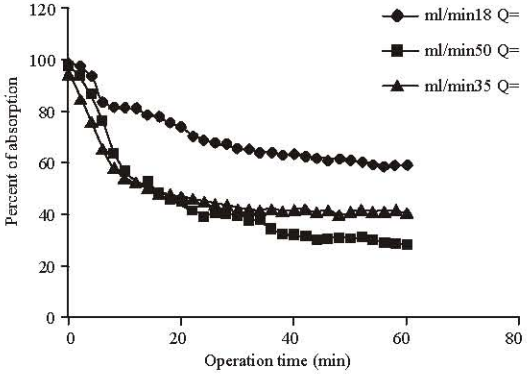

Fig. 6: Effect of flow rate on adsorption of MB

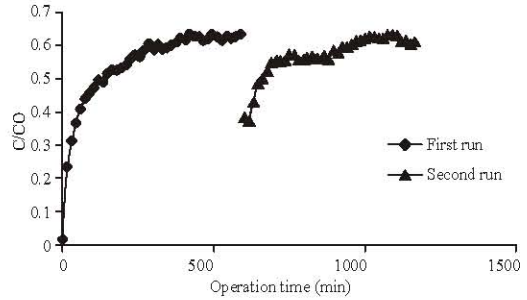

Fig. 7: Breakthrough curve of the continuous adsorption operation

adsorbent from 3.4 to 8.8 *min* increased. Adsorption of MB on the adsorbent needs a relatively long contact time. This is due to the fact that during the adsorption of MB solution, at first the dye molecules reach to the surface of the adsorbent. Then, the dye diffuses into the porous structure of the adsorbent. Hence, decreasing the flow rate of the waste stream and consequently, increasing the contact time, enhanced the dye removal efficiency. Adsorption of MB solution during the first 5 *min* of the operation were 62, 71 and 89 percent for the flow rates of 50, 35 and 18 *ml/min*, respectively. The adsorption at the beginning was high and then after 20-30 *min* of operation, it gradually reduced to a relatively constant value of 45, 47 and 75 percent for the flow rates of 50, 35 and 18 *ml/min*, respectively.

Continuous Adsorption of MB: Breakthrough Curve Development: Figure 7 shows the effect of continuous operation time on adsorption of MB from the aqueous phase. Breakthrough curve showed that during the first 600 *min* of operation with fresh adsorbent, the value of C/C_o reached to 0.65. Although the adsorbents were saturated with MB during the first run, they showed great potential to adsorb significant amount of MB in the second run. As breakthrough curve of the second run depicts, the value of C/C_o reaches from 0.38 to 0.65. This may be due to the interruption of 10 hours between first and second run. During this time, the dye molecules covered the outer surface of the adsorbents had sufficient time to diffuse through the adsorbent. While the system was run for the second round, there were some free binding sites on the surface of the adsorbents to be occupied by MB. Such phenomena had created free binding sites and then the adsorbents interacted with MB in second run as data are presented.

CONCLUSION

Adsorption of MB from aqueous solution using a new fabricated adsorbent was investigated. Results showed that decreasing the flow rate and consequently increasing the contact time, enhanced the adsorption efficiency. It was also concluded that the fabricated adsorbent had heterogeneous surface and inequivalent binding sites as the adsorption data were well fitted with Freundlich adsorption model. For a contact time of 8.8 *min*, maximum adsorption of MB (3.88 *mg/g*) was obtained.

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