

Adsorption of Methylene Blue in Aqueous Phase by Fly Ash, Clay and Walnut Shell as Adsorbents

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Abstract: Methylene Blue (MB) adsorption from aqueous phase was investigated using three types of adsorbents. Granular solid adsorbents were prepared from waste wood fly ash and clay. Experiments were conducted in a batch system for determining sorption equilibria. For continuous process, the adsorbents were packed in a column to remove MB from the synthetic wastewater. The fabricated adsorbents and also pretreated walnut shell were used to compare the performance of the packed adsorbents. The generated wastewater contained 4 mg/l of MB. The wastewater with flow rate of 18 ml/min was continuously pumped through the column using peristaltic pump for removal of dyes from aqueous phase. The effluent samples were collected with respect to time at a time interval of 2 min. The maximum adsorption capacity of clay, fly ash and walnut shell was 7.14, 7.87 and 5.78 mg/g, respectively. Langmuir and Freundlich adsorption isotherms were investigated to interpret the experimental equilibrium data. The obtained results revealed that the sorption data were well described by Freundlich model. Adsorption model represented by Langmuir model also depicted similar results. Results obtained from dynamic study in packed column indicated that the maximum and minimum removal efficiency of 90 and 53% was devoted to walnut shell and clay, respectively.

Key words: Methylene blue • Adsorption model • Clay • Fly ash • Walnut shell

INTRUCTION

Dyes and pigments are used in many industrial processes to colorize the final products. They are widely used in textile, chemical, printing and food industries [1, 2]. The effluents of such industries are highly polluted and usually have high organic content with color pigments. Discharge of the dye effluents to water systems is a major environmental concern due to their toxicity. Dyes usually have complex aromatic structure which makes their biodegradability more difficult. They use the dissolved oxygen required for aquatic life and also inhibit penetration of sunlight into deep water [3, 4]. Hence, treatment of colorful waste streams before their discharge to the environment is essential for safety and assists the bioremediation plans.

Various chemical, physical and biological processes have been implemented to remove dyes from industrial effluents [5]. Some of these conventional waste treatment technologies are: Trickling filter, activated sludge, chemical coagulation and flocculation, oxidation or

ozonation, membrane separation, photodegradation and adsorption processes [6-8]. Among all these waste treatment methods, physical adsorption has attracted considerable attention as an effective technique to remove dye from the effluent streams. Physical adsorption process is cost effective and also simple to operate [2, 9]. 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 [10, 11].

Numerous approaches have been found in the literature regarding the adsorption of chemical dyes on various adsorbents such as activated carbon [6, 10, 12], clay [13], silica [2, 14], metal hydroxides [15], polymers [16], carbonic matter from agricultural wastes [17-19], alumina [20] and zeolites bed [21]. Among all these potential adsorbents, fly ash and clay have received considerable attention. Fly ash is a waste material originated in great amounts in combustion process and clay is a natural scavenger of water pollutants. Walnut shell is also a natural waste material

which is generated from industries dealing with nuts. They are locally available and also practically in low cost [22].

The purpose of present research was removal of MB from an aqueous phase by solid adsorbents. The performance of fly ash, clay and walnut as potential adsorbents to remove dye from waste stream was investigated. Various adsorption isotherm models were experimented to interpret the adsorption data. The coefficients and important parameters of these models were determined.

MATERIALS AND METHODS

Fly ash was locally obtained from workshop (Tonekabon, Iran). It was supplied from burning waste woods. Clay was provided by a ceramic industry, Sophal Tabarestan, Neka, Iran. Fine sands with particle size of $150\pm 50\ \mu\text{m}$ used in the preparation of adsorbents were 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 thoroughly and uniformly blended. In preparation of the granulated adsorbents, 10 ml of distilled water and 10 ml of 5 weight percents poly vinyl alcohol with 99 percent purity (Merck, Germany) were added to 8 g of uniformly mixed solid adsorbent.

Another adsorbent without fly ash was prepared from clay and sand with proportion of 50 and 50 weight percent. The preparation process was similar to previous technique as explained before. The paste material was pelletized in a stainless steel cast and compacted with hydraulic press under a pressure of 10 bars. The pelletized adsorbents were in cylindrical shape. The air dried pellets were placed in a furnace (Nobetherm, Germany) and heated at 600°C for 2 hours. The third type of adsorbent implemented, was pretreated walnut shell. In order to remove the initial brownish color of the shells, they were soaked in a 0.1M NaOH solution, kept for overnight. Then, the shells were boiled in hot water for 2 hours.

In batch experiment, experiments were conducted for each adsorbent in 7 flasks contained 10 ml of synthetic wastewater with a known initial concentration and 3g of adsorbents added to each flask. Samples were collected with respect to time at a time interval of 10 min for duration of one hour. For equilibrium, the last sample data was collected after sufficient contact time (24 h). Standard calibration curve was prepared using the collected data with several MB concentrations (4-18 mg/l).

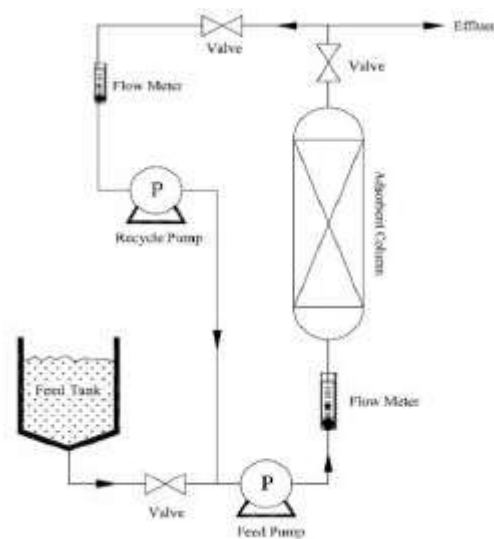


Fig. 1: Schematic diagram of experimental set up for the adsorption process

The dye concentration was determined by spectrophotometer (Unico, 2100 series, USA) at wavelength of 664 nm. The collected data from these experimental runs were incorporated to determine adsorption isotherm models. The amount of MB adsorbed on the adsorbent at equilibrium was calculated based on following relation:

$$q_{eq} = \frac{(C_0 - C_{eq}) \cdot V}{W} \quad (1)$$

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).

To evaluate the performance of the adsorbents to remove MB from the solution, the porous and calcined solid cylindrical pellets were packed separately in a Plexiglas column with internal diameter of 25 mm and height of 80 cm. In a separate experiment the treated walnut shell was packed in the same column for evaluation of its adsorption properties. The schematic diagram of experimental set up is shown in Figure 1.

MB (Merck, Germany) with concentration of 4 mg/l was used as synthetic wastewater. The generated wastewater was pumped through the column using a peristaltic pump (B series peristaltic pump, Italy) at the selected flow rate of 18 ml/min. The effluent samples were collected with respect to time at a time interval of 2 min.

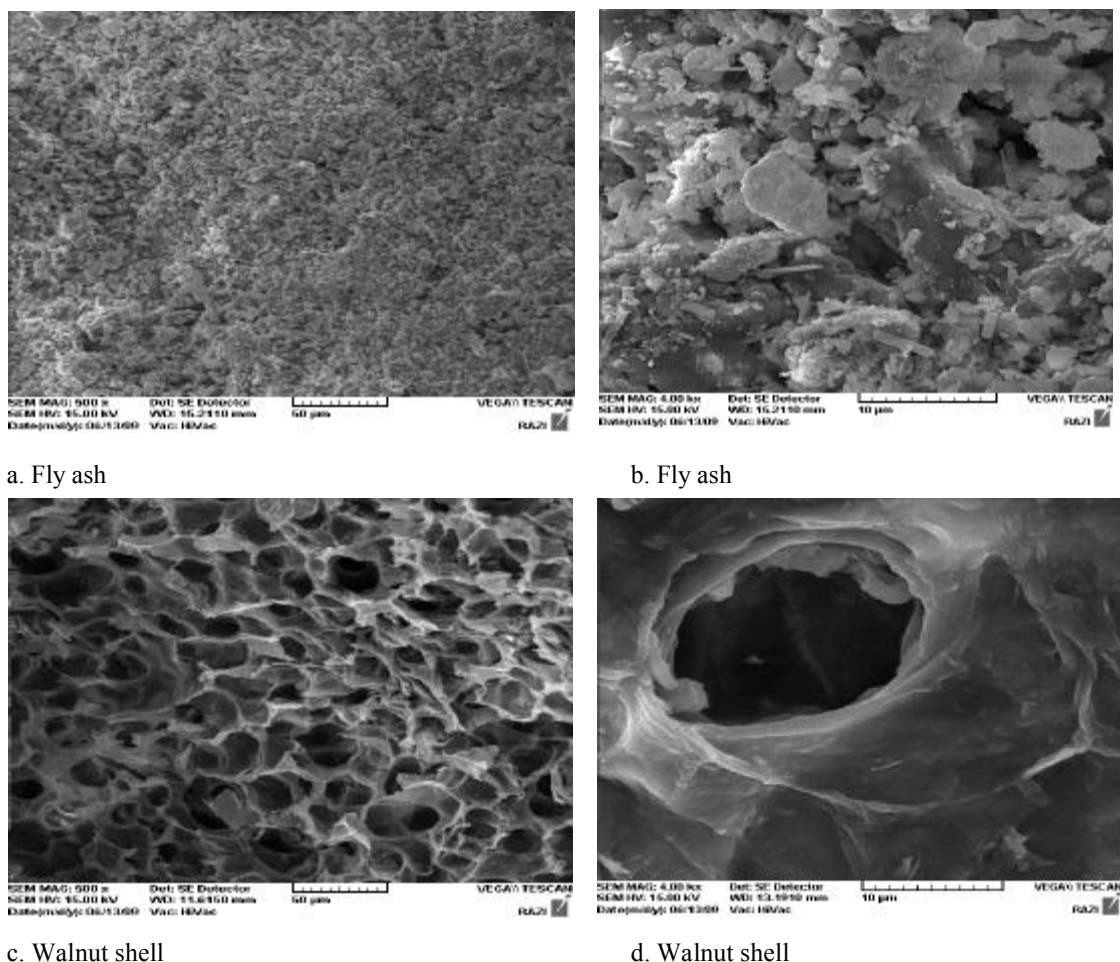


Fig. 2: SEM micrographs of fly ash and treated walnut shell adsorbents

Scanning Electronic Microscope (SEM) was used to observe the interior surface texture of the adsorbents. For the production of conductive films on SEM specimens, the samples were processed through sputtering of Gold / Palladium. The pellet was cut along the length as a half cylinder, vacuum suction was applied and then the sample was coated with Gold layer thickness of 10 nm. The coating device was BAL-TEC, SCD 005 Cool Sputter Coater (Switzerland). The coated sample was scanned with TESCAN Model XMU, VEGA (Czech Republic) with magnification of 30000. Finally, images of the samples were taken under SEM at magnifications of 500 to 4000 and the image had quality of 8192x8192 pixels.

Figure 2 shows the SEM micrographs of fly ash and walnut shell with magnification of 500 and 4000. The inorganic textures with non-uniform shape of particles for fly ash (Figure 2a & b) despite of honeycomb uniform pore size of the treated walnut shell (Figure 2c & d) are obviously demonstrated in the SEM images.

RESULTS AND DISCUSSION

Breakthrough curves were developed for various adsorbents. The role of adsorbent on dye removal efficiency was investigated. Three types of adsorbents were examined. Figure 3 shows the breakthrough curves obtained with various adsorbents. After 60 min of continuous operation, the value of C/C_0 for fly ash reached to a constant value of 0.4. The value of C/C_0 for clay was 0.51 at the beginning of the adsorption process. It was gradually reduced, after 10 min the value has reached to 0.35. After that, the curve has increased to 0.45 and remained nearly constant and then it was stabilized for the rest of the operation. Such behavior may be due to the turbidity caused by the clay texture at the beginning of the process. At first, turbidity created by dissolution of clay, that may increased the color in the waste stream. After a while, dye molecules adsorbed and reached to the surface of the adsorbent,

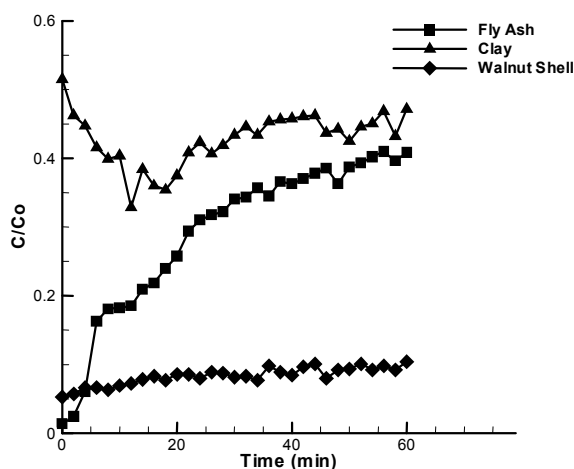


Fig. 3: Breakthrough curves for three types of adsorbents in adsorption process

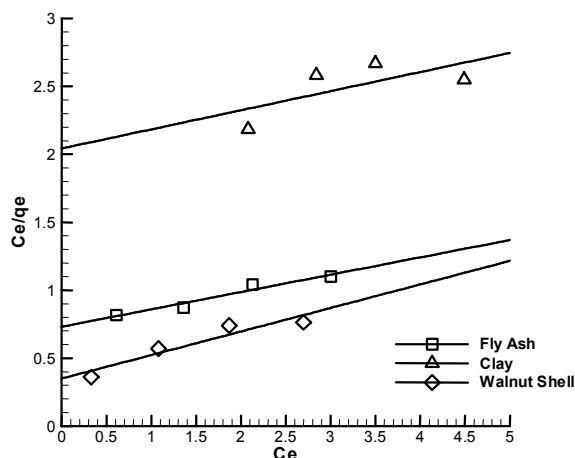


Fig. 4: Linearized Langmuir isotherm model for MB adsorption on various adsorbents

consequently the value of C/C_0 decreased and the breakthrough curve shows normal behavior.

The breakthrough curve for the treated walnut shell as adsorbent is also shown in Figure 3. The value of C/C_0 changed from 0.5 to 0.1 and remained almost constant for the entire operation. The low value of C/C_0 for walnut shell shows the high capacity of this nut shell for adsorption. Thus, the pretreated natural waste material as adsorbent has a fairly good potential to be used for decolorization in the adsorption processes. For operation time of 60 min, adsorption percent of 90, 60 and 53 was obtained for walnut shell, fly ash and clay, respectively. Even, it is a locally available as waste material; the pretreatment walnut shell is only used in small scale plants. Walnut shells may be used for many purposes such as preparation of activated carbon. Fly ash may

have limited use, therefore it is recommended as a new adsorbent instead of activated carbon.

Adsorption isotherms were investigated to evaluate the applicability of the adsorption process for the removal of organic dyes from industrial wastewater. The interactions between the adsorbates and adsorbents have been described by several models for the adsorption isotherms [23]. These adsorption models are used to evaluate the performance of the adsorption process, because they represent the surface properties and affinity of the adsorbent. For the cases where the interaction between the adsorbed solute particles is negligible, Langmuir isotherm is used. This model is valid for monolayer adsorption on a homogenous surface. The linearized equation is given as follows [18, 23]:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Kq_{max}} + \frac{C_{eq}}{q_{max}} \quad (2)$$

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 [18, 23]:

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq} \quad (3)$$

where K_f is the adsorption capacity (mg/g)(l/mg)^{1/n} and n is the adsorption intensity. The coefficients of K_f and n are easily obtained by plot of $\ln q_{eq}$ vs $\ln C_{eq}$.

Figures 4 and 5 show the linearized Langmuir and Freundlich models applied for the obtained experimental data. The collected data were well fitted with Freundlich model with R^2 of 0.995, 0.994 and 0.952 for fly ash, walnut shell and clay, respectively. Langmuir model was also fitted with experimental data, with R^2 of 0.947 and 0.9 for fly ash and walnut shell, respectively. But, this model showed a relatively poor agreement with data obtained for clay; the scattered obtained data points were due to dissolution of clay particles.

Table 1: Langmuir and Freundlich isotherms parameters for MB adsorption

		Clay	Fly ash	Walnut shell
Langmuir	q_{max} (mg/g)	7.143	7.874	5.780
	K_L (l/mg)	0.068	0.174	0.496
	R^2	0.449	0.947	0.900
Freundlich	K_f (mg/g)/(l/mg) ^{1/n}	0.511	1.137	1.809
	n	1.270	1.247	1.600
	R^2	0.952	0.995	0.994

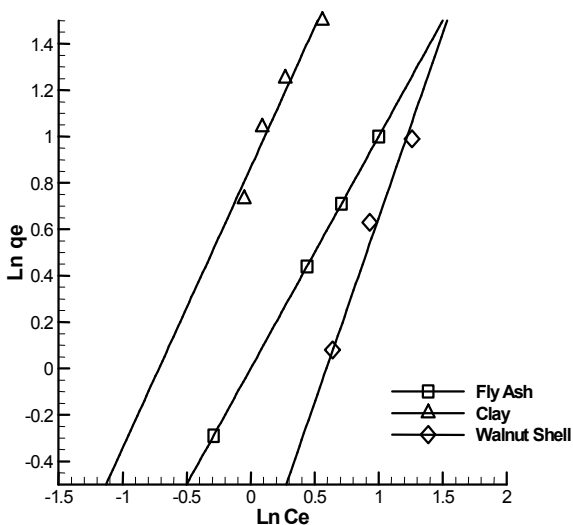


Fig. 5: Linearized Freundlich isotherm model for MB adsorption on various adsorbents

The constants and important parameters of the isotherms are tabulated in Table 1. Maximum adsorption capacity of 7.87 mg/g was obtained using fly ash at the flow rate of 18 ml/min and contact time of 8.8 min. Maximum monolayer adsorption of MB on several sources of granular activated carbon (GAC) is less than granular fly ash adsorption. MB adsorption by GAC from lingocellulosic sources such as almond shell, walnut shell and apricot stones were 1.33, 3.53 and 4.11 mg/g, respectively [18, 19]. MB adsorption by GAC from some other sources was higher than granular fly ash adsorption. The reported adsorption data for GAC originated from hazelnut shell, euphorbia rigida, pistachio shells and sunflower oil cake were 8.82, 114.45 and 129 mg/g, respectively [18, 19].

CONCLUSIONS

Adsorption of MB from aqueous phase using three types of adsorbents was investigated. Results showed that the treated walnut shell had the highest potential to remove dye from wastewater stream. About 90% of MB was removed in a short contact time. It was also

concluded that the adsorbents had heterogeneous surface as the adsorption data were well fitted with Freundlich adsorption model. For a contact time of 8.8 min, maximum adsorption of MB (7.87 mg/g) was obtained using fly ash adsorbents. Based on priorities walnut shell and then fly ash are recommended for the removal of organic dyes from the industrial wastewater.

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