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Removal of Methylene Blue from Aqueous Phase by Pretreated Walnut Shell in a Packed Column

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Abstract: Methylene blue (MB) adsorption from aqueous phase was investigated. Pretreated walnut shell, as adsorbent was used. Experiments were conducted in a batch system for determination of sorption equilibria and then the data were incorporated in a packed column for the removal of MB from synthetic wastewater. The generated wastewater was contained 4 mg/l of MB. The wastewater was pumped through the column with flow rate of 18 ml/min and the effluent samples were collected. The effect of influent MB concentration (4 and 8 mg/l) and pH (5, 7 and 9) of wastewater on removal efficiency of dye were investigated. Langmuir adsorption isotherm model was implemented to interpret the experimental data. The obtained results revealed that the sorption data were well described by Langmuir model at pH value of 9. At contact time of 300 min, maximum equilibrium adsorption of MB uptake 6.7 mg/g adsorbent was achieved.

Key words: Adsorption · Methylene blue · Langmuir isotherm · Walnut shell · Packed column

INTRODUCTION

Dyes and pigments are used in many industries such as printing, textile, chemical and food industries as color additives [1, 2]. In the finishing stages of industries, wastewater that contains dyes and pigments is formed [2, 3]. If dyes flow to rivers and lakes, pollute the natural environment and it is too hazardous for the living creatures and marine aquatic life. Also the dyes and colors cause prevention of sunlight and oxygen to water resources [4]. Natural biodegradation of dyes is not simple because of their aromatic chemical structures [5, 6].

Removal of dyes from industrial effluents may require biological, chemical and physical processes [7, 8]. Trickling filter, activated sludge, chemical coagulation and flocculation, oxidation and ozonation, membrane separation, photodegradation and adsorption processes are the most applicable techniques to eliminate dyes from waste streams [5, 9-11]. Application of these processes involved some constrains such as generation of secondary pollutants, low efficiency or unable to treat large quantities of effluents. In some cases, the process is expensive to operate or requires long time to treat the effluents [12, 13]. Physical adsorption is an efficient and cost effective process to eliminate dyes from waste streams [2, 14]. The specific criterion of organic dyes is deposition of dye molecules on the surface of adsorbents. The porous structure and chemical nature of the adsorbents and also pH of the solution are major parameters involved in the adsorption process [15, 16].

Numerous approaches have been found in the literature regarding the adsorption of dyes on various adsorbents such as activated carbon [5, 15, 17], clay [18-23], silica [2, 24, 25], metal hydroxide [26], polymers [27], carbonic materials from agricultural wastes [28-31], alumina [32], fly ash [33] and zeolite bed [13, 34]. Walnut shell is a natural waste material which is generated from industries dealing with nuts. Walnut shell is locally available and also practically in low costs [35].

The objective of the present research was to investigate the adsorption of MB from aqueous phase using pretreated walnut shell as natural adsorbent. The treat and untreated walnut shells were experimented in a packed column. The ability of adsorbent to remove dye from synthetic wastewater was evaluated.

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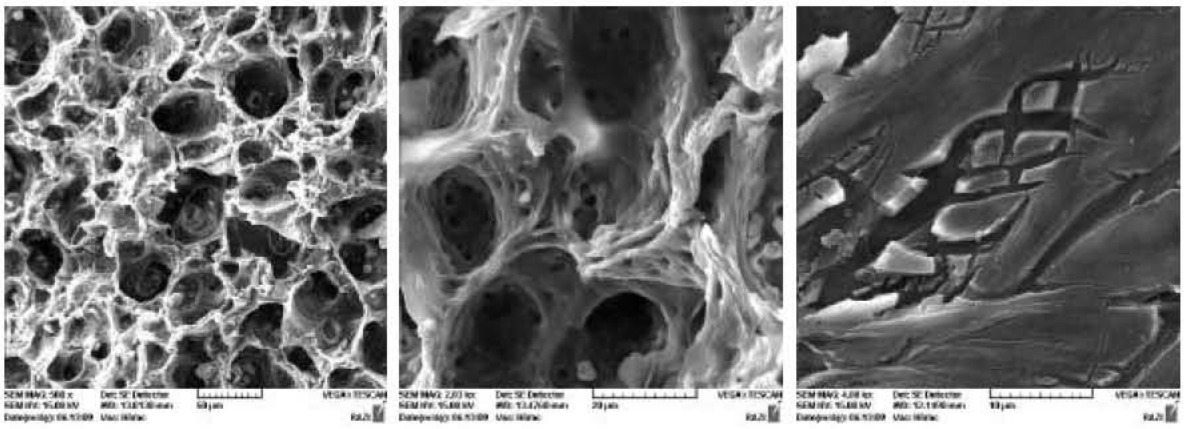
Langmuir isotherm model was used to interpret the experimental data. The effect of dye concentration and pH on color removal efficiency of the adsorption column was investigated.

MATERIALS AND METHODS

Walnut shell was obtained from local market (Tonekabon, Iran). The shells were cracked to size of 0.8-1.5 cm. In order to remove the initial brownish color of the shells, they were overnight soaked in water. The shells were boiled in hot water for 2 hours. Then, the clean shells were pretreated in 0.1M NaOH solution for 20 hours. The soaked and pretreated shells were autoclaved at 121°C, 15psig for 20min washed with distilled water used in the packed column.

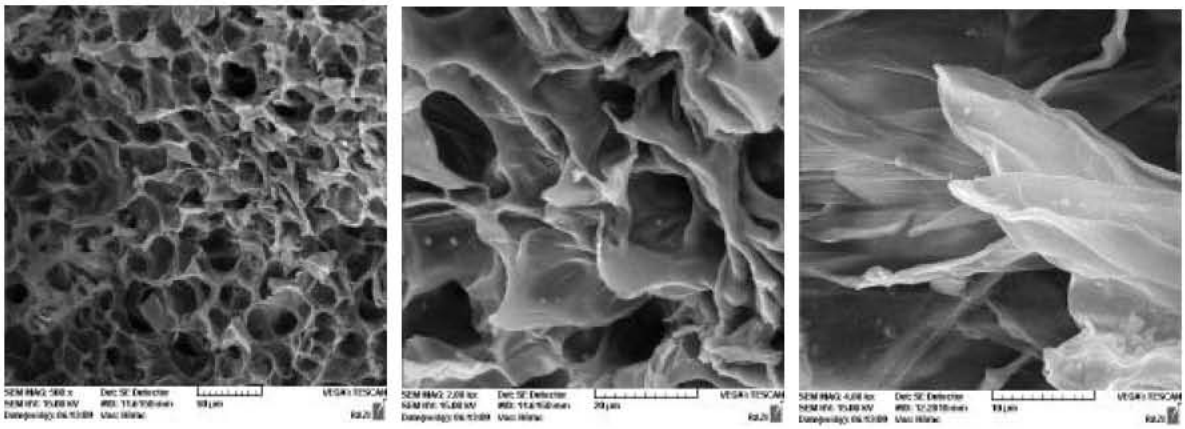
Scanning electron microscope (SEM) was used to observe the interior surface texture of the adsorbents. For the production of conductive films on SEM specimens, the samples were processed through sputtering of Gold / Palladium. The inner and outer surfaces of walnut shell pellet were vacuumed and then the samples were coated with Gold layer thickness of 10 nm using 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 images had quality of 8192x8192 pixels. Figures 1 and 2 show the SEM micrographs of the treated and untreated walnut shells, respectively. The imaged are with magnifications of 500, 2000 and 4000. The treated walnut shell shows more clear and uniform pores. Thus, the treated surface may show more adsorption activities.

In batch system, experiments were conducted for each adsorbent in 11 flasks contained 10 ml of synthetic



(a) (b) (c)

Fig. 1: SEM micrograph of treated walnut shell
a. inside of shell,500x b. inside of shell,2000x c. outside of shell,4000x



(a) (b) (c)

Fig. 2: SEM micrograph of raw walnut shell
a. inside of shell,500x b. inside of shell,2000x c. outside of shell,4000x

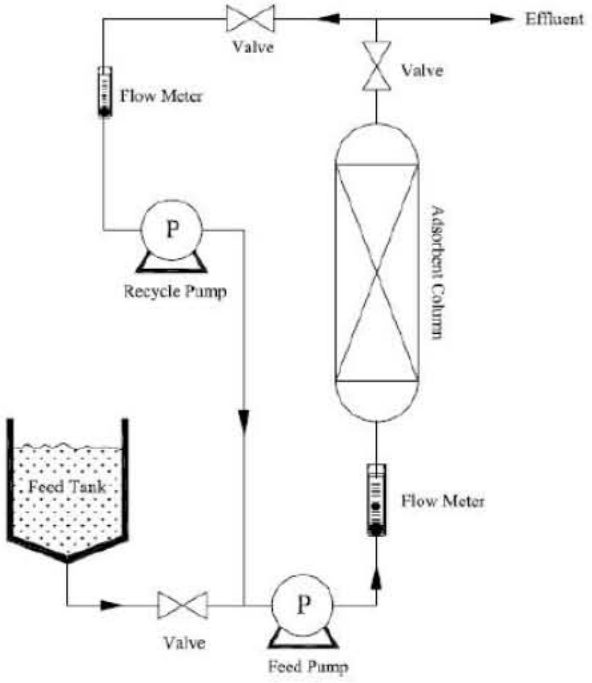


Fig. 3: Schematic diagram of experimental set up in adsorption process

wastewater of MB (Merck, Germany) with a known initial concentration. A 3g of adsorbent were added to each flask. Samples were collected with respect to time at a time interval of 30 min and the last sample was collected for equilibrium after 24h contact time. Standard calibration curve was prepared based on collected data for several MB concentrations. The dye concentration was determined by spectrophotometer (Unico, 2100 series, USA) at wavelength of 664 nm. Similarly, samples from experimental runs were collected for several MB concentrations. The obtained data were incorporated in adsorption model.

Dynamic study was experimented at continuous system. The porous adsorbents were packed in a plexiglas column with internal diameter of 25 mm and height of 80 cm. 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 concentration on dye removal efficiency of the adsorption column, two concentrations of 4 and 8 mg MB/l were selected. The MB solution was pumped through the packed column with a flow rate of 18 ml/min. The effluent samples were collected with respect to time at a time interval of 30 min. The experiments were prolonged for 300 min.

To examine the effect of pH on adsorption of MB, pH meter (Hanna, pH 211, Italy) was used. Three values of pH: 5, 7 and 9 were selected and the experimental run was similar to the previous runs as explained.

RESULTS AND DISCUSSION

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

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

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).

Adsorption Isotherms: 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 adsorbate and adsorbents have been described by several models for the adsorption isotherms [3, 4, 5, 31]. These adsorption models are used to evaluate the performance of the adsorption process, as 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 [3, 31]:

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

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 $1/Kq_{max}$.

Figures 4 shows the linearized Langmuir model applied for the obtained experimental data. The collected data were well fitted with Langmuir model with R^2 of 0.95 for pH of 5, 7 and 9.

The constants and important parameters of the isotherm are tabulated in Table 1. Maximum adsorption capacity of 6.7 mg/g was obtained using pH value of 9 with the flow rate of 18 ml/min and contact time of 300 min.

Table 1: Langmuir isotherm parameters for MB adsorption

pH	q_{max} (mg/g)	K_l (l/mg)	R^2
5	5.77	0.50	0.90
7	6.43	0.52	0.94
9	6.70	0.64	0.95

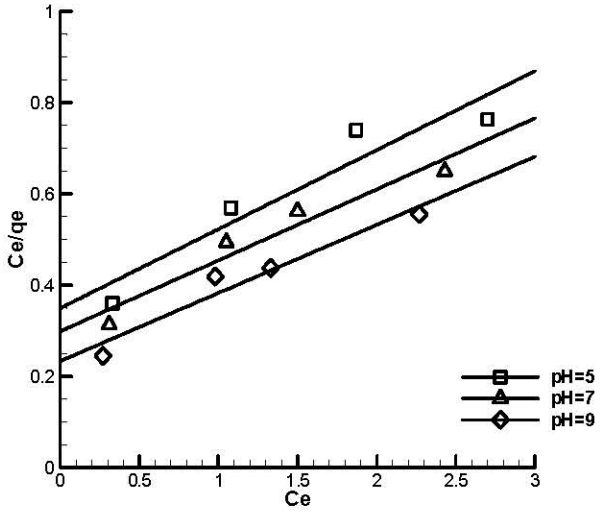


Fig. 4: Langmuir isotherm for MB adsorption with respect to pH of solution

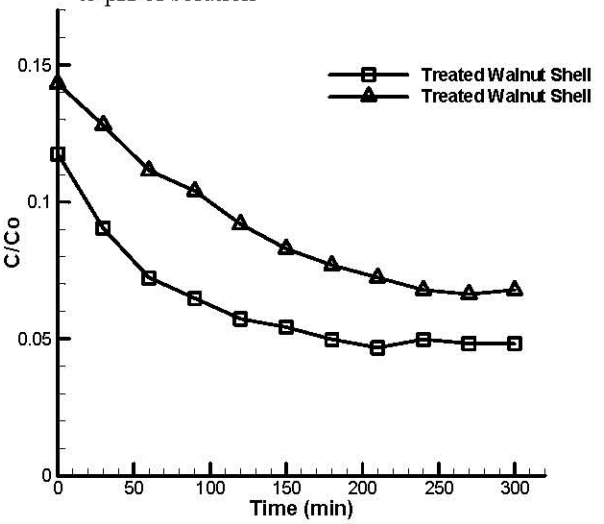


Fig. 5: Effect of pretreatment of adsorbent on adsorption of MB

Effect of Pretreatment of Adsorbent on Adsorption of MB: The effect of pretreatment of adsorbent on adsorption of MB is shown in Figure 5. It was observed that the adsorption capacity increased with the pretreated shells. Pretreatment made the shell to be more porous media. These shells had more specific surface than untreated shells. This is due to the fact that during the adsorption of MB solution, at first the dye molecules

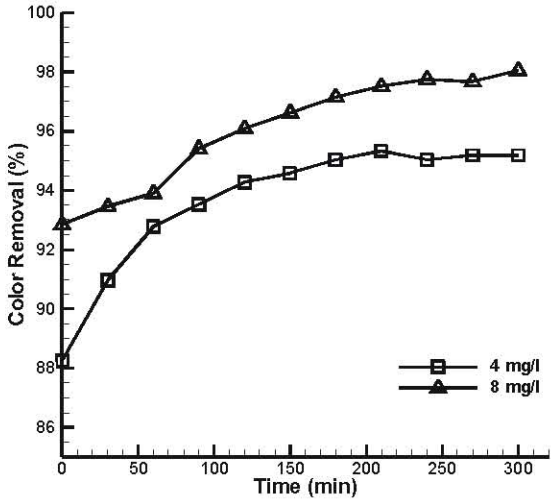


Fig. 6: Efficiency of MB removal from the solution with various initial concentrations

reach and interact with the surface of adsorbent. Then, the dye diffuses into the porous structure of the adsorbent. Hence, pretreatment increased the surface activities and dyes are adsorbed to the surface of adsorbents which enhanced the dye removal efficiency. After 60min operation, the adsorptions of MB solutions for the untreated and pretreated walnut shells were 89 and 93 percent, respectively. The adsorption at the beginning was high (86 and 88 percent for untreated and pretreated shells) but that was increased with an increase in contact time to 93 and 95 percent, respectively. After 200 min of operation, adsorbents were saturated with MB and the efficiency significantly dropped.

Effect of Initial Concentration on Adsorption of MB: Continuous adsorption of MB was conducted while the initial dye concentration in the wastewater was varied. Two different samples with concentration of 4 and 8 mg/l were prepared to perform the experiments. The wastewater was continuously fed into the column at fixed flow rate of 18 ml/min. The effluent samples were collected with respect to time. The amount of dye removed from the wastewater was collected based on following equation:

$$\text{MB Removal Efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (4)$$

The dye removal efficiency at various MB concentrations and flow rate of 18 ml/min is illustrated in Figure 6. It was observed that after 180 min of operation, the dye removal efficiency has reached to 95 and 97 percent for effluent MB concentration of 4 and 8 mg/l,

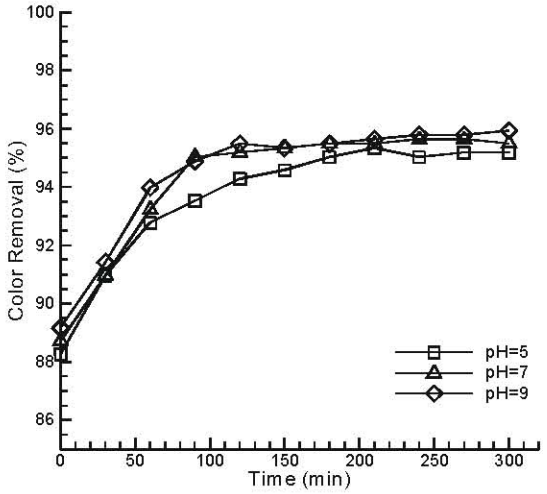


Fig. 7: Efficiency of removal MB with respect to pH of the solution

respectively. Although, there were great driving forces for dye molecules to bind on the active sites of adsorbents that were probably due to concentration gradient exists on multi layer diffusions from the bulk of liquids to the surface of adsorbents. After about 240 min of adsorption operation, the adsorbents were saturated with the dye.

Effect of pH on Adsorption of MB: In another set of experiments, pH of the MB solution was varied; the values of pH for the wastewater were 5, 7 and 9. Diluted NaOH and HCl solutions were used to adjust the pH of the solution. The synthetic wastewater at the selected flow rate of 18 ml/min and concentration of 4 mg/l was pumped through the column, while the pH was varied for each set of experiment. The effluent samples were collected and the pH of the solution was determined by the pH meter.

Figure 7 demonstrates the dye removal efficiency as pH of the wastewater with influent solution of MB with concentration of 4 mg/l and the flow rate was set at 18 ml/min. The achieved results showed that after 300 min of continuous operation, the MB removal efficiency was slightly enhanced to 95.1, 95.5 and 96 as the pH of wastewater was raised from 5 to 7 and then to 9, respectively. It is known that ionic dyes release colored anions or cations while the dye was dissolving in a solution. The amount of dyes adsorbed on the adsorbent surface was mainly influenced by the surface charges, which is in turn affected by the pH of solution. In this experiment, low variation on removal efficiency of several pH, was related to the neutral surface of walnut shell. Lower adsorption of MB at acidic pH was probably due to the presence of excess proton (H^+) ions which is competed with the cationic dye for adsorption on negatively charged surface of the adsorbent.

CONCLUSION

Adsorption of MB from the wastewater using the pretreated natural adsorbent was investigated. The equilibrium data were incorporated in a Langmuir adsorption isotherm model. The obtained experimental data were well fitted with Langmuir isotherm, particularly for the wastewater samples at alkaline pH. The dye solution with pH of 9, had maximum equilibrium adsorption of MB uptake of 6.70 mg/g of the pretreated adsorbent. Based on data presented by this research, the pretreated walnut shell is recommended for the removal of organic dyes from industrial wastewater. Application of treated adsorbent for organic dye removal was more effective for the wastewater at alkaline pH.

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