J. Iran. Chem. Soc., Vol. 7, No. 2, June 2010, pp. 339-350.

JOURNAL OF THE
Iranian
Chemical Society

Removal of Basic Dye Methylene Blue from Aqueous Solutions Using Sawdust and Sawdust Coated with Polypyrrole

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(Received 25 October 2008, Accepted 11 June 2009)

This research deals with the application of wood sawdust obtained from walnut and its polypyrrole (PPy) coated form for the removal of methylene blue (MB) from aqueous solutions. MB, a typical cationic dye, was used as a test probe. Coating of sawdust was carried out chemically *via* direct addition of chemical oxidant ($FeCl_3$) on the sawdust which was previously soaked in monomer solution (0.2 M pyrrole). Adsorption experiments were carried out using both batch and fixed bed column systems. The effects of different system variables such as adsorbent dose, initial dye concentration, pH of test solution, contact time and breakthrough curves were studied. In order to find out the possibility of reuse, desorption study was also carried out in this investigation. It was found that both SD and PPy/SD are efficient and cost-effective adsorbents for the removal of MB dye from aqueous solutions. The collected data in this research indicate that compared with PPy/SD, adsorption of MB by SD is not a very pH dependent process, at least from pH 4 to 10. Higher sorption percentage of MB is obtained for PPy/SD at alkaline pHs.

Keywords: Polypyrrole, Methylene blue, Sawdust, Adsorption, Desorption

INTRODUCTION

Dyes have long been used in dyeing paper and pulp, textiles, plastics, leather, cosmetics and food industries [1]. Colorstuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem [2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade [3]. Some dyes are reported to cause allergy, dermatitis, skin irritation, cancer and mutations in humans [4]. Thus, the removal of dyes from effluents before they are mixed up with unpolluted natural water bodies is important.

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There are various conventional methods for removing dyes. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost, simple design and easy operation, less energy intensiveness, non-toxic, and superior removal of organic waste constituents as compared with the conventional biological treatment processes [5]. The advantages and disadvantages of some methods of dye removal from wastewaters are given in Table 1. MB is a common pollutant material in textile wastewater and is frequently used in dye houses and textile industries. The removal of MB from aqueous solutions using low-cost materials (*e.g.* agricultural wastes) has been investigated by some other researchers [6,7].

Conducting polymers such as PPy and its derivatives have attracted a great deal of attention in recent years due to their interesting electrical conductivity and electroactivity [8-11]. The electroactive nature or the switching properties of PPy

Table 1. Advantages and Disadvantages of Some Methods of Dye Removal from Wastewaters

Physical/chemical methods	Advantages	Disadvantages
Fenton's reagent adsorption [12]	- Effective decolorization - Removal of a wide range of dyes - No sludge generation	- Sludge generation - Absorbent require disposal
Photochemical oxidation [13]	- Rapid process - Good sorption capacity for dyes	- Formation of byproducts - High energy costs
Cucurbituril [14]	- Non-hazardous end products - Highly effective for various dyes	- High cost
Electrochemical [15]	- Effective for basic dyes	- High cost of electricity
Activated carbon [16]	- Removes all dyes - No adsorbent loss	- Very expensive
Silica gel [17]	- Effective decolorization	- Side reactions in effluent - Concentrated sludge production
Membrane technologies [18]	- Environmentally friendly	- Not effective for all dyes
Ion exchange [19]	- Low cost - Good regeneratability	- Less efficient for column or flow adsorption systems
Sawdust (current study)	- Possible recovery of dye - No sludge generation - Effective decolorization - Good sorption capacity for MB	- Poor regeneratability
Coated sawdust by PPy (current study)	- No sludge generation - Effective in both batch and flow systems	- Adsorbent requires disposal

have been utilized as the basis of most proposed applications such as sensors, separation devices, rechargeable batteries, anticorrosion and controlled drug-release [20-24]. Nearly all of the previously reported applications of these conjugated conducting electroactive polymers (*e.g.* separation and sensors) are mostly based on their electrical conductivity and electroactivity which have been used under applied potential or current in an electrochemical cell. Moreover, we have previously reported that these polymeric materials can be used for electroless removal of some heavy metal ions from aqueous solutions with high performance [25-27].

This paper deals with the investigation of another possible application of polypyrrole for the removal of dyes from aqueous solutions. MB as a typical basic textile dye was selected as a test probe. In this study PPy was synthesized from aqueous solution directly on the surface of the sawdust via chemical route at room temperature. Sawdust (SD) and sawdust coated with polypyrrole (PPy/SD) were then used for the removal of MB from aqueous solutions. The sorption capacities of the two selected adsorbents (SD and PPy/SD) were compared.

EXPERIMENTAL

Materials and Equipment

All chemicals used were analytical reagents grade and prepared in distilled water. Pyrrole was obtained from Merck and distilled before use. Sawdust samples (SD) from walnut were obtained from a local carpentry workshop. A solution of 100 mg l^{-1} MB [3,7-bis (dimethylamino) phenothiazin-5-ium ion] (MW = 319.65 g mol^{-1}) was prepared in distilled water as the stock solution. MB shows an intense absorption peak in the visible region at 660 nm. This wavelength corresponds to the maximum absorption peak of the methylene blue monomer. The pH adjustments were made using dilute NaOH and HCl solutions. A single beam Perkin-Elmer UV-Vis spectrophotometer with a 1 cm cell was used for measuring all the absorption data. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for pH measurements.

Determination of Methylene Blue (MB)

Concentrations of methylene blue (MB) in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of the dye (λ_{max} = 660 nm) using the calibration curve shown in Fig. 1. The calibration curve of absorbance against MB concentration was obtained by using standard MB solutions at pH 6. The calibration curve shows that beer's law ($A = \varepsilon bc$) is observed in concentration range (0.0-2.5 mg l^{-1}). The experimental data reported in Fig. 1 were fitted by a straight line with a high regression coefficient value ($r^2 = 0.999$).

Preparation of the Adsorbent

Pyrrole (Merck) was distilled before polymerization. Polymerization was carried out in aqueous solution. In order to prepare polymer coated sawdust (PPy/SD), 5.0 g sawdust (35-50 mesh, 10% humidity) was immersed in 50 ml of 0.20 M freshly distilled pyrrole solution for 12 h before polymerization. The excess of the monomer solution was removed by simple decantation. 50 ml of 0.5 M $FeCl_3$ as the oxidant solution was added into the mixture gradually, and the reaction was allowed to continue for 4 h at room temperature. The polymer coated sawdust (PPy/SD) was filtered, washed with distilled water, dried in an oven at 55-60 °C and sieved before use. The coating percentage of PPy onto sawdust was determined by weight differences of the dried sawdust before and after coating was ~5%.

Adsorption Experiments

Batch mode studies were conducted using 0.2 to 1.0 g of the adsorbents, taken separately. Each adsorbent was shaken in 50 ml aqueous solution of MB of varying concentrations (20-100 mg l^{-1}) at room temperature for definite time periods. At the end of the pre-determined time intervals, the adsorbent was removed by simple filtration. The filtrates were analyzed for the residual (unadsorbed) MB, spectrophotometrically. All the experiments were carried out in triplicate at each condition whose mean values are presented. The maximum RSD was less than 1%.

In column experiments for preparing breakthrough curves, a glass column with 1.0 cm diameter and 15 cm height was employed. 1.0 g of the PPy/SD sorbent was packed into the column (bed volume ~5 cm^3). Dye solution (MB) was passed through the column at a flow rate of 3 ml min^{-1} at room temperature (25 ± 2 °C). The outlet solution was analyzed for

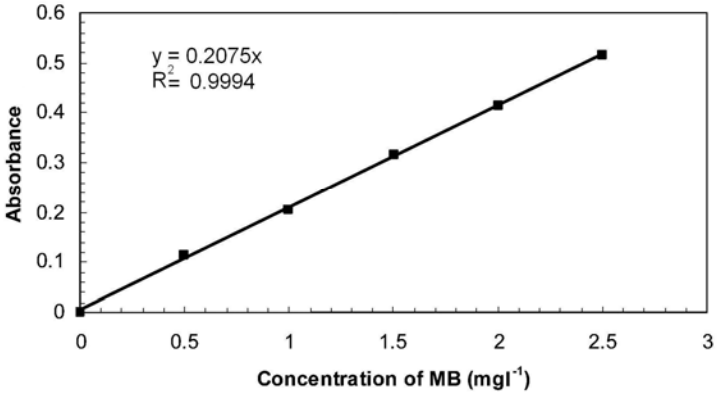

Fig. 1. Calibration curve of absorbance against concentration of methylene blue.

the residual MB. The following equations (Eqs. 1, 2) were used to calculate the percentage of sorption (removal percentage) and the amount of adsorbed MB, respectively:

$$\%\text{Sorption} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$\frac{x}{m_1} = \frac{(C_o - C_e)V_1}{m_1} \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of MB, respectively (mg l^{-1}), m_1 is the weight of the adsorbent (g), x/m_1 is the amount of MB adsorbed onto unit amount of the adsorbent (mg g^{-1}) at equilibrium, and V_1 is the volume of the test solution used in the adsorption experiment (L). Alternatively, regeneration of the used adsorbent was also examined (Eqs. 3, 4).

$$\%\text{Desorption} = \frac{m_2}{m_o} \times 100 \quad (3)$$

$$m_o = (C_o - C_e)V_2 \quad \text{and} \quad m_2 = C_e \times V_2 \quad (4)$$

where m_o is mg of MB sorbed onto the adsorbent, m_2 is mg of MB in the regenerated solution; V_2 is the volume of eluent solution (L). C_o and C_e have the same definitions as above. The effect of some other important factors such as the sorbent dosage, contact time and pH of the solution was also investigated in batch system.

RESULTS AND DISCUSSION

Sorption of MB by SD and PPy/SD in Batch System

A series of experiments was performed to optimize the adsorption conditions for the removal of MB dye using the treated and untreated sawdust. The pH of an aqueous medium is an important factor that may influence the uptake of the many adsorbates such as dyes, so the influence of pH on dye adsorption by the selected adsorbents was studied first.

Effect of pH. In order to find out the effect of pH, 1.0 g of the dried PPy/SD and SD sorbents were treated separately with 50 ml of 50 mg l^{-1} MB at various pH values (from 2 to 12). The pH solution was adjusted in the range of 2-12 by adding dilute HCl or NaOH solutions as required. The results obtained have been summarized in Table 2.

An initial pH in the range of 6-12 was found to be favorable for the MB dye removal by both the adsorbents. It was also noted that increasing solution pH increases the extent of dye removal. Lower adsorption percentage of MB on SD or PPy/SD at highly acidic conditions (pH ≤ 2) is probably due to

Table 2. Effect of Solution pH on Adsorption Percentage of MB by SD and PPy/SD

pH	2	4	6	8	10	12
SD	65.3	98.5	98.6	98.6	99.0	94.4
PPy/SD	50.0	56.0	96.8	98.2	98.3	98.5

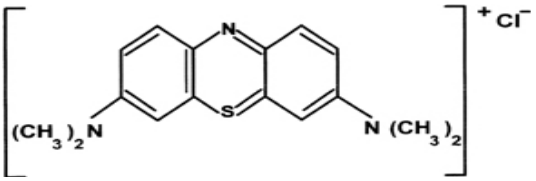

Fig. 2. Chemical structure of methylene blue.

the presence of high concentration of H^+ ions on the surface of adsorbent competing with methylene blue (a cationic dye) for adsorption sites in the adsorbent (Fig. 2). With an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of adsorbent is lowered and consequently the removal efficiency is increased. Adsorption of MB by sawdust could be mainly due to the strong interactions (such as H-bonding) between MB dye molecules and various functional groups (*e.g.* hydroxyl, carbonyl and carboxyl) present in the cellulosic and non-cellulosic (*e.g.* lignin) constituents of sawdust.

Effect of adsorbent dose. To investigate the effect of adsorbent mass on the adsorption of methylene blue dye, a series of adsorption experiments were carried out with different adsorbent dosages (0.20-1.0 g). In order to differentiate the sorption capacity of the employed adsorbents, we chose 100 ml of 50 mg l^{-1} MB solution as test probe in this investigation. Adsorption experiments for uncoated sawdust were carried out at pH 6 (the natural pH of MB solution) and for PPy/SD, the experiments were performed at pH 12. The results obtained have been summarized in Table 3.

The results indicate the expected pattern, in which the percentage sorption increased as the sorbent dose was increased over the range 0.2-1.0 g. This is a result of increased surface area and availability of more adsorption sites. However, no increase in the amount of dye adsorption was observed with increasing the adsorbent dosage above 0.2 g. As the data show (Table 3), PPy/SD is a more efficient adsorbent for the removal of MB from aquatic solutions than the uncoated SD. Of the two adsorbents used in this study, PPy/SD allowed for the greater removal at all levels of the adsorbent dose.

Effect of initial concentration. In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 20 to 100 mg l^{-1}. To perform this experiment, fixed amounts (0.25 g) of SD and PPy/SD adsorbents were treated with 100 ml of 20-100 mg l^{-1} of MB solution at pH 6,12, respectively. The period of contact time was 30 min accompanied by a mild mechanical shaking at room temperature. The results obtained are summarized in Table 4.

Results from this study show that the adsorption process is highly dependent on the initial concentration of the dye in

Table 3. Effect of Amount of Adsorbent on Removal Percentage of MB by SD and PPy/SD

Dosage (g)	0.2	0.4	0.6	0.8	1.0
SD	56.0	63.0	67.1	69.2	71.5
PPy/SD	90.0	93.0	94.5	96.2	97.4

Table 4. Effect of Initial MB Concentration on Its Sorption Percentage onto SD and PPy/SD

Adsorbent	C_o (mg l^{-1}) MB				
	20	40	60	80	100
SD (pH = 6)	84.0	71.2	55.3	44.1	40.0
x/m (mg g^{-1}) (SD)	6.7	11.4	13.2	14.1	18.8
PPy/SD (pH = 12)	99.7	98.0	92.0	88.6	82.0
x/m (mg g^{-1}) (PPy/SD)	8.0	15.8	23.1	30.0	33.2

solution and %removal of MB decreases as its initial concentration increases. However, the total amount of dye (x/m) uptake is increased gradually. As the data clearly show sorption capacity of polymer coated sawdust (PPy/SD) is considerably higher than uncoated sawdust especially at higher initial concentrations of the dye.

Effect of contact time. The effect of period of contact on the removal of MB by the adsorbents was determined by keeping other conditions (particle size, initial concentration, dosage and pH) constant at the optimum. The effect of contact time was investigated by treating 0.25 g of the adsorbents PPy/SD and SD with 100 ml of 50 mg l^{-1} MB solution at pH value of pH 6 for SD and 12 for PPy/SD. The mixture was agitated in a mechanical shaker for different periods of contact time (10-60 min). The results obtained are summarized in Table 5. It was observed that the rate of removal of MB dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material. As the data show the sorption process was rapid for the first 20 min for SD and the first 10 min for PPy/SD. Again, PPy/SD afforded a rapid uptake and greater removal at all periods of contact compared to SD which accorded well with the findings of our previous research presented in this paper.

Adsorption isotherms. The equilibrium adsorption isotherms are of fundamental importance in the design of any adsorption system. In this study Langmuir and Freundlich isotherms were employed for the treatments of the equilibrium adsorption data [28-30]. The Langmuir adsorption isotherm is the best known linear model for monolayer adsorption and most frequently utilized to determine the adsorption parameters. Longmuir model is represented by the following equations:

$$q_e = \frac{K_L C_e}{1 + bC_e} = \frac{Q_o b C_e}{1 + bC_e} \qquad \text{(Nonlinear form)} \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o}\right) C_e \qquad \text{(Linearized form)} \qquad (6)$$

where q_e is the amount sorbate adsorbed per unit mass of adsorbent (mg g^{-1}), Q_o is the maximum amount sorbed (mg g^{-1}) when the monolayer is complete, b is Langmuir's constant related to the affinity of binding sites and is a measure of the energy of adsorption (l mg $^{-1}$). A linearized plot of C_e/q_e against C_e gives Q_0 and b values. Values of Q_0 and b were calculated from the slopes (1/ Q_0) and intercept ($1/bQ_0$) of the linear plots.

The Langmuir model deals with monolayer adsorption and constant adsorption energy. Another widely used equation in adsorption processes is the Freundlich equation [29]. The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. The model is represented by the following equations:

$$q_e = \frac{x}{m} = K C_e^{\frac{1}{n}} \qquad \text{(Nonlinear form)} \qquad (7)$$

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \qquad \text{(Linear form)} \qquad (8)$$

where, as defined previously, x/m is the equilibrium adsorption capacity (mg g^{-1}), C_e is the equilibrium or residual concentration (mg l^{-1}) of MB dye in solution, and K and $1/n$ are empirical Freundlich constants indicating sorption capacity of adsorbent and intensity of adsorption (mg g^{-1}), respectively. The Langmuir model assumes monolayer surface coverage on equivalent sites, the Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available.

The plot of C_e/q_e against C_e in Fig. 3 gave straight lines for all the concentrations which implies that the adsorption for

Table 5. Effect of Contact Time on the Removal of MB by SD and PPy/SD

Time (min)	10	20	30	40	50	60
SD	40.0	60.0	64.0	66.0	66.4	67.0
PPy/SD	96.5	97.0	97.2	97.3	97.5	97.6

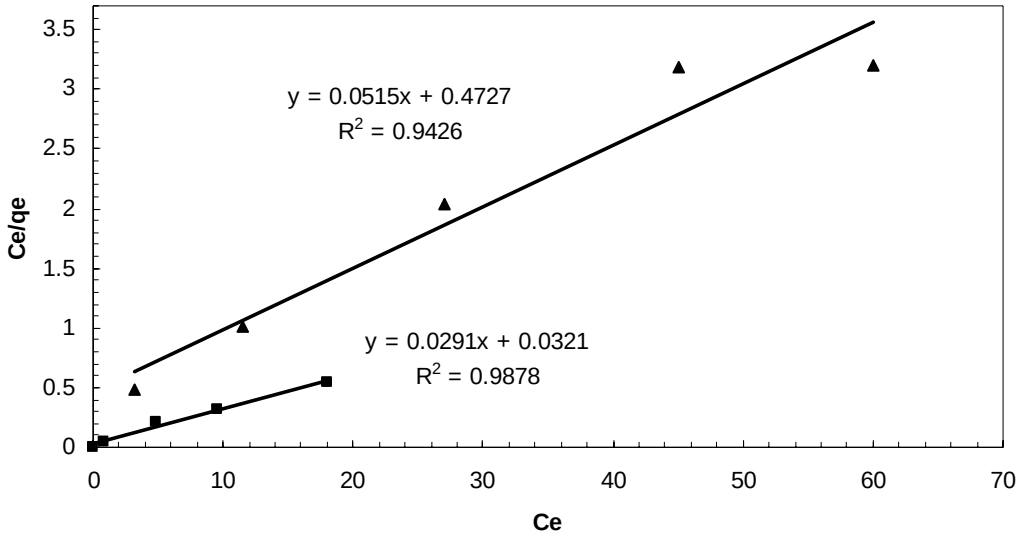

Fig. 3. Langmuir adsorption isotherms for the sorption of MB by PPy/SD (■) and SD (▲).

both adsorbents fitted well to Langmuir isotherm. The high correlation coefficient obtained for PPy/SD (R^2 = 0.9878) indicates high affinity between adsorbent surface and MB which plays the major role in the adsorption mechanism. The Freundlich isotherm (linear forms) obtained for the two adsorbents employed in this research are shown in Fig. 4. Based on the high correlation coefficient obtained for SD (R^2 = 0.9964), it could be concluded that the adsorption isotherm of methylene blue using SD gives a better fit to the Freundlich model.

On the basis of slopes and intercepts of the straight lines, Langmuir and Freundlich constants derived from these straight lines are presented in Table 6. The values of n obtained for PPy/SD and PAni/SD indicate (Table 6) that both SD and PPy/SD are good adsorbents for uptake of MB dye from aqueous solutions. For a suitable sorbent/adsorbate system, the value of n is normally between 2 and 10 [24]. The higher adsorption capacity (Q_o), b and K_L ($Q_o b$) values obtained for PPy/SD indicate a higher sorption capacity and superior performance of PPy/SD adsorbent for MB adsorption from aqueous solution compared to untreated SD (Table 6).

The essential characteristics of Langmuir isotherms may be expressed by a dimensionless constant, named parameter of equilibrium, R_L. The dimensionless separation factor R_L tells the favorability and the shape of the adsorption isotherms by applying the following equation [31]:

$$R_L = 1/ (1 + bC_o) \quad (9)$$

where b signifies the Langmuir constant (l mg^{-1}) and C_o is the initial concentration of the adsorbate (mg l^{-1}). $R_L > 1$ means unfavorable isotherm, $R_L = 1$ means linear isotherm, R_L = 0-1 means favorable isotherm and $R_L = 0$ means irreversible isotherm. In this study, the R_L values were found to be 0.091 to 0.333 (for SD) and 0.011 to 0.052 (for PPy/SD) for concentration ranges of 20-100 mg l^{-1} MB dye. The R_L values obtained are less than unity, confirming that adsorption process is favored in both the cases as well as applicability of Langmuir isotherm.

Adsorption Study Using Column System

Effect of pH. Sorption isotherms which are obtained from batch study do not give an accurate scale-up data for industrial treatment systems since sorption in a column is not normally in a state of equilibrium. Consequently, there is a need to perform flow tests and plot breakthrough curves in order to evaluate the performance of an adsorbent. To this end, 1.0 g of SD or PPy/SD was packed into a glass column, and then 50 mg l^{-1} of MB solution at their optimal pH values (6 and 12 as already reported), was passed through the column at a constant

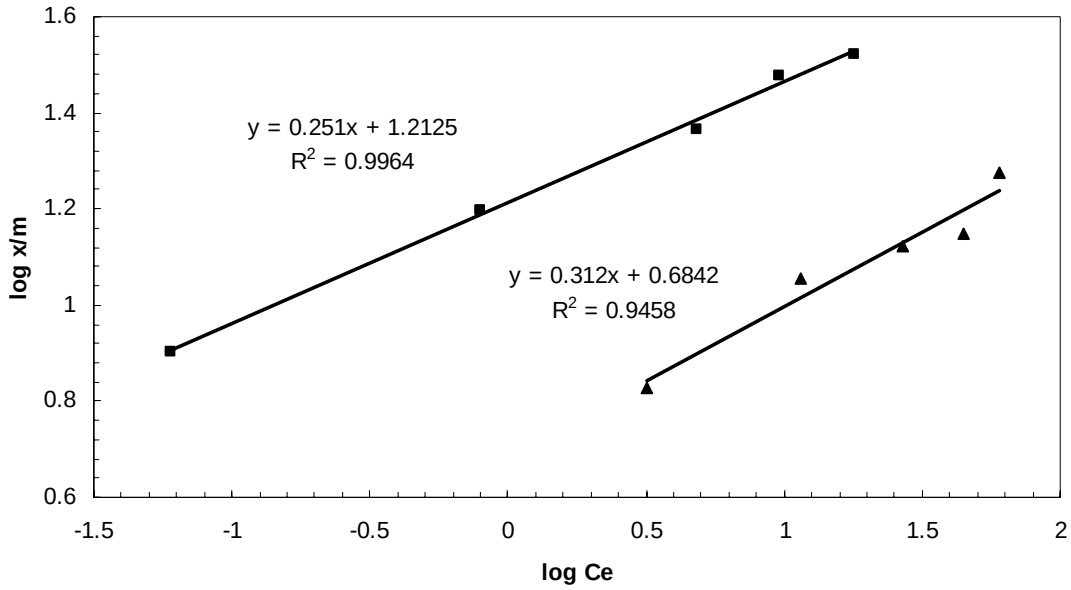

Fig. 4. Freundlich isotherms for the sorption of MB by SD (■) and PPy/SD (▲).

Table 6. Freundlich and Longmuir Isotherms Constants for MB Adsorption onto SD and PPy/SD Using Batch System

Adsorbent	1/*n*	*n*	K_F	*b* (l mg^{-1})	Q_o (mg g^{-1})	K_L (l g^{-1})	R^2 (Langmuir)	R^2 (Freundlich)
SD	0.31	3.2	16.3	0.10	19.41	1.94	0.9426	0.9964
PPy/SD	0.25	4.0	4.8	0.90	34.36	38.2	0.9878	0.9458

flow rate of 3 ml min^{-1}. Sample solutions were withdrawn at predetermined time intervals for the color removal analysis. The breakthrough curves were obtained by plotting C_e/C_o *vs*. the volume of the outlet solution (Fig. 5).

It is interesting to note that 1 g of PPy/SD can remove more than 99% of MB from about 1400 ml of 50 mg l^{-1} MB solution. Break of the curve begins after the passage of about 1500 ml of the MB solution. Sorption capacity of PPy/SD is about three times as that obtained for SD.

Maximum adsorption happened at pH 12 for PPy/SD. Since the pH of solution has a paramount effect on the removal efficiency of MB using the selected adsorbents, so the effect of pH was further studied for the two adsorbents. As there was not much difference in sorption capacity of PPy/SD or SD toward MB at pH 10 or 12, so the next experiment to investigate the influence of pH was performed at the pH ranges of 2-10. Note that neither SD nor PPy/SD is chemically very stable at pH > 12 or at pH = 12 for prolonged exposure time. The breakthrough curves obtained for the adsorbents (SD and PPy/SD) are presented in Figs. 6 and 7, respectively.

Our results (Figs. 6 and 7) clearly show that both adsorbents (SD and PPy/SD) are more effective in dye removal at alkaline pHs. As the pH is increased the sorption capacity of both adsorbents is increased considerably. About 90 percent of MB was removed when about 3500 ml of MB solution (20 mg l^{-1}) of pH 12 was passed through a column containing 1.0 g PPy/SD under the same experimental conditions as used for Fig. 5. PPy/SD is also more efficient

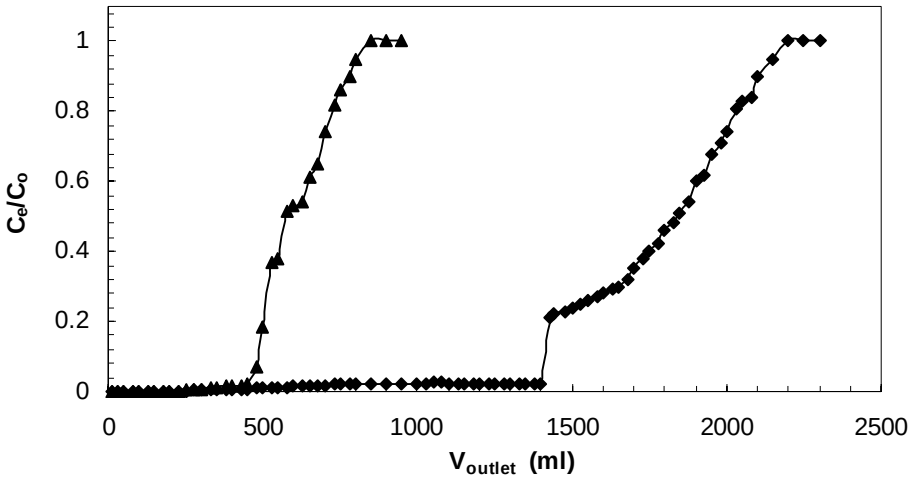

Fig. 5. Breakthrough curves for the sorption of 50 mg l^{-1} of MB onto SD at pH 6 (▲) and PPy/SD at pH 12 (■).

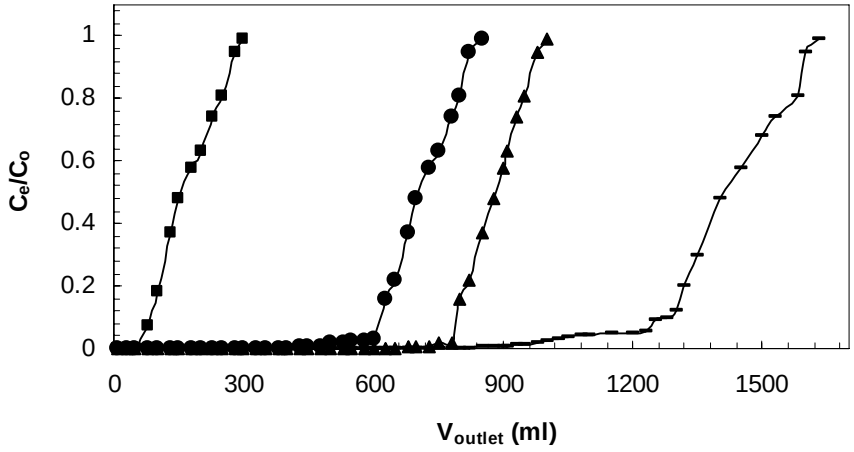

Fig. 6. Breakthrough curves for the sorption of MB by SD at different pHs, 2 (■), 6 (●), 8 (▲) and 10 (─). Experimental conditions used were as described for Fig. 5, except the initial concentration which was 20 mg l^{-1}.

adsorbent for the removal of MB compared to SD when used in column. Using pH above 12 was avoided because of the poor chemical stability of both adsorbents at highly basic conditions. A considerable decrease in dye removal was also observed for both adsorbents when acidic conditions (pH ≤ 4) were used.

Effect of initial concentration of MB on breakthrough curves. To perform this investigation, the column experiments were conducted as described previously (Sec. 3.2) using MB solutions of different concentrations (20-120 mg l^{-1}). The pH of solutions in the case of SD and PPy/SD was selected at 6 and 12, respectively. The results obtained for SD and PPy/SD are presented in Figs. 8 and 9, respectively. Other experimental conditions were kept constant as described previously (3.2.1).

As the results show (Figs. 8, 9), in each initial concentration of MB, higher sorption capacity was observed for PPy/SD. Both adsorbents showed more effectiveness when used for uptake of MB from aqueous solutions at low initial dye concentrations.

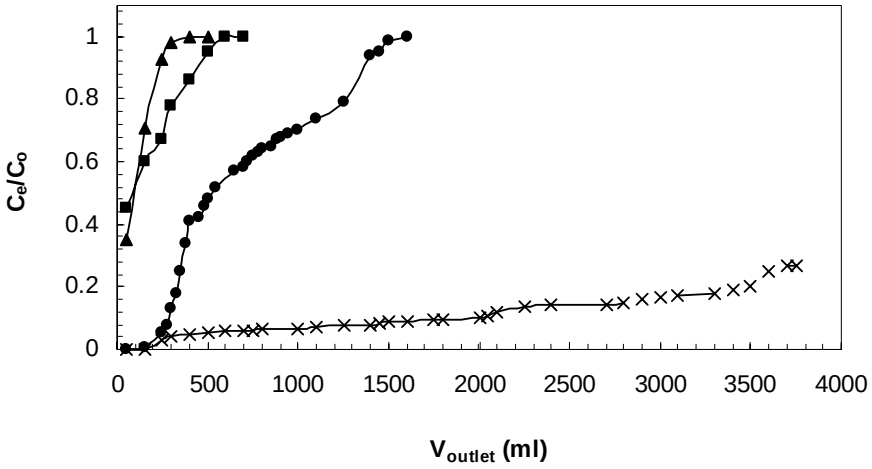

Fig. 7. Breakthrough curves for the sorption of MB by PPy/SD at different pHs, 2 (▲), 6 (■), 8 (●) and 10 (×).

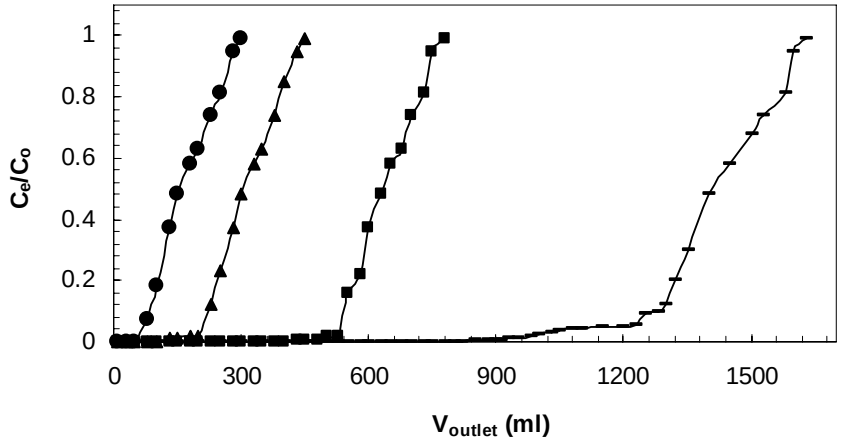

Fig. 8. Breakthrough curves for the sorption of MB by SD at different initial concentrations, C_o: 20 (—), 50 (■), 100 (▲) and 120 mg l^{-1} (●).

Column Regeneration and Dye Recovery

In order to find out the possibility of desorption for frequent applications, the regeneration of the used column was also investigated. Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed through using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. For performing this experiment, 50 ml of 20 mg l^{-1} MB solution was first treated with 1.0 g of PPy/SD for 45 min under mild shaking at room temperature. The analysis of the filtrate showed that more than 90% of MB had been removed.

The regeneration was examined using 50 ml of the selected solvents. The results are summarized in Table 7. As the data show (Table 7), maximum desorption percentage using different desorbing solutions in the case of PPy/SD was found to be about 15%. Poor desorption percentage implies strong interaction between MB and PPy/SD. However, in the case of SD, regeneration percentage improved considerably (~80%) when a hot solution (~60 °C) of 1 M NaCl was used as the

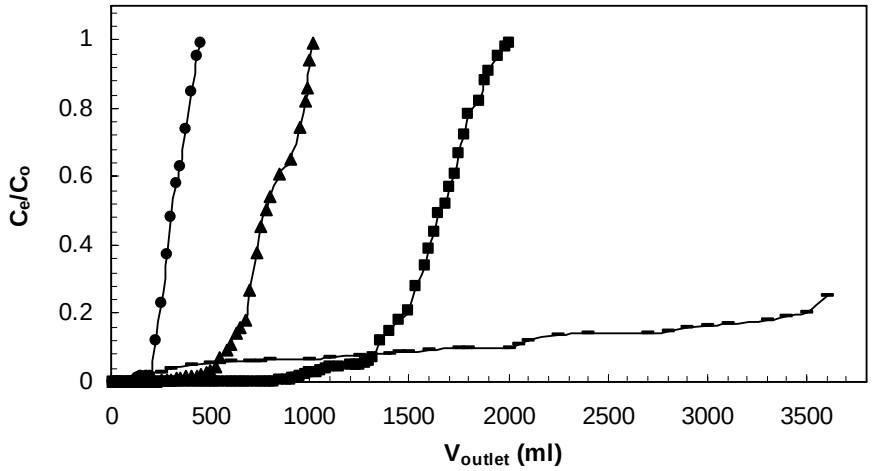

Fig. 9. Breakthrough curves for the sorption MB by PPy/SD at different initial concentrations, C_o: 20 (—), 50 (■), 100 (▲) and 120 mg l^{-1} (●).

Table 7. Effect of Different Chemicals on Desorption or Recovery Percentage of MB

Adsorbent	Regenerant solutions						
	Distilled water	HCl (1M)	NaCl (1M) T = 60 °C	NaOH (0.05 M)	HCl + NaCl	EDTA (0.1 M)	C_2H_5OH (96%)
PPy/SD	2.0	5.0	0.0	0.0	15.0	12.0	10.0
SD	2.0	12.0	80.0	7.0	28.0	6.0	11.0

desorbing agent. Extensive investigation is perhaps needed to find out more suitable conditions for the improvement of the regeneration efficiency. The major disadvantage of PPy/SD seems to be its poor regeneration percentage after use. This can be due to high affinity and the strong interaction between polar functional groups in polymer backbone (PPy) and MB dye. Since the adsorbents used for dye removal are rather cheap and readily available, regeneration does not seem to be really necessary and it can also be burnt with the sorbed dye as a source of energy.

CONCLUSIONS

The adsorption experiments revealed that both adsorbents used in this research were effective in removing methylene blue from aqueous solution. Advantages such as environmentally friendly material, low cost and high regeneration percentage make them suitable adsorbents for the removal of dyes such as MB from textile wastewaters. Equilibrium isotherms were analyzed by the Langmuir models of adsorption and were applicable with maximum monolayer adsorption capacity of 19.41 and 34.36 mg g^{-1} for SD and PPy/SD, respectively. The correlation coefficients in every case were found to be between 0.942 and 0.999. It could be concluded that the sorption isotherms of MB using SD and PPy/SD followed the Langmuir and Freundlich models. The dimensionless factor, R_L of the MB-SD and MB-PPy/SD isotherms revealed that the adsorption process for both adsorbents was very favorable. According to our breakthrough analyses it seems that PPy/SD is an excellent adsorbent for the removal of MB when used at its optimal pH compared with the other adsorbents reported by researchers so far.

This study was performed using synthetic dye solution at laboratory conditions. The results obtained may vary if applied to real samples. The real samples are in fact complicated because textile industries use a mixture of various types of dyes for different applications. Thus, a separate study focusing on the real wastewater is needed. Research in this regard is being continued. The currently introduced adsorbents are both simple and cost-effective which may prove to be of wider application for the treatment of textile wastewaters in our world of rapid technological advancement.

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