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Adsorption of Cationic Dyes from Aqueous Solutions using Polyaniline Conducting Polymer as a Novel Adsorbent

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ABSTRACT

In this research, polyanilline (PANi) as coated film onto sawdust was used for removal of methylene blue (as a typical cationic or basic dye) from aqueous solutions. The experiments were conducted using both batch and column systems. The operating variables studied were initial solution pH, adsorbent mass, initial dye concentration and contact time. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. In order to find out the possibility of reuse, desorption study was also carried out in this investigation. It was found that the currently introduced adsorbents can be used to remove cationic dyes such as methylene blue from aqueous solutions very efficiently. Regeneration of the column or desorption of the dye uploaded adsorbent can also be achieved using very simple and cost effective method with high performance.

Keywords: Removal, methylene blue, polyanilline, sawdust, desorption

INTRODUCTION

Colour is the most obvious indicator of water pollution.The discharge of coloured waste is not only damaging the aesthetic nature of receving streams,but also it may be toxic to aquatic life. In addition,coloure interferes with the transmission of sunlight into the stream and therefore reduces photosynthetic action.According to the U.S. environmental Protection Agency,stringent limits of colour concentration in the effluents are permissible[1]. The removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. The most commonly used methods for color removal are biological oxidation and chemical precipitation. However, these processes are effective and economic only in the case where contaminations concentrations are relatively high. Currently sorption process is proved to be one of the effective and attractive processes for the treatment of this dye-bearing wastewaters[2–6]. Also this method will become inexpensive, if the sorbent material used is of inexpensive material and does not require any expensive additional pretreatment step. 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 intensivness, non-toxic, and superior removal of organic waste constituents as compared to the conventional biological treatment processes[7]. A number of non-conventional, low cost adsorbents have been tried for dye removal. These include wood[4], Fuller's earth and fired clay[5], fly ash[6], biogas waste slurry[7–11], waste Fe(III)/Cr(III) hydroxide[12], waste orange peel[13], banana pith[14-15], peat [16-17], chitin[18], chitosan[19], silica[20] and others[21–26].

Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}ClN_3S$ (MW =319.65 g mol^{-1}). MB is an important basic dye widely used for printing calico, coloring paper, temporary hair colorant, wools, coating for paper stock, dyeing, printing cotton and tannin, indicating oxidation-reduction, and dyeing leather, and in purified zinc-free form, it is used as an antiseptic and for other medicinal purposes, etc[27]. At room temperature MB appears as a solid, odorless, dark green powder, that yields a blue solution when dissolved in water. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue will found cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans.

Adsorption of methylene blue from the aqueous phase is a useful toll for product control of adsorbents. Some kinds of sawdust have been studied as adsorbents for removal of methylene blue from aqueous solutions[28-30]. Polyaniline (PANi) is a poly aromatic amine that can be easily synthesised chemically from bronsted acidic aqueous solutions[31]. It is one of the most potentially useful conducting polymers and has received considerable attention in recent years[32]. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidising agents such as $(NH_4)_2S_2O_8$ as shown in the following (Fig. 1). The oxidation process is accompanied by the insertion of anions of acid electrolyte in order to maintain the charge neutrality of the final polymer product. Ammonium persulfate is a popular and frequently used chemical oxidant for polymerization of aniline in acidic aqueous solutions.

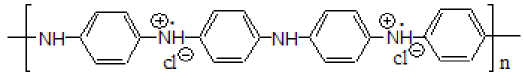

Figure 1. Chemical structure of polyaniline (PANi)

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

EXPERIMENTAL

Materials and Equipments

All chemicals used were analytical reagents grade and prepared in distilled water. Aniline was obtained from Merck and distilled before use. Sawdust samples (SD) from walnut obtained from a local carpentry workshop.

A solution of 100 mg L^{-1} methylene blue [3, 7-bis (dimethylamino) phenothiazin-5-ium ion] was prepared in distilled water as the stock solution (Fig. 2). Methylene blue (MW =319.65 g mol^{-1} termed as MB) shows an intense absorption peak in the visible region at 660 nm (Fig. 3). This wavelength corresponds to the maximum absorption peak of the methylene blue monomer. The pH adjustments were carried out using dilute NaOH and HCl solutions.

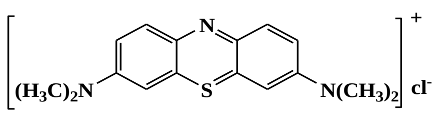

Figure 2 Chemical structure of MB

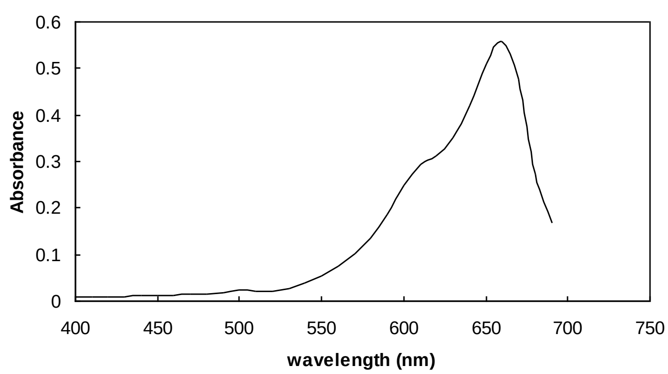

Figure 3 The Vis spectrum obtained for methylene blue in distilled water

A single beam Perkin-Elmer UV–Vis spectrophotometer with a 1 cm cell was used for measuring all of absorption data. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for pH measurements.

Determination of methylene blue

Concentrations of methylene blue (MB) in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of the dye (λ_{max}=660nm) using the calibration curve shown in Fig. 4. 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 obeyed in concentration range (0.0–2.5 mg L^{-1}).

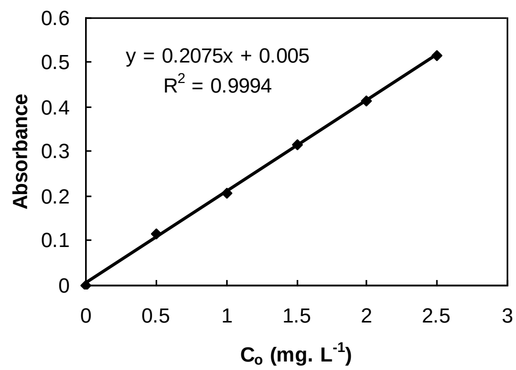

Figure 4: Calibration curve of absorbance against concentration of methylene blue (MB)

Preparation of the polymer

Aniline (Merck) distilled before polymerization. Polymerization was carried out in acidic solution. In order to prepare polymer coated onto sawdust (termed as PANi/SD), 5.0 g sawdust (35-50 mesh, 10 % humidity) immersed in 100 mL of 0.20 M freshly distilled Aniline solution for 12 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50 mL of oxidant solution (5 g ammonium persulphate) was added into the mixture gradually, and the reaction was allowed to continue for 5 hours at room temperature. Polymer coated sawdust (PANi/SD) filtered, washed with distilled water, then dried at temperature about 60 ^{o}C (in an oven) and sieved before use.

Adsorption experiments

Batch mode studies were conducted 0.2 to 1 g of adsorbents, taken separately, were shaken in 50 ml aqueous solution of MB dye of varying concentration (0-100 mg L^{-1}) at room temperature for definite time periods. At the end of pre-determined time intervals, adsorbent was removed by simple filtration. The filtrates were analyzed for the residual (unadsorbed) concentration of methylene blue, spectrophotometerically at 660 nm wavelength.

All experiments were carried out in triplicate with respect to each condition and mean values are presented. The maximum RSD was less than 2%. In column experiments for preparing breakthrough curves, a glass column with dimensions of 1.0 cm diameter and 30 cm height was employed. 1.0 g sorbent (PANi/SD) was packed in the column (bed volume ~5 cm^3). Dye solution (MB) with known initial concentration was passed through the column with flow rate of 3 mL min^{-1} at room temperature (22 ± 2 ^{o}C). The outlet solution was analyzed for residual (unadsorbed) methylene blue. The following equations were used to calculate the percentage of sorption and the amount of adsorbed methylene blue, respectively:

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

$$\frac{x}{m} = \frac{(C_o - C_e)V}{m} \quad \text{(Eq. 2)}$$

Where C_o and C_e are the initial and equilibrium concentrations of the methylene blue, respectively (mg L^{-1}); x/m is the amount of methylene blue adsorbed onto unit amount of the adsorbent (mg g^{-1}) at equilibrium; and V is the volume of the solution used in the adsorption experiment (L). Alternatively, regeneration of the used adsorbent was examined.

$$\% \text{ Desorption} = m / m_o \times 100 \quad \text{(Eq. 3)}$$

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

Where, m_o is mg of the sorbed material (MB) 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 are the initial and equilibrium concentrations of MB, respectively (mg L^{-1}). 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 methylene blue by sawdust (SD), and PANi/SD (batch system)

The Effect of pH on MB sorption by SD and PANi/SD

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. For this investigation, 0.8 g portions of dried sorbents (PANi/SD and SD) were treated separately with 50 mL of methylene blue solution (50 mg L^{-1}). The variation of methylene blue adsorption on SD and PANi/SD over a broad range of pH (2-12) is shown in Table 1.

Table 1: Effect of pH on sorption by SD and PANi/SD

pH	2	4	6	8	10	12
% Sorption (SD)	65.70	96.82	97.20	97.50	96.61	96.70
% Sorption (PANi/SD)	78.0	97.95	98.71	99.20	97.64	96.72

As shown, the adsorption is lower at pH< 2 and then is increased to higher values at pH> 6. More significant enhancement in the adsorption of dye is reached at pH=8 than at pH=6. It is known that ionic dyes upon dissolution release coloured dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH. Methylene blue is a basic dye. In water, it produces cation (C^+) and reduced ions (CH^+). If the solution pH is above the zero point of charge the negative charge density on the surface of the SD and PANi/SD increases, which favours the sorption of cationic dyes. In addition, the basic dye will become protonated in the acidic medium and the positive charge density would be located more on the dye molecules at low pH, resulted to a lower sorption degree[33].

Effect of sorbent dosage

In this experiment different weights of the selected sorbents (PANi/SD and SD), (0.2-1.0 g) were treated with 50 mL methylene blue solutions with concentration of 50 mg L^{-1}. The results obtained have been summarized in Fig 5.

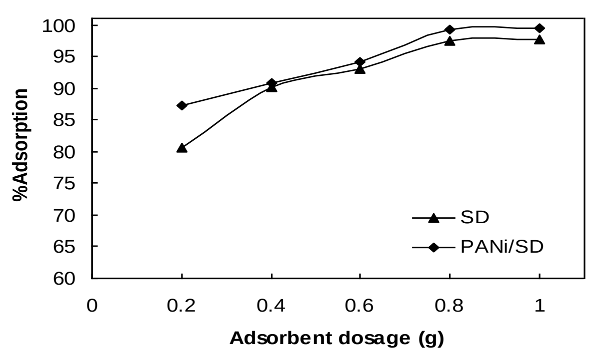

Figure 5. Effect of PANi/SD and SD dosage on the adsorption of MB

As our results the percentage removal of increased with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent[34]. Both SD and PANi/SD adsorbents can remove MB quickly. However in the case of PANi/SD, sorption rate is some higher than SD.

Effect of initial concentration

For performing this experiment 0.8 g sorbents SD and PANi/SD (mesh size 35-50) were treated with 50 mL of methylene blue solution with concentration of 20-100 mg L^{-1} at pH 8 for 40 min accompanied by mild shaking at room temperature. The results obtained are summarized in Table 2. As our results show, with increasing the initial concentration of methylene blue (C_o), total amount of metal sorption (x/m) also increases linearly.

Table 2 Effect of initial concentration of MB on sorption by SD and PANi/SD

adsorbent	C_o (ppm)				
	20	**40**	**60**	**80**	**100**
%Sorption (SD)	98.05	97.80	97.14	96.44	95.70
%Sorption (PANi/SD)	99.20	99.15	98.95	98.24	97.85

As our data clearly show, both coated (PANi/SD) and uncoated sawdust (SD) can effectively and comparably remove MB from aqueous solutions under specified conditions. It is also interesting to note that sawdust as a very low cost agricultural waste material can effectively be used for adsorption or removal of MB. However, our data in later sections show that the total capacity of PANi/SD is much higher than unmodified sawdust.

Effect of contact time

For performing this experiment, 0.50 g of adsorbent (PANi/SD), were treated with 50 mL of 50 mg L^{-1} MB for different periods (10-60 minutes) accompanied by stirring at room temperature. The results of adsorption obtained from the analysis of unabsorbed MB solution are shown in Fig 6.

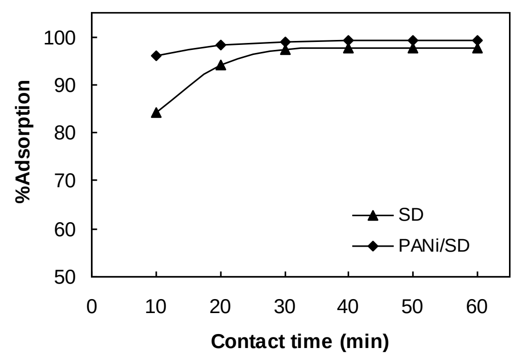

Figure 6 Effect of agitation time on removal of MB using SD and PANi/SD

As the results indicate, removal of MB using the selected adsorbents occurs quickly and is not a very time dependent process. The removal of MB by adsorption on SD and AC was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time. The removal of MB by adsorption on surface of SD and AC was due to MB as MB^+ cationic form. The mechanism for the removal of dye by adsorption may be assumed to involve the following steps:

- Migration of dye from bulk of the solution to the surface of the adsorbent
- Diffusion of dye through the boundary layer to the surface of the adsorbent
- Intra-particle diffusion of dye into the interior pores of the adsorbent particle.

The boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption.

Column studies

Treatment of data using adsorption isotherms [35-36]

The linear form of Langmuir isotherm is represented by the following equation:

$$1/X = 1/X_m + 1/bC_e \quad \text{(Eq. 5)}$$

Where C_e is the equilibrium concentration of MB solution (mgL^{-1}), X is the amount sorbed by adsorbent (mg g^{-1}), X_m is the maximum amount sorbed, b a Langmuir's constant signifying energy of sorption. The Langmuir isotherm obtained for the sorbents are shown in Figure 7.

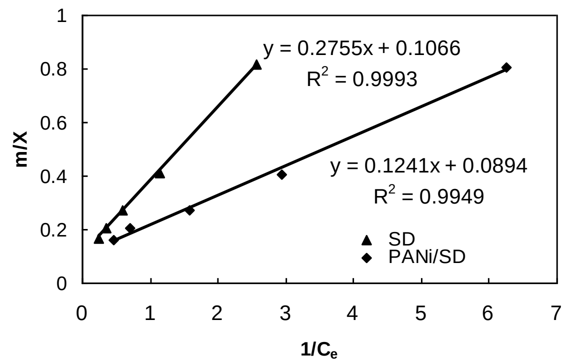

Figure 7 Langmuir adsorption isotherm obtained for sorption of MB by modified and unmodified sawdust

The Freundlich isotherm was also applied to plots of equilibrium adsorption data:

$$X/m = KC_e^{\frac{1}{n}} \quad \text{(Eq. 6)}$$

$$\log X/m = \log K + 1/n \log C_e \quad \text{(linearised form)} \quad \text{(Eq. 7)}$$

Where X is the amount of dye adsorbed (mg), m is the weight of the adsorbent used (g), C_e is the equilibrium concentration of dye in solution (mg L^{-1}), K and n are Freundlich's constants indicating sorption capacity and intensity, respectively. Where K_F is adsorption capacity at unit concentration and 1/n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1) and unfavorable (1/n>1)[37].

Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. In Freundlich adsorption system, the value of n is determined experimentally from the slope of the line which is equal to 1/n. For a good adsorbent it is between 1 and 10 [38]. Adsorption isotherm parameters were calculated from the slope and intercept of the linear plots are presented in Table 3. The Freundlich isotherm obtained for the sorbents employed in this research are shown in Figure 8.

Table 3 Equilibrium isotherm constants for the sorption of methylene blue onto SD and PANi/SD

	Langmuir isotherm parameters			**Freundlich isotherm parameters**		
Adsorbent	**b**	**X_m**	**r^2**	**n**	**K**	**r^2**
SD	0.38	9.38	0.9993	1.53	2.44	0.9884
PANi/SD	0.72	11.12	0.9949	1.57	3.39	0.9616

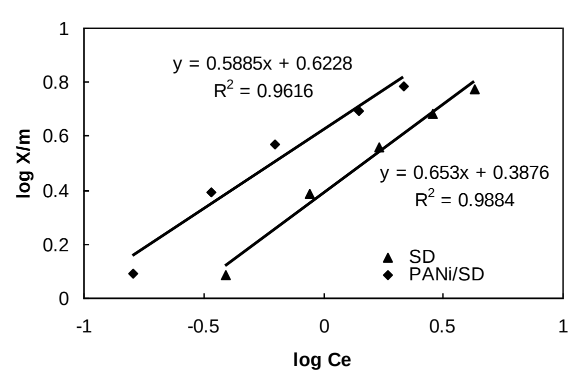

Figure 8 Freundlich isotherm obtained for sorption of MB by SD and PANi/SD

Breakthrough curves for removal of MB using SD and PANi/SD adsorbents

Sorption isotherms which are obtained from batch study do not give 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 using columns to evaluate the performance of adsorbent. The design of packed bed adsorbent in continuous systems, concentration vs. time or volume of solution usually yields as S- shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion.

For performing this experiment, 1.0 g SD and PANi/SD packed in a glass column (fixed bed depth of 5cm^3), and then methylene blue solution with concentration of 50 ppm passed through the column with constant flow rate (3 mL min^{-1}) at pH 8.0. Each time 10 mL was poured into the column. The outlet solution was analyzed for unabsorbed methylene blue solution in order to obtain the breakthrough curve. The breakthrough curves obtained for the SD and PANi/SD used for sorption of methylene blue a column system are shown in Fig 9.

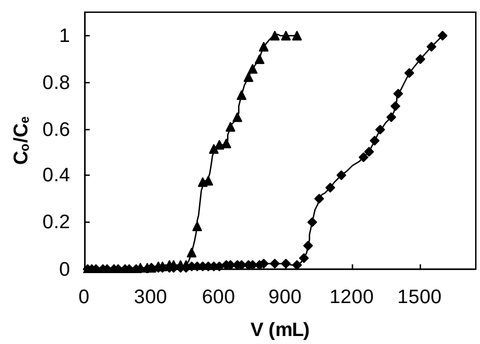

Figure 9 Breakthrough curve obtained for removal of MB using SD (▲) and PANi/SD (▪)

As our data show, PANi/SD is much more efficient in column system compared to SD. Our breakthrough analysis interestingly shows that the breakpoint occurred after passing about 1000 mL of dye solution from PANi/SD column. For SD column this volume is about 400 mL dye solution.

Desorption studies

In this study, 1.0 g of adsorbents PANi/SD was first treated with 50 ml of methylene blue solution with concentration 50 mg.L^{-1} in pH = 8. The analysis of the filtrate showed that more than 95% of MB has been removed. The used column was then treated with different chemicals (used as eluent or desorption agent). The results are summarized in Table 4.

Table 4 Effect of tnereffid slacimehc no noitprosed egatnecrep fo BM

Adsorbent	Regenerant solutions				
	Distilled water	HCl (1M)	NaCl (1M) T=60^{o}C	NaOH (0.05M)	C_2H_5OH (96%)
PANi/SD	0.0	0.0	0.0	0.0	60.0
SD	2.0	12.0	80.0	7.0	11.0

Our further desorption investigation showed that in the case of SD, regeneration percentage improved considerably when a solution of NaCl (1M) was used for regeneration. Also when a hot solution of NaCl 1M (60 ^{o}C) was used, regeneration percentage further increased to about 80%. Poor regeneratability of the used PANi/SD column clearly indicates that intermolecular interactions of MB and PANi/SD adsorbent are stronger than interactions between MB and sawdust, or it might be concluded that removal of MB by PANi/SD is occurred via some chemisorption process too.

CONCLUSION

It was found that sawdust without any modification can be used to remove textile dyes such as methylene blue with moderate efficiency. Advantages such as environmentally friendly material, low cost (almost free) and abundant natural material make it suitable for application as both modified and unmodified for treatment of textile wastewaters. It was also found as a suitable substrate for coating PANi/SD as chemically modified adsorbent. Our results in this investigation also demonstrated that PANi/SD is very efficient adsorbent for removal of the methylene blue from aqueous solutions using both batch and column systems compared to other materials previously reported for removal of MB. The major advantage of PANi/SD is its high sorption capacity in column system. Adsorption capacity of the two employed adsorbents showed that they are good and economical for removal of cationic dyes such as methylene blue from aqueous solutions.

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