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Removal of methylene blue dye by application of polyaniline nano composite from aqueous solutions

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ABSTRACT

This paper deals with application of polyaniline coated on wood sawdust for removal of methylene blue (MB) dye from aqueous solutions. Polyaniline coated onto sawdust (termed as PAn/SD) was prepared via direct chemical polymerization onto sawdust which was previously soaked in the monomer (aniline) solution in acidic (HCl) media. Adsorption experiments were carried out using batch system. The effects of different system variables such adsorbent dose, initial dye concentration, pH, contact time were then studied. It was found that PAn/SD is efficient and cost effective adsorbents for removal of MB dye from aqueous solutions.

Keywords: polyaniline; nano composite ; methylene blue; adsorption; removal of dye

INTRODUCTION

Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes [1-3]. The Textile industry is in the forefront in the use of dyes in its operations with more than 9000 types of dyes incorporated in the colour index [4]. Similarly, it has been reported that more than 70000 tons of approximately 10000 different types of dyes and pigments are produced annually world wide, of which 20-30% are wasted in industrial effluents during dyeing and finishing processes in the textiles industries [5]. The discharge of coloured waste is not only damaging the aesthetic nature of receiving streams, but is also toxic to the aquatic life [6]. In addition, wastewaters from dyeing and textile industries easily produce toxic trihalomethanes when chlorinated. Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack. Hence, their presence in wastewater is unwarranted, and it is desirable to remove coloring material from effluents, before their discharge in the environment, not only for aesthetic reasons. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. As a result of the low biodegradability of dyes, the

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conventional biological treatment process is not very effective in treating dye wastewater.

Some of the physicochemical methods that have been employed to remove dye from wastewater include chemical precipitation, coagulation, membrane filtration, electrolysis and oxidation. However these methods are not economical and are often unable to adequately reduce contaminants concentrations to desired levels. A search is on more effective and economic treatment techniques. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [3-6]. The toxic nature of the dye is still not quantified much but its high content in living systems can prove to be harmful. Thus, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using a novel adsorbent. Polyaniline (PAn) is a poly aromatic amine that can be easily synthesized chemically from bronsted acidic aqueous solutions. It is one of the most potentially useful conducting polymers and has received considerable attention in recent years [7-11]. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidizing agents such as $(NH_4)_2S_2O_8$ as shown in the following (Figure 1).

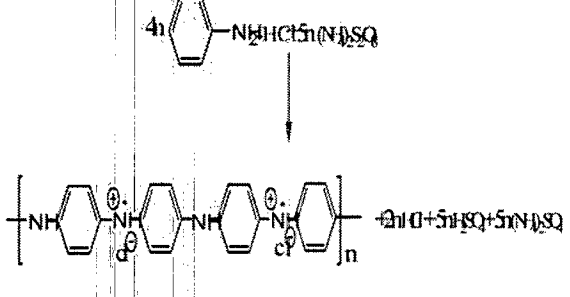

Fig. 1. Chemical polymerization of aniline in aqueous acidic media.

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 per sulfate is a popular and frequently used chemical oxidant for polymerization of aniline in acidic aqueous solutions. 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 [12-16]. However, this paper deals with investigation of another possible application of PAni for removal of dyes from aqueous solutions. MB as a typical basic textile dye was selected as a test probe.

EXPERIMENTAL

Materials and equipments

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 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 which corresponds to its maximum absorption peak as monomer. The pH adjustments were carried out using dilute NaOH and HCl solutions. 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 (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. 2. 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 (0.0–5 mg L^{-1}). The

experimental data reported in Fig. 2 were fitted by a straight line with a high regression coefficient value ($r^2 = 0.991$).

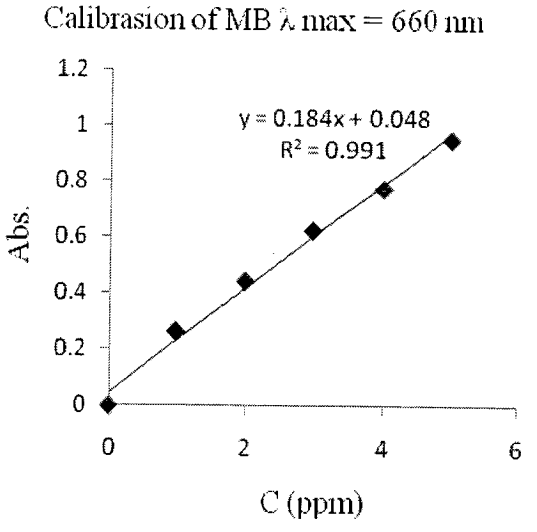

Fig. 2. Calibration curve of absorbance against concentration of methylene blue.

Preparation of the adsorbent

Aniline (Merck) was doubly distilled before polymerization. Polymerization was carried out in aqueous solution. In order to prepare polymer coated onto sawdust (PAn/SD), 5.0 g sawdust (35-50 mesh, 10 % humidity) immersed in 50 mL of 0.20 M freshly distilled aniline in HCl 1M solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50 mL of 0.5 M $(NH_4)_2S_2O_8$ as the oxidant solution was added into the mixture gradually, and the reaction was allowed to continue for 4 hours at room temperature. The polymer coated sawdust (PAn/SD) was filtered, washed with distilled water, dried in an oven at about 60 °C and sieved before use.

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 (10-50 mg L^{-1}) at room temperature for definite time periods. At the end of pre-determined time intervals, the adsorbent was removed by simple filtration. The filtrates were analyzed for the residual (unadsorbed) MB, spectrophotometrically. Adsorption experiments were carried out at room temperature using batch system. All experiments were carried out at least for three times with respect to each condition and mean values are presented. The maximum RSD was less than 2%. The following equations were used to calculate the percentage of sorption and the amount of adsorbed methyl orange, respectively:

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

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

Where, C_0 and C_e are the initial and equilibrium concentrations of the methyle orange, respectively (mg L^{-1}); x/m is the amount of methyl orange 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).

RESULTS AND DISCUSSIONS

Sorption of MB by PAn/SD

A series of experiments has been performed to optimize the adsorption conditions for 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, 0.5 g of the dried PAn/SD sorbents were treated separately with 50 mL of 10 mg L^{-1} MB at various pH values (from 1 to 12) accompanied by mild shaking at room temperature at

constant contact time (1 h). The results obtained have been summarized in Table 1.
As our data show (Table 1 & Fig. 3) increasing solution pH increases the extent of dye removal. Lower adsorption percentage of MB on PAn/SD at highly acidic conditions (pH ≤ 2) is probably due to the presence of high

Table 1. Effect of solution pH on adsorption percentage of MB by PAn/SD

pH	1	2	3	4	9	10	11	12
% Sorption	81	81	91	90	99.5	99	98.5	97
x/m (mg/g)	0.81	0.81	0.90	0.90	0.99	0.99	0.98	0.97

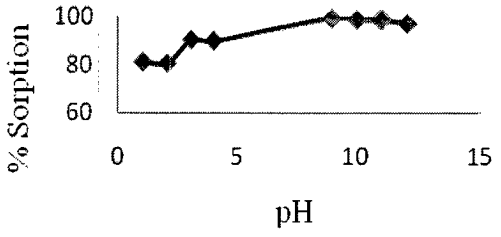

Fig. 3. Graphical display of the effect of solution pH on adsorption percentage of MB by PAn/SD

concentration of H^+ ions on the surface of adsorbent competing with methylene blue (a cationic dye) for adsorption sites in the adsorbent (Fig. 4). With an increase in the solution pH, the electrostatic repulsion between the positively charged methylene blue and the surface of adsorbent is lowered. Consequently removal efficiency is increased.

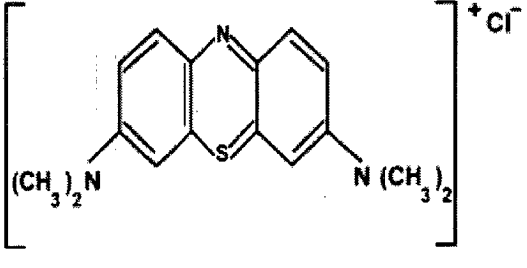

Fig. 4. Chemical structure of Methylene Blue (MB).

Effect of adsorbent dose

For investigating the effect of adsorbent mass on the adsorption of methylene blue dye, a series of adsorption experiment was carried out with different adsorbent dosages (0.10-1.0 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 PAn/SD was carried out at pH 9 of MB solution, the experiments was performed at pH 9. The results obtained have been summarized in Table 2 and Fig. 5 respectively.

Table 2. Effect of amount of adsorbent on removal percentage of MB by PAn/SD

Dosage (g)	0.1	0.2	0.3	0.4	0.5	0.8	1
% Sorption	86.06	86.80	87.70	93.20	93.74	98.72	98.90
x/m(mg/g)	43.03	21.66	14.61	11.71	9.32	6.17	4.95

The results follow the expected pattern, in which the percentage sorption increased as the sorbent dose was increased over the range 0.1 – 1.0 g. This is as a result of increased surface area and availability of more adsorption sites.

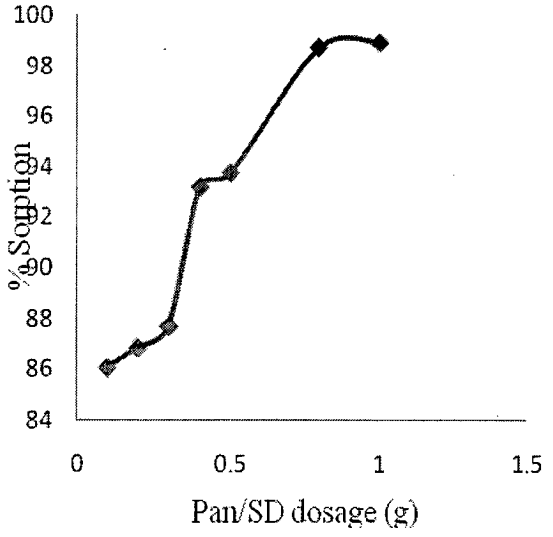

Fig. 5. Graphical display of the effect of amount of adsorbent on removal percentage of MB by PAn/SD.

Effect of initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 50 mg L^{-1}. For performing this experiment, fixed amounts (0.3 g) of PAn/SD adsorbent was treated with 25 mL of 10-50 mg L^{-1} of MB solution at pH 9. The period of contact time was 10 minutes accompanied by a mild mechanical shaking at room temperature. The results obtained are summarized in Table 3. Results from this study show that the adsorption process is highly dependent on the initial concentration of the dye in solution and % removal of MB decreases as its initial concentration increases. However, the total amount of dye (x/m) uptake is increased gradually.

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 0.5 g of the adsorbents PAn/SD and with 50 mL of 50 mg L^{-1} MB solution at pH value of 9. The mixture was agitated in a mechanical shaker for different periods of contact time (30-120 minutes). The results obtained are summarized in Table 4 and Fig.6 respectively.

Table 3. Effect of initial MB concentration on its sorption percentage onto PAn/SD

MB concentration	10	20	30	40	50
% Sorption	99.90	98.85	98.70	98.25	98.42
x/m (mg/g)	0.83	1.65	2.50	3.30	4.10

Table 4. Effect of contact time on the removal of MB by PAn/SD

Time (min)	30	60	90	120
% Sorption	99.5	99.3	99.0	99.1
x/m (mg/g)	4.97	4.96	4.95	4.95

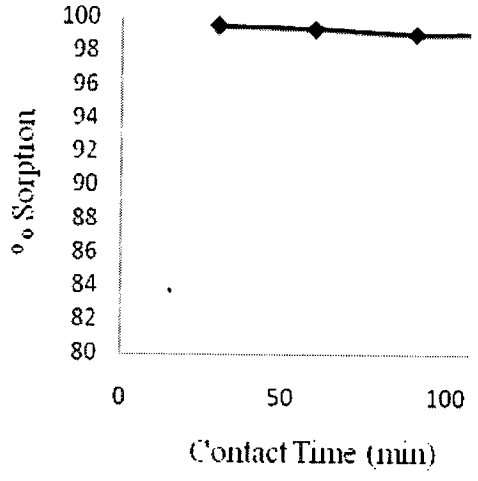

Fig. 6. Graphical display of the effect of contact time on the removal of MB by PAn/SD.

It was observed that the rate of removal of MB dye increases with increase in contact time to some 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 30 min for PAn/SD.

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 treatments of the equilibrium adsorption data [17-18]. 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:

$$\frac{X}{m} = \frac{X_m b C_e}{1 + bC_e} \quad \text{(Nonlinear form)} \qquad (3)$$

$$\frac{m}{x} = \frac{1}{x_m} + \frac{1}{x_m b C_e} \quad \text{(Linearised form)} \qquad (4)$$

Where X/m is the amount of dye adsorbed (mg g-1), represents the adsorptive capacity of the adsorbent for the equilibrium effluent concentration, Xm is the maximum amount sorbed, b is a Langmuir's constant signifying energy of sorption, C_e is equilibrium concentration of MB dye in the aqueous phase (mg L^{-1}). The Langmuir equation (Eq. 5) makes several assumptions, such as monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies. Another widely used equation in adsorption processes is the Freundlich equation. 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:

$$q_e = \frac{x}{m} = K C_e^{\frac{1}{n}} \quad \text{(Nonlinear form)} \qquad (5)$$

$$\log\frac{X}{m} = \log K + \frac{1}{n}\log C_e \quad \text{(Linearised form)} \qquad (6)$$

where, X/m is 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 m/x against $1/C_e$ in Fig. 7 gave straight lines for all the concentrations, implies that the adsorption for adsorbent well fitted to Langmuir isotherm. The high correlation coefficient obtained for PAn/SD (R^2 = 0.987) indicates high affinity between adsorbent surface and MB which plays the major role in the adsorption mechanism.

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 [19].

$$R_L = 1/(1+bC_o) \qquad (7)$$

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 0.084 to 0.020 (for PAn/SD) for concentration ranges of 10-50 mg L^{-1} MB dye. The R_L values obtained are less than unity, confirming that adsorption process is favored in both the cases and applicability of Langmuir isotherm also.

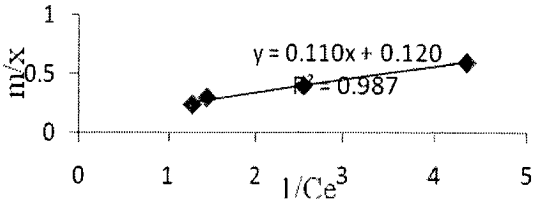

Fig. 7. Langmuir adsorption isotherm for the sorption of MB by PAn/SD.

The Freundlich isotherm (linear forms) obtained for the adsorbent employed in this research is shown in Fig. 8.

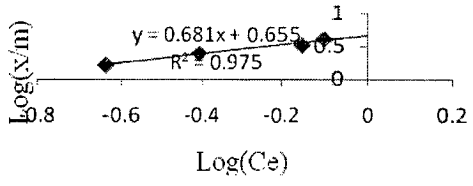

Fig. 8. Freundlich isotherm for the sorption of MB by PAn/SD.

From the high correlation coefficient obtained for PAn/SD (R^2 = 0.975) indicates high affinity between adsorbent surface and MB. It could be concluded that the adsorption isotherm of methylene blue using PAn/SD give a better fit to the Langmuir model.

Table 5. Freundlich and Longmuir Isotherms constants for MB adsorption onto PAn/SD

Adsorbent	n	k	b	X_m
PAn/SD	1.5	4.5	1.1	8.3

CONCLUSIONS

The adsorption experiments indicated that adsorbent used in this paper was effective in removing methylene blue from aqueous solution. Advantages such as environmentally friendly material, low cost and its high regeneration percentage make it a suitable adsorbent for removal of dyes such as MB from textile wastewaters. Equilibrium isotherms were analysed by the Langmuir models of adsorption and were applicable with maximum monolayer adsorption capacity of 8.3 mg g^{-1} for PAn/SD. The correlation coefficients in this case were found in 0.987 and 0.975 for Langmuir model and Freundlich model respectively. It could be concluded that the sorption isotherms of MB using PAn/SD followed the Langmuir and Freundlich models. The dimensionless factor, R_L of the MB-PAn/SD isotherms revealed that the adsorption process for adsorbent is very favorable. In this study, the R_L values were found to be 0.084 to 0.020 (for PAn/SD) for concentration ranges of 10-50 mg L^{-1} MB dye. According to our breakthrough analyses it seems that PAn/SD is an excellent adsorbent for removal of MB when used at its optimal pH compared to the other adsorbents reported by previous researchers so far.

This study was performed using synthetic dye solution at laboratory conditions; the results obtained may vary if apply to real samples. The real samples are in fact complicated because textile industries use a mixture of various types of dyes for different applications, so a separate study focused on the real wastewater is needed. The research in this regard is continued. The currently introduced adsorbents are both simple and cost effective and might have successful application for treatment of textile wastewaters in near future technology.

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