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POLYPYRROLE NANO COMPOSITE – AN EFFICIENT AND NOVEL ADSORBENT FOR THE REMOVAL OF DISPERSE RED 9 FROM TEXTILE WASTEWATER

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ABSTRACT

In this research work, application of Polypyrrole coated onto wood saw dust (PPC) was employed for the removal of Disperse Red 9 (DR) from aqueous solutions. The effects of important parameters such as pH, initial concentration, adsorbent dosage and contact time on the uptake of DR solution were investigated by batch adsorption system. Surface morphology of adsorbent is studied through scanning electron microscopy. The effect of *p*H, initial dye concentration, adsorbent dosage and contact time has been studied at optimum experimental conditions. Results reveal that as the amount of adsorbent increases, the percentage removal of the dye also increased. The adsorption of DR dye onto PPC follows pseudo second order kinetics. Study on the dye by the adsorbent fits Freundlich and Langmuir isotherms well. The present study confirms the potentiality of an abundant low cost adsorbent and its availability for the removal of dyes from aqueous solution.

KEY WORDS : Polypyrrole, Saw dust, Disperse Red, Langmuir, Adsorbent.

INTRODUCTION

Textile industries ranks first in the usage of dyes when compared to other industries like food, paper, cosmetics and carpet industries (O'Neill *et al.*, 1999). Decolourization of textile effluents using conventional technologies is not effective due to their limitations (Willmott *et al.*, 1998). Many physical and chemical methods such as adsorption, coagulation, precipitation and filtration have been used to remove harmful dyes from coloured waste water. Adsorption is the most effective and economical method for removal of dyes. Many researchers have proved several low cost materials such as pear millet husk carbon (Inbaraj *et al.*, 2002), aspergillus niger(Fu *et al.*, 2003), rice husk, banana pith, cotton waste, kaoline (Ghosh *et al.*, 2002), coir pith (Namasivayam *et al.*, 2001), guava seeds (Rahman *et al.*, 2003), neem saw dust (Khatri *et al.*, 2000), clay (Gurses *et al.*, 2004) and mango seed kernel (Vasanth *et al.*, 2005) as suitable adsorbents for the removal of dyes.

In this study, Poly pyrrole saw dust composite is prepared by polymerizing pyrrole on saw dust surface. The main objective of this study is to remove disperse dye namely Disperse red 9 from aqueous solutions by using Polypyrrole nano composite as an adsorbent this study also evaluates the potential of the polymer composite prepared from Casuarina saw dust. The study also includes an evaluation of the effects of various operational parameters such as initial dye concentration, contact time, pH and temperature on the dye removal process. The adsorption kinetic models, equilibrium isotherm models related to adsorption processes were also performed and reported.

MATERIALS AND METHODS

Adsorbent

Preparation of Poly pyrrole composite

Saw dust prepared from Casuarina was used for the preparation of Polymer composite. The saw dust

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was first washed with distilled water in order to remove the impurities and finally dried at 333 K for 2 hours. In order to prepare polymer coated saw dust, 5.0 g of saw dust was immersed in 50 mL of 0.20M freshly distilled pyrrole solution for 12 hours before polymerization. 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 (Ansari, 2005). The polymer coated saw dust was filtered, washed with distilled water, dried in an oven at55-60^0 C and sieved before use (Hsieh *et al*., 2000). The characteristics of PPC were studied as per the standard procedures (Ilhan, 2006 and Abdelwahab, 2008), and the surface morphology was analyzed by Scanning Electron Microscope images.

Adsorbate

Disperse Red 9 (M.Wt: 237.25, Mol.Formula: $C_{15}H_{11}NO_2$, λ max: 503 nm) used in this study is of commercial quality and used without further purification. The structure of Disperse Red 9 dye is shown in Fig. 1.

A stock solution of 1000 mg/L of DR 9 dye was prepared by dissolving appropriate amount of dye in one litre of distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations. The concentration of the dye was determined using Elico make uv-vis spectrophotometer at wavelength 503 nm.

Batch mode adsorption studies

The batch technique was selected because of its simplicity. The experiments were carried out in a mechanical shaker (KHAN shaker - KEMI make) working at a speed of 150rpm. Adsorption experiments were conducted at room temperature by agitating 0.20 gm of adsorbent with 50 ml of dye solutions of 25 to 100 mg/L concentrations in 250 ml stoppered flask. The flasks were sealed to prevent any change in volume during the experiments. It was agitated for predetermined time intervals at room temperature in the mechanical shaker. Blank samples were run under similar experimental conditions without using adsorbent. After shaking, the adsorbent was separated by centrifugation and the supernatant solution was analyzed by measuring absorbance at maximum wavelengths using UV-Visible spectrophotometer (Model: JASCO V) at the wave length of 503 nm.

The mixture was withdrawn at specified intervals, centrifuged using electrical centrifuge (universal make) at 5000 rpm for 20 minutes and the unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make uv-vis spectrophotometer at wavelength 503 nm. The effect of solution pH on the equilibrium adsorption of dyes (50 mg/L) was investigated using dilute HCl and NaOH solutions between pH 2 to 10. The effect of temperature on equilibrium adsorption was studied at 303, 308 and 313 K. The effect of each parameter like adsorbent dose, adsorbent particle size, different dye concentrations and agitation time was studied by fixing the values of other parameters (Vinod *et al*., 1997).To correct any adsorption of dye in container walls, control experiments were carried out in duplicate. There was no adsorption by the container walls. The amount of dye adsorbed by the PPY was calculated using the following equation:

$$qe = \frac{(c_0 - c_e)}{w} v \quad (1)$$

Where q_e(mgg^{-1}) is the amount of dye adsorbed at equilibrium onto PPC; C_o and C_e(mgL^{-1}), the initial and equilibrium liquid-phase concentrations of dye; V(L), the initial volume of dye solution; and W(g), the weight of PPY.

Desorption Studies

Desorption Studies were carried out to analyze the mechanism of adsorption and recovery of the adsorbate and adsorbent. The supernatant liquid was separated after centrifugation and the adsorbent was separated and allowed to agitate with 50 ml of distilled water at pH 2 – 10 above the equilibrium time of adsorption. The desorbed dye solution was estimated as given in the adsorption studies (Ahsan Habib *et al*., 2006).

RESULTS AND DISCUSSION

Characterization Studies

The Physico-chemical characteristics of PPC prepared from Casuarina are summarized in table 1. Physico-chemical characteristics of Poly pyrrole composite were studied as per the standard testing methods. In order to characterize the surface structure and morphology of Poly pyrrole saw dust composite, SEM analysis was carried out using Scanning Electron Microscope as shown in fig.2.

Table 1. Physico-chemical characteristics of PPC

S.No.	Properties	PPC
1.	pH	7.90
2.	Moisture content, %	6.25
3.	Conductivity, mS/cm	5.73
4.	Volatile matter, %	34.6
5.	Methylene Blue Number, mg/g	43
6.	Iodine Number, mg/g	96

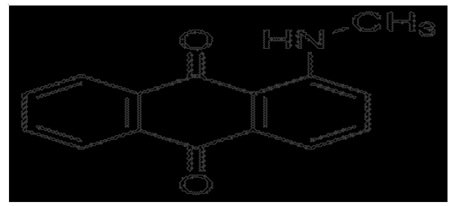

Fig. 1. Structure of Disperse Red 9

Analysis of Adsorption Parameters

Effect of initial dye concentration and agitation time

The rate of adsorption is a function of the initial dye concentration and contact time which is an important factor for effective adsorption. Initial dye concentration of DR ranging from 10mgL^{-1} to 120mgL^{-1} was prepared and adsorption experiments were conducted using 2 g. The effect of time on the removal of DR by PPC is shown in Fig. 3 and this reveals that as the concentration of PPC increases the percentage removal decreases. As expected when the concentration of dye increases, the limited capacity of the adsorbent checks any further adsorption of dye. Hence, the overall percentage removal decreases (Khashayar Badii *et al*., 2010). The equilibrium controls the maximum adsorption and decreases the final removal percentage. Similar results were reported for the adsorption of dyes on activated bleaching earth (Tsai *et al*., 2004).

Effect of pH

The pH of the dye solution has been recognized as one of the most important factors influencing the adsorption process. Adsorption process for the treatment of dye containing waste water is *p*H dependent. To determine the effect of *p*H on the removal of dye, its adsorption was studied at varied *p*H range of 2 – 10. The maximum percentage removal of DR occurs at acidic pH 2 and adsorption decreases with increase in pH. In acidic medium, the surface of the adsorbent is positively charged due to higher concentration of H^+ ions, so the electrostatic attraction between PPC and DR is enhanced. But in alkaline conditions, electrostatic repulsion occurs resulting in decreased adsorption. Similar results have been reported for adsorption of Eosin Y using conducting electro polymers (Ansari, 2005).

Effect of Temperature

The effect of temperature on dye adsorption was studied at 30^o, 35^o and 40^o C. The results indicated that the amount of dye adsorbed at equilibrium increases with increase in temperature. This is due to the increase with mobility of the dye molecules with increase in temperature (Khashayar Badii*et al*., 2010). It has been observed that the percentage removal of DR9 increased from 41.5 % to 82.7 %

Table 2. Isotherm parameters of Disperse Red 9 onto PPC

Temp ^{o}C	Isotherm Models					
	Langmuir			Freundlich		
	Q_0(mg/g)	b_L(L/mg)	r^2	1/n	K_f (mg/g)	r^2
30	7.4896	*0.4516	0.9988	0.4032	2.9307	0.9787
35	9.1177	0.4582	0.9942	0.3985	3.2640	0.9827
40	9.8793	0.5383	0.9977	0.3538	0.8236	0.9959

Table 3. Kinetic Model Values for adsorption of Disperse Red 9

Conc mg/L	First order kinetics			Second order kinetics		
	$k_{1x\,10^{-2}\,(min^{-1})}$	$q_{e\,(mg/g)}$	r^2	k_2X 10^{-4}(g/mg/min)	$q_{e(mg/g)}$	r^2
25	5.581	41.26	0.9653	16.4	36.68	0.9987
50	1.96	117.37	0.9890	12.48	583.00	0.9990
75	1.51	152.15	0.9689	7.8	575.89	0.9954
100	1.25	183.24	0.9756	0.83	759.58	0.9966

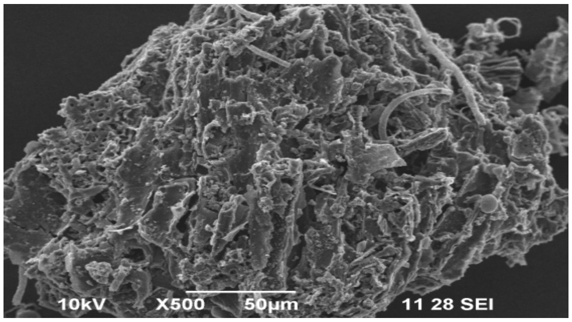

Fig. 2. SEM image of PPC

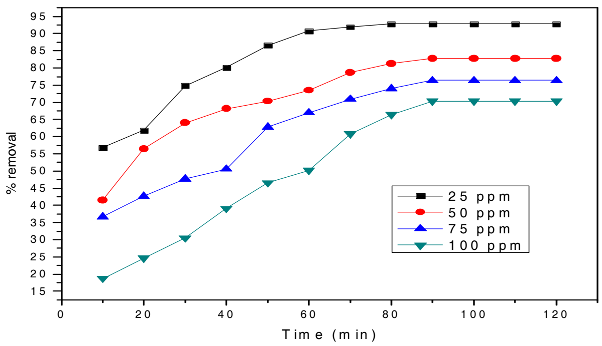

Fig. 3. Effect of initial dye concentration and agitation time for the adsorption of DR9 onto PPC

indicating that the adsorption is endothermic in nature (Alkan *et al.*, 2003). These adsorption data were further analyzed with adsorption isotherm models to find out the suitable model.

Equilibrium Adsorption Isotherm

Adsorption isotherm indicates the relationship between the adsorbate in the liquid phase and the adsorbate on the surface of the adsorbent at equilibrium constant temperatures (Jaikumar *et al.*, 2009). The applicability of the isotherm equation is compared by judging the correlation coefficient (r^2)

Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models were used to describe the adsorption of Disperse Red 9 onto PPC.The Langmuir equation can be written as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \tag{2}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b_L (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The Langmuir isotherm is based on the assumption of structurally homogeneous adsorbent and monolayer coverage with no interaction between the sorbate molecules. Once a dye molecule occupies a site, no further adsorption can take place at that site (Vimonses *et al.*, 2009). The values of Q_0 and b_L calculated from the slopes and intercepts of the linear plots of C_e / q_e and the results are summarized in Table 2.

The values of adsorption efficiency Q_0 and adsorption energy b_L increases with increasing the temperature suggested that the maximum adsorption corresponds to a saturated monolayer of dye molecules on all the adsorbents. Further it confirms the endothermic nature of processes involved in the system (Krishna *et al.*, 2002).

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L(Vermeuln, 1996) that is defined by the following equation

$$R_L = \frac{1}{(1+bC_0)} \tag{3}$$

Where C_0 is the highest initial solute concentration. R_L value indicates the type of adsorption isotherm to be either unfavorable (R_L> 1), favorable (R_L =1) or irreversible (R_L = 0). The R_L values confirm that the adsorption process is favourable. Langmuir model is more appropriate to explain the nature of adsorption of DR9 with correlation coefficient of 0.9988 at 30°C.

The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. Linear form of Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

Where K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent respectively. Q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), Where Ce is the equilibrium concentration (mg/L). The values of K_f and 1/n are calculated from intercepts and slopes of linear plot of log q_e versus log C_e. The value of 1/n is below 1 for DR indicates that the adsorption of dyes is favourable. The results of isotherms are summarized in Table 2.

An analysis of the correlation coefficients obtained for these isotherms showed that both isotherm equations describe the adsorption but Langmuir model was found to be more appropriate to explain the adsorption of DR onto PPC.

Kinetics of Adsorption

Adsorption Kinetics is necessary for the design of adsorption systems (Atef Alzaydien *et al*., 2009). In this present study, the following two kinetic models were applied for the experimental data.

In order to investigate the mechanism of adsorption, characteristic constants of adsorption were determined using Pseudo-first order reaction (Langergren, 1898) of Langergren based on solid capacity and its kinetic equation (Ho *et al*., 1999) can be expressed as follows.

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad .. (5)$$

The integrated form of equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad .. (6)$$

The dye adsorption described by a modified second order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q e^2} + \frac{1}{q_e} \quad .. (7)$$

The values of first order rate constant k_1 and q_e were calculated from the intercepts and slopes of the plot of log (q_e-q_t) vs t and the results are summarized in table 3.

The value of k_2 was found to decrease with increase in dye concentration due to decrease in available vacant sites for adsorption. The values of r^2 suggested that Pseudo-first order equation does not fit well with whole range of adsorption process, as it is applicable for the initial stages of adsorption processes. The values of second order rate constant k_2 and q_e were calculated from the intercepts and slopes of the plot of t/q_t as shown in figure 6.

Based on the values of the correlation co-efficient which is above 0.98, the second order kinetic model was the suitable one to describe the adsorption process for DR adsorption than Pseudo-first order model.

CONCLUSION

The present investigation showed that Poly pyrrole / saw dust composite was effectively used for the removal of Disperse dye from aqueous solution. The adsorption process was dependent on *p*H. Maximum adsorption occurs at pH 2 for DR9. The maximum monolayer adsorption capacities were calculated by Langmuir model for disperse red at 303, 308 and 313K). The pseudo second order kinetics fitted well with dynamical behaviour of anionic dyes suggesting ion exchange adsorption. The adsorption capacity of PPC increased with rise in temperature indicating endothermic nature of adsorption. Based on the results obtained from this study, it can be suggested that Poly Pyrrole Composite is an effective, economic and alternative biomaterial for the removal of disperse dyes from aqueous solutions.

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