

# REMOVAL OF HAZARDOUS REACTIVE VIOLET DYES USING AN ELECTROACTIVE CONDUCTING POLYMER

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## ABSTRACT

Conducting Electroactive polymer, Polypyrrole (PPy/SD) was synthesized chemically on the surface of saw dust (SD) to remove Reactive Violet 5 (RV) from an aqueous solution. The important parameters such as pH, initial concentration, sorbent dosage and contact time on uptake of RV solution were also investigated. The experiments were carried out using batch system at room temperature. It was found that PPy/SD can be used to remove anionic dye such as RV from aqueous solutions very efficiently. The adsorption process using polypyrrole coated onto sawdust termed as PPy/SD was dependent on the pH of the solutions. Kinetic studies revealed that the experimental data correlated well with intra-particle diffusion model and pseudo second-order model possessing regression coefficient of  $R^2 \geq 0.9896$ . The experimental data were also analyzed by the Langmuir and Freundlich models of adsorption. The isotherm data could be well described via Langmuir equation with the correlation coefficient of 0.9866. Scanning Electron Micrographs provided a supporting evidence to evaluate surface area, total pore volume and pore diameter. The present study confirms the potentiality of a carbon embedded in conducting electroactive polymer matrix and its availability for the removal of reactive dyes from aqueous solution.

**Keywords:** Adsorption, Intra-Particle Diffusion, Langmuir Equation, Polypyrrole, Reactive Violet, Saw Dust

## I. INTRODUCTION

The world-wide high level of production and use of dyes generates colored wastewaters, which give cause of environmental concern. Textile companies, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, distilleries, food companies and a host of other industries discharge colored wastewater [1]. Use of reactive dyes has been enhanced due to the increased consumption of cellulose fibers in which other dyes suffer from technical and economical practical limitations in comparison with reactive dyes [2]. Among the treatment options, adsorption appears to have considerable potential for the removal of colour from industrial effluents. Thus, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using novel adsorbents.

Conducting electroactive polymer such as Polypyrrole has attracted a great deal of attention in recent years[3-8]. This class of new polymeric material can be easily synthesized from both aqueous and non-aqueous solutions. The electro-active nature or the switching properties of PPy/SD have been utilized as the basis of most proposed

applications such as sensors, separation devices, rechargeable batteries and controlled drug release. All other applications of these polymers are based on their electrical conductivity and unique electrochemical properties [9-12]. However, this paper deals with a quite different application of this reactive and functional polymer. Our recent studies have shown that these polymers can effectively remove or uptake the ions and dyes from aqueous solutions.

In this study, PPy/SD was synthesized directly on the surface of sawdust via chemical route at room temperature. The anion exchange properties of polypyrrole conducting polymer are well established and documented [10-12]. Sawdust, the same as other biomaterials or agricultural wastes is a good adsorbent for adsorption of basic dyes such as methylene blue, malachite green [13-15]. Our research is mainly focused on Polypyrrole coated sawdust (PPy/SD) for investigation of RV dye removal from aqueous solutions. The main objective of this study is to evaluate the potentiality of PPy/SD, the polymer prepared from saw dust to remove reactive dyes from wastewater. 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 and equilibrium isotherm models related to adsorption processes were also performed and reported.

## II. EXPERIMENTAL SECTION

### 2.1. Materials and Methods

Saw dust prepared from Casuarina wood was used for the preparation of electroactive Polymer. The saw dust 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<sub>3</sub> as the oxidant solution was added into the mixture gradually and the reaction was allowed to continue for 4 hours at room temperature [16]. The polymer coated saw dust was filtered, washed with distilled water, dried in an oven at 55-60<sup>0</sup> C and sieved before use [17]

Reactive violet 5 (M.Wt: 735.58, Mol.Formula: C<sub>20</sub>H<sub>16</sub>N<sub>3</sub>Na<sub>3</sub>O<sub>15</sub>S<sub>4</sub>, λ max: 545 nm) used in this study is of commercial quality and used without further purification. Different initial concentrations were prepared by diluting the stock solution using double distilled water as solvent. Dye concentration was analyzed by measuring the absorbance values with UV-VIS spectrophotometer (Model: JASCO V-570) at a wavelength of 545 nm. The pH measurements were made using pH meter (Model LI 610 ELICO). The pH adjustments of the solution were made by 0.1M HCl or 0.1M NaOH. The chemicals were of analar grade and all the adsorption experiments were carried out at room temperature (27±2<sup>0</sup>C).

Physico-chemical characteristics of PPy/SD were studied as per the standard testing methods [18, 19]. In order to characterize the surface structure and morphology of PPy/SD, SEM analysis was carried out using Scanning Electron Microscope as shown in Fig.1. The experiments were carried out in a mechanical shaker (KHAN shaker - KEMI make) working at a speed of 150 rpm. Dye solutions (50mL) of desired concentrations and initial pH values were used. Blank samples were run under similar experimental conditions without using adsorbents. After shaking, the adsorbents were separated by centrifugation and the supernatant solutions were estimated by measuring absorbance at maximum wavelengths. 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 [20]. The amount of dye adsorbed by PPy/SD was calculated using the following equation:

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

where  $q_e$  ( $\text{mgg}^{-1}$ ) is the amount of dye adsorbed at equilibrium onto PPy/SD;  $C_o$  and  $C_e$  ( $\text{mgL}^{-1}$ ), the initial and equilibrium liquid-phase concentrations of dye;  $V$  (L), the initial volume of dye solution; and  $W$  (g), the weight of PPy/SD.

### III. RESULTS AND DISCUSSION

Initial dye concentration of RV5 ranging from  $10\text{mgL}^{-1}$  to  $120\text{mgL}^{-1}$  was prepared and adsorption experiments were conducted using 2g of PPy/SD. The overall removal percentage decreases [21] since the adsorbent has limited number of active sites which becomes saturated at certain concentration. The amount of RV5 dye removal by PPy/SD is found to be higher due to the heterogeneity obtained by the presence of functional groups present on the surface of the polymer composites [22]. From the literature, it was suggested that the dye removal was high due to the ion exchange mechanism between the oppositely charged functionalities originating from monomer and the ionic dye molecules.

The effect of contact time was studied by agitating 2 g of PPy/SD with  $50\text{mgL}^{-1}$  of RV5 solution. The adsorption efficiency increases with increase in time. PPy/SD shows 77.8 % removal of RV5 within 50 min. The adsorbent attain equilibrium at 90 min and hence it is selected as the equilibrium time for further studies. In the process of adsorption, initially, the dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface. Finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time [23].

Adsorption process for the treatment of dye containing waste water is  $pH$  dependent. The effect of  $pH$  on the dye removal efficiency of PPy/SD was studied at varied  $pH$  range of 2 - 10. The maximum percentage removal of RV5 occurs at acidic  $pH$  2.5 and adsorption decreases with increase in  $pH$ . The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which, in turn, is influenced by the  $pH$  of the solution. Similar results have been reported for adsorption of Eosin Y using conducting electro polymers [24].

The effect of temperature on dye adsorption was studied at 30, 35 and  $40^{\circ}\text{C}$ . The results indicated that the amount of dye adsorbed at equilibrium increases with increasing temperature. This is due to the increase in the mobility of the dye molecules with increase in temperature [25]. The percentage removal of RV5 increased from 42.6 % to 98.4 % for PPy/SD indicating that the adsorption is an endothermic process.

#### 3.1 Kinetics

The pseudo first order model of Lagergren [26] is based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount.

The pseudo-first order equation is expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

The integrated form of equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

Where  $q_e$  ( $\text{mgg}^{-1}$ ) and  $q_t$  ( $\text{mgg}^{-1}$ ) are the adsorption capacity per unit weight of adsorbent at equilibrium and at time  $t$  (min) respectively.  $k_1$  is the pseudo-first order rate constant. Linear plot of  $\log(q_e - q_t)$  versus  $t$  gives the

value of rate constant  $k_1$ . The values of first order rate constant  $k_1$  and  $q_e$  were calculated from the intercepts and slopes of the plot of  $\log (q_e - q_t)$  versus  $t$  and the results are summarized in Table 1. The correlation coefficients are low for PPy/SD and it is found that the 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 and after that it starts deviating from the theory. This infers that the adsorption of RV5 onto PPy/SD does not follow first order mechanism.

The pseudo second order model [27] is based on the assumption that the rate - limiting step involves chemisorption. The dye adsorption described by a modified second order equation is expressed as follows:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

Where  $k_2$  is the pseudo second order rate constant ( $\text{mg}^{-1}\text{min}^{-1}$ ). 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 second order rate constant  $k_2$  and  $q_e$  (Table 2) were calculated from the intercepts and slopes of the plot of  $t/q_t$  versus  $t$  as shown in Fig.2. Based on the values of the correlation co-efficient which is greater than 0.9957, the second order kinetic model is found to be more suitable to describe the adsorption process than Pseudo-first order model.

### 3.2 Intraparticle Diffusion

In a rapidly stirred batch reactor, the transport of adsorbent species takes place from the bulk of the solution into solid phase through intra particle diffusion process [28]. The expression for the intra-particle diffusion model is given by the following equation:

$$q_t = K_{\text{dif}} t^{1/2} + C \quad (5)$$

Where  $C$  ( $\text{mgg}^{-1}$ ) is the intercept; and  $K_{\text{dif}}$  is the intra-particle diffusion rate constant ( $\text{mgg}^{-1}\text{min}^{-1/2}$ ). The values of  $q_t$  are found linearly correlating with values of  $t^{1/2}$  for both the adsorbents and the rate constant  $K_{\text{dif}}$  was directly evaluated from the slope of the regression line. The values of intercept  $C$  provide information about the thickness of the boundary layer. The results are shown in Table 2. The plot  $q_t$  versus  $t^{1/2}$  as shown in Fig.3. indicates that it does not pass through the origin. The correlation coefficient values from Table 3. indicate that pore diffusion [29] plays a major role for the adsorption of RV5 onto PPy/SD.

### 3.3. Isotherm

Langmuir [30] isotherm is used to determine the maximum capacity of the adsorbent. The Langmuir equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \quad (6)$$

Where  $C_e$  is the equilibrium concentration ( $\text{mg/L}$ ),  $q_e$  is the amount of dye adsorbed at equilibrium ( $\text{mg/g}$ ) and  $Q_0$  ( $\text{mg/g}$ ) and  $b_L$  ( $\text{L/mg}$ ) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The value of  $Q_0$  and  $b_L$  for PPy/SD is calculated from the slope and intercept of the linear plot 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 temperature which confirms the endothermic nature of processes involved in the system. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter  $R_L$  which could be defined by the following equation:

$$R_L = \frac{1}{(1 + b C_0)} \quad (7)$$

Where  $C_0$  is the highest initial solute concentration.  $R_L$  value indicates the type of adsorption isotherm either to be unfavorable ( $R_L > 1$ ), favorable ( $R_L = 1$ ) or irreversible ( $R_L = 0$ ). Langmuir model is more appropriate to explain the nature of adsorption of RV5 with correlation coefficient of 0.98341 to 0.9866.

The Freundlich [31] equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. Linear form of Freundlich equation is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

Where  $K_f$  is a constant for the system, related to the bonding energy.  $1/n$  indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The data obtained by plotting  $\log q_e$  vs  $\log C_e$  from linear Freundlich isotherm for the adsorption of RV5 onto PPy/SD is presented in Table 2. The value of  $1/n$  lesser than 1 (Table 2) indicates that the adsorption of RV5 onto PPy/SD is favourable.

#### IV. CONCLUSION

Electroactive conducting Polypyrrole polymers can be easily synthesized via chemical oxidation directly on the surface of sawdust from aqueous solutions. Reactive Violet 5 dye removal by the PPy/SD is supposed to occur mainly through anion-exchange process. The amount of dye adsorbed is found to vary with initial pH, temperature and contact time. Maximum adsorption occurs at pH 2-3 for RV5. Two simplified kinetic models, pseudo-first order and second-order were tested to investigate the adsorption mechanism and concluded that the adsorption of RV5 onto PPy/SD follows pseudo second-order kinetics. The equilibrium data fits very well into the Langmuir isotherm model which indicates monolayer adsorption. The adsorption capacity of PPy/SD increased with rise in temperature indicating endothermic nature of adsorption. An Intraparticle diffusion model predicts that pore diffusion plays a major role for the adsorption of RV5 onto PPy/SD. The adsorption system currently introduced (PPy/SD) seem to be very economical and efficient for the removal of dyes such as RV from aqueous solutions. The findings in this paper seem to be very important from application point of view for water and wastewater treatments in dye removal technology using batch systems compared to other materials previously reported for removal of RV.

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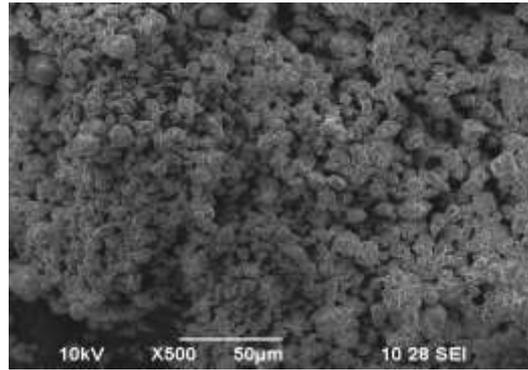


Fig.1. SEM image of PPC

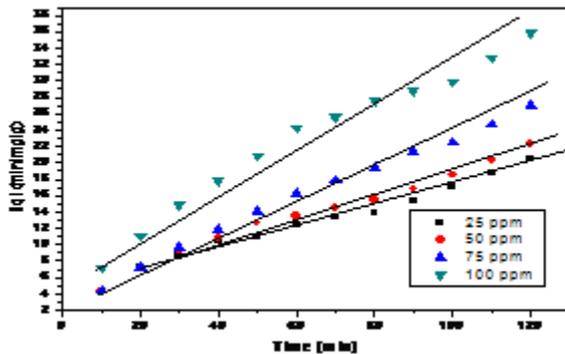


Fig.2 Pseudo Second Order Plot for the Adsorption of RV5 on to PPC

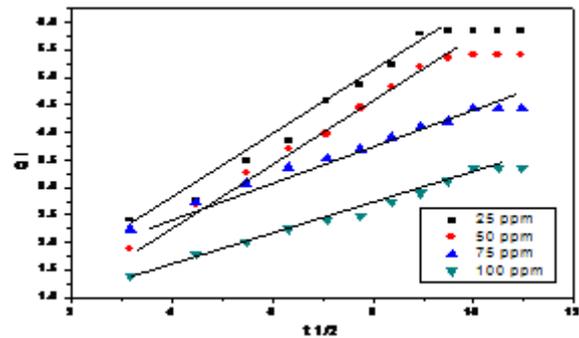


Fig.3 Intra Particle Diffusion Plot for the Adsorption of RV5 on to PPC

TABLES

Table 1 Comparison of First-Order and Second-Order Rate Constants and Correlation Coefficients

Conc mg/L	First order kinetics			Second order kinetics		
	$k_1$ (min <sup>-1</sup> )	$q_e$ (mg/g)	$r^2$	$k_2 \times 10^{-2}$ (g/mg min)	$q_e$ (mg/g)	$r^2$
25	0.02468	0.9331	0.9532	1.178	6.2454	0.9966
50	0.01463	1.5741	0.9627	1.304	5.6197	0.9982
75	0.01024	2.2489	0.9695	0.896	5.1913	0.9957
100	0.00578	3.9856	0.9871	0.834	3.9781	0.9996

**Table 2. The Values of Parameters and Correlation Coefficient for Each Isotherm Model**

Temp <sup>0</sup> C	Langmuir			Freundlich		
	Q <sub>0</sub> (mg/g <sup>-1</sup> )	b <sub>L</sub> (L/mg <sup>-1</sup> )	r <sup>2</sup>	K <sub>f</sub> (mg g <sup>-1</sup> )	1/n	r <sup>2</sup>
30	6.0759	0.0549	0.9838	3.5547	0.2869	0.9383
35	7.7102	0.2218	0.9866	4.0563	0.3283	0.9771
40	8.9369	0.4379	0.9831	4.7483	0.3199	0.9798