



Application of Polyaniline Nano Composite for the Adsorption of Acid Dye from Aqueous Solutions

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Abstract: In this research, Polyaniline coated sawdust (Polyaniline nano composite) was synthesized via direct chemical polymerization and used as an adsorbent for the removal of acid dye (Acid Violet 49) from aqueous solutions. The effect of some important parameters such as pH, initial concentration of dye, contact time and temperature on the removal efficiency was investigated in batch adsorption system. The adsorption capacity of PAC was high (96.84 %) at a pH of 3-4. The experimental data fitted well for pseudo second order model. Langmuir model is more appropriate to explain the nature of adsorption with high correlation coefficient. The Energy of activation from Arrhenius plot suggested that the adsorption of AV49 onto PAC involves physisorption mechanism.

Key words: Sawdust, Langmuir isotherm, polyaniline, Arrhenius plot, acid violet 49.

Introduction

Among the industries, textile industry plays an important role in the economy of country and it accounts for around one third of total export of India. The wastewater from textile industry causes damages to the ecological system of the receiving surface and affects the ground water resources. Most of the dyes are stable to light and non biodegradable¹. Therefore dye bath effluents need to be treated before being discharged to the environment².

Among the physico chemical processes, adsorption is considered to be most effective and proven technology for the wastewater treatment. Activated carbon is the most common adsorbent for this process due to its effectiveness and versatility³. The regeneration and difficulty of separation from the wastewater after use are major concerns associated with activated carbon. There has been growing interest in finding inexpensive and effective

alternative to activated carbon such as rice husk⁴, chitin⁵, orange waste⁶, lemon peel⁷, raw barley straw⁸, egg shell⁹ and sawdust¹⁰ etc.

The present study is an attempt to remove the acid dye, AV49 from aqueous solutions by using polyaniline nano composite as an adsorbent. Polyaniline (PA) is a polyaromatic amine that can be easily synthesized chemically on the surface of sawdust from aqueous bronsted acid solutions. Chemical polymerization of aniline in aqueous acidic media can be easily performed using of oxidizing agents such as (NH₄)₂S₂O₈.

Experimental

Adsorbent

Polyaniline Composite was synthesized on sawdust surface of *Thevetia peruviana*. In order to prepare polymer coated sawdust, 5.0 g sawdust immersed in 50 mL of 0.20 M freshly distilled aniline in 1M HCl solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. Then 50 mL of 0.5 M (NH₄)₂S₂O₈ as an 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 (PAC) was filtered, washed with distilled water, dried in an oven at about 60 °C and sieved before use¹¹. The coating percentage of each polymer onto saw dust determined by weight difference of the dried sawdust before and after coating and it was nearly 5%. The characteristics of the PAC were studied as per the standard procedures^{12, 13} and the surface morphology was analyzed by Scanning Electron microscope images.

Adsorbate

The dye used in this study was Acid Violet 49 having molecular formula C₃₉H₄₀N₃NaO₆S₂ (Mol.Wt:733.87) with CI No. 42640. The molecular structure is given in Figure 1. All the chemicals used were high purity, commercially available analar grade. A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of dye (based on percentage purity) in one litre of double distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

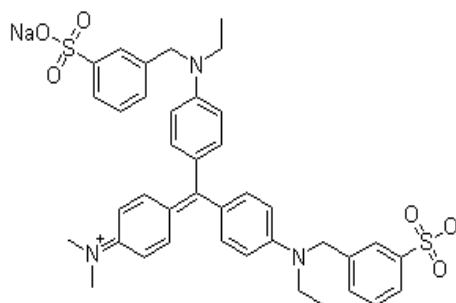


Figure 1 Molecular structure of Acid Violet 49.

Batch mode adsorption experiments

The adsorption experiments were carried out by agitating 100 mg adsorbent with 200 mL of dye solutions of 25 to 100 mg/L concentration at 150 rpm on an Orbital shaker (REMI make). The mixture was withdrawn at specified intervals, centrifuged using electrical centrifuge (Universal make) at 5000rpm for 20 minutes and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make UV Spectrophotometer

(CI 73) at 548 nm. The effect of pH was studied by using dilute HCl and NaOH solutions. The effect of temperature was studied at four different temperatures (30, 35, 40 and 45°C). All experiments were carried out in duplicate and the mean values are reported, where the maximum deviation was within 4%.

Desorption Studies

Desorption studies were carried out to analyse the mechanism of adsorption and recovery of the adsorbate and adsorbent. The supernatant was separated after centrifugation and the adsorbent was separated and allowed to agitate with 100 mL of distilled water at different pH (2 – 11) above the equilibrium time of adsorption. The desorbed dye solution was estimated as given in the adsorption studies¹⁴.

Results and Discussion

Characterization studies

The characteristics of PAC are presented in Table 1.

Table 1: Physico – Chemical characteristics of PAC.

S.No	Properties	PAC
1	pH	7.42
2	Conductivity, mS/cm ²	5.93
3	Methylene Blue Number, mg/g	45
4	Iodine Number, mg/g	87
5	Volatile matter, %	56.3

In the SEM micrograph of Sawdust-PPy composite, it can be seen from the figure 2 that the surface of sawdust is coated with PANi nano particles aggregated in clusters having globular particle shape with an average diameter of about 100nm¹⁵.

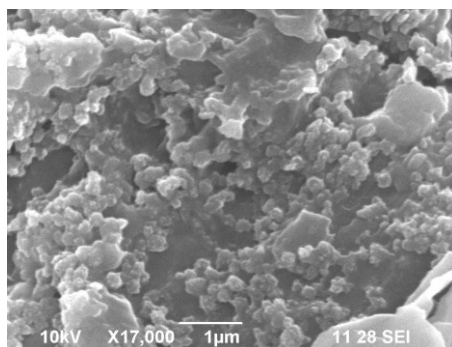


Figure 2 Scanning Electron Microscope of PAC.

Effect of agitation time and initial dye concentration:

The effect of time on the removal of AV49 by PAC is shown in Figure 3. The percentage of removal increases with time and attains equilibrium at 50 minutes for all concentrations studied (25 to 100 mg/L). After that no significant change was observed in the extent of adsorption. The amount of dye adsorption increases from 48.42 mg/g to 173.41 mg/g while increasing the initial dye concentration from 25 to 100 mg/L. This is due to the fact that with

increase in dye concentration, the presence of dye molecules near the adsorbent also increased. Similar results were reported for the adsorption of acid dye on activated bleaching earth¹⁶.

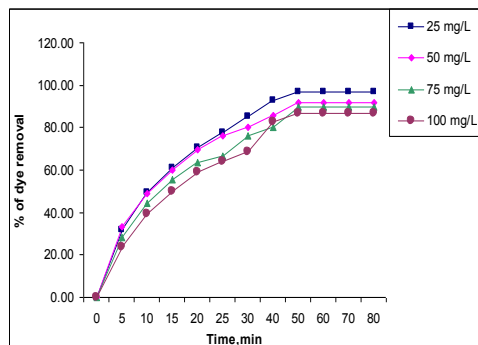


Figure 3 Effect of agitation time on the percentage removal of AV49 dye on PAC at 30° C (adsorbent dosage, 100mg; pH, 3.4).

Effect of pH

It is found that the percentage removal of AV49 was higher when the pH is below 5. After pH 5, the adsorption rate decreased. In acidic conditions, the surface of the adsorbent is positively charged due to high concentration of H^+ , so electrostatic attraction between the adsorbent and the adsorbate (anionic dye) is enhanced. Lower adsorption of AV49 under alkaline conditions is due to the presence of hydroxyl ions on the surface of adsorbents competing with the adsorbate for adsorption sites¹⁷.

PAC has positively fixed charged sites which are balanced with the anions (Cl^- ions) originating from monomer or oxidant solution during their synthesis. The small size dopant anions can be exchanged with other anionic species in treated solutions which have stronger interactions with the polymer¹⁸. It may be suggested that the rate of anionic dye removal is high due to the ion exchange mechanism between mobile Cl^- ions and anionic dye molecules.

Effect of temperature

It has been observed from Figure 4 that the percentage removal of AV49 by PAC increases from 91.96 % to 97.32% on increasing the temperature from 30°C to 45°C. This indicates that the sorption of anionic dyes is endothermic in nature¹⁹. These adsorption data were further analyzed with adsorption isotherm models to find out the suitable model.

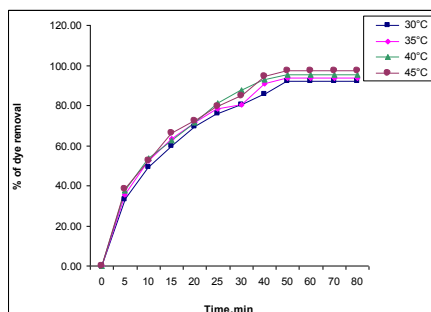


Figure 4 Effect of temperature on the adsorption of AV 49 dye on to PAC at initial concentration of 50 mg/L (adsorbent dosage, 100mg; pH, 3.4).

Equilibrium adsorption isotherm

The Langmuir adsorption isotherm has been used successfully for many adsorption processes of monolayer adsorption. Langmuir model²⁰ is represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{Q_o b_L} + \left(\frac{1}{Q_o} \right) C_e \quad (1)$$

where, q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_o is the monolayer adsorption capacity (mg/g) and b_L is Langmuir constant related to energy of adsorption, C_e is the equilibrium concentration (mg/L).

Figure 5 shows a linear plot of C_e / q_e against C_e for the removal of AV49 by PAC. The Langmuir adsorption capacity varies from 188.67 mg/g to 204.08 mg/g for AV49 onto PAC with increase in temperature from 30°C to 45°C. This indicates that the adsorption is favored at high operating temperature. Similar results were reported for the removal of basic and acidic dyes by the low cost adsorbent²¹. The Langmuir isotherm fits quite well with the experimental data with good correlation coefficient as shown in Table 2.

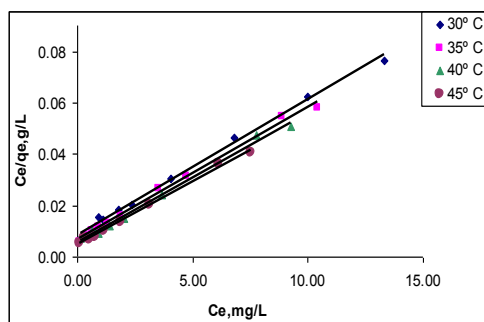


Figure 5 - Langmuir adsorption isotherm plot for the adsorption of AV49 dye onto PAC (adsorbent dosage, 100mg; pH, 3.4; agitation time, 100 min).

The separation factor R_L is calculated by the following equation to confirm the favorability of the adsorption process²². The values of R_L found to be between 0 and 1 and confirm that the adsorption process is favorable.

$$R_L = 1 / (1 + b_L \cdot C_0) \quad (2)$$

The Freundlich isotherm is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. Freundlich²³ model is expressed as

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

A plot of $\log q_e$ versus $\log C_e$ gives a linear line with a slope of $1/n$ and intercept of $\log k_f$ and the results are given in Table 2. From the experimental data, k_f values increased with increasing temperature for AV 49, implying that the adsorption process may be endothermic in nature. Values $n > 1$ represent a favorable adsorption condition. The correlation coefficient values are poor compared to the Langmuir isotherm model.

The D-R isotherm describes the adsorption on a single uniform pore. Dubinin-Raduskevich isotherm²⁴ is generally expressed as follows

$$q_e = q_D \cdot e^{-B \epsilon^2} \quad (4)$$

Table 2: Isotherm Constants for the adsorption of AV49 dye onto PAC at various Temperatures.

Temperature (°C)	Langmuir Isotherm			Freundlich Isotherm			D-R Isotherm		
	Q ₀ (mg/g)	b _L (L/mg)	r ²	n	k _f (mg ^{1-1/n} L ^{1/n} g ⁻¹)	r ²	q _D (mg/g)	E (kJ/mol)	r ²
30	188.68	0.6235	0.9954	2.16	62.9071	0.948 5	121.89	2.6720	0.8765
35	192.31	0.7647	0.9954	2.11	70.3558	0.943 5	126.67	2.8860	0.9418
40	200.00	0.8621	0.9943	2.01	76.6832	0.886 9	137.32	2.6720	0.9373
45	204.08	1.0208	0.9954	2.01	85.6446	0.896 9	141.26	2.8860	0.9030

The linear form of D-R isotherm equation is represented as:

$$\ln q_e = \ln q_D - B\varepsilon^2 \quad (5)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

Where q_D is the theoretical saturation capacity (mol/g), B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/J²), ε is the Polanyi potential, R (J/mol/K) is the gas constant and T(K) is the absolute temperature. The D-R constants q_D and B were calculated from the linear plots of ln q_e versus ε² (figure not shown) are given in Table 2. The constant B gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the following relationship²⁵

$$E = 1/(2B)^{1/2} \quad (7)$$

The adsorption is physisorption if the energy of activation is in the range of 5 – 40 kJ/mol and chemisorption if the energy of activation is between 40- 800 kJ/mol. The results from Table 2 suggest that the adsorption of AV 49 by PAC is physisorption in nature. D-R isotherm is not able to describe the experimental data properly because of the poor linear correlation coefficient for the adsorption of the dye onto PAC at different temperatures.

Kinetics of Adsorption

Adsorption kinetics is necessary for the design of adsorption systems²⁶. In this present study, the following two kinetic models were applied for the experimental data.

Pseudo first - order kinetic model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time²⁷. The rate constant of adsorption is expressed as a first – order rate expression given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (8)$$

Where, k₁ is the pseudo-first-order rate constant (min⁻¹).

The plot of log (q_e-q_t) versus t should give a straight line with slope of -k₁/2.303 and intercept log q_e which allows calculation of adsorption rate constant k₁ and equilibrium adsorption capacity q_e. Calculated values of k₁ and q_e for the adsorption of AV49 dye on

PAC are summarized in Table 3. The pseudo first-order kinetic model of Lagergren does not fit well with the experimental data over the whole range of initial concentrations studied.

Table 3: Kinetic parameters for the adsorption of AV 49 onto PAC.

Parameter	Initial dye concentration, mg/L				Temperature, °C			
	25	50	75	100	30	40	45	50
$q_{e,exp.}(mg/g)$	48.42	91.96	134.59	173.41	91.96	93.75	95.54	97.32
Pseudo first order kinetics								
$k_1 \times 10^{-2} (min^{-1})$	5.48	6.43	7.19	7.76	6.43	6.47	6.49	6.56
$q_{e,cal} (mg/g)$	35.89	76.31	142.96	203.66	76.31	72.18	70.42	76.77
r^2	0.9155	0.9337	0.9183	0.9202	0.9337	0.9194	0.9186	0.9191
Pseudo second order kinetics								
$k_2 \times 10^{-4} (g/mg \text{ min})$	14.45	8.85	4.50	2.74	8.85	9.65	9.66	8.97
h	4.7733	10.0200	11.6959	12.9702	10.0200	11.1607	11.6686	11.3250
$q_{e,cal}(mg/g)$	57.47	106.38	161.29	217.39	106.38	107.53	109.89	112.36
r^2	0.9953	0.9973	0.9957	0.9916	0.9973	0.9971	0.9960	0.9966

The pseudo second-order kinetic equation is expressed as²⁸

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where, k_2 is the rate constant of pseudo second –order adsorption (g/mg min) and q_e is the equilibrium adsorption capacity (mg/g).

Fig 6 shows the pseudo second -order plot for the adsorption of AV49 dye by PAC at various initial dye concentrations (Temperature 30°C). A plot of t/q_t against t should give a linear relationship from which k_2 and q_e can be determined from the intercept and slope of the plot. The correlation coefficient values are greater than 0.99 (Table 3) and the data points give a linear straight line. It indicates that the adsorption of AV49 dye by PAC follow the pseudo second order kinetic model.

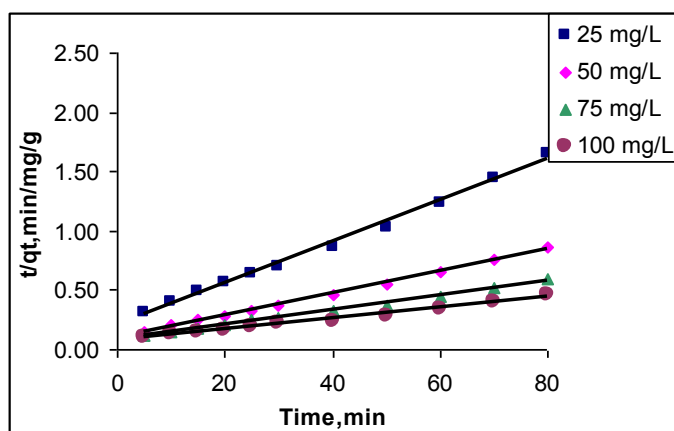


Figure 6 Pseudo second order plot for the adsorption of AV 49 onto PAC at 30 °C (adsorbent dosage, 100mg; pH, 3.4).

Thermodynamics analyses

Langmuir isotherm equation was applied to calculate the thermodynamic parameters as follows:

$$\Delta G^\circ = -RT \ln k_L \quad (10)$$

$$\ln k_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (11)$$

where k_L is the Langmuir equilibrium constant, ΔH° and ΔS° is the standard enthalpy and entropy changes of adsorption respectively.

Thermodynamic parameters like ΔH° , ΔS° and ΔG° were determined from the slope and intercept of Van't Hoff's plot of $\ln k_L$ versus $1/T$ (figure not shown). Table 4 shows the thermodynamic results for the removal of AV49 by PAC. The decrease in the negative values of ΔG° with an increase in temperature (30 to 45°C) indicates that the adsorption becomes more favorable at high temperature. The positive ΔH° values indicate that the adsorption of AV49 dye onto PAC is endothermic process. Furthermore the positive ΔS° indicates that the degrees of freedom increased at the solid – liquid interface during adsorption of acid dye onto PAC. Generally, ΔG° for physisorption is between -20 to 0 kJ/mol and for chemisorption is between -80 to -400 kJ/mol²⁹. The ΔG° Values from Table 4 confirm that the adsorption of AV49 by PAC is physisorption in nature.

Table 4 : Thermo dynamical parameters for the adsorption of AV 49 onto PAC.

Temperature,°C	ΔH° ,kJ/mol	ΔS° ,kJ/K/mol	ΔG° ,kJ/mol
30	30.0285	0.1388	-12.0279
35			-12.7219
40			-13.4159
45			-14.1099

The pseudo second order rate constant K_2 of the dye adsorption is expressed as a function of temperature by Arrhenius relationship using the Equation

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (12)$$

The value of E_a is calculated as 2.225 kJ/mol from the slope of a plot of $\ln k_2$ versus $1/T$ (Figure not shown). This confirmed that physisorption is predominantly operating force along with very weak chemical forces of attraction.

Desorption studies

Maximum desorption of 80.2 % for AV49 dye was observed at a pH range of 8 to 9. Desorption of Anionic dyes from PAC using alkaline solution may imply that physisorption mechanism of the anionic dye molecules along with weak chemical forces of attraction onto PAC.

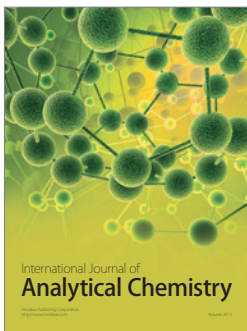
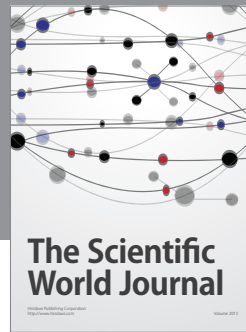
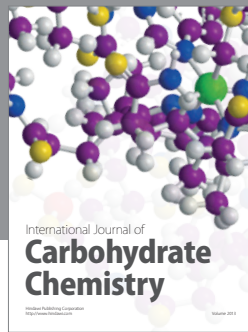
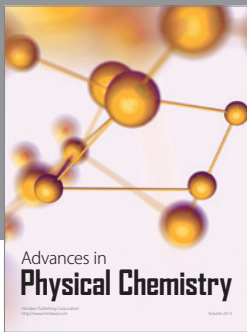
Conclusions

In this investigation, Polyaniline nano composite was easily synthesized by chemical oxidation method directly on the surface of sawdust of *Thevetia Peruviana*. Removal of AV49 is pH dependent and the maximum removal was attained at pH 3-4. The adsorption of the dyes increased with increase in temperature from 30°C to 45°C indicates that the adsorption is endothermic in nature, which was well supported by positive ΔH° values. Kinetic studies showed that adsorption of AV49 followed pseudo-second order model. The data obtained from adsorption isotherms are well fitted with Langmuir model which suggests the monolayer coverage of the dyes on surfaces of PAC. The Langmuir adsorption capacity varies from 188.67 mg/g to 204.08 mg/g for AV49 onto PAC with increase in temperature from 30°C to 45°C. The negative ΔG° values obtained from Van't Hoff plots confirmed that the adsorption of AV49 is spontaneous in nature. It was suggested that PAC can be used as a potential adsorbent for the removal of acidic dyes from aqueous solutions.

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