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Polyaniline Nano Composite for the Adsorption of Reactive Dye from Aqueous Solutions: Equilibrium and Kinetic Studies

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In the present study, polyaniline nano composite was synthesized through direct chemical polymerization. Polyaniline nano composite was tested for the removal of reactive dye, reactive orange 4 from aqueous solutions by batch adsorption technique under varying conditions of agitation time, dye concentration, pH and temperature. Lower solution pH (3 to 5) favoured the adsorption of reactive dye onto polyaniline nano composite. The dye adsorption increases from 45.83 to 143.59 mg/g on increasing the initial concentration from 25 to 100 mg/L. The pseudo second order kinetic model adequately described the kinetics of dye adsorption with high correlation coefficient (0.99). Langmuir isotherm model well fitted to the experimental data. Thermodynamic parameters like free energy (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) were also calculated. Maximum desorption of 78.6 % for reactive orange 4 was observed at a pH range of 8 to 9. The results indicated that polyaniline nano composite is a promising adsorbent for the removal of dyes from aqueous solution.

Key Words: Polyaniline composites, Reactive orange 4, Removal, Kinetics, Isotherms.

INTRODUCTION

The wastewater treatment has been a main problem of the textile industry for long time. These effluents contain various kinds of synthetic dyestuffs. Owing to the good solubility, synthetic dyes are common water pollutants and they are frequently found in trace quantities in industrial wastewater[1]. Dyes may have chronic and acute effects on living organisms, affect the nature of water and inhibit sunlight penetration into the stream which reduces photosynthesis[2].

Reactive dyes are extensively used in dyeing process. However about 10 to 40 % of these dyes remain in the effluent[3,4]. Because of the more solubility of reactive dyes, removal from wastewater is difficult by conventional coagulation and the activated sludge process[5]. Adsorption is an effective treatment method that is widely used for the removal of contaminants from water and wastewater. This method has also been proven to be an important way to treat coloured effluents[6].

Activated carbon is the most commonly used adsorbent due to its high adsorption capacity[7]. However the high cost of activated carbon restricts its use largely in developing countries. This has led many researchers to search for the use of low cost and efficient alternative materials such as coal[8], fly ash[9], rice husk[10], bagasse pith[11], date pits[12], fruit stones and nutshells[13]. However very little data are available on the adsorption kinetics of sawdust.

In this study, polyaniline nano composite 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 $(NH_4)_2S_2O_8$. Polyaniline nano composite used for the removal of reactive orange 4 from aqueous solution.

EXPERIMENTAL

Adsorbate: The dye used in this study was reactive orange 4 having molecular formula $C_{24}H_{13}N_6O_{10}S_3Na_3Cl_2$ (m.w. 781.46) with CI No. 18260. The molecular structure is given in Fig. 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 1 L of double distilled water. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

Adsorbent: Polyaniline composite was synthesized on sawdust surface of *Thevetia peruviana*. In order to prepare polymer coated sawdust, 5 g sawdust immersed in 50 mL of 0.20 M freshly distilled aniline in 1 M HCl solution for 6 h

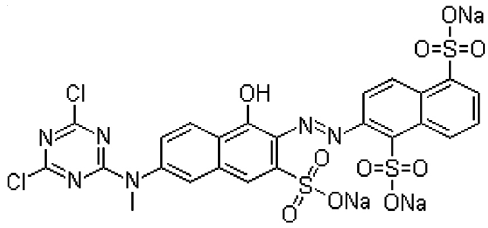

Fig. 1. Molecular structure of reactive orange 4

before polymerization. The excess of the monomer solution was removed by simple decantation. Then 50 mL of 0.5 M $(NH_4)_2S_2O_8$ as an oxidant solution was added into the mixture gradually and the reaction was allowed to continue for 4 h at room temperature. The polymer coated sawdust (polyaniline nano composite) was filtered, washed with distilled water, dried in an oven at *ca.* 60 ºC and sieved before use[14]. 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 polyaniline nano composite were studied as per the standard procedures[15,16] and the surface morphology was analyzed by scanning electron microscope images.

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 5000 rpm for 20 min and unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make UV spectrophotometer (CI 73) at 479 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 ºC). All experiments were carried out in duplicate and the mean values are reported, where the maximum deviation was within 4 %.

The amount of dye adsorbed on polyaniline nano composite was calculated from the following equation:

$$q_t = \frac{(C_0 - C_e)}{M} V \quad (1)$$

where, q_t (mg/g) is the amount of dye adsorbed at time t, C_0 and C_e (mg/L) are the concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of dye solution and W (g) is the mass of dry adsorbent.

Desorption studies: Desorption studies were carried out to analyze 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 studies[17].

RESULTS AND DISCUSSION

Characterization studies: The characteristics of polyaniline nano composite are presented in Table-1. It can be seen from the SEM micrograph (Fig. 2) of sawdust-PPy composite that the surface of sawdust is coated with polyaniline nano composites aggregated in clusters having globular particle shape with an average diameter of about 100 nm[18].

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF POLYANILINE NANO COMPOSITE (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

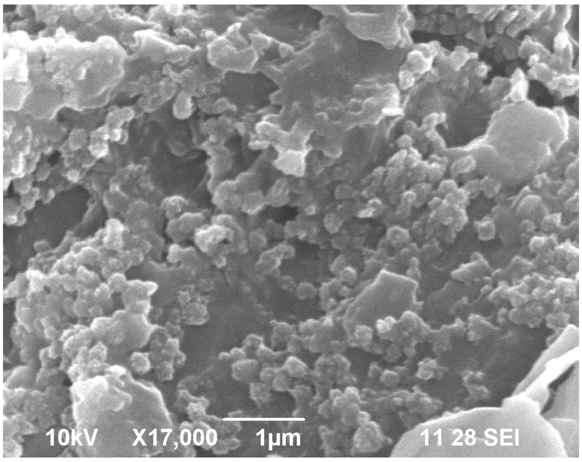

Fig. 2. Scanning electron microscope of polyaniline nano composite

Effect of agitation time and initial dye concentration: The effect of time on the removal of reactive orange 4 by polyaniline nano composite is shown in Fig. 3. The percentage of removal increases with time and attains equilibrium at 50 min 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 45.83 to 143.59 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 textile reactive dye using *Posidonia oceanica* (L) fibrous mass[19].

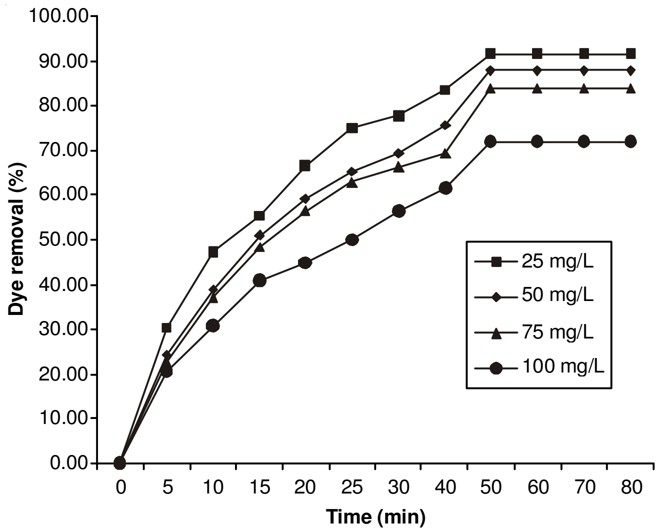

Fig. 3. Effect of agitation time on the percentage removal of reactove pramge 4 dye on polyaniline nano composite at 30 ºC (adsorbent dosage, 100 mg; pH, 4.1)

Polyaniline nano composite 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 polymer[14]. 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 pH: It is found that the percentage removal of reactive orange 4 was higher when the pH is below 5. Above the 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 reactive orange 4 under alkaline conditions is due to the presence of hydroxyl ions on the surface of adsorbents competing with the adsorbate for adsorption sites[20].

Effect of temperature: It has been observed from Fig. 4 that the percentage removal of reactive orange 4 by polyaniline nano composite increases from 87.76 to 97.96 % on increasing the temperature from 30 to 45 ºC. This indicates that the sorption of anionic dyes is endothermic in nature[21]. These adsorption data were further analyzed with adsorption isotherm models to find out the suitable model.

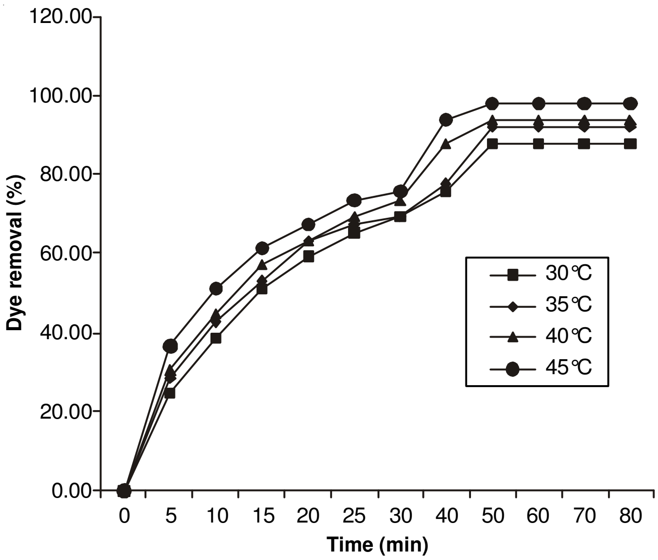

Fig. 4. Effect of temperature on the adsorption of reactive orange 4 dye on to polyaniline nano composite at initial concentration of 50 mg/L (adsorbent dosage, 100 mg; pH, 4.1)

Adsorption kinetics: Adsorption kinetics is necessary for the design of adsorption systems[22]. In 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 time[23]. The rate constant of adsorption is expressed as a first - order rate expression given as:

$$\log\ (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

where, k_1 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 $-k_1/2.303$ and intercept log q_e which allows calculation of adsorption rate constant k_1 and equilibrium adsorption capacity q_e. Calculated values of k_1 and q_e for the adsorption of reactive orange 4 dye on polyaniline nano composite are summarized in Table-2. The pseudo first-order kinetic model of Lagergren does not fit well with the experimental data over the whole range of initial concentrations studied. The pseudo second-order kinetic equation is expressed as[24]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

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. 5 shows the pseudo second -order plot for the adsorption of reactive orange 4 dye by polyaniline nano composite at various initial dye concentrations (temperature 30 ºC). A plot of t/q_t against t should give a linear relationship from which and q_e can be determined from the intercept and slope of the plot. The correlation coefficient values are greater than 0.99 (Table-2) and the data points give a linear straight line. It indicates that the adsorption of reactive orange 4 dye by polyaniline nano composite follow the pseudo second order kinetic model.

Equilibrium adsorption isotherm: The Langmuir adsorption isotherm has been used successfully for many adsorption processes of monolayer adsorption. Langmuir model[25] is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b_L} + \left(\frac{1}{Q_o}\right) C_e \qquad (4)$$

TABLE-2
KINETIC PARAMETERS FOR THE ADSORPTION OF REACTIVE ORANGE 4 ONTO POLYANILINE NANO COMPOSITE

Parameter	Initial dye concentration (mg/L)				Temperature (ºC)			
	25	50	75	100	30	40	45	50
q_e exp (mg/g)	45.83	87.76	125.81	143.59	87.76	91.84	93.88	97.96
Pseudo first order kinetics								
$k_1 \times 10^{-2}$ (min^{-1})	5.34	6.56	7.14	7.42	6.56	6.61	6.68	6.70
q_e cal (mg/g)	35.74	94.30	148.66	181.13	94.30	101.79	95.08	93.37
r^2	0.9324	0.9163	0.9013	0.9029	0.9163	0.9077	0.9241	0.9169
Pseudo second order kinetics								
$k_2 \times 10^{-4}$ (g/mg min)	14.82	5.30	3.56	2.95	5.30	5.39	5.85	6.69
h	4.3783	6.4061	8.9606	9.7656	6.4061	6.9638	7.7340	9.0416
q_e cal(mg/g)	54.35	109.89	158.73	181.82	109.89	113.64	114.94	116.28
r^2	0.9963	0.9942	0.9925	0.9918	0.9942	0.9926	0.9935	0.9946

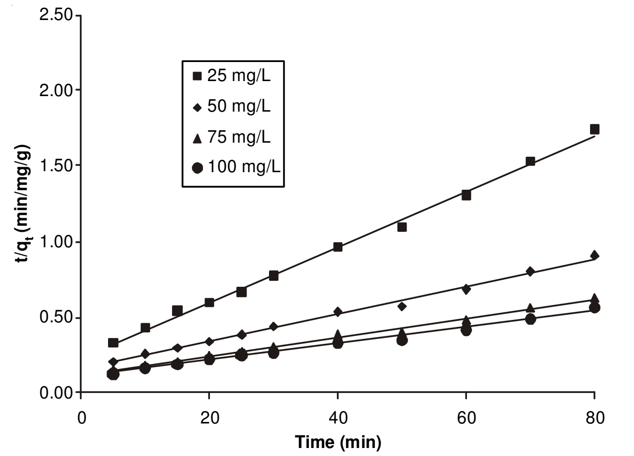

Fig. 5. Pseudo second order plot for the adsorption of reactive orange 4 onto polyaniline nano composite at 30 ºC (adsorbent dosage, 100 mg; pH, 4.1)

where, Q_0 is the monolayer adsorption capacity (mg/g) and b_L is Langmuir constant related to energy of adsorption.

Fig. 6 shows a linear plot of C_e/q_e against C_e for the removal of reactive orange 4 by polyaniline nano composite. The Langmuir adsorption capacity varies from 161.29 mg/g to 200 mg/g for the adsorption of reactive orange 4 onto polyaniline nano composite with increase in temperature from 30 to 45 ºC. This indicates that the adsorption is favoured at high operating temperature. Similar results were reported for the adsorption of reactive brilliant red HE-3B by activated charcoal[26]. The Langmuir isotherm fits quite well with the experimental data with good correlation coefficient as shown in Table-3.

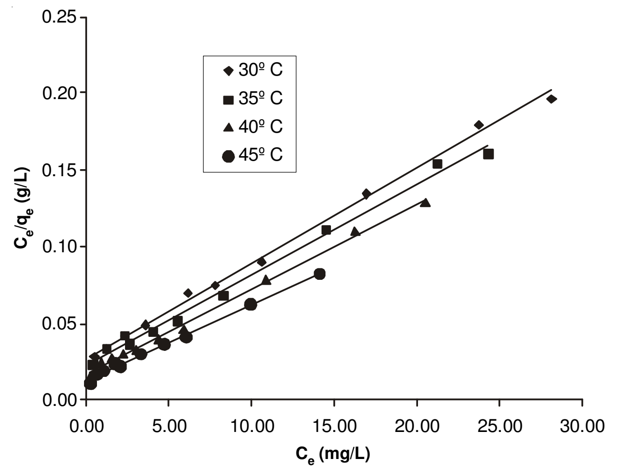

Fig. 6. Langmuir adsorption isotherm plot for the adsorption of reactive orange 4 dye onto polyaniline nano composite (adsorbent dosage, 100 mg; pH, 4.1; agitation time, 100 min)

The separation factor R_L is calculated by the following equation to confirm the favourability of the adsorption process[27].

$$R_L = 1/(1+ b_L \cdot C_0) \qquad (5)$$

The values of R_L found to be between 0 and 1 and confirm that the adsorption process is favourable.

The Freundlich isotherm is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. Freundlich[28] model is expressed as

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \qquad (6)$$

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-3. From the experimental data, k_f values increased with increasing temperature for reactive orange 4, implying that the adsorption process may be endothermic in nature. Values n > 1 represent a favourable adsorption condition. The correlation coefficient values are poor compared to the Langmuir isotherm model.

The Dubinin-Raduskevich (D-R) isotherm describes the adsorption on a single uniform pore. Dubinin-Raduskevich isotherm[29] is generally expressed as follows:

$$q_e = q_D . e^{-B\varepsilon^2} \qquad (7)$$

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

$$\ln q_e = \ln q_D - B\varepsilon^2 \qquad (8)$$

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \qquad (9)$$

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 (mol^2/J^2), 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* ε^2 (figure not shown) are given in Table-3. 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 relationship[30]:

$$E = 1/(2B)^{1/2} \qquad (10)$$

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-3 suggest that the adsorption of reactive orange 4 by polyaniline nano composite 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 polyaniline nano composite at different temperatures.

TABLE-3
ISOTHERM CONSTANTS FOR THE ADSORPTION OF REACTIVE ORANGE 4 DYE ONTO POLYANILINE NANO COMPOSITE AT VARIOUS TEMPERATURES

Temperature (ºC)	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	161.29	0.2305	0.9969	2.05	33.2659	0.9472	102.843	1.29	0.8167
35	169.49	0.2682	0.9926	2.01	37.0169	0.9225	104.752	1.581	0.7656
40	178.57	0.3457	0.9962	2.03	44.2588	0.9372	108.777	2.236	0.7571
45	200.00	0.4065	0.9965	1.88	52.9785	0.9594	117.601	2.236	0.7976

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

$$\Delta G^{o} = -RT \ln k_{L} \quad (11)$$

$$\ln k_{L} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{R}\frac{1}{T} \quad (12)$$

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 reactive orange 4 by polyaniline nano composite. The decrease in the negative values of ΔG° with an increase in temperature (30 to 45 °C) indicates that the adsorption becomes more favourable at high temperature. The positive ΔH° values indicate that the adsorption of reactive dye onto polyaniline nano composite is endothermic process. Furthermore the positive ΔS° indicates that the degrees of freedom increased at the solid-liquid interface during adsorption of reactive dye onto polyaniline nano composite. Generally, ΔG° for physisorption is between -20 to 0 kJ/mol and for chemisorption is between -80 to -400 kJ/mol[31]. The ΔG° values from Table-4 confirm that the adsorption of reactive orange 4 by polyaniline nano composite is physisorption in nature.

TABLE-4
THERMODYNAMICAL PARAMETERS FOR THE ADSORPTION OF REACTIVE ORANGE 4 ONTO POLYANILINE NANO COMPOSITE

Temperature (°C)	ΔH° (kJ/mol)	ΔS° (kJ/K/mol)	ΔG° (kJ/mol)
30	42.2493	0.1693	-9.0486
35			-9.8951
40			-10.7416
45			-11.5881

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:

$$\ln k_{2} = \ln A - \frac{E_{a}}{RT} \quad (13)$$

The value of E_a is calculated as 12.444 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 78.6 % for reactive orange 4 dye was observed at a pH range of 8 to 9. Desorption of reactive dye from polyaniline nano composite using alkaline solution may imply that physisorption mechanism of the anionic dye molecules along with weak chemical forces of attraction onto polyaniline nano composite.

Conclusion

In this present study, polyaniline nano composite was easily synthesized by chemical oxidation method directly on the surface of sawdust of *Thevetia peruviana* and used for the removal of reactive orange 4 from aqueous solutions. Removal of reactive orange 4 is pH dependent and the maximum removal was attained when pH was below 5. The adsorption of the dyes increased with increase in temperature from 30 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 reactive orange 4 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 polyaniline nano composite. The Langmuir adsorption capacity varies from 161.29 to 200 mg/g for reactive orange 4 onto polyaniline nano composite with increase in temperature from 30 to 45 °C. The negative values obtained from van't Hoff plots confirmed that the adsorption of reactive dye (reactive orange 4) is spontaneous in nature. The results showed that polyaniline nano composite can be used as a potential adsorbent for the removal of reactive dye, reactive orange 4 from aqueous solutions.

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