



Polypyrrole Composite - A Potential Material for the Removal of Acid Dyes

P.N. PALANISAMY¹, A. AGALYA^{2,*} and P. SIVAKUMAR³

²Department of Chemistry, Al-Ameen Engineering College, Erode-638 104, India

¹Department of Chemistry, Kongu Engineering College, Erode-638 052, India

³Department of Chemistry, Arignar Anna Government Arts College, Namakkal-637 002, India

*Corresponding author: E-mail: agalarun@rediffmail.com

(Received: 23 May 2012;

Accepted: 16 April 2013)

AJC-13362

The present research work provides information on the dye removal potential of polypyrrole saw dust composite, prepared by reinforcement of natural wood saw dust (obtained from *Euphorbia tirucalli* L wood) and polypyrrole matrix phase. Dye adsorption on polypyrrole composite was characterized in terms of adsorption isotherm, kinetics and the parameters studied were initial dye concentration, contact time, pH and temperature. The kinetic data obtained at different initial dye concentration and temperatures were studied using pseudo-first order and pseudo-second order model. The equilibrium data were analyzed by Freundlich and Langmuir isotherm model. The equilibrium isotherm data were fitted well with Langmuir isotherm model. The maximum monolayer adsorption capacities calculated by Langmuir model were 243.9, 243.90, 250 and 256.41 mg/g for acid orange 10 at 30, 35, 40 and 45 °C respectively. The thermodynamic parameters including ΔG° , ΔH° and ΔS° were evaluated and suggesting the feasible, spontaneous, endothermic nature of ion exchange adsorption with weak van der Waals force of attraction. Activation energy for the adsorption of acid orange 10 by polypyrrole composite was 2.0704 kJ/mol. Isothermic heat of adsorption calculated using Clausius-Clapeyron equation also supported the ion exchange adsorption process in which forces of attraction between dye molecules and polypyrrole composite is weak.

Key Words: *Euphorbia tirucalli* L saw dust, Polymer composites, Acid orange, Isotherm studies, Activation energy.

INTRODUCTION

In the present century, population increase and rapid industrial development results in an increasing consumption of natural habitat. Besides these, water pollution generated by textile industries receiving great attention among all industrial sectors due to huge volume of effluents and its composition. Without adequate treatment, textile dyes can remain in the environment for an extended period of time¹.

Acid dyes comprise the largest class of dye in the colour index (CI). The anionic compounds mainly used for dyeing nitrogen containing fabrics like wool, polyamide, modified acryl and silk. Most of the acid dyes belong to azo and anthraquinone groups and give a wide range of bright colours on textiles and are the most difficult to remove. Therefore, removal of dyes from effluent is very important in terms of environment and many treatment methods such as physical, chemical and biological methods²⁻⁴ have been applied. However these methods have one or more limitations such as low efficiency, high cost, greater energy consumption and generation of sludge. To overcome these problems, there is an urgent requirement for the development of innovative, economic and

effective technology for the removal of dye from the effluent. A great interest has been recently directed to polymer composites for the removal of dyes from waste water. Polymer composites or green composites are a viable alternative for the exiting wastewater treatment technologies. Polymer composites are materials formed by matrix (polymer) and a reinforcement of natural wood fibre derived from renewable resources. These are environmentally friendly, low cost and renewable material. Polymer composites would contribute to solve the water pollution problem around the world and could be the efficient and promising adsorbent for the removal of commercial dyes from aqueous solution. One efficient way of increasing adsorption capacity of saw dust is the polymerization of monomer on the surface of saw dust.

In recent years, conducting electro active polymers such as polyaniline and polypyrrole have attracted with great attention due to their electrical conductivity and electro activity⁵⁻⁷. Polypyrrole, a conducting polymer doped with releasable or exchangeable counter ions coated on saw dust has been utilized for the removal of anionic dyes from aqueous solutions based on ion exchange properties of these polymers. The dye removal technology utilizing polymer composite is a

viable option because of its economic, eco-friendly, abundantly available, green way and efficient technique.

In this study, polypyrrole-saw dust composite prepared by polymerizing pyrrole on saw dust surface *via* chemical route at room temperature. The main objective of this study is to evaluate the potential of polymer composite (PPC) prepared from *Euphorbia tirucalli* wood saw dust. The study 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 and thermodynamic parameters related to adsorption process were also performed and reported.

EXPERIMENTAL

Preparation of polypyrrole composites: *Euphorbia tirucalli* L wood saw dust used for the preparation of polymer composite. The saw dust was first washed with distilled water in order to remove impurities and finally dried at 60 °C for 2 h. The polypyrrole was synthesized on saw dust surface, which was previously soaked in monomer pyrrole solution (0.2 M) for 12 h at room temperature followed by slow addition of chemical oxidants 0.5 M FeCl₃ at room temperature for 4 h⁸.

Polymerization was carried out on the surface of saw dust immediately after the addition of oxidant solution. The polymer coated saw dust designated as PPC were filtered, washed with distilled water and dried.

Adsorbent character studies: Physico-chemical characteristics of polypyrrole composite were studied as per the standard testing methods^{9,10}. In order to characterize the surface structure and morphology of polypyrrole saw dust composite, SEM analysis was carried out using scanning electron microscope and shown in Fig. 1.

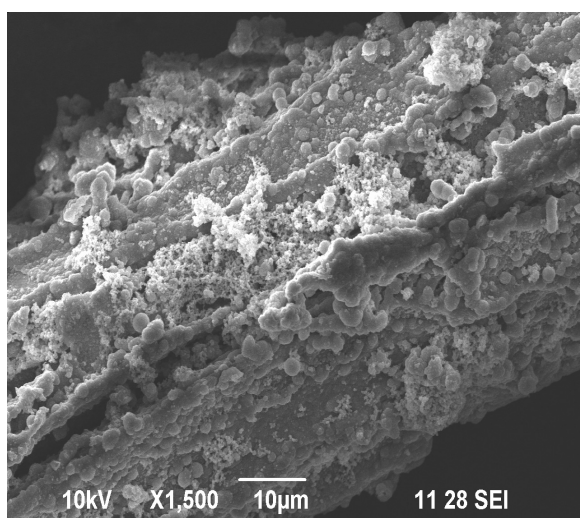


Fig. 1. SEM image of polypyrrole composite

Adsorbate: Acid orange 10 (m.w. 452.38, m.f. C₁₆H₁₀N₂O₇S₂Na₂, λ_{max}: 478 nm), used in this study is of commercial quality and used without further purification. The structure of AO10 shown is in Fig. 2. A stock solution of AO10 (1000 mg/L) was prepared by dissolving appropriate amount of dye (based on the percentage purity) and suitably diluted

as and when required. The concentration of the dye was determined using Elico make UV-visible spectrophotometer at wavelength 478 nm. All chemicals used were analytical reagent grades and used without further purification.

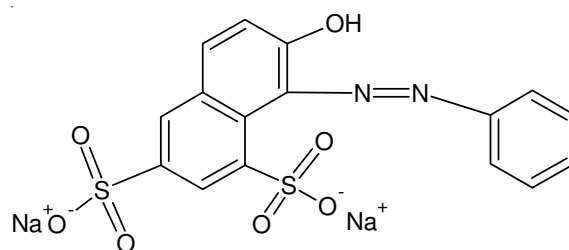


Fig. 2. Structure of acid orange 10

Batch adsorption experiments: Adsorption experiments were conducted at room temperature by agitating 0.10 g of adsorbent with 200 mL of dye solution of desired concentration in 250 mL stoppered flask using a shaker at a speed of 120 rpm for equilibrium time except for contact time experiments. The effect of solution pH on the equilibrium adsorption of dyes (50 mg/L) was investigated under similar experimental conditions between pH 2 to 12. The effect of temperature on the equilibrium adsorption was studied under similar conditions between temperatures of 30 to 45 °C. Equilibrium isotherm studies were conducted by agitating 200 mL of dye solution with 0.1 g of adsorbent at different initial dye concentration (10-170 mg/L) and agitated for equilibrium time.

RESULTS AND DISCUSSION

Analysis of adsorbent characteristics: The physico-chemical characteristics of PPC prepared from *Euphorbia tirucalli* L wood was summarized in Table-1. The SEM analysis is a useful tool for the analysis of the surface morphology of an adsorbent. SEM image of polypyrrole composite is shown in Fig. 2.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF
POLYPYRROLE COMPOSITE

Properties	Polypyrrole composite
pH	7.81
Moisture content (%)	9.85
Conductivity (µS/cm)	5.86
Volatile matter (%)	54.8
Methylene blue value (mg/g)	41.0
Iodine number (mg/g)	98.0

Analysis of adsorption parameters

Effect of initial dye concentration and contact time: The rate of adsorption is a function of the initial dye concentration and contact time which is an important factor for the effective adsorption. Fig. 3 depicts the adsorptions of AO10 by polypyrrole composite at various initial dye concentrations with contact time. On increasing the initial dye concentration from 25 to 100 mg/L, the adsorption capacity of polypyrrole composite increases from 48.15 to 173.74 mg/g and the percentage of dye adsorption decreases from 96.3 to 86.87 % for AO10. The percentage removal of dyes decreases

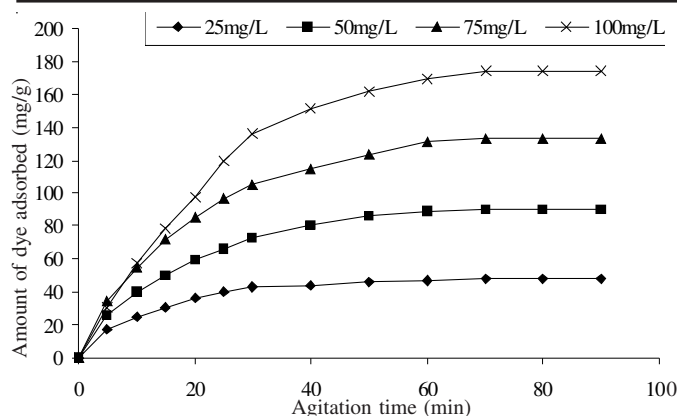


Fig. 3. Effect of initial dye concentration and contact time for the adsorption of AO10 onto polypyrrole composite

when the initial concentration increases from 25 to 100 mg/L for polypyrrole composite because the adsorbent has a limited number of active sites which becomes saturated at a certain concentration. Similar results have been observed for the removal of Eosin Y using conducting electro polymers⁸ and adsorption of reactive orange on loofa activated carbon¹¹. The equilibrium adsorption increased with rise in contact time and equilibrium reached at 70 min for AO10. Initially the rate of adsorption was rapid then it slowly reaches equilibrium, further increase in contact time did not enhance the adsorption. The initial rapid adsorption may be attributed to the presence of large number of available binding sites for adsorption and slower adsorption is due to saturation of binding sites and equilibrium attained.

Effect of pH: The pH of the dye solution has been recognized as one of the most important factors influencing the adsorption process. The effect of initial pH on the dye removal efficiency of polypyrrole composite was studied at different pH ranging from 2-12 and shown in Fig. 4. The adsorption of AO10 was pH dependent. The maximum percentage removal of AO10 occurs at acidic pH 3-4 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 polypyrrole composite and AO10, is enhanced. But in alkaline conditions, electrostatic repulsion occurs resulting in decreased adsorption. Similar results have been reported for the adsorption of Eosin Y using conducting electro polymers⁸.

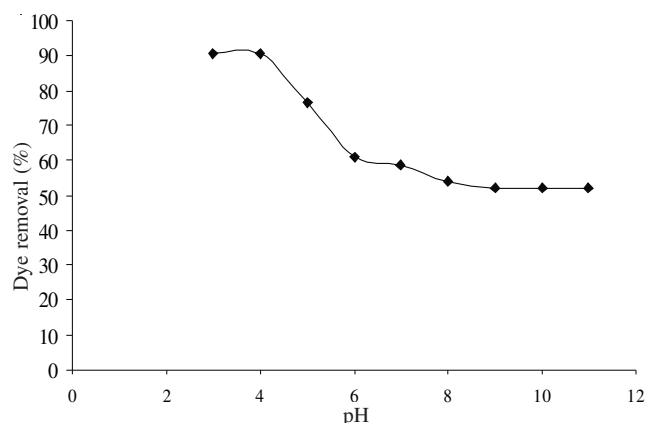


Fig. 4. Effect of pH for Adsorption of AO10 onto polypyrrole composite

Effect of temperature: The effect of temperature on dye adsorption has been studied at 30, 35, 40 and 45 °C. The results indicated that the amount of dye adsorbed at equilibrium increases with increasing temperature. This may be a result of increase in the mobility of the dye molecules with increase in temperature¹². The equilibrium adsorption increased from 90.41 to 96.58 % on increasing the temperature from 30 to 45 °C for AO10, indicates that the adsorption is endothermic process.

Adsorption kinetics: In order to investigate the mechanism of adsorption, characteristic constants of adsorption were determined using pseudo-first order equation¹³ of Lagergren based on solid capacity and pseudo-second order equation¹⁴ based on solid phase adsorption.

Pseudo-first order Lagergren kinetic equation can be expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

The integrated form of equation:

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

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

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

The amount of dye adsorbed at equilibrium q_e and first order rate constant k_1 calculated from intercept and slope of the plot $\log(q_e - q_t)$ vs. time as shown in Fig. 5 and the values listed in Table-2. The value of k_2 decreases 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 processes¹⁵. Based on the values of co-relation co-efficient which is above 0.99, the second order kinetic model was more suitable to describe the adsorption process for anionic dye adsorption than pseudo-first order model. But to identify the mechanism of adsorption, the kinetic results were further analyzed by ion exchange process.

Ion exchange process: In case of polymer saw dust composite the increase in adsorption capacity is due to its ion exchangeable active sites. Polypyrrole has positively fixed

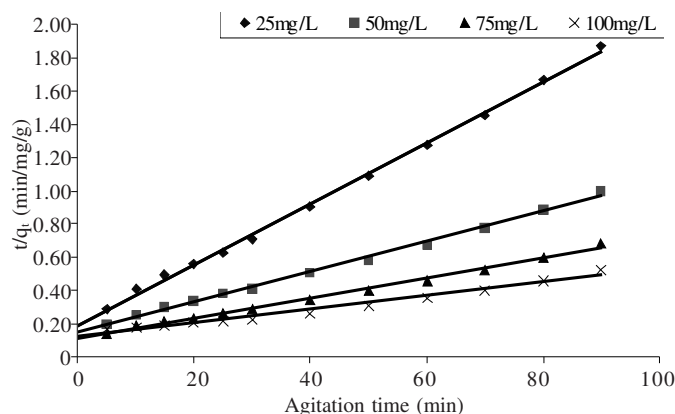


Fig. 5. Pseudo-second order plot for adsorption of AO10 onto PPC

TABLE-2
RESULTS OF KINETIC STUDIES FOR
ADSORPTION OF ACID ORANGE 10

Conc. (mg/L)	First order kinetics			Second order kinetics		
	k_1 (min^{-1})	q_e (cal) (mg/g)	r^2	$k_2 \times 10^{-4}$ (g/mg min)	q_e (cal) (mg/g)	r^2
25	0.0629	43.53	0.9925	17.7049	54.64	0.9981
50	0.0658	106.17	0.9744	5.5689	109.89	0.9964
75	0.0596	150.55	0.9682	3.2347	166.66	0.9964
100	0.0605	216.97	0.9786	1.4174	243.90	0.9787

charged sites which are balanced with the anion. The small size dopant anions can be exchanged with other anionic species in the dye solutions which have stronger interactions with the polymer⁸. Therefore, higher percentage removal of anionic dyes by the polymer saw dust composite is supposed to occur by ion-exchange mechanism due to exchangeable active sites and explained by pseudo-second order kinetics. However, the importance of other processes such as electrostatic interactions between highly polar and positively charged polymer and negatively charged anionic dye molecules also cannot be ignored.

Equilibrium adsorption isotherms

Adsorption isotherm: The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour between adsorbate and adsorbent. It is important for predicting the adsorption capacity of adsorbent, which is one of the main parameters required for design of an adsorption system. The Langmuir¹⁶ and Freundlich¹⁷ models were used to describe the adsorption of anionic dye AO10 onto polypyrrole composite.

The Langmuir equation can be written as:

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{c_e}{Q_0} \quad (4)$$

This equation has been successfully applied to many adsorption processes. The Langmuir isotherm is based on 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 site¹⁸. 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 values of Q_0 and b_L calculated from the slopes and intercepts of the linear plots of C_e/q_e vs. C_e shown in Fig. 6 and the results are summarized in Table-3. 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 system¹⁹. The maximum adsorption capacity Q_0 varies from 243.9 to 256.41 mg/g for AO10 while increasing the temperature from 30 to 45 °C.

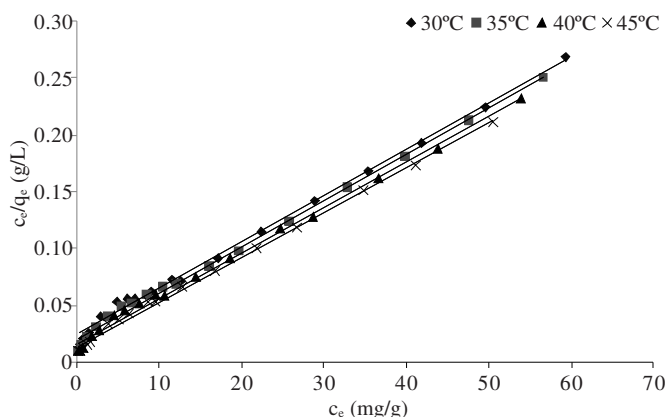


Fig. 6. Langmuir isotherm for adsorption of AO10 onto polypyrrole composite

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L ¹⁹ that is defined by the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

where, C_0 is the highest initial solute concentration. The R_L value indicated the type of adsorption isotherm to be either unfavourable ($R_L > 1$), favourable ($R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). Langmuir model is more appropriate to explain the nature of adsorption of AO10 with correlation coefficient of 0.9961 to 0.9969.

The Freundlich model is employed to describe the heterogeneous system, which is characterized by heterogeneity factor $1/n$. It considers multilayer adsorption with heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. The Freundlich isotherm is expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad (6)$$

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); c_e is the equilibrium concentration of adsorbate (mg/L). The values of K_f and $1/n$ are calculated from intercept and slopes of linear plot of $\log q_e$ versus $\log c_e$ (figure not shown). The value of $1/n$ is below one for AO10 studied indicating that the adsorption of dyes is favourable. The results of isotherms are summarized in Table-3.

TABLE-3
COMPARISON OF THE COEFFICIENTS OF ISOTHERM PARAMETERS OF ACID ORANGE 10

Adsorbent	Temp. (°C)	Isotherm models					
		Langmuir			Freundlich		
		Q_0 (mg/g)	b (L/mg)	r^2	n	k_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	r^2
AO10	30	243.90	0.1694	0.9961	2.4154	50.1418	0.9494
	35	250.00	0.2019	0.9960	2.5106	55.3477	0.9601
	40	256.41	0.2409	0.9956	2.7078	64.1357	0.9706
	45	256.41	0.2786	0.9969	2.7594	69.4704	0.9585

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 AO10 onto polypyrrole composite.

Thermodynamic parameters

Activation energy: The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (7)$$

where, E_a and A refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ vs. $1/T$ as shown in Fig. 7. The activation energy was found to be 2.0704 kJ/mol for adsorption of AO10 onto polymer coated saw-dust respectively. The physisorption usually have energies in the range of 5-40 kJ/mol, while higher activation energies 40-800 kJ/mole suggests chemisorption²⁰. The activation energy < 40 KJ/mol for AO10 dyes indicates the physisorption.

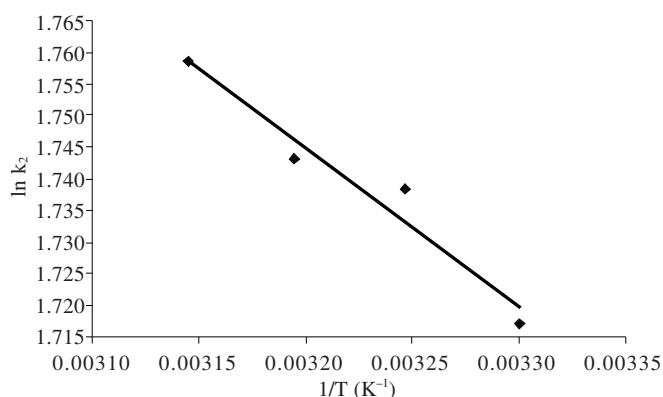


Fig. 7. Arrhenius plot for adsorption of AO10 onto polypyrrole composite

In adsorption process, energy consideration must be taken into account in order to determine what process will occur spontaneously. Thermodynamic parameters values are the actual indicators for practical application of a process²¹.

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be determined by using Vant Hoff's equation:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

where, T is the absolute temperature and K_L (L/g) is the standard thermodynamic equilibrium constant. By plotting a graph of $\ln K_L$ vs. $1/T$, the values of ΔS° and ΔH° can be estimated from

the slopes and intercepts (figure not shown). The results are summarized in Table-4. The Gibbs free energy change (ΔG°) is an indication of spontaneity of a chemical reaction therefore it is an important criterion for spontaneity. The change in free energy for physisorption is between -20 and 0 kJ/mol, but chemisorption is in a range of -80 to -400 kJ/mol^{22,23}. The values of ΔG° for the adsorption of AO10 was with in the range of -20 and 0 kJ/mol, indicating that the physisorption is the dominating mechanism. The positive values of ΔS° confirming physical adsorption nature and increased randomness at the solid-solution interface during adsorption and indicate affinity of the dye onto adsorbents²⁴. Physisorption and chemisorption can be classified to a certain extent by the magnitude of enthalpy change. Bonding strengths of < 84 kJ/mol are typically considered as those of physisorption bonds. Chemisorption bond strengths can be 84-420 kJ/mol²⁵.

Isosteric heat of adsorption: Isosteric heat of adsorption ΔH_x is defined as the heat of adsorption determined at constant amount of adsorbate adsorbed. It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using Clausius-Clapeyron equation²⁶:

$$\ln C_e = \frac{\Delta H_x}{RT} + K \quad (10)$$

where, C_e is the equilibrium dye concentration in solution (mg/L), ΔH_x is the isosteric heat of adsorption (kJ/mol). The isosteric heat of adsorption is calculated from the slope of the plot $\ln C_e$ versus $1/T$. The magnitude ΔH_x of provides an information about the nature and mechanism of the process. For physical adsorption ΔH_x should be below 80 kJ/mol and for chemical adsorption it ranges between 80-400 kJ/mol²⁷. The value of ΔH_x for the adsorption of AO10 onto PPC is 54.4652 kJ/mol which is within the range of physisorption and suggested that the adsorption process is physisorption. Therefore, the values of ΔG° , ΔH° , ΔH_x and E_a all suggest that adsorption of AO10 onto polymer coated saw dust was driven by ion exchange adsorption process involving weak vander Walls force of attraction (as the adsorption energy is very less).

Conclusion

The present investigation showed that polypyrrole - saw dust composites can be effectively and efficiently removed the ionic dyes from aqueous solution. The adsorption process was dependent on pH, maximum adsorption occurs at pH 3-4 for AO10. The pseudo-second order kinetic model fitted well with the dynamical adsorption behaviour of anionic dyes suggested ion exchange adsorption. The equilibrium data showed good agreement with the Langmuir isotherm model. The maximum monolayer adsorption capacities calculated by

TABLE-4
THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES

Adsorbent	Temp. (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/K/mol)	E_a (kJ/mol)	ΔH_x (kJ/mol)
PPC	30	-9.3473	29.5230	0.1283	2.0704	54.4652
	35	-9.9888				
	40	-10.6302				
	45	-11.2716				

Langmuir model were 243.9 mg/g for Acid Orange10 at 30 °C. The adsorption capacity of polypyrrole composite increased with rise in temperature indicating endothermic nature of adsorption. The thermodynamic parameters such as enthalpy change, free energy change indicated the physisorption nature of adsorption process. Arrhenius activation energy calculated was 2.0704 kJ/mol composite and lower values of isosteric heat of adsorption also supported the forces of attraction between dye and polypyrrole composite was weak. Adsorption capacity of polymer composites gets increased due to ion exchangeable sites and ion exchange adsorption occurs. Lower bonding energy suggested that only weak bond is formed between dye and polymer composite. Based on the results obtained in this study, it can be concluded that polypyrrole composite is an effective, economic and alternative material for the removal of acid dyes.

ACKNOWLEDGEMENTS

The first (PNP) and third authors (PS) thank UGC, New Delhi for providing financial assistance under major research project scheme to carryout this research work.

REFERENCES

- J. Li and J.T. Guthrie, *Bioresour. Technol.*, **101**, 4291 (2010).
- G. Crini, *Bioresour. Technol.*, **97**, 1061 (2006).
- A. Mittal, A. Malviya, D. Kaur, J. Mittal and L. Kurup, *J. Hazard. Mater.*, **148**, 229 (2007).
- S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li and C. Li, *Desalination*, **252**, 149 (2010).
- R. Ansari, *J. Electrochem.*, **41**, 950 (2005).
- G.G. Wallac, G.M. Sprinks, L. Kane-Magure and P. Teasdale, *Hand Book of Conductive Electroactive Polymers: Intelligent Materials Systems*, CRC Press, New York, edn. 2 (2003).
- L.X. Wang, X.G. Li and Y.L. Yang, *React. Func. Polym.*, **47**, 125 (2001).
- R. Ansari and Z. Mosayebzadeh, *Iran. Polym. J.*, **197**, 541 (2010).
- C.T. Hsieh and H. Teng, *J. Colloid Interf. Sci.*, **230**, 171 (2000).
- U. Ilhan, *Dyes Pigments*, **70**, 76 (2006).
- O. Abdelwahab, *Desalination*, **222**, 357 (2008).
- M. Alkan and M. Dogen, *Environ. Bull.*, **12**, 418 (2003).
- S. Langergren, *Veternskapsakad. Handl.*, **24**, 1 (1898).
- Y.S. Ho and G. McKay, *Proc. Biochem.*, **34**, 451 (1999).
- M.S. Chiou and H.Y. Li, *J. Hazard Mater.*, **93**, 233 (2002).
- I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
- H.M.F. Freundlich, *J. Phys. Chem.*, **57**, 384 (1906).
- V. Vimonses, S. Lei, B. Jin, C.W.K. Chow and C. Saint, *Appl. Clay Sci.*, **43**, 465 (2009).
- T. Vermeulen, *Ind. Eng. Chem. Fund.*, **5**, 221 (1996).
- H. Nollet, M. Roels, P. Lutgen, P.V.D. Meeran and W. Verstraete, *Chemosphere*, **53**, 655 (2003).
- A. Ozcan, E.M. Onar and A.S. Ozan, *Colloids Surf. A.*, **277**, 90 (2006).
- N.M. Mahmoodi, M. Arami, H. Bahrami and S. Khorramfar, *Desalination*, **264**, 134 (2010).
- M.J. Jaycock and G.D. Parfitt, Ellis Horwood Ltd, Onichester (1981).
- B.P. Kelleher, M. O'Callaghan, M.J. Leahy, T.F.O. Dwyer and J.J. Leahy, *J. Chem. Technol. Biotechnol.*, **77**, 1212 (2002).
- S.D. Faust and O.M. Aly, *Adsorption Processes for Water Treatment*, Butterworth (1987).
- T.S. Anirudhan and P.G. Radhakrishnan, *J. Chem. Thermodyn.*, **40**, 702 (2008).
- M. Dogan and M. Alkan, *J. Colloid Interf. Sci.*, **267**, 32 (2003).