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## Sorptive removal of Congo red by polypyrrole alumina composite

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### ABSTRACT

This study reveals the use of polypyrrole/Alumina (PPy/AIO) composite as an adsorbent for the removal of the dye, Congo red, from aqueous solution. A small amount (0.05 g/50 ml) of the adsorbent could decolorize as much as 18 mg/g of the dye from an aqueous solution (40 mg/L) at 30°C if agitated for an hour. The adsorption of the dye was appreciable in a wide range of pH. This showed that adsorption of the dye could be carried out using polypyrrole/alumina composite without adjusting the pH of the medium. The experimental data yielded good fit with Langmuir when compared to Freundlich isotherm equations. The values of the adsorption coefficients computed indicated the potential of the adsorbent for practical applications in colour removal process. The adsorption of Congo red onto polypyrrole/alumina was spontaneous at higher temperature and lower concentration. Change in enthalpy suggests the process is endothermic in nature. The enthalpy change for the adsorption process was observed to be 8-86 kJ mol<sup>-1</sup>, which indicated the absence of very strong chemical force between the adsorbed dye molecules and the polypyrrole/Alumina surface. Hence, physisorption seems to be the major mode of adsorption.

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### INTRODUCTION

Synthetic dyes are extensively used in many fields of up-to-date technology, e.g., in various branches of the textile industry, in paper production, in food technology, in agricultural research in light harvesting arrays, in photo electrochemical cells and in hair coloring. Moreover, synthetic dyes have been employed for the control of efficiency of sewage and wastewater treatment, for the determination of specific surface area of activated sludge for ground water tracing etc.

Synthetic dyes exhibit considerable structural diversity. The chemical classes of dyes employed more frequently on industrial scale are the azo, anthraquinone, sulfur, indigoid, triphenylmethyl and phthalocyanine derivatives. However, it has to be emphasized that the

overwhelming majority of synthetic dyes currently used in the industry are azo derivatives. It should be noted that azo-keto hydrozone equilibria can be a vital factor in the easy break down of many azo dye system.

Unfortunately, the exact amount of dyes produce in the world is not known. It is estimated over 10,000 tons per year. Exact data on the quantity of dyes discharged in the environment are also not available. It is assumed that a loss of 1-2% in production and 1-10% loss in use are a fair estimate. For reactive dyes, this figure can be about 4%. Due to large-scale production and extensive application synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. Although, the growing impact of environment promotes the development of eco friendly technologies, reduced consumption of fresh

water and lower output of waste water, the release of important amounts of synthetic dyes to the environment causes public concern, legislation problems and is a serious challenge to the environmental scientist.

Because of their commercial importance, the impact and toxicity of dyes that are released in environment have been extensively studied. As several thousand different synthetic dyes that are employed exhibit various biological activities, it is understandable that our knowledge concerning their behavior in the environment and health hazards involved in their use is still incomplete. Traditional waste water treatment technologies have been proven to be markedly ineffective for handling waste water of synthetic textile dyes because of the chemical stability of these pollutants. A wide range of method has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment. The technologies involved adsorption on inorganic or organic matters, decolorization by photo catalysis, and/or by oxidation process, microbiological or enzymatic decomposition, etc. Adsorption<sup>[1-18]</sup> has undoubtedly been one of the most popular technique for the removal of dyes from aqueous solution and is widely used in wastewater treatment applications throughout the world.

### **Importance of polypyrrole**

Since the discovery of conducting polymers three decades ago, a large volume of research work has been performed associated with the physics and chemistry of conducting polymers. Polypyrrole is one of the most environmentally stable known conducting polymer and also one of the most commonly investigated conducting polymer due to its high electrical conductivity and ease of preparation<sup>[19]</sup>. Polypyrrole find applications in various fields such as microelectronics, composite materials, optics and biosensors<sup>[20]</sup> and as adsorbent<sup>[21,22]</sup>. The development of such materials would be useful in making sensors for the identification of certain classes of dyes even at ppm levels. The polypyrrole has been used successfully for the selective removal of anionic dyes from aqueous solution<sup>[23,24]</sup>. The interaction between the negatively charged anion of the dye and the positively charged polymer backbone is responsible for the anionic dye adsorption by polypyrrole from aqueous dye solution.

### **Aim and scope of the present work**

Dyes are widely used in industries to colour their products during which these dyes are invariably left in the industrial waste waters. Dyes even in very low concentrations affect the aquatic life and food chain. Hence, the removal of dye from process or waste effluents becomes environmentally important. Conventional physicochemical and biological treatment methods are ineffective for their removal. This led to the study of other effective materials. The major objective of the present work, therefore, is to investigate the equilibrium, kinetic and thermodynamic aspects of the adsorptive removal of Congo red by polypyrrole/alumina composite. The adsorption process is one of the effective methods used to remove dyes from aqueous solution.

## **EXPERIMENTAL SECTION**

### **Materials**

All chemicals used were of analytical reagent grade (Sd-fine/Merck, India). Doubly distilled water was used throughout the study.

The structure of Congo red (Direct Red, C.I.NO. 22120) is given below.

Congo red ( $C_{32}H_{22}N_6Na_2O_6S_2$ ) is a secondary azodyes bearing R-N=N-R' as the functional group. The solubility of congo red in water 40 gram per litre. The maximum absorption wavelength in the visible light range is 497 nm.

### **Preparation and characterization of polypyrrole/alumina composite**

Polypyrrole/alumina composite (PPy-AIO) was prepared by the method adopted for the preparation of polypyrrole/alumina composite<sup>[25]</sup>. About 2.1 ml of pyrrole was dissolved in 50 ml of methyl alcohol and then alumina (2 g) was added in a 100 ml beaker. This mixture was stirred for 10-15 min using magnetic stirrer. To this stirred mixture, 7.18 g of ferric chloride was added. The colour of the solution gradually changes from dark brown to black. The reaction was allowed to proceed for 16 h at about 0-5°C with stirring. The resulting black product was filtered and washed thoroughly with methyl alcohol until the filtrate is

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colourless. Finally, the product was dried in an oven at 60°C for 24 h. The conducting polymer/alumina composites were characterized using FT-IR, XRD and SEM techniques.

In Figure 1, the band at 1542 cm<sup>-1</sup> is assigned to pyrrole ring i.e., the combination of C=C and C-C stretching vibrations. The peak at 1463 cm<sup>-1</sup> is associated with Al-O stretching vibration. The peaks at 1304 and 1180 cm<sup>-1</sup> are attributed to the in-plane vibrations of C-H. A sharp and intense peak at 924 cm<sup>-1</sup> shows the 2,5 coupling between the monomer molecules of pyrrole in polypyrrole<sup>[26]</sup>. The strong peaks at 1050 and 1451 cm<sup>-1</sup> are the characteristic vibrations of alumina<sup>[27]</sup>. The SEM image of the composite is shown in Figure 1c. In this image polymer as spongy like structure and alumina as crystalline particles<sup>[28]</sup>.

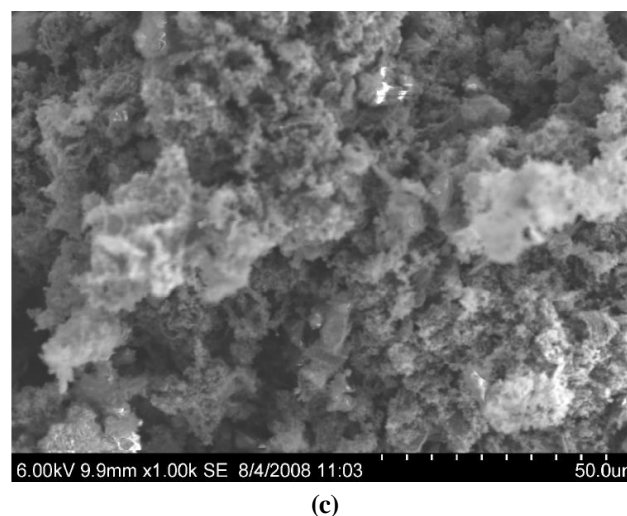
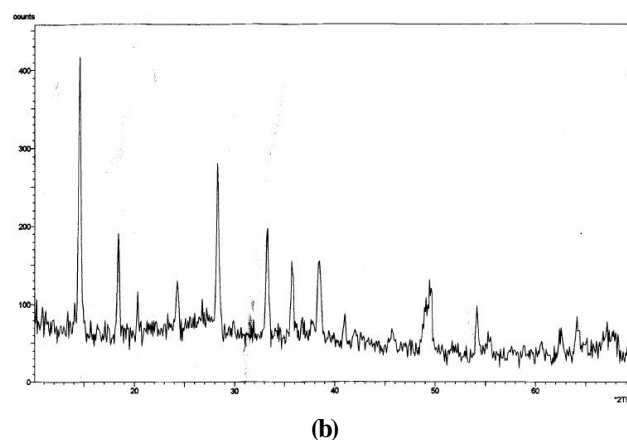
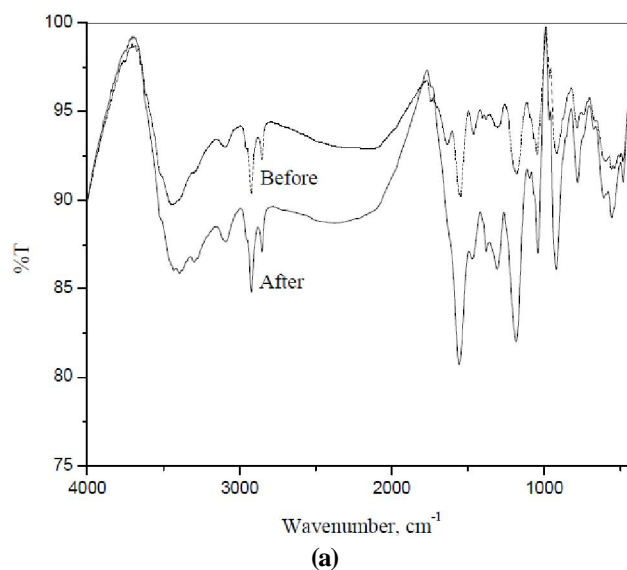
### Methodology

The concentration of dye solutions were measured using UV-Visible Spectrometer (JASCO, V-630). The XRD (X' Pert PRO PANalytical, Netherlands) patterns of PPy was recorded at the National Institute for Science and Technology, Thiruvananthapuram, India. The SEM (HITACHI-S-3400H) image was obtained from Pondicherry University, Pondicherry. FT-IR spectra were recorded using KBr disc on a JASCO FT-IR 460 Plus spectrometer.

### Batch adsorption experiments

Adsorption experiments were performed by agitating 50 mg of adsorbent with 50 ml of dye solution of desired concentrations at 30 ± 0.5°C in different stoppered bottles in a shaking thermostat machine. At the end of pre-determined time intervals the sorbate was filtered and the concentration of dye was determined colorimetrically by employing Shimadzu UV-VIS spectrophotometer. All experiments were carried out twice. Adsorbed dye concentrations were the means of the duplicate experimental results. Experimental variable considered were (i) Initial concentration of dye 20-100 mg/L; (ii) contact time between adsorbent and the dye solution 10-60 min; (iii) pH 3-11; (iv) dosage of adsorbent 25 mg to 250 mg/50ml; (v) temperature 30-50°C and (vi) co-ions Cl<sup>-</sup> and Ca(II).

The amounts of adsorption were calculated based



**Figure 1 :** (a) FT-IR Spectra of the polymer before and after treating with congo red; (b) X-ray diffraction pattern of the polymer/alumina

on the difference of dye concentrations in aqueous solutions before and after adsorption the volume of aqueous solution (50 ml) and the weight of adsorbent

(0.05 g) according to equation 1.

$$\text{Adsorption capacity } Q_e = (C_0 - C_e) V/W \tag{1}$$

Where  $C_0$  is the initial dye concentration (mg/L),  $C_e$  is the equilibrium dye concentration (mg/L),  $V$  is the volume of the dye solution (ml) and  $W$  is the weight of adsorbent (g).

**Data analysis**

The experimental data were analyzed using Microcal Origin (version 6.0) computer software. The goodness of fit was discussed using coefficient of determination,  $r$ , and standard deviation,  $sd$ .

**Adsorption isotherm**

The adsorption isotherms generally used for the design of adsorption system. The Langmuir<sup>[29]</sup> and Freundlich<sup>[30]</sup> equations are commonly used for describing the adsorption isotherms. The linear equation of Langmuir and Freundlich are represented as follows Eqns. (3) and (4), respectively.

$$C_e/Q_e = (C_e/Q^0) + (1/Q^0 b) \tag{3}$$

$$\log Q_e = 1/n \log C_e + \log K \tag{4}$$

Where  $Q_e$  and  $C_e$  have the usual meanings and  $Q^0$  and  $b$  are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively.  $K$  and  $n$  are the empirical constants of the Freundlich isotherm measuring the adsorption capacity and intensity of adsorption respectively.

**Thermodynamic parameters**

The standard free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from the variation of the thermodynamic equilibrium constant  $K_0$ . The  $K_0$  for the adsorption process was determined by the reported method<sup>[31]</sup>. The thermodynamic parameters were calculated using the following equations,

**TABLE 1 : Equilibrium parameter for the removal of dye per unit mass (mg/g) of PPy/AIO**

[Dye] mg/L	$C_e$ (mg/L)			$Q_e$ (mg/g)		
	30 <sup>0</sup>	40 <sup>0</sup>	50 <sup>0</sup> C	30 <sup>0</sup>	40 <sup>0</sup>	50 <sup>0</sup> C
20	8.82	5.31	3.45	11.2	14.7	16.5
40	22.0	17.3	17.2	18.0	22.7	22.8
60	40.7	37.2	35.3	19.3	22.8	24.7
80	47.1	45.3	42.7	32.9	34.7	37.3
100	75.13	69.8	67.3	24.9	30.2	32.7

$$\ln K_0 = (\Delta S^0/R) - (\Delta H^0/RT) \tag{6}$$

$$\Delta G^0 = -RT \ln K_0 \tag{7}$$

$\Delta H^0$  and  $\Delta S^0$  were determined from the slope and intercept of the plot of  $\ln K_0$  versus  $1/T$  respectively.

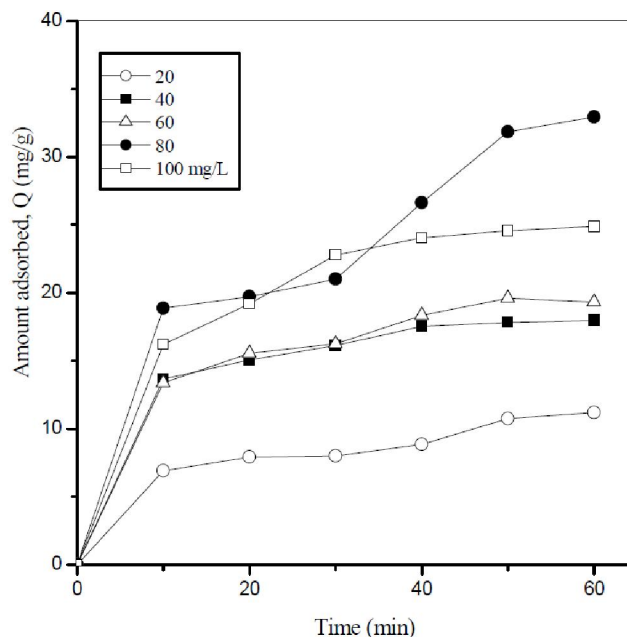
**RESULT AND DISCUSSION**

**Effect of agitation time and initial concentration**

The equilibrium parameters for the adsorption of dye onto PPy/AIO are collected in TABLE 1. The results reveal that, the amount of dye adsorbed per unit mass of the adsorbent increased with increase in concentration and rise in temperature. The variation of  $Q_e$  with temperature indicates that the adsorption process is endothermic in nature. The effect of contact time between the adsorbent and adsorbate is depicted in Figure 2. It is evident from the figure that the equilibrium was established after 40 min for all the concentrations. Further, the curves in Figure 2 are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye onto the PPy/AIO surface<sup>[18]</sup>.

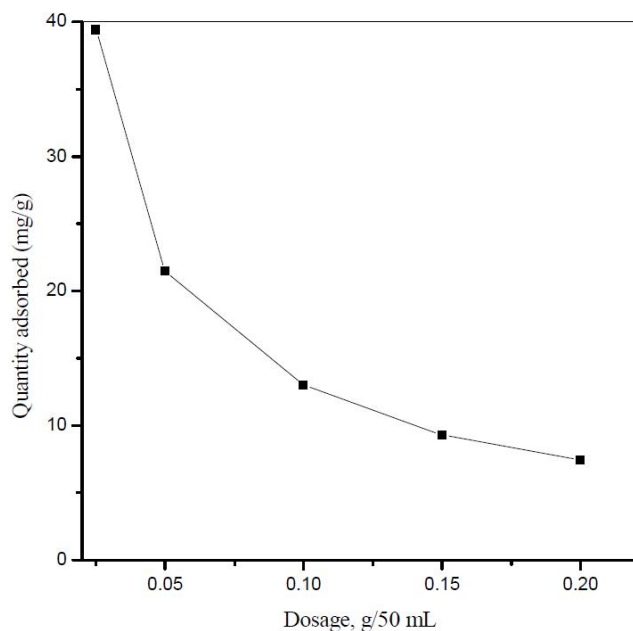
**Effects of adsorbent dosage**

The amount of dye removed as a function of adsorbent dosage at 40 mg/L of initial concentration of dye solution at 30<sup>0</sup> C was shown in Figure 2. Adsorbent



**Figure 2 : Effect of contact time and initial concentration for the adsorption of conged on to PPy/AIO**

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**Figure 3 : Effect of dose of the adsorbent on the removal of congored**

dosage was varied from 25 mg to 250 mg per 50 ml and equilibrated for 60 min. From the result it is evident that optimum dosage of 0.05g/50ml is required for maximum removal for dye solution.

### Adsorption isotherms

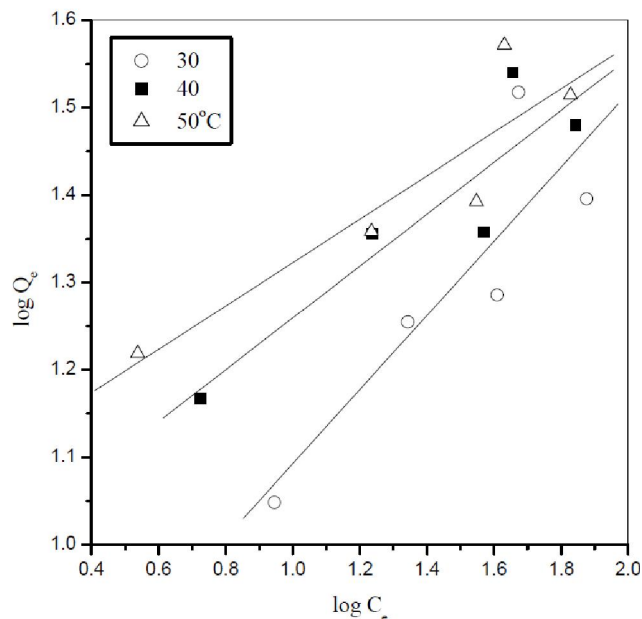
To quantify the adsorption capacity of the chosen adsorbent for the removal of dye from water, the adsorption data have been fitted to the Freundlich isotherm. The linear plots of  $\log Q_e$  versus  $\log C_e$  (Fig 4) indicate the applicability of Freundlich adsorption isotherm. The results (TABLE 2) indicated the value of intensity of adsorption ( $n$ ) is greater than unity signifies that the forces within the surface layer are attractive<sup>[32]</sup>. Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The applicability of Freundlich isotherm to the PPy/AlO implies that heterogeneous surfaces conditions used. The adsorption properties of the adsorbent are thus likely to be complex, involve more than one mechanism<sup>[33]</sup>.

The plot in Figure 5. shows that the Langmuir equation provides an accurate description of the experimental data, which is further confirmed by the extremely high values of the coefficient of determination. In order to find out the feasibility of the isotherm in the essential characteristics of the Langmuir isotherm can be expressed interms of dimensionless constant separation factor or equilibrium parameter  $R_L$ , which is

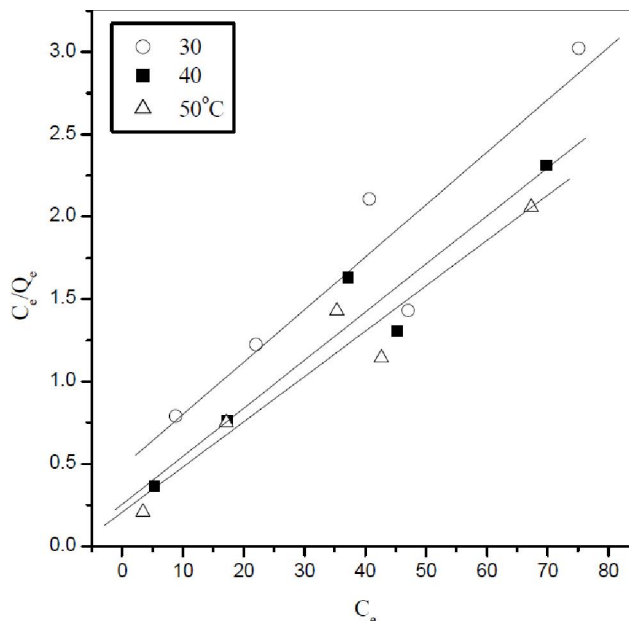
defined by Hall et al.<sup>[34]</sup>, as;

$$R_L = 1 / (1 + bC_0) \quad (5)$$

where  $b$  is the Langmuir constant ( $L \text{ mg}^{-1}$ ) and  $C_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ ). The value of  $R_L$  is computed and presented in TABLE 4. The value of  $R_L$  indicates the shape of the isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). In this case the  $R_L$  values are less than one which suggests the adsorption process



**Figure 4 : Freundlich adsorption isotherm for the removal of dye onto polymer composite**



**Figure 5 : Langmuir adsorption isotherm for removal of dye by polymer composite**

is favorable.

**Thermodynamic parameters**

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were given in TABLE 5. The endothermic nature of adsorption is indicated by an increase in  $K_o$  with rise in temperature. The  $\Delta G^\circ$  values are negative at higher temperature and lower concentration, which mean that the reaction is spontaneous at lower concentration and higher temperature. The values of enthalpy change of a sorption process may be used to distinguish between chemical and physical sorption<sup>[35]</sup>. For chemical sorption, enthalpy values range from 83 to 830 kJ mol<sup>-1</sup>, while for physical sorption they range from 8 to 25 kJ mol<sup>-1</sup>. On the basis of the above distinction, we conclude that dye sorption by the PPy/AIO is a physical process. Positive values of  $\Delta H^\circ$  suggest that the process is endothermic, so an increase of temperature encourages dye adsorption. As indicated in TABLE 5,  $\Delta S^\circ$  values for the adsorption process are positive. This observation suggests a high degree of disorderliness at the solid-solution interface during the adsorption of the dye onto polymer composite. This may be due to the fact that the adsorbed

water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules. Thus allowing the prevalence of randomness in the system. Further the positive values of entropy reflect the affinity of the adsorbent material for the dye<sup>[36]</sup>.

**Effect of pH**

The effect of pH of the dye solution on the amount of Congo red, a cationic dye, adsorbed was studied at pH 3, 5, 7, 9 and 11. The percentage of the dye adsorbed was found to be 13.81, 15.0, 18.2, 17.7 and 17.18 mg/g, respectively. The result indicated that the adsorbent show commendable capacity in wide range of pH.

**Effect of co-ions**

The effect of added co-ions viz. Cl<sup>-</sup>, and Ca<sup>2+</sup> on the amount of dye removed (mg/g) is given in TABLE 6. The results indicated that addition of these common co-ions, does not have any marked effect on the removal of congo red by PPy/AIO composite under the present experimental conditions.

**Kinetics of adsorption**

The sorption of dye form liquid phase to solid phase may be expressed as:



where  $k_1$  is the forward rate constant and  $k_{-1}$  is the backward rate constant. A represents dye remaining in the bulk solution and B represents dye retained on the surface of PPy/AIO. The reaction in the both directions is of first order. The rate constant for the adsorption,  $k_{ad}$  was determined using the Natarajan-Khalaf equation

**TABLE 2 : Equilibrium parameters and isotherm constants for the retrieval of dye by PPy/AIO**

Isotherm	Statistical parameter /constant	Temp (°C)		
		30	40	50
Freundlich	r	0.87	0.91	0.91
	sd	0.098	0.07	0.07
	n	1.49	3.36	4.03
	K	4.66	9.16	11.75
Langmuir	r	0.93	0.96	0.96
	sd	0.38	0.23	0.21
	Q <sub>o</sub>	1.07	34.48	37.03
	b	0.52	8.79	7.66

**TABLE 3 : R<sub>L</sub> values for the removal congored by PPy/AIO composite**

[Dye] mg/L	R <sub>L</sub>		
	30	40	50°C
20	0.088	0.006	0.006
40	0.221	0.816	0.794
60	0.070	0.020	0.021
80	0.151	0.384	0.378
100	0.062	0.025	0.026

**TABLE 4 : Equilibrium constants and thermodynamic parameters for the removal of dye by PPy/AIO composite**

[Dye] mg/L	K <sub>o</sub>			ΔG <sup>o</sup>			ΔH <sup>o</sup>	ΔS <sup>o</sup>
	30°	40°	50°C	30°	40°	50°C		
20	1.27	2.76	4.79	-0.6	-2.64	-4.27	54	181
40	0.82	1.31	1.33	0.51	-0.71	-0.77	20	65
60	0.47	0.61	0.7	1.88	1.27	0.96	16	46
80	0.7	0.77	0.87	0.9	0.69	0.36	15	27
100	0.33	0.43	0.49	2.79	2.18	1.94	16	34

ΔG<sup>o</sup> = (kJ mol<sup>-1</sup>); ΔH<sup>o</sup> = (kJ mol<sup>-1</sup>) and ΔS<sup>o</sup> = (JK<sup>-1</sup> mol<sup>-1</sup>)

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**TABLE 5 : Effect of co-ions on the amount of dye removed (mg/g) by PPy/AIO**

Co-ion	Amount adsorbed, mg/g					
	0	100	200	300	400	500
Chloride	18	17.7	17.5	17.8	16.9	18.4
Calcium	18	18.2	18.7	17.7	18.1	17.2

[dye] = 4 mg/L; Temp = 30°C; pH = 7; Contact time = 30 min

**TABLE 6 : Rate constants for the adsorption of dye and the rate constants for forward ( $k_1$ , min<sup>-1</sup>) and reverse ( $k_{-1}$ , min<sup>-1</sup>) processes**

[Dye] mg/l	10 <sup>3</sup> k <sub>ad</sub>	10 <sup>3</sup> k <sub>1</sub>	10 <sup>3</sup> k <sub>-1</sub>
20	8.1	4.5	3.6
40	3.7	1.6	2.1
60	2.6	0.8	1.8
80	6.1	2.5	3.6
100	2.3	0.6	1.7

as described earlier<sup>[37]</sup>. The rate constants for the adsorption ( $k_{ad}$ ) and forward ( $k_1$ ) and reverse ( $k_{-1}$ ) processes are presented in Table 7. The results indicated that the  $k_{ad}$  values increased with an increase in temperature suggesting endothermic nature of the adsorption process. Further, the values of  $k_1$  were found to be lesser than that of  $k_{-1}$  suggesting desorption is dominant over adsorption in the present experimental condition.

### FT-IR, XRD and SEM studies

The FT-IR spectra (Figure 1 a) and X-ray diffraction pattern of the PPy/AIO before (Figure 1b) and after treatment with Congo red (Figure 1c) are shown in Figure 1. The spectra after adsorption showed no significant change except the hydration of the adsorbent indicating that the removal of the dye may occurred via physisorption.

### CONCLUSION

The polypyrrole/AIO has demonstrated sufficient promise as an adsorbent for the removal of the dye, Congo red, from aqueous solution. A small amount (0.05 g/50 ml) of the adsorbent could decolorize as much as 18 mg/g of the dye from an aqueous solution (40 mg/L) at 30°C if agitated for an hour. The adsorption of the dye was appreciable in a wide range of pH. This showed that adsorption of the dye could be carried out using

polypyrrole/alumina composite without adjusting the pH of the medium. The experimental data yielded good fit with Langmuir when compared to Freundlich isotherm equations. The values of the adsorption coefficients computed indicated the potential of the adsorbent for practical applications in colour removal process. The adsorption of Congo red onto polypyrrole/alumina was spontaneous at higher temperature and lower concentration. Change in enthalpy suggests the process is endothermic in nature. The enthalpy change for the adsorption process was observed to be 8-86 kJ mol<sup>-1</sup>, which indicated the absence of very strong chemical force between the adsorbed dye molecules and the polypyrrole/Alumina surface. Hence, physisorption seems to be the major mode of adsorption.

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