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Polypyrrole/montmorillonite composite used as an adsorbent for the removal of congored from aqueous solution

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ABSTRACT

This study reveals the possibility of the use of Conducting polymer/ inorganic hybrid composites. They have large surface areas, which makes the adsorbent properties of the polymer composites as good the constituents. Polypyrrole/montmorillonite (PPy/MMT) composite was prepared, characterized (Fourier transform infrared, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction patterns) and used as adsorbents for the removal of congored from aqueous solution by batch adsorption method. The spectra of before and after the adsorption are recorded to get better knowledge regarding the mechanism of the adsorption process. The results indicated that the removal of congored from wastewater by PPy/MMT composite occurs via physico-chemical mechanism. The amount of congored removed by PPy/MMT is 46.5 mg/g at 50°C. This study obey Freundlich adsorption isotherm than Langmuir. The adsorption of Congo red onto polypyrrole/Montmorillonite was spontaneous at higher temperature and lower concentration. Change in enthalpy suggests the process is endothermic in nature.

KEYWORDS

Dye;
Congored;
Polypyrrole;
Montmorrillonite;
Composite;
Dye removal;
Isotherms.

INTRODUCTION

Organic dyes are used in many industries like textile, paper, food technology, and also in agricultural industries. The discharge of these industry wastewater may contain maximum amount of dye molecule[1]. 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.

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 behaviour in the environ-

ment 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 has undoubtedly been the most popular technique for the removal of dyes from aqueous solution and is widely used in wastewater treatment applications throughout the world.

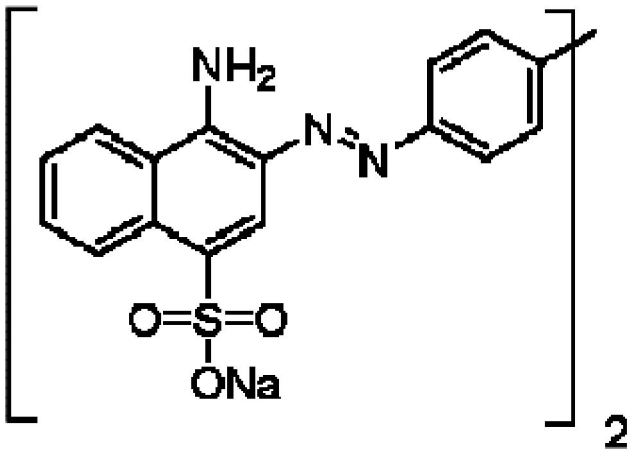
The literature on various adsorbent developed for the adsorption of dyes from aqueous solutions is voluminous. Few of the works in this field of study are methylene blue on kaolinite[2], Orang II, Crystal violet, Reactive blue 5 and p-nitro phenol on Chitosan[3], congored on leaves of Azadirachta indica[4], Reactive yellow on diatomite[5], sugar solution on anionic resins[6], satranine on rice husk carbon[7], remazol black[8], methylene blue on saga un saw dust[9], on cellulose based adsorbent from saw dust[10], acid dyes on bentonite[11], malachite green on proscopis cineraria saw dust[12], dye and related compound on silica[13], anionic dyes on cross linked chitosan beads[14], malachite green on pithophora sp[15], methylene blue on activated carbon from gulmohar tree fruits[16], congo red on pleurotus ostreatus[17], basic dyes on akash kinari coal[18] and supranol yellow 4 GL on Clay[19] were reported by several authors. Recent past reviews suggest the possibilities of using conducting polymer and its composites as adsorbent to remove hazardous chemicals such as dye and other metals present in aqueous solution. The present study reveals the possibility of the using PPy/MMT composite as viable decolourising agent for the removal of congo red.

METHODS

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 is 40 g/litre. The maximum absorption wavelength in the visible light range is 497 nm.

Preparation and characterization of polypyrrole/montmorillonite

Polypyrrole/montmorillonite composite (PPy-MMT) was prepared by the reported procedure[20]. About 2.1 ml of pyrrole was dissolved in 50 ml of methyl alcohol and then montmorillonite (2 g) was added. This mixture was stirred for 10-15 min using magnetic stirrer. To this stirred mixture, 7.18 g of anhydrous 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^{0}C with stirring. The resulting black product was filtered and washed thoroughly with methyl alcohol until the filtrate is colourless. Finally, the product was dried in an oven at 60^{0}C for 24 h.

The conducting polymer/montmorillonite composites were characterized using FT-IR and XRD techniques. The FT-IR spectra of PPy-MMT are shown in Figure 1. The peaks at 1151, 1047 and 913 cm^{-1} corresponds to various vibrations of Si-O group and the peak at 789 cm^{-1} corresponds to Al-OH vibration in MMT[21]. The band at 1542 cm^{-1} is assigned to pyrrole ring i.e., the combination of C=C and C-C stretching vibrations. The peaks at 1304 and 1180 cm^{-1} are attributed to the in-plane vibrations of C-H. A sharp and

intense peak at 924 cm^{-1} shows the 2,5 coupling between the monomer molecules of pyrrole in polypyrrole[20]. The XRD patterns of the composites suggest that the crystallinity is due to the presence of montmorillonite. The SEM image shows the particle size of the polymer composites is less than 100 nm.

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 ± 0.5^0C 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 50 mg to 200 mg/50ml; (v) temperature 30-50^{0}C and (vi) co-ions Cl^- and Ca (II).

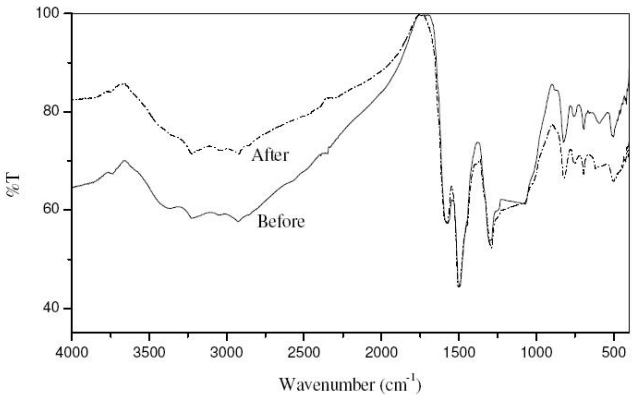


Figure 1a : FT-IR Spectra of the polymer before and after treating with congo red

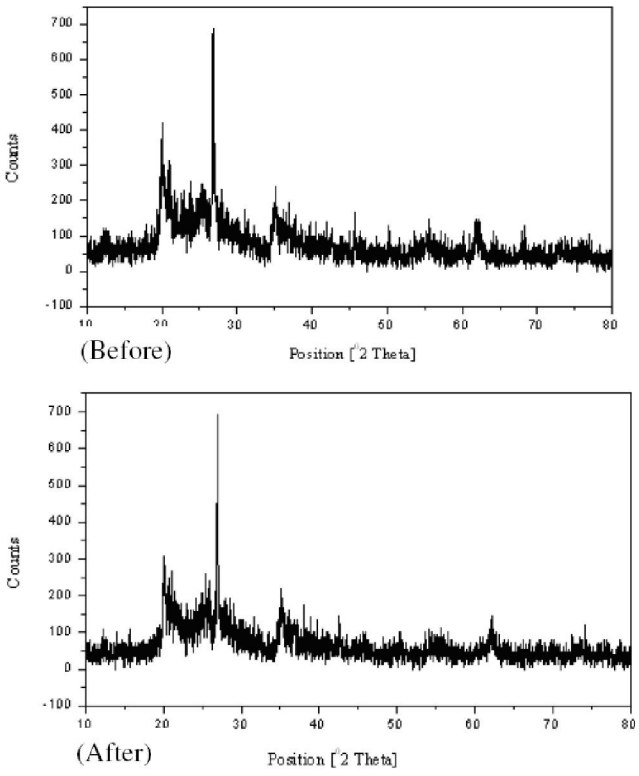


Figure 1b : X-ray diffraction pattern of the polymer/montmorillonite composite

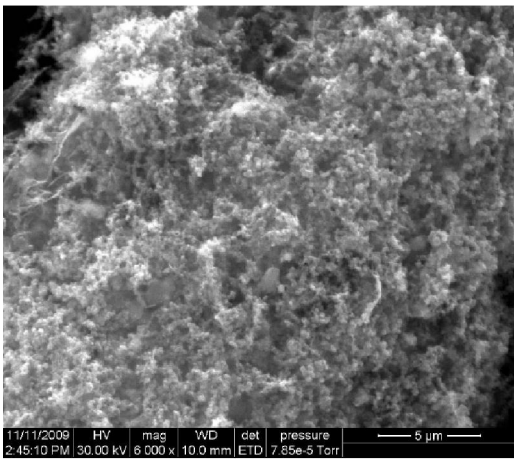


Figure 1c : SEM image of PPy/MMT composite

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.

RESULTS

Effect of agitation time and initial concentration

The equilibrium parameters for the adsorption of

dye onto PPy/MMT 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 Qe 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/MMT surface[19].

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

[Dye] mg/L	C_e (mg/L)			Q_e (mg/g)		
	30^0	40^0	50^oC	30^0	40^0	50^oC
20	14.35	5.55	4.76	5.65	14.45	15.24
40	23.75	18.17	16.04	16.25	21.83	23.96
60	42.32	36.16	29.57	17.69	23.84	30.43
80	53.83	48.02	45.02	26.17	32.0	34.98
100	58.09	55.21	53.53	40.92	44.79	46.47

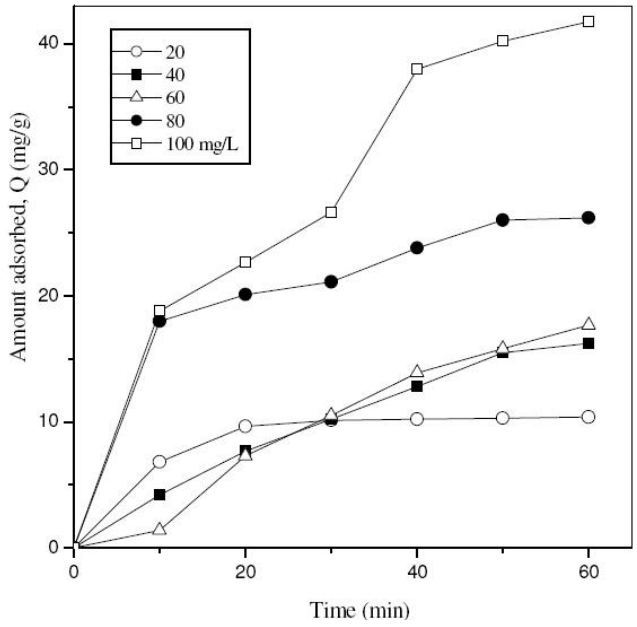


Figure 2 : Effect of contact time and initial concentration for the adsorption of congored onto PPy/MMT

Effects of adsorbent dosage

The effect of adsorbent dose on the amount of fluoride ion removed (Figure 3) was studied at 30°C and at an initial fluoride ion concentration of 40 mg/L by allowing a contact time of 60 min. In both the cases the amount of dye uptake increased with a decrease in adsorbent dose. This increase in congored removal is due to the availability of higher number of fluoride ions per unit mass of the polymer composites, i.e., higher dye molecule/composite ratio. Further experiments were carried out using 50 mg of adsorbent per 50 ml of fluoride ion solution, as it exhibits appreciable removal capacity, for the optimization of adsorption parameters.

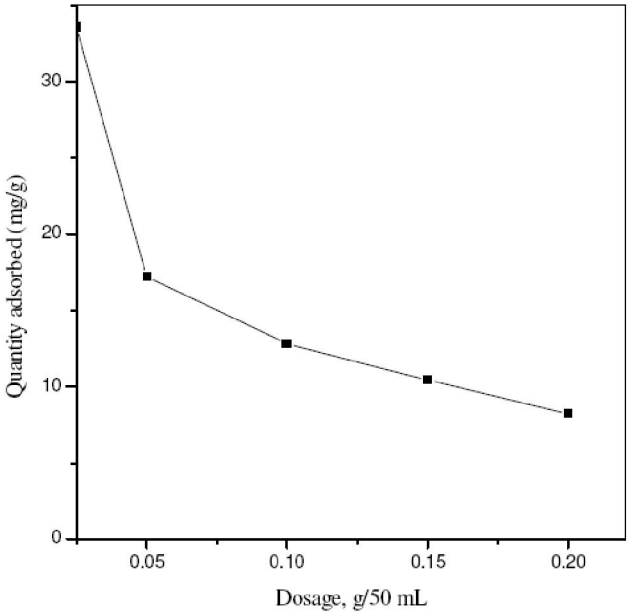


Figure 3 : Effect of dose of the adsorbent on the removal of congored

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 (Figure 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[22]. Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The applicability of Freundlich isotherm to the PPy/MMT implies that heterogeneous surfaces conditions used. The adsorption properties of the adsorbent are thus likely to be complex, involve more than one mechanism[23].

It is evident from the figure (Figure 5) the Langmuir isotherm is Fits poor than Freundlich, which suggests the physico-chemical interaction of the dye onto the

polymer composite.

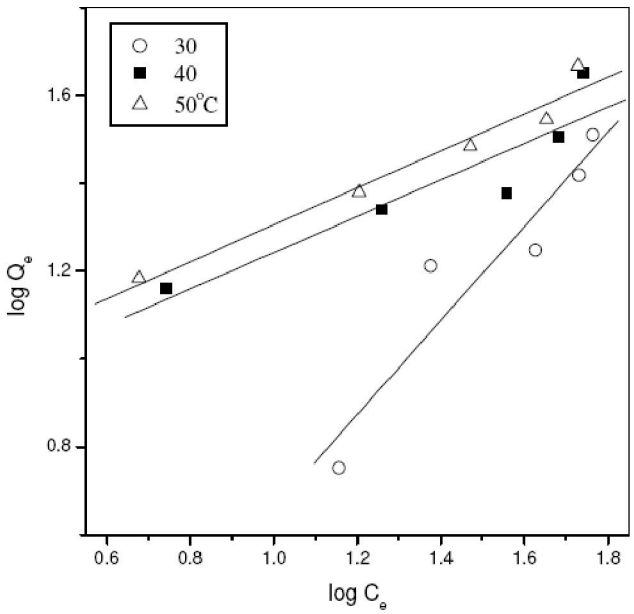


Figure 4 : Freundlich adsorption isotherm for the removal of congored by PPy/MMT composite

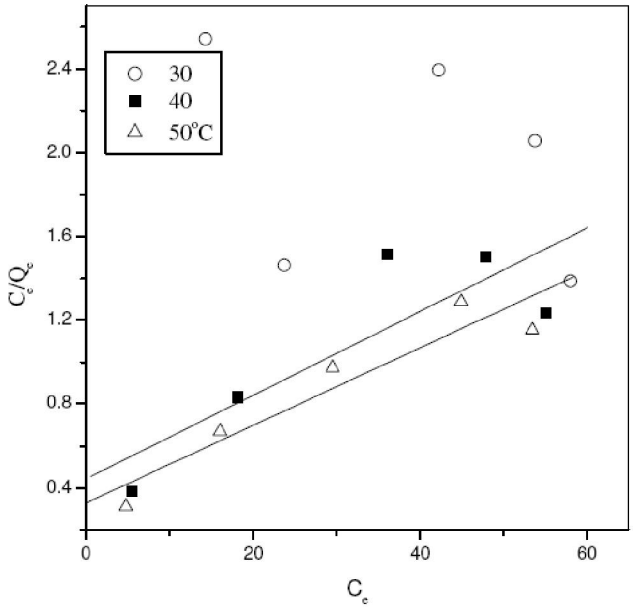


Figure 5 : Langmuir adsorption isotherm for the removal of dye from aqeous solution

Thermodynamic parameters

The standard free energy change, enthalpy and entropy changes along with equilibrium constants were given in TABLE 3. The endothermic nature of adsorption is indicated by an increase in K_o with rise in temperature. The ΔG^o values are negative at higher temperature and lower concentration, which mean that the reaction is spontaneous. The values of enthalpy change of a sorption process may be used to distinguish between chemical and physical sorption[24]. For chemical sorption, enthalpy values range from 83 to 830 kJ mol^{-1}, while for physical sorption they range from 8 to 25 kJ mol^{-1}. On the basis of the above distinction, we conclude that dye sorption by the PPy/MMT is a physical process. Positive values of ΔH^o suggest that the process is endothermic, so an increase of temperature encourages dye adsorption. As indicated in TABLE 3, ΔS^o 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[25].

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

Isotherm	Statistical parameter/ constant	Temp (^{0}C)		
		30	40	50
Freundlich	r	0.94	0.92	0.98
	sd	0.131	0.083	0.041
	n	1.85	1.21	1.13
	K	0.29	6.71	7.66
Langmuir	r	0.37	0.85	0.95
	sd	0.56	0.29	0.15
	Q_o	48	52.63	55.56
	b	0.42	2.27	3.05

TABLE 3 : Equilibrium constants and thermodynamic parameters for the removal of dye by PPy/MMT composite

[Dye] mg/L	K_0			ΔG^0			ΔH^0	ΔS^0
	30°	40°	50°C	30°	40°	50°C		
20	0.39	2.60	3.20	2.35	-2.49	-3.12	86	278
40	0.68	1.20	1.49	0.96	-0.48	-1.08	32	103
60	0.42	0.66	1.03	2.20	1.08	-0.08	37	114
80	0.49	0.67	0.78	1.82	1.06	0.68	19	57
100	0.72	0.81	0.87	0.82	0.54	0.38	8	22

ΔG^0 = (kJ mol^{-1}); ΔH^0 = (kJ mol^{-1}) and ΔS^0 = (JK^{-1} mol^{-1})

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 15.34, 14.16, 17.2, 16.34 and 16.11 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^-, and Ca^{2+} on the amount of dye removed (mg/g) is given in TABLE 4. The results indicated that addition of these common co-ions, does not have any marked effect on the removal of congo red by PPy/MMT composite under the present experimental conditions.

TABLE 4 : Effect of co-ions on the amount of dye removed (mg/g) by PPy/MMT

Co-ion	Amount adsorbed, mg/g					
	0	100	200	300	400	500
Chloride	16.2	16.0	15.1	15.7	15.1	15.2
Calcium	16.2	16.2	16.3	16.7	16.9	17.2

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

Kinetics of adsorption

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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad (6)$$

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/MMT. 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 as described earlier[26,27]. The rate constants for the adsorption (k_{ad}) and forward (k_1) and reverse (k_{-1}) processes are presented in TABLE 5. 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 slightly larger than that of k_1 suggesting desorption is slightly dominant over adsorption in this present experimental condition.

FT-IR, XRD and SEM studies

The FT-IR spectra (Figure 1 a) and X-ray diffraction pattern of the PPy/MMT 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 dsorbent indicating that the removal of the dye may occur via physisorption.

TABLE 5 : Rate constants for the adsorption of dye and the rate constants for forward (k_1, min^{-1}) and reverse (k_{-1}, min^{-1}) processes

[Dye] mg/l	k_{ad}	$10^3 k_1$	$10^3 k_{-1}$
20	0.39	1.45	3.68
40	0.68	3.45	5.05
60	0.42	1.87	4.48
80	0.49	0.99	2.05
100	0.72	3.12	4.32

CONCLUSION

The polypyrrole/MMT 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 46.5 mg/g of the dye from an aqueous solution (100 mg/L) at 50°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/Montmorillonite composite without adjusting the pH of the medium. The experimental data yielded good fit with Freundlich and poorly correlated with Langmuir 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/Montmorillonite 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^{-1}, which indicated the absence of very strong chemical force between the adsorbed dye molecules and the polypyrrole/MMT surface. Hence, physisorption seems to be the major mode of adsorption.

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