Research Article

Removal of Congo Red Dye from Aqueous Solution by Polyaniline-Montmorrillonite Composite

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Abstract

A wide range of methods have been implemented for the removal of synthetic dyes from wastewater to decrease their impact on the environment. The methods such as decolorization by photocatalysis or oxidation process, enzymatic or microbiological decomposition, adsorption on inorganic or organic matters are used for removing various dyes from industrial wastewater. Adsorption method is proved to be the most popular and effective technique for the removal of dyes from aqueous solution. Therefore, we synthesised polyaniline-montmorrillonite composite (PANi-MMT) and it was used to remove congo red dye from industrial wastewater by adsorption method. The equilibrium parameters for the adsorption of congo red dye on PANi-MMT composites are collected which reveal that the amount of congo red dye adsorbed per unit mass of the adsorbent (PANi-MMT) is increased with increase in concentration and rise in temperature. The Langmuir and Freundlich isotherms were used to describe the adsorption equilibrium. The spectral studies of the adsorbents before and after the adsorption are recorded to get better insight into the mechanism of the adsorption process. The results of the equilibrium parameters, FT-IR, XRD, SEM and TGA studies have revealed that the removal of congo red dye from wastewater occurs via a physico-chemical mechanism.

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Keywords: Congo red, Polyaniline, Montmorrillonite, Adsorption, Freundlich& Longmuir Isotherms.

Introduction

Synthetic dyes are extensively used in many fields of up-to-date technologies because of their commercial importance. The impact and toxicity of synthetic dyes on environment have been extensively studied. Traditional waste water treatment technologies have proved to be an ineffective method for removing synthetic textile dyes from waste water because of their chemical stability. A wide range of methods have been adopted for the removal of synthetic dyes from waste water to decrease their impact on the environment. The methods such as decolourization by photo catalysis or oxidation process, enzymatic or microbiological decomposition, adsorption on inorganic or organic matters are used for removing various dyes from industrial waste water. Adsorption method is proved to be the most popular and effective technique for the removal of dyes from aqueous solution. A variety of materials have been tried as adsorbents for the removal of dyes from aqueous solution as given in Table 1[1-18].

Composites of polymers and inorganic materials reported to provide many synergistic properties, which are difficult to attain from individual components [19]. Clay minerals have been adapted to the field of composites with polymers because of their small particle size and intercalation property [20-21]. Among various clay materials, Montmorillonite clay (MMT) has been used for the adsorption of toxic metal ions and organic pollutants from wastewater [22-24]. The main aim of the present endeavour is to investigate the feasibility of Polyaniline-Montmorillonite (PANi-MMT) composite as an adsorbent to remove congo red dye from aqueous solution. The equilibrium and thermodynamic aspects of the adsorption of congo red dye by PANi-MMT composites are presented and discussed.

Experimental

Materials

All the reagents used are of analytical grade (Aldrich/Merck, India) and were used as received. Aniline was purified by distillation. The stock solution of congo red dye was prepared by dissolving congo red dye in doubly distilled water.

Table 1 Various adsorbents used for the removal of dye from aqueous solution

Dye's Name	Adsorbent
Methylene Blue	Kaolinite[1]
Orange II and Crystal Violet	Chitosan[2]
Congo Red	Leaves of Azadirachtaindica[3]
Methylene Blue and Ciabacron Yellow	Diatomite[4]
Sugar solution	Anionic resins[5]
Satranine and Methylene blue	Rice husk carbon[6]
Remazol black-B	Kluyveromycesmarxianus IMB3[7]
Malachite Green and Rhodamine B	Saga un saw dust[8]
Methylene Blue	Cellulose-based adsorbent from saw dust[9]
Acid dyes	Bentonite[10]
Malachite Green	Proscopis cineraria saw dust[11]
Dye and related compounds	Silica[12]
Anionic dyes	Cross-linked chitosan beads[13]
Malachite Green	Pithophorasp[14]
Methylene Blue	Gulmohar tree fruits[15]
Congo Red and Methyl Orange	Pleurotusostreatus[16]
Basic dyes	Akashkinari coal[17]
Supranol Yellow 4 GL	Clay[18]

Preparation and characterization of the composite

Polyaniline-Montmorillonite composite (PANi-MMT) was prepared by the reported procedure [25]. In a typical experiment, about 1 mL of aniline (0.1 M) was dissolved in 1 mL of hydrochloric acid solution and then about 2 g of Montmorillonite was added. This mixture was then stirred for 10-15 minutes by using a magnetic stirrer.To this stirred mixture, Ammonium peroxydisulphate (4.4g, 0.1 M) was added at 0-5^{0}C. After completion of the addition, stirring is continued for 6 h. The greenish black power obtained was washed with deionised water followed by methyl alcohol until the filtrate become colourless and then the power was dried in an oven at 60-80^{0}C for 24 h.

Cheracterization of PANi-MMT composite

The concentration of congo red dye solutions were measured using UV-visible spectrometer of JASCO, V-630. FT-IR spectra were recorded using KBr disc on a JASCO FT-IR 460 Plus spectrometer. The XRD patterns of PANi-MMT composite were measured using X' Pert PRO PANalytical instrument. The SEM images were measured by HITACHI-S-3400H. TGA measurement was recorded by using Universal V4.3A TA Instrument.

Batch adsorption experiments

Adsorption experiments were performed by agitating 50 mg of adsorbent with 50 ml of congo red 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 congo red dye was determined colorimetrically by UV-Vis spectrophotometer. All experiments were carried out twice. Adsorbed congo red dye concentrations were the means of the duplicate experimental results. Experimental variable considered were (i) initial concentration of congo red dye 20–100 mg/L; (ii) contact time between adsorbent and the congo red dye solution 10–60 min; (iii) pH 3-11; (iv) dosage of adsorbent 25 mg to 250 mg/50mL; and (v) temperature 30–50°C.

The amounts of adsorption were calculated based on the difference of congo red dye concentrations in aqueous solutions before and after adsorption the volume of aqueous solution (50ml) and the weight of adsorbent (0.05 g) according to Adsorption capacity, $Q_e = (C_o-C_e)$ V/W Where C_o is the initial congo red dye concentration (mg/L), C_e is the equilibrium congo red dye concentration (mg/L), V is the volume of the congo red 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 [26] and Freundlich[27] equations are commonly used for describing the adsorption isotherms. The linear equation of Langmuir and Freundlich are represented as follows:

$$C_e/Q_e = (C_e/Q^o) + (1/Q^0b)$$

$$\log Q_e = 1/n \log C_e + \log K$$

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 (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^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 [28]. The thermodynamic para -meters were calculated by using the following equations

$$1n\ K_0 = (\Delta S^0/R) - (\Delta H^0/RT)$$

$$\Delta G^0 = -RT\ 1n\ K_0$$

ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of 1n K_0 versus 1/T respectively.

Results and Discussion

Effect of initial dye concentration and contact time for removing congo red dye by PANi-MMT Composite

The equilibrium parameters for the adsorption of dye onto PANi-MMT composite are collected in Table 2. 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 1. It is evident from the Fig.1 that the equilibrium was established after 40 min for all the concentrations. Further, the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the congo red dye onto the PANi-MMT composite surface [18].

Table 2 Equilibrium parameter for the removal of congo red dye per unit mass of PANi-MMT composite

Congo Red	PANi-MMT C_e (mg/L)			Q_e (mg/g)		
mg / L	30°C	40°C	50°C	30°C	40°C	50°C
20	6.59	-	-	13.4	-	-
40	14.94	12.94	10.74	25.1	27.1	29.3
60	27.52	-	-	32.5	-	-
80	36.61	-	-	43.4	-	-
100	43.99	-	-	56.0	-	-

Effect of dosage on the removal of Congo red dye by PANi-MMT composite

The amount of congo red dye removed as a function of adsorbent dosage at 40 mg/L of initial concentration of congo red dye solution at 30°C is shown in Figure 2. Adsorbent (PANi-MMT) dosage is varied from 25 mg to 250 mg per 50 mL and equilibrated for 60 minutes. From the result it is evident that optimum dosage of 50 mg/50 mL is required for maximum removal for congo red dye solution.

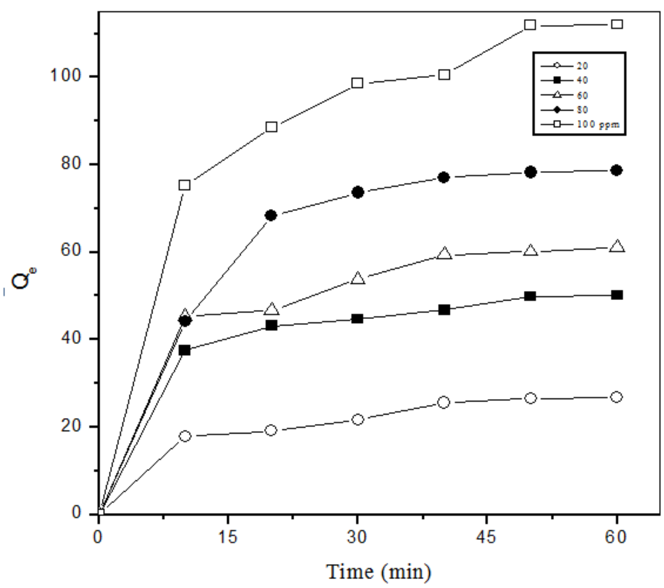

Figure 1 Effect of initial dye concentration and contact time for removing congo red dye by PANi-MMT composite.

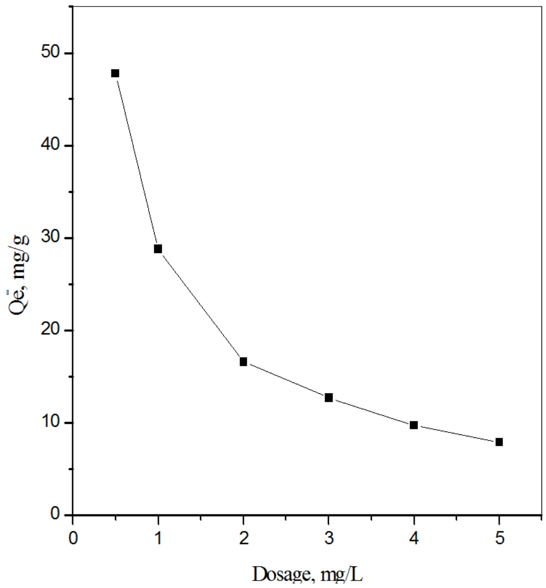

Figure 2 Effect of dosage on the removal of congo red dye by PANi-MMT composite.

Adsorption isotherms

To quantify the adsorption capacity of the chosen adsorbent for the removal of congo red dye from wastewater, the adsorption data have been fitted to the Freundlich isotherm. The linear plots of log Q_e versus log C_e as shown in Figure 3a, indicate the applicability of Freundlich adsorption isotherm. The results (Table 3) indicated that the value of intensity of adsorption (n) is greater than unity signifies that the forces within the surface layer are attractive [29]. Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. The applicability of Freundlich isotherm to the PANi-MMT composite implies that heterogeneous surfaces conditions were used. The adsorption properties of the adsorbent are thus likely to be complex, involve more than one mechanism [30].

Table 3 Isotherm constants for the removal of congo red dye by PANi-MMT composite

Isotherms	Statistical Parameter/ Constants	30^oC
Langmuir	r	0.863
	sd	0.09
	Q_0	2.091
	b	52.91
Freundlich	r	0.988
	sd	0.041
	n (mg/g)	1.419
	K (g/L)	5.064

The plot in Figure 3b 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 in terms of dimensionless constant separation factor or equilibrium parameter R_L, which is defined by Hall et al.[31] as $R_L = 1/(1+bC_o)$ Where, b is the Langmuir constant (L mg^{-1}) and C_0 is the initial congo red dye concentration (mg/L).

The value of R_L is computed and presented in Table 4 and the value of R_L indicates that the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In this case the R_L values are less than one which suggests the adsorption process is favourable.

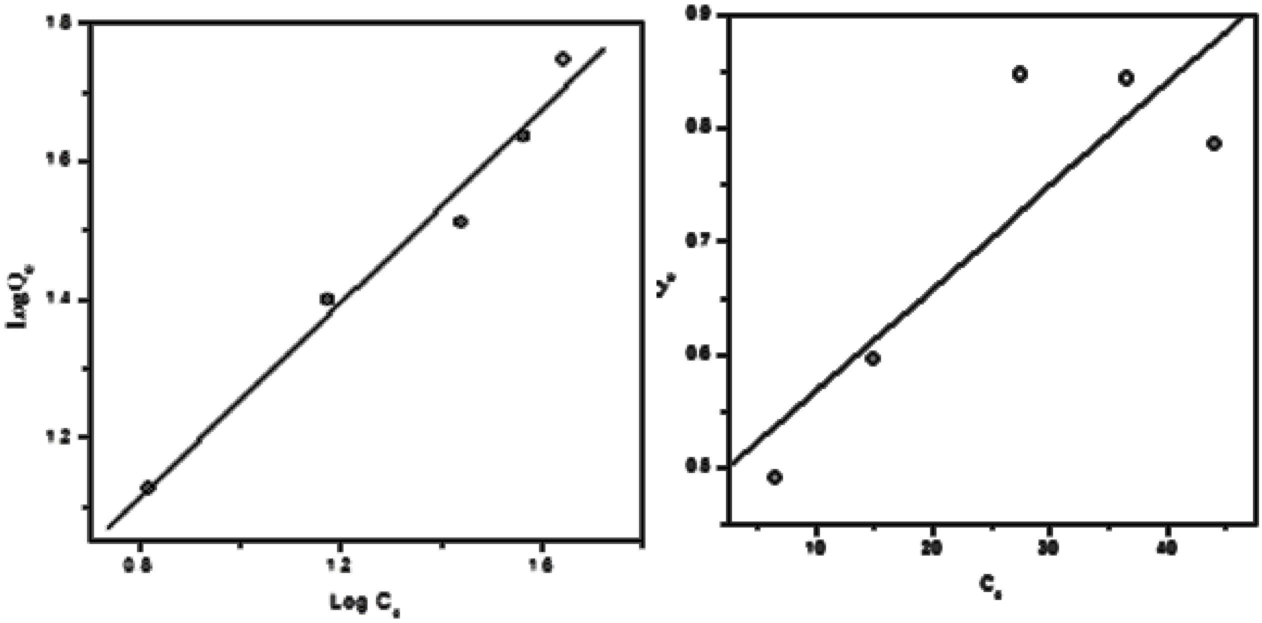

Figure 3.a) Freundlich and **b)** Langmuir adsorption isotherm for the removal of congo red dye by PANi-MMT composite.

Thermodynamic parameters

The standard free energy change, enthalpy and entropy changes along with equilibrium constant are given in Table 4. The endothermic nature of adsorption is indicated by an increase in K_0 with rise in temperature. The ΔG^0 values are negative which mean that the reaction is spontaneous. The values of enthalpy change of a sorption process are used to distinguish between chemical and physical sorption [32]. The chemical sorption takes place at enthalpy values range from 83 to 830 kJ mol^{-1}, while for physical sorption at the range from 8 to 25 kJ mol^{-1}. We conclude, on the basis of the above distinction that congo red dye sorption by the PANi-MMT is a physical process. Positive values of ΔH^0 suggest that the process is endothermic, so an increase of temperature encourages congo red dye adsorption. As indicated in Table 4, ΔS^0 value for the adsorption of congo red dye by PANi-MMT process is positive. This observation suggests a high degree of disorderliness at the solid-solution interface during the adsorption of the congo red dye onto the PANi-MMT composite. This is due to the fact that the adsorbed water molecules which are displaced by the adsorbate species and gain more translational entropy than is lost by the adsorbate molecules. Thus, allowing the prevalence of randomness in the system. Further, the positive value of entropy reflects the affinity of the adsorbent material for the congo red dye [33].

Table 4 Equilibrium constants and thermodynamic parameters for the removal of congo red dye by PANi-MMT composite

Congo Red mg / L	K_0			$-\Delta G^0$			ΔH^0	ΔS^0
	30°C	40°C	50°C	30°C	40°C	50°C		
20	2.03	-	-	1.79	-	-	-	-
40	1.68	2.09	2.72	1.30	1.92	2.69	20	69
60	1.18	-	-	0.42	-	-	-	-
80	1.19	-	-	0.43	-	-	-	-
100	1.27	-	-	0.61	-	-	-	-

Table 5 Effect of pH on the removal of congo red dye by PANi-MMT composite

pH	Qe
3	26.8
5	26.2
7	25.1
9	25.8
11	25.4

Effect of pH

The effect of pH of the dye solution on the amount of congo red dye, a cationic dye, absorbed was studied at pH 3, 5, 7, 9 and 11. The percentage of the dye adsorbed was found to be 26.8, 26.2, 25.1, 25.8 and 25.8 mg/g respectively (Table 5). The results indicate that the PANi-MMT composite (adsorbent) shows commendable capacity in wide range of pH 3-11.

FT-IR, XRD, SEM and TGASTUDIES

The FT-IR spectra of PANi-MMT composite is shown in Figure 4. The characteristic bands at 1573 cm^{-1} arises mainly from both C=N and C=C stretching for quinoid form, while the band near 1483 cm^{-1} is attributed to the C-C aromatic ring stretching of the benzenoid unit. The peaks at 1288 cm^{-1} and 791 cm^{-1} can be assigned to C-N stretching of the secondary aromatic amine and aromatic C-H out-of-plane bending vibration, respectively. The absorption bands at 1549, 1304 and 1180 cm^{-1} are attributed to the polyaniline chain [25].

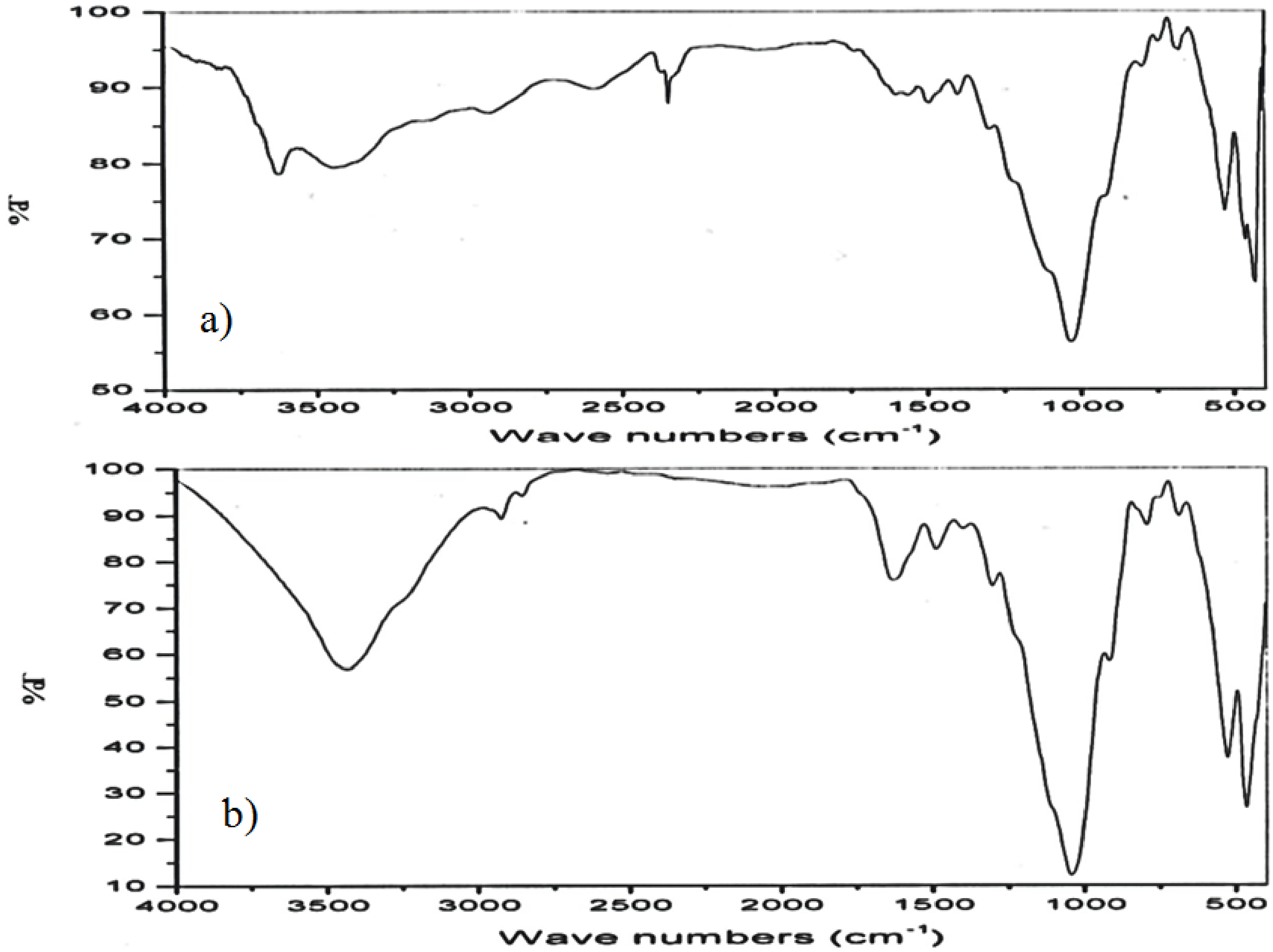

Figure 4 FT-IR spectra of PANi-MMT composite (a) before and (b) after adsorption of congo red dye.

The FT-IR spectra of the composite after the adsorption of congo red dye has showed no significant change except the hydration of the adsorbent indicating that the removal of congo red dye may occurred via physisorption.

The XRD pattern before and after adsorption of congo red dye on PANi-MMT composite (Figure 5) shows the characteristic peaks for the emeraldine structure of PANi [25]. The crystalline nature of the polymer composite and hence there is no observable change would be noticed in the XRD pattern of the polymer composite before and after the adsorption of congo red dye.

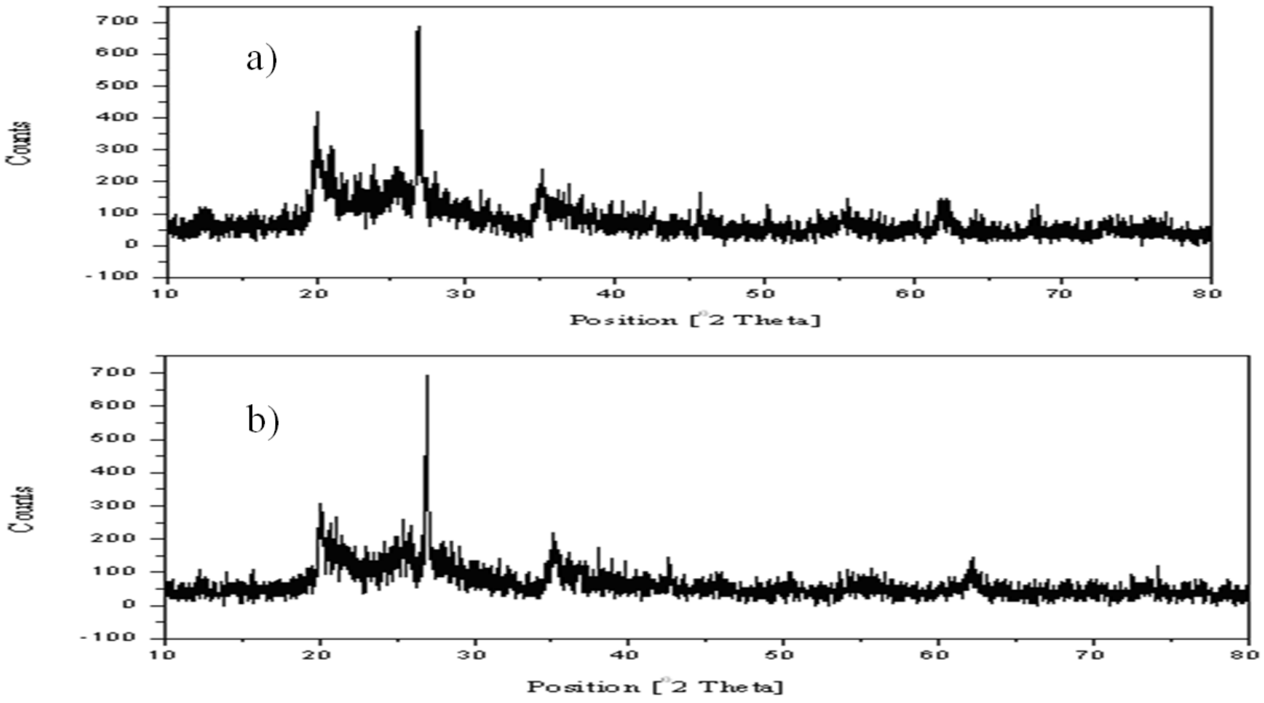

Figure 5 XRD pattern of PANi-MMT composite (a) before and (b) after adsorption of congo red dye.

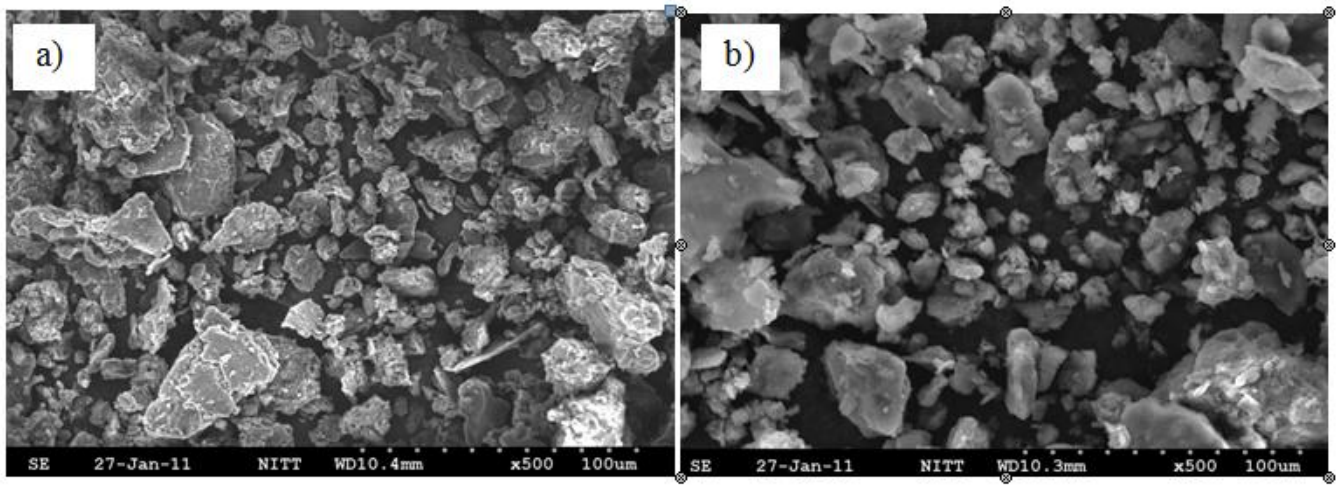

Figure 6 SEM images of PANi-MMT composite (a) before and (b) after adsorption of congo red dye.

The SEM images of PANi-MMT composite before and after adsorption of congo red dye are shown in Figure 6. In this case the sponge-like structure with some bright spots confirms the presence of the polymer and montmorillonite [34]. The flake structure after adsorption may be the congo red dye coverage on the PANi-MMT composites. Hence, the removal of congo red dye is clearly shown in SEM images.

TGA of PANi-MMT composite before and after adsorption of congo red dye are shown in Fig. 7A and B respectively. The TGA curve of sample A shows the weight loss of ~ ~ 4 % is obtained up to 100 ^{0}C due to the presence of moisture. Similarly TGA curve of sample B shows the weight loss of ~ 7% is obtained upto 100^{0}C due to the presence of moisture after adsorption of aqueous congo red dye onto the PANi-MMT composite. The presence of excess water in sample B was also confirmed in FT-IR spectrum. The TGA curve of sample A shows the second weight loss of ~ 8 % is observed at ~280 to 450^{0}C, which is equivalent to the doping level of the dopant in the polymer whereas sample B shows the second weight loss of ~ 10 % is observed at ~ 120 to 490^{0}C due to the decomposition of dopant. The final degradation of the polymer composite starts at ~ 430^{0}C in sample A and for sample B final degradation starts at ~ 490^{0}C.

Figure 7 TGA of PANi-MMT composite (a) before and (b) after adsorption of congo red dye.

Conclusion

The PANi-MMTcomposte has demonstrated sufficient promise as an adsorbent for the removal of Congo red dye from aqueous solution. A small amount (50 mg/50 mL) of the PANi-MMT composite could decolorize as much as 25.1 mg/g of the congo red dye from an aqueous solution (40 mg/L) at 30^{o}C if agitated for 1 h. The adsorption of the congo red dye was appreciable in a wide range of pH. This showed that adsorption of the congo red dye could be carried out using PANi-MMT composite without adjusting the pH of the medium. The experimental data yield good fit with Longmuir when they compared to Freundlich isotherm equations. The values of the adsorption coefficients computed indicated that the potential of the PANi-MMT composite (adsorbent) for practical applications in colour removal process. The adsorption of congo red dye onto PANi-MMT composite was spontaneous at higher temperature and lower concentration and change in enthalpy suggests that the process is endothermic in nature. The enthalpy change for the adsorption process was observed to be 8-86 kJ mol^{-1}, which indicates that, the absence of very strong chemical force between the adsorbed congo red dye molecules and the PANi-MMT composite surface. Therefore, physisorption seems to be the major mode of adsorption.

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Publication History
Received 24th Nov 2013
Revised 11th Jan 2014
Accepted 15th Jan 2014
Online 29th Apr 2014