Thermodynamic study of removal of congored by polyaniline/MnO_2composite

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Abstract

The prepared PANi/MnO_2 is an efficient adsorbent to remove congored from aqueous solution. It decolorize as much as 84 % of the dye from an aqueous solution (40 mg/L) at 30^oC if agitated for an hour. The experimental data yielded perfect fit with Langmuir The enthalpy change for the adsorption process was in the range of 36 to 54 kJ mol^{-1}, which indicate very strong chemical force between the adsorbed dye molecules and the polymer surface. Hence, physisorption seems to be the major mode of adsorption.

Key words: Polymer, adsorption, composite, dye

INTRODUCTION

The textile industry is one of the largest polluters in the world. The World Bank estimates that almost 20% of global industrial water pollution comes from the treatment and dyeing of textiles. Some 72 toxic chemicals reach our water supply from textile dyeing. Many of these chemicals cannot be filtered or removed. The textile industry is second only to agriculture as the biggest polluter of clean water globally. Dyeing, rinsing, and treatment of textiles all use large amount of fresh water. Synthetic dyes are also 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. The dyes release toxic chemicals like aromatic amines (benzidine and toluidine), heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments and chlorine. 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. Activated carbon has undoubtedly been on of the most popular adsorbents for the removal of dyes from aqueous solution and is widely used in wastewater treatment applications throughout the world.

The adsorption process is one of the effective methods used to remove dyes from aqueous solution. Activated carbon is the most widely used adsorbent for dye removal, but it is too expensive. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater. The adsorption of dyes on clay minerals is likely to be dominated by ion exchange processes, many minerals are used for the removal of dye from aqueous solution; such as, Silica, acid activated bentonite, clay. In this present study the equilibrium and thermodynamic studies of the adsorption of Congored (MG) onto the conducting polyaniline/MnO_2 composite has been investigated and discussed in the following pages. The main aim, therefore, of the present work is to scan the suitability of the composite for the removal of Congoredfrom aqueous solution by adsorption method. The adsorption process is one of the effective methods used to remove dyes from aqueous solution.

Aim and scope of the present work

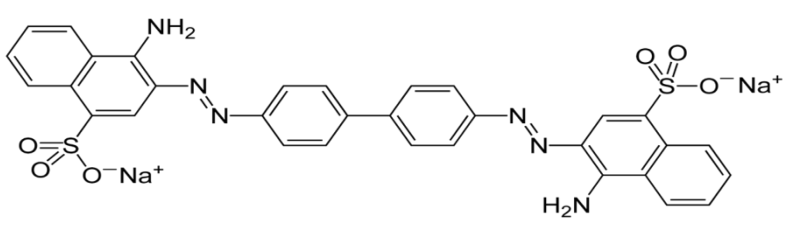
Dyes are widely used in industries such as dyestuff, textiles, rubber, leather, paper, plastics, cosmetics, etc., to colour their products; these dyes are invariably left in the industrial waste waters. Dyes even in very low concentrations affect the aquatic life and food chain. Hence, the removal of dye from process or waste effluents becomes environmentally important. Because of the high degree of organics present in these molecules and the stability of modern dyes. Conventional physicochemical and biological treatment methods are ineffective for their removal. This led to the study of other effective materials.

The adsorption process is one of the effective methods used to remove dyes from aqueous solution. The adsorption of dyes on clay minerals is likely to be dominated by ion exchange processes, many minerals are used for the removal of dye from aqueous solution; such as, kaolinite, Silica, acid activated bentonite, iron humite and alumina. In this present study the equilibrium and thermodynamic studies of the adsorption of congoredonto the polyaniline/MnO_2 composite has been investigated and discussed in the following pages.

EXPERIMENTAL SECTION

Materials

All chemicals used were of analytical reagent grade (Merck/SRL, India). Doubly distilled water was used throughout the study. Polyaniline/MnO_2 composite (PANi-MnO_2) was prepared by reported method [1]. The structure of congoredis given below.



Congored

Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid)(formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol.The maximum absorptionwavelength in the visible light range is 497nm.

Batch adsorption experiments

Adsorption experiments were performed by agitating 30 mg of adsorbent with 50ml of dye solution of desired concentrations at 30 ±0.5^{0}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 Elico photometer. 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 20-100mg/L; (ii) contact time between adsorbent and the dye solution 10-60min; (iii) dosage of adsorbent 25mg to200 mg/50ml; (iv) temperature 30-50^{0}C and (v) co-ions Cl^- and Ca(II).

RESULT AND DISCUSSION

Effect of agitation time and initial concentration

The equilibrium parameters for the adsorption of dye onto PANi/$MnO_2$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 decreased with rise in temperature. The variation of Qe with temperature indicates that the adsorption process is exothermic in nature. The effect of contact time between the adsorbent and adsorbate shows equilibrium was established after 40 min for all the concentrations.

Table 1. Equilibrium parameters and removal efficiency for the adsorption of congored onto PANi/MnO_2 composite

$[CR]_o$ (mg/L)	Ce (mg/L) 30^0	40^0	50^0C	Qe (mg/g) 30^0	40^0	50^0C	Removal (%) 30^0	40^0	50^0C
20	3	6	8	17	14	12	85	70	60
40	6	13	17	34	27	23	85	68	58
60	10	20	26	50.3	40	34	84	67	57
80	15	28	37	65.1	52	43	81	65	54
100	28	36	48	72.3	64	52	72	64	52

Effects of adsorbent dosage

The effect of adsorbent dose on the dye removal at a fixed initial dye concentration shows that the amount of dye removed is decreased with the increase in adsorbent dose. The maximum removal of dye was found to be 34 mg/g at an adsorbent dose of 100 mg/50 ml for PANi/MnO_2 composite. This increase in dye removal is due to the availability of higher number of dye molecules per unit mass of the adsorbent, i.e., higher dye/adsorbent ratio. Further experiments were carried out using 100 mg/50 ml, as it exhibits appreciable removal capacity, for optimization of adsorption parameters.

Adsorption isotherms

To quantify the adsorption capacity of the chosen adsorbent for the removal of dye from water,the Langmuir adsorption equation was applied.The adsorption isotherms were studied at 30, 40 and 50 ^{0}C.The linear plot of Ce/Qe Vs Ce indicates the applicability of Langmuir isotherm. (Fig. 3). Langmuir isotherm [2] suggests this is due to physico-chemical interaction between the adsorbent and adsorbate.

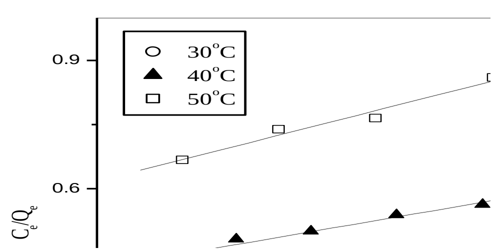


Table 2. Adsorption isotherms

Isotherms	statistical parameters/ constants	Temperature 30°C	40°C	50°C
Langmuir	r^2	0.968	0.98	0.99
	Sd	0.023	0.022	0.042
	Q_o	116	232	158
	b	0.068	0.010	0.104

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^ovalues are negative 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 [3]. For chemical sorption, enthalpy values range from 83 to 830 $kJmol^{-1}$, 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 composite is a physical process. Negative values of ΔH^o suggest that the process is exothermic, so decrease of temperature encourages dye adsorption. As indicated in Table 5, ΔS^o values for the adsorption process are negative. This observation suggests a high degree of orderliness at the solid-solution interface during the adsorption of the dye onto composite.

Table3.Equilibrium constant and thermodynamic parameters for the adsorption of methylene blue on to composite.

$[CR]_o$ (mg/L)	K_o 30°	40°	50°C	$-\Delta G^o$ 30°	40°	50°	$-\Delta H^o$	$-\Delta S^o$
20	5.67	2.33	1.50	4.37	2.20	1.09	54	165
40	5.67	2.08	1.35	4.37	1.90	0.8	58	180
60	5.16	2.00	1.31	4.13	1.80	0.72	56	172
80	4.38	1.86	1.16	3.72	1.61	0.40	54	167
100	2.61	1.78	1.08	2.42	1.50	0.21	36	110

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

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 thedye [4].

Effect of co-ions

The result from table 5 indicate the effect of added Ca(II) ions decrease the amount of dye removed. This may be due to the fact that there is a competition between the cation and cationic dye for the active sites on the adsorbent.Addition of chloride ions also decreases the dye adsorption. This may be due to the fact that at higher concentration of chloride ions the negative ionic atmosphere might have slow down the boundary layer diffusion of the positively charged dye there by decreasing the adsorption percentage.

Table 5. Effect of Co-Ions on the amount of dye remove by polymer/MnO_2 composite

Co-ion	Amount adsorbed, mg/g						
		0	100	200	300	400	500
Chloride	34	32.6	31.2	31.1	31.0	28.8	
Calcium	34	33.7	33.05	30.8	30.5	29.6	

[dye]=40mg/L; Temp: 30^oC; pH=7; Contact time= 60 min

Conclusion

The prepared PANi/MnO_2 is an efficient adsorbent to remove congored from aqueous solution. It decolorize as much as 84 %of the dye from an aqueous solution (40mg/L) at 30^oC if agitated for an hour.The experimental data yielded perfect fit with Langmuir The enthalpy change for the adsorption process was in the range of 36 to 54kJ mol^{-1}, which indicate very strong chemical force between the adsorbed dye molecules and the polymer surface. Hence, physisorption seems to be the major mode of adsorption.

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