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Kinetics, isothermal and thermodynamic studies of adsorption of reactive blue dye from aqueous solution by chitosan modified cobalt ferrite

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Abstract

Adsorption techniques for the remove dyes from water have been widely used since it has been found to be an economical and effective treatment method for removal of dyes due to its sludge free clean operation. Spinel ferrite nanoparticles have attracted much attention because of their magneticproperties and ease of separation. However, high rate oxidative reaction in air, short storage life and low adsorption capacity are limitations to its applications. When magnetic particles are coated with chitosan, they may be protected from oxidation and may have reduced toxicity, aggregation and extended storage life. Hence, this study investigated the potential of chitosan modified cobalt ferrites (Cs-$CoFe_2O_4$) composites for the removal of dye. The Cs-$CoFe_2O_4$ was prepared by in-situ co-precipitation procedure with chitosan in 1% glacial acetic acid. The resulting composite was washed to neutral pH and dried in vacuum and characterized using Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). The composites were used for removal anthraquinone reactive blue dye in batch process. The equilibrium data were subjected to Langmuir and Freundlich adsorption isotherms while pseudo-first order and second order kinetic models were used to analyse the kinetic data. The XRD results revealed the main characteristic peaks of chitosan and that of metal ferrites at 2θ values of 20 and 32° corresponding to 2 0 1 and 3 1 1 planes respectively. The presence of O-H, N-H, C-H and Fe-O stretches are consistent with chitosan and metal ferrites in the FTIR analysis. IR peaks at 3348cm^{-1} is associated to N-H and O-H stretches; while the bands at 2876 and 560 cm^{-1} are consistent with C-H and Fe-O respectively. The SEM results confirmed the microscopic morphology of the prepared composites. Percentage removals increased with increase in adsorbent dosage and the optimum pH for anthraquinone reactive blue dye removal was 11. Langmuir isotherm best described the adsorption with maximum capacity of 35.68 mg/g. The adsorption process followed first order kinetics with correlation coefficient (R^2) closed to unity. The evaluation of free energy and enthalpy changes revealed that the adsorption process was spontaneous and endothermic. Chitosan modified cobalt ferrite is an excellent adsorbent for the removal of anthraquinone reactive blue dye from water with improved recovery of the composite.

Keywords: Chitosan; cobalt ferrite; reactive blue dye; adsorption; kinetics and isotherm.

1. Introduction

Textile industries use large amount of organic and inorganic chemicals as dyes that are directly or indirectly responsible for the production of wastewater. Reactive dyes are frequently used for dyeing cotton, wool and polyamide fibres, they are extensively used either as primary or secondary dyes in commercial dyeing formulations (Epolito *et al*., 2005; Hassan and Hameed, 2011). Effluents from textile, dyeing, paper and pulp, tannery and paint industries contain dyes which pollute the water. Majority of the dyes are toxic and carcinogenic, also they impart colour to water, thereby causing environmental problems and health hazards to humans and aquatic organisms (Alver and Metin

2012; Venkatesha *et al.*, 2012). Dyes are designed to resist breakdown with time, exposure to sunlight, water, soap and oxidizing agent. They are recalcitrant in nature and cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins (Wang *et al.,* 2008; Carielle*t al.* 1995; 1996; Pagga and Brown, 1986).

Adsorption techniques have been widely used for the wastewater treatment, it has been found to be an economical and effective treatment method for removal of dyes due to its sludge free clean operation (Kushwaha et *al.,* 2014). Activated carbon has been remarkably used for the treatment of dyes contaminated wastewater due to their large surface area and porosity; however regeneration and high cost has limited their applications.

Chitosan is a biopolymer that has been extensively studied as adsorbent because of its high adsorption potential, it presents hydroxyl and amino functional groups, which can be protonated in acid solution. However, chitosan can be solubilized in diluted acid solutions, and its separation from the solution after the adsorption process is difficult. The use of magnetic nanoparticles in environmental application are receiving increasing attention due to their large surface area, reduced diffusion resistance and above all, ease of separation (Keyhanian et al., 2016). Cobalt ferrite ($CoFe_2O_4$) is a spinel inverse type that can be easily synthesized via co–precipitation methods with less toxic and high yield (Fariñas et al., 2018).

When magnetic particles are coated with chitosan, they may be protected from oxidation and may have reduced toxicity, aggregation and extended storage life (Donadel*et al.,* 2008). Furthermore, chitosan coating may be used as surface for further functionalization due to abundant amino and hydroxyl group which may improve the adsorption capacity of the magnetic chitosan (Reddy and Lee 2013). Also, chitosan crosslinking can improve the mechanical and chemical properties of the magnetic composite, with greater stability in acid solution, high adsorption capacity and easy to be separated from the liquid after the adsorption operation

This study therefore investigated the potential of chitosan modified cobalt ferrites (Cs-$CoFe_2O_4$) composites for the removal of anthraquinone blue reactive dye from aqueous solutions. The Cs-$CoFe_2O_4$ was prepared by in-situ co-precipitation procedure with chitosan in 1% glacial acetic acid. The resulting composites were characterized using Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). The composites were used for removal of anthraquinone blue dye. The equilibrium data were subjected to Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich, Redlich-Peterson and Sips adsorption isotherms. Pseudo-first order, second order, Elovich and intra-particle diffusion models were used to analyze the kinetic data.

2.0. Materials and methods

2.1 Materials

Reactive blue 4, (C.I. No. 61205; CAS No.13324-20-4), chitosan powder of high molecular weight, glutaraldehyde, ferric nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$) and cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) were from Sigma Aldrich, while NH_4OH and NaOH were procured from Merck, India, other chemicals were Analar grades, while doubly distilled water was used for aqueous solutions preparation.

2.2 Synthesis of Cs-$CoFe_2O_4$ Nanoparticle

The composite was synthesized by co-precipitation procedure by weighing accurately 1.164 g of $Co(NO_3)_2.6H_2O$, 3.232 g of $Fe(NO_3)_3.9H_2O$ and quantitatively transferred them into 100 ml flask, 40 ml doubly distilled water was added under vigorous stirring for 60 min. Solution of chitosan was prepared by activating 0.75 g of the powder in 25 ml of 1% glacial acetic acid solution stirred at 80 °C for 4 hours. Synthesis of Cs-$CoFe_2O_4$ was accomplished by adding the chitosan solution gradually to the salts solution under continual stirring, the pH was adjusted to 11 using 25 ml of 35% NH_4OH solution under continue stirring at 60 °C for 2 hours, 5 ml of 50% glutaraldehyde was added and the allow to cure for 24 hours. The reddish black precipitate was washed with ethanol and distilled water each thrice followed by drying in vacuum oven at 80 °C for 12 hours.

2.3 Characterisation of synthesized Cs-$CoFe_2O_4$

Surface morphology and elemental composition of the material was analysed using scanning electron microscopy (SEM) [VEGA3 TESCAN], X-ray diffraction (XRD) data were collected using a PAN Analytical X' Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.5418Å). Fourier transform infrared (FT-IR) spectra were recorded from 400 to 4000 cm^{-1} in TENSOR 27spectrometer (Bruker, Germany) using KBr pellet technique.

2.4 Adsorption studies

Adsorption studies were carried out has previously described (Adeogun, 2019). The amount of dye adsorbed (mg/g) by the adsorbents as a function of time (Q_t) and at equilibrium (Q_e) were estimated according to equations 1 and 2 below:

$$Q_t = \frac{(C_o - C_t)}{m} \times V \qquad (1)$$

$$Q_e = \frac{(C_o - C_e)}{m} \times V \qquad (2)$$

where C_o, C_t and C_e are the initial, time t and equilibrium concentrations (mg L^{-1}) of the dye respectively, V is volume (L) of the solution and m is the mass (g) of the adsorbent.

3.0 Results and Discussions

3.1 Characterization

Figure 1 shows the scanning electron microscopy (SEM) images and energy dispersive X-ray analysis (EDAX) for Cs-$CoFe_2O_4$. Figure 1a revealed that the structure is an open crystal grains with agglomerated rod-like particles with surface texture and porosity characterized by openings with increasing contact area that can facilitates the pore diffusion during adsorption. After adsorption, the SEM image (Figure 1b) displayed a total collapse structure due to the occupation of adsorption sites which leads to agglomeration of the adsorbent particles. Figure 1c, revealed further information on the elemental composition of the synthesized Cs-$CoFe_2O_4$, the figure displayed higher percentage of carbon, oxygen and nitrogen due to the presence of chitosan. In addition, it contains iron as well as cobalt.

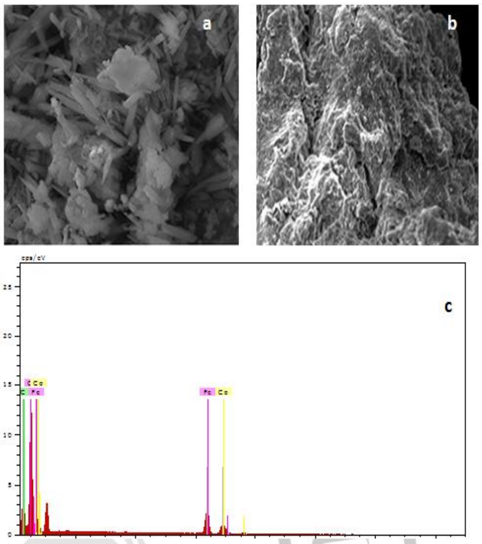

Figure 1: SEM and EDAX analysis of the Cs-$CoFe_2O_4$

The XRD patterns of the Cs exhibit two characteristic peaks at 2θ values of 11.1° and 20.2°. The peak at 20.2° shows the allomorphic tendon form of Cs, which resulted in a strong decrease in the sorption capacities (Nguyen and Huynh, 2014). The XRD patterns of the Cs-$CoFe_2O_4$ exhibited the reflection planes (220), (311), (222), (400), (422), (511) and (440) that indicate the spinel cubic structure (Nejati and Zabih, 2012). XRD pattern of Cs-$CoFe_2O_4$ composites (Fig. 3) shows the mixed peaks of Cs and the pure $CoFe_2O_4$ particles. This is consistent with that reported by Nguyen and Huynh, (2014). However, the diffraction intensity of Cs-$CoFe_2O_4$ composites is lower than that of $CoFe_2O_4$ due to lower $CoFe_2O_4$ content. This result suggests that the $CoFe_2O_4$ nanoparticles are incorporated into the chitosan. The more diffuse scattering is due to the amorphous nature of chitosan coating. Furthermore, the zinc ferrite nanoparticles had partially inverse spinel structure (Shahraki *et al.,* 2014).

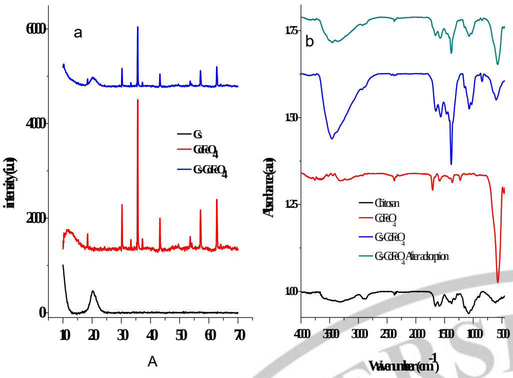

Figure 2: XRD pattern (a) and FTIR spectra (b) of Cs-$ZnFe_2O_4$

FTIR spectra of Cs- $CoFe_2O_4$ nanoparticles is shown in figure 4. On the bases of literature, data in the range of 1000-100 cm^{-1}, the FT-IR bands of solids are usually assigned to vibration of ions in the crystal lattice (Nejati and Zabihi, 2012; Baykal *et al* 2008). Absorption peak at 584 cm^{-1} is assigned to Fe–O group in $CoFe_2O_4$, the characteristic absorption bands which appeared at around 3348 cm^{-1} corresponding to the stretching vibration of O–H and N–H bonds in chitosan. The peaks around 2880 cm^{-1}, 1631 cm^{-1}, 1336 cm^{-1}, 1028 cm^{-1} are ascribed to C–H of alkyl group, C=O of amide , -NHCO of amide and C–OH bond, respectively(Nguyen and Huynh , 2013). In the FTIR spectrum of Cs-$CoFe_2O_4$/Anthraquinone blue, (Fig. 2b) the absorption peak at 3277 cm^{-1} was due to interaction between the composite and anthraquinone blue dye.

3.2 ADSORPTION STUDY

3.2.1. Effect of contact time and initial dye concentration

Figure 3a shows the effects of contact time and initial dye concentration on the adsorption process, the quantity of dye adsorbed increased from 0.29 to 8.36 mg/g with an increase in agitation time (5 – 120 min), and became almost constant after 120 mins. At higher initial dye concentration of 50 mg/L, the amount of adsorbed increased from 4.83 to 26.22 mg/g and then reaches a constant value beyond which no more adsorbate would be further removed from the solutions.

3.2.2. Effect of pH on the dye adsorption

The effect of pH on the adsorption of anthraquinone dye on Cs-$CoFe_2O_4$ is presented in Figure 3b. There is a sharp decrease in adsorption efficiency as the pH increases, possibly due to the competition or interaction of other ions in the solution with dye molecule and available adsorption site. However the highest efficiency was recorded at pH 11, this is similar to what was earlier reported by Mehta *et al*., (2013).

3.2.3 Effect of Adsorbent Dosage

The effect increased adsorbent dosage on the adsorption efficiency is shown in Figure 3c, the figure showed that the efficiency increase with increase dosage possibly due to increase in adsorption sites. However, if the adsorption efficiency is expressed in term of capacity, the inverse would be the case; this can be attributed to aggregation of adsorption with increase quantity (Huang *et al.,* 2017).

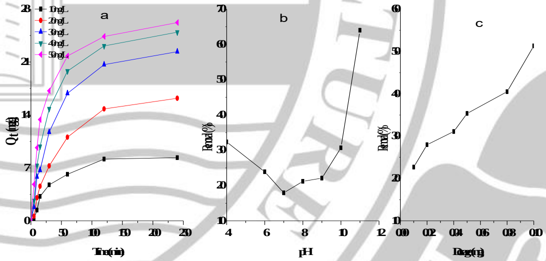

Figure 3: Effect of (a) contact time (b) pH and (c) adsorbent dosage on the dye adsorption

3.3 Kinetic Modelling

Figure 4 show the first order and second order kinetics model fits for adsorption of anthraquinone blue dye by Cs-$CoFe_2O_4$. The kinetic models parameters are shown in the Table 1. The values of R^2 obtained indicated a good correlation for the two kinetic models, however, when the values of experimental adsorption capacity obtained ($Q_{e.exp}$) was compared with calculated adsorption capacity ($Q_{e.calc}$), the values obtained for the first order kinetic model displayed a better relationship with lower values of the %SSE. This implied that the first order kinetic model best fitted the data for the adsorptionof anthraquinone blue dye by Cs-$CoFe_2O_4$.

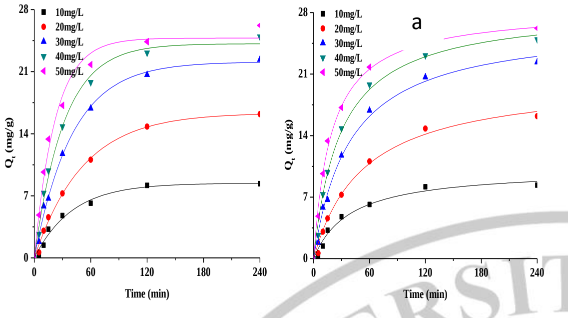

Figure 4: First order and second order kinetic model fits for the adsorption of anthraquinone blue dye by Cs-$CoFe_2O_4$

Table 1: Kinetics parameter of adsorption process

Model	C_0	10	20	30	40	50
First order	Q_e (exp) (mg/g)	8.365	16.206	22.372	24.94	24.967
	Q_e (cal) (mg/g)	8.421	16.348	22.104	24.151	24.226
	k_1 (mins^{-1})	0.025	0.019	0.025	0.032	0.047
	R^2	0.994	0.998	0.999	0.998	0.998
	% SSE	0.002	0.003	0.004	0.011	0.010
Second order	Q_e(cal) (mg/g)	10.224	20.463	26.783	28.512	28.411
	k_2	0.002	0.001	0.001	0.001	0.002
	R^2	0.991	0.997	0.998	0.998	0.999
	%SSE	0.078	0.093	0.070	0.051	0.049

3.3.1 Isotherms studies for adsorption by Cs-$CoFe_2O_4$

Figure 5 represents the adsorption isotherm fits for the adsorption process, the isotherm model parameters in Table 2 shows that the models well fitted the equilibrium data. The maximum adsorption capacity of 35.05 mg/g was obtained with R_L value of less than unity along with **n** value from Frudlinch isotherm model confirming the favourability as well as cooperativity of the adsorption process.

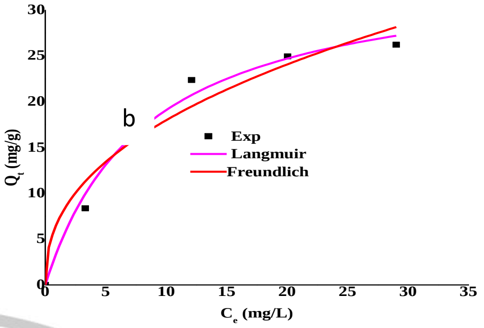

Figure 5: Isotherm model fits for the adsorption process

Table 2: Physical Isotherm Parameter of Adsorption by Cs-$CoFe_2O_4$

Isotherm	Parameter	
Langmuir	$Q_{max\ (mg/g)}$	35.04
	R_L	0.143
	b (mg/L)	0.119
	R^2	0.997
Freundlich	K_F(mg/g)(mg/L)$^{-1/2}$	6.834
	1/n	0.420
	R^2	0.990

3.4 Thermodynamic Studies

The thermodynamic parameters, ΔG°, ΔH° and ΔS° were estimated by using van't Hoff plot of temperature dependent equilibrium studies. The plot of natural logarithms of equilibrium constant, ln K_D versus the reciprocal of temperature, (1/T) is shown in Figure 6, while the thermodynamic parameters are presented in Table 3. The negative value of ΔG and positive value of ΔS indicate the spontaneous and feasible adsorption, while the positive values of enthalpy change indicate that the adsorption process is endothermic in nature. The positive value of ΔS also shows that there is increase in randomness of the solid-liquid interaction during the adsorption process.

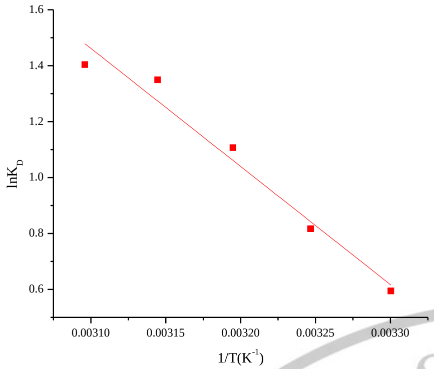

Fig 12 van't Hoff plot for adsorption of anthraquinone blue by Cs-$CoFe_2O_4$

Table 3: Thermodynamic parameters for adsorption process

Temp (K)	K_D	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)	R^2
303	1.812	-1.498	35.112	0.1210	0.959
308	2.263	-2.091			
313	3.024	-2.880			
318	3.856	-3.568			
323	4.071	-3.770			

4.0 Conclusion

Chitosan coated $CoFe_2O_4$ composite was successfully synthesized and confirmed by characterization. The prepared Cs-$CoFe_2O_4$ successfully removed anthraquinone blue dye from water and the adsorbent was easily recovered from the solution with magnetic assistance. The optimum pH for adsorption of anthraquinone blue dye was found to be 11, while the adsorption process was best fitted by first order model. The maximum adsorption capacity of 35.04 mg/g was obtained from the equilibrium isotherm study. The effect of temperature on adsorption process revealed the spontaneity and feasibility of adsorption process. This study showed that Cs-$CoFe_2O_4$ is a promising adsorbent for the removal of pollutants from aqueous solutions with improved recovery of the adsorbent.

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