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An Insight on Kinetic Adsorption of Congo Red Dye from Aqueous Solution using Magnetic Chitosan Based Composites as Adsorbent

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ABSTRACT

In the present research, a series of magnetic chitosan based composites with the general formula of $Ni_xMn_{1-x}Fe_2O_4$/CS were synthesized from spinel-type transition metal ferrites [$Ni_xMn_{1-x}Fe_2O_4$ (where x= 0, 0.2, 0.5 and 1.0)] and chitosan (CS) as a polymer. The structure and composition of the synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The adsorption activity of the synthesized magnetic chitosan based composites was evaluated for the removal of Congo red (CR) dye from aqueous solution. Furthermore, the influence of the Mn content on adsorption capacity of the synthesized magnetic chitosan based composites were studied. The results of adsorption kinetic of CR dye using spinel-type transition metals $Ni_xMn_{1-x}Fe_2O_4$ and $Ni_xMn_{1-x}Fe_2O_4$/CS followed pseudo- second order model. The results indicated that 74% of CR dye solution were removed *via* adsorption using $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS after 180 min. The adsorption performance show that the chitosan based composites can be more efficient than spinel-type transition metals for removal of CR dye. Moreover, the magnetic chitosan based composites can be quickly separated from the aqueous solution by an external magnet after adsorption process.

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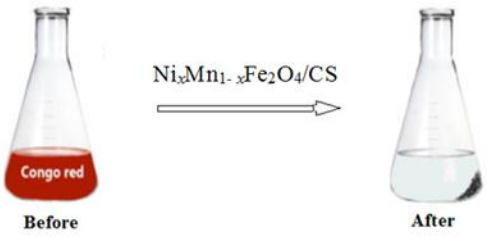
Graphical Abstract



Introduction

The dyes are widely used in industries including textile, cosmetics, leather and food. However, many organic dyes are harmful to human being and toxic to microorganisms, so the removal of dyes has gained more attention in the past few years [1]. Various physical and chemical technologies, such as coagulating sedimentation [2], adsorption [3], and chemical oxidation have been developed to remove the organic dyes from wastewaters. Among these approaches, adsorption is used as an effective and economic method to remove organic dyes from wastewater. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluents. In addition, since the adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process [4, 5]. On the other hand, magnetic separation is a very convenient approach for removing and recycling magnetic particles/composites [6, 7]. Chitosan is a cationic biopolymer derived from chitin and the most abundant biopolymer in nature. Chitosan is an excellent natural adsorbent due to the presence of the amine (NH_2) and hydroxyl (OH) groups [8]. However, raw chitosan presents some major problems in adsorption process such as (i) weak mechanical property, (ii) dissolution in acidic media, (iii) low specific gravity, (iv) high swelling ratios [9]. In order to increase the chemical stability, separation efficiency and adsorption capacity of raw chitosan, chemical crosslinking, magnetic separation and nanotechnology are crucial options. From the viewpoints of environmental protection and high energy saving technology, it is very important and significant to prepare magnetic chitosan composites and explore its adsorption properties in order to expand the utilities as industrial biomaterials. The composites are composed of a magnetic core with a strong magnetic response such as Fe_3O_4 and a chitosan shell to provide favorable functional groups [10, 11-13]. In Compared with Fe_3O_4, spinel-type transition metal ferrites [$Ni_xMn_{1-x}Fe_2O_4$ (where x= 0, 0.2, 0.5 and 1.0)] are stable and their high saturation magnetization will be favorable for magnetic separation [14].To the best of our knowledge, the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite for adsorption application has not been reported. Therefore,

the objectives of our work are to (1) prepare a magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite; (2) characterize the structure of the as prepared composite; (3) investigate the influence of the Mn content on adsorption capacity of synthesized magnetic chitosan based composites were studied in the dye removal. Congo red (CR) was also selected as a model pollutant to examine the adsorption capacity. Our results show that the $Ni_xMn_{1-x}Fe_2O_4$/CS composite can be more efficient in the removal of dye than $Ni_xMn_{1-x}Fe_2O_4$.

Experimental

Materials and Characterization

Congo red (C.I. Direct Red 28), $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, $Mn(NO_3)_2.4H_2O$, Tween 80, acetic acid, ethanol, acetone and NaOH were purchased from Merck Company. Chitosan (with medium MW) from Aldrich Company. The structure of the synthesized samples was characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation).The morphology of synthesized samples were investigated by scanning electron microscope (SEM-VEGA3-TESCAN). The progress of adsorption experiments were measured by UV-Vis spectrophotometer (Shimadzu UV-2550).

Synthesis of spinel-type transition metal ferrites ($Ni_xMn_{1-x}Fe_2O_4$)

Nickel manganese ferrites with formula $Ni_xMn_{1-x}Fe_2O_4$ (where x= 0, 0.2, 0.5 and 1.0) were synthesized by chemical co-precipitation method. The samples with varying x concentration were prepared. All the salts $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ and $Mn(NO_3)_2.4H_2O$ with different quantities for different samples were dissolved in distilled water. The beaker containing 25 ml solution of 4M NaOH was placed on magnetic stirrer of moderate speed (50rpm) at room temperature. The solution of beaker containing NaOH solution was added drop by drop into the beaker containing metallic ions NaOH solution. During the addition, brown precipitates were obtained. The resultant product were collected from the reaction mixture under an external magnetic field, washed with ethanol several times, and dried at 50 °C under vacuum.

Synthesis of chitosan coated spinel-type transition metal ferrites ($Ni_xMn_{1-x}Fe_2O_4$/CS)

For this purpose, spinel type transition metal ferrites $Ni_xMn_{1-x}Fe_2O_4$ (200 mg) were dispersed in mineral oil (50.0 mL) containing Tween 80 by ultrasonication. CS solution (1% w/v, 15.0 mL) was added to the medium and the mixture was sonicated for 30 min. The system was stirred with the rate of 1500 rpm. After 4 h stirring at room temperature, the resultant CS coated spinel type transition metal ferrites ($Ni_xMn_{1-x}Fe_2O_4$/CS) were removed from the reaction mixture by a magnet.

The obtained magnetic composite were washed several times with acetone and dried in vacuum oven at 50°C.

Batch adsorption experiments

In order to investigate the adsorption behavior of the $Ni_xMn_{1-x}Fe_2O_4$ samples and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composites, dark adsorption experiments were carried out. 50 mg adsorbent was added into 100 mL CR solution with fixed concentration (10 mgL^{-1}). The mixtures were standing in a beaker at neutral pH and room temperature for 15, 30, 45, 60, 90,120 and 180 min. At the end of the equilibrium period, aqueous sample (5 mL) was taken from the solution and the concentrations of CR solution were determined by using a UV-vis spectroscopy at a wavelength of 498 nm. The amount of adsorbed dye per gram of adsorbent (mg g^{-1}) at time t (min) was calculated using the following equation [15]:

$$q_t = \frac{(C_o - C_t)V}{m} \qquad \text{Eq. (1)}$$

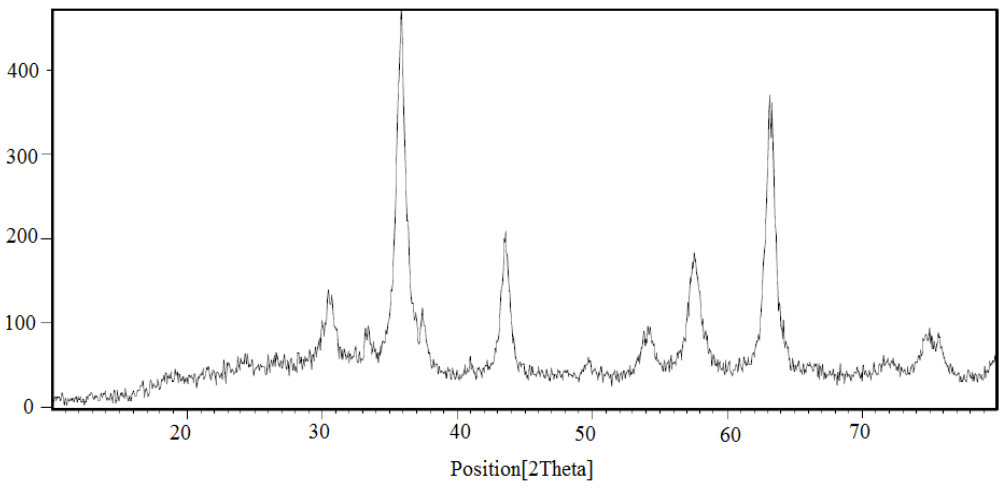
Where q_t (mgg^{-1}) is the amount of adsorbed Congo red per gram of adsorbent at time t (min), C_0 is the initial concentration of Congo red solution (mgL^{-1}), C_t is the concentration of Congo red solution (mgL^{-1}) at time t (min), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

Results and Discussion

Characterization

Figure 1 shows the XRD patterns of the spinel type transition metal ferrites $Ni_xMn_{1-x}Fe_2O_4$. The all of the patterns show all the characteristic peaks of ferrite material with most intense peak (311), which confirms the formation of cubic spinel structure [16]. The diffraction signals located at 2θ = 30.5°, 33.4°, 36°, 43.5°, 53.5°, 57.5° and 63.0° assigned to scattering from (220), (003), (311), (222), (400), (422), (511) and (440) planes of the metal spinels are consistent with the cubic [16].

(a)



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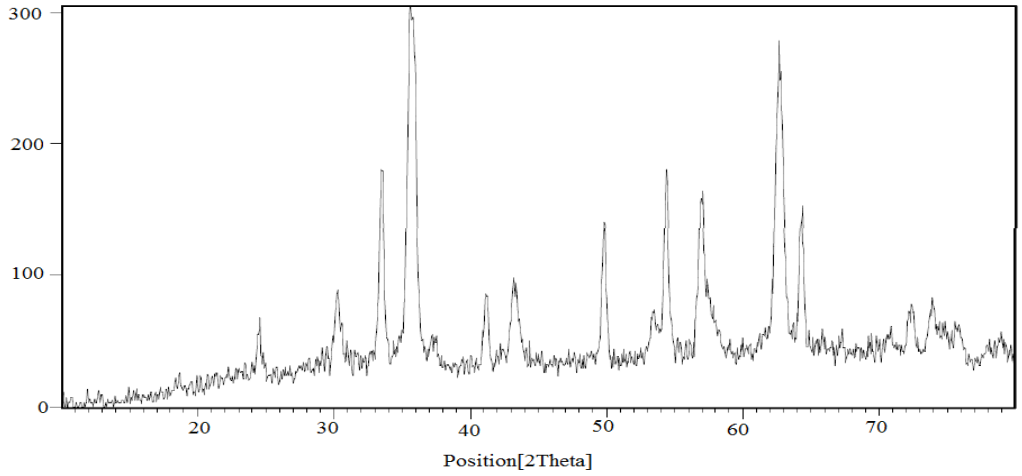

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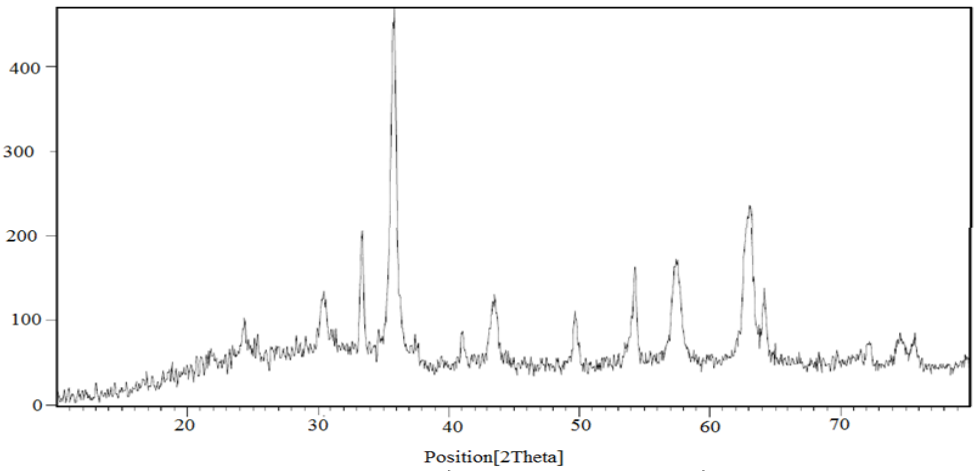


(d)

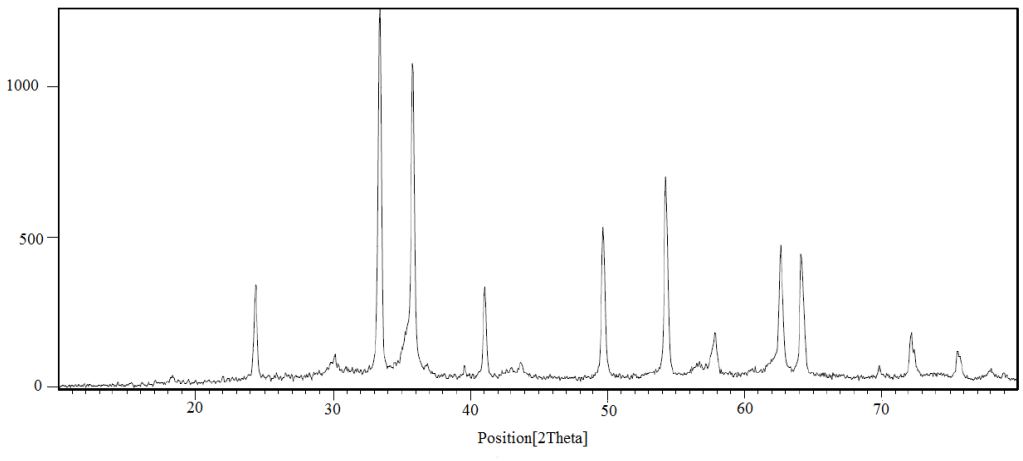


Figure 1. XRD patterns of (a) $NiFe_2O_4$/CS (b) $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS (c) $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS and (d) $MnFe_2O_4$/CS

The SEM images of the spinel type transition metal ferrites $Ni_xMn_{1-x}Fe_2O_4$ are shown in Figure 2. According to SEM images that the grain size of the $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS and $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS is larger than that of pure spinel type transition metal ferrites of $NiFe_2O_4$/CS and $MnFe_2O_4$/CS.

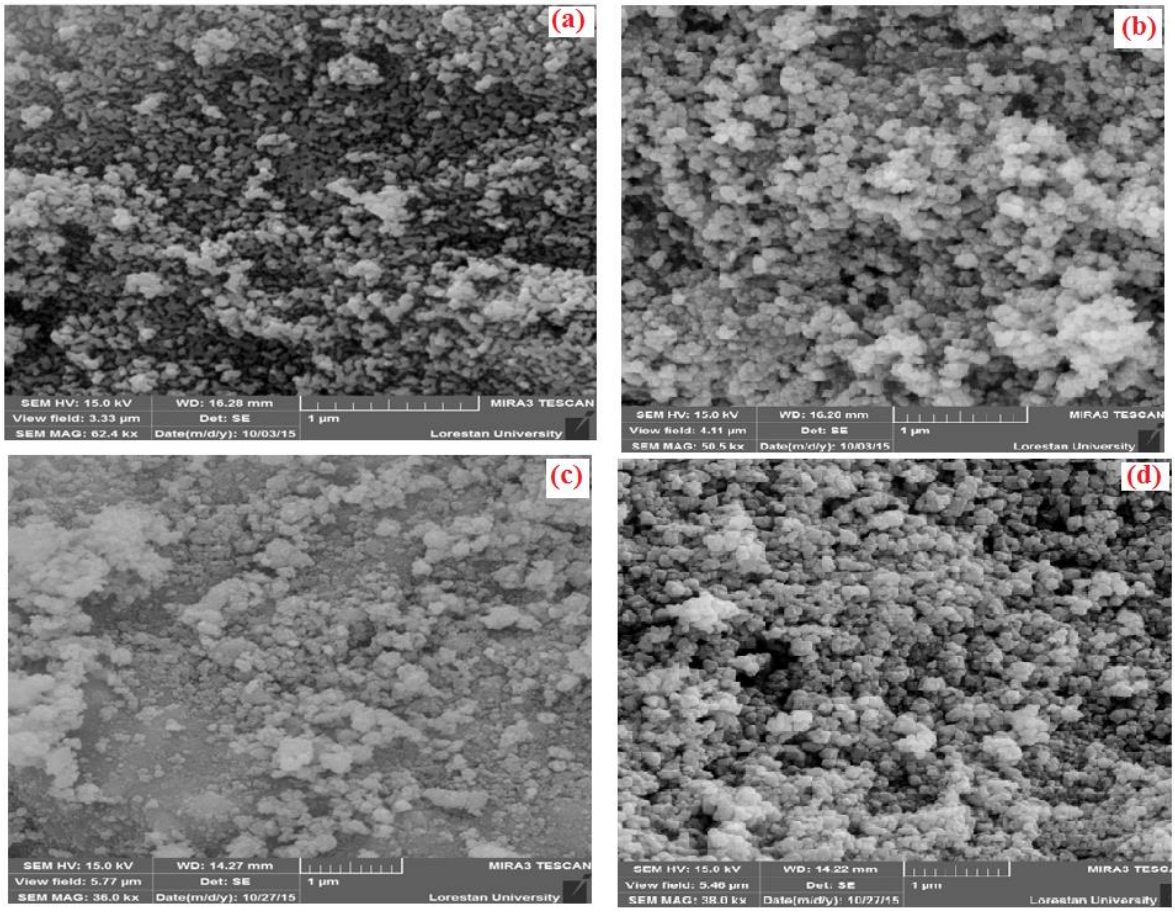


Figure 2. SEM images of (a) $NiFe_2O_4$/CS (b) $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS (c) $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS and (d) $MnFe_2O_4$/CS

The elemental analysis of the $NiFe_2O_4$/CS and $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS as sample was carried out using Energy Dispersive analysis of X-ray (EDX) spectrometer (Figure 3). The C, O, N, Mn, Ni and Fe peaks in Figure 3 (b) in the EDX spectrum showed the presence of carbon, oxygen, nitrogen, manganese, nickel and ferrite. Table 1 summarizes the EDX analysis which indicates the exact composition of the synthesized $NiFe_2O_4$/CS and $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS, therefore confirming the purity of the samples.

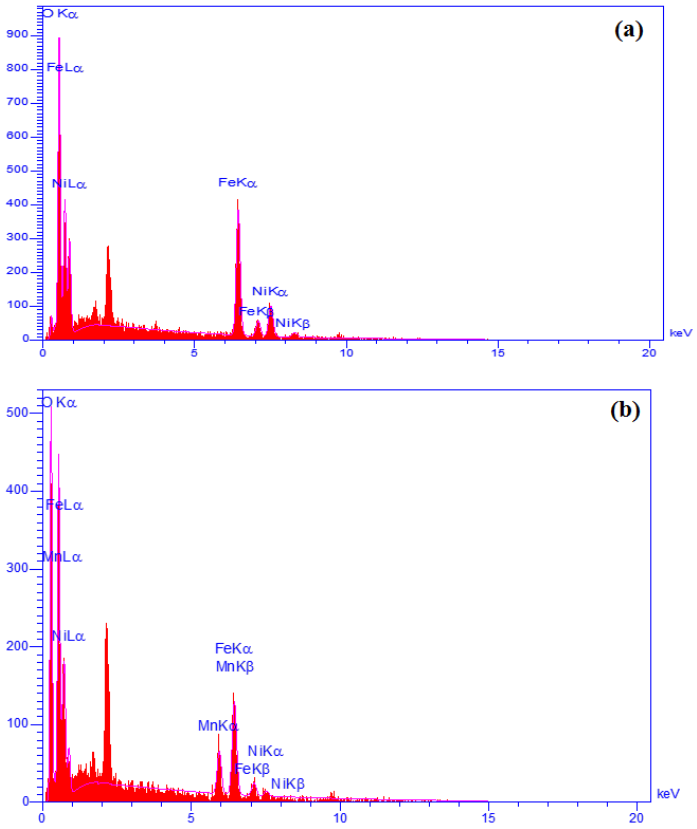


Figure 3. EDX patterns of (a) $NiFe_2O_4$/CS (b) $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS

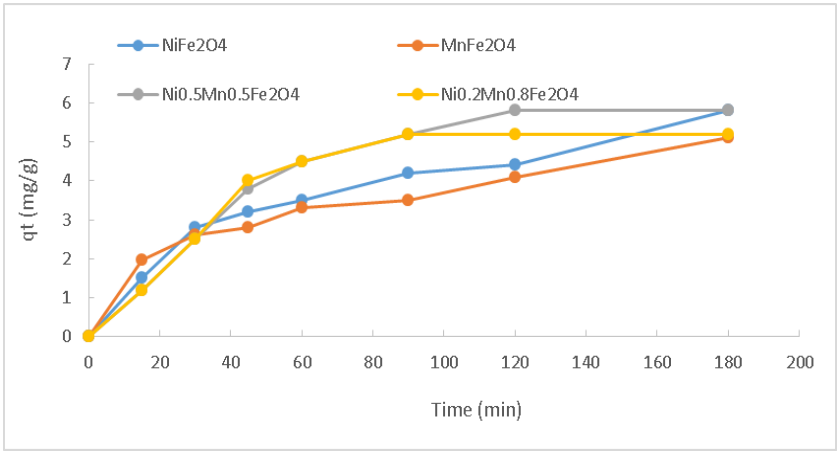
Table1. Composition of the synthesized $NiFe_2O_4$/CS and $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS Obtained from EDX

Sample	Nickel (Wt.%)	Manganese (Wt.%)	Iron (Wt.%)	Oxygen (Wt.%)	Nitrogen (Wt.%)	Carbon (Wt.%)
$NiFe_2O_4$/CS	6.78	-	17.52	58.29	5.78	11.63
$Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS	0.38	1.76	4.5	42.94	8.46	41.93

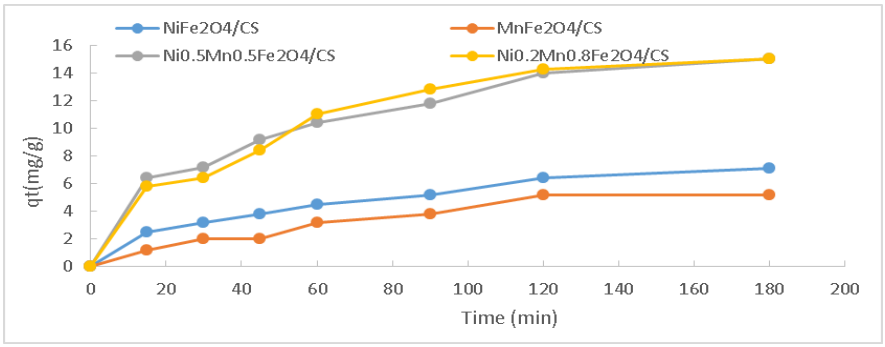
Kinetic Adsorption

The effect of contact time on CR adsorption kinetic of $Ni_xMn_{1-x}Fe_2O_4$ and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite is shown in Figure 4. It was observed that the adsorption capacity of $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS and $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS in comparison to $Ni_{0.5}Mn_{0.5}Fe_2O_4$ and $Ni_{0.2}Mn_{0.8}Fe_2O_4$ increased with increasing contact time and reached equilibrium after 120 min (Figure 4(a) & (b)). The adsorption capacity of $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS and $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS was 14 and 14.3 mg g^{-1}, respectively. The obtained results showed that magnetic $Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS composite exhibit much enhanced adsorption performance. The removal efficiency of CR onto magnetic

$Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS by adsorption for 180 min can reach up to %74. However, the percentage of CR removal by magnetic $Ni_{0.2}Mn_{0.8}Fe_2O_4$ was 28% at 180 min, it indicate that the adsorption capacities of CR onto magnetic $Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS was mainly attributed to chitosan polymer.



(a)



(b)

Figure 4. Effect of contact time on adsorption kinetics of CR on $Ni_xMn_{1-x}Fe_2O_4$ and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite

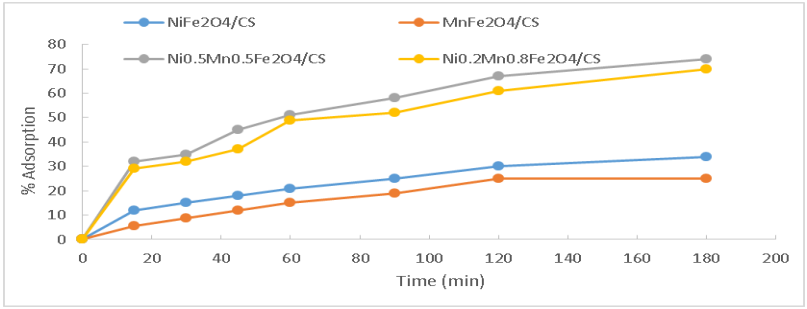
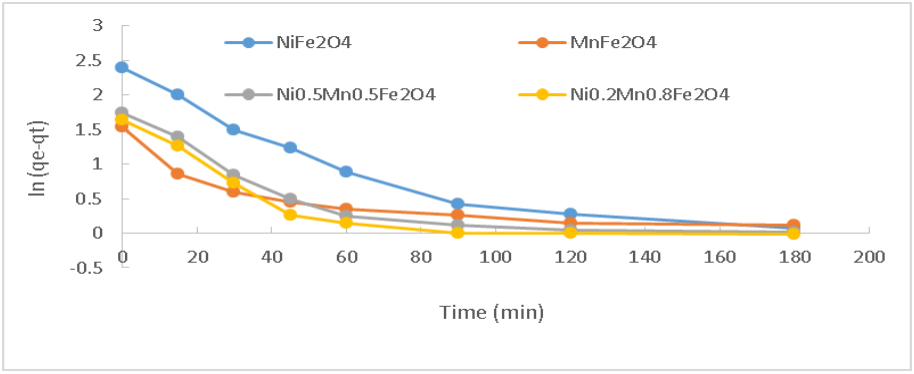


Figure 5. Effect of contact time on percentage adsorption of CR on $Ni_xMn_{1-x}Fe_2O_4$ and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite

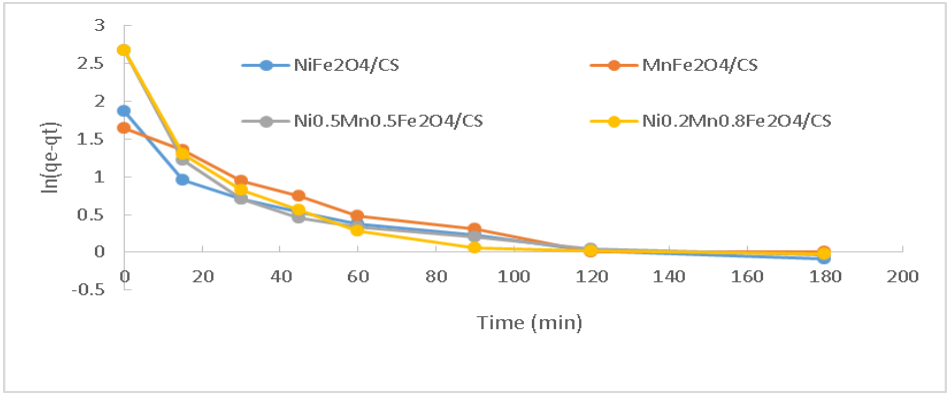
The order of adsorbate–adsorbent interactions has been described by using various kinetic models. In this study, the pseudo-first-order kinetic model and pseudo-second-order model was investigated. The pseudo- first-order model for liquid-solid adsorption is expressed as: [17]

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad \text{Eq. (2)}$$

Where q_t and q_e are the amounts adsorbed (mg/g) at time t (min) and at equilibrium, respectively, and k_1 is the rate constant of pseudo- first-order adsorption process (min^{-1}). The plot of log ($q_e - q_t$) versus t for $Ni_xMn_{1-x}Fe_2O_4$ samples and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composites are showed in Fig. 6 and the calculated parameters of the pseudo-first-order kinetic model are listed in Table 2. The calculated value of R^2 indicates that it is not appropriate to use the pseudo-first-order kinetic model to describe the adsorption kinetics of $Ni_xMn_{1-x}Fe_2O_4$ samples and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composites.



(a)



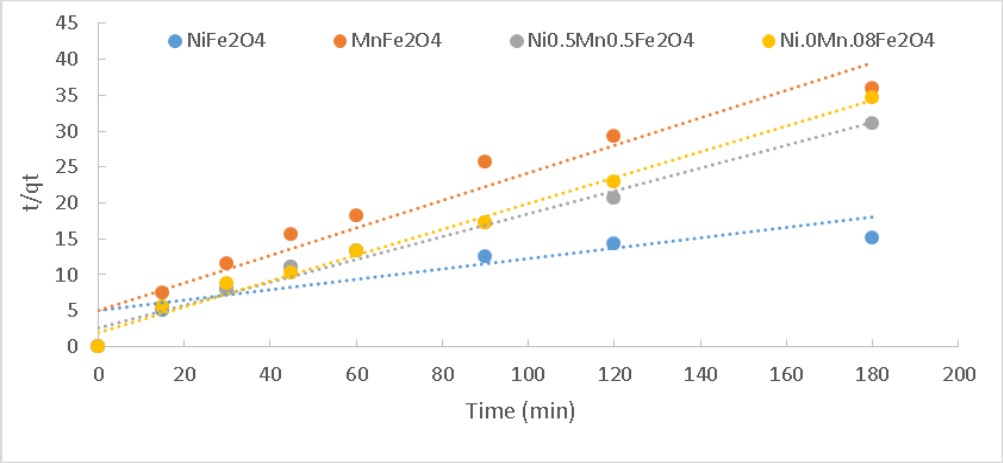
(b)

Figure 6. The pseudo first-order kinetics for CR adsorption on the $Ni_xMn_{1-x}Fe_2O_4$ samples (a) the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite (b) (t=25 °C; adsorbent dose=100 mg; initial concentration = 10mg/L).

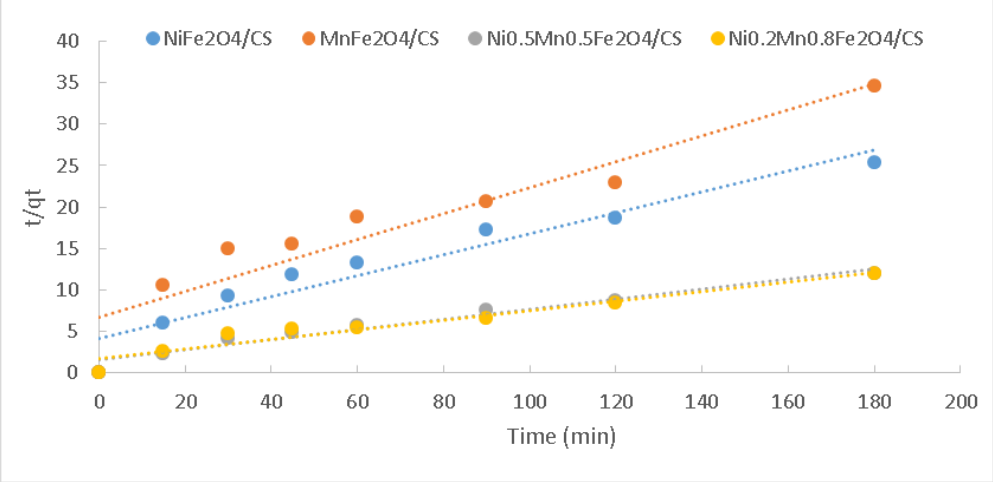
The pseudo- second- order equation can also be expressed as follows [18, 19]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{Eq. (3)}$$

Where k_2 is the second-order rate constant (g mg^{-1} min^{-1}). The plot of t/q_t versus time gives straight lines (Figure 8). The values for q_e and k_2 can be calculated from the slope and intercept.



(a)



(b)

Figure 7. The pseudo second-order kinetics for CR adsorption on the $Ni_xMn_{1-x}Fe_2O_4$ samples (a) the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite (b) (t=25 °C; adsorbent dose=100 mg; initial concentration = 10 mg/L).

As shown from Table 2, the correlation coefficient (R^2) has an extremely high value and closer to unity for $Ni_xMn_{1-x}Fe_2O_4$ and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite and the pseudo second order kinetic model compared to the value of pseudo-first order kinetic model.

Table 2.The calculated parameters of the pseudo first-order and pseudo second-order kinetic model of CR on the $Ni_xMn_{1-x}Fe_2O_4$ samples the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composites

Samples	**Conc. (mg/L)**		**First-order parameter**			**Second-order parameter**	
		K_1 (min^{-1})	**q_e(mg/g)**	**R^2**	**K_2(g/mg min)**	**q_e (mg/g)**	**R^2**
$NiFe_2O_4$	10	0.0129	7.17	0.8554	0.00105	13.75	0.7017
$Ni_{0.2}Mn_{0.8}Fe_2O_4$	10	0.0084	2.918	0.6213	0.01704	5.5	0.9901
$Ni_{0.5}Mn_{0.5}Fe_2O_4$	10	0.0091	3.41	0.6862	0.0213	4.2	0.9818
$MnFe_2O_4$	10	0.0062	2.61	0.6276	0.0074	5.2	0.9405
$NiFe_2O_4$/CS	10	0.0088	3.22	0.7101	0.0038	7.9	0.9277
$Ni_{0.2}Mn_{0.8}Fe_2O_4$/CS	10	0.0117	4.48	0.5864	0.0002	17.17	0.9371
$Ni_{0.5}Mn_{0.5}Fe_2O_4$/CS	10	0.0111	4.26	0.5597	0.0002	16.26	0.9568
$MnFe_2O_4$/CS	10	0.0092	3.68	0.8277	0.00037	6.36	0.8908

These results showed the pseudo-second-order sorption mechanism is predominant for $Ni_xMn_{1-x}Fe_2O_4$ samples and the magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composites and that the overall rate constant of sorption process appears to be controlled by a chemisorption process.

Conclusion

In summary, a novel magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite was prepared in the dispersed $Ni_xMn_{1-x}Fe_2O_4$ suspension and chitosan polymer. This study showed that magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS composite is a promising adsorbent for the removal of CR from aqueous solution

in comparison to the $Ni_xMn_{1-x}Fe_2O_4$, because of the rapid uptake of CR and a high percentage adsorption. The adsorption process of the CR on magnetic $Ni_xMn_{1-x}Fe_2O_4$/CS was found to fit the pseudo second-order model. The $Ni_xMn_{1-x}Fe_2O_4$/CS composite could be easily separated by external magnetic therefore could be used as effective adsorbent for the removal of anionic dye from wastewater.

Acknowledgement

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