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Iranian Chemical Communication

Original Research Article

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MgCaFe- layered double hydroxide (LDH) for congo red dye removal in aqueous solution

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Received: 7 April 2016, Accepted: 15 October 2016, Published: 1 January 2018

Abstract

In this work, the ability of the MgCaFe- Layered double hydroxide (LDH) for congo red (CR) dyeremoval in aqueous solution was investigated. Various parameters such as initial dye concentrations, temperature, adsorbent dosage, pH effect and agitation rate were examined and optimal conditions(10 mgL^{-1} of the dye concentration, 25 °C of temperature, 0.5 gL^{-1} of the adsorbent dosage, pH~7 and 450 rpm of agitation rate) were obtained. Moreover, the reusability of the adsorbent was investigated and promising result was obtained. Furthermore, the result showed the adsorption data on optimal condition was found to follow the pseudo- second order kinetic model with a high degree of correlation coefficient. In sum, this research illustrated that the MgCaFe-LDH can be used as efficient adsorbent for removing anionic dye in waste water.

Keywords: Congo red; removal; MgCaFe-LDH.

Introduction

The dye removal from aqueous solution *via* adsorption has attracted much attention due to its efficiency, simplicity of design and reusability [1-5]. Layered double hydroxides (LDHs) have relatively simple synthesis. LDHs can be represented by the general formula$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n}\ )_{x/n}.yH_2O]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent cations respectively. A^{n-} is an anion and x is (M^{3+}/M_{total}) ranges from 0.17 to 0.33 [6]. Until now various LDHs have been used for catalyst, photocatalyst, adsorbent and drug delivery applications [7-9]. Many studies have focused on the application of LDHs as adsorbent materials [10-13]. In this study the adsorption capacity of MgCaFe-LDH for CR dye removal in aqueous solution was investigated. The effect of some parameters such as initial dye concentrations, temperature, adsorbent dosage, pH effect and agitation rate was investigated.

Experimental procedure

Materials

Congo red dye (C.I. Direct Red 28), $MgCl_2$, $FeCl_3$. 10 H_2O, $CaCl_2$. $2H_2O$, HCl and NaOH were purchased from Merck Company.

MgCaFe-LDH preparation

The procedure used for synthesis of the MgCaFe-LDH followed a coprecipitation method reported previously [14]. In this synthesis 0.025 mol of ($CaCl_2$. $2H_2O$), 0.025 mol of ($MgCl_2$) and 0.02 mol of ($FeCl_3$. 10

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H_2O) were dissolved in 50 mL of deionized water. Then the above solution was slowly added into the 100 mL of alkaline solution which containing 0.12 mol of NaOH under vigorous magnetic stirring. The suspension was aged under magnetic stirring for 18 h at 25 °C. The product was washed with deionized water several times and dried at 50 °C [14].

Instrumentation

The product was characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM, EDX, Vega 2 Tscan). The progress of adsorption experiments was measured by UV-Vis spectrophotometer (Shimadzu UV-2550).

Adsorption experiments

To evaluate the adsorption properties of MgCaFe-LDH, a series of adsorption experiments was performed. Typically, 0.1 g of the MgCaFe-LDH sample was suspended in a 200 mL of CR dye solution with 10 mgL^{-1}concentration. The mixture was continuously stirred for 90 min. The suspension was sampled at regular intervals and immediately remove adsorbent particles. Then, the degree of adsorption (X), as a function of time, is given by $X = (C_\circ - C)/C_\circ$ where $C_\circ$ is the initial dye concentration, and C the dye concentration at time t. The disappearance of peak at λ = 498 nm was chosen for monitoring of CR dye adsorption. The amount of CR adsorbed on the surface of the catalyst at the time t was calculated *via* the following equation [15]:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where, q_t (adsorption capacity, mgg^{-1}) is the adsorbed dye amount on the surface of the catalyst, C_0 and C_t (mgL^1) are the initials and at any time t can be considered as dye concentration, V is the solution volume (L), and m is the adsorbent mass (g).

Results and discussion

Characterization

As shown Figure 1 the XRD pattern for the MgCaFe-LDH sample is in good agreement with that previously reported [14].Figure 2a shows the morphology of the MgCaFe-LDH sample. As shown Figure2a the MgCaFe-LDH is plate shape at a range of (30-100) nm in size. The EDX analysis in Figure 2b reveals that the MgCaFe-LDH is composed of the (Mg, Ca, Fe and Cl) elements.

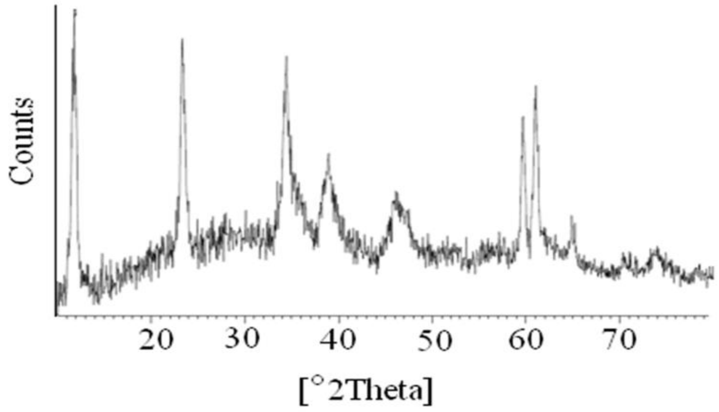

Figure 1. The XRD pattern of the MgCaFe-LDH sample

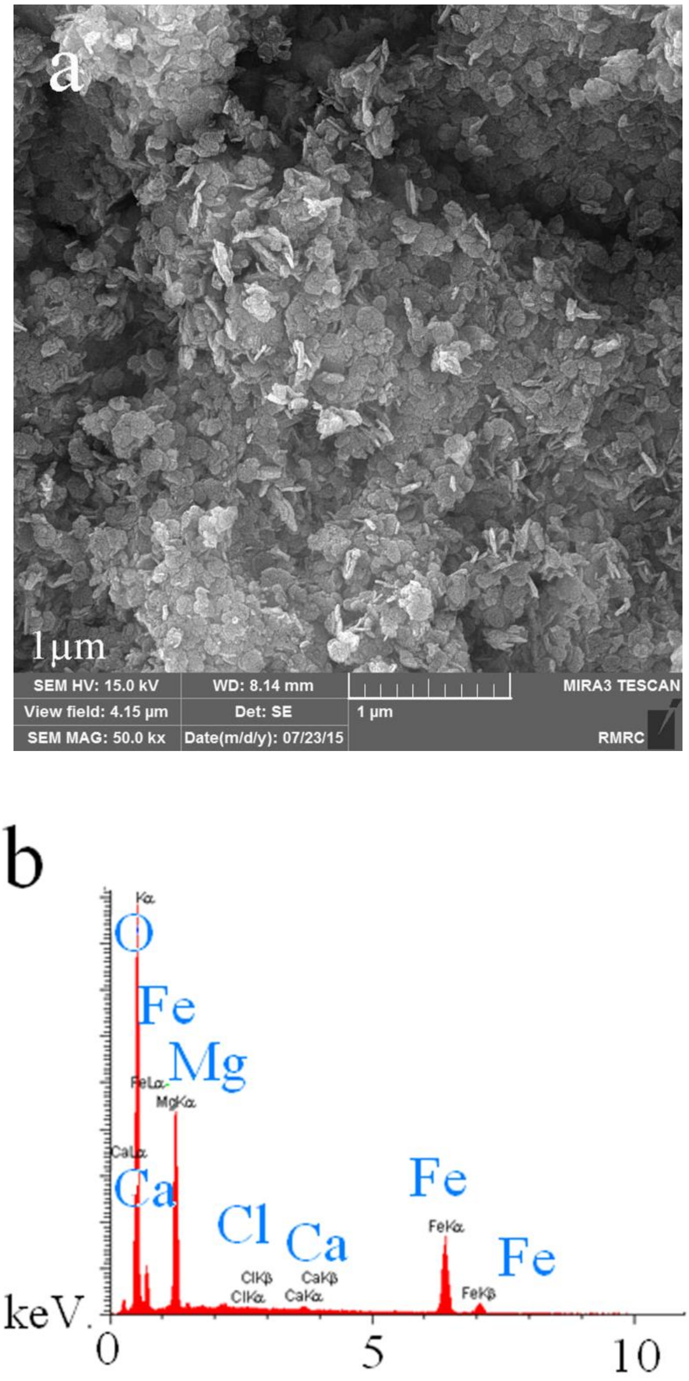

Figure 2. The SEM image (a) and EDX analysis (b) of the MgCaFe-LDH sample

The adsorption behavior of CR on MgCaFe-LDH

Effect of dye concentration

The adsorption experiments of CR dye solution with10, 35 and 50 mgL^{1} concentrations on the MgCaFe-LDH was measured. Figure 3 shows the UV-Vis spectra changes of the CR dye solution during the adsorption experiments.

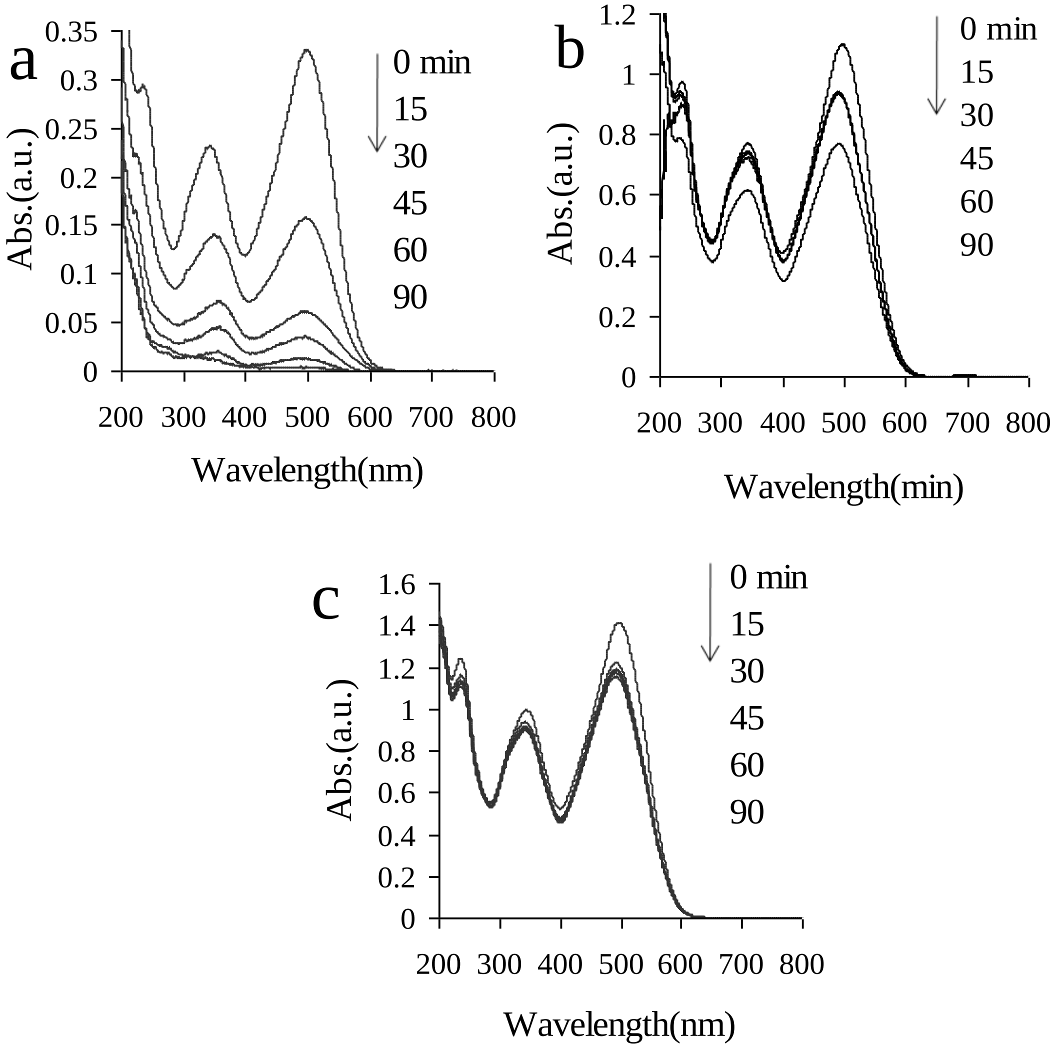

Figure 3. UV-Vis spectra changes of CR dye solutions (a) 10 mgL^{-1} (b) 35 mgL^{-1} and (c) 50 mgL^{-1} during adsorption experiments on MgCaFe-LDH sample

From Figure 3, it is clear that the CR dye removal is dependent on the dye concentration. At low concentrations, adsorption sites took up the available dye more quickly. However, at higher concentrations, dye needed to diffuse to the sorbent surface by intraparticle diffusion. Also, the steric repulsion between the solute molecules could slow down the adsorption process [16]. The experimental results indicate that the CR dye removal percentage was decreased with increased initial dye concentration from 99% for 10 mgL^{-1} to 19% for 50 mgL^{-1}after 90 min (Figure 4A).

The maximum adsorption capacity of the MgCaFe-LDH for CR dye removal with 10, 35 and 50 mgL^{-1} concentration is obtained about 22, 22 and 18 mgg^{-1} after 90 min, respectively (Figure 4B).

Effect of adsorbent dosage

The effect of varying adsorbent dosage from0.25to 1.75 gL^{-1}on the CR dye removal is illustrated in Figure 5. As shown in Figure 5, 0.5 gL^{-1} of the adsorbent is selected to be optimal dosage.

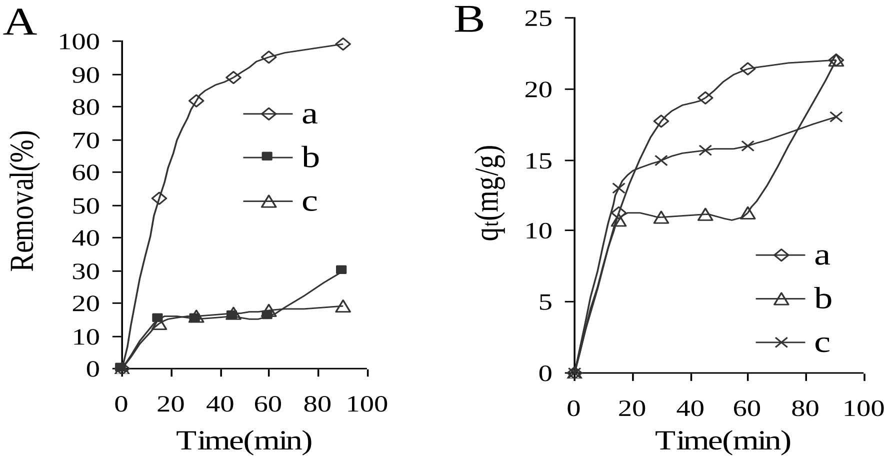

Figure 4. (A) The plots of CR dye removal percentage,(B) Adsorption capacity of the MgCaFe-LDH sample *vs*. time at different dye concentrations: (a) 10 mgL^{-1} (b) 35 mgL^{-1} and (c) 50 mgL^{-}

However, it should be noted that at higher dosages of adsorbent, the aggregation of particles may reduce the adsorbent efficiency [17].

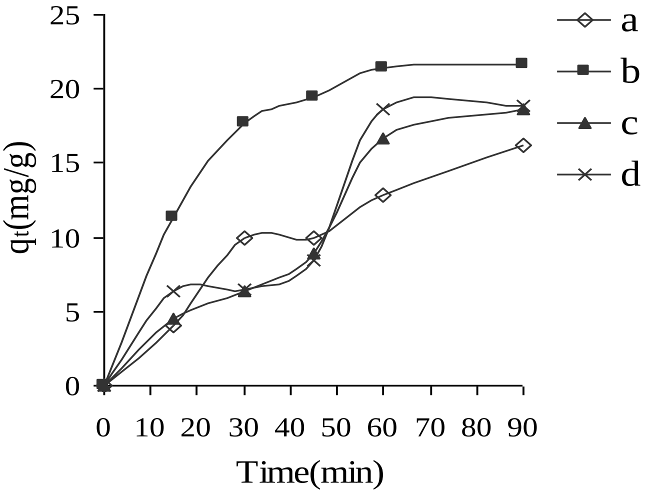

Figure 5. Adsorption capacity of the MgCaFe-LDH sample for CR dye removal, with varying adsorption dosage (a) 0.25, (b) 0.5, (c) 1 and d) 1.75 gL^{-1}

Effect of temperature

The adsorption capacity of the MgCaFe-LDH for CR dye removal at 25, 45 and 55 °C is obtained 22, 18, 17.8 mgg^{-1} respectively (Figure6). The results show adsorption capacity can be decreased with increase of temperature, hence, physical adsorption was occurring. Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding. There is no electron exchange between adsorbent and adsorbate [18].

Effect of agitation rate

The agitation rate effect on the adsorption capacity of the MgCaFe-LDH was also studied. The study was conducted varying the speed from 120 to 450 rpm using a magnetic stirrer. Figure 7 shows that the adsorption capacity increases by increasing of agitation rate from 120 to 450rpm. An increase in the adsorption with increasing of the agitation rate can be attributed to the increasing number of collisions between sorbent site and dye molecule. The adsorption capacity does not show a significant variation at rates above 450 rpm. Thus, 450 rpm is considered as the optimum agitation speed for the CR dye removal.

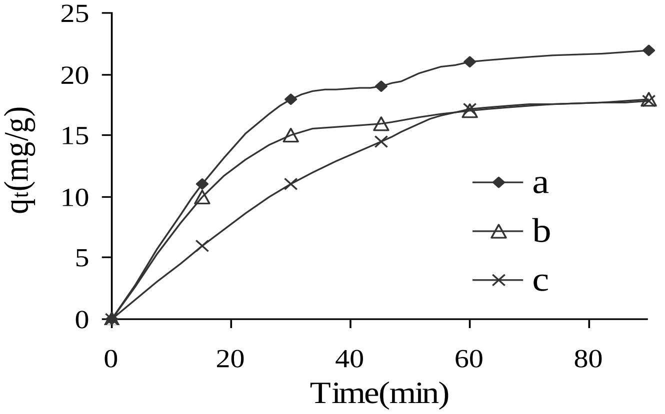

Figure 6. Adsorption capacity of the MgCaFe-LDH sample for CR dye removal (10 mgL^{-1}) at (a) 25, (b) 45 and (c) 55 °C

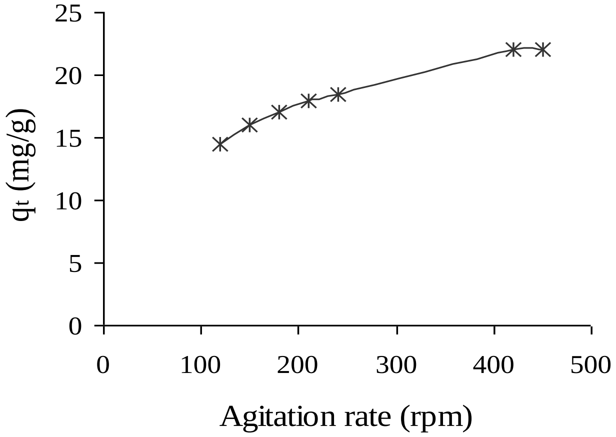

Figure 7. Adsorption capacity of the MgCaFe-LDH sample for CR dye removal at different agitation rates (120, 150, 180, 210, 240 and 450 rpm)

Effect of pH

The effect of pH on CR dye removal was carried out by performing the adsorption experiments in the pH range between 5 and 11. The pH of the solution was adjusted by adding a few drops of NaOH or HCl to reach the desired value, before adsorption experiment. Figure 8 shows the behavior of the MgCaFe-LDH at various pH. The CR dye removal percentage decreased with an increase in the pH from 8 to 11. The maximum CR dye removal is obtained at pH~7.Generally, the effect of pH on dye adsorption can be explained in terms of the point of zero charge (PZC). The PZC can be used as a qualitative for the adsorbent surface charge balance. For pH values blow the PZC, the hydrated surface of the LDH is protonated and is positively charged. The surface of LDH is deprotonated at pH values above the PZC and is negatively charged. For pH values blow the PZC, there may be two possible the mechanism for dye adsorption onto LDH, one of there is an anionic exchange of anions in the interlayer by dye anions. The other is adsorption by means of association between the positively charged surface of LDH and the dye anions. For pH values above the PZC, occurs deprotonation of surface hydroxyls groups and the positive charge on the surface of LDH decrease and dye removal also decreases [19,20].

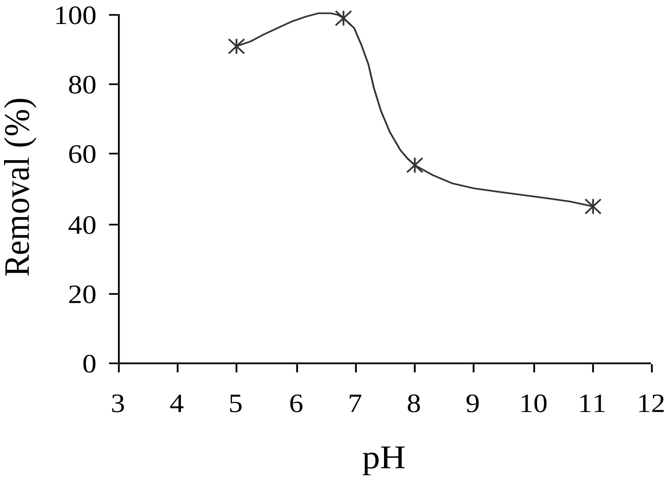

Figure 8. CR dye removal percentage in the pH from 5 to 11

Kinetic models

The kinetic of adsorption can be described using several models. In the present study, the lagergren pseudo- first- and pseudo- second order model was tested. Lagergren's pseudo- first order model for liquid-solid adsorption is generally expressed as: [21]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

here k_1 is rate constant for pseudo- first order adsorption. After definite integration by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, Eq. (2) becomes:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad (3)$$

The above linear equation can usually be used be estimated equilibrium adsorption capacity (q_e) from intercept and k_1 from the slope.

A pseudo- second order equation can be expressed as follows [22,23]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

Where k_2 is rate constant for pseudo- second order adsorption. After definite integration by applying the initial conditions, we have a linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

The plot of t/q_t versus time gives straight lines. The values for qe and k_2 can be calculated from the slope and intercept.

The pseudo- second order equation is often successfully used to describe the kinetics of pollutants on the adsorbent [24,25]. This model assumes that chemisorption might be the rate limiting step in adsorption processes [23]. Figure 9 represents pseudo- first-and pseudo- second order kinetic models for adsorption data on optimal condition (25 °C, 0.5 gL^{-1} of the adsorbent dosage, 10 mgL^{-1} of the dye concentration). The kinetic parameters obtained from the models for CR dye removal is given in Table 1. The correlation coefficient (R^2) for the pseudo- first order model did not fit very well for the MgCaFe-LDH and calculated q_e value was quite different with the experimental data, which implies that the adsorption did not follow the model. For pseudo- second order kinetic, the R^2 is closer to unity. The calculated q_e value also agrees with the experimental data. These results show that the pseudo-second order model is predominant. This model assumes that chemisorption might be the rate limiting step in adsorption processes.

Table 1. Kinetic adsorption parameters obtained using pseudo-first and pseudo- second order models

Sample	q_e^{exp}	Pseudo-first-order			Pseudo-second-order		
		k_1(min^{-1})	q_{e1}(mg/g)	R^2	k_2(g/mg min)	q_{e2}(mg/g)	R^2
MgCaFe-LDH	22	0.0063	1.62	0.5561	0.0024	26	0.99

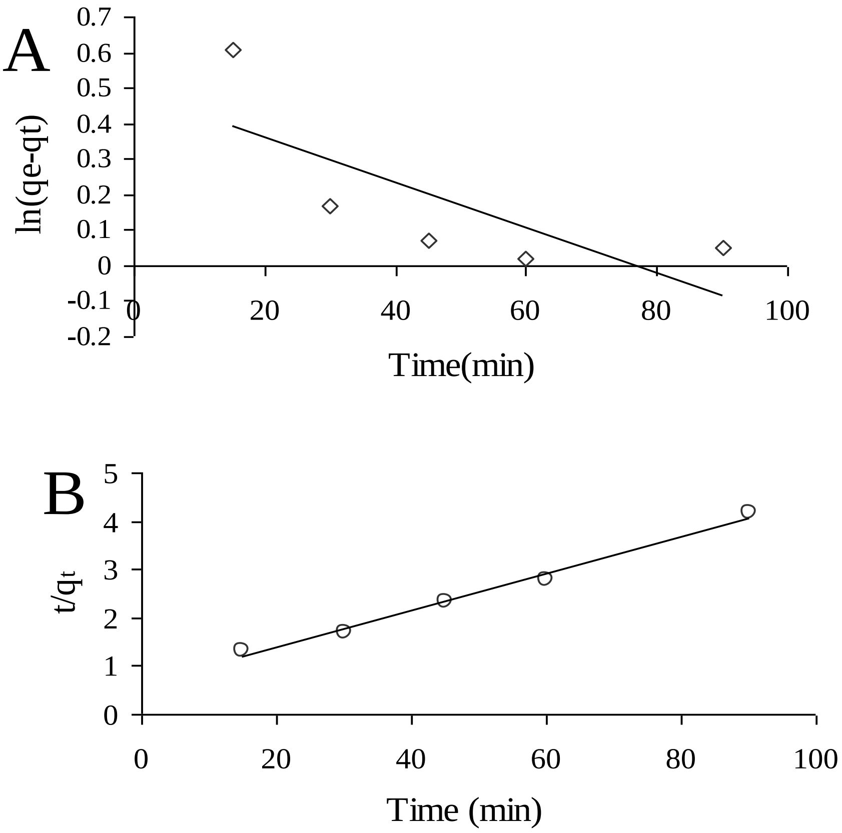

Figure 9. (A) ln(q_e–q_t) (B) t/q_t *v.s* time for the CR dye removal

Reusability

The reusability of the adsorbent was investigated through 4 cycles of experiments. The reusability of the adsorbent after four consecutive uses was obtained to be 97, 93, 90, 88% (Figure10). These results show that the MgCaFe-LDH can be used as efficient adsorbent for removing anionic dye in waste water due to its high anionic exchange capacities and high layer charge densities.

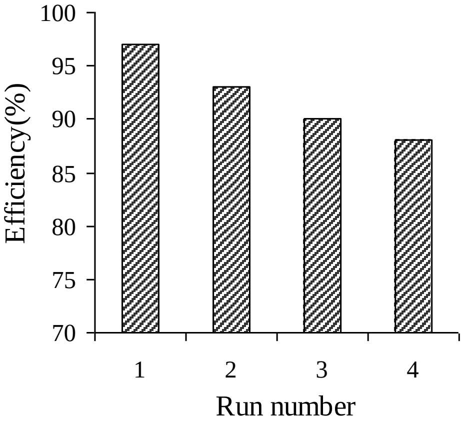

Figure 10. The reusability of the MgCaFe-LDH sample after four consecutive uses

Conclusion

From the present study it can be seen that MgCaFe-LDH can be used effectively for removal of the anionic CR dye from wastewater. The MgCaFe-LDH catalyst (0.5 gL^{-1}) was selected to be optimal dosage to remove of the CR dye solution with $10mgL^{-1}$ concentration. The effective pH range for dye removal was between 5 and 7. The result shows the adsorption data on optimal condition was found to follow the pseudo- second order kinetic model.

Acknowledgments

We are grateful to Payame Noor University for its financial support.

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How to cite this manuscript: Zeynab Soltani, Hossein Salavati, Maryam Movahedi, Zahra Sadeghi. "MgCaFe- layered double hydroxide (LDH) for congo red dye removal in aqueous solution".
Iranian Chemical Communication, 2018, 1, 39-48.