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## Original Research Article

# Enhanced adsorption of anionic diazo dye by magnetic layered double hydroxide ( $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-CrLDH$ ) from aqueous solution

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### ARTICLE INFORMATION

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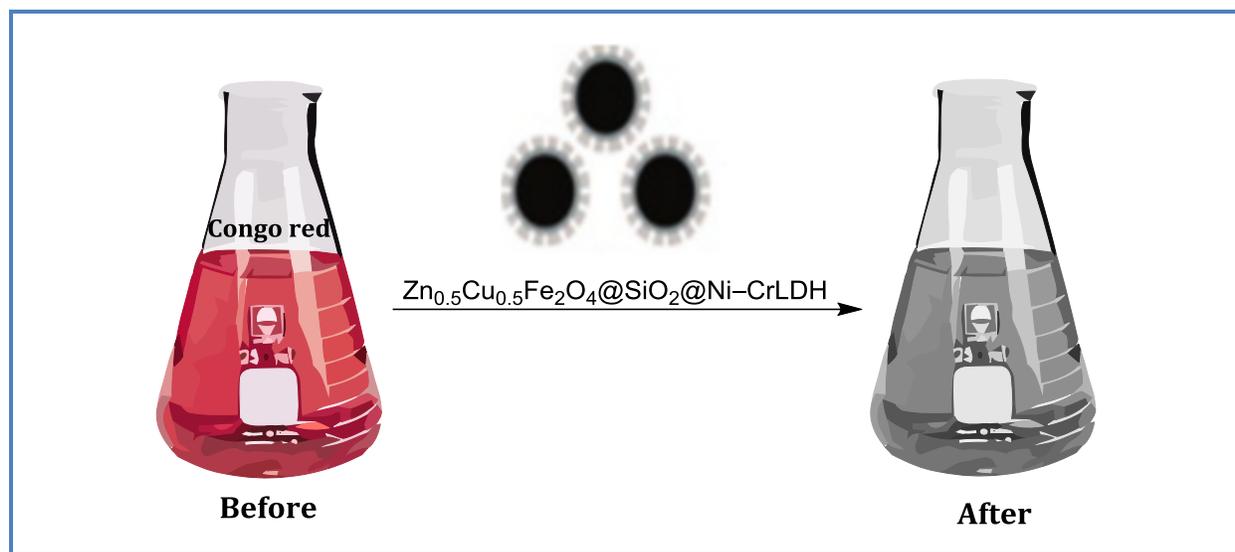
### KEYWORDS

Layered double hydroxide  
Magnetic separation  
Adsorption kinetics  
Anionic diazo dye

### ABSTRACT

A novel magnetic layered double hydroxide known as  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-Cr$  layered double hydroxide was synthesized with  $Zn_{0.5}Cu_{0.5}Fe_2O_4$ ,  $SiO_2$  and  $Ni-CrLDH$  by using coprecipitation method. In order to compare the adsorption efficiency, the  $Ni-CrLDH$  sample also was synthesized. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and fourier transform infrared spectroscopy (FT-IR). The adsorption of Congo red (CR) by magnetic layered double hydroxide depended upon the contact time, initial dye concentration and pH. The adsorption of the Congo red (CR) reached equilibrium at 180 min and followed the pseudo-second-order kinetic equation. The adsorption capacity of the magnetic layered double hydroxide changed significantly between pH 4–10 and the maximum dye removal were 88% for CR. Moreover, the magnetic layered double hydroxide can be quickly separated from the aqueous solution by an external magnet before and after adsorption process. This indicated that the  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-CrLDH$  composite was an effective adsorbent for CR dye removal with quick separation. The adsorption performance of the synthesized  $Zn_{0.5}Cu_{0.5}Fe_2O_4$ ,  $SiO_2$  and  $Ni-CrLDH$  and comparing with  $Ni-CrLDH$  show that the  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-CrLDH$  can be more efficient than  $Ni-CrLDH$  for removal of CR dye.

## Graphical Abstract



## Introduction

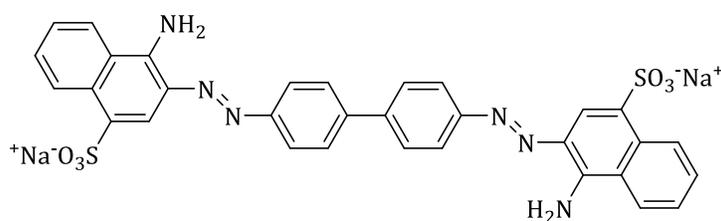
Environmental pollution is known as one of the major problems in the world. Wastewater effluents from industries containing synthetic azo dyes cause a potential pollution to the environment. The presence of toxic compounds in the industrial wastewater results in major environmental problems. Also, azo dyes undergo reductive splitting of the azo bond and converted into aromatic amines [1, 2]. Congo red as an anionic diazo dye is considered as a mutagen and reproductive effector. It also has a considerable effect on the blood factors such as clotting, resulting in somnolence and respiratory problems [3]. Therefore, an increased interest has been focused on removing the dyes from the wastewater. In this regard, many researchers have studied various techniques in order to remove the azo dyes from the wastewaters [4, 5].

The adsorption processes due to its low cost, simple process, ease of operation, and insensitive to toxic substances, is considered as an effective separation technique for water treatment. Recent studies showed that Layered double hydroxides (LDHs,  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(An^-)_{x/n} \cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are metal cations that occupy octahedral sites in the hydroxide layers,  $An^-$  is an exchangeable anion, and  $x$  is the ratio  $M^{3+}/(M^{2+} + M^{3+})$  and the layer charge will depend on the  $M^{2+}/M^{3+}$  ratio) as a class of anionic clay have been considered as excellent adsorbent materials for wastewater treatment because of their layered structure, high surface area, non-toxicity and interlayer ion exchange [6, 7] and wide applications in different fields such as catalysts, biological agents, energy storage and conversion [8, 9]. A great number of studies have been conducted on the

application of layered double hydroxides as adsorbent using different interlayer anions [10, 11] and as a host for intercalation chemistry [12].

Despite the high adsorption capacity of the dyes by LDH, there is a great difficulty in separating and reclaiming the adsorbents at the end of the reaction in liquid systems. Magnetic auxiliary adsorption separation technology has been considered as an effective method to separate the powdery adsorbents from solution [13–15]. Magnetic adsorbents can be used to adsorb contaminants from the aqueous solutions and easily separate them by using a simple magnetic separation process after adsorption [15]. Several magnetic adsorbent materials have been reported in literature [16, 17]. For this purpose, magnetic  $Zn_{0.5}Cu_{0.5}Fe_2O_4$  was synthesized and used due to its unique magnetic properties, stability, and large surface area [18]. Recently, the combination of  $Fe_3O_4$  nanoparticle and LDH has developed to enhance the separation and re-dispersion performance of the LDH in aqueous solution [19].

To the best of our knowledge the magnetically modified layered double hydroxide ( $Zn_{0.5}Cu_{0.5}Fe_2O_4 @SiO_2@Ni-CrLDH$ ) have not been reported in literature for the adsorption of anionic dyes such as congo red. Therefore, the purpose of this study was to synthesis the Ni-CrLDH with magnetic properties, and evaluate the adsorption performance of the synthesized  $Zn_{0.5}Cu_{0.5}Fe_2O_4 @SiO_2@Ni-CrLDH$  composite and compare it with the Ni-CrLDH sample. Our experimental results showed that the  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-CrLDH$  composite was successfully synthesized and it was suggested to be more efficient as adsorbent in comparison with the Ni-CrLDH.



## Scheme 1.

### Experimental

#### Materials and methods

Congo red (C.I. Direct Red 28),  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Cr(NO_3)_3 \cdot 9H_2O$ , cetyltrimethylammonium bromide,  $Na_2CO_3$  and  $NaOH$  were purchased from Merck company. The structure of the synthesized samples was characterized by using X-ray diffraction analysis (Holland Philips Xpert, with  $Cu-K\alpha$  radiation). The morphology of synthesized samples was investigated by scanning electron microscope (SEM-VEGA3-TESCAN). The FT-IR spectra were

recorded by a Fourier transform infrared spectroscopy (JASCO FT/IR-4200, Japan). The progress of adsorption experiments were measured by UV-Vis spectrophotometer (Shimadzu UV-2550).

#### *Synthesis of $Zn_{0.5}Cu_{0.5}Fe_2O_4/SiO_2/Ni-CrLDH$*

In a typical procedure, 0.2 g of cetyltrimethylammonium bromide was dissolved in 50 mL distilled water at 80 °C (Solution 1). 10 mmol of  $Fe(NO_3)_3 \cdot 9H_2O$ , 5 mmol of  $Zn(NO_3)_2 \cdot 6H_2O$  and 5 mmol of  $Cu(NO_3)_2 \cdot 3H_2O$  was dissolved in 50 mL distilled water (Solution 2). Then, the solution 2 was added into the solution 1 under constant stirring. After that, 15 mL of the NaOH 4M solution was added drop wise into the above solution. After stirring the mixture for 2 h at room temperature, then the precipitate was poured into beaker to neutralize its pH. Finally, heat treatment of the product was carried out at 900 °C for 1 h. In order to improve stability of the magnetic core and generate regular LDH shell, the sample of  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2$  were synthesized by sol-gel method. In this procedure, zinc-copper ferrite  $Zn_{0.5}Cu_{0.5}Fe_2O_4$  (0.85 g) was dispersed in a round-bottom flask in ethanol (200 mL), water (50 mL) and concentrated ammonia solution (3.60 mL, 28 wt.%) and the suspension was ultrasonicated for 30 min. Then, 2.5 mL of tetraethylorthosilicate (TEOS) was added dropwise followed by continuous mechanical stirring for 8 h. The resultant  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2$  product were collected from the reaction mixture by external magnetic field, washed with ethanol several times, and dried at 50 °C under the vacuum. In the final stage, 0.1 g of  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2$  were dispersed in 50 mL deionized water, with the pH adjusted to 10 (the pH buffered solution for adjusting was obtained by dissolving 1.28 g  $Na_2CO_3$  and 1.6 g NaOH in 100 mL of a 1:1 (v:v) methanol-water solution). Then 20 mL aqueous solution containing 1.44 mmol  $Ni(NO_3)_2 \cdot 6H_2O$  and 0.48 mmol  $Cr(NO_3)_3 \cdot 9H_2O$  was added drop-wise to the suspension of  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2$  under vigorous stirring and the solution pH maintained at pH 10 and was ultrasonicated for 1 h, then the products were collected and redispersed in 70 mL of deionized water for 1 h. The synthesized  $Zn_{0.5}Cu_{0.5}Fe_2O_4@SiO_2@Ni-Cr$  LDH was collected from the reaction mixture by external magnetic field, and dried at 50 °C under vacuum.

#### *Synthesis of Ni-CrLDH*

The Ni-CrLDH sample was prepared as described in the literature [20]. A mixture of  $Ni(NO_3)_2 \cdot 6H_2O$  (0.034 mol) and  $Cr(NO_3)_3 \cdot 9H_2O$  (0.05 mol) with Cr to Ni molar ratio (1:1) was dissolved into the deionized water to form a clear solution. Subsequently, aqueous sodium hydroxide (0.4 mol) was added to the above solution under constant stirring until reaching pH=8 to complete

precipitation. Then, the synthesized Ni–Cr LDH was stirred for 24 h at 60 °C. After filtration and washing with distilled water several times, the solid was dried in an oven at 80 °C overnight.

### Adsorption experiments

In order to investigate the adsorption behavior of the Ni–Cr LDH and  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH, dark adsorption experiments were carried out. 100 mg adsorbent was added into 200 mL CR solution with fixed concentration ( $32 \text{ mgL}^{-1}$ ). 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 ( $\text{mg g}^{-1}$ ) at time  $t$  (min) was calculated using the following equation [21]:

$$qt = \frac{(C_0 - C_t)V}{m} \quad \text{Eq. (1)}$$

Where  $qt$  ( $\text{mg g}^{-1}$ ) 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 ( $\text{mgL}^{-1}$ ),  $C_t$  is the concentration of congo red solution ( $\text{mgL}^{-1}$ ) at time  $t$  (min),  $V$  is the volume of the solution (L) and  $m$  is the mass of the adsorbent (g).

## Results and discussion

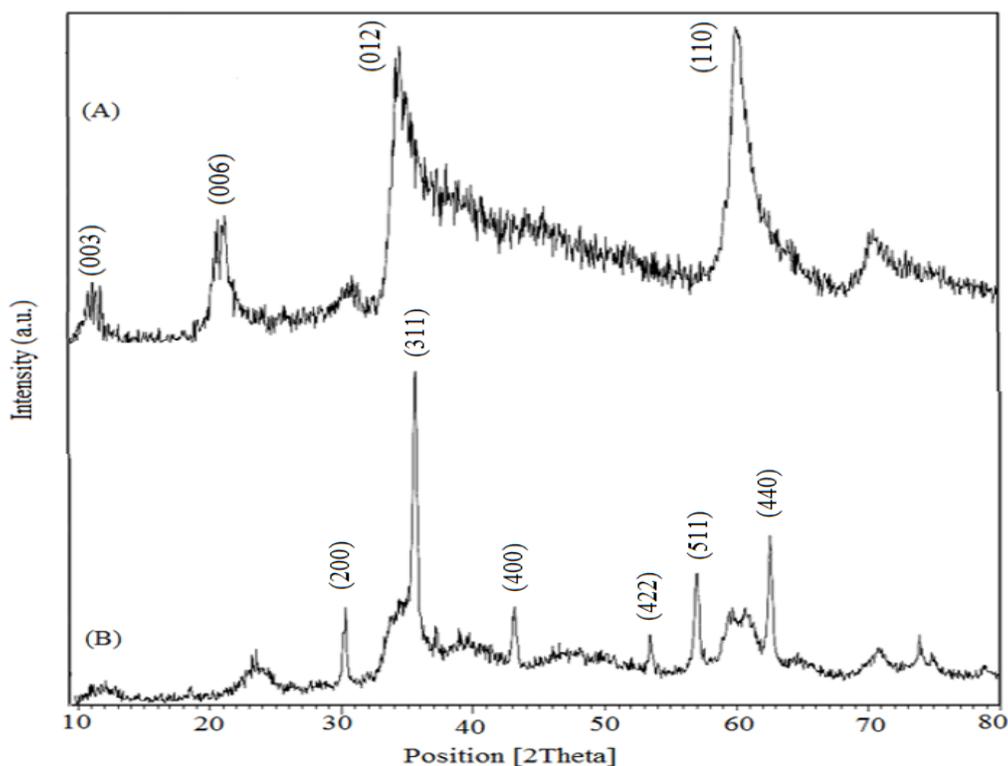
### Characterization

Figure 1 illustrates the XRD pattern of the Ni–Cr LDH and  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH samples. The both of the XRD patterns exhibit lamellar structure of LDH materials, consisting of three intense lines at low angles corresponding to planes (003), (006), (012) and (110) [22]. The diffraction signals located at  $2\theta=30.1^\circ$ ,  $35.4^\circ$ ,  $43.1^\circ$ ,  $53.5^\circ$ ,  $57.0^\circ$  and  $62.6^\circ$  assigned to scattering from (220), (311), (400), (422), (511) and (440) planes of the mixed metal oxide  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$  are consistent with the reported data (JCPDS card No.77–0012), [23]. There is only one broad peak centered at  $2\theta=23.2^\circ$ , suggesting that amorphous  $\text{SiO}_2$  was formed in the  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH sample.

The SEM images of Ni–CrLDH and  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH samples shown in Figure 2. As can be seen in Figure 2, the Ni–CrLDH sample has a defined belt structure. While the SEM image of the synthesized  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH showed a smooth surface with some agglomeration (Figure 2b).

The FT-IR spectra of the  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ ,  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2$  and  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-Cr}$  LDH samples are shown in Figure 3. The broad bands around  $3455 \text{ cm}^{-1}$

<sup>1</sup> of the spectra for all samples are attributed to the O–H stretching mode of the layer surface and interlayer water molecules. Also, the band at  $1636\text{ cm}^{-1}$  is attributed to the H–O–H deformation mode [24]. An intense absorption at  $1381\text{ cm}^{-1}$  of the spectra of  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-CrLDH}$  are ascribed to the asymmetric stretching of nitrate anion in the interlayer of Ni–CrLDH [25]. The very strong and broad IR band at  $1111\text{ cm}^{-1}$  with a shoulder at  $1188\text{ cm}^{-1}$  is usually assigned to the Si–O–Si asymmetric stretching vibrations that is decreased in the FT-IR of  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-CrLDH}$  due to the successful coating of the  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2$  sample with LDH layer. The bands at  $1465$ ,  $1371$ , and  $1129\text{ cm}^{-1}$  can be assigned to either the appearance of new M–O (M = Cu, Zn, Fe) bonds and/or to the combinations of OH librations and lattice modes of ternary mixed metal oxides [26]. The bands at low frequency region (below  $1000\text{ cm}^{-1}$ ) are related to Fe–O, Ni–O and metal-oxygen-metal vibrational modes in LDH [27].

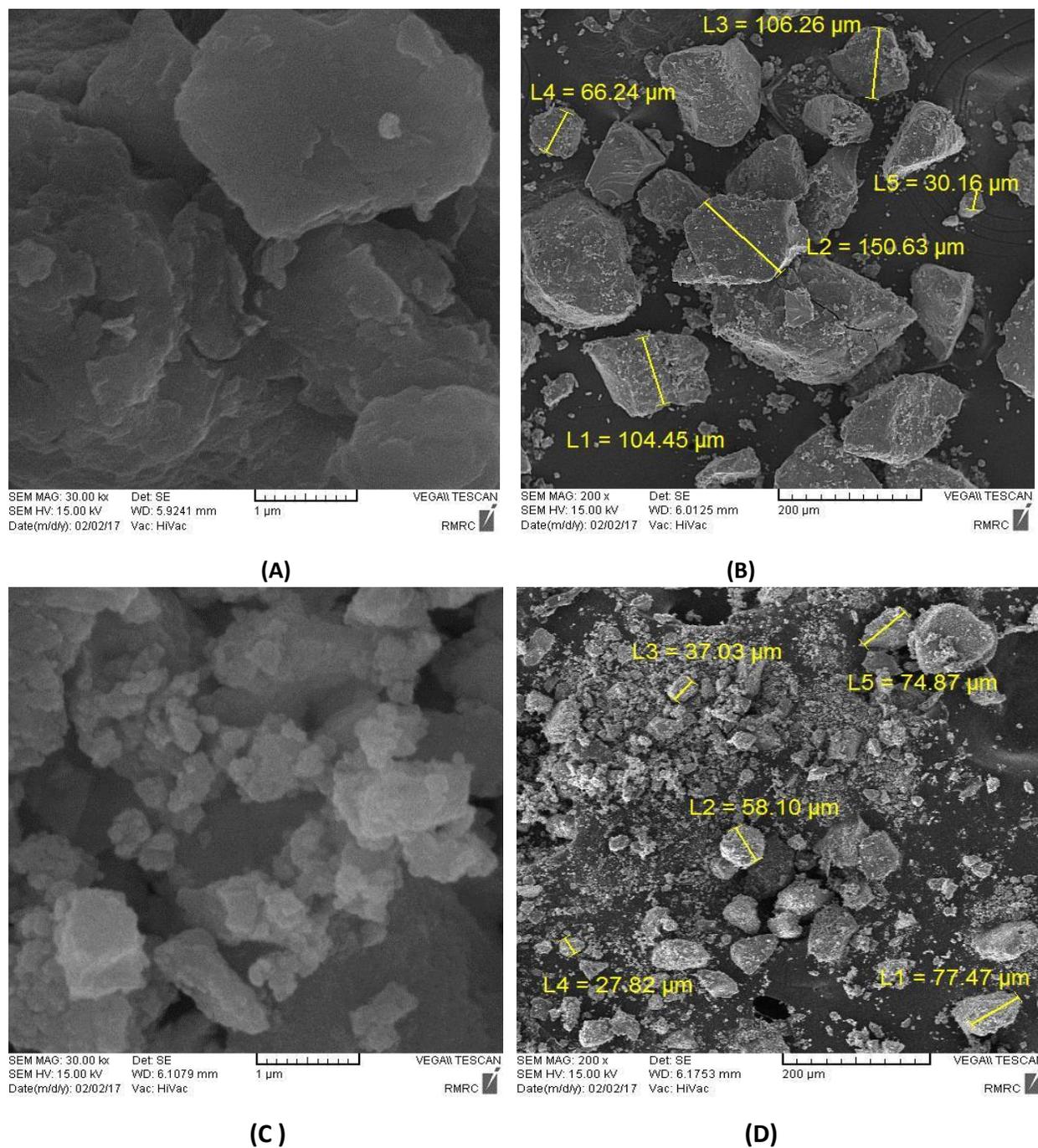


**Figure 1.** a) XRD patterns of Ni–Cr LDH and b)  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-CrLDH}$

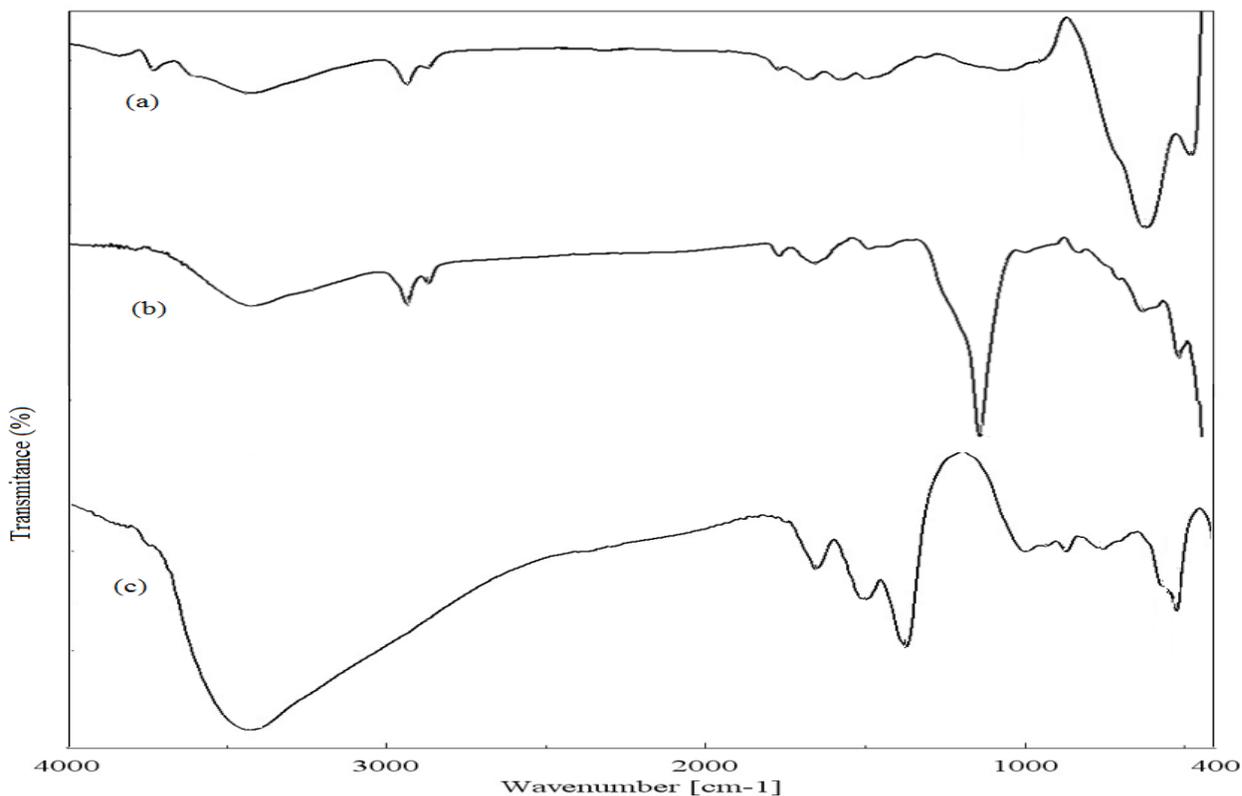
### *Kinetic Adsorption*

The effect of contact time on CR adsorption kinetic is demonstrated in Figure 4. It was observed that the adsorption capacity increased with increasing the contact time and reached equilibrium after 180 min. The adsorption rates were initially rapid due to readily accessible sites and subsequently

became much slower. So, the adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. The adsorption capacity of the Ni-CrLDH and Zn<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ni-CrLDH was 17.8 and 38.6 mg g<sup>-1</sup>, respectively. The obtained results showed that the magnetic Ni-CrLDH exhibits better adsorption performance.



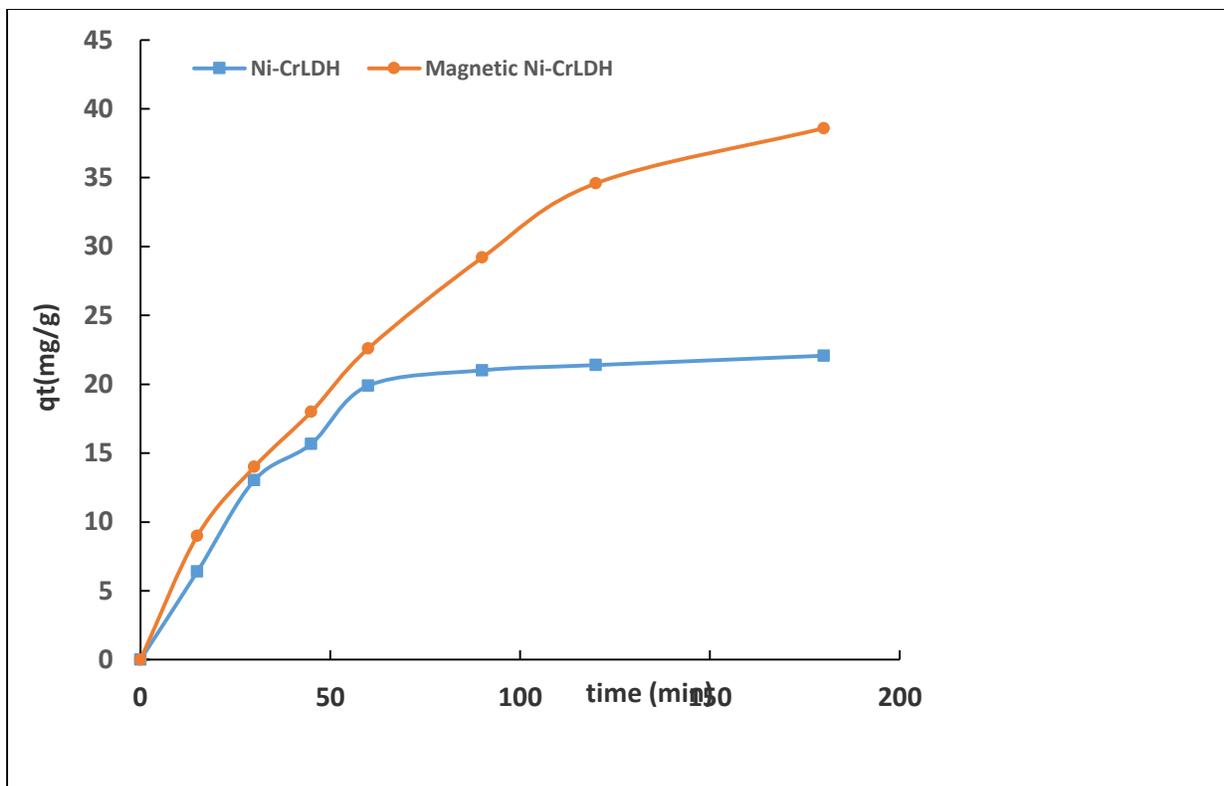
**Figure 2.** SEM images of a) & b) Ni-Cr LDH and c) & d) Zn<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ni-CrLDH



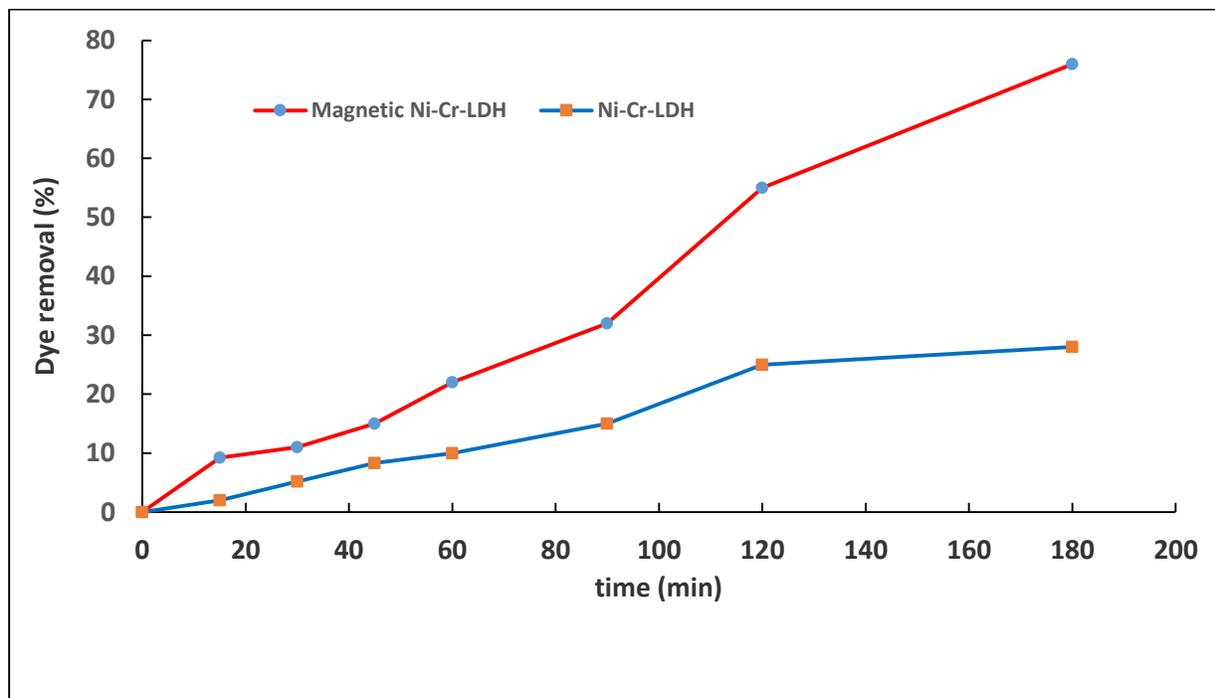
**Figure 3.** FT-IR spectra of a)  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ , b)  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2$  and c)  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-CrLDH}$

Also, as seen in [Figure 5](#), the adsorption percentage of CR onto magnetic Ni-CrLDH increased substantially from the beginning of the adsorption and thereafter it proceeded at a slower rate and finally reached to equilibrium. As illustrated in [Figure 5](#), the removal efficiency of CR onto magnetic Ni-CrLDH by adsorption for 180 min can reached up to 78%. However, the percentage of CR removal by the magnetic Ni-CrLDH was 28% at 180 min, it indicates that the adsorption capacities of CR onto the magnetic Ni-CrLDH was mainly attributed to  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ . There are four common steps involved in the adsorption process. The first step is bulk diffusion process in which adsorbate migrates from the bulk solution onto the surface of the adsorbent. Second is the film diffusion where the adsorbate diffuses through boundary layer to the adsorbent surface. Then intraparticle diffusion takes place which allows the adsorbate to diffuse from the surface to the inner part of the adsorbent particles and finally adsorbed on the active sites. That is why the adsorption becomes slower near the equilibrium [28].

[Figure 6](#) reveals the adsorption of initial CR at different pH solution. It can be observed that the adsorption efficiency of the adsorbents increases with a decrease in pH of the initial solution (pH=

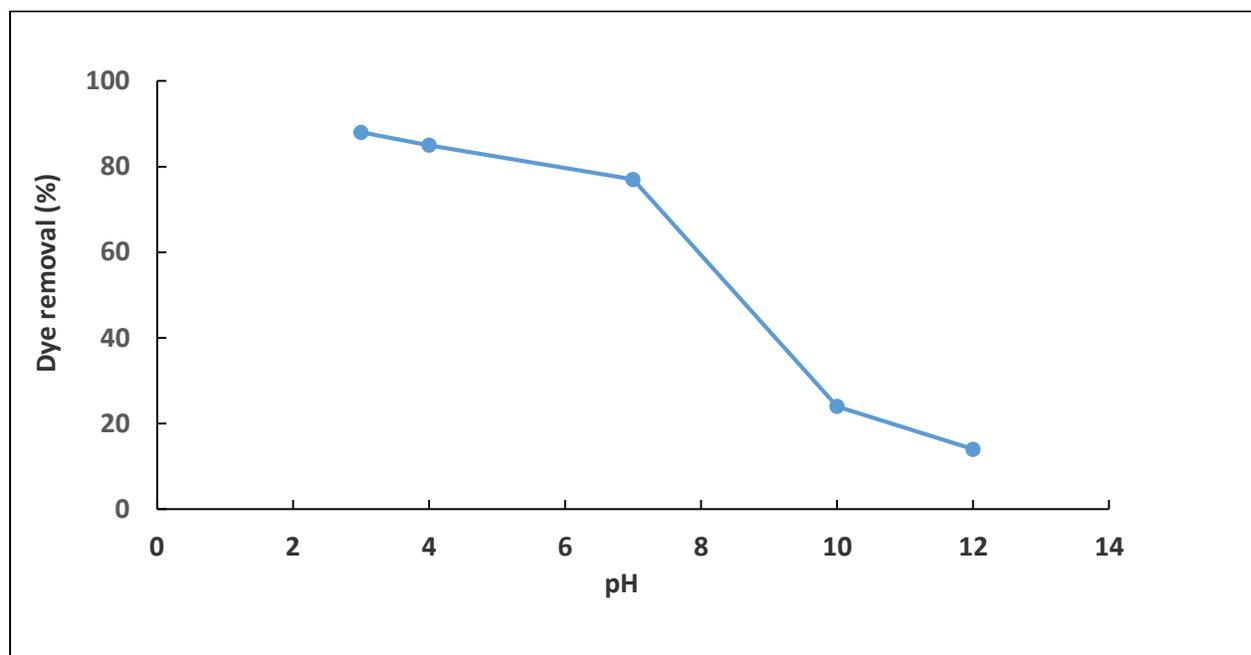


**Figure 4.** Effect of contact time on adsorption kinetics of CR on Ni-CrLDH and magnetic Ni-CrLDH



**Figure 5.** Effect of contact time on percentage removal of CR on Ni-CrLDH and magnetic Ni-CrLDH

3; %A = 88), because of electrostatic interaction between the adsorbent and the anionic group in the CR molecule [29]. However, the adsorption percentage decreases from 78% to 14% with increases in initial pH of CR solution from 6 to 12 due to successive deprotonation of the positive charged groups on the adsorbent and electrostatic repulsion between negatively charged sites on the adsorbent and CR molecules. Moreover, the decrease in percentage adsorption could also be interpreted by formation of OH<sup>-</sup> ions in the alkaline solution that compete with the anionic azo dyes for the adsorption sites.

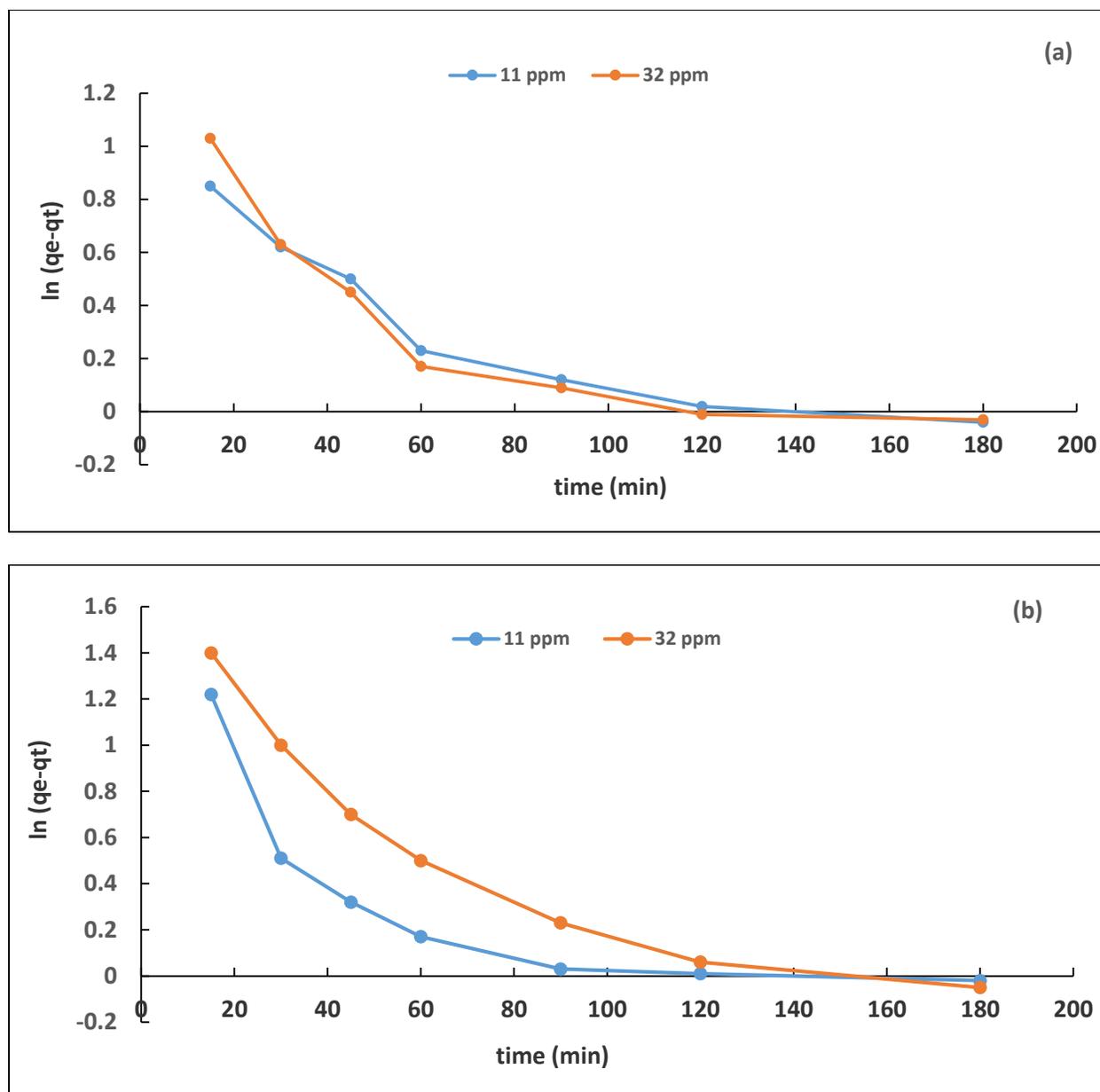


**Figure 6.** Influence of pH on adsorption

The order of adsorbate-adsorbent interactions has been described by using various kinetic models. In this study, the pseudo- first- order kinetic model, pseudo- second- order model and intraparticle diffusion model was investigated. The pseudo- first-order model for liquid-solid adsorption is expressed as: [30]

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

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 ( $\text{min}^{-1}$ ). The plot of  $\log (q_e - q_t)$  versus  $t$  for Ni-CrLDH and magnetic Ni-CrLDH are showed in [Figure 7](#) and the calculated parameters of the pseudo- first- order kinetic model are listed in [Table 1](#). The calculated value of  $R^2$  indicates that



**Figure 7.** The pseudo first-order kinetics for CR adsorption on the Ni-CrLDH sample a) and Zn<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ni-CrLDH, b) ( $t=25$  °C; adsorbent dose = 100 mg; initial concentration = 11, 32 mg/L)

it is not appropriate to use the pseudo-first-order kinetic model to describe the adsorption kinetics of Ni-CrLDH and magnetic Ni-CrLDH samples.

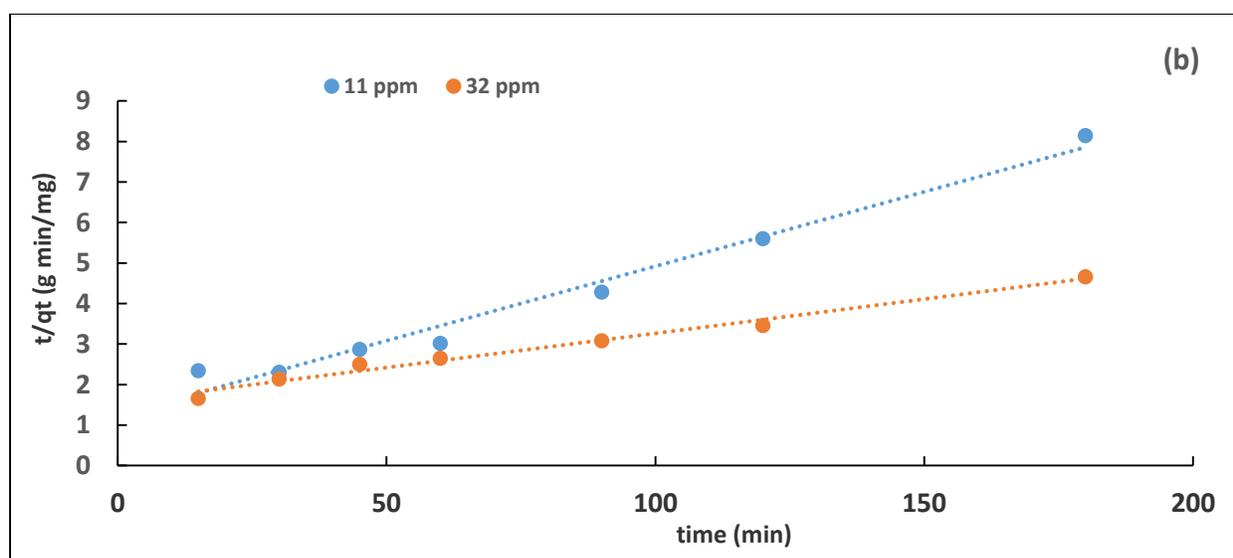
The pseudo- second- order equation can also be expressed as follows [31, 32]:

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

**Table 1.** The calculated parameters of the pseudo first-order and pseudo second-order kinetic model of CR onto Ni–CrLDH

Samples	Conc.(mg/L)		First-order parameter		Second-order parameter			$q_e$ exp.(mg/g)
Ni-CrLDH	11	0.0052	5.358	0.8034	0.00195	13.57	0.9896	11.8
Ni-CrLDH	32	0.0057	5.896	0.6976	0.00121	21.88	0.9938	18.3
Magnetic Ni-CrLDH	11	0.0057	5.767	0.5612	0.00109	27.17	0.9766	22.7
Magnetic Ni-CrLDH	32	0.0082	15.36	0.8223	0.00018	59.17	0.9853	39.6

Where  $k_2$  is the second-order rate constant ( $\text{g mg}^{-1}.\text{min}^{-1}$ ). 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. As shown from Table 1, the correlation coefficient ( $R^2$ ) has an extremely high value (0.9938) and closer to unity for the pseudo second order kinetic model compared to the value of pseudo-first order kinetic model.

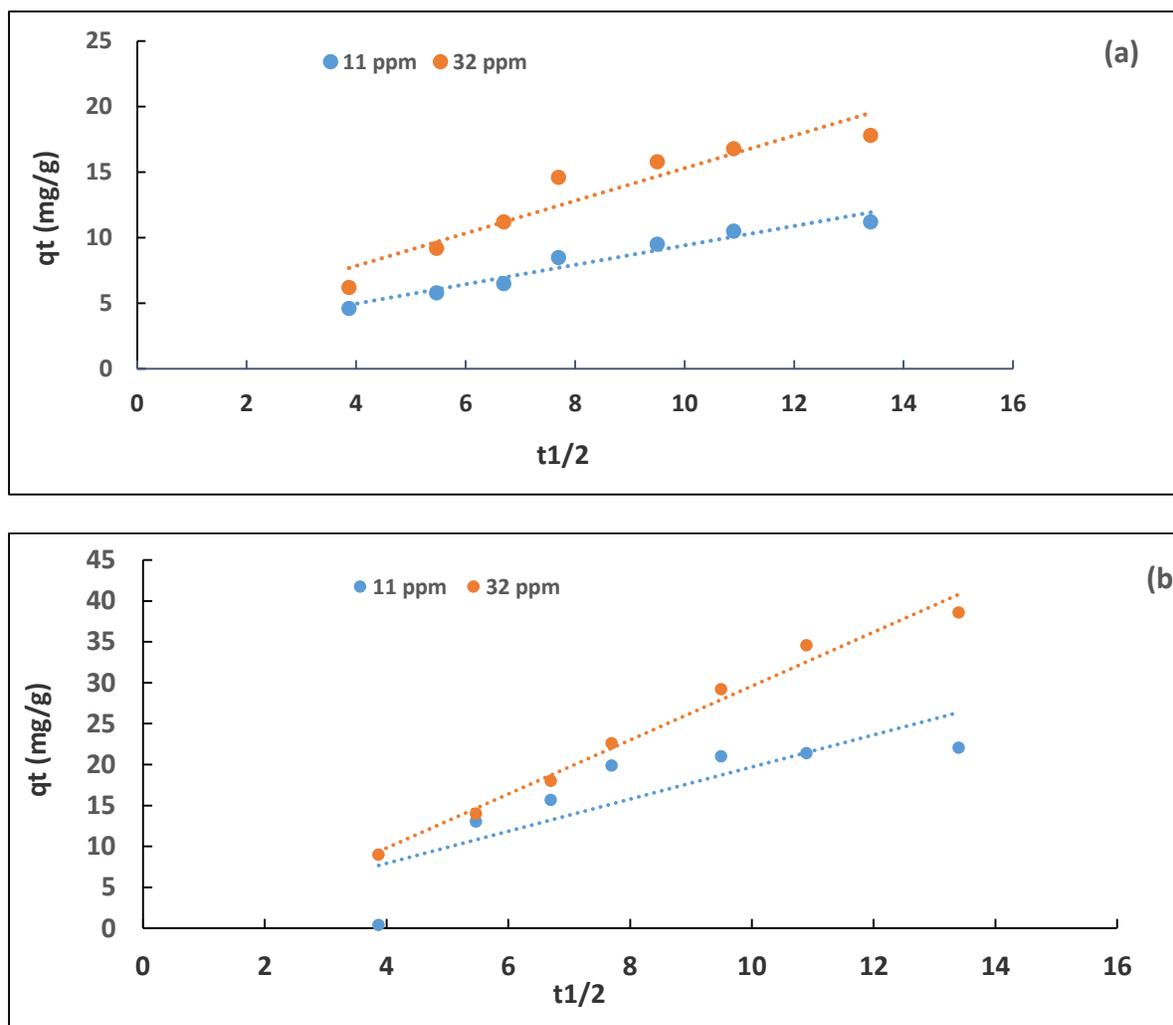
**Figure 8.** The pseudo second-order kinetics for CR adsorption on the Ni–CrLDH sample a) and  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni-CrLDH}$ , b) ( $t=25$  °C; adsorbent dose = 100 mg; initial concentration = 11, 32 mg/L)

The calculated equilibrium sorption capacity ( $q_e$ ) is consistent with the experimental data. These results showed the pseudo-second-order sorption mechanism is predominant for the Ni–CrLDH and magnetic Ni–CrLDH and that the overall rate constant of sorption process appears to be controlled by a chemisorption process.

The effect of intra particle diffusion resistance on adsorption can be evaluated by the following equation:

$$q_t = k_{di}\sqrt{t} + C_i \quad \text{Eq. (4)}$$

Where  $k_{di}$  is the rate constant of intra particle diffusion ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ). Values of  $C_i$  give the information regarding the thickness of boundary layer. The plots of  $q_t$  vs  $t^{1/2}$  as shown in Figure 9, were found to yield straight lines for Ni-CrLDH and magnetic Ni-CrLDH samples. The intra particle diffusion rate constant  $k_{di}$  and regression coefficient are listed in Table 2.

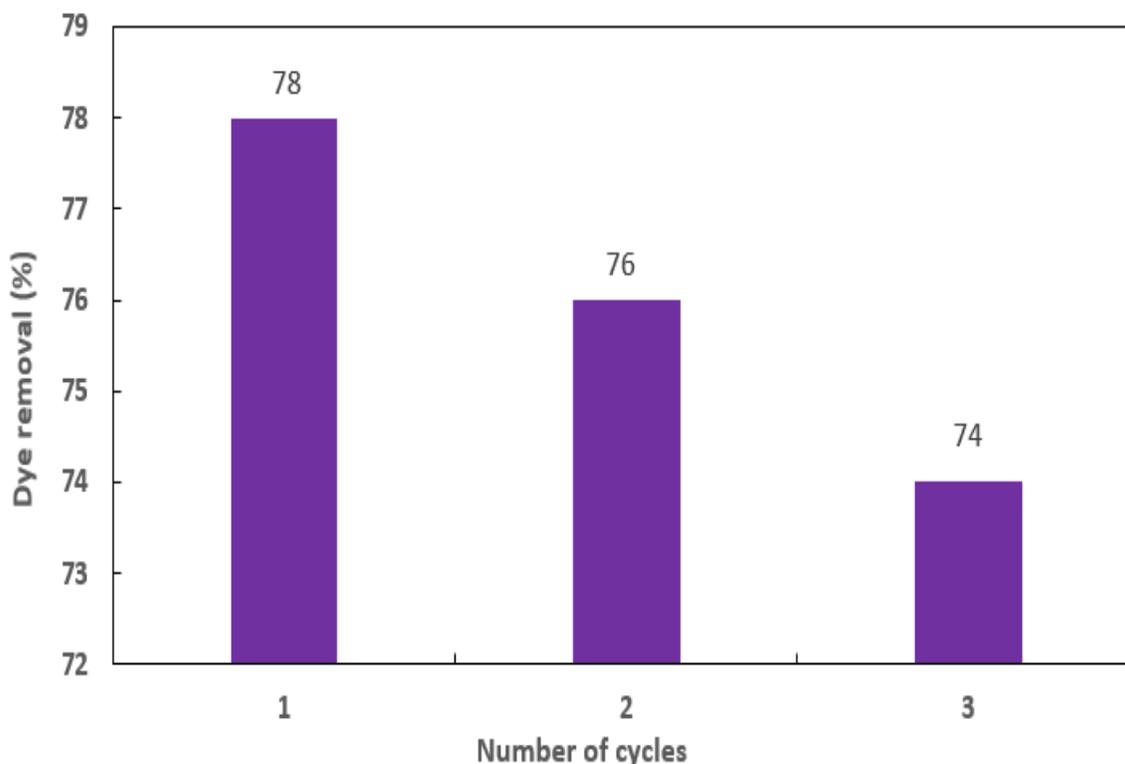


**Figure 9.** Intraparticle diffusion kinetics for CR adsorption on the Ni-CrLDH sample a) and Zn<sub>0.5</sub>Cu<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>@Ni-CrLDH, b) ( $t=25$  °C; adsorbent dose = 100 mg; initial concentration = 11, 32 mg/L)

**Table 2.** Intraparticle diffusion model constants for CR adsorption on all samples

Samples	$C_o$ (mg/L)	$k_{id}$ (mg/g min <sup>-1/2</sup> )	$C_i$	$R^2$
Ni-CrLDH	11	0.742	1.982	0.9493
Ni-CrLDH	32	1.244	2.853	0.8975
Magnetic Ni-CrLDH	11	1.96	0.105	0.6937
Magnetic Ni-CrLDH	32	3.295	3.375	0.9832

The linearity of the plots showed that intra particle diffusion might have a significant role in the adsorption of the CR dye onto Ni-CrLDH and magnetic Ni-CrLDH samples (Figure 9). From an industrial point of view, it is important for adsorbents to be recyclable after regeneration. So, it is desirable to regenerate the adsorbent for another cycle of application. For this purpose, methanol was selected to remove the CR. The dye adsorption percentage of magnetic Ni-CrLDH for three consecutive adsorption-desorption cycles are presented in Figure 10. It can be seen that slight decrease in adsorption percentage might be due to the incomplete desorption of desorption experiments [33]. These results revealed that magnetic Ni-CrLDH could be used as an efficient recyclable adsorbent for the removal of CR from the aqueous solution.

**Figure 10.** Adsorption percentage of magnetic Ni-CrLDH after three cycle regeneration

## Conclusion

A novel magnetic layered double hydroxide ( $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni}-\text{CrLDH}$ ) composite was prepared by co-precipitation method in the dispersed  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2$  suspension. This study showed that the magnetic  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni}-\text{CrLDH}$  is a promising adsorbent for the removal of CR from aqueous solution in comparison with the Ni-Cr-LDH. The kinetic adsorption of the CR on magnetic  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni}-\text{CrLDH}$  was investigated and was found to fit the pseudo second-order model. The  $\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4@\text{SiO}_2@\text{Ni}-\text{CrLDH}$  could be easily separated by external magnetic, therefore could be used as effective adsorbent for the removal of anionic CR dye from wastewater.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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