Adsorption of chromium (VI) ion using zeolite NaA/Fe₃O₄ composite derived from rice husk ash

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Abstract. In this study, zeolite NaA was fabricated from rice husk ash before combining with Fe₃O₄ to form a magnetic NaA/Fe₃O₄ composite. NaA/Fe₃O₄ composite was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), and Brunauer Emmett Teller (BET). The surface area and the pore size of zeolite NaA/Fe₃O₄ was 24.11 m².g⁻¹ and 23.04 Å. In addition, batch adsorption studies were carried out for the removal of chromium (VI) ion in aqueous solution. The effects of adsorption parameters, including pH solution, initial concentration of Cr (VI) ions, mass of adsorbent, and contact time were investigated. The maximum equilibrium adsorption capacity of zeolite NaA and NaA/Fe₃O₄ was 22.554 mg.g⁻¹ and 13.722 mg.g⁻¹, respectively. The pseudo-first order kinetic model fitted well to the experimental data. The regeneration of the adsorbent was also investigated for three cycles.

1. Introduction
Heavy metal ions such as chromium, lead, mercury, cadmium ions, which result from industrial processes, lead to severe water pollution [1]. The heavy metal ions can cause a detrimental impact on our ecosystem as well as people’s health when releasing them into the environment without treatment. For the human, chromium is mainly present in the trivalent state Cr(III) in the blood and maintains the metabolism of blood through food, water and respiratory system [2]. Allowable safe limits of chromium (VI) in drinking water sources is 50 µg.L⁻¹ in water [3]. However, the World Health Organization stipulates that Cr (IV) concentration limits in wastewater are 0.2 mg.L⁻¹ and in drinking water must be less than 0.05 mg.L⁻¹ [4]. Therefore, reducing the Cr(VI) content from contaminated water to below the allowable limit is urgent.

In the recent years, many conventional treatment processes have been applied to remove or reduce hexavalent chromium from solution such as flocculation [5], membrane filtration [6], ultrafiltration [7] bio and microbial reduction [8], photo-catalytic degradation [9], reverse osmosis [10], ion exchange [8], electrocoagulation methods [11], and adsorption [12]. Adsorption is a common treatment process to remove heavy metal ions. Zeolite is commonly used due to its good adsorption capacity and low cost. However, the generation of the recycle of the absorbent is time-consuming, and expensive on the
industrial scale [13]. These issues can be overcome by combining the adsorbent with magnetic. Recently, zeolite/Fe$_3$O$_4$ composite has been synthesized and used as an adsorbent [14-17]. Khodadadi used NaA zeolite-coated magnetic nanoparticles to remove Pb (II) and Cu (II) ions from aqueous solutions [18,19]. Liu and co-workers studied the effect of adding Fe$_3$O$_4$ addition zeolite NaA to remove ammonium ions [20,21]. Tran and co-workers synthesized magnetic Fe$_3$O$_4$/zeolite NaA nanocomposite and applied for removal of methylene blue in wastewater treatment [15,22]. Rice husk is an agricultural waste abundant in rice producing areas like Mekong Delta, Vietnam. It has been used as fuel in small plants [23-26]. However, the disadvantage of this combustion is the accumulation of residue namely rice husk ash (RHA), which contains crystalline silica up to 80-90% [24,26]. To make the most of a waste like RHA, it has been used as a natural source of silica for the process of fabricating silica powder [23], silica nanosphere [22,27], ceramic composites [28,29] and NaA zeolites [30,31]. In this study, RHA was applied as an available SiO$_2$ source for the synthesis of zeolite NaA. Zeolite NaA/Fe$_3$O$_4$ composite was prepared and applied for the removal of Cr(VI) in aqueous solution. Effects of several conditions in the adsorption process including pH solution, initial concentration of Cr (VI) ions, mass of adsorbent, and contact time were studied. In addition, the isotherm and kinetic studies on Cr(VI) adsorption were also investigated. Finally, adsorbent regeneration was tested to evaluate its behavior in recycling.

2. Materials and methods

2.1. Materials
Sodium hydroxide (96%), hydrochloric acid (36-38%), sodium chloride (≥99.5%), iron (II) chloride tetrahydrate (96%), iron (III) chloride hexahydrate (97%) potassium dichromate (99.8%) were purchased from Xilong. Aluminum foil was obtained from Union Chemical Industry Company Ltd., 99%. Distilled water was used in all experiments. RHA was collected from Tra Noc Industrial Park, Can Tho city, Vietnam.

2.2. Preparation of NaA and magnetic zeolites NaA/Fe$_3$O$_4$

Zeolite NaA preparation
The synthesis of zeolite NaA followed a reported process [15]. A slight modification was applied. 10 g of RHA was reacted with 100 mL NaOH 5 M at boiling temperature to obtain silicate solution. 50 mL of the silicate solution was mixed with a sodium aluminate solution 0.83 M with the molar ratios of SiO$_2$/Al$_2$O$_3$=2.0, Na$_2$O/SiO$_2$=6.0, H$_2$O/Na$_2$O=50.0 for 8 h at 95 °C to form a powder (zeolite NaA particles). The powder was washed several times with distilled water until the pH of the solution was 7. Then, the obtained powder was dried at 65 °C for 5 h and calcined at 660 °C for 6 h [15].

Synthesis of zeolite NaA/Fe$_3$O$_4$ composite
6.379 g of the mixture (FeCl$_3$.6H$_2$O and FeCl$_2$.4H$_2$O with molar ratio of 2:1) was dissolved in 400 mL of distilled water and stirred at 70 °C for 1 h to obtain a transparent solution. A NaOH 2M solution was slowly dropped to the solution until the homogeneous suspension was obtained. Then, 3 g of zeolite NaA was added to the suspension while stirring. Next, the resulting powder was separated using a permanent magnet and it was washed several times with distilled water until pH reaches 7. Finally, the obtained powder was dried at 50 °C and heated in a furnace at 550 °C for 6 h. The effects of the reaction time, the mass ratio of zeolite NaA/Fe$_3$O$_4$ and the concentration of NaOH solution were investigated.

Material characterization
The crystalline phase of zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite was investigated by X-ray diffraction (XRD, D8 Phaser, Bruker, Germany) over 2 theta (2θ) range from 5° to 70° with a scanning speed of 0.05° /min using CuK$_\alpha$ radiation (λ = 1.5406 Å). The surface morphology and elemental compositions of zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite were analyzed under a field-
emission scanning electron microscope (FE-SEM, Hitachi, S-4800) at an accelerating voltage of 10 kV after gold coating and energy dispersive X-ray spectroscopy (EDX). The formation of zeolite NaA and zeolite NaA/Fe₃O₄ composite was observed by Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 6700) using KBr pellets with the scanned spectra of 4000 – 400 cm⁻¹. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area of zeolite NaA and zeolite NaA/Fe₃O₄ composite at 77 K of liquid nitrogen. The zeolite NaA and zeolite NaA/Fe₃O₄ composite were degassed at 573.15 K in vacuum prior to analysis on a NOVA 2200e - Surface Area and Pore Size Analyzer, Quantachrome Instruments (USA).

2.3. Adsorption experiments

Batch adsorption studies were carried out to evaluate the effects of pH, contact time, adsorbent dosage on the chromium (VI) ion removal efficiency of zeolite NaA and zeolite NaA/Fe₃O₄ composite. To investigate the effect of solution pH on the Cr(VI) adsorption, 0.1 g adsorbent was added to 30 mL of 12 mg.L⁻¹ Cr(VI) solution with various pH values (3, 4, 5, 6, 7, 8, 9), adjusted by using amount of 0.01 M HCl and 0.01 M NaOH. The mixtures were stirred at 300 rpm for 10 min. To study the effects of initial Cr (VI) concentration, the experiments were carried out with different initial Cr (VI) concentrations of 6, 8, 10, 12, 14 and 20 mg.L⁻¹ at pH 4 and 0.1 g adsorbent in 20 min. To examine the effects of adsorbent mass, different amounts of the adsorbent (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g) were used at pH 4 and 12 mg.L⁻¹ of initial Cr (VI) concentration, contact time 20 min. To determine the adsorption rate, adsorption kinetic was conducted at various time intervals from 5 to 60 min, at pH 4, an initial Cr (VI) concentration of 12 mg.L⁻¹, and an adsorbent dosage of 0.2 g. The final concentration of Cr (VI) was measured at the wavelength of 361 nm by a UV-visible spectrometer (Shimadzu UV-1800).

In all experiments, the percentage of Cr(VI) removal (R, %) and the adsorption capacity (qₑ, mg.g⁻¹) were calculated according to the equation 1 and 2:

\[ R = \frac{C_0 - C_e}{C_0} \times 100\% \]  
\[ q_e = \frac{C_0 - C_e}{m} V \text{, mg.g}^{-1} \]  

where \(C_0\) and \(C_e\) are the initial concentration and equilibrium concentration of Cr(VI) (mg.L⁻¹); \(V\) is the volume of Cr(VI) solution (L), and \(m\) is the mass of adsorbent (g).

2.4. Desorption experiments

After the adsorption, the solid was separated and dried. 0.2 g solid was added to 30 mL of 0.1 M NaOH solution for regeneration. Next, the mixture was shaken at 300 rpm at room temperature for 30 min. Then, the adsorbent was washed with distilled water several times before being filtered and dried at 60 °C overnight and reused in the next cycle.

3. Results and Discussions

3.1. Preparation of zeolite NaA and zeolite NaA/Fe₃O₄

XRD of zeolite NaA and zeolite NaA/Fe₃O₄ composite

Figure 1 shows XRD patterns of zeolite NaA and zeolite NaA/Fe₃O₄ composite calcined at 660 °C for 6 h. The characteristic peaks of zeolite NaA at 20 values of 7.18°, 10.3°, 12.6°, 16.2°, indexed to (200), (220), (222), (420) crystalline planes, agreeing well with JCPDS reference card number of 01-073-2340 for zeolite NaA. The characteristic peaks of zeolite NaA/Fe₃O₄ composite at 20 values of 30.1°, 35.4°, 43.1°, 53.4°, 57.0°, and 62.6° belong to crystal indexes of (220),(311), (400), (422),(511), and (440) were attributed to Fe₃O₄ with the standard pattern (JCPDS, card number 89-691). The results were in agreement with previous reports [20,21,25,26]. Thus, zeolite NaA and zeolite NaA/Fe₃O₄ composite were successfully prepared.
Figure 1. XRD patterns of zeolite NaA and zeolite NaA/Fe₃O₄ composite calcined at 660 °C, 6 h

SEM and EDX of zeolite NaA and zeolite NaA/Fe₃O₄ composite
FE-SEM images and EDX analysis of the zeolite NaA and zeolite NaA/Fe₃O₄ composites are provided in Figure 2. Zeolite NaA crystallized well in uniform cubic shape with average size of 2 μm (Figure 2a). The morphology of NaA is in good agreement with previous studies [22]. When NaA was modified with Fe₃O₄, the observed morphology comprises of fine nanoparticles attached to NaA surface (Figure 2b) [29]. Figure 2c present the SEM-EDX data for zeolite NaA/Fe₃O₄ composites. The atomic percentages of major elements include 7.41% carbon, 57.81% oxygen, and 5.03% iron. These results prove the presence of Fe₃O₄ nanoparticles on the surface of NaA zeolite.

Figure 2. SEM images of zeolite NaA (a) and zeolite NaA/Fe₃O₄ composites (b); EDX mapping of zeolite NaA/Fe₃O₄ composites (c)
FTIR

Figure 3 shows FTIR spectra of zeolite NaA and zeolite NaA/Fe$\text{O}_4$ composites. The spectra at position 3420 cm$^{-1}$ and 3429 cm$^{-1}$ indicate the presence of absorbed water in zeolite NaA framework and zeolite NaA/Fe$\text{O}_4$ composite [31]. The peaks at 1600 cm$^{-1}$ can be attributed to the stretching vibration indicating the presence of hydroxyl groups [32]. The high intensity vibration frequencies at the band positions 1000 cm$^{-1}$ and 999 cm$^{-1}$ found between the ranges of 1250 and 950 cm$^{-1}$ and the 668 cm$^{-1}$ found between 720 and 650 cm$^{-1}$ represent the internal vibrations due to the asymmetric stretching of Si-O-Al tetrahedral. The absorption band at 553–557 cm$^{-1}$ is associated with the Si-O and Al-O groups [33]. The bands at 460 cm$^{-1}$ and 570 cm$^{-1}$ are assigned to the specific vibrations of Fe-O [34,35]. The FTIR result indicates that the zeolite NaA/Fe$\text{O}_4$ composite was successfully prepared.

BET results of zeolite NaA/Fe$\text{O}_4$ composite

Figure 4 represents the nitrogen adsorption–desorption isotherms at liquid nitrogen temperature and correspondingly obtained pore size distribution of zeolite NaA and zeolite NaA/Fe$\text{O}_4$ composite. Adsorption data were obtained with a relative pressure $P/P_0$ range from 0 to 0.9. The adsorption isotherm curve exhibits a type IV for zeolite NaA (Figure 4a) and type III for zeolite NaA/Fe$\text{O}_4$ composite ((Figure 4b) based on the International Union of Pure and Applied Chemistry (IUPAC) [36]. Type IV isotherm with hysteresis loop is characterized by porous adsorbents with pores in the range of 1.5–100 nm [36]. At higher pressures, the uptake of adsorbate was increased because zeolite NaA contains a certain number of mesopores, multilayer adsorption [37]. The type III isotherms are ascribed to a macroporous with the weak adsorbent–adsorbate interactions compared to relatively strong adsorbate–adsorbate interactions [38]. Moreover, type III is also confined to monolayers of adsorbate molecules distributing unevenly on the adsorbent surface and located in most active sites with high concentration [39]. The specific surface areas were calculated by the BET method. The specific surface area of the zeolite NaA was 9.130 m$^2$.g$^{-1}$ and pore volume 0.005 cm$^3$.g$^{-1}$, which is smaller than that of zeolite NaA/Fe$\text{O}_4$ composite (24.11 m$^2$.g$^{-1}$) with a pore volume of 0.031 cm$^3$.g$^{-1}$ and an average pore size of 23.40 Å. These results are consistent with those of previous studies [40,41]. The specific surface area of zeolite NaA/Fe$\text{O}_4$ composite is increased due to the coating of Fe$\text{O}_4$ nanoparticles on the NaA surface. Besides, the recovery of the NaA/Fe$\text{O}_4$ composite is much easier due to the magnetic properties of the Fe$\text{O}_4$ nanoparticles.
Figure 4. BET adsorption-desorption isotherms and pore size distribution of zeolite NaA (a) and zeolite NaA/Fe$_3$O$_4$ composites (b).

3.2. Removal of Cr (VI) studies

Effects of parameters

Effect of pH

Figure 5 shows the effects of pH on the adsorption of Cr(VI) ions by 0.1 g zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composites in 30 mL of 12 mg.L$^{-1}$ Cr(VI) solution after 10 min. The removal efficiency increases with increasing pH from 3 to 4 and decreases from 4 to 9. At low pH values, chromium in the form Cr$_2$O$_7^{2-}$ dominates the form HCrO$_4^-$ in the solution [42]. The percentage of the removal efficiency was high because the attraction between the ionic species and the surface of the adsorbent increased. When increasing pH above 5, the adsorption capacity decreases due to the changes of adsorbent surface charge and the chromium species. Besides, high pH (above 6) also causes chromium precipitation [19,43-47]. Therefore pH 4 was chosen to investigate the effect of other parameters.
Effects of pH on Cr(VI) adsorption by the zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composites

Figure 5 depicts the relationship between percentage removal of Cr(VI) ions and the initial Cr (VI) concentration. With an increase in the initial concentration of Cr (VI) from 6 to 20 mg.L$^{-1}$, the removal efficiency of Cr(VI) ions of both adsorbents decreases significantly from 14 mg.L$^{-1}$ to 20 mg.L$^{-1}$. It can be related to the active site and the surface area of the absorbents. Therefore, the 12 mg.L$^{-1}$ of initial Cr(VI) concentration was chosen to study the effect of other parameters.

Effects of initial Cr (VI) concentration

Figure 6 depicts the relationship between percentage removal of Cr(VI) ions and the initial Cr (VI) concentration. With an increase in the initial concentration of Cr (VI) from 6 to 20 mg.L$^{-1}$, the removal efficiency of Cr(VI) ions of both adsorbents decreases significantly from 14 mg.L$^{-1}$ to 20 mg.L$^{-1}$. It can be related to the active site and the surface area of the absorbents. Therefore, the 12 mg.L$^{-1}$ of initial Cr(VI) concentration was chosen to study the effect of other parameters.

Effects of adsorbent mass

Figure 7 shows the effects of adsorbent mass on Cr (VI) removal of zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composites. When increasing the adsorbent mass from 0.05 g to 0.5 g, the removal efficiency increases and reaches 80.77 % and 69.23 % at 0.2 g zeolite NaA and zeolite NaA/Fe$_3$O$_4$, respectively. However, if higher mass of adsorbents are added, the Cr(VI) removal efficiency increases slowly. This may be due to the higher the amount of adsorbent, the higher the number of active sites is obtained. Meanwhile, the Cr(VI) ion concentration is maintained unchanged. Since there was no significant difference in the removal efficiency for higher amounts of adsorbent, 0.2 g of the adsorbent was chosen for further experiments.
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Figure 7. Effects of adsorbent mass on Cr(VI) removal by the zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composites [ion concentration = 12 mg.L$^{-1}$, pH 4, contact time = 20 min.]

**Kinetic models**
To obtain the rate-controlling step in the adsorption mechanism, the pseudo-first-order and pseudo-second-order models were used to analyze the kinetic data. The kinetic models (Equation 3 and 4) were used to investigate Cr (VI) ion adsorption kinetics on zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite.

**Pseudo-first-order model:**

$$
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
$$

**Pseudo-second-order model:**

$$
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
$$

where $k_1$ is the pseudo-first-order kinetics model rate constant (min$^{-1}$) and $k_2$ is the pseudo-second-order kinetics model rate constant (g mg$^{-1}$ min$^{-1}$).

The effect of contact time on Cr(VI) removal by the zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composites is shown in Figure 8a. The effect of adsorption time was investigated by varying the amount of zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite from 5 to 60 min. The adsorption process is very rapid at the initial stage, then decreases slowly after 20-30 minutes. The adsorbent time increased from 5 to 30 min, the removal efficiency Cr(VI) of material zeolite NaA increased and reached a maximum value of 74.34±0.89 % at 20 min. Similarly, when using zeolite NaA/Fe$_3$O$_4$ composite, the removal efficiency Cr (VI) reached the maximum value of 61.91±0.71 after 20 min.

In this study, the pseudo-first-order kinetics is not suitable because the correlation coefficients ($R^2$) obtained were less than those obtained for pseudo-second-order kinetic models (Figure 8b-c). Thus, the present adsorption study obeyed the pseudo-second-order kinetics and the adsorption rate is controlled by chemical interactions.
Figure 8: a) Adsorption rate of Cr(VI) onto the zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite, (b) kinetic fitting of pseudo-first order kinetic model and (c) pseudo-second order kinetic model [ion concentration=12 mg.L$^{-1}$, amount of adsorbent = 0.2 g, pH 4]

Isotermal adsorption

Adsorption isotherm models, namely Langmuir, Freundlich, were applied for the adsorption capacity on zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite, according to the equation 5 and 6.

The Langmuir equation:

$$\frac{1}{q_e} = \left( \frac{1}{K_Lq_{\text{max}}} \right) \times \frac{1}{C_e} + \frac{1}{q_{\text{max}}}$$

(5)

The Freundlich equation:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

(6)

where $K_L$, $K_F$ are equilibrium adsorption constants (mg.L$^{-1}$); $q_{\text{max}}$ is the maximum adsorption capacity (mg.g$^{-1}$); $n$ is Freundlich isotherm model constants.

Experiment data for zeolite NaA fits the Langmuir isotherm model better than the Freundlich (Figure 9a and 9b). The plot of $C_e/Q_e$ against $C_e$ for Langmuir model which fits the linear equation (5) ($C_e/Q_e = 0.534 + 0.263 \times C_e$ with correlation coefficients $R^2 = 0.976$. $Q_m$ was 22.554 mg.g$^{-1}$. For the NaA/Fe$_3$O$_4$ composite, Freundlich isotherm model seems dominant since the plot of $\log(Ce/Qe)$ against $C_e$ for the experiment data which the linear equation (6) is $\log(Qe) = -0.186 + 0.528 \times \log(C_e)$ with $R^2 = 0.882$, which is better than Langmuir isotherm model (Figure 9c and 9d). The Cr (VI) adsorption on the zeolite NaA/Fe$_3$O$_4$ composite fitted well to the Freundlich isotherm model. $Q_m$ was 13.722 mg.g$^{-1}$, determined by the slope. Table 1 shows the comparison of Langmuir and Freundlich adsorption capacity of Cr(VI) ions using various adsorbents. The results show that the adsorption
capacity of Cr(VI) ions of zeolite NaA/Fe$_3$O$_4$ composite is higher than that of Cr(VI) ions using kaolin, clay minerals, rice husk ash and smaller than that of Cr(VI) ions using modified activated carbon and PANi/PEG composite.

Figure 9: (a) Langmuir isotherm plot of zeolite NaA, (b) Freundlich isotherm plot of zeolite NaA, (c) Langmuir isotherm plot of zeolite NaA/Fe$_3$O$_4$, (d) Freundlich isotherm plot of zeolite NaA/Fe$_3$O$_4$

3.3. Regeneration studies
The regeneration of adsorbents is one of the most significant indicators for engineering applications. Iron oxide nanoparticles decorated with zeolite NaA allow a simple method of magnetic separation. Zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite were reused for three adsorption-desorption cycles, and the results are illustrated in Figure 10. The removal efficiency declined slowly with increasing cycle numbers. After three cycles, the removal efficiencies of Cr(VI) were 79.11% and 61.68% for zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite, respectively. However, the adsorption capacity of adsorbents was reduced only by less than 4% for zeolite NaA and 4.5% for zeolite NaA/Fe$_3$O$_4$ composite. Thus, the zeolite NaA and zeolite NaA/Fe$_3$O$_4$ composite have an excellent regeneration capacity.

Table 1. Comparison of Langmuir and Freundlich adsorption capacity of Cr(VI) ions, using various adsorbents

| Adsorbents                      | Adsorption conditions | $q_{\text{max}}$ (mg.g$^{-1}$) | Adsorption isotherms | References |
|--------------------------------|-----------------------|------------------------|----------------------|------------|
| Modified activated carbon      | pH 3, t=4 h, $m_{\text{ads}}$=75 mg.L$^{-1}$, $C_0$=1 mg.L$^{-1}$ | 18.519 | Langmuir | [48] |
| Kaolin                         | pH 4.6, t=120 min, $m_{\text{ads}}$=3 g L$^{-1}$, $C_0$=50 mg.L$^{-1}$ | 11.16 | Langmuir | [49] |
| Clay minerals                  | pH 4.6, t=4 h, $m_{\text{ads}}$=2 g L$^{-1}$, $C_0$=50 mg.L$^{-1}$ | 10.6-13.9 | Langmuir | [50] |
| PANi/PEG composite             | pH 5, t=30 min, $m_{\text{ads}}$=1 g L$^{-1}$, $C_0$=50 mg.L$^{-1}$ | 68.97 | Langmuir | [51] |
| Rice husk ash                  | pH 2, t=180 min, $m_{\text{ads}}$=40 g L$^{-1}$, $C_0$=10 mg.L$^{-1}$ | 0.49 | Langmuir | [52] |
| Polyaniline/Zeolite nanocomposite | pH 2, t=10 min, $m_{\text{ads}}$=5 g L$^{-1}$, $C_0$=100 mg.L$^{-1}$ | 25 | Freundlich | [53] |
| Zeolite NaA                    | pH 4, t=30 min, $m_{\text{ads}}$=0.2 g, [Cr (VI)]=30 mg.L$^{-1}$, $C_0$=12 mg.L$^{-1}$ | 22.554 | Langmuir | This study |
| Zeolite NaA/Fe$_3$O$_4$        | pH 4, t=20 min, $m_{\text{ads}}$=0.2 g, v=30 mg.L$^{-1}$, $C_0$=12 mg.L$^{-1}$ | 13.722 | Freundlich | This study |

4. Conclusions
This work aimed to study the synthesis of zeolite NaA/Fe$_3$O$_4$ composite for the removal of Cr(VI) in an aqueous solution. The specific surface area of NaA/Fe$_3$O$_4$ material was 24.11 m$^2$g$^{-1}$, the pore size was 23.04 nm. Adsorption experiments were conducted at pH of 4, in 20 min, with an initial concentration of 12 mg.L$^{-1}$ and at adsorption mass of 0.2 g. The maximum capacity of Cr(VI) adsorption was 69.23% for zeolite NaA/Fe$_3$O$_4$ composite. The adsorption process obeyed the pseudo-second-order kinetic model. After three cycles of regeneration, the removal efficiency was 61.68%. Adsorption data obeyed the Langmuir isotherm model for NaA zeolite and Freundlich isotherm model for NaA/Fe$_3$O$_4$ composite.

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