Scientific Research

Adsorption of Fe(III) from Aqueous Solution by Linde Type-A Zeolite

Saeedeh Hashemian[*]**, Seyed Hossein Hosseini, Hamila Salehifar, Khaterah Salari**

Chemistry Department, Yazd Branch, Islamic Azad University, Yazd, Iran
Email: [*]sa_hashemian@yahoo.com

ABSTRACT

Linde Type-A (LTA) zeolite was prepared from sodium aluminate and sodium metasilicate by hydrothermal process precursors. Sodium metasilicate prepared from molten NaOH and SiO_2. The zeolite was characterized by FTIR, XRD, XRF and SEM. The adsorption of Fe(III) from aqueous solution by zeolite A was studied. Different parameters like contact time, pH and concentration of iron were investigated. The results show that at contact time of 60 min and pH of 6 maximum adsorption of iron onto zeolite was observed. The kinetic data was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The adsorption kinetics of Fe(III) were fitted well with the pseudo-second-order kinetic model.

Keywords: Adsorption; LTA Zeolite; Sodium Metasilicate; Fe(III) Removal

1. Introduction

Porous solids are interest of researcher and scientist because of their ability to interact with atoms, ions and molecules not only at their outer surfaces, but also throughout the inner porous network. This involves ion exchange, adsorption (for separation) and catalysis; many of these processes actually benefit from the high order that can be achieved in solids such as zeolites. Zeolites represent one of the most commercially relevant categories of crystalline microporous solids. Zeolites are hydrated aluminosilicates of the alkaline and alkaline-earth metals with fully cross-linked open framework structures made up of corner sharing SiO_4 and AlO_4 tetrahedral. There are about 40 natural zeolites which have been identified during the past 200 years and more than 150 zeolites have been synthesized. For synthetic zeolites; the most common are zeolites A, X, Y andZSM-5. Zeolites, with their permanent negative charges as well as the interconnection of channels and cages that run through their secondary framework structure, are efficient adsorbents for positively charged pollutants such as heavy metals [1-3]. Both natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve and catalytic properties.

The application of zeolites to environmental pollution control in terms of heavy metal removal has received

very little attention, possibly due to the low pH solution that is often necessary [4-10]. Adsorption is a special characteristic of zeolites which is usually quite a complex process, generally involving much more than simple ion exchange into the pore openings of the ion exchanger. The amount of metal ion to be adsorbed is strongly affected by nature and concentration of the counter ion (metal ion), pH, metal solubility, presence of competing and complexing ions [11,12]. Since it is considered to be a particularly effective technique, adsorption is the preferred method for heavy metal removal.

In this study, first Linde Type-A zeolite was synthesized, and then the adsorption behavior of Fe(III) by zeolite was studied.

2. Experimental

2.1. Materials and Methods

Silicon Dioxide (99.8 wt%) was used as a silica source (Prepared from Glass Company Mazroof Yazd). Sodium aluminate was used as aluminum source (Riedel), sodium hydroxide, $FeCl_3 \cdot 6H_2O$ and other compound were obtained from Merck. All compounds were use as received without any purification.
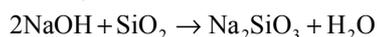
The crystalline structure of the synthesized zeolite seeds was determined by FTIR, XRF and XRD. FTIR spectra of synthesized LTA zeolites were recorded with

[*]Corresponding author.

spectrophotometer (Bruker, Tensor27) using pellet technique. A mixture of 5.0 mg LTA zeolite and 200.0 mg of KBr were pressed into a disk for IR measurement. XRD was carried out on a PW3719 Philips X'Pert diffractometer using Cu Kα (λ = 1.54° A) radiation, operated at 30 mA and 40 kV. The diffraction patterns of the products were obtained for a 2θ range of 0° - 50°. Fluorescence Bruker S4 Pioneer XRF wavelength dispersive spectrometer equipped with an array of up to 8 analyzing crystals and fitted with an Rh X-ray tube target was used. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles. Scanning electron microscopy (SEM) was carried by XL30 Philips.

2.2. Preparation of Zeolite

Sodium metasilicate is the most stable of silicic acid sodium salts and can be prepared from molten or hot aqueous NaOH and SiO_2 (preferably in powder, so that it has more reaction area). The reaction is as follows:

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

The crucible is loaded with 10 g NaOH and 7.6 gsilicon dioxide powder, and completely mixed together. Crucible placed in the furnace for 30 minutes in air at 1073 K to reaction completed. Greenish white powder (Sodium metasilicate) isobtained at 25°C. The LTA was prepared by the procedure reported [13].

First, sodium hydroxide (0.72 g) was dissolved in 80 ml of distilled water. This solution was divided into two parts. To the first part of the solution of sodium aluminate (8.25 g) was added. To the second part, (15.48 g) sodium metasilicate was added. These mixtures were stirred for 30 min. Then the two parts were poured simultaneously into a teflon container, resulting in the formation of a creamy gel. The Teflon container was sealed in an autoclave (hydrothermal bomb) and heated at 100°C for 24 hours. After cooling, the precipitate was collected by filtration. The obtained white precipitate was washed with water DI until the pH value of the wash liquor decreased from 13 to 10 and then the produced materials were dried overnight at 100°C.

3. Results and Discussion

3.1. Characterization of LTA Zeolite

FTI R spectra of LTA zeolite is shown in **Figure 1**. The bands at 450 to 1200 cm^{-1} are known to assignable to Si-O-Al, Si-O-Si, Si-O, Si-Al and T-O species [13]. In the other hand, the broad bands at 3350 to 3700 cm^{-1} are attributed to Si-OH, Si-OH-Al and -OH hydroxyl groups. The band at 668 cm^{-1} is known to assignable to Si-O-M where Misthe exchangeable Na$^+$ ion metal species. The absorption band at 668 cm^{-1} in LTA is visible which is in corporate with Na atoms in the zeolite framework [12].

XRD patterns of LTA zeoliteis shown in **Figure 2**. XRD result is shown high purity and a good crystallinity of zeolite. These results are in good agreement with those reported in the literature [12]. After indexation of XRD patterns of prepared zeolites, all diffraction planes (hkl) correspond to LTA phases. The synthesis product matched the characteristic peaks of zeolite A at 2θ values of 7.2°, 10.3°, 12.6°, 16.2°, 21.8°, 24°, 26.2°, 27.2°, 30°, 30.9°, 31.1°, 32.6°, 33.4° and 34.3° that were reported previously by Treacy and Higgins [14]. The results of X-ray Fluorescence (XRF) analysis is shown in **Table 1**. The XRF is offered molar ratio of Si/Al about 1 for LTA zeolite. Scanning electronic micrographs show the cubic shape of particles for LTA zeolite. **Figure 3** shows the SEM image of zeolite.

3.2. Adsorptive Properties of the LTA Zeolite

3.2.1. Effect of pH on the Adsorption of Fe(III)

The effect of solution pH is important factor for adsorption process. A solution containing 70 and 100 mg·L^{-1} of Fe(III) was prepared using deionized water. The 0.1 g of zeolite and 30 mL of Fe(III) was used. The pH was adjusted to a range of 2 - 7. The sample was shaken for 60 min on a shaker. The suspension was then filtered. Metal ion concentrations in the filtrate were analyzed using a varian 220 atomic absorption spectrometer. The results show that, the adsorption capacity of LTA zeolite for adsorption of Fe(III) increased with increasing the pH of the medium from 2 to 6, but it is nearly constant from 6 to 8, and after than decrease to pH of 10. Therefore, the maximum adsorption capacity was observed at pH 6 (**Figure 4**). pHs more than 8 case the precipitation of iron hydroxide.
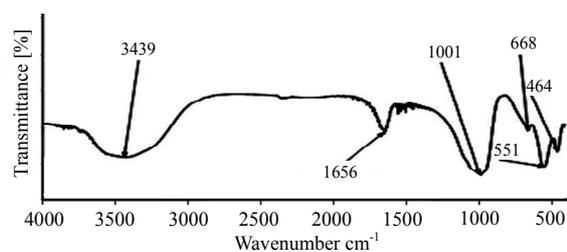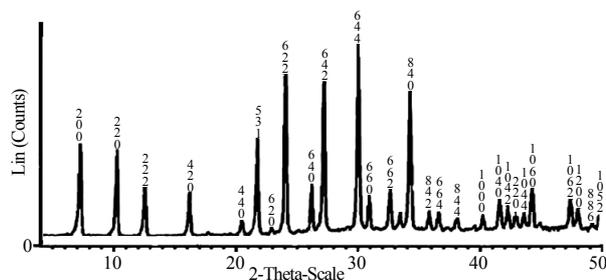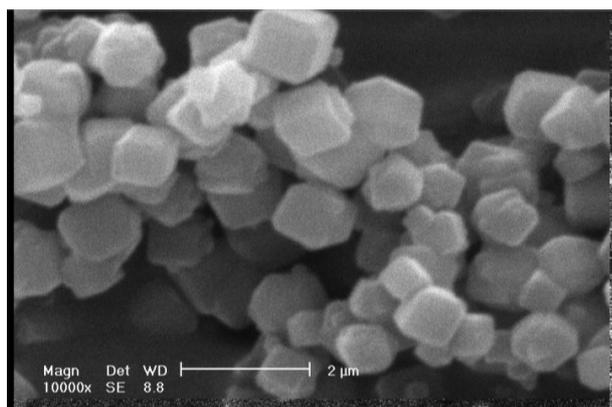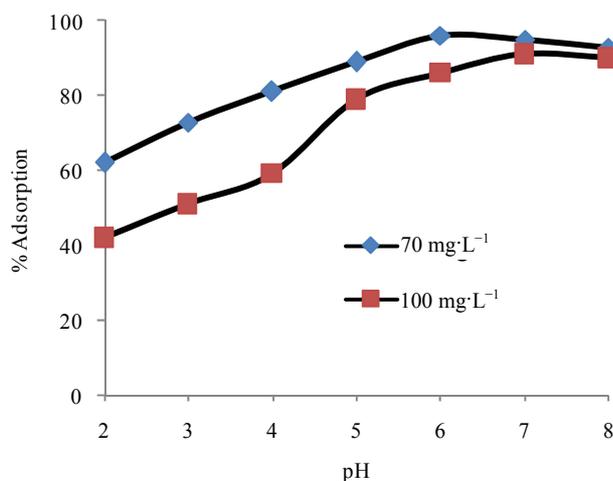

Figure 1. FTI R spectra of LTA zeolite.

Figure 2. XRD pattern of LTA zeolite.

Table 1. XRF analysis of LTA zeolite.

Compound	Concentration (%W/W)
SiO_2	32.86
Al_2O_3	30.48
Na_2O	19.28
K_2O	0.043
CaO	0.042
Fe_2O_3	0.038
CO	0.006
LOI[*]	17.22
Total	99.97

[*]Loss on ignition (1000°C, 2 h).

Figure 3. SEM image of LTA zeolite.

Figure 4. Effect of pH on the adsorption of Fe(III) onto LTA zeolite.

3.2.2. Effect of Contact Time

The effect of contact time on adsorption of Fe(III) with concentration 70 and 100 mg·L^{-1} was studied. The results show that initial adsorption was rapid due to the adsorption of iron onto exterior surface, after that metal ions enter into pores (interior surface), relatively slow process. The adsorption rate decreased substantially with time further than 60 min. The adsorption process was attained to equilibrium at 90 min of contact time. The increasing of shaking time more than 90 min has no significant effect on adsorption of metal ions. Therefore, the best shaking time is 90 min at which adsorption of iron metal is 92% and 96%, for Fe(III) 100 and 70 mg·L^{-1}. **Figure 5** shows the effect of contact time for adsorption of Fe(III) onto LTA zeolite.

3.3. Kinetics of Adsorption

The kinetic data of the adsorption of Fe(III) onto LTA zeolite was evaluated using pseudo-first order and pseudo-second-order kinetic models. The pseudo-first order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time [15].

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{1}$$

where q_e and q_t are the amounts of dye adsorbed per unite mass of the adsorbent (mg·g^{-1}) at equilibrium and time t, respectively and k_1 is the rate constant of adsorption (min^{-1}). When $\ln\left(q_e - q_t\right)$ was plotted against time, a straight line should be obtained with a slope of k_1, if the first order kinetics is valid.

The pseudo-second order model as developed by Ho and McKay [15,16] has the following form:

$$t/q_t = t/q_e + 1/\left(k_2 q_e^2\right) \tag{2}$$

where q_e and q_t represent the amount of dye adsorbed (mg·g^{-1}) at equilibrium and at any time. k_2 in the rate constant of the pseudo-second order equation (g·mg^{-1} min^{-1}). A plot of t/q versus time (t) would yield a line with a slope of $1/q_e$ and an intercept of $1/\left(k_2 q_e^2\right)$, if
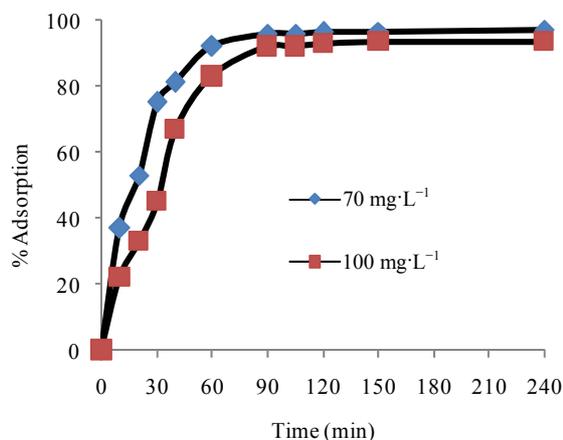

Figure 5. Effect of contact time on the adsorption of Fe(III) onto LTA zeolite.

Table 2. Pseudo-first order and Pseudo-second order kinetics rate constants for Iron(III) on zeolite LTA.

First order kinetic model		Second order kinetic model	
R^2	k_1 (min^{-1})	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)
0.697	0.03	0.976	2×10^{-5}

the second order model is a suitable expression.

From the plot between $\ln(q_e - q_t)$ versus time t and the plot of t/q versus time t, the rate constant of firs and second order of adsorption, also R^2 were determined. **Table 2** shows the kinetic parameters of adsorption of Fe (III) onto LTA zeolite. The kinetic model with a higher correlation coefficient R^2 was selected as the most suitable one. Results are shown the adsorption of Fe(III) onto LTA zeolite is followed by pseudo-second order.

4. Conclusion

LTA zeolite was successfully obtained in two steps. FTIR, XRD and SEM results confirmed the formation of crystalline form of LTA zeolite. The LTA zeolite was used for iron removal from water. Results show that at contact time 60 min and pH of 6, the maximum iron removal falls down.

5. Acknowledgments

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