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Removal of Fe^{3+} from Aqueous Solution by Natural Apatite

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ABSTRACT

The feasibility of natural apatite for adsorptive removal of Fe^{3+} from aqueous solution was investigated. Batch experiments were performed as function of process parameters such as contact time, initial concentration of Fe^{3+}, temperature, apatite dosage and pH. The natural apatite exhibited a high performance for the removal of Fe^{3+} from aqueous solution. The pH value clearly affects the removal mechanism of Fe^{3+} by natural apatite. At low pH value, dissolution/precipitation is the main effect. The effect of hydrolyzation increased with the pH value. After the pH value above 5.0, hydrolyzation is the main effect. The adsorption isotherms demonstrated that the adsorbent behaved in a favorable manner for Fe^{3+} adsorption. The experimental data were well fitted with Langmuir isotherm.

KEYWORDS

1. Introduction

The tremendous increase in the use of heavy metals over the past few decades has eventually resulted in an increased flux of metallic substances in the environment. The heavy metals are of special concern because they are non-degradable and persistent. From the view of environmental protection, heavy metal ions should be removed from the source to avoid pollution of natural waters and subsequent metal accumulation in food chain. Various technological methods, such as precipitation, cementation, sedimentation, filtration, coagulation, flotation, complexing, solvent extraction, membrane separation, electrochemical technique, biological process, reverse osmosis, ion exchange and adsorption have been used for the removal of toxic heavy metals from wastewater. Among these methods, adsorption is a cost-effective technique and simple to operate [1-3]. The adsorption process usually used natural organic or inorganic materials which are particularly abundant and inexpensive. These natural materials include bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/ algae/alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton [4].

The presence of iron ions as one of the heavy metals in ground and industrial water becomes toxic at high level and then may cause environmental and human health problems [5-8]. Iron ions are attracting wide research attention since they are found in many manufacturing industries such as coatings, car, aeronautic and steel industries [9]. Many absorbents have been reported for removal of iron ions (Fe^{2+} or Fe^{3+}), such as bacterias [9, 10], chitin [11], palm fruit bunch and maize cob [12], *Bengal gram* husk [13], tur dal husk [14], eggshells [15], ash [16], sawdust [17], activated carbon [18], natural zeolite [19], bentonite and quartz [20], and apatite [21-23].

The general formula of apatite is $M_{10}(XO_4)_6Y_2$ (M = Ca^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, ...; $XO_4 = PO_4^{3-}$, VO_4^{3-}, AsO_4^{3-}, ...; Y = F$^-$, OH$^-$, Cl$^-$, ...) [23-30]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) is a member of apatite mineral family. It is an ideal adsorptive material for long-term containment because of its high sorption capacity for heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability and low cost [24]. There are many reports on the use

of HAP for stabilizing a variety of metals such as Co, Pb, Cu, Zn, Cd, Sb, Cr [23-28]. Different mechanisms for metal cations retention such as ion exchange, adsorption, dissolution/precipitation and formation of surface complexes have been proposed [26,29,30].

Ma *et al*. [23] have reported the use of hydroxyapatite for removal of heavy metals (Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Fe^{2+} and Al^{3+}) in batch experiments. In Fe^{2+} removal experiments, these authors only observed some retention of Fe^{2+} on new phases but no Fe^{2+} solids were detected by XRD. Gschwend and Reynolds [31] have reported the *in-situ* subsurface formation of colloidal Fe phosphate solids, which were attributed to the interaction of different phosphate species combined with Fe^{2+} released from the solids of the aquifer. It was suggested that the colloidal solids were vivianite. Oliva *et al*. [21] have studied the sorption of Fe^{2+} onto biogenic hydroxyapatite with pH 4.5 and 75 mg/L Fe^{2+}. The results indicated that apatite is an effective absorbent for the removal of Fe^{2+}. The study of iron adsorption by eggshells indicated the reversible and exothermic nature of sorption [15]. However, so far there has been no report on the use of natural apatite for removing Fe^{3+} from aqueous solution.

In this work, we presented the use of natural apatite for removal of Fe^{3+} from aqueous solution. The influencing factors such as pH, initial concentration, contact time, dosage of the adsorbent and temperature have been systematically investigated. And the removal mechanism of Fe^{3+} by natural apatite was discussed.

2. Materials and Methods

2.1. Materials

Natural apatite used here comes from a phosphate rock in Yichang, China. The sample was ground in a ball mill and sized by wet sieve analysis separately for experimental work. In the present studies, rock phosphate of 74 - 150 μm size range was used for the removal of Fe^{3+} from aqueous solution. Mineralogical analysis of rock phosphate sample reports mainly of apatite and quartz. Dolomite, calcite and iron oxide are the other associated gangue minerals.

2.2. Experimental Procedure

Iron solutions were prepared by dissolving Fe(NO$_3$)$_3$ analytical grade. Adsorption experiments were carried out in the batch reactors (200 mL) containing natural apatite as adsorbent and 50 mL of Fe^{3+} solutions having different concentrations (10, 50, 100, 150 and 200 mg/L) and pH (1 - 7) was adjusted with 0.1 M HNO$_3$ and 0.1 M NH$_3$·H$_2$O. In order to investigate the effect of the temperature on the adsorption, four adsorption temperatures (273, 293, 303, and 323 K) were studied. The suspen-

sions were stirred with a magnetic stirring bar inside the reactor for different time. Then, the suspensions were filtered through a 0.45 μm membrane filter and the Fe^{3+} concentration in the filtrate was analyzed using UV/Vis spectrophotometer (Shimadzu, UV-2550) at 510 nm [32].

The morphologies and microstructures of natural apatite and the reaction production were observed by using a JSM-5510 scanning electron microscopy (JEOL, Japan). The crystalline phase of natural apatite and the reaction production were detected by powder X-ray diffraction (Bruker D8 ADVANCE, Germany) using Cu Kα radiation.

3. Results and Discussions

3.1. Effect of Initial Fe^{3+} Concentration

The effect of initial Fe^{3+} concentration in the range of 10 to 200 mg/L on adsorption was investigated (**Figure 1**). It is evident from **Figure 1** that the removal efficiency of Fe^{3+} decreased with the increasing initial Fe^{3+} concentration. And the equilibrium adsorption capacity increased with increasing initial concentration indicating that higher initial concentration of Fe^{3+} can enhance the adsorption process. The initial Fe^{3+} concentration provides the necessary driving force to overcome the resistances to the mass transfer of iron between the aqueous phase and the solid phase. The increase in initial Fe^{3+} concentration also enhances the interaction between iron and apatite powder. Therefore, an increase in initial Fe^{3+} concentration enhances the adsorptive uptake of Fe^{3+}. This is due to increase in the driving force of concentration gradient, as an increase in the initial Fe^{3+} concentration. The percentage of Fe^{3+} removal efficiency was found to be 92.90% for 10 mg/L Fe^{3+} and 40.03% for 200 mg/L Fe^{3+}. The experimentally derived maximum removal capability of natural apatite was 0.179 mmol/g.
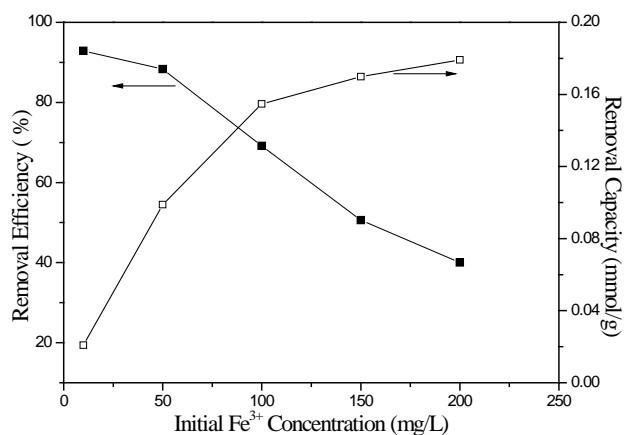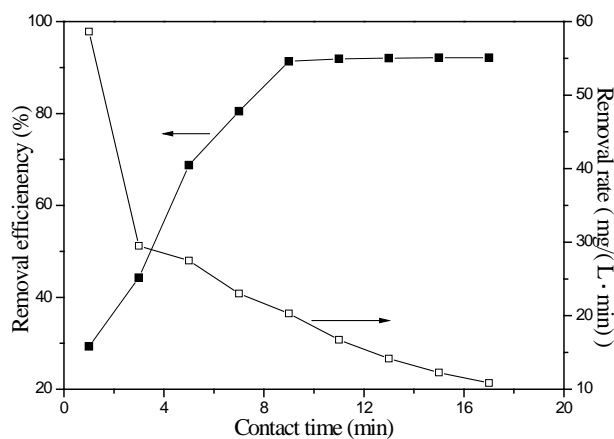

Figure 1. Effect of initial concentration on the removal Fe^{3+} by natural apatite (the dosage = 8 g/L, initial pH = 2 and contact time = 10 min).

3.2. Effect of Contact Time

The effect of contact time was investigated in the range of 1 min to 17 min. The result (**Figure 2**) indicated that the removal rate of Fe^{3+} increased at initial period of contact time and it decreased gradually with time until the removal rate reached an equilibrium point. The equilibrium time was established within 9 min. This is probably due to the number and availability of natural apatite surface active sites, as well as the highest driving force for the mass transfer, caused the rapid Fe^{3+} uptake at the beginning. Another reason is that the addition of natural apatite increases the pH of solution, which leads to the facile hydrolyzation of Fe^{3+}. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the natural apatite particles.

3.3. Effect of Natural Apatite Dosage

The effect of apatite dosage was studied in the range of 1 g/L to 28 g/L for the initial Fe^{3+} concentration of 200 mg/L at pH 2.85. The variation of the removal efficiency of Fe^{3+} ions and the pH of filter with natural apatite dosage is shown in **Figure 3**. It can be observed that the removal efficiency increases quickly with the increase in natural apatite dosage initially; but beyond a certain value 20 g/L, the removal efficiency reaches almost a constant value. This trend is expected because the number of adsorbent particles increases with increasing the natural apatite dosage which leads to more Fe^{3+} attached onto their surfaces. The significant increase in uptake was observed when the dose was increased from 4 to 20 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. A maximum removal efficiency of 98.10% was observed at ad-
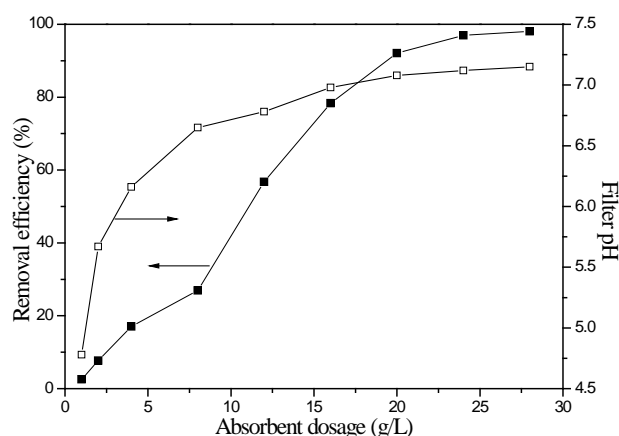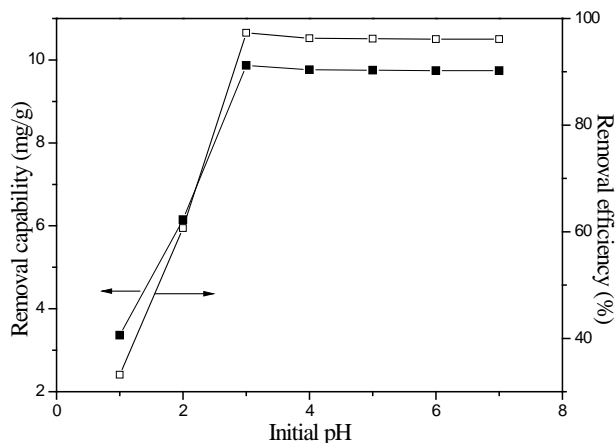

Figure 3. Effect of dosage on the removal efficiency of Fe^{3+} and filter pH.

sorbent dosage of 28 g/l. The red brown insoluble iron hydroxide increased with increasing the dosage of natural apatite was observed in the filtration residue. That is to say, the hydrolyzation of Fe^{3+} increased very dramatically with increasing the dosage of natural apatite. The reason is that the addition of natural apatite can increase the pH of solution, as a result of sorption of H$^+$ ions from the acid solution by surface active sites [33]. The result (**Figure 3**) indicates that the natural apatite dosage has an obvious effect on pH up to 16 g/L. The surface sorption active sites of H$^+$ ions are increased with increasing the dosage of natural apatite. The active sites can adsorb most of H$^+$ ions in the solution at the dosage 16 g/L which leads to the change of filter pH to 7. Any further addition of the natural apatite beyond this did not cause any significant change in the pH. From the discussion above, the adsorption effect and precipitation effect are may be exist together to remove Fe^{3+} in aqueous solution.
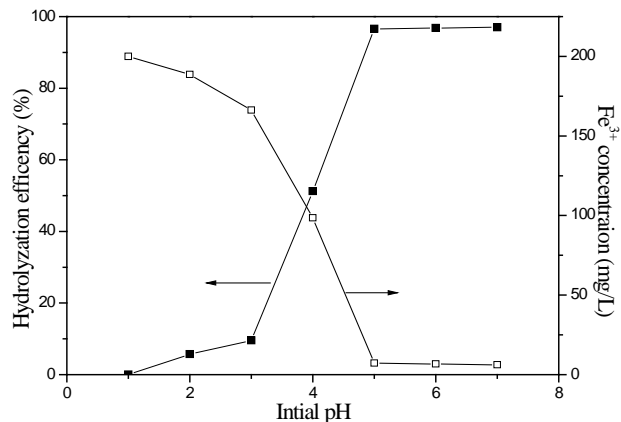
3.4. Effect of Initial pH

One of the most critical parameters in the adsorption process of metal ions from aqueous solutions is the pH of the medium. Hence, the effect of initial pH on removal of Fe^{3+} ions from aqueous solution on natural apatite was studied. The initial pH values was ranged from 1 to 7 at room temperature (20 °C) and the initial concentration of Fe^{3+} ions was chosen at 200 mg/L. The natural apatite dosage was taken as 20 g/L. The variation of the removal efficiency of Fe^{3+} ions and removal capability of Fe^{3+} ions with initial pH is shown in **Figure 4**. It can be observed that the removal efficiency is increased dramatically with increasing the initial pH, but beyond a certain value 3.0, the removal efficiency reaches almost a constant value. It is known that heavy metal ions convert to insoluble hydroxide and precipitated from the solution at higher value, which lead to the reduction of metal ions. Therefore, both adsorption and precipitation may be re-


Figure 2. Effect of contact time on the removal Fe^{3+} by natural apatite (initial pH = 2.85, the dosage = 20 g/L, initial Fe^{3+} concentration = 200 mg/L).

Figure 4. Effect of initial pH on the removal Fe^{3+} by natural apatite (contact time = 10 min).

sponsible to remove Fe^{3+} in aqueous solution.

To understand the removal mechanism, the effect of pH on the hydrolyzation of Fe^{3+} was investigated. The initial concentration of Fe^{3+} ions was 200 mg/L whereas the initial pH values were adjusted to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 by HNO$_3$ and NH$_3$·H$_2$O solutions. The solutions were filtered after stirred 10 min and the Fe^{3+} concentration in the filtrate was analyzed. The result (**Figure 5**) indicated that initially the reduction of Fe^{3+} ions in the solution was not strongly. But beyond pH 3.0, the reduction increased dramatically with increasing pH and almost reached a constant value after the pH beyond 5.0. That is to say, the insoluble iron hydroxide increased with increasing pH. After pH 3.0 the hydrolyzation increased dramatically with increasing pH and almost reached a constant value after the pH beyond 5.0. The SEM images of the natural apatite and the reaction production between natural apatite and aqueous Fe^{3+} at pH 1 and pH 5 are shown in **Figure 6**. The XRD pattern of the natural apatite and the reaction production between natural apatite and aqueous Fe^{3+} at pH 1 and pH 5 are shown in **Figure 7**. It can be seen that natural apatite dissolved clearly at pH 1 solution (**Figure 6(b)**), and the XRD pattern of the reaction production (**Figure 7**) revealed the presence of FePO$_4$.2H$_2$O corresponding to the respective diffraction angles as 17.03°, 17.91°, 20.88°, 22.06°, 24.27°, 32.33°, 63.49°, 64.07° and 65.48°. The SEM images of the reaction production between natural apatite and aqueous Fe^{3+} at pH 5 (**Figure 6(c)**) indicated that there are some gel covered on the natural apatite surface, and the XRD pattern of reaction production (**Figure 7**) revealed the presence of β-FeOOH corresponding to the respective diffraction angles as 24.13°, 35.66°, 56.06°, 61.97° and 64.33°. Accordingly, we conclude that the pH value clearly affects the removal mechanism of Fe^{3+} by natural apatite. At low pH value, dissolution/precipitation is the predominant mechanism. The effect of hydrolyza-

Figure 5. Effect of initial pH on the hydrolyzation efficiency and the concentration of Fe^{3+} in the solution.
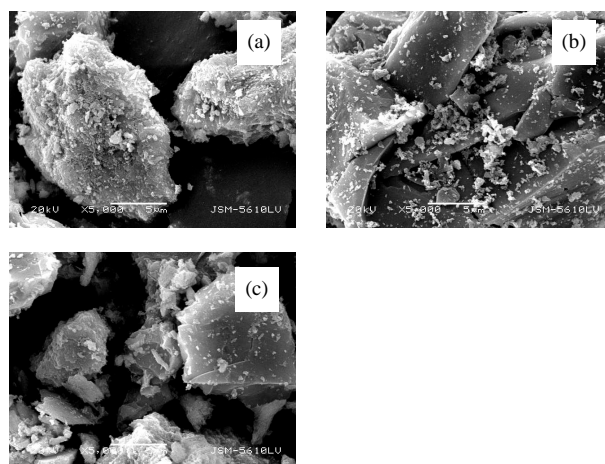
Figure 6. SEM images of natural apatite (a) and the reaction production between natural apatite and aqueous Fe^{3+} at pH 1 (b) and pH 5 (c).
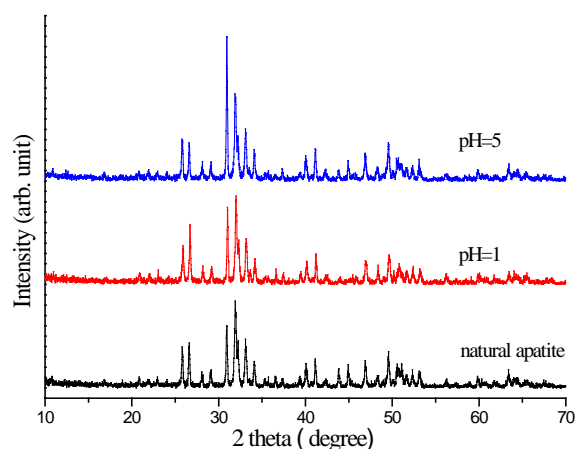
Figure 7. XRD pattern of the natural apatite and the reaction production between natural apatite and aqueous Fe^{3+} at pH 1 and pH 5.

tion increased with the pH value. After the pH value above 5.0, hydrolyzation is the predominant mechanism.

3.5. Effect of Temperature

The temperature effect on removal of Fe^{3+} at 273 K, 293 K, 303 K, and 323 K was studied for the initial Fe^{3+} concentration 200 mg/L at pH 2.85. **Figure 8** shows the relationship between the removal efficiency of Fe^{3+} and temperature. It is found that the adsorption of Fe^{3+} increases with increasing temperature. The increase in the removal efficiency of Fe^{3+} at increased temperature indicates that the adsorption of Fe^{3+} ions onto natural apatite is endothermic in nature.
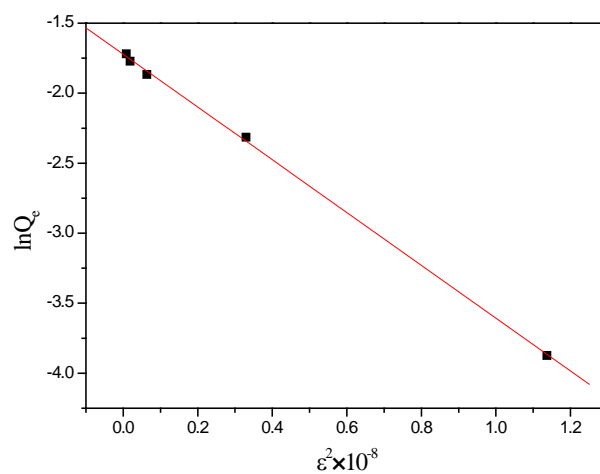
3.6. Adsorption Isotherms

The capacity of the adsorption isotherm plays an important role in the determination of the maximum capacity of adsorption. It also provides a panorama of course taken by the system under study in a concise form and indicates how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbent commercial applications for the specified solute. In order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained. The experimental equilibrium data were fitted using Langmuir, DKR and Freundlich models (**Table 1**). Sorption parameters are as follows: C_e (mmol/L) is the equilibrium concentration of Fe^{3+} in the solution, Q_e (mmol/g) is the equilibrium concentration of Fe^{3+} at natural apatite surface, q_m (mmol/g) is the maximum sorption capacity, K_L (L/mmol) the Langmuir constant related to the energy of adsorption, β (mol^2/J^2) the DKR constant related to adsorption energy, ε (J/mol) the Polanyi potential, and K (mmol^{1-n} L^n g^{-1}) and n are the Freundlich constants related to the capacity and intensity of the sorption process. The graphical illustration of the linear data fitting is shown in **Figure 9**, while calculated sorption parameters and the degree of correlation between the sorption data and applied models are listed in **Table 1**.
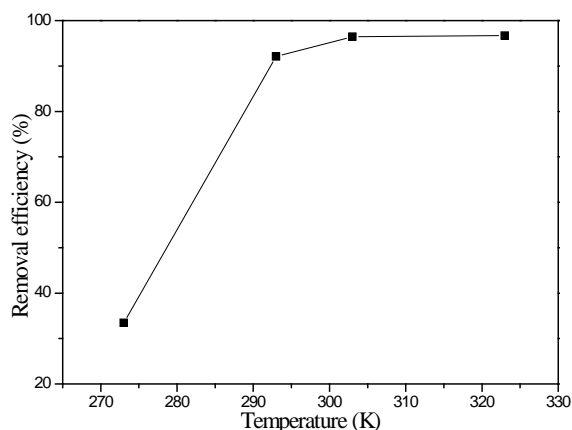
Figure 8. Effect of temperature on the removal efficiency of Fe^{3+} (the natural apatite dosage = 20 g/L, contact time = 10 min).
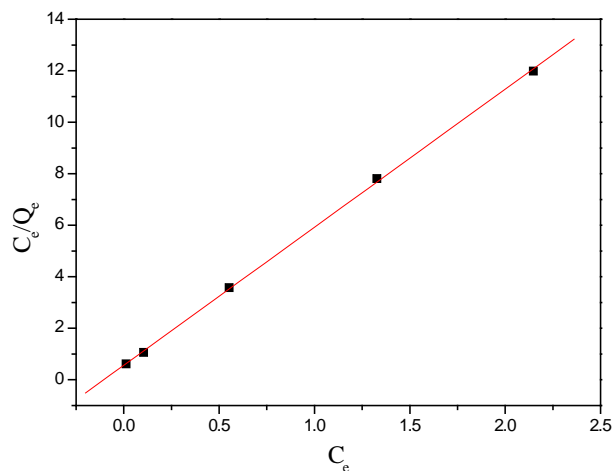
(c)

(b)
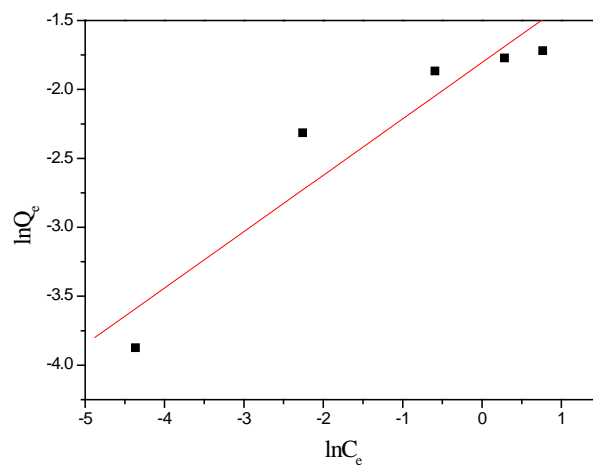
(c)

Figure 9. Langmuir(a), DKR(b) and Freundlich (c) isotherms for the adsorption of Fe^{3+} onto natural apatite.

It is obvious from **Table 1**, that the highest correlation coefficient was obtained using Langmuir model, suggesting that the Fe^{3+} ions were sorbed by natural apatite

Table 1. Correlations coefficients and sorption parameters obtained using Langmuir, DKR and Freundlich model.

Model	Equation	Sorption Parameters	R^2
Langmuir	$\dfrac{C_e}{Q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{q_m K_L}$	$q_m = 0.174$ (mmol/g) $K_L = 10.027$ (L/mmol)	0.999
DKR	$\ln Q_e = \ln q_m - \beta \times \varepsilon^2$ $\varepsilon = R \times T \times \ln\left(1 + \dfrac{1}{C_e}\right)$	$q_m = 0.170$ (mmol/L) $\beta = 1.736 \times 10^{-8}$ (mol^2/J^2)	0.980
Freundlich	$n\,Q_e = \ln K + n \ln C_e$	$K = 0.152$ (mmol^{1-n}L^{n}g^{-1}) $n = 0.394$	0.946

in a monolayer. Furthermore, the q_m value calculated by this equation corresponds well with the experimentally obtained sorption capacity which indicates that the Langmuir equation better fits the experimental data.

Knowing the Langmuir constant, K_L, the dimensionless separation factor (R_L) can be derived using the expression [34]:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 (mol/dm^3) denotes the initial solution concentration. R_L values indicate that the sorption process is: unfavorable for $R_L > 1$, linear for $R_L = 1$, favorable for $0 < R_L < 1$, or irreversible for $R_L = 0$.

For initial Fe^{3+} concentration range from 1.8×10^{-4} to 3.6×10^{-3} mol/dm^3, used in this study, calculated R_L values were between 0.353 and 0.027, which indicated that the adsorption of Fe^{3+} by natural apatite was favorable.

4. Conclusion

The present investigation showed that natural apatite was an effective adsorbent for the removal of Fe^{3+} from aqueous solutions. The removal of Fe^{3+} by natural apatite was found to be dependent upon pH, contact time, initial Fe^{3+} concentration, dosage of the adsorbent and temperature. The removal efficiency of Fe^{3+} increases with the increase of adsorbent dosage and decreases with the increase of initial Fe^{3+} concentration. The pH value clearly affects the removal mechanism of Fe^{3+} by natural apatite. At low pH value, dissolution/precipitation is the predominant mechanism. The effect of hydrolyzation increased with the pH value. After the pH value above 5.0, hydrolyzation is the predominant mechanism. The equilibrium data were analyzed using Langmuir, DKR, and Freundlich isotherms. The experimental data yielded excellent fits within the following isotherms order Langmuir > DKR > Freundlich, based on its correlation coefficient values.

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