

EQUILIBRIUM ADSORPTION ISOTHERM OF U(VI) AT pH4 AND pH5 ONTO SYNTHETIC MAGNETITE NANOPARTICLES

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ABSTRACT

The adsorption features of synthetic magnetite nanoparticles have been investigated for removal of uranyl ions from nitric solutions. These magnetic nanoparticles can be used to adsorb contaminants in wastewater and can subsequently be removed from the medium by a magnetic process because their superparamagnetic behavior. The magnetite nanoparticles were synthesized by simultaneous precipitating of Fe^{2+} and Fe^{3+} ions in a NaOH solution. Batch experiments were carried out to investigate the adsorption of UO_2^{2+} ions from nitric solution, pH 4 and 5, onto magnetic nanoparticles. The adsorption equilibrium was attained with 30 min of contact time. Two min of application of a magnetic field were sufficient for the removing of magnetite nanoparticles from the liquid medium. Equilibrium adsorption isotherm was evaluated using Freundlich and Langmuir models. The adsorption isotherm fitted well to the Langmuir equation with maximum adsorption capacity of 27 mg g^{-1} . The adsorption was between 40% and 80% under conditions studied. The results showed that the nanoparticles of synthetic magnetite have high adsorption capacity for uranyl ions so they present good perspectives of application for the processes of uranium liquid waste treatment.

1. INTRODUCTION

Elevated levels of U are introduced in rivers, soils and groundwater by the release from uranium mill and milling, by agricultural application of phosphate fertilizers [1] and by the phosphogypsum, a by-product from the production of phosphoric acid from natural phosphate rock, which are associated with uranium [2, 3]. Furthermore, activities related to nuclear industry [4] are possible sources of release of radioactive wastewaters to the environment. Due to its radioactivity and toxicity, uranium is a hazardous contaminant in the environment. Therefore, it is of great importance the eliminating uranyl ions from wastewaters and the need of economic and effective methods not only for the removal of uranyl ions, but also for other metals from environmental samples, has resulted in the development of new separation technologies.

Adsorption process combined with magnetic separation has been used in a variety of processing of separation of minerals, organic compounds and metals and more recently as magnetic nanotechnology in wastewater treatment and environmental remediation processes. Magnetic nanotechnology is the combination of adsorptive and magnetic properties in a particle type [5]. The advantages of this separation technology are that the contaminant adsorbed onto magnetic particles can be removed, for example, from the wastewater when an external magnetic field is applied. After magnetic separation, the contaminant can be

desorbed from the magnetic particles, and the recovered magnetic particles can turn back to the wastewater and be reused.

These magnetic particles generally consist of nanoparticles of magnetite that have superparamagnetic properties [6] and the modified surface to enhance the adsorption efficiency.

In this work synthetic magnetite nanoparticles of non-modified surface were prepared and some adsorption features for removal of uranyl ions from nitric solutions were investigated.

2. EXPERIMENTAL

2.1. Materials

All chemicals used ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ArsenazoIII, NaOH and HNO_3) were analytical grade and obtained from Merck (USA). Standard solution of uranyl nitrate was prepared by dissolution of U_3O_8 nuclear pure obtained from Environment and Chemistry Centre at Nuclear and Energy Research Institute (IPEN), BR.

2.2. Preparation of Magnetic Nanoparticles

Magnetic nanoparticles studied were synthesized using chemical precipitation method [7]. First, an aqueous solution of Fe^{2+} and Fe^{3+} was prepared with a molar ratio of 1:2. Then 5 mol L^{-1} NaOH was added drop-wise into the solution until reaches pH 11. After that, the stirrer was switched off and the precipitate settled gradually. The precipitate was isolated by an external magnetic field and the supernatant was decanted. To obtain pure and neutral pH product, synthesized material was rinsed with distilled water and the rinse was discarded. The rinsing was repeated until it reaches pH~7 and the precipitate was then dried. Finally, the magnetite nanoparticles, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, were obtained.

2.3. Batch Adsorption Studies

The batch adsorption experiments were carried out on a rotary shaker using 15 mL glass flasks containing 1 mL solution of uranyl nitrate and 15 mg of magnetic nanoparticles. The mixtures were shaken at room temperature of $27 \pm 2^\circ\text{C}$ and 360 rpm for a time interval. The mixture was separated via external magnetic field for 2 min and the final concentration of uranium in the supernatant was measured at 650 nm using a spectrophotometer UV-Vis, mod. B582 Micronal, by arsenazo III method [8]. An investigation for the effect of agitation time on U adsorption, from nitric solution of pH 4 and 5, was performed to determine the equilibrium time. The removal percentage was determined by the Eq. 1. All experiments were performed in duplicate and the averaged values were taken.

$$\text{Removal \%} = (C_0 - C) \times 100/C_0 \quad (1)$$

Where C_0 is the initial concentration of U ions (mg L^{-1}) in the solution and C is the final concentration of U ions (mg L^{-1}) after contact by shaking.

Studies of adsorption equilibrium isotherm were conducted varying the U concentration from 50 to 500 mg L^{-1} at pH 5, for 40 min of shaking at room temperature. These data were evaluated by Langmuir and Freundlich adsorption isotherm equations to interpret the efficiency of metal sorption [9].

Langmuir isotherm model assumes monolayer adsorption, and is presented by the Eq. 2 and 3.

$$\text{Langmuir model: } q_{\text{eq}} = Q_{\text{max}} * K_L * C_{\text{eq}} / (1 + K_L * C_{\text{eq}}) \quad (2)$$

$$\text{Langmuir model in linear form: } C_{\text{eq}}/q_{\text{eq}} = 1/(Q_{\text{max}} * K_L) + 1/Q_{\text{max}} * C_{\text{eq}} \quad (3)$$

Where q_{eq} is the metal amount adsorbed per unit mass of adsorbent (mg g^{-1}), C_{eq} is the equilibrium concentration of metal in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L is the constant related to the free energy of adsorption. A straight line is obtained by plotting $C_{\text{eq}}/q_{\text{eq}}$ against C_{eq} and the slope and intercept are used to calculate the Q_{max} and K_L , respectively.

The Freundlich model is presented by the Eq. 4 and 5, which indicates that the surface of adsorbent is heterogeneous [9].

$$\text{Freundlich model: } q_{\text{eq}} = K_F * C_{\text{eq}}^{1/n} \quad (4)$$

$$\text{Freundlich model in linear form: } \log q_{\text{eq}} = \log K_F + 1/n * \log C_{\text{eq}} \quad (5)$$

Where K_F is a parameter of relative adsorption capacity of the adsorbent related to the temperature and n is a characteristic constant for the adsorption system. A plot of $\log q_{\text{eq}}$ against $\log C_{\text{eq}}$ gives a straight line and the slope and intercept correspond to $1/n$ and $\log K_F$, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Contact Time

The suspended particles of the magnetite exhibited a strong magnetization in the presence of a magnetic field, being easily attracted and removed from aqueous solutions using a magnet, so indicating the possibility of application of the magnetic separation process. Two min of application of a magnetic field were sufficient for the removing of magnetite nanoparticles from the liquid medium.

The effect of the contact time on uranium adsorption from nitric solutions (100 mg L^{-1}) at pH 4 and 5 was investigated and shown in Fig. 1. The removal percentage increases with shaking time and reveals a rapid removal during the first few minutes of contact until a state of equilibrium is reached in 30 min at room temperature. The uptake percentages attained after equilibrium are 40% and 80% for U adsorption onto magnetite nanoparticles from nitric solutions pH 4 and 5, respectively. The results showed that the sorption of U(VI) on magnetite, in form of UO_2^{2+} ions, is favored at higher pH. Although the amount adsorbed at equilibrium differs at different pH, the time for attaining equilibrium remains almost unaffected in both cases of pH studied. Based on these results, a shaking time of 40 min was assumed to be suitable for subsequent experiments of sorption isotherm in solutions of pH 5.

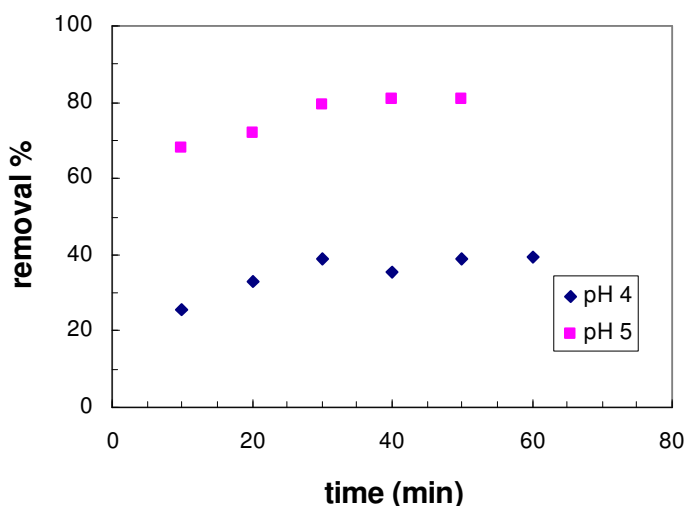


Figure 1. Influence of the contact time on UO_2^{2+} adsorption from nitric solutions (100 mg L^{-1}) at pH 4 and 5 by magnetite nanoparticles.

3.2. Adsorption Isotherm

The equilibrium adsorption isotherm was obtained by plotting the amount of U sorbed on magnetite (q_{eq}) against equilibrium concentration (C_{eq}) in the solution, and was presented in Fig. 2. The Figure shows that the amount of U sorbed increases with an increase in equilibrium concentration and attains a value related to the maximum adsorption capacity of the magnetite. The linearized Langmuir and Freundlich isotherms were applied for the experimental data and the parameter values were calculated and presented in Table 1. The Langmuir and Freundlich plots were put in Fig.3.

Table 1 shows that the value of $1/n$ is less than one, indicating a nonlinear sorption of U in the concentration range studied. The observed values of K_F as $2.88 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{1/n}$ confirms a significant affinity of uranyl ions by magnetite.

The value of the correlation coefficient of the Langmuir model is higher than of the Freundlich model. This indicates the adsorption phenomenon was best described by this model over the concentration range studied. According to the Langmuir model, a monolayer of adsorbed U was formed with a maximum adsorption capacity of magnetite of 27 mg g^{-1} .

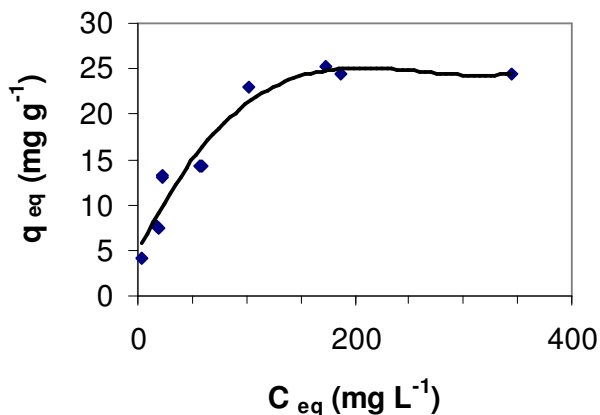


Figure 2. Equilibrium adsorption isotherm for UO_2^{2+} adsorption onto magnetite nanoparticles at $27\pm 2^\circ\text{C}$.

Fig. 3 compares the predicted data by the models of Langmuir and Freundlich with the experimental data. The Figure shows that the Freundlich model fitted the experimental data reasonably well, and the Langmuir model fitted best, being very close to experimental isotherm corroborating the value of r^2 of the Langmuir higher than the Freundlich model.

Table 1. Parameter values of the models of Langmuir and Freundlich isotherms for adsorption of UO_2^{2+} ions onto magnetite nanoparticles at $27\pm 2^\circ\text{C}$, from nitric solutions in pH 5.

Isotherm model	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	$1/n$	K_F ($\text{mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{1/n}$	correlation coefficient, r^2
Langmuir	27	0.0316	-----	-----	0.978
Freundlich	-----	-----	0.405	2.88	0.920

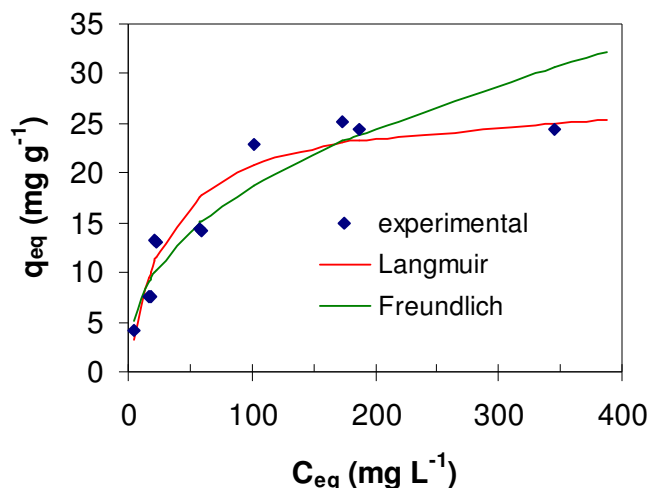


Figure 3. Comparison between the experimental equilibrium adsorption isotherm for UO_2^{2+} ions onto magnetite nanoparticles and the isotherm models, at $27\pm 2^\circ C$.

4. CONCLUSIONS

Nanoparticles of magnetite were prepared and investigated for U removal as an alternative magnetic adsorbent for UO_2^{2+} ions from radioactive wastewaters.

From the uranium nitric solution of 100 mg L^{-1} (pH 5), it was possible to remove 80% of U(VI) by 15 g L^{-1} magnetite nanoparticles, and the maximum uranium adsorption capacity of the magnetite nanoparticles was obtained to be 27 mg U per g of dry magnetite. The magnetite nanoparticles can be easily attracted and removed from aqueous solutions using a magnet. The results showed that the nanoparticles of synthetic magnetite have high adsorption capacity for uranyl ions so they present good perspectives of application for the processes of uranium liquid waste treatment. They are inexpensive, no toxic and environmentally safe.

Magnetic nanotechnology of magnetite nanoparticles is a promising alternative of treatment process for the removal of uranium from the wastewater. But, further studies are needed, including influence of others metals and multi-component adsorption tests in order to study adsorption under competition, for application in wastewater treatment.

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