



Uranium removal from groundwater by natural clinoptilolite zeolite: Effects of pH and initial feed concentration

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ABSTRACT

Adsorption of uranium (VI) on a natural clinoptilolite zeolite from Sweetwater County, Wyoming was investigated. Batch experiments were conducted to study the effects of pH and initial feed concentrations on uranium removal efficiency. It was found that the clinoptilolite can neutralize both acidic and low basic water solutions through its alkalinity and ion-exchange reactions with U within the solution, and adsorption of uranium (VI) species on clinoptilolite not only depends on the pH but also the initial feed concentration. The highest uranium removal efficiency (95.6%) was obtained at initial uranium concentration of 5 mg/L and pH 6.0. The Langmuir adsorption isotherm model correlates well with the uranium adsorption equilibrium data for the concentration range of 0.1–500 mg/L. From the experimental data obtained in this work, it was found that the zeolite sample investigated in this work is a mixture of clinoptilolite-Na zeolite and mineral impurities with a relatively large specific surface area (BET of 18 m²/g) and promising adsorption properties for uranium removal from contaminated water.

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1. Introduction

Uranium is present in the environment as a result of leaching from natural deposits, discharge from mill tailings, emissions from the nuclear industry, combustion of coal and other fossil fuels, and use of uranium-containing phosphate fertilizers. Naturally occurring uranium is a mixture of three radioisotopes (234U, 235U and 238U), but majority of them are 238U isotope (99.27%). Uranium is a radioactive heavy metal that can cause cancer. Its primary toxic effect when consumed in water is that of heavy metals [1,2]. Heavy metals, like uranium, lead, cadmium, and arsenic, are deposited in the kidneys and cause irreparable damage to the main filtering mechanism of the body. The maximum uranium level in drinking water recommended by the World Health Organization [3] is 15 µg/L, and the maximum contaminant level (MCL) set by the USEPA [4] for drinking water standard is 20 µg/L.

Several methods are available for removing uranium from drinking water. Ion-exchange is the most efficient removal method because it can remove about 98% of the uranium from water. However, it generates concentrated liquid wastes that must be disposed of. Other methods for removing uranium include chemical clarification that uses ferric sulfate or aluminum sulfate [5], precipitation [6], membrane filtration [7], and reverse osmosis [8]. The major limitation for these methods is the proper disposal of the resulting

sludge that contains high levels of the metal and other contaminants.

Natural zeolites, a group of crystalline alumina-silicates with adsorption and ion-exchange capabilities, have gained increasing attention in drinking water purification [9,10,11]. Studies have been conducted to investigate the effects of sorption kinetics, pH, concentration, and temperature on uranium removal efficiency [12,13,14]. However, the initial concentrations reported in these studies covered a very limited range and no definite conclusion was drawn regarding its effect on uranium removal efficiency in the adsorption process.

The objective of this study was to investigate the effect of pH and initial concentration on the adsorption of uranium by a natural clinoptilolite zeolite from Sweetwater County, Wyoming. Batch adsorption equilibrium studies were carried out with aqueous solutions having initial uranium concentrations ranging from 0.01 mg/L to 500 mg/L. The experimental results obtained in this work will help us to understand the adsorption equilibrium and kinetics of uranium adsorption on natural clinoptilolite zeolite, and provide valuable insights on adsorption breakthrough process development and implementation.

2. Materials and methods

2.1. Characterization of adsorbent material

The natural clinoptilolite zeolite used in this study came from a zeolite deposit located Southeast of Bitter Creek in Sweetwater

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County, Wyoming. It was supplied by Gas Separation Technology, LLC, Denver, Co., USA. Physical and chemical properties of the clinoptilolite zeolite were determined by SEM, XRF, XRD, and N₂-adsorption analyses. Prior to SEM analysis the sample was sieved (mesh size 14 × 30), washed with distilled water, and dried at room temperature for 48 h. The dried zeolite sample was then coated with a gold film to alleviate charging and improve resolution, and placed in a scanning electron microscope (Hitachi S-3400N) for analysis.

Sample for crystal phase structure and crystal size analysis was crushed in a mortar and sieved (<325 mesh). Analysis was performed in a desktop Rigaku XRD apparatus (MiniFlex-II). The XRD pattern was obtained on a powder clinoptilolite zeolite sample (mesh <350) with a CuKα X-ray tube operated at 30 kV and 15 mA. By matching the XRD pattern with the built-in ICDD database in the equipment, we determined the crystal phase structure for the natural clinoptilolite zeolite.

Elemental analysis for major and trace elements in the clinoptilolite was made by using a Rigaku X-ray fluorescence analyzer (XRF) (ZSX, 100-e). Sample for major elemental analysis was prepared by mixing calcined natural clinoptilolite zeolite powder (325 mesh, 900 °C) with lithium tetraborate and lithium metaborate, and by placing the mixture in a muffle furnace at 1100 °C for 30 min. Sample for trace elemental analysis was prepared by mixing zeolite powder (325 mesh) with a binder solution (Ultra bind) in a steel pellet and by pressing the mixture at 20 ton in a press plate for 1 min. The dried samples were then placed in the XRF apparatus.

The BET and Langmuir specific surface area, pore size distribution, and pore volume of the natural clinoptilolite zeolite were determined in an accelerated surface area and porosimetry instrument (Micromeritics ASAP 2020). All the calculations were performed with the built-in software of the ASAP 2020 instrument. The Barrett–Joyner–Halenda (BJH) [15] and Horvath–Kawazoe (H–K) [16] models were selected for the calculation of the volume and pore size distribution.

2.2. Variation of pH with adsorption time

A 500 mg/L uranium stock solution was prepared from a calibration standard solution for ICP-MS containing 1000 mg/L of uranium (VI) oxide in 4% nitric acid. The calibration standard solution was provided by SPC Science, USA. Two 100 mL uranium solutions with 50 mg/L of concentration were prepared from the stock solution and adjusted with 0.10 M NaOH or 0.1 M HCl solution to pH 6.0 and 7.0 respectively. The solutions were then mixed with 1 g of clinoptilolite zeolite in 200 mL high density polyethylene plastic bottles. The bottles were tightly closed and placed in an automatic shaker (model lab-line Orbit No. 359) at 100 rpm for 100 h. A standard pH meter (Accumet Excel XL25, Fisher Scientific) was used during the batch adsorption experiments to monitor the changes on pH in the solutions, every half an hour during the first eight hours and then with decreasing frequency.

2.3. Effect of pH on uranium adsorption

The effect of pH on the uranium adsorption equilibrium was investigated at acidic and basic conditions. The initial pH of 100 mL uranium solutions with 10 mg/L of concentration was adjusted to 3.0, 5.0, 6.0, 7.0, and 9.0 by adding 0.1 M HCl or 0.1 M NaOH solution. The solutions were then mixed with 1 g of clinoptilolite zeolite in 200 mL plastic bottles, closed tightly, and placed in the automatic shaker at 100 rpm. The experiment was conducted under batch conditions for five days to ensure that adsorption equilibrium was obtained. Initial and final pH values were recorded. After stabilization, samples were removed, filtered (0.45 μm nylon) and analyzed with an ICP-MS Spectrometer (Elan DRC-e, Perkin Elmer).

Table 1
Elemental analysis for the natural clinoptilolite zeolite.

Major elements	Concentration wt (%)	Trace elements	Concentration (mg/g)
SiO ₂	64.9	Rb	84
TiO ₂	0.2	Th	19.8
Al ₂ O ₃	12.9	Nb	25
Fe ₂ O ₃	1.4	Sr	415
MnO	0.01	Zr	262
MgO	0.7	Y	24.9
CaO	1.7	Pb	23.1
Na ₂ O	4.4	U	4.2
K ₂ O	1.6	Cr	23
P ₂ O ₅	0.04	Ni	11
Loss on ignition	11.5	Cu	96
		Zn	71
		Ga	16.4

2.4. Equilibrium adsorption of uranium on clinoptilolite zeolites

Uranium solutions with initial concentration ranging from 0.01 mg/L to 500 mg/L were prepared by diluting the corresponding volume of the standard stock solution of 500 mg/L with deionized water (Milli-Q System, resistivity of 18.2 MΩ cm, TOC ≤10 μg/L) to complete 195 mL in 200 mL plastic bottles. The pH of the solutions was adjusted to 6.0 to mimic the drinking water purification condition by adding 0.10 M NaOH or 0.1 M HCl solution. The pH of all solutions was measured with the standard pH meter, and the uranium concentration in the water samples was analyzed with ICP-MS. Two grams of the natural clinoptilolite zeolite sample were added to each bottle. The bottles were then closed tightly and placed in the automatic shaker that was set at a shaking speed of 100 rpm. Based on observed pH variations in the solutions in contact with clinoptilolite after 100 h, the batch adsorption experiments conducted in this work were run continuously for five days to ensure the adsorption equilibrium point for each concentration analyzed. The water samples were then removed from the shaker, filtered (0.45 μm nylon), and analyzed with ICP-MS for uranium concentration. A simple mass balance on the water solution and the adsorbent was carried out to calculate the adsorption amount on the natural clinoptilolite zeolite for each solution concentration. The final uranium concentration remaining in solution was defined as the equilibrium concentration. The adsorption capacity (mg/g) in equilibrium with the final concentration was obtained by dividing the adsorbed amount (mg) with the mass of the adsorbent (2 g).

3. Results and discussion

3.1. Characterization of clinoptilolite

The major and trace elements of the natural clinoptilolite zeolite investigated in this work were determined by XRF elemental analysis and summarized in Table 1. Except for the major components Si and Al, Na is the next component with 4.4 wt.%. The silica to alumina ratio (Si/Al = 5.0) for the clinoptilolite studied provides relatively high negative charges for attracting positive uranium (VI) species. The Si/Al ratio is the most important parameter that determines the crystal structure and ionic charges of the clinoptilolite zeolite as an adsorbent material.

The XRD data of the clinoptilolite zeolite were processed with the Jade 8 XRD analysis software. The data matches well with that of Na-Clinoptilolite (sodium form of clinoptilolite), which has the empirical chemical formula (Na, K, Ca)₂-3(Si,Al)₁₈O₃₆·11H₂O [17]. This finding is consistent with the XRF elemental analysis results listed in Table 1. Some small amorphous particles surrounding the clinoptilolite crystal clusters can be seen in the SEM image of the natural clinoptilolite zeolite shown in Fig. 1. The presence of quartz

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