

# Removal of Uranium from Aqueous Solutions using Ammonium-modified Zeolite

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## ABSTRACT

Batch experiments were conducted to study the effects of contact time, pH (3 to 8), initial concentration, presence of carbonate, sulphate, and competing ions ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$ ) on the adsorption of U(VI) on ammonium-modified zeolite (AMZ). The structural features of the modified zeolite were assessed by Fourier Transform Infra Red Spectroscopy (FTIR) while the metal content was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The removal of uranium was effective and maximal under acidic conditions (pH 3 to 5). The kinetics of adsorption of U-nitrate and U-sulphate on AMZ were described by the pseudo-second-order model ( $R^2 \geq 0.9820$ ). In the presence of  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ , a significant reduction of 67.88 % and 71.63 %, respectively, in uranium uptake was observed. The distribution coefficient,  $K_d$  ( $\text{L g}^{-1}$ ), was in the order of: U-nitrate (1.116) > U-sulphate (0.029) > U-carbonate (0.019), suggesting that AMZ had a high affinity for U-nitrate. The presence of  $\text{Fe}^{3+}$  enhanced the removal of U(VI) from U-nitrate, U-sulphate and U-carbonate by 20.18 %, 72.48 % and 82.43 %, respectively, while the presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  reduced the removal to 19.57 %, 31.60 % and 23.65 %, respectively. AMZ is an effective adsorbent for uranium removal from aqueous solutions dominated by nitrate, carbonate and sulphate.

## KEYWORDS

Adsorption, zeolite-ammonium, uranyl, carbonate, sulphate, nitrate, aqueous solutions.

## 1. Introduction

Gold, platinum, diamond and coal are amongst several minerals that are commonly mined in South Africa. A large proportion of gold (98 %) in South Africa is mined in the Witwatersrand goldfields.<sup>1</sup> When gold is extracted, large amounts of rocks are crushed and processed, producing large quantities of waste in the process. The improper management of this waste has led to many environmental concerns such as erosion and the production of acid mine drainage.<sup>2</sup> Uranium is one of the metals of concern occurring in significant amounts in gold mining waste. The Witwatersrand gold ores have significant concentrations of uranium between 30 and 2000 ppm since uranium occurs as an accessory mineral in the gold ores.<sup>3</sup> The discharges of uranium and associated radionuclides from waste and tailing dumps in abandoned uranium mining and processing sites pose contamination risks to surface and groundwater.<sup>4,5</sup>

The toxic effects due to uranium exposure are based on its chemical and radioactive characteristics. The presence of high levels of uranium (U) compounds in the human body has been reported to affect renal functions, leading to kidney failure.<sup>6</sup> Uranium is also associated with toxicity to crops, livestock as well as aquatic organisms.<sup>7</sup> The maximum uranium level in drinking water recommended by the World Health Organization and the South African Bureau of Standards is  $15 \mu\text{g L}^{-1}$ ,<sup>8,9</sup> the maximum contaminant level (MCL) set by the USEPA for drinking water standard is  $20 \mu\text{g L}^{-1}$ .<sup>10</sup>

Under oxidizing geochemical conditions, the most stable oxidation state of uranium is U(VI)<sup>11</sup> which exists in acidic aqueous solution as the linear uranyl ion,  $\text{UO}_2^{2+}$ . At higher pH, the uranyl ion hydrolyzes extensively, forming monomers [ $\text{UO}_2(\text{OH})^+$ ] and dimers [ $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ]. Both the migration and retardation of uranyl ions in geological environments are

controlled primarily by the sorption of these toxic species to mineral surfaces.<sup>12</sup> Hence, predicting the future fate and transport of uranyl in contaminated sites requires an understanding of the factors affecting their sorption onto minerals. Many parameters govern uranyl sorption behaviour onto minerals; these include: pH, initial uranium concentration, presence and absence of complexing ligands such as sulphates, carbonates, phosphates, nitrates, chlorides and organic acids. Uranyl has been reported to be strongly adsorbed onto many soil constituents including clay minerals such as zeolites under appropriate chemical conditions. Such materials can be used for uranium (VI) remediation of aqueous solutions.<sup>13-15</sup>

Adsorbents such as natural zeolite are cost-effective for the removal of uranium, although their modified versions tend to perform better.<sup>13-14</sup> It should be noted that at times this modification is not deliberate, but may be a result of natural processes in environments where the adsorbents are deployed. For instance, ammonium is one of the dominant components in aqueous systems and may influence the surface properties of such adsorbents. It is on this premise that this study was conducted. It was aimed at assessing the capability of ammonium-modified zeolite (AMZ) to adsorb uranium occurring in different aqueous systems, e.g. nitrate-, sulphate- and carbonate-dominated systems. The latter two of these systems would typically be acid mine drainage (AMD)-impacted and lime-neutralized systems while the former would be expected to dominate in most natural water systems. The adsorption behaviour of uranium on AMZ was studied under various conditions, namely: contact time, pH, uranium initial concentration, solid/liquid (S/L) ratio and the presence of  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$ . Desorption of uranium from the AMZ was also studied to assess the potential re-use of the adsorbent.

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## 2. Materials and Methods

### 2.1. Synthesis and Characterization of AMZ

The natural zeolite used in the study was purchased from Merck, South Africa. The chemical treatment of the zeolite was performed by adding 1 L of 2 M  $\text{NH}_4\text{Cl}$  solution to 100 g of zeolite (fraction 2–3 mm) at 25 °C. The mixture was shaken for 24 h. The solid phase was separated from the solution, washed until all chloride ions had been removed (checked using  $\text{AgNO}_3$  solution). The samples were then dried at 105 °C and stored for further experiments.

Natural and modified zeolites were characterized using X-ray fluorescence (chemical composition, performed in the School of Geosciences at Wits University) and FTIR (Tensor 27, Bruker, Germany) (for the identification of functional groups) while the surface area and cationic exchange capacity (CEC) were determined by the Brunauer-Emmet-Teller (BET surface area and porosity analyzer, (Tristar 3000 Analyzer, Micromeritics, USA) and  $\text{BaCl}_2$  methods<sup>16</sup>, respectively.

### 2.2. Reagents and Standards

Uranium stock solution of 100 mg  $\text{L}^{-1}$  was prepared by dissolving an appropriate amount of uranyl nitrate hexahydrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) obtained from Sigma Aldrich. Working solutions were prepared by serial dilution of the stock solution. Other metal ions stock solutions ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$ ) were prepared by dissolving a known mass of metal chloride salt in deionized water and then diluting to the desired concentration.

### 2.3. Batch Experiments

Batch adsorption experiments were carried out by shaking 1 g of AMZ with 50 mL of U(VI) solution at varying experimental conditions in 250 mL plastic bottles at a speed of 150 rpm. When the adsorption equilibrium was reached, the solution was filtered to separate AMZ and the concentration of uranium in the filtrate was determined using ICP-OES (Spectro, Kleve, Germany).

#### 2.3.1. Effect of Adsorbent Mass (0.5 g to 5 g)

Different amount (0.5, 1, 2 and 5 g) of AMZ was added to 50 mL of 20 mg  $\text{L}^{-1}$  of uranium solution. The contents were shaken for 180 min at room temperature at 150 rpm using an automated SHAKER (Labcon, USA). The remaining uranium concentration in the filtrate was determined.

#### 2.3.2. Effect of U(VI) Concentration

Adsorption isotherms were evaluated at different initial concentration of uranium-nitrate solutions, varying from 10 to 50 mg  $\text{L}^{-1}$  at pH 3 and 25 °C while keeping the adsorbent mass (1 g) and the solution volume (50 mL) constant. The mixture was shaken for 180 min at room temperature. At equilibrium, the solutions were filtered and the equilibrium concentrations of U(VI) determined.

#### 2.3.3. Effect of pH

The effect of pH on the adsorption capacity of uranium onto AMZ was investigated by adding 1 g of AMZ to 50 mL of 20 mg  $\text{L}^{-1}$  uranium solution. The pH was adjusted using  $\text{HNO}_3$  and  $\text{NaOH}$  to obtain the desired pH (3–8). Then the mixture was shaken for 180 min at room temperature at 150 rpm. The uranium concentration in the filtered supernatant solution was determined.

#### 2.3.4. Effect of Carbonates and Sulphates

0.2 M of  $\text{Na}_2\text{CO}_3$  solution and 20 mg  $\text{L}^{-1}$  of uranyl-nitrate solution were mixed in ratios of 4:1 (40 mL: 10 mL) and 1:1 (25 mL:

25 mL). Each mixture was added to bottles containing 1.0 g of AMZ. The contents were then shaken for 180 min at room temperature. In the same way, 20 mg  $\text{L}^{-1}$  of uranyl solution was mixed with different concentrations of  $\text{H}_2\text{SO}_4$  solution (1 M, 0.1 M and 0.01 M) in the ratios of 4:1 and 1:1. The different mixtures were added into bottles containing 1.0 g AMZ. The contents were then shaken for 180 min at room temperature at 150 rpm.

#### 2.3.5. Effect of Fe, Mg, Sr and Ca on U(VI) Adsorption

The study of competitive adsorption was performed at an initial pH of 3 at 25 °C. 20 mg  $\text{L}^{-1}$  of uranyl-nitrate solution was mixed with solutions of  $\text{FeCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{SrCl}_2$  and  $\text{CaCl}_2$  at different concentrations (1.0, 0.1 and 0.01 M) in a ratio of 1:1 to make 50.0 mL solution and the different mixtures were added to bottles containing 1.0 g of AMZ. The contents were shaken for 180 min at room temperature.

#### 2.3.6. Effect of Contact Time

The effect of contact time was assessed by adding 500 mL of 20 mg  $\text{L}^{-1}$  U(VI) solution to a 1-L beaker containing 25 g of AMZ. The mixture was shaken using an automated checker at 150 rpm and the temperature was kept constant at 25 °C for the study. Samples (5 mL) were withdrawn at pre-determined time intervals (30, 60, 90, 120 and 180 min), the volume drawn being <10 % of the total volume. This was to minimize the change in the ratio between the metal concentration and the sorbent mass. The change in solution volume with each sampling was taken into account during the calculations. Samples were filtered and analyzed for the residual U(VI) concentration.

#### 2.3.7. Desorption Studies

Batch desorption tests to regenerate AMZ from different solutions (U-nitrate, U-sulphate and U-carbonate) were conducted using 50.0 mL of 0.1 M  $\text{Na}_2\text{CO}_3$ . The mixture was agitated in 250 mL bottles at 150 rpm for 12 h using a mechanical automated shaker. The concentration of uranium in the filtrate was determined.

## 2.4. Data Processing

The amount of uranium adsorbed onto AMZ was calculated using the mass balance equation expression:<sup>14-15</sup>

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

where  $q_e$  (mg  $\text{g}^{-1}$ ) is the adsorption capacity;  $C_o$  and  $C_e$  (mg  $\text{L}^{-1}$ ) are the initial and equilibrium metal concentrations, respectively;  $V$  is the solution volume (L) and  $M$  is the amount of adsorbent (g).

The Langmuir and Freundlich models (Equations 2 and 3, respectively), were used to fit the adsorption data.<sup>17-19</sup>

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $q_m$  (mg  $\text{g}^{-1}$ ) is the monolayer adsorption capacity and  $b$  ( $\text{L mg}^{-1}$ ) is the adsorption equilibrium constant related to the free energy of adsorption.  $K_F$  ( $\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$ ) and  $n$  are empirical Freundlich constants.

The isotherms were also evaluated using the Dubinin-Radushkevich (DR) model:<sup>20</sup>

$$\ln q_e = \ln X_m + \beta \cdot F^2 \quad (4)$$

$$F = R \cdot T \cdot \ln \left( 1 + \frac{1}{C_e} \right) \quad (5)$$

where:  $X_m$  is the maximum sorption capacity of sorbent ( $\text{mol g}^{-1}$ ) and  $F$  is the Polanyi potential.  $\beta$  is the constant ( $\text{mol}^2 (\text{kJ})^{-2}$ ) related to mean sorption energy;  $R$  is the gas law constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ) and  $T$  the absolute temperature (K).

The free energy change ( $E_s$ ,  $\text{kJ mol}^{-1}$ ) required to transfer one mole of ion from infinity in the solution to the solid surface was derived from Equation 6:<sup>18</sup>

$$E_s = \frac{1}{\sqrt{-2 \cdot \beta}} \quad (6)$$

The pseudo-second-order kinetic (Equation 7) and intraparticle diffusion rate or Weber Morris (Equation 8) models were applied for the time dependence of adsorption to assess the controlling mechanism of the adsorption process.<sup>21</sup>

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} \quad (7)$$

$$q_t = K_p \cdot t^{0.5} + I_d \quad (8)$$

where:  $q_t$  and  $q_e$  are the adsorbed amounts ( $\text{mol kg}^{-1}$ ) at time  $t$  (experimentally obtained) and at equilibrium (obtained from the second-order model),  $k_2$  and  $k_p$  are the rate constants,  $I_d$  is a constant used to examine the relative significance of the two transport mechanisms of the solute, intraparticle diffusion and external mass transfer.

The distribution coefficients ( $K_D$ ) were derived from  $K_D = q_e/C_e$ .

A normalized standard deviation ( $\Delta q$ ) was used in order to compare the validity of each model.  $\Delta q$  (%) is calculated by the following expression:<sup>22</sup>

$$\Delta q (\%) = 100 \cdot \sqrt{\frac{\sum_{i=1}^n \left( \frac{q_{\text{exp}} - q_{\text{cal}}}{q_{\text{exp}}} \right)^2}{n - 1}}$$

where:  $q_{\text{exp}}$  is the experimental metal ion uptake,  $q_{\text{cal}}$  the calculated amount of metal ions adsorbed and  $n$  is the number of data points. The goodness-of-fit of the models to the experimental data was determined by comparison of the correlation coefficients ( $R^2$ ). Speciation of uranium was assessed using MEDUSA software (freeware by KTH, Sweden),<sup>23</sup> assuming thermodynamic equilibrium.

### 3. Results and Discussion

#### 3.1. Characteristics of Natural and Modified Zeolites

The natural zeolite had the following chemical composition:

$\text{SiO}_2$  – 77.36 %,  $\text{Al}_2\text{O}_3$  – 12.96 %,  $\text{Fe}_2\text{O}_3$  – 0.13 %,  $\text{FeO}$  – 1.08 %,  $\text{CaO}$  – 1.42 %,  $\text{MgO}$  – 0.92 %,  $\text{TiO}_2$  – 0.15 %,  $\text{Na}_2\text{O}$  – 1.62 %,  $\text{K}_2\text{O}$  – 4 % and LOI – 11.96 %. The high silica content of the natural zeolite makes it more selective for cations with lower charge density (e.g.  $\text{NH}_4^+$ ) and efficient for the formation of AMZ. The cationic exchange capacity ( $\text{meq } 100 \text{ g}^{-1}$ ) of zeolite and AMZ was 23.16 and 31.65, respectively.

Figure 1 shows the FT-IR spectra of natural zeolite, Na-zeolite as well as ammonium-modified zeolite (AMZ). The presence of strong peaks of N-H around  $3180 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$  for AMZ spectrum was the evidence of the presence of amino groups on the surface of zeolite.

#### 3.2.1. Effect of AMZ Mass (0.5 g to 5 g)

Figure 2 presents the adsorption of uranium on various amounts of AMZ (0.5 g to 2 g). The uranium uptake decreases with the increase of AMZ, likely due to the metal shortage in solution as more binding active sites were available for uranium adsorption. As shown in Fig. 2, the maximum uranium uptake was attained with a solid/liquid ratio of 0.5 g:50 mL.

#### 3.2.2. Effect of Initial Uranium Concentration

Uranium removal increased with the increase of initial uranium concentration (U-nitrate) from 10 to  $50 \text{ mg L}^{-1}$  at pH 3. The maximum adsorption capacity was  $2.116 \text{ mg g}^{-1}$  with the initial uranium concentration of  $50 \text{ mg L}^{-1}$ . This increase could be attributed to an increase in the driving force of the concentration gradient rather than an increase in the initial metal ion concentration. Under the same conditions, if the concentration of uranium in the solution is higher, the active sites of the adsorbent are surrounded by more metal ions, making the adsorption process more effective. Therefore, the value of  $q_e$  increased with increasing initial metal ion concentration.

#### 3.2.3. Adsorption Isotherms

The adsorption isotherms represent the relationship between the amounts of solute adsorbed by a unit mass of solid and the amount of solute remaining in the solution at equilibrium.

The parameters determined from the isotherm models, namely Langmuir, Freundlich and DR models are listed in Table 1.

The best correlation coefficient ( $R^2 = 0.9992$ ) was obtained with the Langmuir isotherm. The model is based on the assumption that maximum adsorption corresponds to saturated monolayer of uranium(VI) molecules on the adsorbent surface, that the

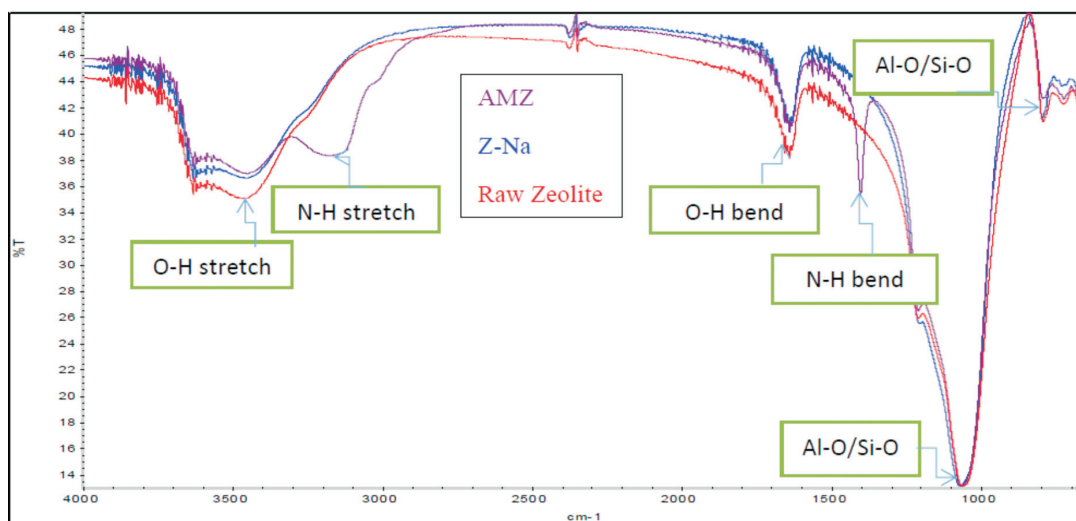
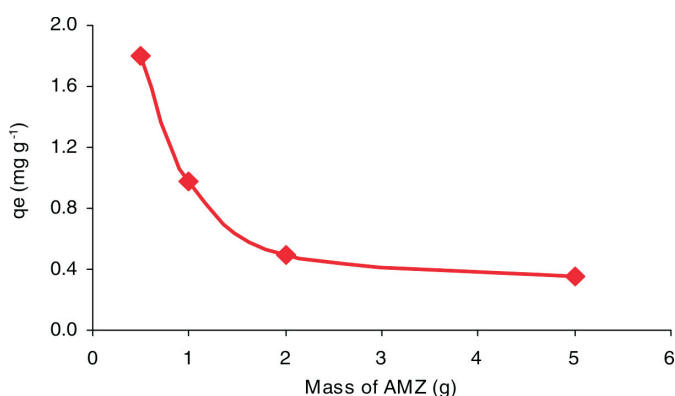


Figure 1 FTIR spectra of natural zeolite (raw zeolite – red), Z-Na (Na-zeolite – blue) and AMZ (purple).

**Table 1** Langmuir, Freundlich and D-R parameters for uranium ion adsorption on AMZ.

	Langmuir				Freundlich			D-R				
	$q_m$ /mg g <sup>-1</sup>	$b$ /L mol <sup>-1</sup>	$R^2$	$\Delta q$ /%	$K_f$ /mg g <sup>-1</sup>	$n$	$R^2$	$\Delta q$ /%	$X_m$ /mol g <sup>-1</sup>	$E_s$ /kJ mol <sup>-1</sup>	$R^2$	$\Delta q$ /%
UO <sub>2</sub> <sup>2+</sup>	2.056	2217	0.9992	17.89	0.980	2.397	0.9625	32.74	0.005	10.09	0.9772	67.22

**Figure 2** Effect of AMZ mass on the adsorption of uranium (VI) ( $n = 3$  and RSD < 10 %).

energy of adsorption is constant and that there is no transmigration of adsorbate on the surface of AMZ.<sup>14,24</sup>

When comparing the statistical results ( $\Delta q\%$ ) of the three models applied in this work, it would appear that the Langmuir and Freundlich isotherms better predicted the equilibrium of uranium(VI) adsorption onto AMZ in the studied concentration range.

The high value of the Langmuir parameter,  $b$ , indicated the high affinity of uranium towards AMZ. The experimental adsorption capacity (2.116 mg g<sup>-1</sup>) was similar to the one obtained from the Langmuir model (2.056 mg g<sup>-1</sup>). The Freundlich constant ( $K_f$ ) was 0.98 and the subunitary value of ratio  $1/n$  suggests that the adsorption was favourable.

The experimental equilibrium data of uranium (VI) were also compared with the theoretical equilibrium data obtained from these adsorption models. The plots (not shown in this paper) confirmed that the adsorption equilibrium data fitted well to the Langmuir model in the studied conditions. The isotherm was found to be linear over the entire concentration range studied. The Dubinin-Radushkevich isotherm model provides information about the physical or chemical character of biosorption process.

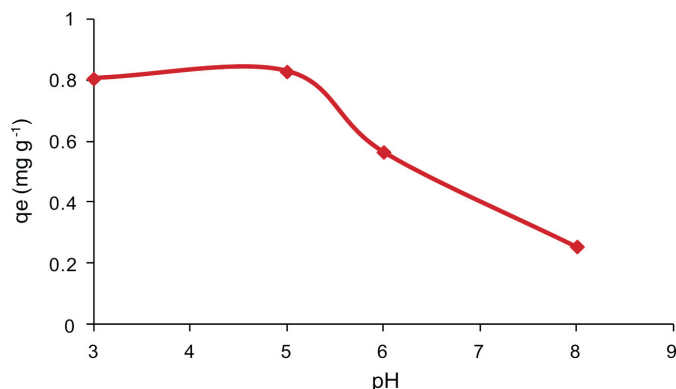
The adsorption energy ( $E_s$ ) value obtained for the experiment data was 10.09 kJ mol<sup>-1</sup>, depicting an ion exchange mechanism.<sup>25</sup>

### 3.2.4. Effect of pH

The solution pH affects the solubility and speciation of uranium in solution as well as the overall charge of the sorbent. The removal of uranium by AMZ was studied in the pH range between 3 and 8 and the results are presented in Fig. 3.

The adsorption of uranium was observed to be strongly dependent on the solution pH. A high uptake was observed under acidic conditions (pH 3–5) with a maximum adsorption obtained at pH 5. As pH increased from 5 to 8, the fraction of U(VI) adsorbed decreased.

At pH between 3 and 5, various monomeric and polymeric hydrolyzed species of UO<sub>2</sub><sup>2+</sup> are formed (Fig. 4a). These include: UO<sub>2</sub><sup>2+</sup>, (UO<sub>2</sub>)OH<sup>+</sup>, (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub><sup>+</sup>, among others.

**Figure 3** Effect of pH on adsorption of UO<sub>2</sub><sup>2+</sup> from aqueous solution by AMZ (temp = 25 °C, conc = 20 mg L<sup>-1</sup>, contact time = 3 h) ( $n = 3$  and RSD < 10 %).

At pH 5, UO<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O(c) is the main species, indicating that the removal of uranium could be a combination of adsorption and precipitation. The decrease in the uptake of uranium at pH > 5 could be attributed to the formation of negatively charged soluble uranium complexes with lower adsorption affinities, i.e. UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup>, UO<sub>2</sub>(OH)<sub>4</sub><sup>2-</sup>, (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>7</sub><sup>-</sup>. The neutral or anionic species depend on the hydroxide groups bonded to the uranium and thus decreasing the possibility of being adsorbed by the AMZ since the electrostatic force between the uranium complexes and AMZ is negligible.<sup>26</sup>

A similar trend was obtained by Sert and Eral<sup>27</sup> as well as Bachmaf and Merkel<sup>28</sup> when using aminopropyl-modified mesoporous sorbent and clay minerals for the adsorption of uranium, respectively.

### 3.2.5. Effect of Carbonates and Sulphates on the Adsorption of U(VI)

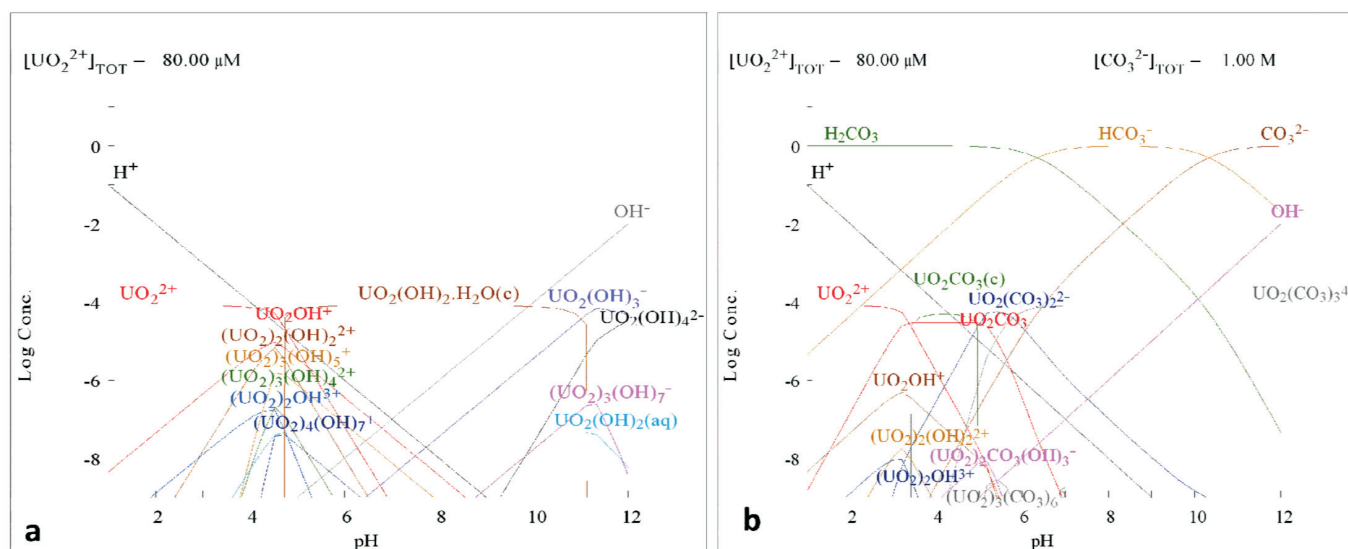
The effect of the presence of carbonates and sulfates on the removal of uranium by AMZ was studied as these ions are usually present in water-system. The results of the adsorption capacity and the distribution coefficient are given in Table 2.

As shown in Table 2, both carbonates and sulphates reduced U(VI) uptake to 67.88 % and 71.63 %, respectively. Experiments were run at different concentration ratios (carbonate/sulphate: uranium), the ratio 1:1 gave the optimum results for both sulphate and carbonate solutions. The presence of carbonates in the solution changes totally the uranium speciation. As shown in Fig. 4b, carbonate is an important ligand in uranyl speciation, particularly at high pH values, where UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> complexes tend to dominate.

At pH > 5, the adsorption of U(VI) onto AMZ decreased sharply in the presence of carbonate, probably due to the formation of negatively-charged complexes such as UO<sub>2</sub>(OH)<sub>3</sub><sup>-</sup>, UO<sub>2</sub>(OH)(CO<sub>3</sub>)<sup>-</sup> which could be repelled by the negative adsorbent surface.<sup>29</sup>

These results are in agreement with those reported on U(VI) sorption onto montmorillonite<sup>29–30</sup> and hydrous silicon dioxide.<sup>31</sup> The authors observed that under alkaline conditions, sorption was inhibited due to the formation of nega-





**Figure 4** Speciation of uranium in a uranium-water system at 25 °C and  $I = 0\text{ M}$  (a), and in the presence of carbonates (b), calculated using Hydra and Medusa speciation modelling free ware versions.

**Table 2** Adsorption capacity of U-nitrate, U-sulphate and U-carbonate complexes on AMZ.

U-solution	Concentration/Ratios	$q_e/\text{mg g}^{-1}$	$K_D/\text{L g}^{-1}$
U-nitrate		0.825	1.116
U-sulphate	0.01 M–4:1	0.258	0.029
	1:1	0.314	
	0.1 M–4:1	0.079	
	1:1	0.265	
	1 M–4:1	0.061	
	1:1	0.263	
U-carbonate	0.2 M–4:1	0.034	0.019
	1:1	0.234	

tively charged U(VI)-carbonate complexes.<sup>30–32</sup>

In the presence of sulphate ions, uranium complexes such as  $\text{UO}_2(\text{SO}_4)_2^{2-}$  and  $\text{UO}_2\text{SO}_4$  are formed in the acidic region, with a small fraction of  $\text{UO}_2\text{OH}^+$  and  $(\text{UO}_2)_3(\text{OH})_5^+$  also present.

The U-sulphate complexes would typically form in acidic mine leachates. The results reported here support the observation of Bachmaf *et al.*,<sup>12</sup> who concluded that the presence of sulphate substantially decreased U(VI) uptake by montmorillonite. Similarly, findings by Venkataramani and Gupta showed that a strong complexing ligand such as  $\text{SO}_4^{2-}$  could substantially decrease U(VI) sorption on hydrous oxides at low pH, either by forming uranyl-sulfate complexes or by competing for available sites.<sup>33</sup>

The distribution coefficient ( $K_D$ ) was higher for U-nitrate ( $1.116\text{ L g}^{-1}$ ) indicating the high affinity and selectivity towards the sorbent (AMZ). The affinity of uranium complexes towards AMZ is in the following sequence:

uranium-nitrate > uranium-sulphate > uranium-carbonate.

### 3.2.6. Effect of $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Sr}^{2+}$ and $\text{Fe}^{3+}$ on Uranium Adsorption

It is important to assess the effect of competing cations in the study of uranium adsorption. The results of the uptake of uranium in the presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  are shown in Fig. 5.

The presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  resulted in a decrease of uranium (U-nitrate system) uptake by AMZ. A significant

reduction was observed even at relatively low concentrations (0.1 M) of these ions. The amount of uranium adsorbed was reduced to 19.57 %, 31.60 % and 23.65 % in the presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$ , respectively. This trend could be attributed to the competitive effect between uranium(VI) and cations for the binding sites available for the adsorption process. Another factor could be the formation of negatively charged Sr-, Ca- and Mg-uranium complexes.<sup>34</sup>

This is a phenomenon of importance in geochemical modelling of uranium transport in aquifers as the presence of calcite ( $\text{CaCO}_3$ ) has been found to reduce adsorption of uranium significantly, resulting in pollution of down gradient boreholes.

A different trend was observed when  $\text{Fe}^{3+}$  was added to uranium solutions as seen in Table 3. The results show an increase of 20 %, 72 % and 82 % for U-nitrate, U-carbonate and U-sulphate, respectively. This increase might be described by two processes, namely: the formation of complexes between  $\text{Fe}^{3+}$  and  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , thus releasing uranium from these complexes which in turn is adsorbed on AMZ; or the binding of uranium complexes to  $\text{Fe}^{3+}$  as well as onto AMZ, a situation resembling a salt bridge set up (surface-uranium complex–Fe-uranium complex). Further investigation into these processes would be required.

**Table 3** Effect of  $\text{Fe}^{3+}$  on adsorption of different uranium complexes.

Solution	Ratio	$q_e/\text{mg g}^{-1}$	% Increase
U-nitrate		0.825	
U-nitrate + 0.1 M $\text{Fe}(\text{NO}_3)_3$	(1:1)	0.991	20.18
U-sulphate		0.265	
U-sulphate + 0.1 M $\text{Fe}(\text{NO}_3)_3$	(1:1)	0.458	72.48
U-carbonate		0.234	
U-carbonate + 0.1 M $\text{Fe}(\text{NO}_3)_3$	(1:1)	0.400	82.43

### 3.2.7. Effect of Contact Time

In order to determine the equilibrium time for uranium (VI) adsorption on AMZ, the kinetics of the adsorption was investigated. The kinetic sorption was characterized by a rapid initial uptake followed by a slower rate of uptake. After 30 min of contact, more than 90 % of uranium had been adsorbed. In addition, no systematic decrease in adsorption percentage



of U(VI), largely due to the formation of negatively charged uranyl-carbonate complexes.

The adsorption of uranium onto AMZ for the U-nitrate system was described by the Langmuir isotherm. The presence of Ca, Sr and Mg ions led to the decrease of the adsorption of uranium (an average drop of 24.94 %) due to competition for binding sites. The presence of Fe<sup>3+</sup> in polluted acidic water enhanced the removal of uranium *in situ* using AMZ. An increase of up to 82.43 % was observed for the U-carbonate system.

The adsorption of uranium from U-nitrate and U-sulphate systems followed the pseudo-second-order kinetic, whilst the intraparticle diffusion described the adsorption for U-carbonate system. Uranium loaded in the AMZ can potentially be desorbed (between 12.33 % and 75.21 %) in order to regenerate the sorbent for further re-use. As such, AMZ are promising materials for the removal of uranium(VI) from contaminated soils and water systems in acidic environments.

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