

## Removal of uranium from aqueous solutions by diatomite (Kieselguhr)

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In this study, the removal of uranium from aqueous solutions by diatomite earth (Kieselguhr) fine particules has been investigated. Diatomite earth is an important adsorbent material in chromatographic studies. Uranium adsorption capacity of four different types of diatomite was determined. The adsorption of uranium on the chosen diatomite sample was examined as a function of uranium concentration, solution pH, contact time and temperature. The adsorption of uranium on diatomite followed a Langmuir-type isotherm.

### Introduction

Adsorption is an effective and convenient technique in the separation and isolation of elements. The greatest advantage of adsorption is the possibility to separate of small amounts of substances from a very large volume of solution.<sup>1</sup> Knowledge of the adsorptive properties of inorganic materials has become of considerable importance in many fields. The adsorption of trace amounts of various ions on inorganic and organic adsorbents from aqueous solution has been studied by numerous scientists.<sup>2–9</sup>

Diatomite earth (Kieselguhr) is the anorganic skeleton of the fossils of certain species of *Diatomaceae* which have a single cell. The use of powdered diatomite earth in filtration, described by SLATER as early as 1876, is now widespread.<sup>10</sup> The scores of industries which find diatomite earth of advantage as a filtration powder include especially sugar refining, petroleum, edible oils, varnish, alcohol fermentation, and fruit juices.<sup>10–11</sup> High grade diatomite earth is almost white. As occurring in commercial quantities, it varies in colour with the nature and amounts of impurities present.

In this study, the sorption of uranium on diatomite has been investigated. The effects of the solution pH, concentration of uranium, contact time and temperature on the adsorption process were examined. The Langmuir isotherm was formed and discussed.

### Experimental

Calcined diatomite samples were supplied from Turkish Sugar Factories Inc., Kieselguhr Factory, Etimesgut – Ankara, Turkey. For improving their mechanical properties, these diatomite samples were calcined with Na<sub>2</sub>CO<sub>3</sub> at 1600 °C by Kieselguhr Factory. The chemical composition and the physical

properties of all the diatomites which were determined by the Kieselguhr Factory, were given in Tables 1 and 2, respectively.<sup>12</sup>

### Preparation of uranium solution

The standard uranium solution 0.01M (2380 mg/l) was prepared by dissolving analytical grade UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salt, adding some drops of concentrated nitric acid. All chemicals used in the experiments are of analytical reagent grade.

### Instrumentation

The pH of the solution was measured using pH meter model 8521 by Hanna Instruments. The shaking was carried out in a thermostated shaker bath, GEL-1083 model and all measurements were carried out by a Shimadzu UV-VIS 260 spectrophotometer.

### Adsorption experiments

The sorption of uranium (VI) on kieselguhr was studied by a batch technique. The general method used for these studies is described below.

A known weight, i.e., 0.1 g, of the adsorbent was equilibrated with 25 ml of the metal solution of known concentration in a stoppered Pyrex glass flask at a fixed temperature in a thermostated shaker water bath for a known period of time. After adsorption, the sorbent was separated by filtration. Then the residual uranium in the filtrate was determined by the spectrophotometer using the Arsenazo III method at  $\lambda = 665$  nm.<sup>13</sup> Adsorption yield (%) was calculated according to:

$$\text{Adsorption yield (\%)} = (C_i - C_a / C_i) \times 100 \quad (1)$$

where  $C_i$  and  $C_a$  are the concentrations of uranium in the initial and equilibrated solutions, respectively.

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Table 1. Chemical composition of diatomites<sup>12</sup>

Chemical composition, %	No. 2 (C)	No. 2 (FC)	No. 3 (FC)	No. 4 (FC)
SiO <sub>2</sub>	92.68	89.81	92.75	93.47
Fe <sub>2</sub> O <sub>3</sub>	1.83	1.72	1.39	1.10
Al <sub>2</sub> O <sub>3</sub>	2.60	2.40	1.66	1.13
CaO	0.66	1.02	0.76	0.66
MgO	0.44	0.30	0.24	0.20
Na <sub>2</sub> O	0.89	3.49	2.25	2.13
K <sub>2</sub> O	0.34	0.26	0.22	0.20
Ignition loss, %	0.50	0.50	0.50	0.50

C: Calcine.  
FC: Flux calcine.

Table 2. Physical properties of diatomites<sup>12</sup>

	No. 2 (C)	No. 2 (FC)	No. 3 (FC)	No. 4 (FC)
Colour	Pink	White	White	White
Loose wt, g/l	95.00	100.00	90.00	80.00
pH (20 °C)	7.00	10.00	10.00	10.00
Average diameter, µm	15.00	20.00	10.00	7.00
Specific surface area, m <sup>2</sup> /cm <sup>3</sup>	0.65	0.60	0.90	1.15

Table 3. Uranium adsorption capacities of diatomite samples

Sample	Uranium capacity, mmol UO <sub>2</sub> <sup>2+</sup> /g
No. 2 (C)	0.2692
No. 2 (FC)	0.3984
No. 3 (FC)	0.3514
No. 4 (FC)	0.3514

#### Determination of adsorption capacity

0.125 g of adsorbent was equilibrated with 50 ml of concentrated uranium nitrate solution (2380 mg/l) at 30 °C for 24 hours. Then the loaded adsorbent was filtered, and the uranium in the filtrate was determined by spectrophotometry using the salicylic acid method at  $\lambda = 468$  nm.<sup>14</sup> The uranyl adsorption capacity of diatomites were determined and shown in Table 3.

The further adsorption experiment was carried out with No. 2 (FC) diatomite sample because of higher uranium adsorption capacity.

### Results and discussion

The analysis of some factors which influence uranium adsorption, such as pH, uranium concentration, contact time and temperature, is necessary for the purpose of understanding the removal process of uranium from aqueous systems.

#### Effect of pH

The effect of pH on the adsorption of uranium in the pH range of 2–7 which was adjusted by 0.1M HNO<sub>3</sub> and NaHCO<sub>3</sub> solutions, for 24 hours at 30 °C was investigated. The results obtained are shown in Fig. 1. It was observed that the amount of uranium adsorbed on No. 2 (FC) was slightly increased until pH 5, after this point, the uranium adsorption began to decrease in the pH range of 6–7. From these result it may be considered that the depression of uranium adsorption below pH 5 is due to the presence of UO<sub>2</sub><sup>2+</sup> ions. Near pH 7, the UO<sub>2</sub><sup>2+</sup> ion forms stable complexes with carbonate such as UO<sub>2</sub>CO<sub>3</sub>, [UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup>.<sup>15</sup> The results of the experiments showed that the adsorbed uranium was dependent on the final pH of the test solutions. The highest uranium adsorption yield was achieved around 77% at pH 5.0 (Fig. 1).

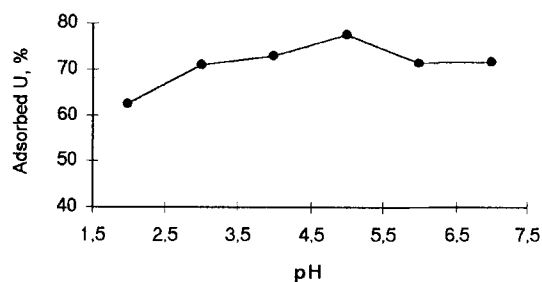


Fig. 1. Adsorption of uranium on diatomite as a function of pH (pH 2–7, [U] = 75 mg/l,  $t = 1$  h,  $T = 25$  °C)

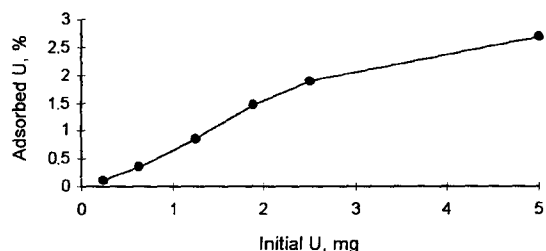


Fig. 2. Adsorption of uranium on diatomite as a function of initial uranium concentration ([U] = 10–200 mg/l,  $v = 25$  ml, pH 5,  $t = 1$  h,  $T = 25$  °C)

*Effect of initial uranium concentration*

The adsorption of uranium on diatomite from aqueous solution of different uranium concentrations is presented in Fig. 2. It was observed that the percentage of the adsorbed  $UO_2^{2+}$  complex increases with increasing uranium concentration of the aqueous solutions. These results indicate that energetically more favourable sites become involved with increasing uranium concentration. These results are similar to those previously reported for the sorption of uranium ions on a variety of sorbents.<sup>16–17</sup> Thus, high uranium concentration in the feed means faster adsorption and greater system efficiency.

*Effect of contact time*

The effect of contact time on the adsorption of uranium on diatomite was checked by employing No. 2 (FC) which has the maximum uranium adsorption capacity. The studies show a decrease in the amount of adsorbed uranium with increasing the contact time which reaches a plateau, as seen in Fig. 3. The adsorption of uranium reached about 97% within 15 minutes.

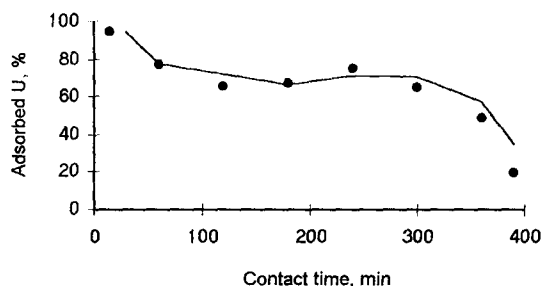


Fig. 3. Adsorption of uranium as a function of contact time (pH 5, [U] = 75 mg/l,  $T = 25$  °C)

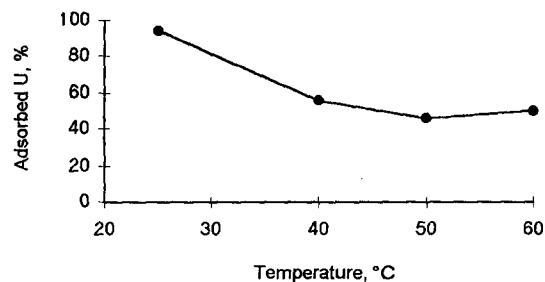


Fig. 4. Adsorption of uranium as a function of temperature (pH 5, [U] = 75 mg/l, contact time: 15 min)

The adsorption of uranium from a 75 mg/l solution at pH 5.0 is very rapid, the percentage adsorption reach a maximum value almost immediately after mixing and then it remains almost constant up to 300 minutes. On the basis of these results a 15-minute shaking period was selected for all further studies.

*Effect of temperature*

The effect of temperature on the adsorption of uranium was investigated between 25 and 60 °C. As shown in Fig. 4, uranium adsorption decreases with increasing temperature. From these results, we can assume that the adsorption of U on diatomite occurs via physisorption.

*Adsorption isotherm*

Figure 5 shows the Langmuir plot for the adsorption of uranium on diatomites. The Langmuir equation is given by

$$C_e/y = (1/Q^\circ \cdot b) + (C_e/Q^\circ) \quad (2)$$

where  $C_e$ , is the concentration of solute in the solution phase at equilibrium (g/l),  $y$  is the amount of solute adsorbed per unit weight of sorbent (mg/g),  $b$  is the

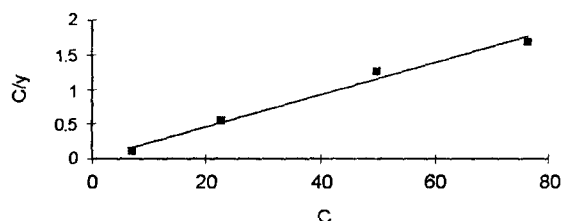


Fig. 5. Langmuir adsorption isotherm ( $Q^\circ = 0.1621$  mmol  $UO_2^{2+}$ /g,  $b = 6.8679$  l/g,  $r^2 = 0.9897$ )

Langmuir constant and, being the ratio of adsorption and desorption rate coefficients ( $l/g$ ),  $Q^\circ$  is the maximum sorption capacity ( $mg/g$ ). At low concentrations, the Langmuir equation is reduced to a linear relationship, while the maximum sorption capacity,  $Q^\circ$ , is attained at concentrations corresponding to monolayer coverage. As the value of  $b$  becomes larger, the limiting sorption capacity is attained at lower solution phase concentration.<sup>18</sup>

Sorption data were expressed as the amount of uranium sorbed per unit weight of sorbent ( $C_e/y$ ) versus the concentration of uranium in the solution phase at equilibrium ( $C_e$ ). The sorption data were fitted to the linear form of Eq. (2) to obtain the values of  $Q^\circ$ , and  $b$  shown in Fig. 5. In Fig. 5, the amounts of uranium were available in the range from 6.75 to 81 mg. Linear regression gives a slope of  $<1$  for the diatomite sample, indicating a concentration dependent sorption of uranyl ions on diatomite sample in this concentration range used.

### Conclusions

The adsorption of uranium was studied by diatomite. From the results it is evident that diatomite has the ability to accumulate relatively large amounts of uranium from aqueous solution. It has also been shown that the adsorption of uranium varies with some factors such as pH, initial uranium concentration, contact time and temperature. The adsorption of uranium from the dilute aqueous solution by diatomite varies with the chemical species of uranyl ion, depending on pH of solution, and it was found that the adsorption of uranium on diatomite is maximum at pH 5.

We have so a cheap, good sorption capacity, and available geological adsorbing agent for the removal of uranium that may be present in the waste water of uranium refining, mine waste water, sea water and in other water sources.

The goodness of fit of the Langmuir model would tend to increase as the contributing sorption component

increases. Once monolayer coverage is achieved, sorption no longer significantly influences solute transport.

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