

Equilibrium and Kinetics of U(VI)_{aq} Adsorption on *in situ* Generated Fe₂O₃ · nH₂O

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The paper aims to present research results obtained at the study of equilibrium and kinetics of U(VI) sorption on in situ generated Fe₂O₃ · nH₂O from model solutions. The studied systems represent U(VI) solutions with C_{U(VI)} = 5-30 mg·L⁻¹ for which maximum U(VI) removal efficiencies (%R_{U(VI)} = 95.98) on in situ generated Fe₂O₃ · nH₂O were obtained in the following working conditions: pH = 8.75, t_{contact} = 30 min, [U(VI)] : [Fe(III)] = 1:75 and stirring rate 250 RPM. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were used to study U(VI) sorption equilibrium. Langmuir isotherm with the correlation coefficient R² (0.9808) suggests that it involves physical interactions. Freundlich (R² = 0.8349) and Temkin (R² = 0.8715) models describe well the sorption process suggesting that there also exists a chemical component, complexing and/or co-precipitation. The kinetic modelling according to the pseudo-first and pseudo-second order models, respectively has demonstrated that the U(VI) sorption equilibrium follows the pseudo-second order equation suggesting a chemical component of the process.

Keywords: uranium, sorption/precipitate flotation, adsorption isotherms modelling, kinetics

Uranium mining activity continues to be a major source of radioactive environmental pollution by producing huge amounts of low radioactive wastes heaped around the mining galleries and large quantities of wastewaters [1]. It is also present in the sea-water and it can contaminate the fish [2]. The radioactive pollution is also faced by other countries such as Serbia in the spa waters [3], Greece in the Axios River's case [4] and Italy in the building materials [5]. This undesired phenomenon challenges the scientific community to discover the most effective solutions for ecological rehabilitation of polluted sites [1].

Uranium is nephrotoxic and accumulates in bones, liver and kidneys causing permanent damages to the affected organs [6]. Uranium contaminated mine water with low content of U(VI) (1-10 mg·L⁻¹) is a challenge for the classic treatment methods such as ion exchange, solvent extraction, adsorption on different supports due to their specific drawbacks [1]. The solution to this problem is sorption/precipitate flotation process [1]. The process has two stages. Firstly, the pollutant metallic ion is adsorbed on a specific inorganic or organic sorbent and secondly a surfactant is added to increase the up-loaded support's hydrophobicity, which is subsequently subjected to flotation [7]. *In situ* generated Fe₂O₃ · nH₂O was chosen to remove U(VI) from a synthetic solution as natural analogue, considering that the system U(VI)-Fe-H₂O is natural occurring one and was largely investigated [8-15].

For the separation process optimization is important to understand the reaction mechanism.

Although the interaction between U(VI) and different sorbents besides natural occurring Fe (II, III) compounds was extensively studied [8-27], those processes' mechanism is not fully understood yet.

Therefore, the present work aims to study U(VI) sorption equilibrium on *in situ* generated Fe₂O₃ · nH₂O, which is the first stage of U(VI) removal by sorption/precipitate flotation process, from the equilibrium and kinetic point of view.

Adsorption isotherms modelling is useful in getting information concerning the sorbent affinity towards the adsorbed species, interaction nature, maximum adsorption capacity and checking the studied process applicability as unit operation [25-29].

Experimental part

Materials and methods

Experiments were conducted in batch system. All the reagents were analytical grade. The stock solution Na₄[UO₂(CO₃)₃] (C_{U(VI)} = 1g · L⁻¹) was prepared using known amounts of uranyl acetate (UO₂(CH₃COO)₂ · H₂O, MERCK) and anhydrous sodium carbonate (Na₂CO₃, MERCK), which was used to obtain the work solutions (C_{U(VI)} = 5, 10, 15, 20, 25 and 30 mg · L⁻¹). For pH adjustment 0.01 M and 0.1 M NaOH (MERCK) solutions were prepared. For the sorbent *in situ* generation 0.1 M FeCl₃ solution (FeCl₃ · xH₂O, MERCK) was prepared.

Equipment

The HeidolphVibramax 100 stirrer with variable speed was used to contact the sample with the sorbent. The 290A ORION pH-meter was used to measure the pH. CINTRA 404 UV-Vis spectrophotometer was used for U(VI) residual concentration in solution determination with Arsenazo III at wavelength λ = 650 nm [30].

Working conditions were: C_{U(VI)} = 5-30 mg·L⁻¹; V_{sample} = 200 mL; molar ratio [U(VI)]:[Fe(III)] = 1:75; stirring rate: 250 RPM; t_{contact} = 1-30 min; T = 298 K; pH = 8.75.

Results and discussions

Adsorption isotherms

In order to study U(VI) sorption equilibrium on *in situ* generated Fe₂O₃ · nH₂O using adsorption isotherms samples with different uranium content (C_i = 5, 10, 15, 20, 25, 30 mg·L⁻¹) were contacted with the corresponding amounts of sorbent to the molar ratio [U(VI)]:

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[Fe(III)]=1:75 for 30 min at pH=8.75, T=298 K and 250 RPM.

The residual concentration of U(VI) was analyzed to calculate the equilibrium adsorption capacity according to the following equation [31]:

$$Q_e = \frac{(C_i - C_e)}{m} \times V \quad (1)$$

where Q_e is the equilibrium adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$); C_i and C_e are the initial and final/equilibrium concentrations of the ionic species ($\text{mg} \cdot \text{L}^{-1}$), respectively; V is solution volume (L) and m is the dried sorbent mass (g).

Langmuir model

The Langmuir isotherm assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption and a constant sorption potential [28, 29].

The linearized form [29-33] is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (2)$$

where: Q_e is equilibrium adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), Q_m is maximum monolayer adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), K_L is Langmuir empirical constant ($\text{L} \cdot \text{g}^{-1}$), which depends on sorption energy and quantitatively assess sorbent's affinity towards the adsorbed specie, C_e is the equilibrium metallic ion concentration ($\text{mg} \cdot \text{L}^{-1}$).

The Langmuir adsorption model parameters are useful to determine the separation factor R_L defined by the following equation [28-33]:

$$R_L = \frac{1}{1 + K_L C_i} \quad (3)$$

where C_i is the initial concentration ($\text{mg} \cdot \text{L}^{-1}$). The value of this dimensionless parameter, R_L , provides information regarding the adsorption process type [31]: when $R_L=0$ it is irreversible, when $R_L \in (0,1)$ it is favorable, when $R_L=1$ it is linear and when $R_L > 1$ it is unfavorable.

The Langmuir model parameters (Q_m and K_L) were calculated from the slope and the intercept of the plot C_e/Q_e versus C_e shown in figure 1.

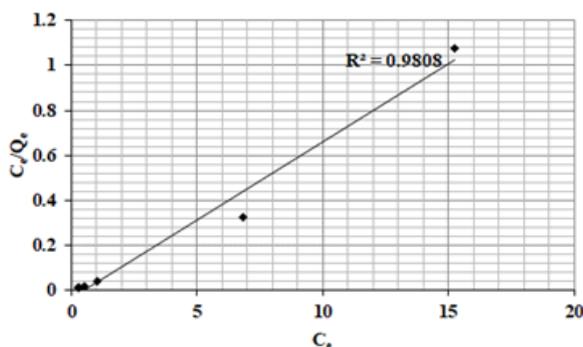


Fig. 1. Linearised Langmuir isotherm model corresponding to the U(VI) equilibrium sorption on *in situ* generated $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($C_{\text{U(VI)}} = 5\text{-}30 \text{ mg} \cdot \text{L}^{-1}$, $T = 298 \text{ K}$, $t_{\text{contact}} = 30 \text{ min}$, $\text{pH} = 8.75$, 250 RPM, molar ratio [U(VI)]:[Fe(III)]=1:75)

The correlation coefficient R^2 value (0.9808) suggests that the adsorption process might involve physical interactions.

The dimensionless parameter, R_L , tends to 0 suggesting that the process is irreversible. This is in good agreement with U(VI) and Fe (III) species possible interactions [34, 35]. So that, the possible chemical interactions involve the following probable species: for U(VI): $\text{UO}_2(\text{OH})_2$, $[\text{UO}_2(\text{OH})_3]^-$, $[(\text{UO}_2)_3(\text{OH})_7]^-$, UO_2CO_3 , $[\text{UO}_2(\text{CO}_3)_2]^{2-}$, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ and $[(\text{UO}_2)_2\text{CO}_3(\text{OH})_3]^-$; for Fe(III): $[\text{Fe}(\text{OH})_2]^+$, $\text{Fe}(\text{OH})_3$ and $[\text{Fe}(\text{OH})_4]^-$ [13, 36].

Freundlich model

This adsorption model may be applied to the sorption processes on heterogenous surfaces under nonideal conditions or to the multi-layer ones to evaluate the adsorption process in solid-liquid system and the linearized form of the equation, that describes it, is [31, 33, 35, 37]:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F is the relative adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$) and n is the adsorption intensity.

The Freundlich isotherm model parameters (K_F and n) were calculated from the slope and the intercept of the plot $\log Q_e$ versus $\log C_e$ shown in fig.2.

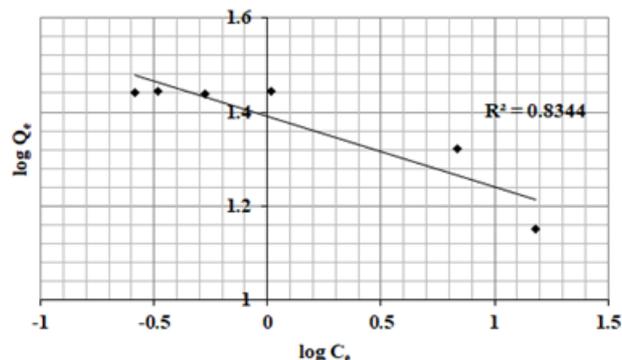


Fig. 2. Linearised Freundlich isotherm model corresponding to the U(VI) equilibrium sorption on *in situ* generated $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($C_{\text{U(VI)}} = 5\text{-}30 \text{ mg} \cdot \text{L}^{-1}$, $T = 298 \text{ K}$, $t_{\text{contact}} = 30 \text{ min}$, $\text{pH} = 8.75$, 250 RPM, molar ratio [U(VI)]:[Fe(III)]=1:75)

Temkin model

This type of model contains a factor, which considers the interactions between the adsorbent and the adsorbed ionic species [31, 33, 35, 37] and has the linearized form:

$$Q_e = B_T \ln A_T + B_T \ln C_e \quad (5)$$

where: $B_T = RT/b_T$ is Temkin isotherm constant and it is related to the adsorption heat ($\text{kJ} \cdot \text{mol}^{-1}$), R is universal gas constant ($8.314 \text{ J} \cdot \text{mol} \cdot \text{K}^{-1}$), T is working temperature (K), b_T is adsorption heat and A_T is the constant equivalent to the maximum binding energy at equilibrium.

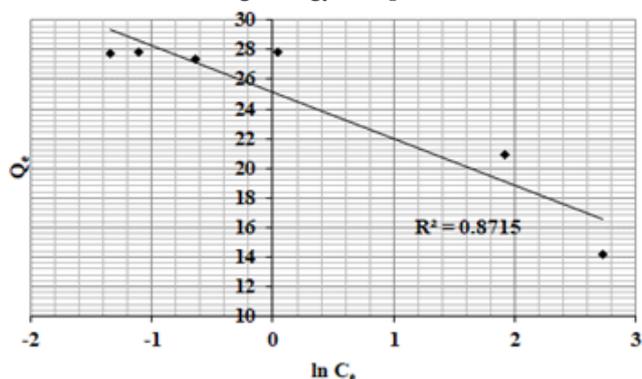


Fig. 3. Linearised Temkin isotherm model corresponding to the U(VI) equilibrium sorption on *in situ* generated $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($C_{\text{U(VI)}} = 5\text{-}30 \text{ mg} \cdot \text{L}^{-1}$, $T = 298 \text{ K}$, $t_{\text{contact}} = 30 \text{ min}$, $\text{pH} = 8.75$, 250 RPM, molar ratio [U(VI)]:[Fe(III)]=1:75)

The values of Temkin model parameters (A_T , B_T and b_T) were obtained from the slope and the intercept of the plot Q_e versus $\ln C_e$ and the positive value of A_T confirms the adsorption efficiency of *in situ* generated $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. The correlation factor R^2 value close to 1 ($R^2 = 0.8715$) confirms that between U(VI) species and Fe(III) ones the chemisorption may occur.

Dubinin - Radushkevich model

This model is used to describe the adsorption mechanism as a function of Gauss energy distribution on a heterogenous surface and the linearized form of the corresponding equation is [30, 32, 34, 36]:

$$\ln Q_e = \ln Q_m - K\varepsilon^2 \quad (6)$$

where ε - Polanyi potential, Q_m - maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), K - Dubinin-Radushkevich constant ($\text{mol}^2\cdot\text{kJ}^{-2}$).

From the value of Dubinin - Radushkevich constant, K , the adsorption energy value, E ($\text{kJ}\cdot\text{mol}^{-1}$), may be determined according to the equation [31, 33, 35, 37]:

$$E = \frac{1}{\sqrt{-2K}} \quad (7)$$

Depending on its value the type of the adsorption process may be determined as follows: for $E \in [1,16]$ is physical adsorption and for $E > 16$ is chemisorption, respectively.

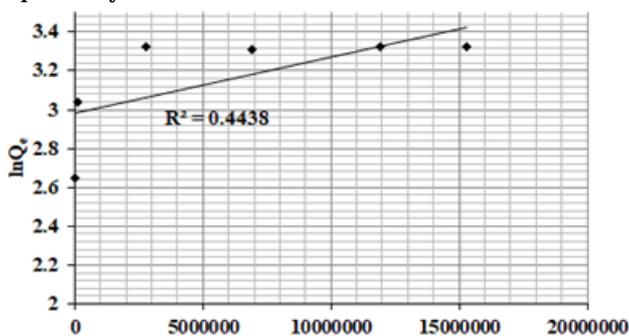


Fig. 4. Linearised Dubinin-Radushkevich isotherm model corresponding to the U(VI) equilibrium sorption on *in situ* generated $\text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O}$ ($C_{\text{U(VI)}} = 5\text{-}30 \text{ mg}\cdot\text{L}^{-1}$, $T = 298 \text{ K}$, $t_{\text{contact}} = 30 \text{ min}$, $\text{pH} = 8.75$, 250 RPM, molar ratio $[\text{U(VI)}]:[\text{Fe(III)}] = 1:75$)

The Dubinin - Radushkevich model parameters (K , ε and E) were calculated from the slope and the intercept of the plot Q_e versus ε^2 displayed in figure 4. The positive calculated value of the adsorption energy higher than 16 $\text{kJ}\cdot\text{mol}^{-1}$ suggests that the studied process involves chemisorption and is endothermal.

The calculated parameters of the adsorption isotherms models are summarized in the table 1.

In table 1 it is noticed that K_F value corresponding to the studied process is $25.09 \text{ mg}\cdot\text{g}^{-1}$, which is close to those obtained ($Q_{e, \text{calc}} = 27.32 \text{ mg}\cdot\text{g}^{-1}$) using the pseudo-second order kinetic model and to the experimental values ($Q_{e, \text{exp}} = 27.27 \text{ mg}\cdot\text{g}^{-1}$), (table 2).

Kinetic models

The kinetic study was conducted in batch system. Samples with different initial concentrations ($C_i = 10$ and $30 \text{ mg U(VI)}\cdot\text{L}^{-1}$) were contacted with the appropriate amount of sorbent at the molar ratio $[\text{U(VI)}]:[\text{Fe(III)}] = 1:75$ for different contact times ($t_{\text{contact}} = 1, 2, 3, 4, 5, 10, 15, 20, 25$ and 30 min), $T = 298 \text{ K}$, $\text{pH} = 8.75$ and stirring rate 250 RPM. They were subsequently analyzed for U(VI) residual concentration determination.

For the kinetic correlation of the obtained experimental data the pseudo-first order and the pseudo-second order kinetic models were used.

The linearized form of the equation corresponding to the pseudo-first order kinetic model is [33]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (8)$$

where Q_e and Q_t are the adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium and t (min.) moment respectively, and k_1 is the constant rate (min^{-1}). From the plot $\log(Q_e - Q_t)$ versus t displayed in fig. 5 results that the correlation coefficient R^2 is less than 0.94 suggesting that the U(VI) sorption process does not follow the pseudo-first order kinetic model.

The linearized form of the equation corresponding to the pseudo-second order kinetic model is [33]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (9)$$

The plot t/Q_t versus t (fig.6), the slope and the intercept values were used to determine the equilibrium adsorption capacity Q_e ($Q_{e, \text{calc}}$) and the constant rate k_2 (table 2.) respectively.

The obtained data confirm that U(VI) sorption on *in situ* generated $\text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O}$ follows the pseudo-second order model because the correlation coefficient's value tends to 1 and the equilibrium adsorption capacity's calculated

Langmuir	Freundlich	Temkin	Dubinin-Radushkevich
$Q_m = 29.07 (\text{mg}\cdot\text{g}^{-1})$	$K_F = 25.06 (\text{mg}\cdot\text{g}^{-1})$	$B_T = -3.1469$	$Q_m = 19.78 (\text{mg}\cdot\text{g}^{-1})$
$K_L = -0.49 (\text{L}\cdot\text{mg}^{-1})$	$n = 6.7$	$b_T = -787.30$	$K = -3\text{E-}08 (\text{mol}^2\cdot\text{kJ}^{-2})$
$R_L = 0.25$	$R^2 = 0.8344$	$A_T = 3.35\cdot 10^{-4}$	$E = 4082.5 (\text{kJ}\cdot\text{mol}^{-1})$
$R^2 = 0.9808$		$R^2 = 0.8715$	$R^2 = 0.4438$

Table 1
ADSORPTION MODELS PARAMETERS

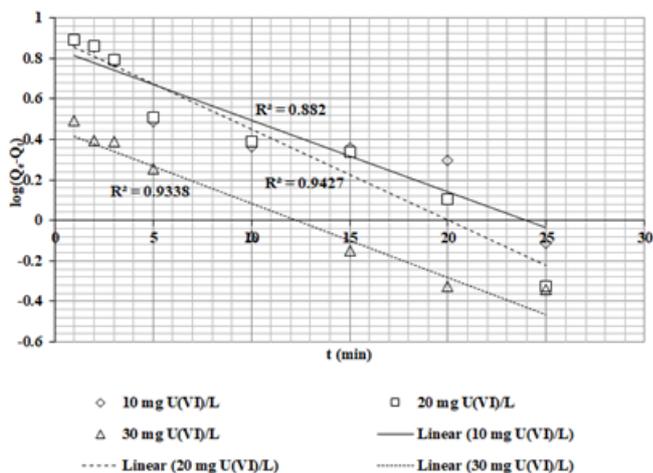


Fig.5 The linearised form of pseudo-first order kinetic model corresponding to U(VI) sorption on *in situ* generated $\text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O}$ ($T = 298 \text{ K}$, $t_{\text{contact}} = 30 \text{ min}$, $\text{pH} = 8.75$, stirring rate = 250 RPM, molar ratio $[\text{U(VI)}]:[\text{Fe(III)}] = 1:75$)

Table 2

PSEUDO-SECOND ORDER KINETIC MODEL PARAMETERS CORRESPONDING TO U(VI) SORPTION ON *in situ* GENERATED Fe₂O₃ · nH₂O AT T=298 K

C _{U(VI)} (mg·L ⁻¹)	Q _{e,exp} (mg·g ⁻¹)	k ₂ (g·mg ⁻¹ ·min ⁻¹)	Q _{e,calc} (mg·g ⁻¹)	R ²
10	27.27	0.0392	27.32	0.9981
20	27.20	0.0421	28.17	0.9989
30	14.14	0.1196	14.18	0.9994

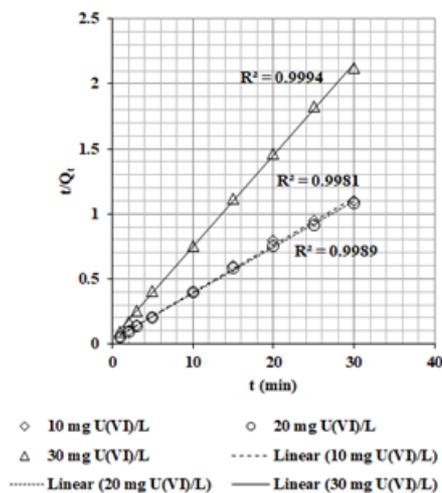


Fig. 6 The linearised form of pseudo-second order kinetic model corresponding to U(VI) sorption on *in situ* generated Fe₂O₃·nH₂O (T = 298 K, t_{contact} = 30 min, pH=8.75, stirring rate = 250 RPM, molar ratio [U(VI)]:[Fe(III)]=1:75)

values are close to those experimentally determined (table 2), suggesting the U(VI) sorption involves chemisorption. This correlation is confirmed by other kinetic studies as well [8, 11, 13, 23].

Conclusions

The present work has investigated U(VI) sorption on *in situ* generated Fe₂O₃ · nH₂O using the adsorption isotherm and the kinetic models, respectively.

The obtained results suggest that the process is mixed and involves both physical and chemical interactions. Based on the correlation coefficients (R²), the sorption equilibrium data fitted to the isotherm models in the following order: Langmuir (0.9808) > Temkin > (0.8715) > Freundlich (0.8344).

All the models have pointed out the process's high complexity [6-10] involving chemical interactions. Adsorption isotherms models parameter values might be explained by the process mechanism [23].

It can be assumed that the U(VI) separation process is not only physical adsorption but might also involve other chemical interactions between U(VI) and Fe (III) aqueous species (co-precipitation). The close values of K_F, Q_{e,exp} and Q_{e,calc} suggest that the process involves chemisorption in good agreement with the fact that it has followed the pseudo-second order kinetics as confirmed by other studies [25, 28].

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