Box–Behnken design for removal of uranium(VI) from aqueous solution using poly(ethylene glycol) based dicationic ionic liquid impregnated chitosan

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Abstract: Poly(ethylene glycol) bis(methylimidazolium) di[bis(trifluoromethylsulfonyl)imide] was synthesized as an ionic liquid and impregnated onto chitosan. The removal of uranium(VI) ions from aqueous solution was investigated with batch sorption tests using ionic liquid impregnated chitosan. Response surface methodology based on 3 level Box–Behnken design was applied to analyze the effect of initial pH (4–6), initial concentration (20–60 mg L\(^{-1}\)), contact time (15–105 min), and temperature (30–50 °C) on the uptake capacity of uranium(VI). Main effect of initial concentration, quadratic effect of contact time, and dual effect of initial pH and contact time were found statistically significant based on analysis of variance (ANOVA). Probability F-value (F = 1.49 × 10\(^{-6}\)) and correlation coefficient (R\(^2\) = 0.96) point out that the proposed model is compatible with experimental data. The maximum uptake capacity of uranium(VI) was found as 28.48 mg g\(^{-1}\) at initial pH 4, initial concentration 60 mg L\(^{-1}\), contact time of 70 min, and a temperature of 50 °C. Sorption kinetics followed a pseudo-second-order model and Freundlich model was obtained to fit the sorption data. The presence of competing ions slightly reduced uranium(VI) sorption and the selectivity order can be given as \(\text{UO}_{2}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}\).

Key words: Uranium(VI), sorption, dicationic ionic liquid, poly(ethylene glycol), chitosan, Box–Behnken design

1. Introduction

Uranium is a naturally occurring radioactive element and chemically toxic heavy metal. During the stages of nuclear fuel production such as mining, purification, and enrichment, large amount of uranium polluted wastewater is produced. Additional uranium sources are natural deposits and depleted uranium ammunitions [1]. Uranium exists mostly in the valence states of uranium(IV) and uranium(VI) depending on the environment. However, the oxidized state uranium(VI) can highly migrate and it is more soluble. Therefore, the direct discharge of uranium polluted waste streams is hazardous for environment and human health. Uranium can enter the human body via food chain. It can cause harmful effects on skin, kidneys, liver, and may even lead to death [2]. Consequently, it is highly important to remove uranium from wastewater prior to discharge and to prevent its mobilization into the environment.

Several methods including ion exchange, adsorption, chemical precipitation and solvent extraction [3–6] have been used for the separation of uranium from aqueous waste streams. These methods have some disadvantages due to technical, economic, and environmental issues. Among those methods, solvent extraction is one of the most commonly used methods for the separation of uranium ions. It has recently attracted more attention with the use of ionic liquids (ILs). ILs have well-known properties such as low volatility and vapor
pressure, high thermal stability, ionic conductivity, and miscibility with solvents [7,8]. However, liquid–liquid extraction has also some disadvantages such as using large quantities of ILs and the loss of IL in the aqueous phase because of insufficient phase separations [9]. The utilization of IL in solid–liquid separation processes can be proposed as a solution to overcome the problems of the liquid–liquid extractions. By the immobilization and impregnation of ILs in a suitable solid support, the consumed amount of ILs can be minimized and the loss of ILs in the aqueous phase can be reduced. Moreover, the solid support can enhance the properties of ILs for the metal ion removal [10–12].

Many types of organic and inorganic support materials have been under research for the impregnation of ILs. Macroporous organic polymers such as Amberlite type resins [13–15] (XAD 2, XAD 4, XAD 7, XAD 8) are well-known with their high surface area, uniform pore size distribution, and good mechanical and chemical stability. However, their thermal degradation generates toxic compounds. This issue could be fixed by using biopolymers such as alginate [16], cellulose [17,18], and chitosan [9,19] as a solid support. These polymers have a thermal degradation which is less harmful to the environment in comparison with synthetic resins.

Chitosan, which is a natural biopolymer, is recognized as an excellent sorbent for heavy metal ions because of its high surface area and active sites such as amino and hydroxyl groups [10,20]. It is utilized extensively for the sorption of metal ions in aqueous solutions [21,22]. The properties of chitosan can be modified and improved, so it can be used in a large number of applications. Wang et al. [23] investigated uranium(VI) adsorption behavior on cross-linked chitosan. Liu et al. [24] prepared chitosan/ZIF-8 composite beads for the efficient removal of U(VI). Lupa et al. [9] conducted a research on the adsorption of cesium and strontium ions by 1-ethyl-3-methyl imidazolium chloride impregnated chitosan. Eliodorio et al. [25] investigated the chromium adsorption behaviors of chitosan treated with two new ILs. Sorption kinetics of zinc and nickel on modified chitosan were investigated by Tripathi et al. [26].

In a surface response experiment, the independent variables or factors can be varied over a continuous range. The aim is to determine the factor settings that produce a maximum or minimum response or to map the relationship between the response and factors. Response surface methods have found considerable use in industry especially in chemical processes where the reaction yield or cost of production can be optimized as a function of controllable process factors. Box and Behnken (1960) developed some three level designs that will allow estimation of the general quadratic model. These designs consist of $2^2$ factorials in each pair of factors with all other factors held constant at their mid-level plus a few center points. Box Behnken designs require factors be varied over three levels and they usually require less total runs than the central composite design. This may make experimentation less costly [27].

In the present study, a novel IL, poly(ethylene glycol) bis(methylimidazolium) di[bis(trifluoromethylsulfon yl)imide] was synthesized and impregnated onto chitosan. The prepared sorbent was characterized by FTIR, SEM-EDX and TGA analysis. Box–Behnken design (BBD) was employed to analyze the effect of initial pH, initial concentration, contact time and temperature on the uptake capacity of uranium(VI). Sorption kinetics, isotherms and the effect of competing ions in mixed metal solutions were studied. Desorption experiments were carried out.

2. Materials and methods

2.1. Reagents and instrumentation

Uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$.6H$_2$O) and bis(trifluoromethane)sulfonimide lithium salt (CF$_3$SO$_2$NLiSO$_2$CF$_3$) were purchased from Sigma-Aldrich (Switzerland). 1-methylimidazolium (C$_4$H$_7$N$_2$) was sup-
plied by Merck (Germany). Chitosan was supplied by Sigma-Aldrich (Japan). Poly(ethylene glycol) 600 (H(OCH$_2$CH$_2$)$_n$OH) was obtained from Alfa Aesar (Germany). Pyridine (C$_5$H$_5$N) was purchased from Carlo Erba (France). Thionyl chloride (SOCl$_2$) was obtained from Acros Organics (Germany). All solvents used were of analytical grade and were supplied by Merck (Germany). The desired concentration of test solutions were obtained by diluting stock solution in appropriate volumes. pH of the test solutions were adjusted by adding nitric acid and ammonia solutions.

Fourier transform infrared (FTIR) data (400-4000 cm$^{-1}$) were acquired by Spectrum Two model FTIR spectrometer with attenuated total reflectance accessory (Perkin Elmer, USA). The thermal stability and weight loss of IL impregnated chitosan were investigated in the temperature range 20-800 °C using SDT Q600 model thermogravimetric analyzer (TGA) & differential scanning calorimeter (DSC), (TA Instruments, USA). The analysis was conducted with a linear heating rate of 10 °C min$^{-1}$ in a nitrogen gas flow. Scanning electron microscopy (SEM)-energy dispersive X-ray analysis (EDX) was performed using Apreo S model SEM coupled with EDX detector (Thermo Scientific, USA). The analysis of uranium(VI) was carried out by Optima 2000DV model Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), (Perkin Elmer, USA).

2.2. Preparation of IL impregnated chitosan
As a first step, poly(ethylene glycol) was converted to poly(ethylene glycol) dichloride. Consequently, this material was reacted with 1-methylimidazolium and poly(ethylene glycol) bis(methylimidazolium) dichloride IL was obtained. This IL was mixed with bis(trifluoromethane)sulfonimide lithium salt and poly(ethylene glycol) bis(methylimidazolium) d[bis(trifluoromethylsulfonyl)imide] was synthesized (Figure 1). Then the synthesized IL was impregnated onto chitosan.

2.2.1. Preparation of poly(ethylene glycol) dichloride
Poly(ethylene glycol) 600 and pyridine were dissolved in toluene and the resulting mixture was heated up to 87 °C and thionyl chloride was slowly added. The obtained mixture was stirred at 87 °C for 15 hours. The resulting solid was filtered and the solvent was removed from the mixture by evaporator [28]. The poly(ethylene glycol) dichloride was obtained in 90% yield.

2.2.2. Preparation of poly(ethylene glycol) based dicationic ionic liquid
The synthesized poly(ethylene glycol) dichloride and 1-methylimidazolium was stirred at 80 °C for 16 hours at a molar ratio of 1:2. Excess of 1-methylimidazolium was then removed by washing with ethyl acetate. The obtained poly(ethylene glycol) bis(methylimidazolium) dichloride was washed with ethyl ether and purified deionized water and dried in a vacuum oven at ~60-65 °C [28]. Then this IL was mixed with bis(trifluoromethane)sulfonimide lithium salt in methanol and stirred for 24 hours at room temperature. The product was separated and washed with deionized water. After that, poly(ethylene glycol) bis(methylimidazolium) d[bis(trifluoromethylsulfonyl)imide] was dried in a vacuum oven at 60 °C [29] and 65% efficiency was achieved from the reaction.

2.2.3. Preparation of sorbent
1 g of chitosan and 45 mL of ultra pure water were mixed and pH of the solution was adjusted to 3 with 1 mol L$^{-1}$ HCl. The mixture was stirred for 1 hour at room temperature. On the other hand, 0.75 g poly(ethylene glycol) bis(methylimidazolium) d[bis(trifluoromethylsulfonyl)imide] was dissolved in 5 mL of dichloromethane. Following this step, IL solution was added to chitosan solution and the mixture was stirred for 24 hours at room
temperature. After that, the mixture was filtered and the sorbent was washed with dichloromethane and dried in a vacuum oven at ~50-60 °C [30]. Thus, the sorbent to be used for the sorption of uranium(VI) ions was prepared.

2.3. Design of experiments

Box and Behnken (1960) have offered some three level designs by associating $2^k$ factorials with incomplete block designs [31]. In this study, BBD has been used to optimize the sorption conditions. The effect of four independent process variables (initial pH ($X_1$), initial concentration ($X_2$), contact time ($X_3$), and temperature ($X_4$)) on uranium(VI) sorption was investigated by making 27 experiments in a temperature controlled shaker at 150 rpm. Batch sorption studies of uranium(VI) ions on IL impregnated chitosan were carried out with 50 mg sorbent in 25 mL of liquid phase. The samples were then filtered with qualitative filter paper and uranium(VI) concentrations in the solution were analyzed before and after equilibrium by ICP-OES. The operating conditions of ICP-OES are summarized in Table 1. The sorption capacity ($Q$) was calculated using Eq. (1):

$$\text{Capacity}(Q) = (C_0 - C_e) \times \frac{V}{m},$$  

(1)
where $C_0$ and $C_e$ are the initial and equilibrium concentrations of uranium(VI) ion in solution (mg L$^{-1}$). $V$ is the volume (mL) and $m$ is the mass of the sorbent (g).

The range and levels of variables (low, center, high) examined in this study are presented in Table 2.

### Table 1. Operating conditions of ICP-OES.

| Parameter                          | Condition |
|------------------------------------|-----------|
| Plasma gas flow rate (L min$^{-1}$) | 15        |
| Auxiliary gas flow rate (L min$^{-1}$) | 0.2       |
| Nebulizer gas flow rate (L min$^{-1}$) | 80        |
| RF power (W)                       | 1000      |
| Sample flow rate (mL min$^{-1}$)   | 1.5       |
| Read delay (s)                     | 15        |
| Replicates                         | 2         |
| Element                            | Detection wavelength (nm) |
| U                                  | 385.958   |
| Zn                                 | 206.200   |
| Ni                                 | 231.604   |

### Table 2. Range and levels of variables

| Variable                        | –1 | 0 | +1 |
|---------------------------------|----|---|----|
| Initial pH                      | $X_1$ | 4 | 5 | 6 |
| Initial concentration (mg L$^{-1}$) | $X_2$ | 20 | 40 | 60 |
| Contact time (min)              | $X_3$ | 15 | 60 | 105 |
| Temperature (°C)                | $X_4$ | 30 | 40 | 50 |

The design matrix of four variables was changed at three levels (–1, 0, +1). The model equation including linear and quadratic terms for the estimation of optimum response is shown in Eq. (2).

$$ y_i = b_0 + b_1 X_i + b_{ii} X_{ii}^2 + b_{ij} X_i X_j , $$

where $y_i$ represents the response (uranium(VI) sorption capacity), $X_i$ and $X_j$ independent coded variables, and $b_0, b_1, b_{ii}, b_{ij}$ the intercept term, linear, quadratic, and dual interaction effects, respectively. Design-Expert 12 software was used to perform statistical, regression, and graphical analysis of the data.

The second-order polynomial equation can be written as in Eq. (3).

$$ y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{11} X_1^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{22} X_2^2 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{33} X_3^2 + b_{34} X_3 X_4 + b_{44} X_4^2 $$

### 3. Results and discussion

#### 3.1. Characterization studies

The FTIR spectrum of poly(ethylene glycol) bis(methylimidazolium) di[bis(trifluoromethylsulfonyl)imide] was compared with the spectrum of starting materials. The characteristic peaks in the FTIR spectrum of dicationic
IL were observed as follows FTIR (cm\(^{-1}\)): \(\nu_{C=H} = 3125\), \(\nu_{C\equiv H} = 2928-2875\), \(\nu_{C=N} = 1562\), \(\nu_{C=C} = 1474\), \(\nu_{C\equiv F} = 1428\), \(\nu_{C\equiv O} = 1195\), \(\nu_{C\equiv N} = 1142\), \(\nu_{C=S} = 1057\), \(\nu_{S=O} = 1035\), \(\nu_{C-S} = 735\).

The FTIR spectrum of IL impregnated chitosan was also compared with the spectrum of IL. The characteristic peaks were as follows FTIR (cm\(^{-1}\)): \(\nu_{OH}\) and \(\nu_{NH_2} = 3335\), \(\nu_{C-H} = 3299\), \(\nu_{C\equiv H} = 2875\), \(\nu_{C=N} = 1654\), \(\nu_{C=C} = 1579\), \(\nu_{C\equiv F} = 1349\), \(\nu_{C\equiv O} = 1196\), \(\nu_{C\equiv N} = 1148\), \(\nu_{C\equiv C} = 1050\), \(\nu_{S=O} = 1026\), \(\nu_{C-S} = 892\). The presence of vibration bands of \(=C-H\), \(C=N\), \(C=C\), \(C-F\), \(C-O\), \(S=O\), and \(C-S\) groups in the FTIR spectrum of IL-based chitosan sorbent showed that the IL was impregnated onto chitosan. Moreover, the vibration bands of \(C-F\), \(S=O\), and \(C-S\) groups in the sorbent changed according to the IL.

The surface characteristics of chitosan, IL-impregnated chitosan, and IL-impregnated chitosan after uranium(VI) sorption were examined with SEM analysis. While the morphology of chitosan has a layered structure (Figure 2a), the surface has become porous after the impregnation of IL (Figure 2b). Changes on the surface of the sorbent after sorption showed that uranium(VI) ions were successfully sorbed (Figure 2c). Additionally, the presence of uranium(VI) on the surface of IL impregnated chitosan was confirmed by energy dispersive X-ray spectroscopy (EDX) measurement. The determination of carbon, oxygen, nitrogen, fluorine, sulfur, and uranium proved that IL was impregnated onto chitosan and uranium(VI) ions are sorbed on the sorbent (Figure 2d).

![Figure 2](image_url)

Figure 2. SEM images with 5000×magnification; chitosan (a), IL-impregnated chitosan (b), IL impregnated chitosan after uranium(VI) sorption (c), and EDX spectra of IL-impregnated chitosan after uranium(VI) sorption (d).

The thermal stability of IL-impregnated chitosan was also investigated with TGA curve. It was seen that the prepared sorbent was stable at the studied temperature.
In order to examine the stability of IL-impregnated chitosan in acidic solutions, weighed amount of particles were immersed into the nitric acid solutions in the pH range of 3–5 for 5 days. The particles were dried at 40 °C and the weight losses (%) were calculated. It was determined that the IL impregnated chitosan has a weight loss of 1.6%, 2.2%, and 2.0% at pH 3, pH 4, and pH 5, respectively. The results prove that IL-impregnated chitosan has a good chemical stability under experimental conditions. However, chemical properties of the sorbent should be improved for the utilization in concentrated acidic solutions.

### 3.2. Box–Behnken design

BBD consists of 24 factorial and 3 replicate points. Experimental variables in coded and actual form along with predicted and actual responses were shown in Table 3. The second-order polynomial equation indicated the relation between independent variables and response. The regression coefficients were determined using a second-order polynomial equation (Eq. 4).

\[
y = 18.96 - 0.31 X_1 + 8.49 X_2 + 0.65 X_3 + 0.40 X_4 - 0.49 X_1^2 - 0.59 X_2^2 - 2.36 X_3^2 + 0.58 X_4^2 \\
- 0.43 X_1 X_2 - 2.18 X_1 X_3 - 0.13 X_1 X_4 - 1.13 X_2 X_3 + 0.14 X_2 X_4 - 0.60 X_3 X_4
\]  

(4)

ANOVA is a statistical method used to check the importance and fitness of the model [32]. Table 4 summarizes ANOVA for uranium(VI) sorption capacity of IL impregnated chitosan. The model F value of 23.43 suggests that the model is important. The capacity values obtained from experimental tests were compared with the predicted ones according to the model. As seen in Figure 3, correlation coefficient (R^2) value of 0.96 points out the good agreement between experimental and predicted values.

![Figure 3](image-url)

**Figure 3.** The predicted and actual responses for uranium(VI) sorption.

Coefficients of independent variables and P-values for the examined parameters (initial pH, contact time, initial concentration, temperature) are also shown in Table 4. The smallest level of importance leading to rejection of the null hypothesis is described as P-value. When P <0.05, the main effect of each factor and dual effects are regarded as statistically significant [33].
Table 3. Box–Behnken model for uranium(VI) sorption onto IL impregnated-chitosan.

| No | Coded variable | Actual variable | Experimental capacity (mg g\(^{-1}\)) | Predicted capacity (mg g\(^{-1}\)) |
|----|----------------|-----------------|--------------------------------------|-----------------------------------|
|    | X\(_1\) X\(_2\) X\(_3\) X\(_4\) | X\(_1\) X\(_2\) X\(_3\) X\(_4\) |                                      |                                   |
| 1  | -1 -1 0 0      | 4 20 60 40      | 9.56                                 | 9.26                              |
| 2  | 1 -1 0 0       | 6 20 60 40      | 9.86                                 | 9.52                              |
| 3  | -1 1 0 0      | 4 60 60 40      | 27.98                                | 27.11                             |
| 4  | 1 1 0 0      | 6 60 60 40      | 26.54                                | 25.62                             |
| 5  | 0 0 -1 -1      | 5 40 15 30      | 14.80                                | 15.52                             |
| 6  | 0 0 1 -1      | 5 40 105 30     | 19.59                                | 18.02                             |
| 7  | 0 0 -1 1      | 5 40 15 50      | 17.18                                | 17.52                             |
| 8  | 0 0 1 1      | 5 40 105 50     | 19.58                                | 17.64                             |
| 9  | -1 0 0 -1      | 4 40 60 30      | 17.47                                | 18.82                             |
| 10 | 1 0 0 -1      | 6 40 60 30      | 18.85                                | 18.46                             |
| 11 | -1 0 0 1      | 4 60 60 50      | 18.28                                | 19.88                             |
| 12 | 1 0 0 1      | 6 40 60 50      | 19.15                                | 19.01                             |
| 13 | 0 -1 -1 0      | 5 20 15 40      | 6.82                                 | 5.74                              |
| 14 | 0 1 -1 0      | 5 60 15 40      | 23.23                                | 24.98                             |
| 15 | 0 -1 1 0      | 5 20 105 40     | 9.85                                 | 9.31                              |
| 16 | 0 1 1 0      | 5 60 105 40     | 21.73                                | 24.02                             |
| 17 | -1 0 -1 0      | 4 40 15 40      | 15.34                                | 13.58                             |
| 18 | 1 0 -1 0      | 6 40 15 40      | 17.30                                | 17.32                             |
| 19 | -1 0 1 0      | 4 40 105 40     | 19.26                                | 19.24                             |
| 20 | 1 0 1 0      | 6 40 105 40     | 12.51                                | 14.28                             |
| 21 | 0 -1 0 -1      | 5 20 60 30      | 9.13                                 | 10.19                             |
| 22 | 0 1 0 -1      | 5 60 60 30      | 28.07                                | 26.89                             |
| 23 | 0 -1 0 1      | 5 20 60 50      | 9.54                                 | 10.73                             |
| 24 | 0 1 0 1      | 5 60 60 50      | 29.04                                | 27.98                             |
| 25 | 0 0 0 0      | 5 40 60 40      | 18.78                                | 18.96                             |
| 26 | 0 0 0 0      | 5 40 60 40      | 18.83                                | 18.96                             |
| 27 | 0 0 0 0      | 5 40 60 40      | 19.26                                | 18.96                             |

Main effect of initial concentration (P = 7.2 × 10\(^{-10}\)), quadratic effect of contact time (P = 7.4 × 10\(^{-3}\)) and dual effect of initial pH and contact time (P = 2.5 × 10\(^{-2}\)) were found statistically significant (Table 4).

pH is one of the most significant parameters controlling the speciation of uranium(VI) and the surface properties of IL impregnated chitosan. Since speciation depends on pH, adsorbed species are also significantly affected by pH change. Uranium(VI) and UO\(_2^{2+}\) are the most stable oxidation state and chemical form at pH <5, respectively. Low adsorption capacity at low pH is associated with the competition of H\(^+\) ions with uranium(VI) ions on active surface sites [34]. Uranyl ion starts to hydrolyze above pH 3.0 according to Eq. (5) and the amount of UO\(_2\) (OH)\(^+\) \(\text{UO}_2\) (OH)\(^2+\) and (UO\(_2\))\(_3\) (OH)\(^5+\) tend to increase until the UO\(_2\) (OH)\(_2\)
precipitates [35]. Therefore, \( \text{UO}_2^{2+}, \text{UO}_2(\text{OH})^+, \text{UO}_2(\text{OH})_2^{2+}, \text{and (UO}_2)_3(\text{OH})^{5+} \) are the species likely to exist in solution at pH 3.0–5.0.

\[
\text{UO}_2^{2+} + n\text{H}_2\text{O} \left[\text{UO}_2(\text{H}_2\text{O})_{n-m}\right]^{2-m} + m\text{H}^+.
\]

Initial pH \((X_1 = -0.31)\) has a negative effect on sorption capacity. However, the positive value of the coefficients belonging to initial concentration \((X_2 = 8.49)\), contact time \((X_3 = 0.65)\), and temperature \((X_4 = 0.49)\) indicated that initial concentration, contact time, and temperature have a positive effect on the sorption of uranium(VI). It means that the sorption capacity of uranium(VI) decreases with the increasing initial pH, whereas uranium(VI) capacity increases as initial concentration, contact time, and temperature increase (Figures 4a–4d).

In order to determine the dual effects of variables on the uranium(VI) sorption capacity, response surface methodology (RSM) has been utilized. Dual effects of independent variables are illustrated with 3D surface plots in Figures 5a–5f. In each 3D surface plot, two variables are altered while other two variables are hold at center levels.

Figure 5a illustrates the dependence of sorption on initial pH \((X_1)\) and initial concentration \((X_2)\). Maximum Q was found to be 27.14 mg g\(^{-1}\) at initial pH 4.2 and initial concentration of 60 mg L\(^{-1}\) by fixing the contact time at 60 min and the temperature at 40 °C. Figure 5b shows the interaction between initial pH \((X_1)\) and contact time \((X_3)\). Maximum Q was obtained as 19.62 mg g\(^{-1}\) at initial pH 4 and contact time of
Figure 4. Main effects on uranium(VI) sorption capacity; effect of initial pH (a), effect of initial concentration (b), effect of contact time (c), effect of temperature (d).

87 min by holding the initial concentration and temperature at 40 mg L$^{-1}$ and 40 °C, respectively. Figure 5c presents the dependency of sorption on both initial pH ($X_1$) and temperature ($X_4$). Maximum Q of 20.04 mg g$^{-1}$ was obtained at initial pH 4.6 and temperature of 50 °C by fixing initial concentration and contact time at center levels. Figure 5d shows the interaction between initial concentration ($X_2$) and contact time ($X_3$). Maximum Q was achieved as 26.88 mg g$^{-1}$ at 60 mg L$^{-1}$ and 55 min by holding the pH and temperature at center levels. Figure 5e indicates the interaction between initial concentration ($X_2$) and temperature ($X_4$). Maximum Q was obtained as 27.98 mg g$^{-1}$ at 60 mg L$^{-1}$ and 50 °C by fixing the pH at 5 and contact time at 60 min. Figure 5f demonstrates the dependence of sorption on contact time ($X_3$) and temperature ($X_4$).
Maximum Q was found to be 19.94 mg g\(^{-1}\) at 60 min and 50 °C by fixing initial pH at 5 and initial concentration at 40 mg L\(^{-1}\).
3.3. Kinetic studies

Kinetic studies were conducted in order to determine the behavior of IL-impregnated chitosan towards uranium ions. Experiments were carried out between 5 and 360 min of contact time. The experimental kinetic data were evaluated using pseudo-first and pseudo-second-order kinetic models. Pseudo-first-order model is expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$  \hspace{1cm} (6)

Integrated form of the equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t,$$  \hspace{1cm} (7)

where \( k_1 \) is the first-order rate constant (min\(^{-1}\)), \( q_t \) and \( q_e \) are amount of metal ion sorbed (mg g\(^{-1}\)) at time \( t \) and at equilibrium, respectively \([36,37]\). \( k_1 \) and \( q_e \) can be obtained from the slope and the intercept of the plot. Pseudo-second-order model \([38]\) is based on sorption capacity of solid phase and is given in Eq. (8):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t),$$  \hspace{1cm} (8)

where \( k_2 \) is the second-order rate constant (g mg\(^{-1}\) min\(^{-1}\)). Integrated linear form of the equation is expressed in Eq. (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (9)

The experimental data of uranium(VI) sorption can be explained well with pseudo-first-order and pseudo-second-order kinetic models. However, pseudo-second-order kinetic model has a slightly higher correlation coefficient value \((R^2 = 0.999)\). The determined \( q_e \) values were in accordance with the experimental data.

The kinetic plot of \( t/q_t \) versus \( t \) for uranium(VI) sorption is presented in Figure 6. \( q_e \) and \( k_2 \) can be determined from the slope and the intercept of the plot. Pseudo-first-order model parameters \( q_e, k_1, R^2 \) and pseudo-second-order model parameters \( q_e, k_2, \) and \( R^2 \) are displayed in Table 5.

![Figure 6. Pseudo-second-order kinetic plot.](image-url)
### Table 5. Kinetic model parameters for uranium(VI) sorption

| Kinetic model       | k₁ (min⁻¹) | qₑ (mg g⁻¹) | R²  |
|---------------------|------------|-------------|-----|
| Pseudo-first-order  | 0.016      | 11.09       | 0.991 |
| Pseudo-second-order | 0.005      | 30.30       | 0.999 |

### 3.4. Sorption isotherms

The effect of initial concentration on uranium(VI) sorption was examined between 25 and 800 mg L⁻¹. Sorption isotherm is presented in Figure 7. Uranium(VI) uptake increased from 12.07 to 233.51 mg g⁻¹ with a rise in the initial uranium(VI) concentration from 25 to 600 mg L⁻¹. After this point, uranium(VI) uptake capacity of the sorbent reached a plateau and remained almost constant. This behavior can be interpreted as the saturation of active sites on the sorbent.

![Sorption isotherm of uranium(VI) on IL-impregnated chitosan (initial pH: 4, temperature: 50 °C, contact time: 70 min, sorbent amount: 50 mg).](image)

**Figure 7.** Sorption isotherm of uranium(VI) on IL-impregnated chitosan (initial pH: 4, temperature: 50 °C, contact time: 70 min, sorbent amount: 50 mg).

Sorption isotherms determine the relation between quantity of the metal sorbed and the metal concentration in the solution at equilibrium.

According to the Langmuir theory, sorption takes place at specific homogeneous sites on the sorbent. Langmuir model in its linear form [39] is described by Eq. (10):

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}
\]  

(10)

where \(q_m\) is the maximum amount of the metal ion per unit weight of sorbent to form a monolayer (mg g⁻¹), \(C_e\) is the equilibrium concentration of metal ion (mg L⁻¹), and \(b\) is a constant related to the sorption energy (L mg⁻¹). \(q_m\) and \(b\) can be determined from the slope and intercept of linear plot between \(C_e/q_e\) and \(C_e\).

\(q_m\), \(b\), and correlation coefficient (R²) values determined from the isotherm are given in Table 6. \(q_m\) value was estimated to be 312.5 mg g⁻¹ for uranium(VI).
Table 6. Isotherm model data for uranium(VI) sorption onto IL impregnated chitosan

| Isotherm model | Parameter | Value |
|----------------|-----------|-------|
| Langmuir       | $q_m$ (mg g$^{-1}$) | 312.5 |
|                | $b$ (L mg$^{-1}$)    | 0.01  |
|                | $R^2$           | 0.88  |
| Freundlich     | $K_f$         | 8.97  |
|                | $n$           | 1.62  |
|                | $R^2$           | 0.97  |

Freundlich isotherm points out the multisite adsorption on heterogeneous surfaces. Freundlich adsorption isotherm [40] and its linear form are represented by Eq. (11) and Eq. (12), respectively:

$$q_e = K_f C_e^\frac{1}{n},$$  (11)

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e,$$  (12)

where $q_e$ is the equilibrium sorption capacity (mg g$^{-1}$), $C_e$ is the equilibrium concentration of the metal in solution, $K_f$ and $n$ are constants related to sorption capacity and intensity, respectively. The calculated values of $n$ and $K_f$ are given in Table 6. Among the adsorption isotherms tested, Freundlich isotherm gave the best fit with a $R^2$ value of 0.97.

The comparison of uranium(VI) sorption capacity of poly(ethylene glycol)-based dicationic IL-impregnated chitosan with some other sorbents reported in the literature is presented in Table 7.

Table 7. Comparison of uranium(VI) sorption capacities of various sorbents

| Sorbent                                    | Initial pH | Time (min) | Uranium(VI) capacity (mg g$^{-1}$) | Reference |
|--------------------------------------------|------------|------------|-------------------------------------|-----------|
| IL-impregnated diatomite                   | 4.2        | 240        | 88.00                               | [41]      |
| Chitosan impregnated with magnetite nanoparticles | 5          | 40         | 42.00                               | [42]      |
| Magnetite nanoparticles                    | 7          | 360        | 5.00                                | [43]      |
| DTPA-functionalized magnetic chitosan nano-particles | 5          | 60         | 157.08                              | [44]      |
| Cysteine functionalized magnetic chitosan microparticles | 3.6        | 60         | 99.96                               | [45]      |
| Ion-imprinted magnetic chitosan resin      | 5          | 180        | 188.02                              | [46]      |
| Poly(ethylene glycol)-based dicationic IL-impregnated chitosan | 4          | 70         | 251.52                              | Present study |

Pure chitosan can be used for the sorption of metal ions and as a result of preliminary tests, we have confirmed that it has an affinity for uranium(VI). However, impregnation of IL enhanced the sorption capacity of chitosan for uranium(VI) ions by approximately 25%. From the data in Table 7, it can be seen that the
the poly(ethylene glycol)-based dicationic IL-impregnated chitosan has a relatively high absorption capacity of 251.52 mg g\(^{-1}\) for uranium(VI) compared to other reported sorbents. Therefore, IL-impregnated chitosan can be used as a high capacity sorbent for the removal of uranium(VI) from acidic aqueous solution.

3.5. Effect of competing ions

The effect of competing ions on the selective sorption of uranium(VI) was investigated in mixed ion solutions containing zinc(II) and nickel(II). IL-impregnated chitosan was mixed with the metal mixture solutions of uranium(VI), zinc(II), and nickel(II) at pH 4. In the experiments, concentrations of zinc(II) and nickel(II) were varied between 6 and 60 mg L\(^{-1}\) while the concentration of uranium(VI) was kept constant at 60 mg L\(^{-1}\). The compositions of test solutions are shown in Table 8.

**Table 8.** The effect of competing ions on uranium(VI) sorption: Q, \(K_d\) and \(k\) values

| Solution | Ion \(\text{UO}_2^{2+}\) | \(C_o\) (mg L\(^{-1}\)) | \(C_e\) (mg L\(^{-1}\)) | Q (mg g\(^{-1}\)) | \(K_d\) (mL g\(^{-1}\)) | \(k\) |
|----------|----------------|----------------|----------------|----------------|----------------|---|
| A        | \(\text{UO}_2^{2+}\) | 60.08 | 5.27 | 26.80 | 5086.44 | - |
|          | Zn\(^{2+}\) | 6.11 | 5.80 | 0.15 | 26.21 | 95.81 |
|          | Ni\(^{2+}\) | 6.00 | 5.35 | 0.32 | 59.29 | 42.35 |
| B        | \(\text{UO}_2^{2+}\) | 60.4 | 9.84 | 24.71 | 2511.00 | - |
|          | Zn\(^{2+}\) | 6.11 | 5.80 | 0.15 | 26.21 | 95.81 |
|          | Ni\(^{2+}\) | 6.00 | 5.35 | 0.32 | 59.29 | 42.35 |
| C        | \(\text{UO}_2^{2+}\) | 60.19 | 14.89 | 22.38 | 1502.90 | - |
|          | Zn\(^{2+}\) | 29.80 | 28.64 | 0.57 | 20.07 | 74.87 |
|          | Ni\(^{2+}\) | 29.81 | 26.05 | 2.14 | 71.22 | 21.10 |
| D        | \(\text{UO}_2^{2+}\) | 60.25 | 17.50 | 20.85 | 1191.15 | - |
|          | Zn\(^{2+}\) | 60.19 | 52.7 | 3.65 | 69.30 | 17.19 |
|          | Ni\(^{2+}\) | 59.62 | 49.21 | 5.08 | 103.13 | 11.55 |

*Initial pH = 4, contact time = 70 min, temperature = 50 °C, \(V = 25\) mL, \(m = 0.05\) g.

The distribution coefficient \((K_d)\) is defined as the ratio of metal ion concentration in the solid phase to metal ion concentration in the solution at equilibrium. It is used to estimate the selectivity coefficient \((k)\) for the sorption of a metal ion in the presence of other competing ions and expressed by Eq. (13) [47]:

\[
K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m},
\]

where \(C_o\) and \(C_e\) are the initial and equilibrium concentration of ions (mg L\(^{-1}\)), respectively, \(V\) is the volume of the solution (mL), and \(m\) is mass of the sorbent (g).

Selectivity coefficient \((k)\) for a specific metal ion is determined as follows [48]:

\[
k = \frac{K_d(U)}{K_d(M)},
\]

where \(K_d(U)\) and \(K_d(M)\) are the distribution coefficient of uranium(VI) and competing ion (mL g\(^{-1}\)), respectively.

The experimental data along with the sorption capacity\((Q)\), distribution coefficient \((K_d)\) and selectivity coefficient \((k)\) values are presented in Table 8. Although uranium(VI) sorption capacity is slightly decreased
with the increase in the concentration of zinc(II) and nickel(II) ions, it is considerably high compared to that of zinc(II) and nickel(II). K_d values are in the order of UO_2^{2+} > Ni^{2+} > Zn^{2+} at all concentration ranges which indicates the affinity of material towards UO_2^{2+} ion.

According to the k values in Table 8, selectivity order can be given as UO_2^{2+} > Zn^{2+} > Ni^{2+}. These results suggest that IL impregnated chitosan can be used successfully in the treatment of radioactive wastewater polluted with uranium(VI) in the presence of competing ions.

3.6. Desorption studies

From an environmental and economic perspective, desorption efficiency and reuse of a sorbent are important parameters for adsorption processes. The desorption of uranium(VI) was investigated by using mineral acids (HNO_3 and H_2SO_4). As a first step, each 50 mg of sorbent was contacted with 60 mg L^{-1} uranium(VI) solution at 50 °C for 70 min. Following solid–liquid separation, the uranium(VI)-loaded sorbent was washed with deionized water and dried at 50 °C.

For desorption step, uranium(VI)-loaded sorbents were contacted with dilute concentrations (0.01–0.5 M) of HNO_3 and H_2SO_4 solutions at 25 °C for 60 min. IL-impregnated chitosan decomposed and dissolved in nitric acid solutions. Therefore, it was concluded that nitric acid is not suitable for desorption in the studied concentration range. On the other hand, IL-impregnated chitosan is insoluble in H_2SO_4; thus, H_2SO_4 can be used as a desorption agent as reported in literature [49,50]. Desorption efficiency increased with the increase in H_2SO_4 concentration. It was determined that 74% and 98% of uranium(VI) ions were desorbed using 0.5 M H_2SO_4, in one and two steps, respectively.

4. Conclusion

In this study, a novel poly(ethylene glycol)-based dicationic IL-impregnated chitosan was synthesized and characterized by FTIR, SEM-EDX, and TGA analysis. Sorbent was found to be chemically stable in the pH range studied. The effect of initial pH, initial concentration, contact time, and temperature on uranium(VI) sorption capacity was determined using 3 level BBD. Initial concentration, quadratic effect of contact time, dual effect of initial pH and contact time were found statistically significant. High correlation coefficient (R^2) of 0.96 reveals that actual and predicted sorption capacity values are in a good agreement. The model F value of 23.43 implies that BBD model is significant. 3D surface plots were drawn to analyze the effect of dual interactions on sorption. Maximum uranium(VI) sorption capacity of IL impregnated chitosan was found as 28.48 mg g^{-1} at the following conditions: initial pH, 4; initial concentration, 60 mg L^{-1}; contact time, 70 min and temperature, 50 °C. Kinetic data fit the pseudo-second-order kinetic model better. By the evaluation of sorption isotherm, uranium(VI) sorption was found as a Freundlich type isotherm (R^2 = 0.97). IL-impregnated chitosan has been demonstrated to be a selective sorbent for uranium(VI) ions in the presence of zinc(II) and nickel(II).

It can be said that there is electrostatic and hydrophobic interactions and hydrogen bonding between chitosan and IL. Moreover, impregnated sorbent had an alkaline character before sorption; thus, interaction between sorbent and acidic uranium(VI) solution was electrostatic. Overall results indicate that poly(ethylene glycol) bis(methylimidazolium) di[bis(trifluoromethylsulfonyl)imide] impregnated chitosan can be utilized as a high-capacity and selective sorbent for the removal of uranium(VI) ions in acidic solutions.
References

1. Xiao-teng Z, Dong-mei J, Yi-qun X, Jun-chang C, Shuai H et al. Adsorption of uranium(VI) from aqueous solution by modified Rice Stem. Journal of Chemistry 2019; 2019: 1-10. doi: 10.1155/2019/6409504

2. Zhang L, Zhang X, Lu Q, Wu X, Jiang T et al. Adsorption of U(VI) ions from aqueous solution using nanogoethite powder. Adsorption Science & Technology 2019; 37 (1-2): 113-126. doi: 10.1177/0263617418816202

3. Phillips DH, Gu B, Watson DB, Parmele CS. Uranium removal from contaminated groundwater by synthetic resins. Water Research 2008; 42: 260-268. doi: 10.1016/j.watres.2007.07.010

4. Chen S, Hong J, Yang H, Yang J. Adsorption of uranium (VI) from aqueous solution using a novel graphene oxide-activated carbon felt composite. Journal of Environmental Radioactivity 2013; 126: 253-258. doi: 10.1016/j.jenvrad.2013.09.002

5. Kim K-W, Kim Y-H, Lee S-Y, Lee J-W, Joe K-S et al. Precipitation characteristics of uranyl ions at different pHs depending on the presence of carbonate ions and hydrogen peroxide. Environmental Science and Technology 2009; 43 (7): 2355-2361. doi: 10.1021/es802951b

6. Kumar JR, Kim J-S, Lee J-Y, Yoon H-S. A brief review on solvent extraction of uranium from acidic solutions. Separation & Purification Reviews 2011; 40 (2): 77-125. doi: 10.1080/15422119.2010.549760

7. Anderson L, Armstrong DW, Wei GT. Ionic liquids in analytical chemistry. Analytical Chemistry 2006; 78 (9): 2892-2902. doi: 10.1021/ac060934o

8. Nakashima K, Kubota F, Maruyama T, Goto M. Ionic liquids as a novel solvent for lanthanide extraction. Analytical Sciences 2003; 19: 1097-1098. doi: 10.2116/analsci.19.1097

9. Lupa L, Voda R, Popa A. Adsorption behavior of cesium and strontium onto chitosan impregnated with ionic liquid. Separation Science and Technology 2018; 53 (7): 1107-1115. doi: 10.1080/01496395.2017.1313274

10. Chen J. Application of Ionic Liquids on Rare Earth Green Separation and Utilization. Berlin, Germany: Springer, 2016. doi: 10.1007/978-3-662-47510-2

11. Fontanals N, Borrull F, Marce RM. Ionic liquids in solid-phase extraction. Trac-Trends in Analytical Chemistry 2012; 41: 15-26. doi: 10.1016/j.tac.2012.08.010

12. Yusuf NYM, Masdar MS, Ishaak WNRW, Nordin D, Husaini T et al. Impregnated carbeneionic liquid as innovative adsorbent for H2/CO2 separation from biohydrogen. International Journal of Hydrogen Energy 2019; 44: 3414-3424. doi: 10.1016/j.ijhydene.2018.06.155.

13. Gallardo V, Navarro R, Saucedo I, Avila M, Guibal E. Zinc(II) Extraction from hydrochloric acid solutions using Amberlite XAD-7 impregnated with Cyphos IL 101 (Tetradecyl(Trihexyl)Phosphonium Chloride). Separation Science and Technology 2008; 43 (9-10): 2434-2459. doi: 10.1080/01496390802119002

14. Navarro R, Alba J, Saucedo I, Guibal E. Hg(II) removal from HCl solutions using a tetraalkylphosphonium ionic liquid impregnated onto Amberlite XAD-7. Journal of Applied Polymer Science 2014; 131 (22): 1-11. doi: 10.1002/app.41086

15. Yang X-Y, Zhan J-P, Guo L, Zhao H, Zhang Y et al. Solvent impregnated resin prepared using ionic liquid Cyphos IL 104 for Cr(VI) removal. Transactions of Nonferrous Metals Society of China 2012; 22 (12): 3126-3130. doi: 10.1007/S10003-6326(12)61764-6

16. Guibal E, Figuerola PA, Ruiz M, Vincent T, Jouannin C et al. Immobilization of Cyphos ionic liquids in alginate capsules for Cd(II) sorption. Separation Science and Technology 2010; 45 (12-13): 1935-1949. doi: 10.1080/01496395.2010.493113
17. Zhong L-x, Peng X-w, Yang D, Sun R-c. Adsorption of heavy metals by a porous bioadsorbent from lignocellulosic biomass reconstructed in an ionic liquid. Journal of Agricultural and Food Chemistry 2012; 60 (22): 5621-5628. doi: 10.1021/jf301182x

18. Wang A, Li S, Chen H, Hu Y, Peng X. Synthesis and characterization of a novel microcrystalline cellulose-based polymeric bio-sorbent and its adsorption performance for Zn(II). Cellulose 2019; 26: 6849-6859. doi: 10.1007/s10570-019-02563-1

19. Ren H, Li B, Neckenig M, Wu D, Li Y. Efficient lead ion removal from water by a novel chitosan gel-based sorbent modified with glutamic acid ionic liquid. Carbohydrate Polymers 2019; 207: 737-746. doi: 10.1016/j.carbpol.2018.12.043

20. Guibal E. Interactions of metal ions with chitosan-based sorbents: A review. Separation and Purification Technology 2004; 38 (1): 43-74. doi: 10.1016/j.seppur.2003.10.004

21. Pivarciova L, Rosskopfova O, Galambos M, Rajec P. Sorption of nickel on chitosan. Journal of Radioanalytical and Nuclear Chemistry 2014; 300 (1): 361-366. doi: 10.1007/s10967-014-3007-3

22. Singh P, Nagendran R. A comparative study of sorption of chromium (III) onto chitin and chitosan. Applied Water Science 2016; 6 (2): 199-204. doi: 10.1007/s13201-014-0218-2

23. Wang GH, Liu JS, Wang XG, Xie ZY, Deng NS. Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan. Journal of Hazardous Materials 2009; 168: 1053-1058. doi: 10.1016/j.jhazmat.2009.02.157

24. Liu L, Yang W, Gu D, Zhao X, Pan Q. In situ preparation of chitosan/ZIF-8 composite beads for highly efficient removal of U(VI). Frontiers in Chemistry 2019; 7: 607. doi: 10.3389/fchem.2019.00607

25. Eliodorio KP, Andolfatto VS, Martins MRG, de Sa BP, Umeki ER et al. Treatment of chromium effluent by adsorption on chitosan activated with ionic liquids. Cellulose 2017; 24 (6): 2559-2570. doi: 10.1007/s10570-017-1264-3

26. Tripathi N, Choppala G, Singh RS, Srivastava P, Seshadri B. Sorption kinetics of zinc and nickel on modified chitosan. Environmental Monitoring and Assessment 2016; 188 (9): 507. doi: 10.1007/s10661-016-5499-5

27. Lawson J. Design and Analysis of Experiments with SAS. United States: CRC Press, 2010.

28. Goodajdar BM, Soleimani S. One-pot and efficient synthesis of triazolo[1,2-a]indazole-triones catalyzed by poly(ethylene glycol) based magnetic dicationic ionic liquid. Iranian Journal of Catalysis 2016; 6 (1): 43-49.

29. Bazito FFC, Kawano Y, Torresi RM. Synthesis and characterization of two ionic liquids with emphasis on their chemical stability towards metallic lithium. Electrochimica Acta 2007; 52: 6427-6437. doi: 10.1016/j.electacta.2007.04.064

30. Seyhan Bozkurt S, Erdogun D, Antep M, Tuzmen N, Merdivan M. Use of ionic liquid based chitosan as sorbent for preconcentration of fluoroquinolones in milk, egg, fish, bovine, and chicken meat samples by solid phase extraction prior to HPLC determination. Journal of Liquid Chromatography & Related Technologies 2016; 39 (1): 21-29. doi: 10.1080/10826076.2015.1116010

31. Montgomery DC. Design and Analysis of Experiments. United States: John Wiley & Sons, Inc., 2001.

32. Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Zaïni M, El Hamri R et al. Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology. Journal of Saudi Chemical Society 2015; 16 (6): 603-615. doi: 10.1016/j.jscs.2012.03.003

33. Carmona MER, Silva MAP, Leite SGF. Biosorption of chromium using factorial experimental design. Process Biochemistry 2005; 40: 779-788. doi: 10.1016/j.procbio.2004.02.024

34. Yang T, Zhang W, Liu H, Guo Y. Enhanced removal of U(VI) from aqueous solution by chitosan-modified zeolite. Journal of Radioanalytical and Nuclear Chemistry 2020; 323: 1003-1012. doi: 10.1007/s10967-019-06993-w
35. Wang J, Chen Z, Shao D, Li Y, Xu Z et al. Adsorption of U(VI) on bentonite in simulation environmental conditions. Journal of Molecular Liquids 2017; 242: 678-684. doi: 10.1016/j.molliq.2017.07.048

36. Lagergren S. About the theory of so-called adsorption of solution substances. Kungliga Svenska Vetenskapsakademiens Handlingar 1898; 24: 147-156.

37. Ho YS, McKay G. Sorption of lead(II) ions on peat. Water Research 1999; 33: 578-584. doi: 10.1016/S0043-1354(98)00207-3

38. Mahajan G, Sud D. Kinetics and equilibrium studies of Cr(VI) metal ion remediation by Arachis Hypogea shell: a green approach. Bioresource Technology 2011; 6: 3324-3338. doi: 10.15376/biores.6.3.3324-3338

39. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society 1918; 40: 1361-1403.

40. Freundlich HMF. Over the adsorption in solution. The Journal of Physical Chemistry 1906; 57: 385-471.

41. Sprynsky M, Kowalkowski T, Tutu H, Cukrowska EM, Buszewski B. Ionic liquid modified diatomite as a new effective adsorbent for uranium ions removal from aqueous solution. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2015; 465: 159-167. doi: 10.1016/j.colsurfa.2014.10.042

42. Stopa LCB, Yamaura M. Uranium removal by chitosan impregnated with magnetite nanoparticles: adsorption and desorption. International Journal of Nuclear Energy Science and Technology 2010; 5 (4): 283-289. doi: 10.1504/IJNEST.2010.035538

43. Das D, Sureshkumar MK, Koley S, Mithal N, Pillai CGS. Sorption of uranium on magnetite nanoparticles. Journal of Radioanalytical and Nuclear Chemistry 2010; 285 (3): 447-454. doi: 10.1007/s10967-010-0627-0

44. Sheng L, Zhou L, Huang Z, Liu Z, Chen Q et al. Facile synthesis of magnetic chitosan nano-particles functionalized with N/O-containing groups for efficient adsorption of U(VI) from aqueous solution. Journal of Radioanalytical and Nuclear Chemistry 2016; 310 (3): 1361-1371. doi: 10.1007/s10967-016-5014-z

45. Galhoum AA, Mahfouz MG, Gomaa NA, Abdel-Rehem SS, Atia AA et al. Cysteine-functionalyzed chitosan magnetic nano-based particles for the recovery of uranium(VI): uptake kinetics and sorption isotherms. Separation Science and Technology 2015; 50 (18): 2776-2789. doi: 10.1080/01496395.2015.1085405

46. Zhou L, Shang C, Liu Z, Huang G, Adesina AA. Selective adsorption of uranium (VI) from aqueous solutions using the ion-imprinted magnetic chitosan resins. Journal of Colloid and Interface Science 2012; 366: 165-172. doi: 10.1016/j.jcis.2011.09.069

47. Anderson PR, Christensen TH. Distribution coefficients of Cd, Co, Ni and Zn in soils. European Journal of Soil Science 1988; 39: 15-22. doi: 10.1111/j.1365-2389.1988.tb01190.x

48. Gu S, Kang X, Wang L, Lichtfouse E, Wang C. Clay mineral adsorbents for heavy metal removal from wastewater: a review. Environmental Chemistry Letters 2019; 17 (2): 629-654. doi: 10.1007/s10311-018-0813-9

49. Bhuvaneswari S, Sruthi D, Sivasubramanian V, Kanthimathy K. Regeneration of chitosan after heavy metal sorption. Journal of Scientific & Industrial Research 2012; 71: 266-269.

50. Schwarz S, Schwarz D, Ohmann W, Neuber S. Adsorption and desorption studies on reusing chitosan as an efficient adsorbent. Proceedings of the 3rd World Congress on Civil, Structural, and Environmental Engineering (CSEE’18) 2018; 1-4. doi: 10.11159/awspt18.128