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## RESEARCH ARTICLE

## Separation of Uranyl Ion from Different Media Using a New Cellulose Hydrazone: Adsorption Isotherms, Kinetic and Thermodynamic Studies

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### Abstract

Cellulose dialdehyde has been prepared and reacted with thiosemicarbazide to give thiosemicarbazone modified cellulose (CTSC). A new and a relatively green methodology have been developed for the selective separation and/or preconcentration of uranyl ions. Batch and column modes were applied. The newly designed cellulose quantitatively sorbed UO<sub>2</sub>(II) ions at pH 4. While,  $t_{1/2}$  is 15 min which decreased with increasing temperatures and the sorption rate constant  $R_d$  equal  $18.565 \text{ mg g}^{-1} \text{ min}^{-0.5}$ . The recovery, relative standard deviation and detection limit are found to be  $> 98\%$ ,  $< 1.7\%$  and  $5 \text{ mg ml}^{-1}$ , respectively. Optimum flow rate is  $5 \text{ ml min}^{-1}$  which reflect higher tendency toward complexation. Desorption was effective with  $0.3 \text{ mol l}^{-1} \text{ HNO}_3$  and/or HCl prior to detection. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were applied to analyze the experimental data. The best interpretation for the experimental data was given by the Langmuir isotherm and the maximum adsorption capacity was found to be  $90.04 \pm 1.00 \text{ mg/g}$  for UO<sub>2</sub>(II) ions. Kinetic data correlated well with the pseudo first-order kinetic model, which results as  $k = 0.046 \text{ min}^{-1}$ ; indicating that the chemical sorption was the rate-limiting step. Thermodynamic parameters like Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were evaluated by applying the Van't Hoff equation. The thermodynamic study indicated that the adsorption process is spontaneous and endothermic in nature. The modified cellulose (CTSC) was highly ion-selective in nature even in the presence of large concentrations of electrolytes or organic media, with a preconcentration ability for UO<sub>2</sub>(II) ions in presence of DETPA. From the column mode HETP and the number (N) of theoretical plates were found to be  $0.194 \pm 0.02 \text{ mm}$ ,  $226 \pm 4 \text{ plates g}^{-1}$ ; respectively, from breakthrough curve and  $0.20 \pm 0.05 \text{ mm}$ ,  $214 \pm 2 \text{ plates g}^{-1}$ ; respectively, from elution of column curve. The utility of the modified cellulose to synthetic and real samples showed RSD values of  $< 3\%$  reflecting its accuracy and reproducibility

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## INTRODUCTION

Radioactive ions often cause pollution, as they accumulate in both water and environment. Hence, the presence of radioactive ions poses an environmental challenge. About 40,000 – 50,000 tons of uranium are produced every year [1]. Uranium is considered to be not only an irreplaceable raw material for nuclear energy, but also a

serious long-term potential environmental hazard [2]. Uranium ions often accumulate in both water and the environment because of its long half-life. Hence, its presence poses an environmental challenge. As the water constitutes an indispensable element life, the removal of radioactive ions from water sources and from waste water becomes important, and many studies have been conducted to develop novel techniques for this purpose [3-6]. Over the past few decades, a variety of technologies including chemical and physical precipitation [7-8], solvent extraction [9] ion exchange [10], membrane processes [11] and adsorption [12] have been developed for the removal and recovery of uranium from nuclear fuel effluents, mine tailings, seawater and other waste sources. Lately, adsorption due to its high efficiency and readily has been gradually utilized [13]. A considerable amount of work has been carried out regarding the extraction of uranium by solvent extraction techniques, using various composites; tetraethylenepentamine modified magnetic chitosan [14], carboxyl-terminated hybrid adsorbent composite [15], pass cement dust [16], solvent-impregnated foam [17], soils [18], activated carbon [19], zeolite volcanic tuff [20], and unsaturated polyester-styrene polymeric beads [21].

The use of many of the solvent extraction techniques has been limited because they are expensive, often require long processes times, and cause the release of toxic materials. A physicochemical method, adsorption, on the other hand, that appears to be a much more cost-effective and environmentally friendly techniques [22-25], has been used for the recovery of metal ions selectively in remediation processes [26-27].

In a previous study, a novel, low-cost, date pits (DP) was prepared and used for the selective removal of  $\text{UO}_2^{2+}$  ions from aqueous solution both a batch and column system [28].

To address this objective in this study we use cellulose modified with thiosemicarbazide (CTSC) for  $\text{UO}_2(\text{II})$  removal from aqueous media. The adsorptive capacity of CTSC was then tested with  $\text{UO}_2^{2+}$  ion; after testing, the physicochemical parameters (pH, concentration, time and temperature) for the adsorption were optimized.

## 2. Experiment

### 2-1. Apparatus

A Perkin-Elmer model 2380 (USA) Atomic Absorption Spectrometer was used. The IR spectra were carried out using Mattson 5000 FTIR Spectrophotometer in the range  $4000\text{-}400\text{ cm}^{-1}$  as KBr disc. The UV-Visible measurements were performed on a Unicam 2001 UV-Vis Spectrophotometer using a 1 cm quartz cell for determination of  $\text{UO}_2^{2+}$  using Arsenazo III. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of  $\pm 0.01$  and standardized with  $0.05\text{ mol l}^{-1}$  potassium hydrogen phthalate (pH 4.01) and standard Tablet (pH = 9.2) at  $25\pm 1\text{ }^\circ\text{C}$ . Glass columns (40x6 mm) and variable mechanical Shaker (Corporation Precision Scientific, Chicago, USA) with shaking rate in the range 10-250 rpm were used for the retention experiments of uranium (VI) species at different pH.

### 2-2. Reagents and materials

A stock solution of uranium (VI) ( $1000\mu\text{g.ml}^{-1}$ ) was prepared by dissolving an appropriate amounts of uranyl acetate dehydrate (Fluka Chemie, AG, Buchs, Switzerland) in double distilled water. Stock solutions ( $1000\mu\text{g ml}^{-1}$ ) of the metal ions (as chloride or nitrate salts) were prepared in double-distilled water.

Arsenazo (III) (0.1%w/v) (Fluka Chemie, AG) was prepared in ethanol and completed with water. Solutions of pH 1- 8 were prepared by using Hydrochloric acid in double distilled water and adjusting the solutions to be required value with Sodium hydroxide. All of these materials were analytical grade.

### 2-3. Synthesis of Modified Cellulose

To prepare the dialdehyde cellulose, potassium periodate was used to oxidize its  $\text{-CH}_2\text{-OH}$  glycol group [29-31]. Cellulose is stirred in a 0.5%  $\text{KIO}_4$  solution for 6h. The precipitate is washed with bidistilled water and then dried, ground, sieved size of - 25 mesh, and stored in a polypropylene container.

### 2-4. Batch Mode

A sample solution (100 ml) containing known concentration of  $\text{UO}_2^{2+}$  ion ( $50\text{ }\mu\text{g/ml}$ ) is transferred to a glass stoppered bottle (250 ml) and 50 mg of the modified cellulose added after adjusting its pH to the optimum value,. The mixture is shaken for 30 min, filtered and washed with bidistilled water at  $25\pm 1\text{ }^\circ\text{C}$ . After equilibrium, the amount of  $\text{UO}_2^{2+}$  ions retained on the solid sorbent was determined from the difference between the absorbance of uranyl (II) ion-Arsenazo III complex before ( $C_i$ ) and after ( $C_f$ ) shaking with the CTSC. The sorption percentage (%E) and the distribution coefficient ( $K_d$ ) were then determined employing the equations:

$$E\% = \frac{C_i - C_f}{C_f} \times 100 \quad (1)$$

$$K_d \text{ (ml g}^{-1}\text{)} = \frac{\% E}{100 - \% E} \times \frac{v}{w} \quad (2)$$

Where; V and W are the sample volume (ml) and weight of the dried CTSC in grms.

Following these procedures, the effect of different parameters e.g. shaking time, temperature, sorbent dose and  $\text{UO}_2^{2+}$  on the retention of  $\text{UO}_2^{2+}$  was carried out. The data are the average of three independent measurements and the precision in most cases was  $\pm 2\%$ . The sorbed  $\text{UO}_2^{2+}$  ion is eluted with 5 ml of a suitable concentration of  $\text{HNO}_3$  and the resulting solution is completed to 100 ml and determined spectrophotometric using Arsenazo III.

## 2-5. Column Mode

The modified cellulose (5.0 g) is firstly swollen for 24 h and packed in a glass column (40x6 mm). A sample solution (100 ml) of 100  $\mu\text{g/ml}$   $\text{UO}_2^{2+}$  ion buffered to the conditional pH is passed through the column at the optimum flow rate. After sorption, the column is washed with 100 ml bidistilled water to remove any uncomplexed  $\text{UO}_2^{2+}$  ion from the modified cellulose bed.  $\text{HNO}_3$  solution was used to stripping  $\text{UO}_2^{2+}$  ion from the modified cellulose. The eluted solution is collected in a 100 ml calibrated flask and analyzed. The same procedures were also applied in the blank experiment. The HETP, N and breakthrough capacity were then calculated from the output of the chromatograms.

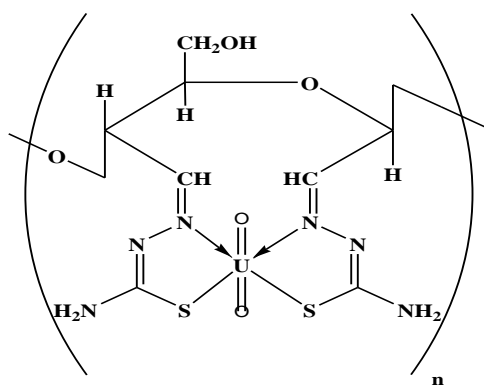
## 3. Results and Discussion

### 3.1. Characterization of CTSC and its $\text{UO}_2^{2+}$ Complex

The IR spectrum of the modified cellulose (**Fig.1**) showed strong bands at 3370, 3266, 3213, 1640, 1620, and  $800 \text{ cm}^{-1}$  assigned to  $\nu_{(\text{OH})}$ ,  $\nu_{(\text{NH}_2)}$ ,  $\nu_{(\text{NH})}$ ,  $\delta_{(\text{NH}_2)}$ ,  $\nu_{(\text{C}=\text{N})}$ , and  $\nu_{(\text{C}=\text{S})}$ ; respectively. The absence of any bands due to aldehydic group with the appearance of these characteristic bands is taken as a strong evidence for the immobilization process.

Comparison between the IR spectrum of  $\text{UO}_2^{2+}$  complex with that of CTSC (**Fig.1**) showed that, each unit of CTSC acts as a binegative tetradentate ( $\text{N}_2\text{S}_2$ ) ligand coordinating *via* C=N and C-S from each side with replacement of the thiol proton. This mode of chelation is supported by complete disappearance of the bands assigned to  $\nu_{(\text{C}=\text{S})}$  and  $\nu_{(\text{NH})}$  with the appearance of bands at 1634 and  $668 \text{ cm}^{-1}$  due to  $\nu_{(\text{C}=\text{N}^*)}$  and  $\nu_{(\text{C}=\text{S})}$ . The azomethine band [ $\nu_{(\text{C}=\text{N})}$ ] in the modified cellulose is shifted to lower wavenumber indicating the coordination *via* nitrogen [30]. The bands due to  $\nu_{(\text{NH}_2)}$  and  $\delta_{(\text{NH}_2)}$  are still more or less at the same position. The strong broad band centered at  $3350 \text{ cm}^{-1}$  may be due to hydrated water.

**Scheme 1** represents a speculative structure for the formed complex.



**Scheme 1:** Structural formula of  $\text{UO}_2^{2+}$  modified cellulose complex ( $\text{UO}_2^{2+}$ -CTSC).

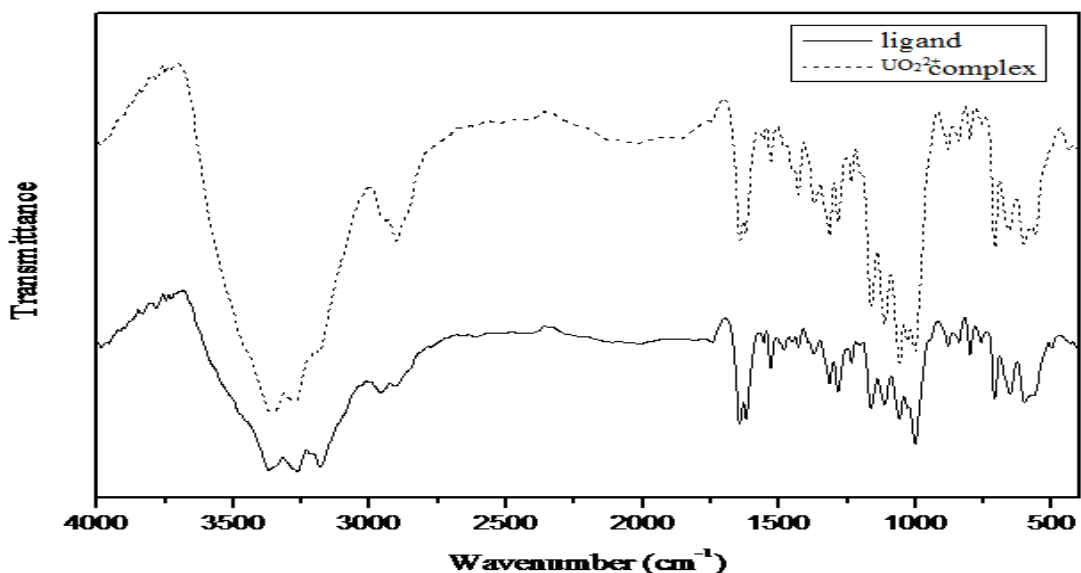


Fig. 1- IR spectra of thiosemicarbazone modified cellulose ( \_\_\_ ) and its  $\text{UO}_2^{2+}$  complex (-----) in KBr.

### 3.2. Batch Technique

#### 3.2.1. Influence of pH on Adsorption

The pH medium is one of the most important factors that commonly controls and strongly influence the retention of the metal ions by the solid sorbents. The effect of pH on the sorption of  $\text{UO}_2^{2+}$  ion has been investigated in the pH range 1-8 by batch equilibrium experiments. The experiments were elaborated by shaking the solution containing the ion with the modified Cellulose of variable pH for sufficient equilibrium time. The pH was adjusted using suitable buffer solutions. The data represented in Fig.2, indicates that the adsorption behavior of  $\text{UO}_2^{2+}$  ions are sensitive to pH changes, especially at a lower pH level [32].  $\text{UO}_2^{2+}$  ion adsorption is pH dependent. Adsorption was observed to increase at elevated pH values, reaching a maximum at pH 4. This maximum value is approaches that of solutions containing metal ions [33].

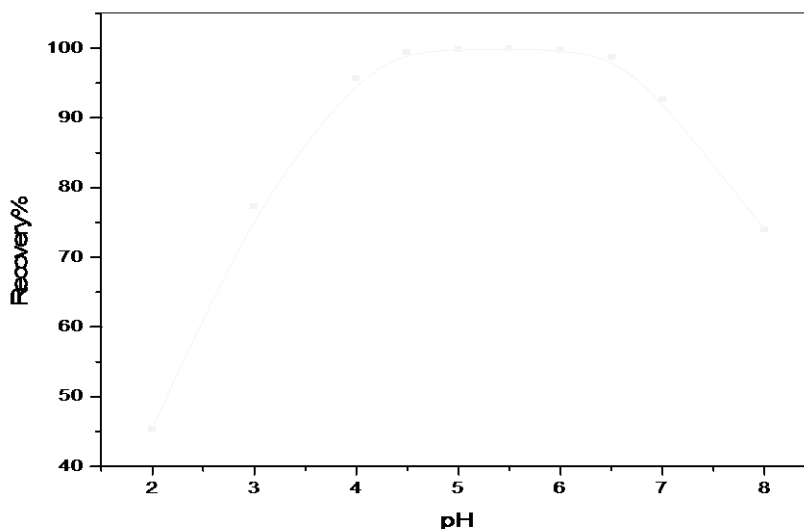
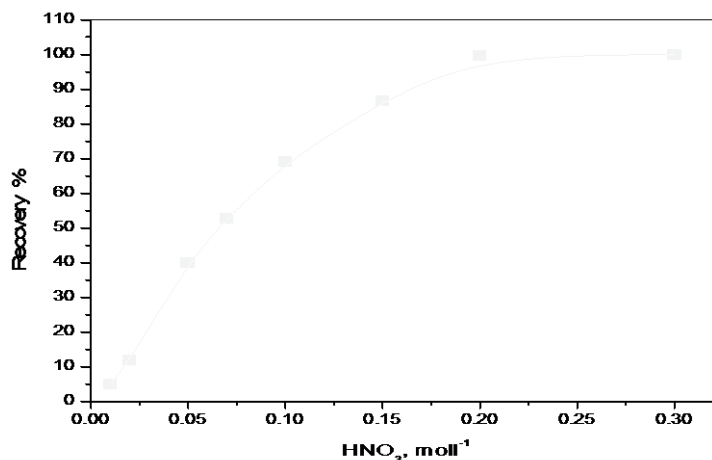


Fig. 2: Effect of pH on the recovery % of  $\text{UO}_2^{2+}$  using 50 mg CTSC and stirring time= 30 min at  $25\pm 1^\circ\text{C}$ .

### 3.2.2. Choice of Eluent

Choice of the effective eluent for the quantitative stripping of the retained  $\text{UO}_2^{2+}$  ion on CeTSC is of special interest. The  $\text{UO}_2^{2+}$  ion sorbed on CeTSC is eluted with different acid solutions (HCl,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ ). The data drawn in Fig. 3 indicate that,  $0.3 \text{ mol l}^{-1}$  of  $\text{HNO}_3$  affords quantitative elution of  $\text{UO}_2^{2+}$  ion from the modified cellulose.



**Fig. 3:** Effect of  $\text{HNO}_3$  concentration (5 ml) on the recovery of  $\text{UO}_2^{2+}$  using 50 mg CTSC and stirring time 10 min at  $25 \pm 1^\circ\text{C}$ .

### 3.2.3. Determination of Sorption Capacity

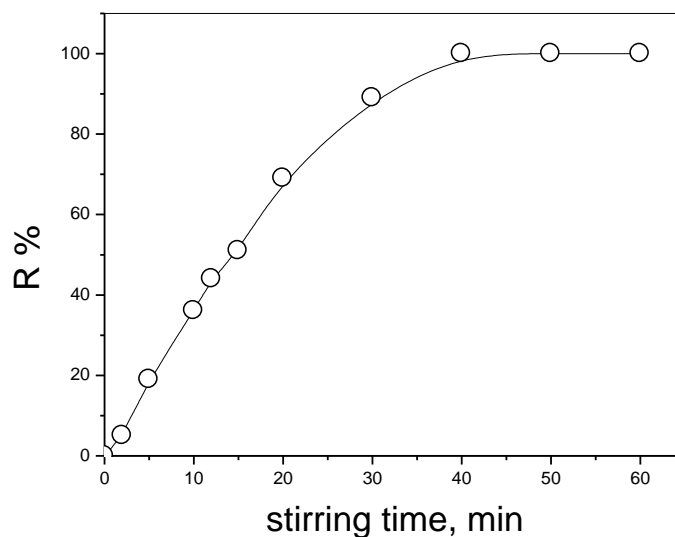
The sorption capacity of the modified cellulose towards  $\text{UO}_2^{2+}$  ion is determined by shaking excess  $\text{UO}_2^{2+}$  ion with 50 mg of CTSC at pH 4.0. The sorption capacity was calculated by the following Eq.:

$$q = \frac{C_i - C_f}{w} \times V \times 1000 \quad (3)$$

Where,  $q$  (mg/g) represents the amount of  $\text{UO}_2^{2+}$  adsorbed onto adsorbent;  $C_i$  and  $C_f$  (mg/L) represent  $\text{UO}_2^{2+}$  concentration before and after adsorption, respectively;  $V$  (mL) is  $\text{UO}_2^{2+}$  solution volume used and  $W$  (g) is the weight of adsorbent. The data indicate  $90 \text{ mg g}^{-1}$  is the maximum sorption capacity for  $\text{UO}_2^{2+}$  ion with CTSC.

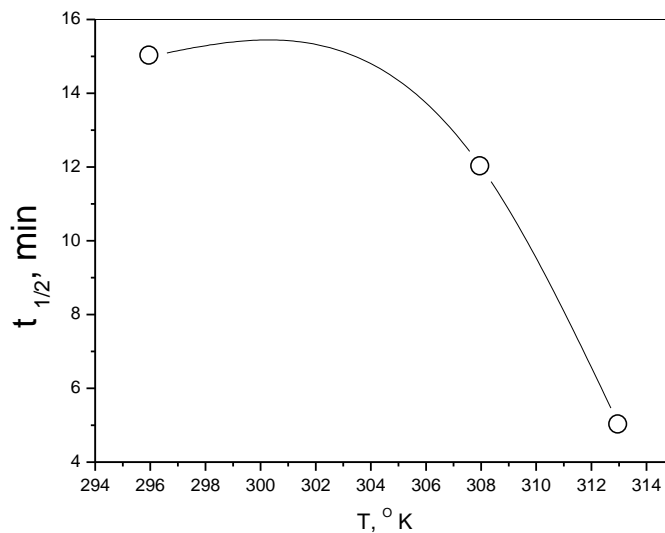
### 3.2.4. Sorption Kinetics

To determine the rate of sorption of metal ion on the modified polymer, batch experiments were elaborated by shaking the solution containing the ion with 50 mg of the modified polymer at room temperature ( $25^\circ\text{C}$ ). Aliquots of 1 ml solution were taken out for analysis at pre-determined intervals. The concentration of metal ion in the supernatant solution was determined and the amount of metal ion sorbed on the modified polymer was calculated by mass balance. The sorption half-time ( $t_{1/2}$ ) defined, as the time needed to reach 50% of the total sorption capacity was estimated from Fig. 4. From the data obtained, it was observed that the maximum sorption of  $\text{UO}_4$  (II) ion with CTSC reached its equilibrium time after about 40 min, respectively. However, the time required for 50% sorption of  $\text{UO}_4$  (II) ion was 15 min for the modified cellulose.



**Fig. 4:** Effect of stirring time on the recovery % of  $\text{UO}_2^{2+}$  using 50 mg CTSC, pH = 4.0 at  $25 \pm 1^\circ\text{C}$ .

The sorption half-time ( $t_{1/2}$ ) is decreased from 15 to 5 min; with increasing temperatures as represented in **Fig. 5**.



**Fig. 5:** Relation between  $t_{1/2}$  and  $T$  ° K.

The sorbed concentration at time  $t$ ,  $q_t$  ( $\text{mg g}^{-1}$ ) amount of metal ion sorbed at time  $t$ , is plotted against  $t$  to test the Morris-Weber equation [34]:

$$q_t = R_d \sqrt{t} \quad (4)$$

For up to 35 min, eq. (1) relationship holds good but deviates as the stirring time is increased. From the slope of the plot in the initial stage (**fig. 6**), the value of  $R_d$ , the rate constant of intraparticle transport, is estimated to be  $18.565 \text{ mg g}^{-1} \text{ min}^{-0.5}$  which reflects the high film diffusion, intraparticle diffusion and a fast reaction between  $\text{UO}_2(\text{II})$  ion and modified cellulose.

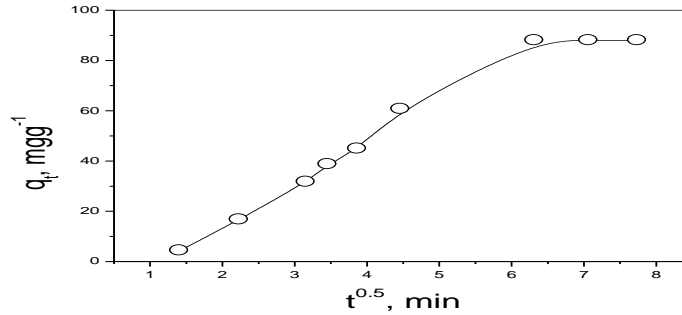


Fig. 6: Effect of Rate law on sorption of UO<sub>2</sub>(II) ion.

Moreover, the kinetic data were also evaluated using the Lagergren equation [35]:

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{k t}{2.303} \tag{5}$$

Where,  $q_e$  is the sorbed UO<sub>4</sub> (II) ion onto CTSC at equilibrium (mg/g) and  $k$  is the overall rate constant. The sorption of UO<sub>4</sub> (II) ion onto modified cellulose follows Lagergren equation shown in Fig. 7 is linear and the slope gives a value of the first-order overall rate constant  $k = 0.046 \pm 0.02 \text{ min}^{-1}$  and from intercept  $q_e = 89.12 \pm 1.50 \text{ mgg}^{-1}$ .

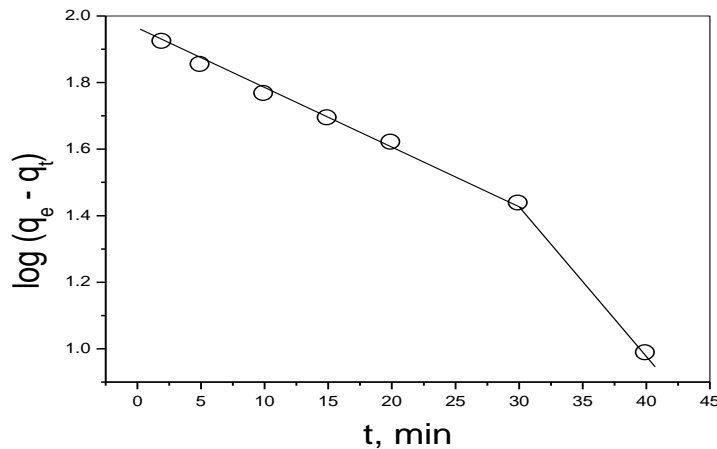
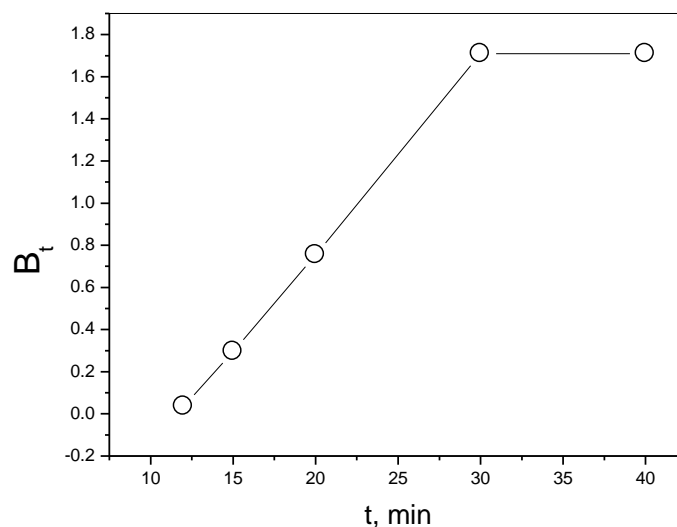


Fig. 7: Lagergren plot of the kinetics of UO<sub>2</sub>(II) ions onto CTSC.

The value of  $B_t$  which is a mathematical function (F) of  $\frac{q_t}{q_e}$  can be calculated for each value of F, as shown by Reichenberg equation [36]:

$$B_t = -0.4977 - 2.303 \text{ log}(1 - F) \tag{6}$$

A linear plot shown in fig. 8 of  $B_t$  versus time at 27 °C was found linear up to 30 min and the straight line does not pass through the origin.



**Fig. 8:** Reichenburg plot of the kinetics of  $\text{UO}_2(\text{II})$  ions onto CTSC.

### 3.2.5. Sorption Isotherm Models

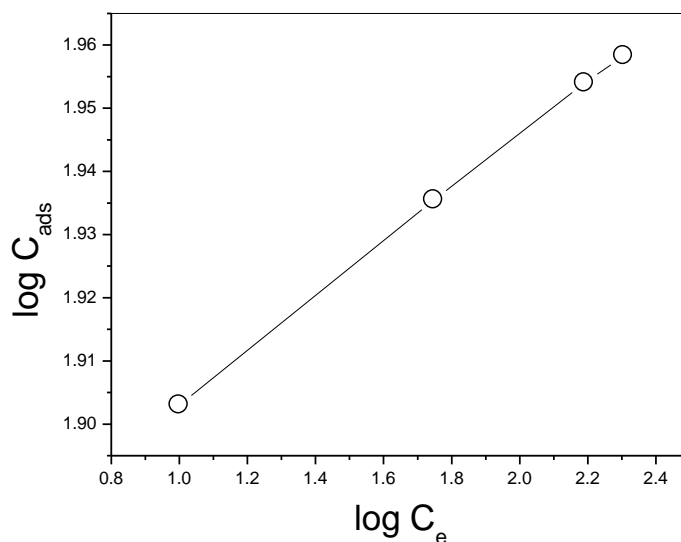
The sorption data were subjected to different sorption isotherms, namely; Freundlich, Langmuir and Dubinin-Radushkevich (D-R) [37 - 39]; the data followed all three isotherms over the entire concentration of  $\text{UO}_4(\text{II})$  ions and temperature range investigated.

Freundlich isotherm equation  $\frac{C_e}{C_{ads}} = K_F C_e^{1/n}$  can be written in the linear form as given below.

$$\log \frac{C_e}{C_{ads}} = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

Where,  $\frac{C_e}{C_{ads}}$  and  $C_e$  are the equilibrium concentrations of  $\text{UO}_2(\text{II})$  ion in the modified cellulose (mg/g) and liquid phases (mg/l), respectively.  $K_F$  and  $1/n$  are the Freundlich constants which are related to sorption capacity and intensity, respectively. These constants can be calculated from the slope and intercept of linear plot, with  $\log \frac{C_e}{C_{ads}}$  versus  $\log C_e$ . From **fig. 9**,  $K_F$  equal  $80.60 \pm 2 \text{ mg g}^{-1}$  and  $1/n = 0.0226$  which  $< 1$  reflects favorable sorption.





**Fig. 9:** The Freundlich sorption isotherm of UO<sub>2</sub>(II) ions onto CTSC.

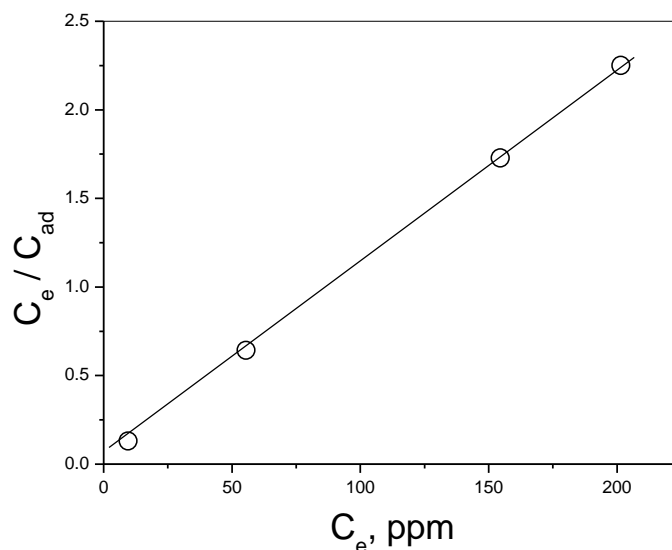
The Langmuir sorption isotherm equation on linearization becomes

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (8)$$

Where, Q and b are Langmuir constants which are related to the sorption capacity and energy of sorption, respectively and can be calculated from the intercept and slope of the linear plot, with  $\frac{C_e}{C_{ads}}$  versus C<sub>e</sub>.

From **fig.10**; Q = 90.04 mg g<sup>-1</sup> and b = 0.888 ± 0.002 Lmg<sup>-1</sup>. Another dimensionless equilibrium parameter, R<sub>L</sub> can be estimated using the following relationship:  
 $R_L = 1 / 1 + b C_i$

Where, b is the Langmuir constant and C<sub>i</sub> is the initial concentration of UO<sub>2</sub>(II) ion in solution. The value of R<sub>L</sub> found be in the range 0.0431 to 5.6 × 10<sup>-3</sup> and according to 0 < R<sub>L</sub> < 1; so; the sorption is favored [40].



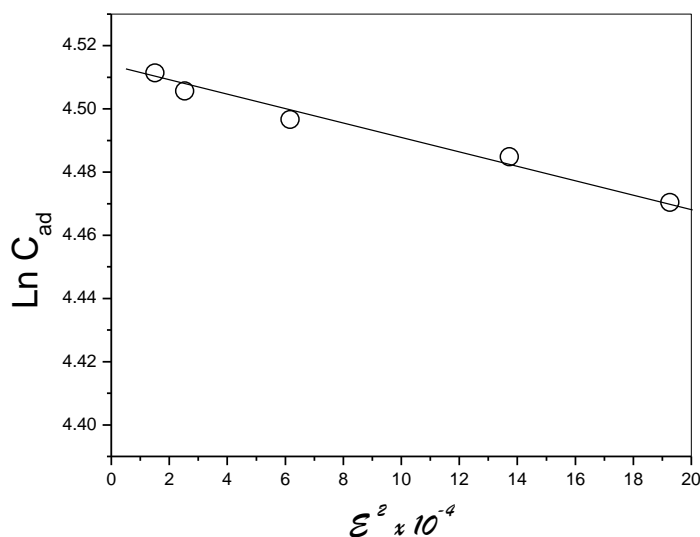
**Fig. 10.** Langmuir sorption isotherm of UO<sub>2</sub>(II) ions onto CTSC.

The Dubinin–Radushkevich isotherm is postulated within and sorption “space” close to the polymer surface [39]. The model features the heterogeneity of energies over the surface. The linear form of the D-R isotherm, which was plotted as,

$$\ln C_{ads} = \ln X_{DR} - \beta \varepsilon^2 \quad (9)$$

Where,  $X_{DR}$  is the total sorption capacity in (mg/g),  $\beta$  is activity coefficient, related to the mean sorption energy as;

$E = 1 / \sqrt{-2\beta}$  in (KJ mol<sup>-1</sup>); that E is the energy of transfer one mole of solute from infinity to the surface of modified cellulose; and  $\varepsilon$  is Polanyi potential, which equal  $RT \ln [1 + (1/C_e)]$ . Plot  $\ln C_{ads}$  versus  $\varepsilon^2$  was linear at all temperatures investigated;  $X_{DR}$  may represent total specific micro pores volume of the polymer. From **fig. 11**;  $X_m = 90 \text{ mgg}^{-1}$  from the intercept,  $\beta = -0.008 \pm 0.002 \text{ mol}^2/\text{KJ}^2$  from the slope and  $E = 1 / (-2\beta)^{0.5} = 1 / (0.016)^{0.5} = 16.66 \pm 0.20 \text{ KJ mol}^{-1}$  which not lie between 8-16 KJ/mol but also higher which reflects that chemisorptions prevails [41].



**Fig. 11:** The Dubinin-Radushkevich sorption isotherm of  $\text{UO}_2(\text{II})$  ions onto CTSC.

### 3.3.6. Effect of Temperature

The influence of temperature on the sorption behavior of  $\text{UO}_2(\text{II})$  ions on modified cellulose using 40 min stirring time from 23 – 45°C has also been studied. Different thermodynamic parameters being evaluated using Van't Hoff equation in the form:

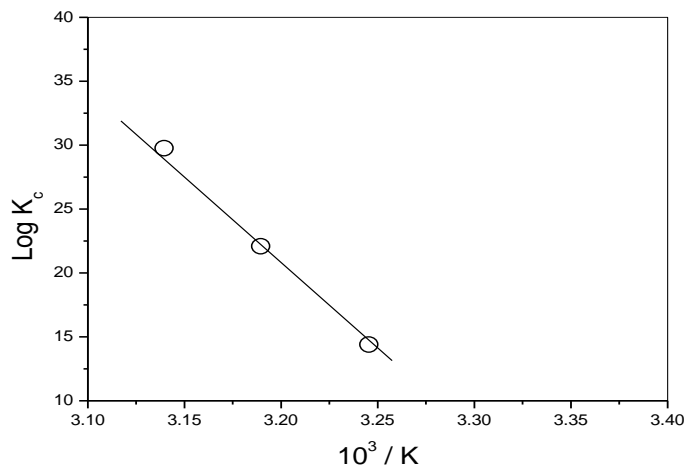
$$\text{Log } K_c = \frac{-\Delta H}{2.303 RT} + \frac{\Delta S}{2.303 R} \quad (10)$$

$$\text{and } \Delta G = -RT \ln K_c \quad (11)$$

The value of  $K_c$  equilibrium constant was worked out at each temperature using the relationship  $K_c = F_e / (1 + F_e)$ , where  $F_e$  is the fraction of  $\text{UO}_2(\text{II})$  ions sorbed at equilibrium. The plot  $\log K_c$  versus  $1/T$  is shown in **Fig. 12**. From the slope and intercept of plot (**Fig. 12**), the numerical values of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) are 2.6245 kJ mol<sup>-1</sup> K<sup>-1</sup>, 593 J mol<sup>-1</sup>; respectively and the Gibbs free energy ( $\Delta G$ ) lie between -37.76 and -180.65 KJ mol<sup>-1</sup> K<sup>-1</sup>. These values indicate spontaneous nature of sorption, while positive value of  $\Delta H$  reflects the endothermic sorption behaviour.

The higher positive value entropy change favors the stability of the sorption *via* chemisorption type [42]. The source of this entropy gain is due to liberation of water molecules from the hydrated shells of the sorbed species [42]. The numerical values of the terms  $-T\Delta S > \Delta H$ , also supports the “entropy driven” sorption due to the decrease in the hydration shells of  $\text{UO}_2(\text{II})$  ions in the polymer which increase the randomness of the system, resulting in the positive entropy change contribution. The positive value of enthalpy ( $\Delta H$ ) reflects

predominantly electrostatic bond formation between metal ion and polymer. Overall, the positive values of  $\Delta H$  and  $\Delta S$  imply that the dehydration is more significant in these terms than reported values in the literature.



**Fig. 12:** The variation of  $\log K_c$  versus  $1/T$  ( $K^{-1}$ ) for  $UO_2(II)$  ions onto CTSC.

### 3.2.7. Interferences

Several cations and anions were placed individually and in combination to study their influence on the sorption and determination of  $UO_2^{2+}$ . The results are summarized in (Table 1) most of them did not interfere;  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Co^{2+}$  interfered only in the determination process. The interference is eliminated or reduced using DETPA by forming a stable complex with most interfering ions, but with  $UO_2^{2+}$ , the modified cellulose has the ability to replace  $UO_2^{2+}$  from its DETPA complex.

**Table 1:** Influence of interfering ions on the R% of  $10 \mu g \text{ ml}^{-1} UO_2^{2+}$  using 50 mg of CeTSC at pH 4.5 and  $25 \pm 1^\circ C$

Coexisting ion (s)	Concentration ( $\mu g \text{ ml}^{-1}$ )	$UO_2^{2+}$ (Recovery %)
$K^+$ , $Cl^-$ , $NO_3^-$ , $NH_4^+$ , $CH_3COO^-$ , $F^-$	500	100.00
$Ca^{2+}$ , $Al^{3+}$ , $Mg^{2+}$	350	100.00
$Ni^{2+}$	200 <sup>a</sup>	99.82
$Mn^{2+}$ , $Co^{2+}$	200 <sup>a</sup>	99.64
$Cu^{2+}$	200 <sup>a</sup>	99.80
$Fe^{3+}$ , $Zn^{2+}$	200 <sup>a</sup>	99.55
$Pb^{2+}$	200 <sup>a</sup>	99.45
$Cd^{2+}$	200 <sup>a</sup>	98.68
		99.80

<sup>a</sup> in presence of  $2 \times 10^{-3} \text{ mol l}^{-1}$  DETPA.

### 3.3. Column Technique

#### 3.3.1. Effect of Flow Rate

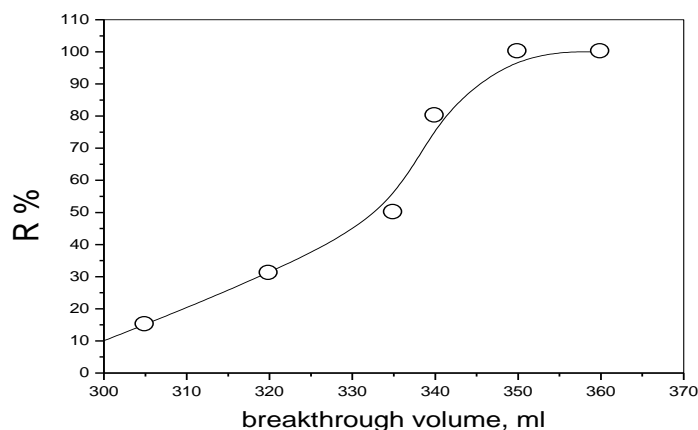
The effect of flow rate on  $UO_2^{2+}$  sorption was investigated at different flow rates ( $1 - 10 \text{ ml min}^{-1}$ ) under the optimum conditions. It is found that, the optimum flow rate for the maximum sorption capacity of  $UO_2^{2+}$  is  $5 \text{ ml min}^{-1}$ . Using flow rate  $> 5 \text{ ml min}^{-1}$ ,  $UO_2^{2+}$  ions do not reach equilibrium. The faster sorption of  $UO_2^{2+}$  is taken as an indication for its higher reactivity with thiosemicarbazone- modified cellulose (CTSC). However, at a flow rate greater than  $5 \text{ ml/min}$ ., there was a decrease in the percentage of sorption, as  $UO_2^{2+}$  ion probably could not equilibrate properly with the resin bed.

### 3.3.2. Breakthrough Volume and Elution Curve

It was used to evaluate the amount of metal ion sorbed per gram on the modified resin under the operating optimum conditions. In order to obtain a breakthrough volume, a glass column was packed with 0.5 g of the modified resin, 100  $\mu\text{g ml}^{-1}$  of  $\text{UO}_2(\text{II})$  ions solution at the optimum pH was passed through the column with the selected flow rate. The receiving effluent after 5 minutes was fractionalized into 5 ml portions and each metal ion was determined. The breakthrough capacity presented (**Fig.13**) indicates that, the column is exhausted with 70 mg  $\text{UO}_2(\text{II})$  per gm polymer. The performance of the date pits packed column is generally described by the number of theoretical plates (N) and height equivalent to the theoretical plates (HETP) calculated from the breakthrough volume curve (**fig.13**) employing the equation:

$$N = \frac{V_{50} \times V^-}{(V_{50} - V^-)^2} = \frac{L}{\text{HETP}} \quad (12)$$

Where,  $V_{50}$ : volume of the effluent solution at the center of the breakthrough curve where the concentration is one-half the initial concentration and  $V^-$ : the volume at which the effluent solution has a concentration 0.1578 of the initial concentration. The HETP and N were in the range  $0.194 \pm 0.02$  mm and  $226 \pm 2$  plates ; respectively.

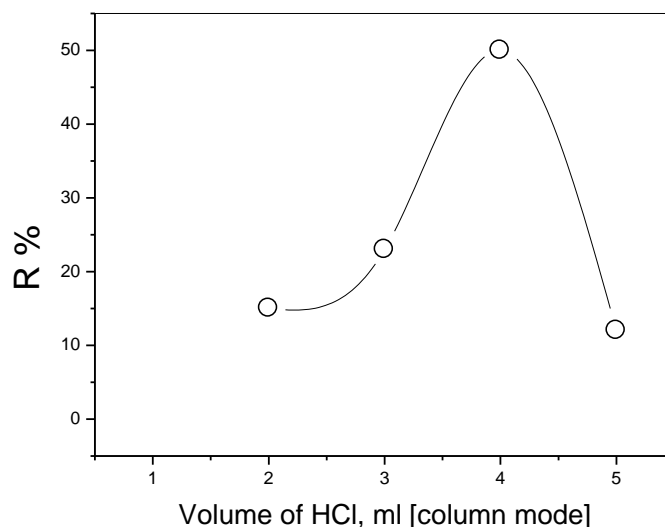


**Fig. 13:** Effect of breakthrough volume on the recovery of  $\text{UO}_2(\text{II})$  ions.

Also, HETP and N were calculated from the elution curve employing Glueckauf [43] equation:

$$N = \frac{8 V_{\max}^2}{W^2} = \frac{L}{\text{HETP}} \quad (13)$$

Where;  $V_{\max}$  is the volume of eluate to peak maximum, W the width of the peak at 1/e times the maximum solute concentration and L is the length of the polymer beds in mm. from **Fig. 14** and applying Glueckauf equation HETP and N also equal  $214 \pm 5$  plates  $\text{g}^{-1}$  and  $0.20 \pm 0.02$  mm; respectively in a good agreement with the values obtained from breakthrough curve[45]. The results confirmed the good performance of proposed modified cellulose sorbent in flow mode for the separation of uranyl(II) ions in complicated matrix.



**Fig. 14:** Effect of elution volume on the recovery of  $\text{UO}_2(\text{II})$  ions.

### 3.3.3. Column Reuse

To test the long-term stability of the column containing the modified cellulose, successive sorption and desorption cycles were subjected by passing the  $\text{UO}_2^{2+}$  solution through the column at  $5 \text{ ml min}^{-1}$  flow rate. The sorbed  $\text{UO}_2^{2+}$  is then eluted from the resin with 5 ml of  $0.3 \text{ mol l}^{-1} \text{ HNO}_3$ . The procedure was repeated several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed  $\text{UO}_2^{2+}$  ion. The results of fifty sorption/desorption cycles indicated that, the recovery decreases by 2–3 % for  $\text{UO}_2^{2+}$ , which reflect good stability of the modified cellulose.

### 3.3.4. Effect of Volume and Preconcentration Factor

To the column, 0.1 - 1.5 L aqueous solution containing  $5 \mu\text{g}$  of  $\text{UO}_2^{2+}$  was passed, eluted with 5 ml of  $0.3 \text{ mol l}^{-1} \text{ HNO}_3$  and determined. It is found that,  $\text{UO}_2^{2+}$  could be removed quantitatively from volume up to 1000 ml then the recovery decreases remarkably. Therefore, a practical maximum of 200 folds preconcentration factor for  $\text{UO}_2^{2+}$  was obtained using 5 ml of  $0.3 \text{ mol l}^{-1} \text{ HNO}_3$ .

### 3.3.5. Detection Limit of $\text{UO}_2^{2+}$

It means the lowest concentration of  $\text{UO}_2^{2+}$  below which its quantitative sorption by the modified cellulose is not perceptibly seen. It was investigated for  $\text{UO}_2^{2+}$  at  $10^{-1} - 10^{-3} \mu\text{g ml}^{-1}$  passed through the column at  $5 \text{ ml min}^{-1}$  flow rate. The limit of detection (LOD) for  $\text{UO}_2^{2+}$  is 5 ppb, showing high sensitivity of the modified cellulose for preconcentration of trace  $\text{UO}_2^{2+}$ .

## 3.4. Applications

### 3.4.1. Selective Separation of $\text{UO}_2^{2+}$ from Binary Mixtures

To investigate the selective separation and determination of  $\text{UO}_2^{2+}$  from its mixture with diverse metal ions (**column mode**), an aliquot of aqueous solution (500 ml) containing 1 mg  $\text{UO}_2^{2+}$  and 25 mg of another cation was taken and the recommended procedure was followed. The results summarized in **Table 2** showed that  $\text{UO}_2^{2+}$  in the binary mixtures is almost sorbed by the modified cellulose up to 25 mg of the diverse ions. It is interesting to note that, no effect on the recovery of  $\text{UO}_2^{2+}$  in the presence of DETPA under the optimum conditions.

**Table 2:** Separation of  $\text{UO}_2^{2+}$  from binary mixtures

Diverse ions	Recovery% of $\text{UO}_2^{2+}$ ions
$\text{Na}^+$	100.0 (0.056)
$\text{Mg}^{2+}$	99.7 (0.210)
$\text{Ca}^{2+}$	99.4 (0.553)
$\text{Co}^{2+}$	99.5 (0.480)
$\text{Ni}^{2+}$	100.0 (0.380)
$\text{Cu}^{2+}$	99.6 (0.850)
$\text{Zn}^{2+}$	99.2 (1.180)
$\text{Pb}^{2+}$	100.0 (0.652)
$\text{Cd}^{2+}$	99.6 (0.800)

Initial sample containing 1 mg  $\text{UO}_2^{2+}$ , 25 mg of diverse ions in 500 ml water (column mode)

Values in parentheses are RSD's based on three replicate analyses.

### 3.4.2. Selective Separation of $\text{UO}_2^{2+}$ from Natural Water

Surface water samples were collected from Nile River water (Mansoura, Dameitta, and Ras EL-Bar) and tap water from Mansoura city. The samples were acidified with concentrated  $\text{HNO}_3$  to pH ~ 2 and preserved in polyethylene vessel. The organic matter was digested prior to the separation process. In a 1 L calibrated flask, 0.5 g of  $\text{K}_2\text{S}_2\text{O}_8$  and 5 ml of 98% (w/v)  $\text{H}_2\text{SO}_4$  were added and completed to the mark with water sample and heated for 30 min at 95 °C. After cooling to room temperature, 1 ml of  $5 \times 10^{-3}$  DETPA solution was added to the sample and the pH was adjusted to 2 and passed through the column. The sorbed  $\text{UO}_2(\text{II})$  ion was then eluted by 5 ml of  $0.3 \text{ mol l}^{-1}$   $\text{HNO}_3$ , to give a concentration factor of 100 folds and the eluate was analyzed as previously described. From **Table 3**; it could be concluded that, The RSD % was found < 3; A reasonable recovery percentage ( $99.66 \pm 0.30$ ) of Uranyl ion was achieved confirming the accuracy of the developed procedures and its independence from matrix effects.

**Table 3:** Analysis of water samples for determination of a spiked  $\text{UO}_2^{2+}$  in  $5 \text{ mg ml}^{-1}$  (otherwise indicated) after preconcentration with CTSC at pH 5, stirring time 30 min at  $25 \pm 1^\circ\text{C}$  (column mode).

Sample (location)	Recovery %	RSD (%)
Tap water (Mansoura city)	100.00	1.1
Nile river (Mansoura city)	99.98	1.00
Wastewater (Talkha from Meat Antar)	99.66	1.68
Nile water (Dameitta city)	99.94	1.52
Wastewater (Ras El-Bar from Elborg)	99.70	1.62
Sea water (Port Said from Suez Canal)	99.80	1.50

ND: not detected

\*presence of DETPA

### 3.4.3. Analytical Performance and Application of the Proposed Method

The validation of the developed method was successfully assessed by comparing the capacity of the used sorbent with the most of other sorbent DCQ-naphthalene [32], PAN-benzophenone [33], Q- Amberlite XAD-4 [34], azo-oxime ion exchanger [35], DAB-AC [36] and date pits [23] towards uranium (VI) uptake. The results are summarized in Table 5 the capacity of the used CTSC is ( $90.00 \text{ mgg}^{-1}$ ) towards uranium (VI) is much better than the all solid sorbent in **Table 4**

**Table 4:** Retention Capacities of the investigated CeTSC and other solid sorbents towards uranyl (II) ions from aqueous media by batch mode\*

SPE	Retention / binding Capacity (mgg <sup>-1</sup> ) of SPE	Reference
DCQ-naphthalene	1.88 ± 0.02	[44]
PAN-benzophenone	2.34 ± 0.01	[45]
Q-Amberlite XAD-4	2.74 ± 0.02	[46]
Azo-oxime ion exchanger	7.14 ± 0.01	[47]
DAB-AC	18.35 ± 0.2	[48]
Date Pits	10 ± 0.02	[28]
CTSC	70.448 ± 0.02	Present work

\*Average of the six measurements ± standard deviation.

#### 4. Conclusion

In this research, the new modified Cellulose was synthesized and its adsorptive features were investigated for UO<sub>2</sub><sup>2+</sup> ions. The adsorptive of UO<sub>2</sub><sup>2+</sup> ions on modified cellulose was investigated for, concentration, pH, ionic strength, kinetic, temperature, storage and reusability. The methodology offered a simple and fast mean for selective sorption and preconcentration of UO<sub>2</sub><sup>2+</sup>. The method was found free from interferences and the quantitative recoveries (better than 98%) from binary mixtures and natural water samples were achieved. No need for organic solvents or higher concentration of acids as in other procedures in the elution step. In comparison with other modified cellulose, CeTSC has the following advantages:

1) higher preconcentration factor and sorption capacity; 2) low matrix effect; 3) short loading time (t<sub>1/2</sub>), 4) suitable for preconcentration of UO<sub>2</sub><sup>2+</sup> in complicated and variable matrices (seawater); 5) low cost compared to other modified polymers; and 6) good precision. The results showed a quantitative sorption of low concentration of UO<sub>2</sub><sup>2+</sup>. Also, beside its stability in different media, it could be recycled for many cycles without change in its sorption properties. From the economic point of view, the sorption capacity of CeTSC, after its versatile uses, has found practically unchanged.

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