

## Radioactive Element Removal from Contaminated Groundwater by Agricultural Waste-Based Activated Carbon

Omotayo Sarafadeen Amuda<sup>1</sup>, Isiaka Adekunle Amoo<sup>2</sup> and Yung-Tse Hung<sup>3</sup>

<sup>1</sup>Analytical/Environmental Chemistry Unit, Department of Pure and Applied Chemistry,  
Ladoke Akintola University of Technology Ogbomosho, 210001, Nigeria

<sup>2</sup>Department of Chemistry, Federal University of Technology, P.M.B. 704, Akure, Nigeria

<sup>3</sup>Department of Civil and Environmental Engineering,  
Cleveland State University, Cleveland, Ohio 44115, USA

**Abstract:** Removal efficiency of activated carbon derived from the shell of *Chrysophyllum albidum* seed was evaluated for its ability to remove uranium from contaminated groundwater. Batch and field column experiments revealed the efficiency of the activated carbon in removing uranium from groundwater with pH range of 6.5 – 7.5 and nitrate level of 280 mg L<sup>-1</sup>. Equilibrium studies were conducted on the groundwater spiked with uranium in the range 20 mg L<sup>-1</sup>. At 60 min. equilibrium time, adsorption capacity was 93.16 mg L<sup>-1</sup>. The study revealed that the activated carbon is capable of removing uranium from groundwater with low to high nitrate concentrations. A field column test using groundwater containing low to high concentrations of nitrogen revealed that the activated carbon was able to remove up to 93 % of the uranium from the feed when 2 g of the carbon was used. Fourier Transforms infrared spectroscopy studies were performed for the characterization of the activated carbon. The experimental data were found to be in good agreement with the isotherm models of Fredunlich and Langmuir. Thermodynamic studies gave  $\Delta G$  and  $\Delta H$  negative response. Adsorption data fitted well with pseudo-second-order kinetic model.

**Key words:** Activated carbon · *Chrysophyllum albidum* seed shell · Groundwater treatment · Uranium  
· Kinetics

### INTRODUCTION

Even before its formal discovery by the German chemist, Martin Klaproth, in 1789, uranium (U) has been used for a variety of purposes starting from colouring glass and ceramics to its use in military and public industries. However, the centuries of mining and milling of uranium and of other elements during their exploitation, have resulted in the production of considerable amounts of radioactive waste materials which are perceived to threaten the environment and public health. Generally, a mine capable of producing 100,000 t of uranium ores annually will simultaneously produce 100,000–600,000 t waste tailings. In addition to mining activities, some radioactive contamination of the environment has also resulted from the extractive industries, such as those for

phosphorus, oil, iron, coal and mineral sands. Direct application of uranium-rich phosphate rock as an alternative to commercially processed phosphorous fertilizers over years may have led to large-area contamination of arable soil, specifically in developing countries [1]. Human beings and animals are exposed to uranium mainly by direct contact (e.g. contaminated drinking water). Besides ionic radiation, uranium behaves similarly to heavy metals, especially for Pb. Uranium is chemically toxic to kidneys and the insoluble uranium compounds are carcinogenic.

A number of media have been shown to be effective in removing uranium from groundwater. These include granulated activated carbon modified with hydrophobic silica, zero-valent iron (ZVI), phosphate rock, zeolites and coal-based sorbents [2-5]. The use of reverse osmosis, ion

exchange, precipitation and coagulation methods has also been employed in the removal of uranium from groundwater. However, these methods are quite expensive and are not effective if the radionuclide is in low concentrations. Synthetic resin has also been reported to be efficient in adsorbing uranium from contaminated groundwater [6].

This study is aimed to investigate the adsorption efficiency of carbon derived from the shell of *Chrysophyllum albidum* seed on near-neutral pH (6.5) and high-pH (8)- low-nitrate-containing groundwater, also, to conduct batch experiments on the activated carbon to evaluate its sorption capacity and selectively to remove uranium from both low- and high-nitrate containing contaminated groundwater with varying pH values.

## MATERIALS AND METHODS

**Preparation of Adsorbent:** The seeds of *Chrysophyllum albidum* were picked at various locations in Ogbomosho town, Oyo State Nigeria. Debris and stones were separated from the seeds by hand-picking. The seeds were washed and dried on laboratory bench for 72 h. Shells were removed, ground and dried in an oven (Memmert Model OV-160, England) at 105°C to constant weight. *Chrysophyllum albidum* seed shells were pyrolyzed in a furnace (Carbolite, CTE 12/75). During pyrolysis, nitrogen gas at a flow rate 0.1m<sup>3</sup>/h was used as purge gas. The furnace temperature of 500°C was maintained for 2 h. The weight before and after pyrolysis gave the weight loss of the sample. The pyrolyzed sample was crushed into powder form. The adsorbent was activated by soaking in excess 0.3 M HNO<sub>3</sub> for 24 h. This was followed by washing the activated adsorbent thoroughly with distilled-deionized water until the solution pH was stable at 7.02±0.1. It was soaked in 27 % NaHCO<sub>3</sub> (w/v) until any residual acid has been removed. It was then dried overnight in an oven (Memmert, England) at 105°C, cooled at room temperature and stored in desiccators until ready for use. The activation process removes any debris or soluble biomolecules that might interact with metal ions and also, all biogenic metal ions in the adsorbent [7].

**Surface Characterization of Adsorbent:** The parameter that denote the accessibility of these pores is on the BET surface areas ( $S_{BET}$ ) of the adsorbent determined from N<sub>2</sub> adsorption isotherms, at 77 K with a Coulter Omnisorp 100 CX apparatus [8]. The cation-exchange capacities

Table 1: Characteristics of the ACASC

| Parameters  | Results |
|---|---------|
| Bulk density (g L <sup>-1</sup> )                       | 0.46    |
| Ash content (%)   | 2.21    |
| pH  | 6.70    |
| Moisture content (%)                                    | 2.10    |
| Surface area (m <sup>2</sup> g <sup>-1</sup> )          | 413.00  |
| Water soluble matter (%)                                | 0.72    |
| HCl soluble matter (0.25 m) (%)                         | 1.16    |
| Decolorizing power (mg g <sup>-1</sup> )                | 25.40   |
| Volatile matter (%)                                     | 6.10    |
| Ion-exchange capacity (milliequiv 100 g <sup>-1</sup> ) | 6.22    |
| Calcium (%)   | 23.00   |
| Sodium (mg kg <sup>-1</sup> )                           | 0.009   |
| Potassium (mg kg <sup>-1</sup> )                        | 0.019   |
| Iodine number (mg g <sup>-1</sup> )                     | 160.00  |
| Fixed carbon (%)  | 87.00   |

(CEC) were determined by the Kjeldhal method. Table 1 shows some characteristics of the new adsorbent prepared from the shell of seed of *Chrysophyllum albidum*.

**Field Column Test:** A field column containing the C. albidum shell activated carbon was tested for uranium removal using a groundwater around Ajaokuta Steel Rolling Industry, Ajaokuta, Kogi State, Nigeria. The pressure gauges were designed to be at the inlet and outlets of the columns (Fig. 1).

The flow meters that were used to adjust the flows to the columns are situated at the right-hand side wall of the panel. The column was constructed from polyvinyl chloride (PVC), 80 pipes were schedule in two segments operating serially to allow sampling at the middle of the column. Each segment was 3.81 cm in diameter and 38.1 cm in length. The empty bed volume (MTBV) was 0.43 L in the column.

**Field Column Operation:** The field column test on the ACASC ran for a duration of 4 weeks. The water was pumped down-flow for runs 1 and 2 to provide more opportunities to separate gas bubbles from the groundwater so that they would not enter the medium in the column. ACASC was tested at 150mLmin<sup>-1</sup>. The superficial velocity for the ACASC test at 100–150mLmin<sup>-1</sup> (usually 150mLmin<sup>-1</sup>) in the 3.81cm diameter column is 0.24cms<sup>-1</sup>, 0.47 fmin<sup>-1</sup> or 627 ft day<sup>-1</sup>. The volume of water treated was verified by collecting the outlet water in an open tube and measuring its volume. Once analytical results consistently showed that the first column gave excellent outlet quality,

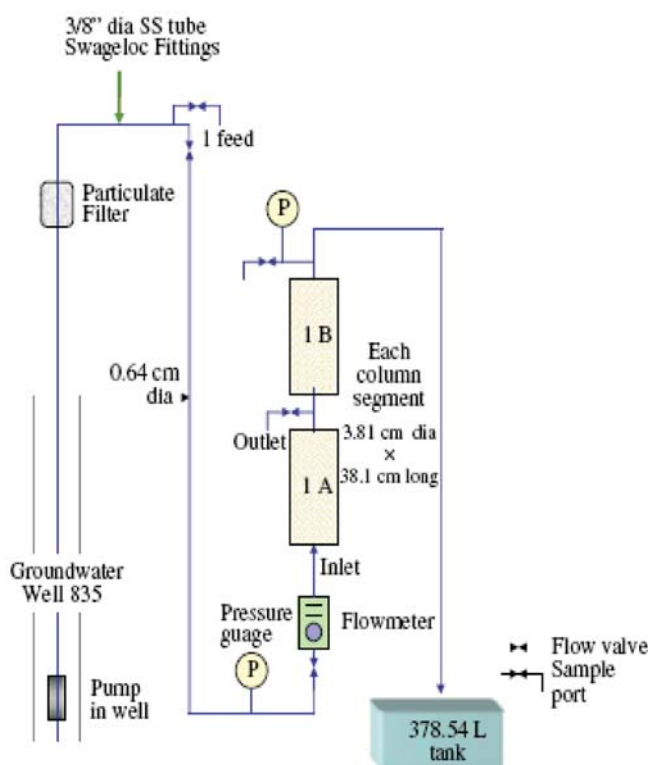


Fig. 1: Schematic diagram of the column test

Table 2: Geochemistry of the groundwater under study

| Groundwater                              | U    | NO <sub>3</sub> <sup>-</sup> | HCO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | pH  |
|--|------|------------------------------|-------------------------------|-----------------|-------------------------------|-----|
| Low-nitrate –                            |      |                              |                               |                 |                               |     |
| Containing water High-nitrate-           | 1.1  | 24                           | 740                           | -               | 100                           | 6.5 |
| Containing water (A)                     | 6.5  | 280                          | 720                           | 760             | -                             | 5.8 |
| (B) (spiked with 20 mg L <sup>-1</sup> ) | 26.5 | 280                          | 720                           | 760             | -                             | 5.8 |

Values in mg L<sup>-1</sup>

sampling for the second column was deferred until further results showed that it should be continued again. Later, when loading capacity (as measured by the outlet column sample) was above the capacity measured in the batch tests, the second column was removed from the system to eliminate the possibility of the mid-column sample being contaminated with back-flow of clean water from the second column during sampling.

During the run, there was no reduced hydraulic flow due to plugging even at high superficial velocities. The pressure at the feed (i.e. the bottom) of the column varied from 0 to 3 psig. However, this pressure was influenced much more by the discharge height of the outlet tubing than by gradual reduction in hydraulic head of the ACASC.

Feed and outlet samples were collected periodically to measure the concentrations of uranium by SAIC. Nitrate, total dissolved solids (TDS) and total suspended

solids (TSS) were measured for the first month of operation. Nitrate, TDS and TSS analyses were not performed for most of the rest of the operation because it was previously showed that the ACASC had very little impact on these three parameters. Total uranium was measured by inductively coupled argon plasma/ mass spectrometry using the standard EPA Method 200.8 [9].

**Batch Test:** Groundwater containing high-nitrate was spiked with 20 mg L<sup>-1</sup> uranium to determine if the ACASC removed uranium similarly under high contaminant loading conditions. A near-neutral-pH (6.5)-low-nitrate-containing groundwater was also used for the study and additional uranium was added to these batch tests because of a relatively high sorption capacity of the activated carbon (ACASC) for uranium (Table 2).

**Sorption Equilibrium:** The removal of uranium by the activated carbon on the field and simulated groundwater conditions was investigated in batch experiments by shaking 0.1 – 3.0 g of ACASC (dry weight) in 100 mL of groundwater in 250 mL capacity plastic scintillation vials on an end-over-end shaker. A separate batch experiment was carried out on groundwater spiked with 20 mg L<sup>-1</sup> uranium to determine if the activated carbon performed similarly at higher uranium concentrations. In these batch experiments, 1 mL of sample solution was taken periodically at different contact time (1 – 2 h). Each of the 1 mL extractions was added to 20 mL of deionized water (Millipore-Q Plus) water in separate scintillation vials and stored under refrigeration. More detailed kinetic studies were conducted on the activated carbon in the batch studies by shaking 0.1 g (dry weight) of carbon in 100 mL of groundwater (26.5 mg L<sup>-1</sup> uranium) in plastic bottles (250 mL capacity). In this experiment, the initial removal rate of uranium from groundwater was investigated by extracting and analyzing 1 mL of the solution from the bottles at different contact time (1 – 2 h). All reagents used were analytical grade. The amount of uranium sorbed onto the carbon was calculated by the difference between the amounts added and/or already present in the water and that left in solution after equilibrium.

The amount of U adsorbed ‘qt’ (mg L<sup>-1</sup>) at time ‘t’ was calculated by using the following equation

$$qt = \frac{\{C_i - C_f\}V}{m} \quad (1)$$

Where  $C_i$  and  $C_f$  are the U concentrations in mg L<sup>-1</sup> initially and at given time,  $t$ , respectively.

The percentage U removed ( $R_{(U)}$  %) from solution was calculated by using the following equation.

$$R_{(U)}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

All the experiments were duplicated to ensure accuracy, reliability and reproducibility of the collected data. Relative error did not exceed 1%.

The samples were purified and pre-concentrated using UTEVA® resin (100–150 mm) 2 mL extraction columns (Eichrom Technologies, Darten, IL) to remove the interference (or quenching effects) of elements such as Cl- and Ca<sup>2+</sup> (Phillips *et al.* 2008). Total uranium (VI) was measured with the laser-induced kinetic phosphorescence analyzer (KPA-11 ChemChek Instruments, Inc., Richland, WA) (with detection limit better than 0.01 mg L<sup>-1</sup>) from a

solution of 1 mL of leachate and 1.5 mL of URAPLEX® (ChemChek Instruments, Inc., Richland, WA) reagent at ORNL [10]. The method used was used to analyze the uranium in batch which gives compatible results with the EPA method was [11] D5174-0.

## RESULTS AND DISCUSSION

### Field Column Tests

**Breakthrough Curve for ACASC:** The breakthrough curve for uranium and cumulative uranium loading are shown in Fig. 2 for the ACASC in field columns using low-nitrate containing groundwater (Table 2) ACASC effectively remove uranium from contaminated groundwater with a high cumulative loading capacity. The performance of the ACASC was so high that three 2-week runs were completed and a fourth run was begun before breakthrough started. Although the cumulative loading capacity at total breakthrough is not known, the cumulative loading capacity at the point when the column was shut down was 57.8 mg g<sup>-1</sup> and uranium. ACASC was still removing 594% of the uranium from the feed at the end of the operation even though the feed from groundwater containing low-nitrate had a lower pH (6.5 beforehand) and a higher iron concentration (20-150 mg L<sup>-1</sup> and Fe vs. 0.20 mg L<sup>-1</sup> and Fe beforehand). The reason for such a high performance is due to the presence of the bicarbonates and about neutral pH conditions of the groundwater. Under oxic and suboxic conditions, uranium exists in groundwater primarily as uranyl cations, which form strong complexes with carbonates in groundwater and form anionic species such as UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup> [10].

### Batch Tests

**Unspiked Acidic-pH (5.8)-high-nitrate-containing Groundwater:** Because of limited data, distribution coefficients ( $K_d$ ) were estimated for the activated carbon based on a single batch test with varying concentration of Uranium.

The  $K_d$  is defined as the ratio of the amount of uranium sorbed (as mg g<sup>-1</sup> carbon) to the concentration of uranium remaining in the equilibrium solution (as mg mL<sup>-1</sup>). On the basis of these data, the carbon removed more uranium (at 5.8 and 6.5 mg L<sup>-1</sup>) from the acidic-pH (5.8)-high-nitrate-containing site groundwater. Uranium was removed from the contaminated groundwater at over 90% with 1 h equilibration by the carbon (Fig. 3). The carbon derived from *C. albidum* therefore appears promising in remediating acidic-pH (5-6) - high-nitrate-containing groundwater at the site.

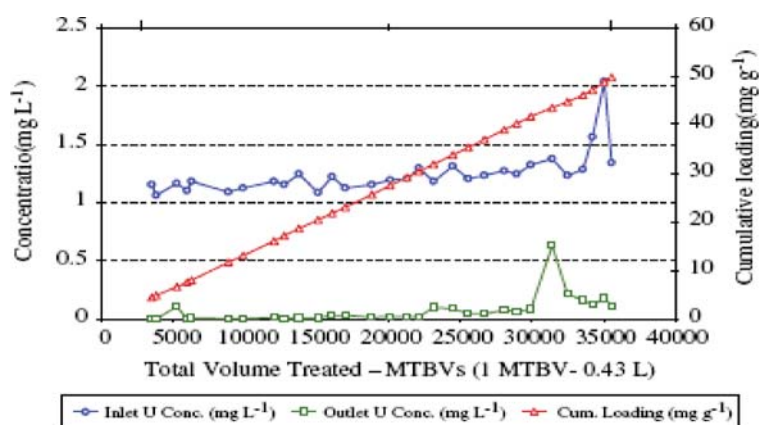


Fig. 2: Breakthrough curve for ACASC in the field column study

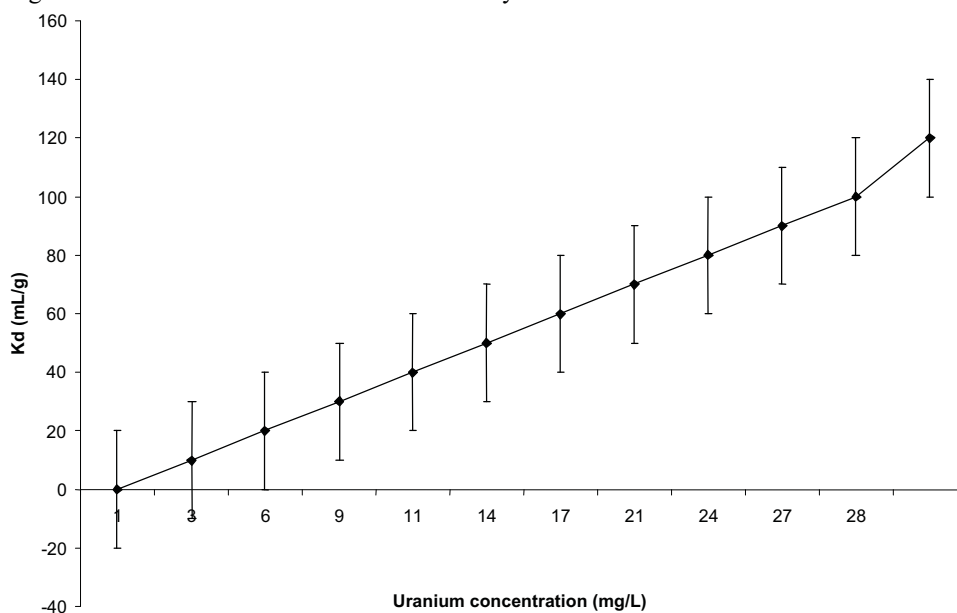


Fig. 3: Distribution ratio of the adsorbents as function of Uranium concentrations.

It was reported that uranium can be extracted from freshwater and seawater by a Chelex-100 resin by careful control of the resin pH [12]. In his study, Chelex-100 removed 93% uranium from seawater samples after conditioning to a pH 7.0 with 1M ammonium acetate solution. Uranium removal was also reported in 25 mL aliquots of seawater and freshwater at pH 5.6, which is similar to the pH of the studied acidic high-nitrate-containing groundwater.

**Effects of ACSC Mass on Uranium Sorption:** The quantity of adsorbent is a significant factor to be considered for effective adsorption. The performance of the ACASC was evaluated for the percentage removal of U. The dose of the ACASC was varied between 1.0 and 3.0 g/100mL. Percentage uranium removal

increased significantly as the amount of adsorbent added increased (Figure 4). Adsorbent dosage of (2.0g/100mL) was required to remove 93% of U in aqueous solution. This is expected because as the dose of ACASC increased, there was increase in the available exchangeable sites for the U. At 2.0 g/100mL dose of the adsorbent, the maximum adsorption set in and hence, the concentration of free ions remained constant even with further increase in the dose of the adsorbent.

**Effect of Contact Time on Uranium Sorption:** In the batch study conducted on the 100 mL of spiked (20 mg L<sup>-1</sup> U) acidic-pH (5.8)-high-nitrate-containing groundwater from the site, ACASC exhibited greatest removal of uranium for the first 7.5 min. when in contact with the uranium containing water (Fig. 5). [13] reported a high sorption of

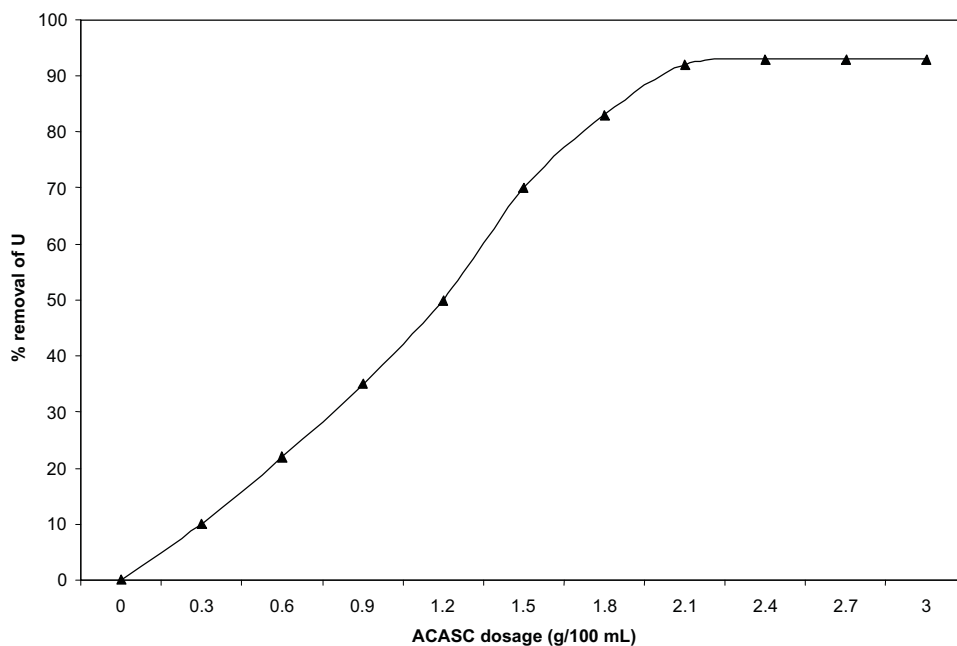


Fig. 4: Percentage removal of Uranium as a function of ACASC

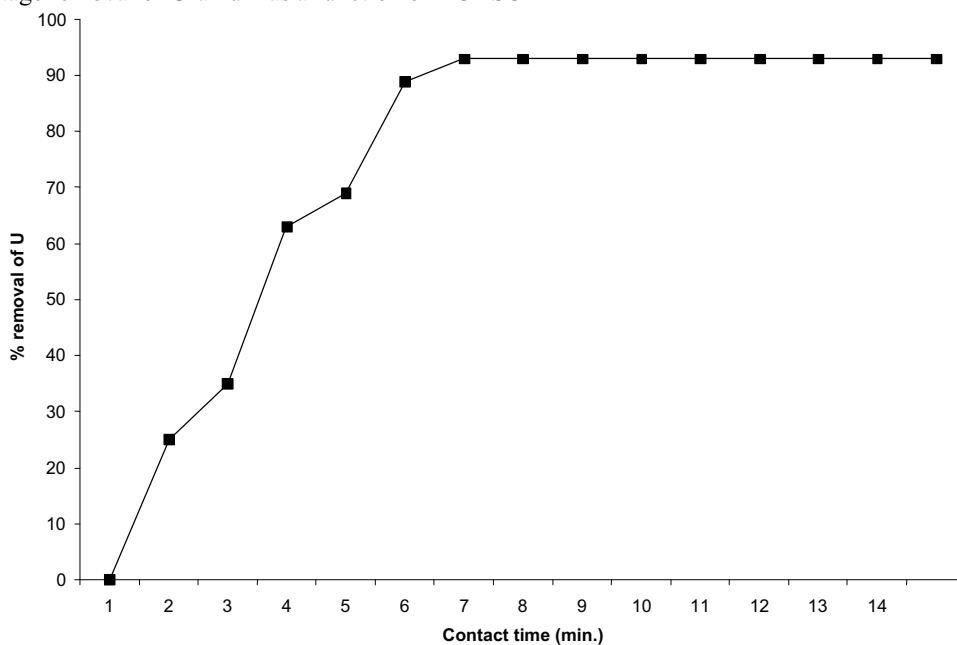


Fig. 5: Percentage removal of Uranium as a function of contact time

uranium by Diphonix resin in near-neutral solutions similar in pH to the groundwater under study (pH 5). The results from the 100mL batch test are probably more reliable than the 15 mL batch test because a relatively large volume of sample solution was used for the experiment to lower the experimental error; this is similar to previous results [11]. Also, high sorption may be due to probability of Uranyl to form weak anionic

complexes with nitrate, which is present at high concentrations in groundwater even in acidic (pH 5) conditions [14].

This may also be attributed to the instantaneous utilization of the most readily available sorbing sites on the adsorbent surface. Increased contact time increased percentage removal of lead until equilibrium adsorption was established. Equilibrium adsorption was established

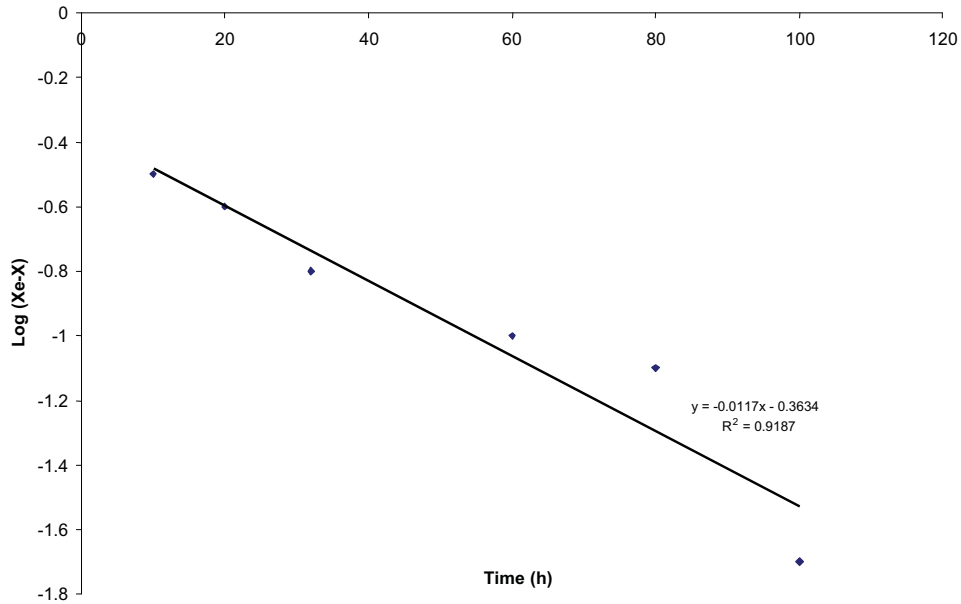


Fig. 6: Lagergren plot for sorption of Uranium

within 60 min. The kinetic data was fitted to the Lagergren equation [15].

$$\text{Log } (X_e - X) = \text{Log } X_e - K_{ads} t / 2.303 \quad (3)$$

$X$  = the amount of solute, U, (mg/L) removed at time  $t$ ,  $X_e$  = amount removed at equilibrium and  $K_{ads}$  = the rate constant of adsorption ( $\text{h}^{-1}$ ). The linear plot of  $\text{Log } (X_e - X)$  vs  $t$  shows the applicability of the above equation for metal sorption by the adsorbent (Fig. 6). The rate constant value ( $K_{ads}$ ) calculated from the slope of the plot was  $1.632 \times 10^{-2} \text{ h}^{-1}$ . The regression coefficient ( $R^2$ ) was 0.9187. Other parameters that determine the sorption rate, such as agitation rate in the aqueous phase, adsorbent structural properties, adsorbate properties (e.g. hydrated ionic radices), initial concentration of ion and chelate-formation rate may also have played a role in this study [16].

The adsorption data was also subjected to pseudo – second order kinetic model, described as:

$$\frac{dq}{dt} = K_2 (qe - qt)^2 \quad (4)$$

Where  $K_2$  is the rate constant of pseudo-second order adsorption ( $\text{g/mg min}$ ).

Integrating and applying boundary conditions  $t = 0$  and  $qt = 0$  to  $t = t$  and  $qt = qe$ , then, Eq. 4 linearly becomes

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{1}{qe} t \quad (5)$$

If the initial sorption rate is

$$h = K_2 qe^2 \quad (6)$$

then Eqs. (4) and (5) become

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe} t \quad (7)$$

Applicability of pseudo-second order kinetics gives the plot of  $t/qt$  against  $t$  (Fig. 7). This gives a linear relationship from which the constant  $qe$ ,  $h$  and  $K_2$  was determined as  $124.92 \text{ mg g}^{-1}$ ,  $144.327 \text{ mg g}^{-1} \text{ min}$  and  $2.56 \times 10^{-3} \text{ g/mg min}$ . The data show good compliance with the pseudo-second order kinetic model ( $r^2 > 0.986$ ). The values of the rate constant  $K_2$  decreased from  $1.24 \times 10^{-2}$  to  $2.56 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ , as the initial concentration increased from 5 to  $30 \text{ mg L}^{-1}$ , for ACASC.

The values of  $qe$ ,  $K_2$  and  $h$  for different values of  $C_0$  were regressed for the following equations:

$$qe = \frac{C_0}{A_q C_0 + B_q} \quad (8)$$

$$K_2 = \frac{C_0}{AK_2 C_0 + BK_2} \quad (9)$$

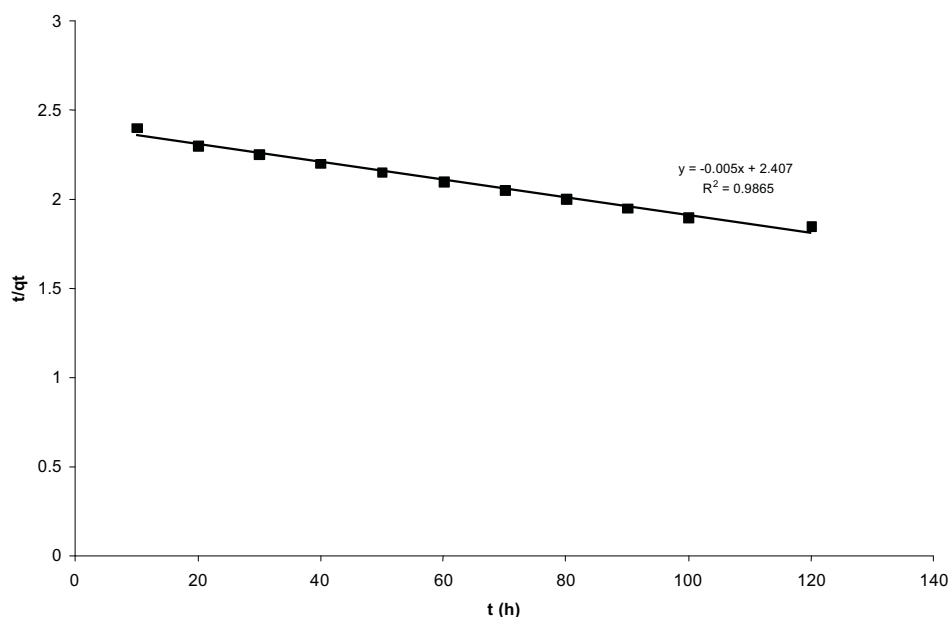


Fig. 7: Pseudo-second-order rate reaction kinetics for adsorption of Uranium

$$h = \frac{C_0}{A_h C_0 + B_h} \quad (10)$$

The values of  $q_e$ ,  $K_2$  and  $h$  can be substituted into Eqs (5), (6) and (7) to obtain the empirical parameters in the equations. The values of  $A_q$ ,  $B_q$ ,  $AK_2$ ,  $BK_2$ ,  $A_h$  and  $B_h$  were obtained as  $7.54 \times 10^{-2} \text{ g mg}^{-1}$ ,  $2.0 \text{ g L}^{-1}$ ,  $1.13 \times 10^2 \text{ mg min g}^{-1}$ ,  $-5.32 \times 10^2 \text{ mg}^2 \text{ min g}^{-1}$ ,  $7.52 \times 10^{-1} \text{ g min mg}^{-1}$  and  $107.9 \text{ g min L}^{-1}$  respectively. The values of correlation coefficients,  $r^2$ , were 0.986.

Substituting the values of  $q_t$  and  $h$  into Eqs. (8) and (10) and then into Eq. (9), the rate law for a pseudo-second order and the relationship of  $q_t$ ,  $C_0$  and  $t$  can be represented as follows for U.

$$qt = \frac{C_0 t}{0.742C_0 + 7.35 + (7.61 \times 10^{-2} C_0 + 3.15)t} \quad (11)$$

Eq. (11) represents generalized predictive model for U adsorbed at any contact time, initial ion concentration, at a given pH and within the range of concentration of adsorbent. There was indication that U adsorbed at any contact time is higher for a greater initial ion concentration. This is obvious for higher  $C_0$  values, because more efficient utilization of the sorptive capacities of the adsorbents is expected due to greater driving force (by a higher concentration gradient pressure) [16]. These equations can be used to derive the amount of U adsorbed at any given U concentration and the contact time.

**Adsorption Isotherms:** Adsorption isotherm models are widely employed to present the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature. The equilibrium data obtained from U sorption capacity of the ACASC were fitted to Langmuir and Freundlich isotherms.

**The Langmuir Isotherm:** The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm.

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (12)$$

Where  $q$  is milligrams of metal accumulated per gram of the adsorbent material;  $C_{eq}$  is the metal residue concentration in solution;  $q_{max}$  is the maximum specific uptake corresponding to the site saturation and  $b$  is the ratio of adsorption and adsorption rates. The Langmuir isotherm is based on the following assumptions: (a) metal ions are chemically adsorbed at a fixed number of well defined sites; (b) each site can hold one ion; (c) all sites are energetically equivalent and; there is no interaction between the ions [17].

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants. This is given by the following equation:



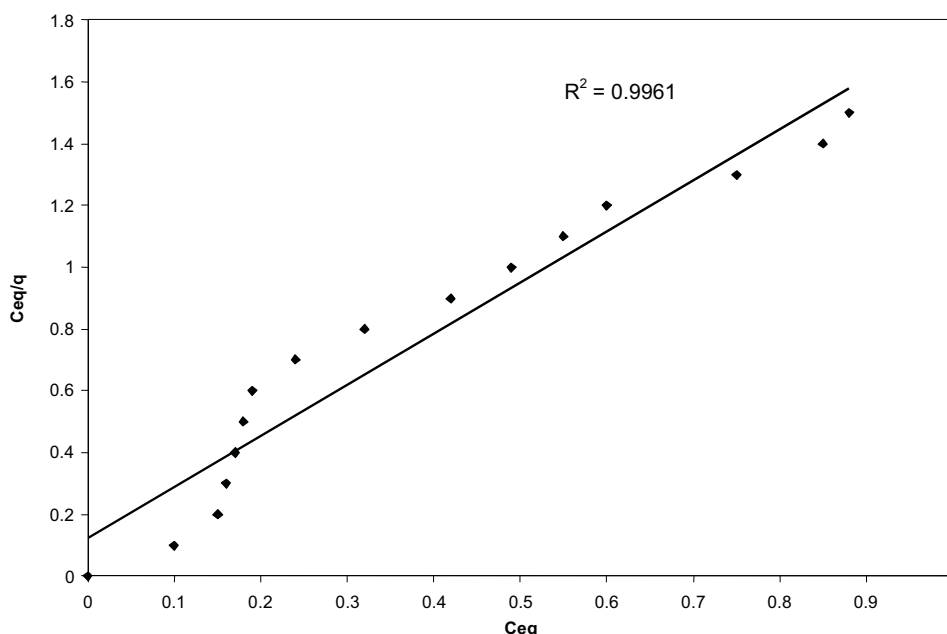


Fig. 8: Langmuir isotherm for adsorption of Uranium

$$C_{eq}/q = I/q_{max} \cdot b + C_{eq}/q_{max} \quad (13)$$

The linear plots of  $C_{eq}/q$  Vs  $C_{eq}$  show that adsorption followed the Langmuir model (Figure 8). The correlation coefficient is 0.997.  $q_{max}$  and  $b$  were determined from the slope and intercept of the plot and were found to be 93.46 mg g<sup>-1</sup> and 0.009 L/mg respectively.

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,  $R_L$ , which is defined as

$$R_L = \frac{I}{I + bC_0} \quad (14)$$

Where  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of U ion. The  $R_L$  value indicates the shape of isotherm, in which case  $R_L$  value is unity. According to [17],  $R_L$  values between 0 and 1 indicate favorable adsorption. In this study, the  $R_L$  values were found to be 0.9248 to 0.1483 for concentrations of 100-1000 mg L<sup>-1</sup> U.

**Effect of Temperature:** The adsorption study was conducted on U at ambient temperature. The results were analyzed and it was found that the adsorption process was endothermic and best fitted to Langmuir model. From the linear plots of  $C_{eq}/q$  vs  $C_{eq}$ ,  $q_{max}$ ,  $b$  and  $R_L$  values for different particle sizes of the adsorbent were calculated and  $R_L$  values were between 0 and 1. This confirms that adsorption process fits Langmuir model.

The Gibbs free energy ( $\Delta G^\circ$ ) for the adsorption process for the aqueous solution containing U was obtained from the following equation.

$$\Delta g^\circ = -RT \ln b \quad (15)$$

Enthalpy change ( $\Delta H^\circ$ ) can be calculated by using the thermodynamic equation,

$$\ln [b_1/b_2] = \Delta H^\circ / RT \quad (16)$$

Equation 7 can be rewritten as:

$$\Delta g^\circ = [\Delta H^\circ - \Delta S^\circ] / T \quad (17)$$

The results of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are presented in Table (3).

The negative values of  $\Delta G^\circ$  at all temperatures indicate the spontaneous nature of the adsorption of U on the adsorbent. The positive values of  $\Delta H^\circ$  indicate that the adsorption is involved with weak forces of attraction. It was observed that the  $\Delta H^\circ$  values increased with decrease of particle size, also the adsorption was found to be endothermic. The  $\Delta S^\circ$  values were positive, this shows the increased randomness at the solid/solution interface during the adsorption process, thus suggesting that U replace some water molecules from the solution previously adsorbed on the surface of the adsorbent. The  $\Delta S^\circ$  values increased as particle size decrease. This describes the new adsorbent as effective towards sorption of U.

Table 3: Thermodynamic parameters for the adsorption of Uranium onto ACASC at pH 5.8

| T°C | K <sub>c</sub> | ΔG° (KJ/mol) | ΔH°(KJ/mol) | ΔS° (Jmol/K) |
|-----|----------------|--------------|-------------|--------------|
| 10  | 1.8792         | -1.6103      |             |              |
| 25  | 1.4343         | -0.7471      | 53.69       | 172.43       |
| 40  | 1.1663         | -0.1304      |             |              |

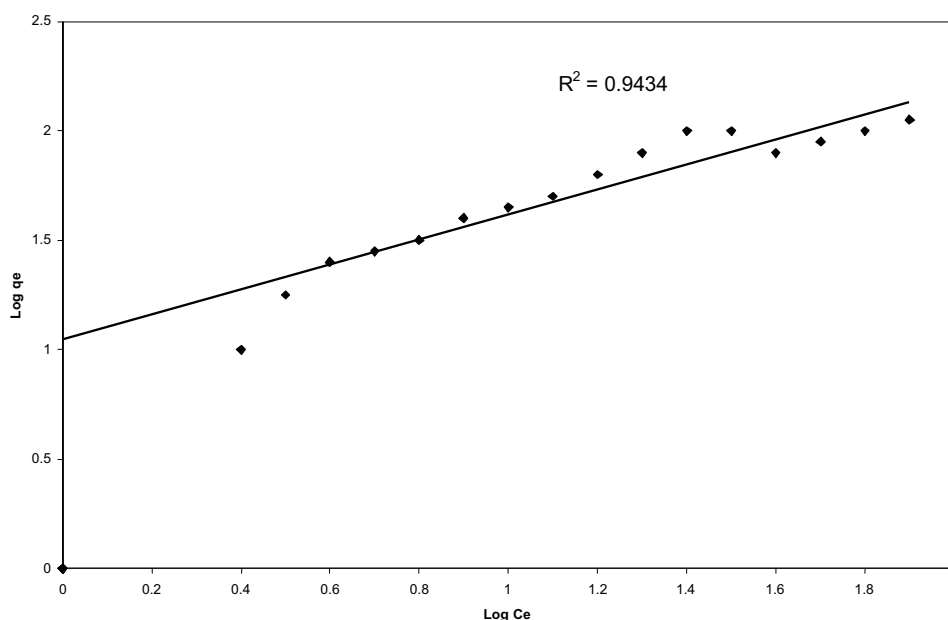


Fig. 9: Freundlich isotherm for adsorption of Uranium

**The Freundlich Isotherm:** The Freundlich isotherm is represented by the equation:

$$C_a = \ln k C_e^{1/n} \quad (18)$$

Where  $C_a$  is the amount adsorbed ( $\text{mg g}^{-1}$ )  $C_e$  is the equilibrium concentration and  $k$  and  $1/n$  are empirical constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised form of Freundlich adsorption isotherm was used to evaluate the relationship between the concentration of U adsorbed by the adsorbent and U equilibrium concentration in groundwater and is given as

$$\ln C_a = \ln k + 1/n \ln C_e \quad (19)$$

Parameters  $k$  and  $1/n$  are respectively equal to the intercept and slope of the plot of  $\ln C_a$  Vs  $\ln C_e$  and were found to be 91.16 and 0.47 respectively. According to [18] a larger value of  $k$  indicates good adsorption efficiency for a particular adsorbent, while a larger value of  $1/n$  indicates a larger change in effectiveness of adsorbent over different equilibrium concentrations. The correlation coefficient is 0.943 (Fig. 9).

In this study, Langmuir isotherm had a better fitting model than Freundlich because the former has higher correlation coefficient than the later (Langmuir,  $R^2 = 0.997$  and Freundlich,  $R^2 = 0.943$ ).

**Infrared Spectral Analysis:** Fourier Transform Infra Red, (FTIR) analysis of the new adsorbent was performed and the percentage transmission for various wave numbers is presented in Figure 10. The FTIR spectra of the adsorbent, showed the presence of amine  $\text{R-NH}_2$  (amino acids, protein, glycoprotein etc), carboxylic acids (fatty acids; lipopoly saccharides etc) and phosphates. The characteristic absorption bands of hydroxyl and amine were identified at  $3427.61 \text{ cm}^{-1}$ , indicating the presence of exchangeable  $\text{OH}^-$  and  $\text{NH}^+$  group respectively, alkyl chain at  $2926.06 \text{ cm}^{-1}$ , amide and phosphate groups at  $1637.14 \text{ cm}^{-1}$  and between  $1197.59$  and  $1124.75 \text{ cm}^{-1}$ , respectively and P-O vibration of  $\text{C-PO}_3^{2-}$  moiety at  $1041.32 \text{ cm}^{-1}$ . The absorption bands identified in the spectra and their assignment to the corresponding functional groups in the adsorbent could enhance the surfaces on which adsorption would take place.

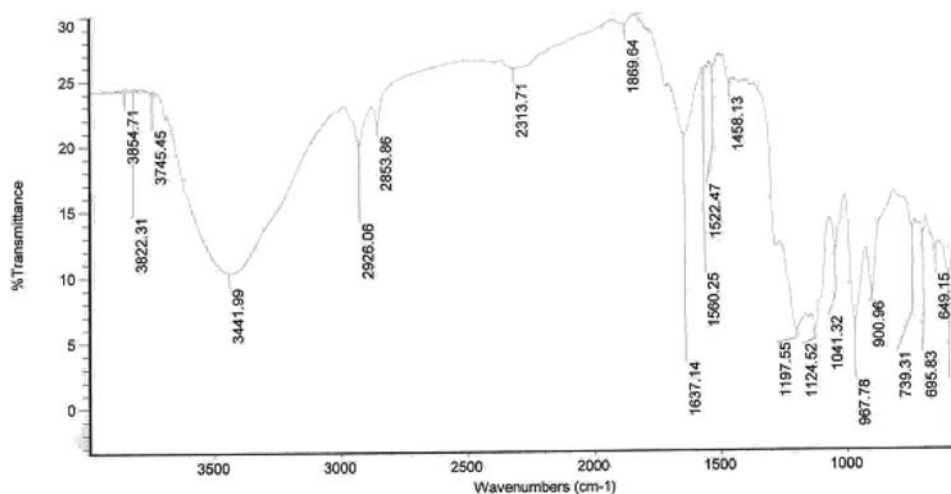


Fig. 10: Fourier transform infrared analysis of ACASC

### CONCLUSIONS

Based on the present study, it can be concluded that the use of chemically activated low-cost agricultural products, such as shells of the seed of *Chrysophyllum albidum* have potential application in the remediation of U-contaminated groundwater. ACASC was more effective in removing uranium from both near-neutral-pH (6.5)- and -high-pH (8)-low- nitrate-containing groundwaters.

A field column test using near-neutral-pH (6.5)-low-nitrate- containing groundwater revealed that ACASC was capable of removing 490 % of the uranium from the feed and uranium breakthrough was not achieved at the cumulative loading capacity of 49.8 mg g l. This is due to the presence of the bicarbonates and close to neutral pH conditions.

In the batch test, In the acidic-pH (5)-high-nitrate-containing groundwater removed 83% uranium with 1-h equilibration and over 90% uranium with 2-h equilibration. ACASC removed more uranium in the first 7.5 min in 100 mL of groundwater (26.5 mgL and uranium).

The optimum conditions of U ion uptake by the adsorbent were: pH value of 5.8, adsorbent mass of 2.0g/100mL, contact time of 60 min and particle size of 1.00 – 1.25 mm. Langmuir isotherm has better fitting model than Freundlich because the former has a higher correlation coefficient than the latter.

These preliminary studies suggest that adsorbent prepared from shell of *Chrysophyllum albidum* seed can be used effectively for the remediation of Uranium in groundwater. Cost analysis for the preparation of

activated carbon of shells of the seed of *Chrysophyllum albidum* has not been performed. The seed of *Chrysophyllum albidum* is available abundantly and can be obtained for nominal price as agricultural by-product in the country.

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