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Removal of U(VI) from aqueous and polluted water solutions using magnetic *Arachis hypogaea* leaves powder impregnated into chitosan macromolecule





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ABSTRACT

In this study m-AHLPICS (magnetic *Arachis hypogaea* leaves powder impregnated into chitosan) was prepared and utilized as an adsorbent to remove U(VI) from aqueous and real polluted wastewater samples. m-AHLPICS was characterized by using the BET, XRD, FTIR, SEM with elemental mapping and magnetization measurements. Different experimental effects such as pH, dose, contact time, and temperature were considered broadly. Chitosan modified magnetic leaf powder (m-AHLPICS) exhibits an excellent adsorption capacity (232.4 \pm 5.59 mg/g) towards U(VI) ions at pH 5. Different kinetic models such as pseudo-first-order, and pseudo-second-order models were used to know the kinetic data. Langmuir, Freundlich and D-R isotherms were implemented to know the adsorption behavior. Isothermal information fitted well with Langmuir isotherm. Kinetic data followed by the pseudo-second-order kinetics (with high R² values, i.e., 0.9954, 0.9985 and 0.9971) and the thermodynamic data demonstrate that U(VI) removal using m-AHLPICS was feasible, and endothermic in nature.

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1. Introduction

With the development of industrial activities, there is a huge demand for the energy throughout the world. To overcome this issue utilization of nuclear energy has received extensive attention in recent years. Uranium (U(VI)) is of the main source for nuclear energy, and it was entered into nature through nuclear activities such as power plants, atomic tests, atomic power plant mishap [1]. Uranium is mainly found in two oxidation stages in the earth's crust, i.e. U(IV) and U(VI). U(VI) seems to be extremely water-soluble and can quickly develop complexes with carbonate in groundwater and U(IV) is precipitated into $UO_2(s)$. The cancer-causing effects of uranium ingestion are well recorded and exposure of people to uranium can cause intense toxicological impacts and dangerous diseases such as damaging the brain, liver and kidneys, causing a wide assortment of malignant growths, and prompting hereditary changes if in direct contact with the skin [2–4]. After entering into the body, uranium can quickly interacts with the

* Corresponding authors. *E-mail addresses*: cdy@gzhu.edu.cn (D.-Y. Chen), kongl_jun@163.com (L.-J. Kong). blood system and tie-up with red platelets, forming a uranyl-albumin white complex that can gather in kidneys and bones [5]. So U(VI) removal is a dire essential to save the ecosystem and human wellbeing.

Up to now, a variety of methods, such as complexation [6], reduction [7], solid phase extraction [8], ion-exchange [9], solvent extraction [10], and membrane processes [11] have been used to remove uranium from the contaminated water sources. The inborn hindrances of the above techniques are fragmented in metal removal, high reagent and essentialness necessities and time of deadly slop close by other waste things, which require further deliberate transfer pathways [12]. Adsorption is simple and cost effective methodology which is extensively utilized in wastewater applications in light of its idealness and practicality. Distinctive sorts of adsorbents have been accounted in past investigations, include green algae [13], Bacillus subtilis/Fe3O4 nanocomposite [14], activated sludge-graphene oxide composites [15], modified Hottentot Fern [16] and modified chitosan composites [17–28] applied for U(VI) removal. It is dire essential to develop new and novel adsorbents to remove U(VI) ions from aqueous and real polluted solutions.

Basically chitosan can exhibit effective sorption performances because of active functional groups on the surface moiety, and it can attract the undesirable metal/dye or some other contaminants from the wastewater. Specifically, chitosan exhibits high selectivity towards metal particles because of the amine and hydroxyl groups which may shape solid bonds with the metal particles [29]. Both (-NH₂ and -OH) groups can act as a chelation sites to attract U(VI) ions. Chelating or coordinating groups can form complexes with metal particles [30]. As a result, economical and eco-friendly sorbents with good sorption capacity and selectivity are urgently required to remove U(VI) contaminants from the surroundings of nuclear industrial sites. In recent years, magnetic nanoparticles have pulled in an ever increasing number of considerations for its remarkable low poisonous quality and simple partition properties.

In this study both, low-cost and environmental friendly m-AHLPICS was prepared by impregnation strategy with the effectively accessible farming waste leaf powders. This combination is attractive because the chitosan is blended with the leaf powder, and gained significance for less harmfulness and simple task process with low level usage of synthetic chemicals for sorbent preparation. Pure and U(VI) loaded m-AHLPICS was undergone through BET, XRD, FITR, and SEM with EDS analysis have been switched to study the surface properties of the m-AHLPICS. Owing to its low cost, easily accessible the adsorbent material exhibited the outstanding adsorption performances. Chitosan and leaf powder were used as a raw material in this study there is no harmful effects to the aquatic environment. Preparation of adsorbent is simple and easy. There is no usage of harmful chemicals to prepare adsorbent. Different experimental effects such as pH, dose, contact time, and temperature were considered broadly. Different kinetic models such as pseudo-first-order, and pseudo-second-order models were used to know the kinetic data. Langmuir, Freundlich and D-R isotherms were implemented to know the adsorption behavior.

2. Materials and methods

2.1. Materials

Chitosan obtained from Sigma–Aldrich with deacetylation degree of 75–85%. Glacial acetic acid, sodium hydroxide sodium (NaOH, S.L., Spain), sulfuric acid (H₂SO₄, Sigma–Aldrich, Germany), FeCl₃·2H₂O, FeCl₃·6H₂O (Sigma–Aldrich, Germany) and U(VI) (UO₂(NO₃)₂·6H₂O 98%, Sigma–Aldrich, Germany) were used without further purification. Uranium stock solution was prepared by dissolving uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) in double distilled water.

2.2. Preparation of m-AHLPICS

m-AHLPICS was prepared by impregnation method. 2 g of $FeCl_2 \cdot 2H_2O$ and 2 g of $FeCl_3 \cdot 6H_2O$ were dissolved 50 mL of distilled water and the solution was stirring continuously to make the clear solution. *Arachis hypogaea* leaves were took from the Guangzhou university surroundings. The leaves were washed, dried and made into fine powder. Then 2 g of leaves powder was added to the above solution with stirring. 0.2 g of NaOH was dissolved in 25 mL of water and it was added to the solution. The solution was turned into black color immediately. It was vigorously stirred for 30 min. Then the magnetic leaf powder was washed thoroughly with distilled water and dried in an oven at 323 K for 7 h.

2 g of chitosan powder was dissolved in 100 mL of glacial acetic acid solution. The solution was kept at constant stirring for 3 h to make the clear chitosan solution. To the chitosan solution the magnetic leaf powder was added and stirred for 4 h. With the help of micro-pipette the solution was dropped into the beaker containing 0.1 N NaOH solution to make beads. After falling into the NaOH solution the material was formed into the beads. The beads were separated from the NaOH solution and washed thoroughly with distilled water. Finally, the beads were dried at 323 K temperature for 12 h and it was named as mAHLPICS for further representation. The total m-AHLPICS preparation process was presented in Fig. 1.

2.3. Batch sorption experiments

All the U(VI) sorption experiments were performed in batch method. The pH of solutions was adjusted to get the desired value (5) by using 0.1 M HCl/M NaOH. pH (1 to 10) and adsorbent mass experiments (0.1 to 0.7 g) were examined with 50 mg/L of U(VI) concentration at 303 K. Contact time (0–180 min) experiments were studied with 25, 50 and 75 mg/L of adsorbate solution (20 mL) at constant pH and dose values. After reaching the equilibrium the adsorbent material was isolated from the solution with filter paper and U(VI) concentrations were determined by ICP-AES.

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where, q_e (mg/g) was the adsorption capacity at equilibrium, C_i and C_e were initial and equilibrium level of U(VI) (mg/L), M (g) was the adsorbent dose, and V (L) was solution volume.

2.4. Desorption and regeneration studies

U(VI) desorption from m-AHLPICS was examined at specific NaOH (0.1–0.4 M) concentrations. 0.3 g of m-AHLPICS was mixed in 50 mL U (VI) solution (250 mg/L) at pH 3.0 and kept it for shaking around 2 h. After that it was filtered and then the filtrate was analyzed with ICP-AES to know how much amount of U(VI) was adsorbed. The reusability tests were performed after U(VI) sorption, and the adsorbent was taken out, rinsed well with the distilled water and dried. Desorption process was carried out by adding 50 mL of desorption eluent to the dried adsorbent and subsequently shaken up and for a certain time. At the end the filtrate was separated and it was assessed how much U(VI) was desorbed by m-AHLPICS. Once m-AHLPICS were desorbed, the same studies were repeated for four times during the adsorption studies. By using the following equation the performance of the U(VI) desorption was assessed.

Desorption efficiency =
$$\frac{Amount of U(VI) desorbed}{Amount of U(VI) adsorbed} \times 100$$
 (2)

2.5. Characterization of adsorbent

From BET and D-R equations, the specific surface area and pore volume of the adsorbent was calculated. In order to study the overall pore volumes, which correspond to the sum of micropores and mesopores, N₂ adsorbed at relative pressure (P/Po = 0.98) was used. XRD with Cu K α radiation ($\lambda = 1.5418$ Å) operated at 2000 W power and a scanning rate of 10°/min in the 2 θ range from 10 to 90. To evaluate the functional groups, the adsorbent was characterized by FTIR studies with Nicolet IS10, Thermo Scientific, USA. 10 mg sample was blended with 100 mg of KBr and ground into a pellet for IR spectral studies. A plain KBr pellet was taken to measure the background absorbance. Surface morphology and elemental compositions of B-BHA samples were measured using a JEOL JSM-7001F Japan, scanning electron microscope (SEM). Magnetic nature of the adsorbent was performed with a vibrating sample magnetometer (VSM, LakeShore-7404).

3. Results and discussion

3.1. BET analysis

Surface properties of *Arachis hypogaea* leaf powder (AHLP), magnetic leaves powder (m-AHLP) and m-AHLPICS beads, was done





through the adsorption/desorption isotherms. Specific surface area of the AHLP, m-AHLP and m-AHLPICS was found to be 58.36, 75.45 and 119.37 m²/g. In addition to this, the pore size distributions curve obtained by BJH method and the average pore sizes of AHLP, m-AHLP and m-AHLPICS were found to be 9.36, 13.61 and 31.32 nm. The pore volume of the AHLP, m-AHLP and m-AHLPICS were found to be 0.025, 0.0519 and 0.0865 cm³/g. Generally, if an adsorbent having the large surface area, pore size and high pore diameter it can exhibit highest sorption capacity. Hence m-AHLPICS can be considered as a prominent sorbent for U(VI) removal.

3.2. XRD analysis

XRD analysis of Arachis hypogaea leaves powder (AHLP), m-AHLP, m-AHLPICS and U(VI) loaded m-APICS were represented in Fig. 2A-D. For Arachis hypogaea leaves powder the main 2 characteristic broad diffraction peaks. The first broad peak appeared in between 6 and 12 and the second broad peak was appeared in between 19 and 23 respectively. For m-APICS the two broad peaks were turned into amorphous nature and 4 new peaks appeared ($2\theta = 38.37, 41.26, 52.76$ and 76.39) in m-AHLP. This 4 peaks represents the magnetic nature of the material. It means that magnetization was properly done on the surface of the AHLP. The same 4 signals were present on the m-AHLPICS. This conforms that the m-AHLP was successfully impregnated into chitosan without changing the magnetic property of the m-AHLP and it is having the amorphous nature. After U(VI) sorption the four signal were disappeared in U(VI) loaded m-AHLPICS. It indicates that the uranyl ions were sorbed successfully and then the U(VI) ions were distributed throughout the sorbent surface.

3.3. FTIR analysis

Fig. 3 represents the FTIR analysis of *Arachis hypogaea* leaves powder (AHLP), m-AHLP, m-AHLPICS and U(VI) loaded m-AHLPICS and it was done in the range of 500–4000 cm⁻¹. Broad band appears 3431 cm⁻¹, reveals the stretching vibration of –OH and -NH groups. For AHLP

(Fig. 3A) peaks at 2925 cm⁻¹ represents the -CH symmetrical stretching vibrations. While, the bands at 1649 and 1074 cm⁻¹ represents the -NH₂ and C—O groups. The band at 1319 cm⁻¹ corresponds to the C—N stretching vibration. For m-AHLP (Fig. 3B) the overlapping of the stretching vibrations of N—H and -OH groups of chitosan can be seen at 3445 cm⁻¹. A new peak appeared at 570 cm⁻¹, corresponds to the Fe—O group, indicating that AHLP was successfully turned into m-AHLP. AHLP peaks at 3431, 2925. 1649, 1319, 1074 cm⁻¹ were shifted to 3445, 2927, 1656, 1414, 1082, and 1028 cm⁻¹ in m-AHLP.

For m-AHLPICS (Fig. 3C) the broad peak at 3451 represents the hydroxyl and amine stretching vibrations. And the peak at 2927 cm⁻¹ corresponded to stretching vibrations of O-H/N-H and C—H. However, peak at 1656 cm⁻¹ is for amide group. The peak at 1570 cm⁻¹ attributed to the chitosan amide groups. The peaks at 1082 and 1028 cm⁻¹, corresponding to the stretching vibration of the primary –OH group and the secondary –OH group, respectively. m-AHLP peaks at 3445, 2925. 1649, 1319, 1074 cm⁻¹ were shifted to 3451, 2927, 1656, 1414, 1082, and 1028 cm⁻¹ in m-AHLPICS.

For U(VI) loaded m-AHLPICS (Fig. 3D) the peak at 2925 shifts to 2935 $\mbox{cm}^{-1}\mbox{,}$ and the broad peak of $\mbox{-}NH_2$ and O—H shifts from 3451 $\rm cm^{-1}$ to 3464 $\rm cm^{-1}.$ This might be involvement of intra- and inter-hydrogen bonds decrease; and -NH₂ and -OH groups increase, which leads to better sorption. The peaks at 1612 cm^{-1} are attributed to imine C=N stretching vibration. 2935 cm⁻¹ is assigned to aliphatic C-H stretching vibrations. After U(VI) adsorption, a new peak at 913 cm⁻¹ was found and it represents the linear structure of [O= $U^{VI}=O^{2+}$. And it will also confirm that there is a strong chemical bond was formed between the (UVI) ions with CCMB [31]. Oxygen atom of the hydroxyl (CCMB-OH), and the nitrogen atom of the amino $(m-AHLPICS = NOH and m-AHLPICS - NH_2)$ participated U(VI) sorption. The peaks 3445, 2927, 1570, 1656, 1082, 1028 and 570 cm^{-1} present at m-AHLPICS was shifted to 3464, 2935, 1654, 1612, 1467, 1133, 1037 and 913 cm⁻¹ after U(VI) loaded m-AHLPICS. The band 1414 cm⁻¹ (m-AHLPICS) was shifted to 1467 cm⁻¹ drastically after U(VI) sorption and it represents the C-N-C bonding. At the end of the U(VI) sorption the band intensity of NH₂, -OH, -CN, C=O and C-O stretching/bending



Fig. 2. XRD analysis of (A) AHLP; (B) m-AHLP; (C) m-AHLPICS; and (D) U(VI) loaded m-AHLPICS.

vibrations were increased/decreased. This represents that oxygen, sulphur, and nitrogen atoms were actively participated in U(VI) sorption.

3.4. SEM with elemental mapping

SEM analysis of m-AHLPICS beads and U(VI) loaded m-AHLPICS beads was shown in Fig. 4A–B. m-AHLPICS (Fig. 4A) beads having round shape with smooth surface. After U(VI) sorption (Fig. 4B) the surface of the m-AHLPICS beads was totally changed. An irregular rough surface was found. The rough surface of the adsorbent is more favorable for U(VI) sorption. In addition to the SEM analysis, the elemental mapping (Fig. 5) was also carried out to know the presence of the elements in the adsorbent. Leaf powder exhibited the presence of C, N, O, and S elements on it. And m-AHLPICS beads having the C, N, O, S, and Fe groups in it. In m-AHLPICS a new Fe elemental group was observed. This represents that the magnetization was successfully done. After U(VI) sorption U was also found along with the C, N, O, and S groups. It indicates that U (VI) sorption was done successfully with m-AHLPICS.

3.5. Magnetic analysis

Magnetic property of m-AHLP, m-AHLPICS and U(VI) loaded m-AHLPICS was done with VSM analysis and the results were kept in Fig. 6. Magnetic leaf powder (m-AHLP), m-AHLPICS and U(VI) loaded m-AHLPICS having the 29.71, 24.62 and 21.42 emu/g values. The above value suggesting that magnetic leaf powder and m-AHLPICS exhibits the ferromagnetism nature. The magnetization value of m-AHLPICS is lower than the magnetic leaf powder (m-AHLP). The main reason for this one is due to the functionalization of the chitosan with the magnetic leaf powder during the reaction. After U(VI) sorption the magnetization values is less than the m-AHLPICS. It reveals that the U (VI) sorption was done successfully on the adsorbent surface.

3.6. Effect of pH

pH is a key point in adsorption process because it will influence the performance of the adsorbent. The sorption efficiency of an adsorbent was to be pH dependent, and it can impact the surface chemistry of the sorbent. In the present study we performed the pH experiments by varying pH from 1.0 to 10.0 and the mechanism results have been depicted in Fig. 7A. U(VI) removal percentage is low at lower pH values and it was reasonably attributed to the protonation of NH₂ and COOH present on the exterior of the adsorbent, hence there is no electron transfer to the uranyl cations. From the results it is very clear that the U(VI) removal was poor at low pH values and it can be ascribed that there is a strong conflict of H^+ with UO_2^{2+} ions for the protonated active sites of the adsorbent. During this period a couple of amino groups were combined with U(VI). UO_2^{2+} is the primary species when solution pH was below 4. U(VI) removal proficiency increases with increasing the pH and reaches the extreme removal at pH 5.0. After achieving the extreme value, the effectiveness of U(VI) decreases gradually with further increment in pH. Moreover hydrolysis will occur and forms the soluble hydrolysis products such as $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^{3+}$, and $(UO_2)_2(OH)_2$ when pH > 6.0 [32]. Hence in this study pH 5 is considered as an ideal pH for the further U(VI) removal tests.

3.7. Effect of adsorbent dose

Selection of adsorbent is the big task to the scientists because the capability of the adsorbent relies upon the effectiveness of the metal/dye removal from aqueous and real polluted samples. Functional groups and active sites are the primary sources to enhance the adsorption capacity of any adsorbent. Adsorbent dose studies were performed by changing the mass of the adsorbent (0.1–0.7 g) at constant pH (5.0) of 50 mg/L concentration of U(VI) solution (20 mL) at 303 K and the



Fig. 3. FTIR spectral analysis of (A) AHLP; (B) m-AHLP; (C) m-AHLPICS; and (D) U(VI) loaded m-AHLPICS.

results has been depicted in Fig. 7B. In this investigation we can see that U(VI) removal increased from 79.46.8 to 91.62% respectively, when the adsorbent portion increased from 0.1 to 0.4 g. This might be because of the rapid involvement of active sites with the U(VI) ions. After reaching an equilibrium there is no considerable amount of U(VI) removal. This might be because of the way that the surface dynamic destinations present in the adsorbent gets totally involved by the U(VI) particles and

prompted the immersion of active sites. In this study 0.4 g was chosen as an ideal adsorbent portion for further U(VI) tests.

3.8. Effect of contact time

Contact time is a standout among the most basic parameter in adsorption process since it decides the take-up limit of the solute from the solvent (solid-liquid inter actions) under specific time. Contact time experiments were performed in range of 0–180 min, with the 25, 50 and 75 mg/L of U(VI) concentration and the obtained results were shown in Fig. 7C. U(VI) removal efficiency increases with increasing contact time. U(VI) removal using CCMB will takes in three steps, i.e. initial fast/rapid step, slow step (moderate) and finally reaches to the equilibrium. The first rapid step might be ascribed to the accessibility of bulk active surface sites to remove U(VI) from aqueous and real polluted water samples. The second moderate step was credited to the staying less active sites and repulsion was occurred when the sorbent material in the bulk phase. If there are anything left active sites the final equilibrium step was achieved and there is no considerable amount of U(VI) removal percentage was carried out in this stage. From Fig. 7C we can see that the U(VI) removal by using m-AHLPICS reaches equilibrium after 90 min reaction. After equilibrium there is no considerable change in adsorption capacity of the adsorbent. Hence the contact time 90 min was chosen an ideal equilibrium time for batch sorption tests.

3.9. Kinetic experiments

Kinetic experiments were studied to find out the adsorption rate and its behaviour with the adsorbent material. Even though the sorption capacity of m-AHLPICS was influenced by different pH, dose, solute nature and concentration, kinetic models are the only one which will concentrate or elucidate the rate of reaction. So kinetic studies can be considered as an important parameter in sorption process. Pseudo-firstorder (Eq. (3)) [33], and Pseudo-second-order (Eq. (4)) [34] models were utilized to investigate the kinetic data of the reaction.

$$q_t = q_{e1}(1 - \exp(-k_1 t)) \tag{3}$$

$$q_t = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t} \tag{4}$$

where qe (mg/g) and qt (mg/g) are the amounts of U(VI) sorbed at equilibrium and at time t. K_1 , and K_2 represents the rate constants for first-order, and second-order process. The values K_1 and K_2 were acquired from q versus t (Fig. 7D) and the obtained results were shown in Table 1. There are so many factors which influences the sorption

Fig. 4. Morphological analysis (SEM) of (A) m-AHLPICS, and (B) U(VI) loaded m-AHLPICS.



Fig. 5. Elemental mapping of AHLP; m-AHLPICS; and U(VI) loaded m-AHLPICS.

capacity of the sorbent including the pH, particle size, dose and the nature of the solute. Among them kinetic model is considered to be one of the most important tool to observe the rate of the reaction. Pseudo-first-order correlation coefficient values were compared with pseudo-second-order values. Pseudo-first-order kinetic model having lower correlation coefficient values and there is huge difference between calculated (q_e _{cal}) and experimental (q_e _{exp}) values suggests that the pseudo-first-order kinetic model was not applicable for U(VI) removal. Pseudo-second-order kinetic model having higher correlation coefficient values. Kinetic results reveals that U(VI) removal followed well with the pseudo-second-order model and implies that the rate-



Fig. 6. Magnetization measurement of m-AHLP, m-AHLPICS and U(VI) loaded m-AHLPICS.

limiting step was chemisorption through the interchanging of lone pair electrons of adsorbent with sorbate.

3.10. Isotherm experiments

Generally, the sorption capacity, and the nature of adsorbent with adsorbate, can be determined from the equilibrium isotherm models. At the same time these experiments were useful to know the adsorption mechanism, surface property of the adsorbent with adsorbate and the affinity towards adsorbent at equilibrium stage. Langmuir [35], Freundlich [36] and D-R isotherms [37] were utilized to know how much percentage of U(VI) sorption was done on the external surface of the adsorbent. Langmuir, Freundlich and D-R isotherms were shown in Fig. 7E. Langmuir model assumes that the sorption was done uniformly on the adsorbent without any transmigration of sorbate onto the plane surface [38] and the isotherm was expressed by the following equation.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_e (mg/g) is the quantity of sorbate adsorbed at equilibrium, q_m (mg/g) is the maximum adsorbate uptake at equilibrium, K_L (L/mg) is the constant and C_e (mg/L) is the equilibrium concentration of adsorbate in the solution. Langmuir isotherm exhibits the highest sorption capacity of m-AHLPICS at 328 K and the lowest at 298 K, which represents that higher temperature is progressively ideal for U(VI) sorption. Langmuir isotherm model possesses higher R² values (Table 2) than the Freundlich isotherm model. This indicates that active sites were distributed homogeneity on the surface of the sorbent. In the present examination we observed that the Q_{max} and K_L values increases with increasing the temperature might be ascribe to increase in the stability of the complex formed between the active sites of adsorbent with U(VI) ions.





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Fig. 7. (A) Effect of pH; (B) adsorbent dose; (C) contact time; (D) kinetic evaluation plots (25, 50 and 75 mg/L); (E) Isothermal study; (F) temperature effect; (G) Thermodynamics (H) Desorption % of NaOH at different concentrations (0.1 to 0.4 M) and (J) adsorption-desorption of U(VI) onto m-AHLPICS.

Freundlich isotherm was applied to find out the heterogeneous system and the isotherm was expressed by the following equation.

$$q_e = K_f C_e^{1/n} \tag{6}$$

where C_e (mg/L) represents equilibrium concentration, q_e (mg/g) is the amount of adsorbate adsorbed per unit weight of adsorbent, K_f is the Freundlich constant and n is the Freundlich exponent. R^2 and K_F values of Freundlich isotherm were compared with the Langmuir isotherm and Freundlich isotherm (Table 2) has the lowest values than the Langmuir isotherm. It indicates that the Freundlich isotherm is not applicable for U(VI) removal in the present study.

D–R isotherm model was also used to know the nature of sorption processes as physical or chemical. D–R isotherm can be expressed by

Isotherm evaluation of U(VI) onto m-AHLPICS.

Isotherm	Parameters	Values
Langmuir	$q_m (mg/g)$ $K_L (L/mg)$ R^2 γ^2	$\begin{array}{c} 232.4 \pm 5.59 \\ 0.0018 \pm 0.0011 \\ 0.9977 \\ 13.6 \end{array}$
Freundlich	$ \frac{\kappa}{K_f(mg/g)} $ n $ \frac{R^2}{\gamma^2} $	25.1 ± 3.501 2.591 ± 0.326 0.9582 244.2
Dubinin-Radushkevich	$\hat{Q}_m (mg/g)$ K R^2 χ^2	$\begin{array}{c} 188.4 \pm 6.631 \\ 0.034 \pm 0.006 \\ 0.8347 \\ 677.3 \end{array}$

the following equations.

$$q_e = q_m \exp(-K\varepsilon^2) \tag{7}$$

where
$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$
 (8)

where q_m (mg/g) is the amount of U(VI) adsorbed onto a unit mass of adsorbent, ε is the Polanyi potential, C_e (mg/L) is the equilibrium concentration, R is the ideal gas constant (8.314 J/mol K) and T is the absolute temperature in Kelvin. The mean free energy of the U(VI) sorption can be determined by the following equation:

$$E = \frac{1}{\sqrt{2K}} \tag{9}$$

Free energy values describe the type of sorption mechanism. If E values existed 1–8 kJ/mol the sorption system can be considered as a physisorption processes and the E value lies between 8 and 16 kJ/mol, the sorption procedure can be considered as ion exchange. In this study the free energy values were calculated to be 3.835 kJ/mol, respectively. Hence the results indicate that the U(VI) removal in the present study is a physisorption process.

3.11. Effect of temperature with thermodynamic study

Temperature plays a key role and it controls the sorption process. Temperature effect graph was shown in Fig. 7F. The sorption capacity (increased and decreased) of the sorbent mainly depends on the temperature. Because it determines the sorption process whether it is endothermic or exothermic nature. In this study the sorption capacity of m-AHLPICS increased to 232.4 mg with increasing the temperature from 298, 308, 318 to 328 K. This might be due to the fact that the interaction between the U(VI) ions and the active groups of m-AHLPICS was stronger at higher temperatures.

Thermodynamic parameters namely, Gibbs free energy (ΔG°), enthalpy (ΔH^{0}) and entropy (ΔS^{0}) values were obtained from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{10}$$

Tuble 1			
Kinetic evaluation	of U(VI)	onto	m-AHLPICS

Table 1

Adsorbent	Conc.	q _{e,exp}	Pseudo-first-	Pseudo-first-order model		Pseudo-secor	Pseudo-second-order model		
		(mg/g)	q _{e,cal} (mg/g)	k ₁ (L/min)	R ²	$q_{e,cal} \ (mg/g)$	k ₂ (g/mg. min)	R ²	
m-AHLPICS	25 50 75	58.4 84.3 106	50.33 66.52 85.42	0.0444 0.0256 0.0368	0.9839 0.9789 0.9826	59.8 83.7 104.6	0.0008 0.0006 0.0005	0.9954 0.9985 0.9971	

Table 3Thermodynamic evaluation of U(VI) onto m-AHLPICS.

Temperature (K)	∆G ^o	ΔH ^o	∆S°
	(kJ/mol)	(kJ/mol)	(kJ/mol K)
298 308 318 328	-0.1474 -1.0170 -2.2316 -3.2931	31.06	0.106

$$\Delta G^{o} = -RT \ln K_{c} \tag{11}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
(12)

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{13}$$

where, C_{Ae} is the amount of U(VI) adsorbed on the solid phase at equilibrium, C_e is the equilibrium (final) concentration of U(VI), where, *R* is the universal gas constant (8.314 × 10⁻³ kJ/mol K), and *T* is the temperature (*K*). Thermodynamic parameters namely ΔG° and ΔH° can be utilized as a primary source to know the sorption procedure. ΔH^{0} and ΔS^{0} values were obtained from the plot of ln K_c versus 1/T (7G). From the Table 3 we can see that the ΔG° values became more negative with increasing the temperature, suggesting that U(VI) is more favorable at higher temperatures. This is mainly due to the dehydrated nature of the cations with increasing the temperatures [39]. Positive ΔH° value represents that the sorption procedure is endothermic. Whereas the positive ΔS° represents the increase in randomness of adsorption process during the solid-solution interaction.

3.12. Desorption and regeneration studies

The reusability of materials is crucial in order to evaluate financially effective and ecologically sustainable use. Stability is essential in various adsorption and desorption cycles, if the same adsorbent is reused. In this study NaOH solution (0.1 to 0.4 M) was acted as good eluent to desorb U(VI) from the m-AHLPICS. Thus the reusability of adsorption was investigated based on the ability of adsorption/desorption. The obtained data were kept in Fig. 7H and I. In the first cycle, 91.12% desorption effectiveness was achieved with 0.1 M NaOH as an eluent, which indicates that adsorbents are appropriate for reuse. After that it was decreased upto 56.54% (in 0.4 M of NaOH). With an increase in the number of cycles, the quantity of the U(VI) adsorption/desorption was observed with number of cycles increased. The desorption efficiency of U(VI) decreased slowly from

89.36% (first cycle) to 69.32% in the final regeneration cycle (fourth cycle). The adsorption efficiency of U(VI) decreased slowly from 91.26% (first cycle) to 74.32% in the final regeneration cycle (fourth cycle). Therefore, the 0,1 M NaOH solution was used to carry out all reusability studies. This implies that m-AHLPICS is highly reusable sorbent and is also essential for real polluted solutions.

3.13. Real sample analysis

To know the potential of m-AHLPICS, we did our experiments on real polluted U samples. We took three different concentrations of U contaminated samples from the uranium mines. The U concentrations (1.43, 1.72 and 2.12 mg/L) and pH (3.2, 3.4 and 3.2) in the polluted samples were tested before starting the sorption experiments. All the polluted U sorption experiments were performed in batch method. And the pH and adsorbent dose effect of real polluted samples were compared with aqueous U(VI) samples and the results were given in Fig. 8. U removal percentage increases with increasing the adsorbent mass. The sorption capacity of m-AHLPICS was decreased with polluted samples (8B-D) and the sorption capacity increases with increasing the dose in aqueous U(V) solutions (8A). While doing the experiments we observed that the U removal percentage was low with the polluted sample compare with the aqueous U(VI) solutions. After we maintain the constant pH the removal level was increased. The main reason for this one is the involvement of some other matrix ions. At the same time presence of other matrix ions is more and there is a competition for the active sites by matrix ions. m-AHLPICS can exhibits high sorption capacity towards real U polluted samples containing the salinity and multi-ionic solutions. Hence m-AHLPICS can be considered as a potential sorbent to remove U from uranium polluted solutions.

3.14. Adsorption mechanism

Sorption mechanism of U(VI) onto m-AHLPICS was explained from the FTIR analysis and pH of the solution. m-AHLPICS having the hydroxyl, amino, carboxyl and carbonyl groups on its surface. These groups may involve in the adsorption mechanism. The involvement of functional groups in the mechanism of U(VI) sorption system by m-AHLPICS was elucidated well with ion exchange, electrostatic attraction, and complexation/coordination. Nitrogen and oxygen are having lone pair of electrons. They can form the complex with the metal U(VI) through an electron pair sharing. During the mechanism the carboxyl group was deprotonated and the m-AHLPICS surface became negative. Hence automatically the negative surface can attract the positive U (VI) ions through electrostatic attraction forces. During the electrostatic attraction the U(VI) removal percentage was less and it was shown in Fig. 9.



Fig. 8. Real sample pH and adsorbent dose analysis of U(VI) onto m-AHLPICS.



Fig. 9. Mechanism of m-AHLPICS with U(VI) ions.

 Table 4

 Comparison study of m-AHLPI CS with other adsorbents.

Adsorbents	Experimental conditions (K)	$Q_{max}\left(mg/g\right)$	Reference
Catechol-functionalized aminopropyl silica gel	pH = 5.0, T = 298	15.94	[40]
Bentonite modified with polyacrylamidoxime	pH = 4.0, T = 298	33.3	[41]
Amine modified silica gel	pH = 4.0, T = 302	35.86	[42]
SA@SiO2	pH = 4.0, T - 298	44.5	[43]
PA-SMM	pH = 5.0, T = 240	76.9	[44]
PVA-VPA	pH = 4.5,	32.1	[45]
PO4/PE	pH = 8.2,	173.8	[46]
TMP-g-AO	P = 360 pH = 8.2, T = 298.15	35.37	[47]
CTPP beads	pH = 5, T = 298.15	236.9	[24]
IMCR and NIMCR	pH = 5, T = 298	187.26 and 160 77	[25]
Raw aloe vera wastes	pH = 4.0, T = 298	201.2	[26]
NaOH treated aloe vera wastes	pH = 4.0, T - 298	370.4	[26]
$\rm H_3PO_4$ treated aloe vera wastes	pH = 4.0, T = 208	208	[26]
m-AHLPICS	pH = 5.0, T = 303	232.4 ± 5.59	Present study

3.15. Comparison study of U(VI) sorption capacity with other adsorbents

m-AHLPICS sorption capacity was compared with other sorbents (Table 4). From Table 4, we can see that m-AHLPICS obtained highest adsorption capacity ($232.4 \pm 5.59 \text{ mg/g}$ at 303 K) compare with other adsorbents [40-47]. This can be attributed that the surface active sites of the adsorbent interacted with the U(VI) ions. In this study m-AHLPICS adsorbent has been prepared by using a simple impregnation method. Chitosan and leaf powder were used as a raw material in this study and they can be easily available with low-cost. Preparation of adsorbent is simple and easy. There is no usage of harmful chemicals to prepare adsorbent. Based on the above advantages, one can conclude that m-AHLPICS is a worthy adsorbent material to remove U(VI) from aqueous and real polluted water samples.

4. Conclusions

m-AHLPICS was prepared through impregnation method. In this study a novel, low-cost, eco-friendly m-AHLPICS beads were prepared and utilized as adsorbent to remove U(VI) from aqueous and real polluted samples. m-AHLPICS was characterized by BET, XRD, FTIR, SEM with elemental mapping and magnetization (VSM) analysis. Oxygen atom of the hydroxyl (m-AHLPICS-OH), and the nitrogen atom of the amino (m-AHLPICS=NOH and m-AHLPICS-NH₂) participated U(VI) sorption. U(VI) removal was studied as a function of pH, adsorbent dose, contact time, and temperature in batch system. The ideal pH for U(VI) adsorption was considered to be 5.0. And 0.4 g of m-AHLPICS was chosen as an ideal adsorbent dose for U(VI) tests. Contact time 90 min was chosen an ideal equilibrium time for batch sorption tests. The extreme sorption capacity of m-AHLPICS was observed to be 232.4 \pm 5.59 mg/g at 303 K. The kinetic data follows the pseudosecond-order model (with high R² values, i.e., 0.9954, 0.9985 and

0.9971), and the equilibrium data fitted well with the Langmuir isotherm model. The thermodynamics parameters show that the adsorption process is feasible, spontaneous and endothermic.

CRediT authorship contribution statement

Gutha Yuvaraja: Writing - original draft, Writing - review & editing, Data curation, Methodology,Ning-Chao Zheng:Conceptualization. Yixiong Pang:Conceptualization.Minhua Su:Conceptualization.Di-Yun Chen:Supervision.Ling-Jun Kong:Supervision.Sajid Mehmood:Conceptualization.Munagapati Venkata Subbaiah:Validation.Jet-Chau Wen:Conceptualization.

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References

- [1] Y.S. Wang, Y.T. Chen, C. Liu, F. Yu, J. Nucl. Mater. 504 (2018) 166-175.
- [2] X. Wang, R.M. Li, J.Y. Liu, R.G. Chen, H.S. Zhang, Q. Liu, Z.S. Lia, J. Wang, New J.Chem. 41 (2017) 10899-10907.
- [3] Y. Liu, Z. Zhao, D. Yuan, Y. Wang, Y. Dai, Y. Zhu, J.W. Chew, Appl. Surf. Sci. 466 (2019) 893-902.
- [4] S. Duan, X. Xu, X. Liu, Y. Wang, T. Hayat, A. Alsaedi, Y. Meng, J. Li, J. Colloid Interf. Sci. 513 (2018) 92-103.
- [5] P.R. Sharma, A. Chattopadhyay, S.K. Sharma, B.S. Hsiao, Ind. Eng. Chem. Res. 56 (2017) 13885-13893.
- [6] M.O. Barnett, P.M. Jardine, S.C. Brooks, Environ. Sci. Technol. 36 (2002) 937–942. [7] D.S. Alessi, B. Uster, H. Veeramani, E.I. Suvorova, J.S. Lezama-Pacheco, J.E. Stubbs, J.R.
- Bargar, R. Bernier-Latmani, Environ, Sci. Technol. 46 (2012) 6150-6157.
- [8] C.S.K. Raju, M.S.A. Subramanian, J. Hazard. Mater. 145 (2007) 315-322.
- [9] J. Li, Y. Zhang, Procedia Environ. Sci. 13 (2012) 1609-1615.
- [10] A. Yao, T. Chu, J. Nucl, Phys. Mater 480 (2016) 301-309.
- [11] C. Zhou, A. Ontiveros-Valencia, L.C. de Saint Cyr, A.S. Zevin, S.E. Carey, R. Krajmalnik-Brown, B.E. Rittmann, Water Res. 64 (2014) 255-264.
- [12] S. Tripathi, A. Roy, S. Nair, S. Durani, R. Bose, Environ. Nanotechnol. Mon. Manag. 10 2018) 127-139
- [13] E. Bagda, M. Tuzen, A. Sari, J. Environ. Radioactiv 175-176 (2017) 7-14.
- [14] W. Hu, Li Me, T. Chen, Z. Zhang, D. Chen, H. Liu, J. Mol. Liq. 258 (2018) 244-252.
- [15] C. Zhao, J. Liu, G. Yuan, J. Liu, H. Zhang, J. Yang, Y. Yang, N. Liu, Q. Sun, J. Liao, J. Mol. Liq. 271 (2018) 786-794.
- K. Zhou, Y. Liu, Z. Yang, H. Liu, J. Environ. Radioactiv. 167 (2017) 13-19. [16]

- [17] X. Yi, I. He, Y. Guo, Z. Han, M. Yang, I. Jin, J. Gu, M. Ou, X. Xu, Ecotox, Environ, Saf, 147 (2018) 699-707.
- [18] J. Liu, C. Zhao, G. Yuan, Y. Dong, J. Yang, F. Li, J. Liao, Y. Yang, N. Liu, Hydrometallurgy 175 (2018) 300-311
- [19] P.S. Barber, S.P. Kelley, C.S. Griggs, S. Wallace, R.D. Rogers, Green Chem. 16 (2014) 1828-1836.
- Z. Chen, J. Wang, Z. Pu, Y. Zhao, D. Jia, H. Chen, T. Wen, B. Hu, A. Alsaedi, T. Hayat, X. [20] Wang, Chem. Eng. J. 320 (2017) 448-457
- [21] D. Pan, Q. Fan, F. Fan, Y. Tang, Y. Zhang, W. Wu, Sep. Purif. Technol. 177 (2017) 86-93
- [22] T.S. Anirudhan, G.S. Lekshmi, F. Shainy, J. Colloid Interf. Sci. 534 (2019) 248-261.
- [23] Y. Sun, C. Ding, W. Cheng, X. Wang, J. Hazard. Mater. 280 (2014) 399-408. [24] M.K. Sureshkumar, D. Das, M.B. Mallia, P.C. Gupta, Adsorption of uranium from
- aqueous solution using chitosan-tripolyphosphate (CTPP) beads, J. Hazard. Mater. 184(2010)65-72
- [25] L. Zhou, C. Shang, Z. Liu, G. Huang, A.A. Adesina, Selective adsorption of uranium(VI) from aqueous solutions using the ion-imprinted magnetic chitosan resins, J. Colloid Interf Sci 366 (2012) 165-172
- F. Noli, E. Kapashi, M. Kapnisti, Biosorption of uranium and cadmium using sorbents [26] based on Aloe vera wastes, J. Environ. Chem. Eng. 7 (2019) 102985.
- [27] R.A.A. Muzzarelli, Potential of chitin/chitosan-bearing materials for uranium recovery: an interdisciplinary review, Carbohyd. Polym. 84 (2011) 54-63.
- [28] C.F. Carolin, P.S. Kumar, A. Saravanan, G.J. Joshiba, M. Naushad, Efficient techniques for the removal of toxic heavy metals from aquatic environment: a review, J. Environ. Chem. Eng. 5 (2017) 2782-2799.
- [29] J. Deng, Y. Liu, S. Liu, G. Zeng, X. Tan, B. Huang, X. Tang, S. Wang, Q. Hua, Z. Yan, J. Colloid Interf. Sci. 506 (2017) 355-364.
- A.A. Galhoum, M.G. Mahfouz, A.A. Atia, S.T. Abdel-Rehem, N.A. Gomaa, T. Vincent, E. [30] Guibal, Ind. Eng. Chem. Res. 54 (2015) 12374-12385.
- [31] Y. Wu, D. Chen, L. Kong, D.C.W. Tsang, M. Su, J. Hazard. Mater. 371 (2019) 397-405.
- [32] K.Z. Elwakeel, A.A. Atia, J. Clean. Prod. 70 (2014) 292-302.
- S. Lagergren, K. Sven, Vetenskapsakad. Handl 24 (1898) 1-39.
- [34] Y.S. Ho, G. McKay, Process Biochem. 34 (1999) 451-465.
- [35] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361-1403.
- [36] H.M.F. Freundlich, J. Phys. Chem. 57 (1906) 385-470. [37]
- M.M. Dubinin, Chem. Rev. 60 (1960) 235-266.
- H. Hallaji, A.R. Keshtkar, M.A. Moosavian, J. Taiwan Inst. Chem. Eng. 46 (2015) [38] 109-118
- [39] S. Song, S. Huang, R. Zhang, Z. Chen, T. Wen, S. Wang, T. Hayat, A. Alsaedi, X. Wang, Chem. Eng. J. 325 (2017) 576-587.
- [40] B.P. Metilda, J.M. Gladis, T.P. Rao, Radiochim. Acta 93 (2005) 219-224.
- [41] S. Simsek, U. Ulusoy, J. Radioanal. Nucl. Chem. 292 (2012) 41-51.
- K.A. Venkatesan, V. Sukumaran, M.P. Antony, P.R.V. Rao, J. Radioanal. Nucl. Chem. [42] 260 (2004) 443-450.
- F. Fan, D. Pan, H. Wu, T. Zhang, W. Wu, Ind. Eng. Chem. Res. 56 (2017) 2221-2228. [43] L.M. Zhou, H.B. Zou, Y. Wang, Z.R. Liu, Z.W. Huang, T.A. Luo, A.A. Adesina, J. [44]Radioanal. Nucl. Chem. 310 (2016) 1155.
- [45] S.X. Duan, X.T. Xu, X. Liu, J. Sun, T. Hayat, A. Alsaedi, J.X. Li, Appl. Surf. Sci. 448 (2018) 297-308.
- [46] Y. Liu, Z. Zhao, D. Yuan, Y. Wang, Y. Dai, J.W. Chew, Ind. Eng. Chem. Res. 57 (2018) 14551-14560.
- J. Zeng, H. Zhang, Y. Sui, N. Hu, D. Ding, F. Wang, J. Xue, Y. Wang, Ind. Eng. Chem. Res. [47] 56 (2017) 5021-5032.