

Adsorption of UO_2^{2+} on Fibrous Cerium Phosphate and its Alanine and Arginine Intercalated Materials

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Article History

Received: 20 September, 2022

Revised: 3 November, 2022

Accepted: 29 November, 2022

Published: 6 December, 2022

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Abstract

Amorphous fibrous cerium (IV) phosphate (f-CeP) was prepared and characterized. Batch sorption method was performed to investigate uptake of uranyl ion (UO_2^{2+}) aqueous solution by amorphous fibrous cerium phosphate f-CeP, using different variables in order to elucidate its applicability as a uranium sorption medium. Sorption of Uranyl ions were measured spectrophotometrically after its extraction by 8-hydroxy quinoline, implementing best adsorption conditions (pH, contact time, ionic strength, amount of adsorbent and initial uranyl ion concentration) for estimation. Exchange capacity of f-CeP was 4.25meq/g. Its x-ray powder diffraction pattern showed an amorphous material with d_{001} spacing value of 10.76 Å. While its amino acid intercalates showed a significant increase in the d_{001} to 11.33Å for f-CeP / alanine and 14.19Å for f-CeP / arginine. From spectrophotometric analysis, the results showed that the maximum uranyl ion adsorption capacity reached at the initial concentration of 50ppm, pH 4.5, contact time 3hrs and adsorption dosage of 2 g/L. However, amino acid intercalates showed less adsorption efficiency than their parent analogue.

Keywords: Amorphous fibrous cerium phosphate; Alanine; Arginine; Intercalates; Uranyl ions uptake.

1. Introduction

Uranium(VI) is the crucial source for the production of nuclear power and is found in nature at a concentration of 4ppm [1]. Uranium (VI) is usually released to the environment during nuclear fuel processing, uranium mining and nuclear accidents [2, 3]. Uranium is a toxic element, uranium toxicity may target important organs in the body such as the kidney [4].

Uranium nowadays is widely used in different fields such as nuclear energy generators, catalysts, staining pigments burning of fossil fuel and uranium containing phosphate minerals [5-7].

In terms of environmental protection and human health, the separation of uranyl ions from aqueous solutions is critical. Many methods have been developed for removal of uranium from waste water such as chemical precipitation/flocculation, electrochemical treatment, oxidation-reduction, reverse osmosis and membrane nanofiltration [8]. However, these methods have inadequacies, such as expense, incomplete removal and generation of secondary contaminants.

Adsorption protrudes as one of the most effective methods in waste water treatment due to its low cost, easily obtainable sources, ecofriendly.

Inorganic exchangers have received much attention nowadays compared to the organic resins [9]. Inorganic ion exchangers have excellent recognition in the field of radioactive waste treatment due to their unique properties such as their ability to withstand high temperatures and radiation doses.

Insoluble salts of tetravalent metal phosphates(TVMP) of high exchange capacity, high thermal stability highly stable in strong acids, oxidizing solutions and ionizing radiations. They show selectivity for certain metal ions [10]. In particular, they are attractive for applications where organic resins cannot be used because of their degradability [11]. The layered tetravalent metal phosphates nanomaterials are receiving great attention because of their size, structure, and possible biochemical applications [12, 13], that have been proven to be good carriers for organic polar molecules. These materials have good thermal stability and do not change on aging. Examples of these are zirconium phosphates. Taking advantage of the expandable interlayer distance. Cerium phosphates have been studied for a long time as ion exchangers, their structures remains unknown until recently [14-16].

Tetravalent metal phosphates have been previously prepared both in crystalline and amorphous forms [12]. They are usually obtained by the combination of tetravalent metal salts with compounds containing anions like phosphate, molybdate, arsenate, antimonate, tungstate etc. They have the general formula $M(IV) (HXO_4)_n H_2O$ where $M(IV) =$

Zr, Ti, Hf, Sn, Ce, Th and X = P, Mo, W, As, Sb etc. These compounds have structural hydroxyl groups, the H of the hydroxyl group (-OH) acts as the exchangeable sites [13].

Cerium(IV) phosphate compounds have been prepared and used for the separation of some radionuclides [17] from hazardous waste solutions.

Cerium phosphate, first reported in the early sixties in its crystalline and amorphous form, was used as a cation exchanger for a series of heavy metals [16, 18, 19].

Later it was reported as the first acid salt of the tetravalent metals with fibrous morphology [20-22] with unique properties, since flexible sheets may be simply obtained via filtration of its aqueous suspension [20].

In the present endeavor amorphous fibrous cerium phosphate was prepared, characterized, and used as a sorbent for the separation of uranyl ions UO_2^{+2} from its aqueous solution. Batch sorption method was used to investigate the effect of pH, contact time, sorbent mass, time and ionic strength on sorption activity.

2. Experimental Work

2.1. Chemicals

All chemicals are used without further purification. Orthophosphoric acid (REACHIM, 85%), H_2SO_4 (CaroErba 96%), NaOH (GPR, 96%), NaCl (Merck, 99.5%), KClO_3 (Riedel-de Haën, 99%), KNO_2 (Chemking, 97%), KCl (Merck, 99.5%), $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (MERCK, 98%), 8-Hydroxyquinoline (MERCK, 99%), $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AnalaR, 99.0%) alanine, arginine, HNO_3 (Riedel-de Haën, 65%), CHCl_3 (Scharlau, 99.0-99.6%).

2.2. Instruments Used for Characterization

Philips analytical PW1800 Diffractometer with Cu $\text{K}\alpha$ Radiation generated at voltage and current were 40 kV, 30 Ma respectively, FT-IR (Bruker TENSOR II) in the range (4000 to 400 cm^{-1}) equipped with MIRacle ATR device and processed with the computer software program OPUS7, DR3900 HACH laboratory Spectrophotometer.

2.3. Preparation of Starting Material

300ml of 0.05M Cerium sulfate solution (in 0.5M H_2SO_4 solution) were added dropwise to 300ml of 6M phosphoric acid at 80°C , the mixture was kept stirring for 4hrs. The resultant material was then dispersed in 3L hot distilled water and kept stirring for 1 hour at 60°C . The resultant product, in form of sheet, Figure (1.a), was washed thoroughly with distilled water up to pH~3, filtered and air dried.

Figure-1.a. Sheet of f-CeP



2.4. Inclusion of Alanine and Arginine

40ml of 0.1M amino acid were added to 0.5g cerium phosphate at room temperature $\sim 25^\circ\text{C}$, kept stirring for 72 hours. The product was filtered, washed with distilled water and air dried.

2.5. Ion Exchange Capacity

0.1g of cerium phosphate was immersed in 25ml of 0.1M NaCl solution with constant stirring for 24 hours, then the mixture was titrated with 0.1M NaOH solution.

2.6. Uptake of Uranium

A group of batch experiments were conducted under different parameters such as pH, contact time, initial ion concentration, and adsorbant mass. This is conducted by taking a known mass of f-CeP into a sealable glass vial with 40ml of several concentrations of Uranyl nitrate at variable conditions as stated previously and kept stirring for 24 hrs. The mixture is filtered. The uranium concentration is determined spectrophotometrically after extraction from the filtrate using 8-HQ in chloroform at $\lambda 460\text{nm}$.

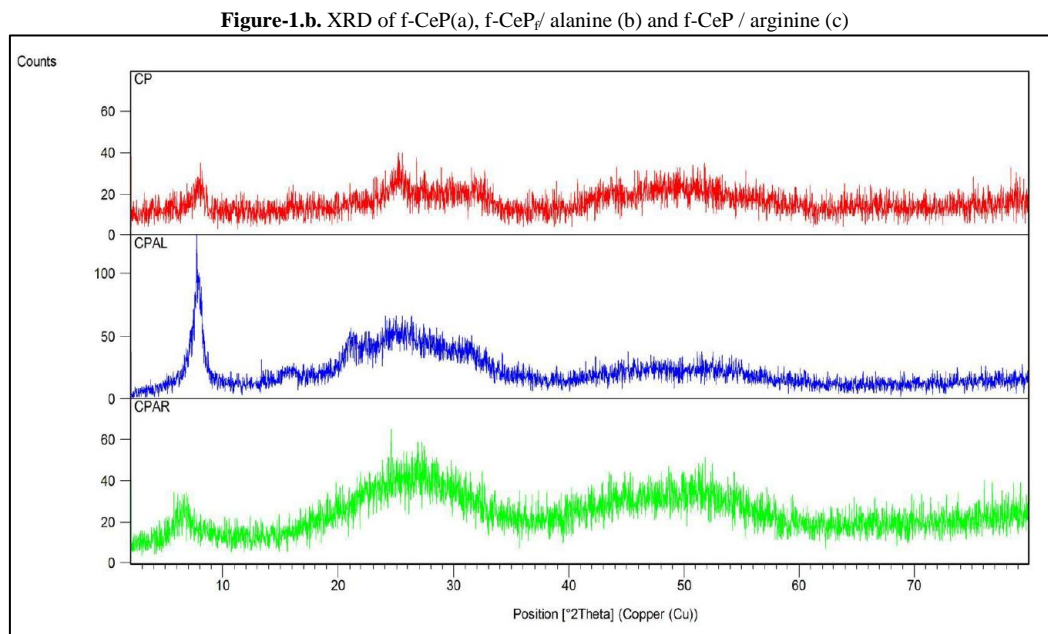
3. Results and Discussion

3.1. Characterisation of Fibrous Cerium Phosphate

Fibrous cerium phosphate was prepared and characterized using FTIR, XRD and SEM.

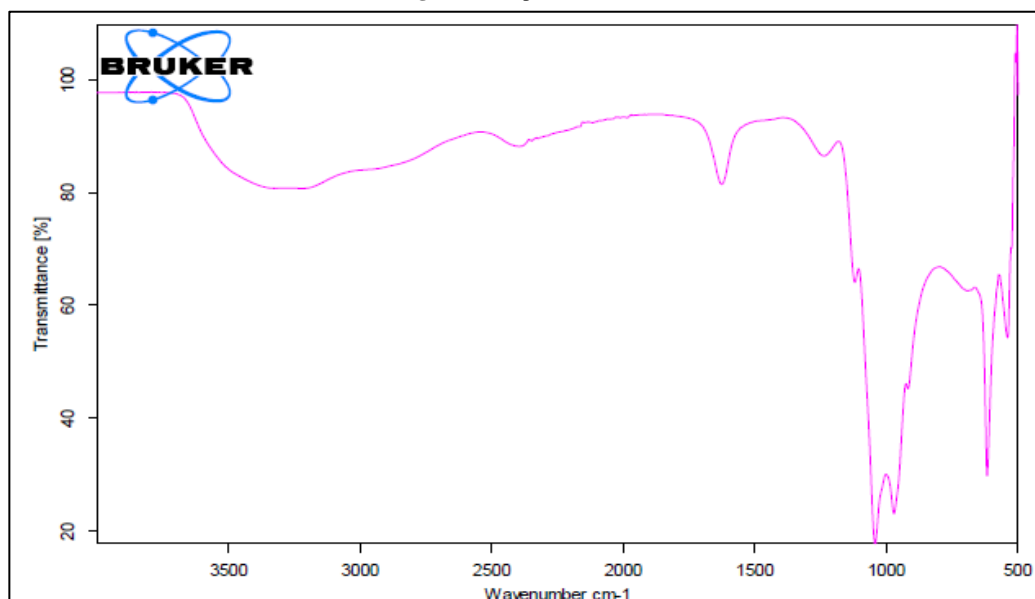
3.2. X-Ray Diffraction

The X-Ray diffractogram pattern of f-CeP and its alanine and arginine intercalates is shown in [figure 1b](#). XRD of pure f-CeP exhibited a diffraction maximum with basal spacing of $d_{001}=10.76 \text{ \AA}$ consistent with that reported previously [21] and also revealed an amorphous structure, while its amino acid intercalates showed a significant interplanar expansion to 11.33\AA and 14.19\AA for f-CeP_f /alanine and f-CeP / arginine respectively.



[Figure 2](#) shows FT-IR spectrum of fibrous cerium phosphate follow similar trend to that of the M(IV) phosphates. The broad band at 3328 cm^{-1} is assigned to interstitial water and OH groups. The bands at 2396 and 1625 cm^{-1} are due to P-OH asymmetry stretching of the phosphate group and occluded H-O-H bending modes respectively [21]. The sharp broad peak at the range $1237\text{-}917 \text{ cm}^{-1}$ is due to phosphate group vibrations (P-O symmetric and antisymmetric stretching). While the two bands in the $500\text{-}600 \text{ cm}^{-1}$ region are connected to Ce-O bond vibrations [9].

Fig-2. FT-IR spectrum of f-CeP



The FTIR spectrum for the amino acid intercalates ([Figure 3,4](#)) exhibited additional intense bands in the range $1650\text{-}1421 \text{ cm}^{-1}$ which are not observed for pure cerium phosphate corresponding to the protonated amines, H-N-H asymmetric and symmetric modes. The arginine intercalate shows a significant intensity loss of the band attributed to the P-O-H mode (2396 cm^{-1}), this phenomenon suggests a proton transfer, resulting from acid –base reaction.

Figure-3. FTIR spectrum for f-CeP / Arginine

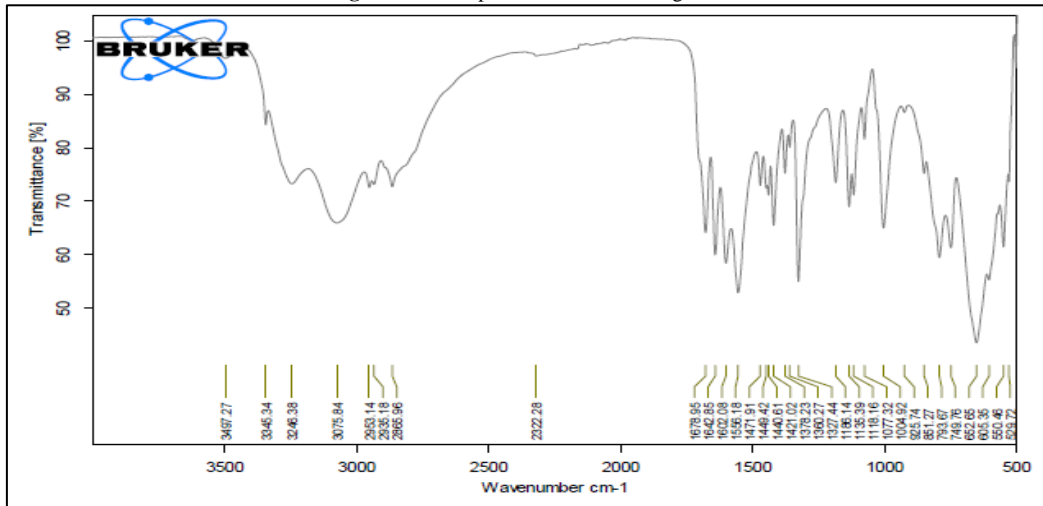
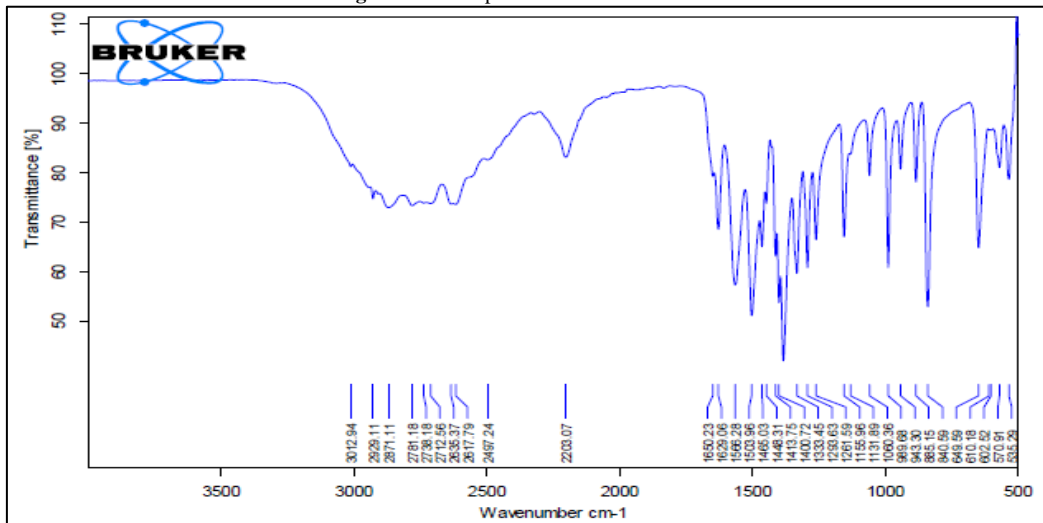


Figure-4. FTIR spectrum for f-CeP /Alanine

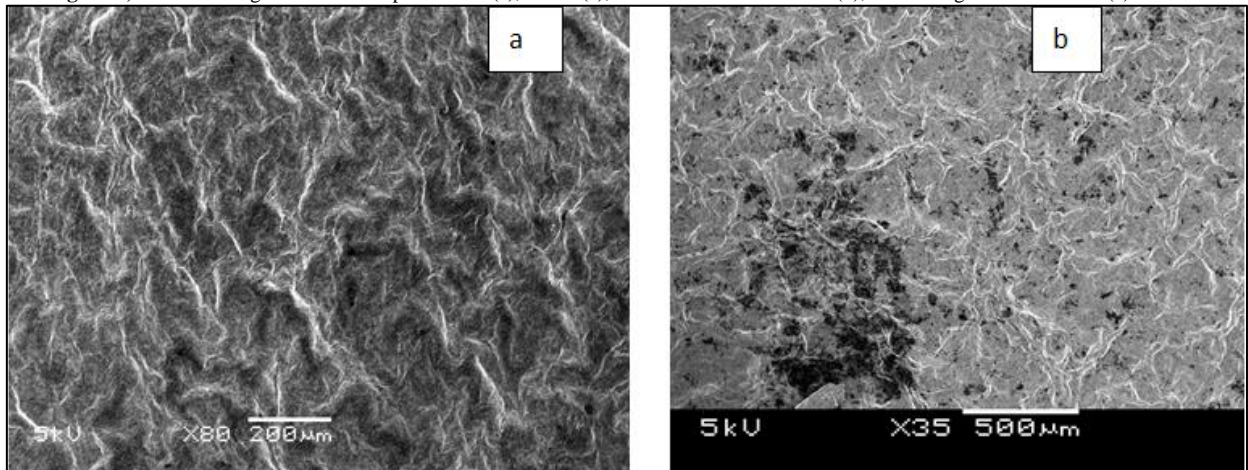


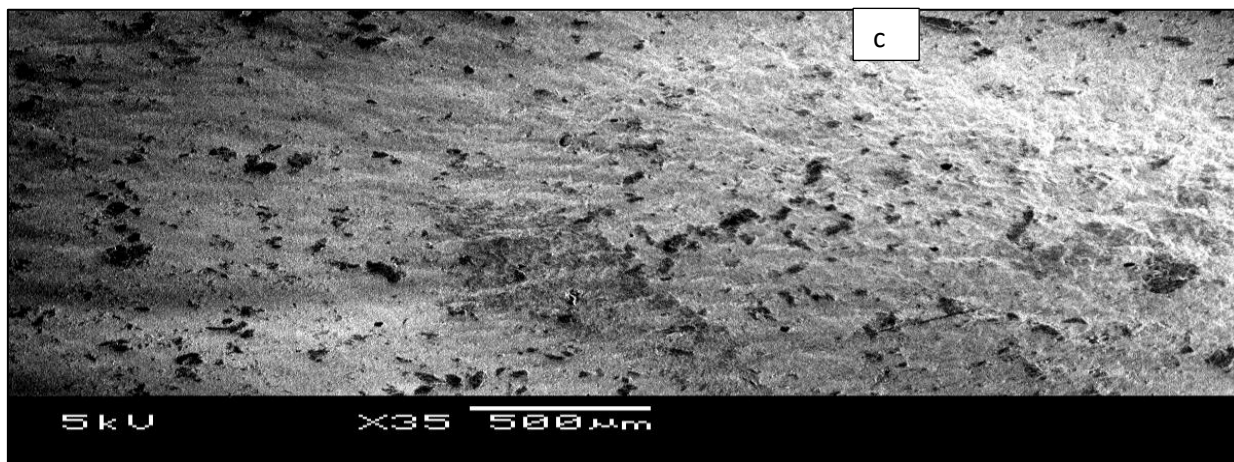
It is clear that the interactions between f-CeP and its host arginine have a predominant coulomb-type component whereas the neutral amino acid (alanine) intercalate does not show a similar behavior. Similar consequences are reported for cerium phosphate with n-alkylamines, suggesting the formation of strong bonds energetically favors insertion of the host [22].

3.3. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) images obtained for pure cerium phosphate and its amino acid intercalates are pictured in figure. Pure cerium phosphate shows fibre morphology. The alanine intercalate shows some modifications in the f-CeP morphology, nevertheless, the fiber structure remains showing the distribution of the inserted alanine. In contrast, the arginine intercalate resulted in drastic changes in its morphological features.

Figure-a,b,c. SEM images obtained for pure f-CeP (a), f-CeP (a), f-CeP / alanine intercalate(b), f-CeP / arginine intercalate (c)

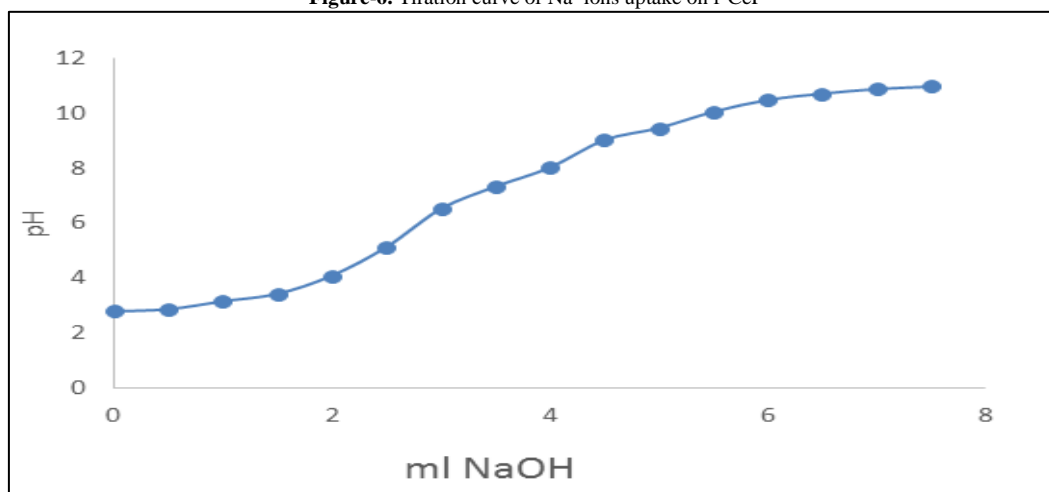




3.4. Exchange Capacity

The exchange capacity of fibrous cerium phosphate, f-CeP was determined by Na^+ titration. Figure 6 shows the titration curve of fibrous cerium phosphate. The exchange capacity found to be 4.25 Meq/g similar to that reported previously [17].

Figure-6. Titration curve of Na^+ ions uptake on f-CeP



3.5. Adsorption of Uranium

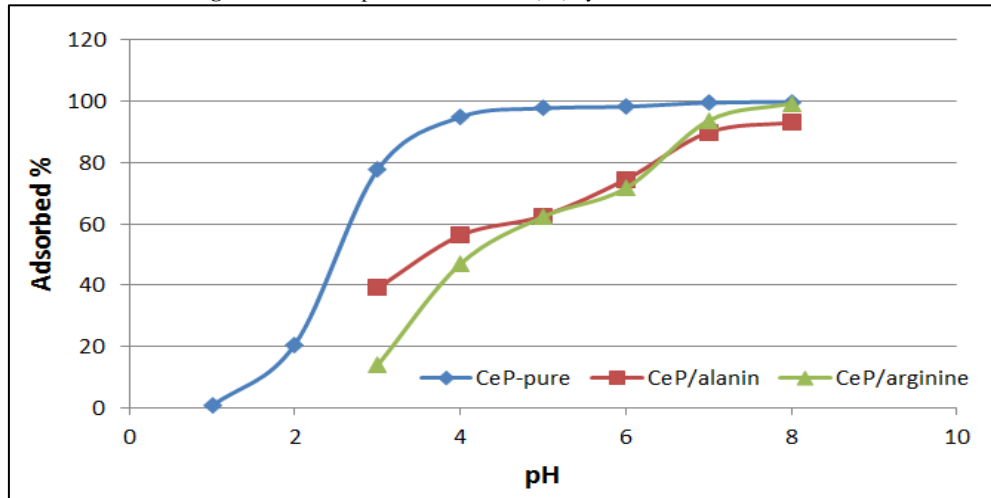
There are various parameters affecting the adsorption characteristics of uranyl ion onto fibrous cerium phosphate as described below:

3.6. Aqueous Phase pH

The pH of a solution influences the charge of the adsorbent, the degree of ionization and surface binding sites [20, 21].

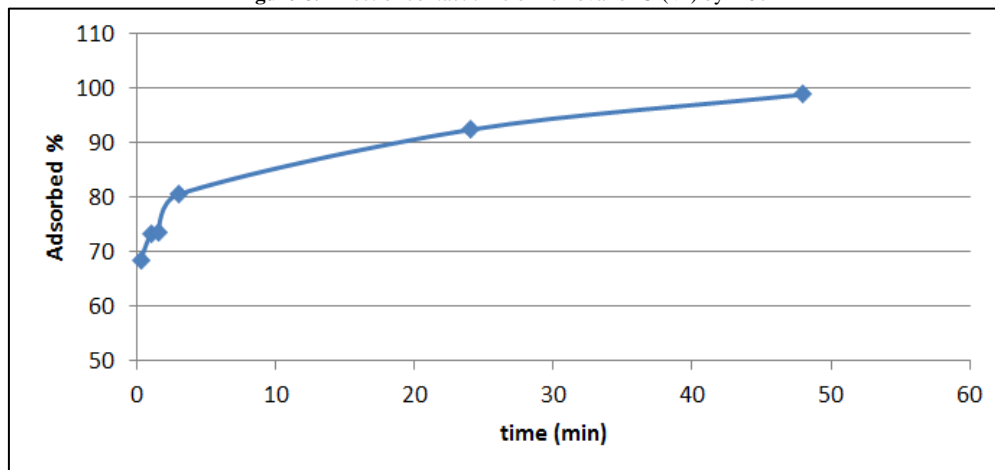
Sorption of uranium ion on fibrous cerium phosphate in aqueous solutions is investigated at pH values in the range of 1-8 (fig7). The results showed a dramatic increase in the adsorption percentage from ~1% at pH 1 to almost complete uptake at pH 4.5 above that it remained almost constant. This may be explained as follows: at low pH the active functional groups on the fibrous cerium phosphate (phosphate groups, hydroxyl groups) are protonised and the uranium at low pH exists as the uncoordinated form of uranyl ions (UO_2^{2+}) in the aqueous solution leading to strong repulsion forces between the aforementioned ions. As the pH increases these active sites on the fibrous cerium phosphate, are deprotonised and negatively charged, promoting the electrostatic affinity between the active sites on the f-CeP and the uranyl ions, thus leading to increased U(VI) removal. As the solution pH further increases above 5 formation of stable hydrolyzed U(VI) ions are formed as reported previously [22]

Whereas the amino acid intercalates showed a different behavior the adsorption of uranyl ion increased at higher pH. For f-CeP /arginine, the sorption percent showed an increase from 14% to almost 100% in the pH range from 3 to 8. While for Cep/alanine the sorption % increased from ~39% to ~93% in the same pH range as its arginine analogue. At $\text{pH} < 4$, pure f-CeP showed higher adsorption affinity to uranium ion than that for Alanine and Arginine intercalated forms.

Figure-7. Effect of pH on removal of U(VI) by f-CeP and its intercalates

3.7. Contact Time

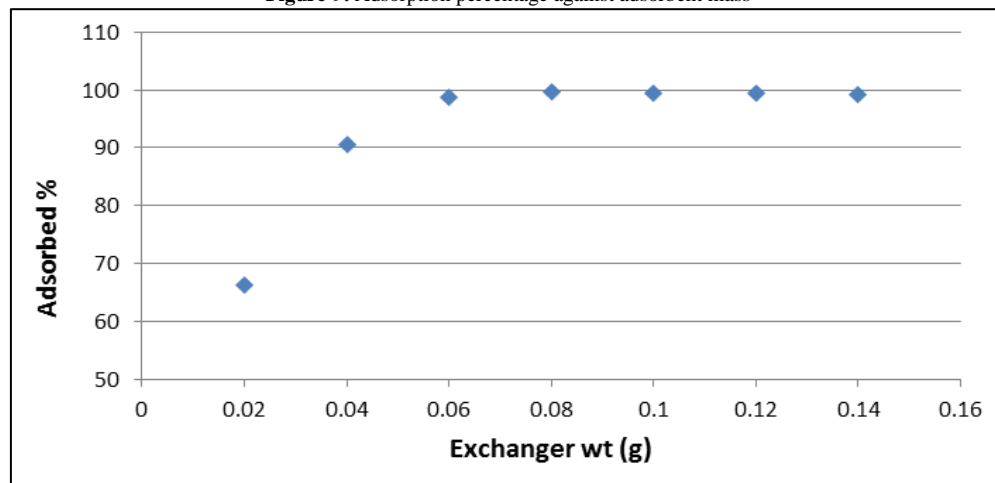
To investigate the time dependency on the uranyl ion uptake on cerium phosphate from aqueous solution (40ml, 60ppm, pH4) as a function of shaking time 15-2880 min was determined. The obtained results disclose that the adsorption process is relatively fast and a contact time of 3hrs was sufficient to attain equilibrium, above 3hrs there is no significant change in the adsorption process. However, the reaction was very fast during the initial stage and slowed down as the reaction approached equilibrium as it is clearly shown in [figure 8](#).

Figure-8. Effect of contact time on removal of U (VI) by f-CeP

3.8. Adsorbent Dose

To investigate the effect of adsorbent mass on the sorption of uranyl ion, varying adsorbent mass doses from 0.5g/L to 3.5g/L in increments of 0.5g/L were used at initial concentrations of 60 mg/L and pH4. The adsorbed % of the uranyl ion increased from 66 to 98.6 as the adsorbent mass increase as presented in [figure 9](#).

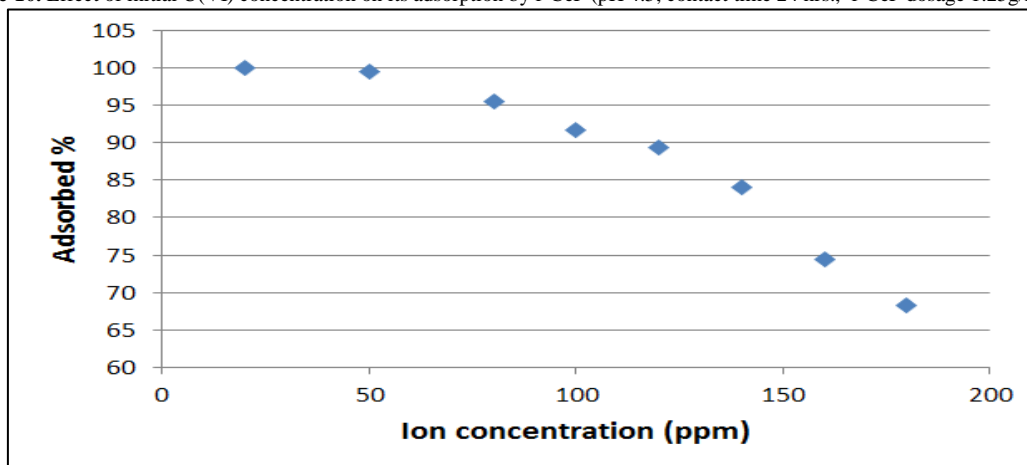
However, no appreciable adsorption was observed at a dose higher than 0.08g.

Figure-9. Adsorption percentage against adsorbent mass

3.9. Effect of Ion Concentration

In this section, adsorption experiments were carried out at the initial U(VI) concentration range of 20 mg/L to 180 mg/L, the sorption affinity is reduced from 100% to 80% [figure 10](#). This phenomenon is expected according to the congestion of uranium ion on small surface area where there are no enough negative sites to be occupied by positive uranium ions.

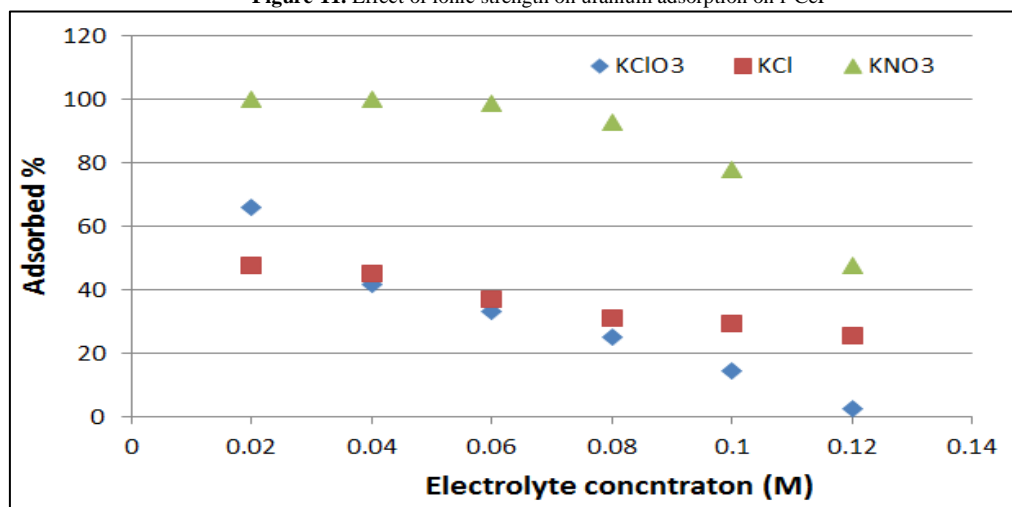
Figure-10. Effect of initial U(VI) concentration on its adsorption by f-CeP (pH 4.5, contact time 24 hrs., f-CeP dosage 1.25g/L)



3.10. Effect of Ionic Strength

In general, the presence of foreign ion can diminish the adsorption of uranium ion on fibrous cerium phosphate, as shown in [figure 11](#). At low concentration (0.04 - 0.08 M) the effect of $KClO_3$ and KCl is almost equal, and higher than that in the presence of KNO_3 . On the other hand, the damping rate along the concentration axes of $KClO_3$, KCl and KNO_3 is 97, 47 and 53% when the electrolyte concentration increased from 0.02 to 0.12M. Evidently, it can be seen from [figure 11](#) that ClO_3^- ion can severely affect the uptake of U(VI) onto f-CeP at concentration higher than 0.08M. Counter wise, Cl^- and NO_3^- ions caused a moderate effect [\[23\]](#).

Figure-11. Effect of ionic strength on uranium adsorption on f-CeP



Having considered the negative impact of ClO_3^- , Cl^- and NO_3^- ions on f-CeP exchanger performance, it is recommended that before using f-CeP for uranium sorption, a pertinent process for eliminating these ions from the solution should be achieved.

This effect can be attributed to the formation of various ionic complexes between uranium and those anions which prevent the sequestering uranium complex to the active sites of the exchanger [\[23\]](#).

4. Conclusion

In this work, fibrous cerium phosphate f-CeP and its alanine and arginine intercalates were successfully prepared and characterized using XRD, FTIR and SEM. The batch adsorption method was conducted to study uranyl ion adsorption under different conditions. The adsorption of U(VI) was investigated as a function of pH, contact time, adsorbent mass, initial concentration and ionic strength. The obtained results showed that pH, contact time, adsorbent mass, initial concentration and ionic strength have considerable effects on U(VI) removal. The optimum pH for the maximum removal of uranyl ion on pure fibrous cerium phosphate was pH 4.5, contact time 3hrs and adsorbent dosage of 2 g/L. Whereas the cerium phosphate alanine and arginine intercalates relatively showed less adsorption affinity than the pure cerium phosphate and slightly different behavior. We conclude that the most

promising adsorbent is the pure cerium phosphate which showed high adsorption affinity to U(VI) and can therefore be used in the treatment of uranium contaminated waste water which is a primary environmental concern.

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