Preparation of un-tanned pig skin waste-loaded metal ions adsorbents and their adsorption behaviors to fluoride, Phosphate and arsenate in aqueous solutions

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Abstract: Leather making process inevitably produce skin wastes due to the operation of splitting, trimming and shaving. The production of un-tanned skin waste is increasing since the wet-white technology is widely adopted. The un-tanned skin wastes are characterized by a high content of collagen protein. Considering the high activity of collagen protein towards many metal ions, it is feasible to obtain low-cost adsorbents by the reaction of un-tanned skin waste with different metal ions such as Fe(III) and Zr(IV), which can be applied for the effective removal of fluoride, phosphate and arsenate from aqueous solutions. In this study, two kinds of adsorbents, un-tanned pigskin waste-loaded Fe(III) or Zr(IV) (denoted as: UPW-Fe or UPW-Zr), were prepared and batch adsorption experiments were carried out to evaluate their adsorption behaviors, including the effect of pH, adsorption isothermal, as well as the adsorption kinetics. As a result, both UPW-Fe and UPW-Zr exhibited excellent adsorption capacities and fast adsorption rate to fluoride, phosphate and arsenate in aqueous solutions. These investigations provide a promising alternative utilization of un-tanned skin waste.

Keyword: Un-tanned skin waste; Metal ions; adsorbents; Adsorption; Fluoride; Phosphate; Arsenate

1 Introduction

In leather making process, skin and leather wastes are inevitably produced due to the operations of splitting, trimming and shaving [1]. About 1,500,000 metric tons of these kinds of tannery wastes are generated merely in China each year [2-4], which not only leads to environmental impact, but also produces huge waste of natural resource. It was estimated that about 25% and 35% of wet salted skins are changed into chrome-containing and un-tanned skin wastes in leather making processes, respectively [5-9]. Recently, the percentage of un-tanned skin waste is increasing significantly since the wet-white technique is widely adopted. It has been reported that un-tanned skin waste can be hydrolyzed by enzyme, acid and alkaline to obtain peptide and amino acid, which might be used as additives in foodstuff, medicine and cosmetic etc [6-9]. However, the utilization of the hydrolyzed products from these wastes is more and more limited in China and other countries due to their potential negative effect to domestic animals and human beings. Although un-tanned skin waste can be used as raw material for the production of regenerated leather, the market demand for regenerated leather is not large enough to consume the considerable amount of un-tanned skin waste. Therefore, it is significant to develop alternative utilization of un-tanned skin waste.

On the other hand, the effective removal of fluoride, phosphate and arsenate from aqueous solutions is still a great challenge of wastewater treatment. There are many methods have been used for the removal of these anions such as chemical precipitation, ion exchange, electrolysis, and adsorption. Among these methods, chemical precipitation and adsorption are two commonly used techniques. Although the method of precipitation is simple and economical, but the final concentrations of fluoride, phosphate and arsenate

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in solutions greatly depend on the solubility of the formed precipitation and precipitation reagent, and therefore often lead to supplementary difficulties of eliminating excess chemicals. Comparatively, adsorption seems to be the most suitable method for the removal of fluoride, phosphate and arsenate due to its significant advantages of availability, easy operation and efficiency [10-12]. However, the cost of the adsorbent is the key factor that should be considered in view of industrial application and thus adsorbents with low-cost are highly desired. Many attempts have been made to prepare low-cost adsorbents by using industrial by-products as the raw materials. It has been reported that blast furnace slag from steel industry [13], dewatered alum sludge from wastewater treatment plants [14] and fly ash from power station [15] have be successfully applied for the preparation of low-cost adsorbents.

The metal ions loaded on porous adsorbents or carrier materials have shown promising results for the adsorptive removal of fluoride, phosphate and arsenate. It has been reported that the adsorption capacity of fluoride on tartrazine modified carbon is 3-5 times higher than that of plain carbon [16]. It was also found that some metal ions, such as Fe(III) and Zr(IV), bearing materials exhibited a specific affinity for arsenic species [17-18]. As we know, un-tanned skin waste is characterized by very high content of collagen protein and exhibits specific affinity towards many metal ions such as Al(III), Zr(IV), Fe(III), according to leather making principles [19]. Therefore, it is also possible to prepare low-cost adsorbent using un-tanned skin waste as the raw material to react with metal ions such as Fe(III) and Zr(IV) and their high adsorption capacity to fluoride, phosphate and arsenate can be expected.

The main purpose of this work is to evaluate the feasibility of un-tanned skin waste used as raw material for the preparation of low-cost adsorbent. Herein, two kinds of adsorbents were prepared by the reaction of un-tanned pigskin wastes with $Fe_2(SO_4)_3$ or $Zr(SO_4)_2$, and their fundamental adsorption behaviors to fluoride, phosphate and arsenate from aqueous solution were investigated.

2. Materials and methods

2.1. Materials

The un-tanned pigskin wastes (UPW) were collected from a local tannery. $Fe_2(SO_4)_3$, $Zr(SO_4)_2$ and all other chemicals were analytical grade reagents. Na_3PO_4, NaF and As_2O_3 were used to prepare fluoride, phosphate and arsenate solutions. Diluted HNO_3 and NaOH solutions were used for adjusting the initial pH of solutions.

2.2. Preparation of adsorbents

The procedures for the preparation of the adsorbents are similar with the tanning process for leather making. Briefly, 15.0 g of UPW were fully washed with deionzied water, and then suspended in 400 mL of deionzied water. The pH of the suspension was adjusted to pH 1.70-2.00 by HCOOH and H_2SO_4 solutions. After being stirred at room temperature for 2 h, 0.1 mol of $Fe_2(SO_4)_3$ or $Zr(SO_4)_2$ was added and the reaction was undertaken with constant stirring at 30^oC for 6 h. Then, a proper amount of $NaHCO_3$ solution (15%, w/w) was gradually added within 2 h in order to increase the pH of the solution to 4.00-4.20, and the reaction was continued at 45^oC for another 4 h. When the reaction was completed, the product was collected by filtration, washed with distilled water, dried in vacuum at 50^oC for 12 h, and ground into particle of 0.5-1.0 mm. Then the UPW-loaded Fe(III) and UPW-loaded Zr(IV) adsorbents were obtained (denoted as UPW-Fe and UPW-Zr, respectively).

The concentration of Fe(III) or Zr(IV) in the residual solution after reaction was determined by means of Inductively Coupled Plasma-atomic Emission Spectroscopy (ICP-AES, Perkin-Elmer Optima 2100DV, German), and the content of metal ion loaded on UPW was determined by mass balance calculation. The

denaturation temperatures of UPW-Fe and UPW-Zr were determined by Differential Scanning Calorimetry (DSC, PC 200DSC, NETZSH Company, Germany). The specific areas of UPW-Fe and UPW-Zr were determined by Surface Area and Porosity Analyzer (TriStar 3000, Micromeritics, U. S.) and other physical properties of the adsorbents were tested by common methods.

2.3. Effect of initial pH on the adsorption of fluoride, phosphate and arsenate on UPW-loaded adsorbent.

The effect of initial pH on the adsorption of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr were conducted according to the experimental conditions summarized in Table 1. The adsorption capacities of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr were determined by mass balance calculation.

Tab.1 Experimental conditions for the study of pH effect on the adsorption of UPW-Fe and UPW-Zr to fluoride, phosphate and arsenate.

Parameters	UPW-Fe			UPW-Zr		
	Fluoride	Phosphate	Arsenate	Fluoride	Phosphate	Arsenate
pH range	2-12	2-12	2-12	2-12	2-12	2-12
Dose (g/mL)	0.1/100	0.1/100	0.05/100	0.1/100	0.1/100	0.05/100
Initail conc. (mmol/L)	2.0	1.0	1.0	2.0	1.0	1.0
Adsorption temp. (^{o}C)	30	30	30	30	30	30
Adsorption time (h)	24	24	24	24	24	24
Measurement	FSE[a]	ICP-AES[b]	ICP-AES	FSE	ICP-AES	ICP-AES

[a]: FSE=fluoride selective electrode [b]: ICP-AES=Inductively Coupled Plasma-atomic Emission Spectroscopy.

2.3. Adsorption isothermal studies.

Isotherm studies of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr were conducted according to the experimental conditions summarized in Table 2.

Tab. 2 Experimental conditions for the adsorption isotherm studies of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr.

Parameters	UPW-Fe			UPW-Zr		
	Fluoride	Phosphate	Arsenate	Fluoride	Phosphate	Arsenate
pH	6.0	6.0	6.0	6.0	6.0	6.0
Dose (g/mL)	0.1/100	0.1/100	0.05/100	0.1/100	0.1/100	0.05/100
Initail conc. (mmol/L)	1.0-6.0	0.2-2.0	0.1-0.7	1.0-6.0	0.2-2.0	0.1-0.7
Adsorption temp. (^{o}C)	30	30	30	30	30	30
Adsorption time (h)	24	24	24	24	24	24
Measurement	FSE[a]	ICP-AES[b]	ICP-AES	FSE	ICP-AES	ICP-AES

[a]: FSE=fluoride selective electrode [b]: ICP-AES=Inductively Coupled Plasma-atomic Emission Spectroscopy.

2.4. Adsorption kinetics studies.

Adsorption kinetics studies of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr were conducted according to the experimental conditions summarized in Table 3. During adsorption process, the concentration of fluoride, phosphate or arsenate in filtrate was analyzed at a regular interval.

Tab. 3 Experimental conditions for the adsorption kinetics studies of fluoride, phosphate and arsenate on UPW-Fe and UPW-Zr.

Parameters	UPW-Fe			UPW-Zr		
	Fluoride	Phosphate	Arsenate	Fluoride	Phosphate	Arsenate
pH	6.0	6.0	6.0	6.0	6.0	6.0
Dose (g/mL)	0.1/100	0.1/100	0.05/100	0.1/100	0.1/100	0.05/100
Adsorption temp. (^{o}C)	2.0	1.0	1.0	2.0	1.0	1.0
Adsorption time (h)	30	30	30	30	30	30
Measurement	FSE[a]	ICP-AES[b]	ICP-AES	FSE	ICP-AES	ICP-AES

[a]: FSE=fluoride selective electrode [b]: ICP-AES=Inductively Coupled Plasma-atomic Emission Spectroscopy.

2.5. Column adsorption studies.

Considering the fact that UPW-Zr has higher adsorption capacity than UPW-Fe, three UPW-Zr columns were adopted in the following column studies and the corresponding experimental conditions were presented in Table 4.

Tab. 4 Experimental conditions for the studies of column adsorption.

	Fluoride/UPW-Zr*	Phosphate/UPW-Zr*	Arsenate/UPW-Zr*
Column height (cm)	30.0	15.0	15.0
Column diameter (cm)	1.1	1.1	1.1
Flow rate (mL/h)	51.4	40.0	4.0.0
Adsorbent dose (g)	5.0	2.5	2.5
Initail pH of inlet flow	6.0	6.0	6.0
Initail conc. of adsorbate (mmol/L)	6.0	1.0	4.0

*****: The effluent was collected by an automatic collector and the concentration of adsorbate in the effluent was analyzed.

3. Results and discussion

3.1. Characterization of adsorbents

The physical properties of UPW-Zr and UPW-Fe were summarized in Table 5. Due to the tanning effects of $Fe_2(SO_4)_3$ or $Zr(SO_4)_2$, the thermal stabilities of UPW-Fe and UPW-Al are remarkably improved. The denaturation temperature UPW-Zr and UPW-Fe are high up to 83-88^{o}C and 80-83^{o}C, respectively. Thus, it can be reasoned that UPW-Zr and UPW-Fe should be stable during the practical application

Tab. 5 Physical properties of UPW-Zr and UPW-Fe.

Parameters	UPW-Zr	UPW-Fe
Metal ion content (mmol/g)	5.32	6.02
Specific area (m^2/g)	5.0-6.0	4.5-5.5
Denaturation temperature (^oC)	83-88	81-83
Bulk density (in dry state) (g/cm^3)	0.14-0.16	0.16-0.17
Water absorptivity (g/g)	3.20-3.38	1.60-1.90
Isoelectric point	11.00	10.50

The surface morphologies of UPW-Zr and UPW-Fe were analyzed by scanning electronic microscopy (SEM). As shown in Figure 1a, Zr(IV) was uniformly loaded on collagen fibers without stack of Zr(IV) salt precipitation, and similar trend can be observed in Figure 1b (UPW-Fe). These facts indicated that Zr(IV) and Fe(III) were well dispersed on collagen fibers, which may favor the adsorption of phosphate, fluoride and arsenate on UPW-Fe and UPW-Zr. It has been reported that the reaction between Fe(III)/Zr(IV) and collagen mainly takes place through the chelating of Fe(III)/Zr(IV) with -COOH and-NH_2 groups on the side chains of collagen peptide, and as a result the chemical stability of the collagen fiber will be improved [20].

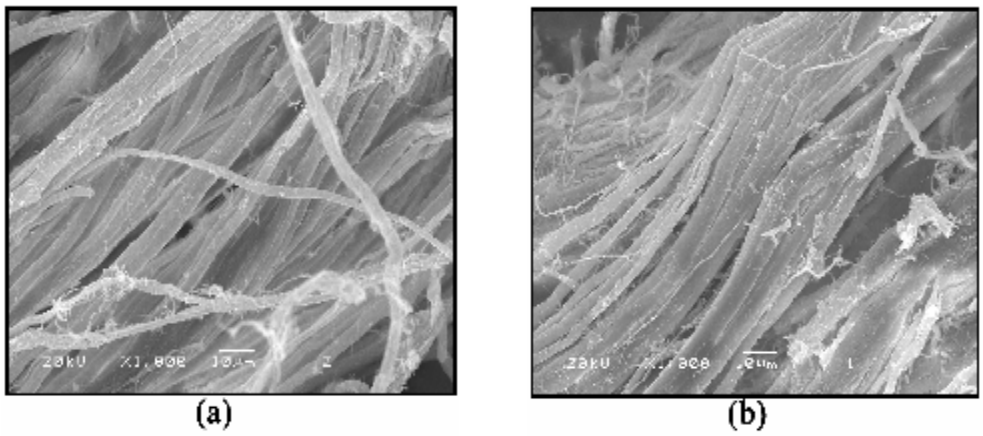

Fig. 1 SEM images of UPW-Zr (a) and UPW-Fe (b).

3.2. Effect of initial pH on the adsorption of phosphate, fluoride and arsenate.

As shown in Fig. 2a, UPW-Zr exhibited adsorption ability to fluoride, phosphate and arsenate in a wide pH range. The optimal pH range for the adsorption of fluoride on UPW-Zr is 3.0-8.0, while those for the adsorption of phosphate and arsenate on UPW- Zr are 2.0-9.0 and 2.0-7.0, respectively. On the other hand, the adsorption capacities of fluoride, phosphate and arsenate on UPW-Zr are remarkable. The adsorption capacities of fluoride on UPW-Zr are higher than 1.30 mmol/g in the pH range of 3.0-8.0, and those of phosphate and arsenate are higher than 0.7 mmol/g in the pH range of 2.0-9.0 and 0.6 mmol/g in the pH range of 2.0-7.0, respectively.

With regard to the adsorption of UPW-Fe to fluoride, phosphate and arsenate, similar adsorption curves can be observed in Figure 2b. Compared with UPW-Zr, UPW-Fe has relatively lower adsorption capacities, but still much higher than those of commonly used adsorbents such as actived carbon [21], metal oxides [22] and resins [23].

According to literature, the effect of initial pH on the adsorption of UPW-Zr (or UPW-Fe) to fluoride,

phosphate and arsenate can be attributed to the influence of pH to the surface charges of UPW-Zr (or UPW-Fe) and the existing species of those anions. The surface of UPW-Zr and UPW-Fe is characterized by positive charges when the pH of solutions is lower than the isoelectric point of UPW-Zr (11.0) and UPW-Fe(10.5), which favors the adsorption of anionic fluoride, phosphate and arsenate species. Thus, the optimal adsorption capacities of UPW-Zr/UPW-Fe to fluoride, phosphate and arsenate are obtained at lower pH range (below isoelectric point of UPW-Zr and UPW-Fe), and relatively lower adsorption capacities were obtained at higher pH range. On the other hand, the different chemical species of fluoride, phosphate and arsenate in solutions also affected their adsorption capacity. Thermodynamic calculations revealed that the dominated chemical species of phosphate in aqueous solutions was $H_2PO_4^-$ in the pH range of 2.0-6.0. Therefore, $H_2PO_4^-$ is favorable for the adsorption of phosphate on UPW-Zr and UPW-Fe. Moreover, the higher adsorption capacity of UPW-Zr over UPW-Fe can be explained by the higher chelating ability of Zr(IV), imparting UPW-Zr higher affinity to anionic fluoride, phosphate and arsenate. Considering that UPW used in this study is solid waste generated by leather industry, UPW-Zr and UPW-Fe could be classified as low-cost and high effective adsorbents for the remedy of wastewater contaminated by fluoride, phosphate or arsenate.

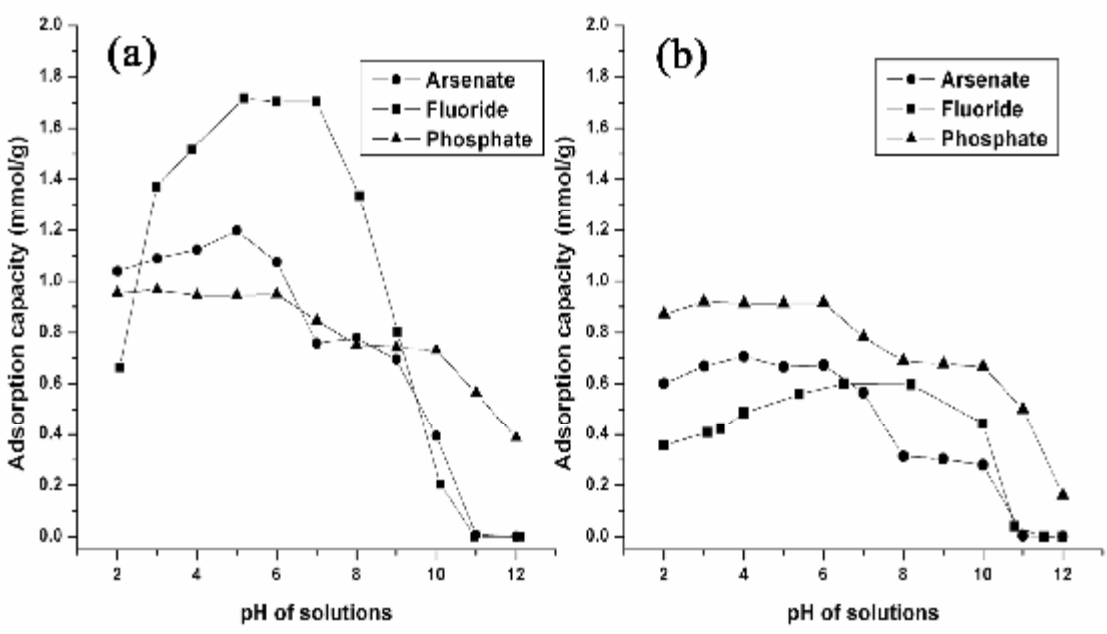

Fig.2 Effect of initial pH on the adsorption of phosphate, fluoride and arsenate on UPW-Zr (a) and UPW-Fe (b).

3.3. Adsorption isothermal studies.

Fig. 3 shows the adsorption isotherms of phosphate, fluoride and arsenate on UPW-Fe and UPW-Zr at 30^{o}C. Generally, UPW-Zr showed much higher adsorption capacities than UPW-Fe for the adsorption of phosphate, fluoride and arsenate. The maximum adsorption capacity of fluoride, phosphate and arsenate on UPW-Zr are 2.96, 1.10 and 1.22 mmol/g, respectively, while those of fluoride, phosphate and arsenate on UPW-Fe are 0.72, 1.02 and 1.00 mol/g, respectively. Compared with other commonly used adsorbents, UPW-Zr and UPW-Fe showed extremely high adsorption capacities, implying their great potential in practical application.

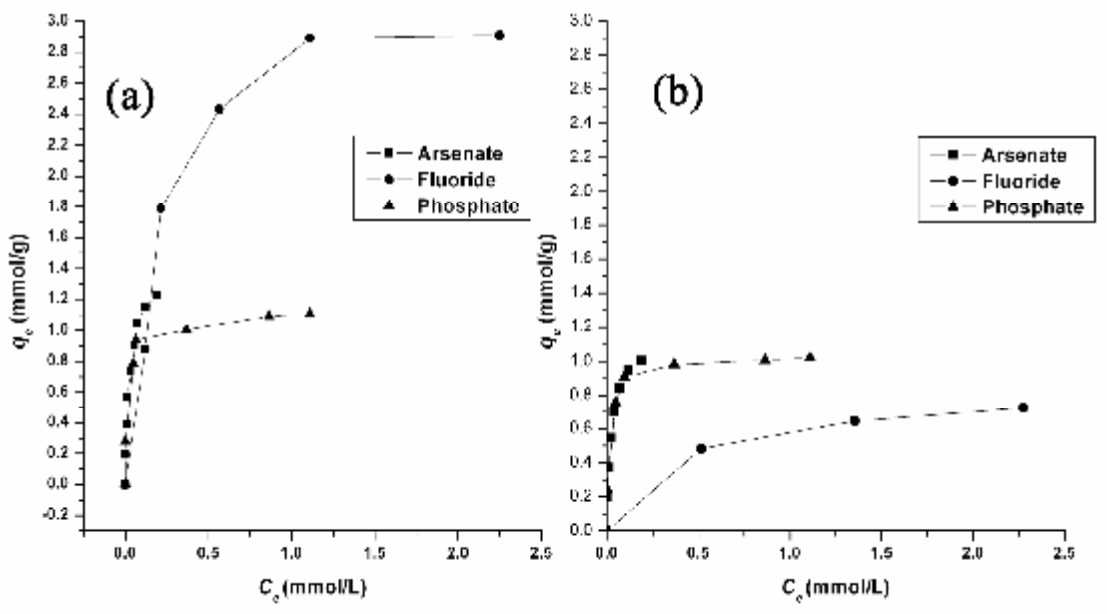

Fig. 3 Adsorption isotherms of fluoride, phosphate and arsenate on UPW-Zr (a) and UPW-Fe (b).

The adsorption isothermal data were further analyzed by Langmuir equation [24] (eq 1), which can be expressed as following:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (1)$$

where C_e is the equilibrium concentration (mmol/L), q_e is the equilibrium adsorption capacity (mmol/g), $q_{\max}$ and b are the maximum adsorption capacity (mmol/g) and Langmuir constants relating to the strength of adsorption, respectively. It was found that the Langmuir equation gave satisfactory fitting to the adsorption isotherms, and the parameters of the Langmuir fitting are summarized in Table 6. It can be seen that all the correlation constant (R^2) are higher than 0.96, and the calculated maximum adsorption capacities are close to those determined from experiments. These facts suggest that the chemical adsorption mechanism may be involved in the adsorption of fluoride, arsenate and phosphate on the UPW-Zr and UPW-Fe.

Tab. 6 Parameters of Langmuir fitting.

	UPW-Zr				UPW-Fe			
	$q_{e,exp}$	q_{max}	b	R^2	$q_{e,exp}$	q_{max}	b	R^2
Fluoride	2.96	3.03	4.27	0.98	0.72	0.82	2.87	0.99
Phosphate	1.10	1.02	227.7	0.98	1.02	0.97	207.4	0.96
Arsenate	1.22	1.32	48.26	0.97	1.00	1.02	39.6	0.99

$q_{e,exp}$(mmol/g)= $q_{e,experiments}$(mmol/g), q_{max}(mmol/g)= $q_{maximum}$(mmol/g)

3.4. Adsorption kinetics studies.

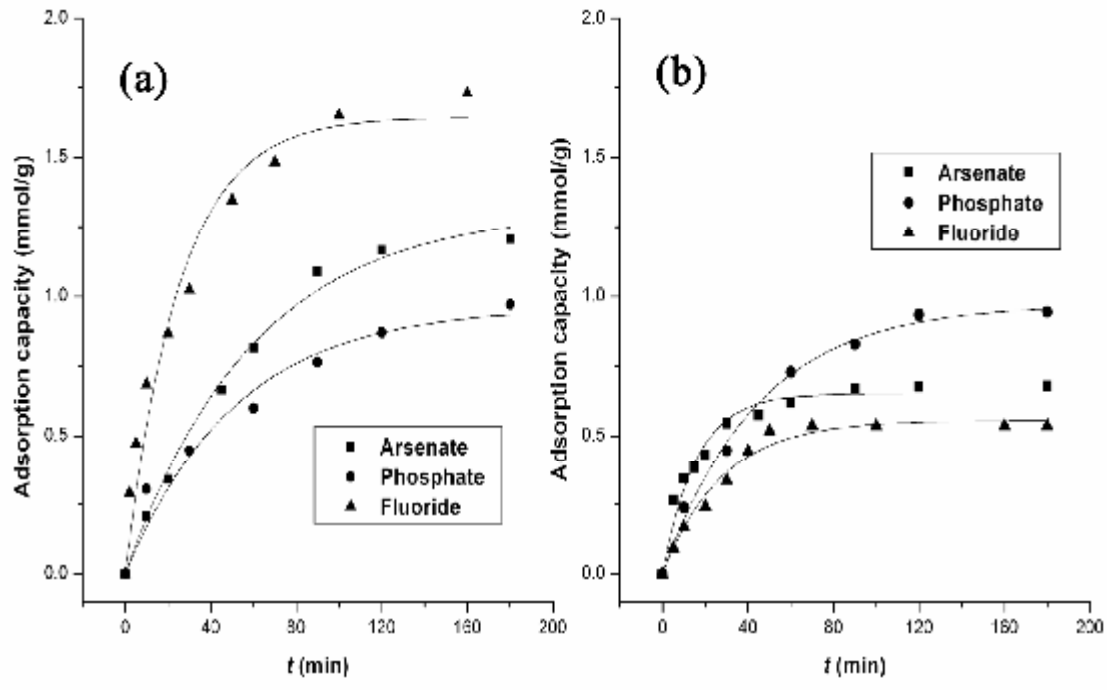

Fig.4 Adsorption kinetics of fluoride, phosphate and arsenate adsorbed on UPW-Zr (a) and UPW-Fe (b).

The adsorption kinetic data are illustrated in Figure 4. It can be observed that all the UPW-loaded adsorbents showed fast adsorption rates to the adsorbates. For example, the adsorption of phosphate on UPW-Zr can reach its adsorption equilibrium within 3 h. The adsorption kinetic data were further analyzed using pseudo-first-order rate (eq 2), pseudo-second-order rate (eq 3) and intraparticle diffusion models (eq 4), which are expressed as following equations [25,26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_{e,cal}} tR^2 \qquad (3)$$

$$q_t = k_3 t^{0.5} \qquad (4)$$

where q_e and q_t (mmol/g) are the amount of arsenate (or fluoride and phosphate) adsorbed on UPW-Zr (or UPW-Fe) at equilibrium and time t (min), and k_1 (min^{-1}), k_2 (mmol/g/min) and k_3 ($mmol/g/min^{0.5}$) are the rate constants of models 1, 2 and 3, respectively. It was found that pseudo-first-order model gives a satisfied fitting to the experimental data with correlation coefficient (R^2) higher than 0.96, and the calculated equilibrium adsorption capacities are very close to those the determined by adsorption experiments, as shown in Table 7. All these facts indicated that the adsorption of fluoride, phosphate and arsenate on UPW-Zr/UPW-Fe should belong to rate-controlling process, and the inner-diffusion resistance of mass transfer can be neglected.

Tab. 7 Pseudo-first-order model parameters for the adsorption of fluoride, phosphate and arsenate on UPW-Zr and UPW-Fe.

	UPW-Zr				UPW-Fe			
	$q_{e,\exp}$	$q_{e,cal}$	$k_2 \times 10^3$	R^2	$q_{e,\exp}$	$q_{e,cal}$	$k_2 \times 10^3$	R^2
Fluoride	1.72	1.75	39.5	0.96	0.54	0.56	36.2	0.98
Phosphate	0.97	0.98	19.4	0.99	0.93	0.94	23.9	0.96
Arsenate	1.218	1.31	16.7	0.99	0.67	0.65	54.4	0.98

$q_{e,exp}$(mmol/g)= $q_{e,experiments}$(mmol/g), q_{max}(mmol/g)= $q_{maximum}$(mmol/g)

3.5. Column adsorption studies.

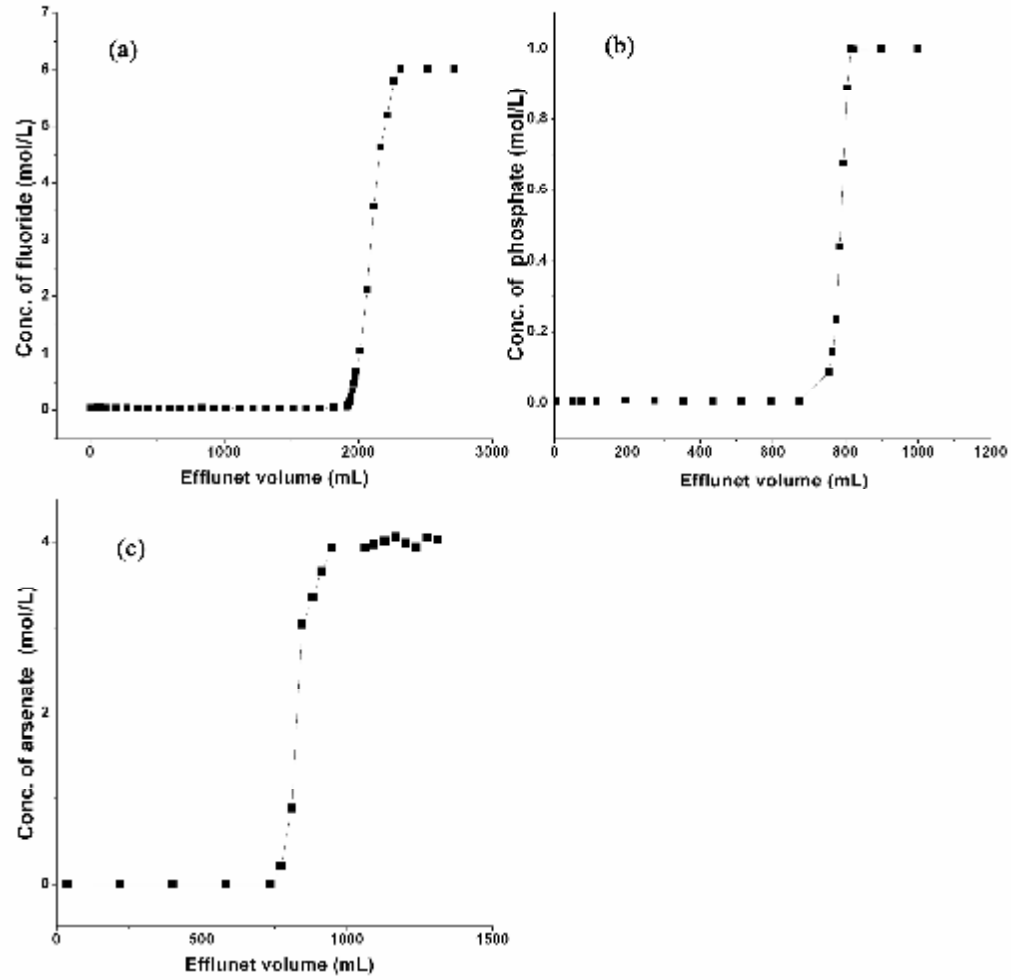

Fig .5 Breakthrough curve of fluoride (a), phosphate (b) and arsenate (c) on UPW-Zr column.

As shown in Fig. 5, the breakthrough points of these three column are located at 1910 mL (column a), 755mL (column b) and 772 mL (column c), and the corresponding adsorption capacities are 2.28, 0.56 and 0.31 mmol/g, respectively. In addition, all the breakthrough curves of fluoride, phosphate and arsenate are very sharp after the breakthrough point. All these facts suggested that the UPW-Zr columns have high availabilities. The obtained adsorption capacities in columns are lower than those of obtained in batch experiments, which can be attributed to the inadequate contact time in column adsorption. Large

adsorption capacities and high efficiency can be expected by adjusting the column parameters, such as flow rate of inlet solution and bed height of the column.

4 Conclusion

This paper presented a potential alternative utilization of un-skin pigskin split wastes (UPW) by using these solid wastes as raw materials to prepare low-cost adsorbents. Two kinds of adsorbent, UPW-Zr and UPW-Fe, were prepared and their fundamental adsorption behaviors to arsenate, fluoride and phosphate were investigated. The excellent adsorption results obtained from batch and column experiments confirmed the feasibility of UPW-Zr and UPW-Fe, which can be used as low-cost and effective adsorbents for the removal of fluoride, phosphate and arsenate from waste water. Consequently, we firmly believed that the proposed method could bring significant environmental and economic benefits.

Acknowledgements

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