ADSORPTIVE REMOVAL OF AS(V) FROM AQUEOUS SOLUTION BY ZR(IV)-LOADED SKIN SHAVINGS

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ABSTRACT

Wet-white shavings are one of the main solid wastes produced in the leather industry. In this paper, Zirconium (IV)-loaded adsorbent (ZrLA) was prepared by using wet-white shavings as the supporting matrix. The fundamental adsorption behaviors of this new adsorbent for arsenic [As(V)] were investigated. It was found that the adsorption capacity of ZrLA for As(V) in aqueous solution was 60.90 $mg \cdot g^{-1}$, when the initial concentration of As(V) was 75.0 $mg \cdot L^{-1}$ at pH 4.0 and the dosage of ZrLA was 1.0 $g \cdot L^{-1}$. The initial pH of As(V) solution significantly affected adsorption capacity of ZrLA to As(V) and the optimal pH for adsorption was in the range of 3.0-6.0. The adsorption isotherms of As(V) could be well fitted by the Langmuir equation, and the maximum adsorption capacities calculated by the Langmuir equation were close to those determined by experiments. The adsorption kinetics of As(V) on ZrLA could be satisfactorily described by the pseudo-second-order rate model. The adsorption capacity was increased with the increase of the zirconium content in ZrLA, and the highest adsorption capacity was obtained when zirconium content of ZrLA was 90-110 $mg \cdot g^{-1}$.

RESUMEN

Rebajaduras del “wet-white” es uno de los principales desechos sólidos producidos por la industria del cuero. En esta obra, un adsorbente (ZrLa) fue preparado utilizando las rebajaduras cargadas de Circonio (IV), como matriz portante. El comportamiento fundamental adsorbente de este nuevo material hacia el arsénico [As (V)] fue investigado. Se encontró que la capacidad de adsorción de ZrLA del As (V) en soluciones acuosas fue 60,90 $mg \cdot g^{-1}$, cuando la concentración inicial del As (V) fue 75,0 $mg \cdot L^{-1}$ a pH 4,0 y la dosis del ZrLA fue 1,0 $g \cdot L^{-1}$. El pH inicial de la solución de As (V) significantemente afecta la capacidad de adsorción de ZrLA hacia As (V) y el pH óptimo para adsorción se encuentra entre el rango de 3,0-6,0. La adsorción isotérmica de As (V) encaja bien en la ecuación de Langmuir, y la máxima capacidad de adsorción calculada por la ecuación de Langmuir coincidió con los valores determinados experimentalmente. La cinética de la adsorción de As (V) sobre ZrLa podría ser satisfactoriamente describible por un modelo de pseudo segundo orden. La capacidad de adsorción aumentó con el incremento del contenido de circonio en ZrLA, y la máxima capacidad de adsorción se obtuvo con un contenido de circonio en ZrLa de 90-110 $mg \cdot g^{-1}$.

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INTRODUCTION

Leather manufacture inevitably produces a huge amount of solid wastes due to the operations of splitting, trimming and shaving. Usually, the processing of one metric ton of wet salted hide only yields 200 kg of leather, together with about 250 kg of tanned waste and 350 kg of un-tanned waste[1]. These wastes are traditionally landfilled or burned, which might impose problems on environment. Considering their high collagen content, many approaches have been developed to reuse these wastes in recent years. It has been found that chrome tanned waste can be reused as insulating and building materials, as well as the raw material of artificial leather.[2, 3] Un-tanned waste is easy to be hydrolyzed. So it has been used for manufacturing glue and gelatin,[4] producing auxiliary tanning agent of leather making,[5] and preparing additives of fodder, food and cosmetics.[4] However, the quantity of the solid wastes utilized by these approaches is limited. Meanwhile, the use of these hydrolyzed products as additives of fodder, food and cosmetic has been forbidden in some countries, due to the potentially negative effects on domestic animals and human beings. Hence, it is necessary to explore alternative utilizations of these wastes.

On the other hand, the contaminations of inorganic anions, such as arsenic, fluoride and phosphate, are common environmental problems. Arsenic and its compounds are commonly used reagents in smelting, petroleum-refining, pesticide, herbicide, glass, and ceramic manufacturing industries.[6] As a result, huge amount of arsenic containing wastewaters are discharged from these industries each year. It has been reported that the arsenic emissions reached 453.20 tons from industrial wastewater in China in 2005.[7] In addition, millions of people are exposed to naturally occurring As-contaminated groundwater, which they use as their only source of drinking water in many countries,[8] such as Bangladesh, India, Vietnam, China and Chile.[9-12] Epidemiological investigation indicated that the toxicity of arsenic to human health is so serious that it causes various diseases ranging from skin lesions to cancer of brain, liver, kidney and stomach.[13, 14] Due to its high toxicity, WHO and EPA have revised the guideline for arsenic content in drinking water to 10 $\mu g \cdot L^{-1}$.[15, 16] Therefore, the removal of hazardous arsenic from water is essentially important in the view of environmental protection and human health.

It has been proved that adsorption is one of the most efficient methods for treating wastewater containing hazardous chemicals in low concentration.[17] Many investigations have indicated that Zr(IV), Fe(III) and some rare earth metals loaded adsorbents exhibit specific affinity to all of arsenate, fluoride and phosphate ions.[18] It has been testified that many adsorbents loaded with these metals are effective in removal of arsenic from water. For example, the content of As(V) and As(III) could be reduced to below 10 $\mu g \cdot L^{-1}$ by using Fe(III) loaded activated carbon when the initial concentration of arsenic was 50 $\mu g \cdot L^{-1}$.[19] Alumina impregnated silica presented higher adsorption capacity to As(V) than that of activated alumina.[20] The adsorption capacities of Zr(IV) and Fe(III) loaded chelating resins to As(V) were 49.15 $mg \cdot g^{-1}$ and 55.44 $mg \cdot g^{-1}$, respectively.[21, 22] Although many adsorbents for removing arsenic from aqueous solution have been prepared, it is still an attractive challenge to develop more effective and low cost adsorbents for this purpose.

The main component of un-tanned skin wastes in tannery is collagen fiber which has abundant functional groups (–COOH, $-NH_2$ and –OH) along the side chain of collagen molecule. According to the principle of leather manufacturing, these functional groups are capable of chemically reacting with many metal ions, such as Cr(III), Zr(IV), Fe(III), and so on.[23] Therefore, it can be inferred that the low cost Zr(IV) or Fe(III) loaded adsorbents can be prepared by using the un-tanned wastes as supporting matrix. In deed, our previous work indicated that Zr(IV)-loaded collagen fiber (prepared by using hide powder) exhibits excellent performance in adsorption of phosphate from aqueous solution.[24] Both phosphorus and arsenic belong to group 5B elements. Thus, their ionic species and chemical behaviors in water should be quite similar. In fact, the acid dissociation constants of phosphoric acid and arsenic acid are mutually very close.[25] Hence, the preparation of new adsorbents for adsorption of arsenic can be expected by loading Zr(IV) or Fe(III) onto un-tanned wastes.

In Chinese tanneries, it is popular that the pelts are first pre-treated by using Na_2SO_4, so that splitting and shaving operations can be carried out before tanning. This technique can save tanning agents and reduce chrome containing wastes. The shavings from shaving operation of the pre-treated pelt are called wet-white shavings. It has been estimated that approximately 0.3 million tons of wet-white shavings are produced each year in China,[26, 27] while the emission of wastewaters which contain arsenate, fluoride, phosphate is about 2.5 billion m^3 each year only in China (account for 5% of total of 50 billion m^3 wastewater each year.)[28] Supposing the average concentration of arsenate, fluoride, phosphate in wastewater is 30 $mg \cdot L^{-1}$, and adsorption capacity of Zr(IV)-loaded wet-white shavings is 60 $mg \cdot g^{-1}$ and it can be repeatedly used 5 times, it can be calculated that about 0.25 million tons of wet-white shavings, 80% of the wet-white wastes in tanneries, would be theoretically consumed.

In this study, Zr(IV) loaded adsorbent (ZrLA) was prepared by using pigskin wet-white shavings as supporting material, and its fundamental adsorption performances to As(V) were investigated.

EXPERIMENTAL METHODS

Materials

Pigskin wet-white shavings containing about 8% Na_2SO_4 was collected from a local tannery. $Zr(SO_4)_2$ was a commercial product and its content of ZrO_2 was 31.5%. As_2O_3 and other chemicals were all analytical reagents.

Preparation of Zr(IV)-loaded absorbent based on wet-white shavings

15 g wet-white shavings (on dry basis) were fully washed and then suspended in 400 ml of water at pH 2.0 adjusted by a mixture of 10% formic acid and 10% sulphuric acid (v/v, 6:4). After being stirred for 2 h, a predetermined amount of $Zr(SO_4)_2$ was added and the reaction was undertaken with stirring for 6 h at 298 K. Then, the pH of the solution was gradually adjusted to 4.0 using 10% $NaHCO_3$ solution (wt %), and the reaction was continued for another 6 h at 318 K. When the reaction was completed, the product was collected by filtration, washed with distilled water, vacuum-dried at 323 K for 12 h, ground into particles of 0.5-1.0 mm to produce Zr(IV)-loaded adsorbent (ZrLA). The ZrLAs with different zirconium contents were obtained by using different dosages of $Zr(SO_4)_2$ in the reaction.

The zirconium content of ZrLA was determined by ICP-AES analysis (ICP-AES, Perkin-Elmer Optima 2100DV, America), after ZrLA was degraded by nitric acid and hydrochloric acid mixture (1:3, V/V). The adsorption behaviors were investigated by using the ZrLA with Zr content 112.05 $mg \cdot g^{-1}$ except when the effect of Zr content on adsorption was studied.

Preparation of As(V) stock solution

As(V) stock solution was prepared by oxidation of As_2O_3. As_2O_3 was dissolved in 1 M NaOH solution and then oxidized by a mixture of nitric acid and hydrochloric acid (1:3, V/V). The concentration of As(V) in stock solution was determined by using standard As(V) solution.

Effect of initial pH on adsorption capacity of ZrLA to As(V)

0.100 g ZrLA was suspended in 100 ml As(V) solutions in which the concentration of As(V) was 75.0 $mg \cdot L^{-1}$. The initial pH values of the As(V) solutions were adjusted to the range of 3.0 to 11.0 by using 0.1 M HNO_3 and 0.1 M NaOH solutions. The adsorption experiments were conducted by constant shaking at 303 K for 24 h (pre-experiments indicated that this time is long enough to reach adsorption equilibrium). Then the solution was filtered through filter paper with 30-50 μm pore size, and the concentration of As and Zr(IV) in filtrates were analyzed by ICP-OES. The adsorption capacities at different initial pH were obtained by mass balance calculation, and denoted as q_e ($mg \cdot g^{-1}$ adsorbent).

Adsorption isotherms

0.100 g ZrLA was suspended in 100 ml As(V) solutions with initial concentrations of As(V) ranged from 7.50 $mg \cdot L^{-1}$ to 75.0 $mg \cdot L^{-1}$. The pH was adjusted to 4.0 by using 0.1 M HNO_3 and 0.1 M NaOH solutions, and the adsorption temperatures were 303 K, 313 K and 323 K respectively. The adsorption procedures were the same as former procedures.

Effect of zirconium content in ZrLA on adsorption capacity

0.100 g ZrLA with different zirconium contents was suspended in 100 ml As(V) solutions (pH 4.0, concentration 75.0 $mgAs \cdot L^{-1}$).The adsorption procedures were the same as former procedures.

Adsorption kinetics

The initial concentration of As(V) solution was 75.0 $mg \cdot L^{-1}$ at pH 4.0. The adsorption procedures were similar to former procedures. But the concentration of As(V) in solution was measured at a regular interval during the adsorption process.

RESULTS AND DISCUSSION

Effect of initial pH on adsorption capacity of ZrLA to As(V)

The effect of initial pH on As(V) adsorption by ZrLA is shown in Figure 1. The adsorption capacity was greatest, 55-60 mg·g-1, in the 3.0-6.0 pH range, with the maximum adsorption capacity observed at pH 4.0. The adsorption capacity decreased remarkably as initial pH was increased from 6.0 to 11.0. Thus, the suitable pH for adsorption of As(V) by ZrLA should be in the range of 3.0-6.0. In addition, no Zr(IV) was released from ZrLA in the pH range of 3.0-11.0 during the adsorption process.

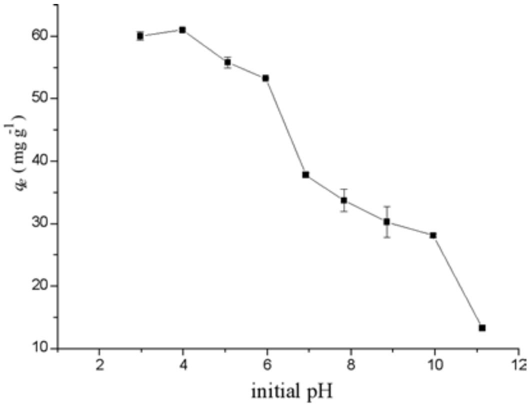


Figure 1. – Effect of initial pH on adsorption capacity of As(V) on ZrLA (303 K).

The pH value of As(V) solution significantly affects the chemical speciation of As(V) in solution. In general, As(V) in aqueous solution mainly exists in the chemical species of H_3AsO_4 (pH<2), $H_2AsO_4^-$ (2<pH<7) and $HAsO_4^{2-}$ (7<pH<11).[29] It can be observed in Figure 1 that the adsorption capacity was higher in the pH range of 3.0-6.0 where the chemical species of $H_2AsO_4^-$ is dominant, and then greatly decreased at pH>6.0. This suggests that the chemical species of As(V) in aqueous solution considerably affects the adsorption of As(V), and that $H_2AsO_4^-$ is favored for the adsorption of As(V) on ZrLA. Therefore, the adsorption capacity at pH 4 is not significantly different from that of pH 3, due to the fact that the predominant chemical species of As(V) in aqueous solution is $H_2AsO_4^-$ at both pH 3 and pH 4.

The effect of pH on adsorption behavior of As(V) on ZrLA is similar to those on Fe(III)-loaded LDA resin and Zr(IV)-loaded resin.[21, 22] That is, a ligand exchange reaction may be involved in the adsorption of As(V) on ZrLA,[21, 22] similar to the adsorption mechanism of As(V) on the resins. In addition, it was found that the pH values of the As(V) solutions were lowered after adsorption, as shown in Figure 2, which implies that H^+ was released during the adsorption process. Hence, the adsorption mechanism could be suggested as in scheme 1.

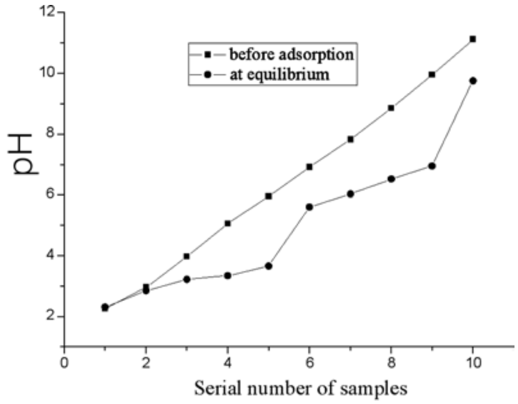


Figure 2. – pH values of As(V) solutions before adsorption and at equilibrium.

$$\equiv \text{Zr-OH}_2^+ + H_2AsO_4^- \rightleftharpoons \equiv \text{Zr-(HAsO}_4^-) + H^+ + H_2O \quad (2.0<\text{pH}<6.0)$$

$$\equiv \text{Zr-OH}_2^+ + HAsO_4^{2-} \rightleftharpoons \equiv \text{Zr-(AsO}_4^{2-}) + H^+ + H_2O \quad (7.0<\text{pH}<11.0)$$

Scheme 1

In addition, it was found that Fe(III) and Al(III) loaded wet-white shavings can also remove As(V) from aqueous solutions. However, the adsorption capacity of Fe(III) and Al(III) loaded wet-white shavings are lower than that of Zr(IV) loaded one. Therefore, our investigation was focused on the adsorption behaviors of Zr(IV) loaded wet-white shavings.

Adsorption isotherm

The adsorption isotherms of As(V) on ZrLA are presented in Figure 3. The adsorption capacity of As(V) on ZrLA increased with the increase of temperature. The adsorption capacity was 60.90 mg·g^{-1} at 303 K, while it was increased to 63.10 mg·g^{-1} at 313 K. Therefore, chemical adsorption mechanism could be suggested for the adsorption of As(V) on ZrLA.

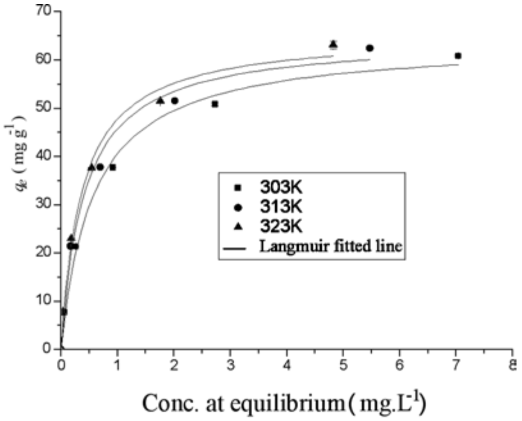


Figure 3. – Adsorption isotherms of As(V) on ZrLA (0.100g adsorbent, pH=4.0).

The Langmuir equation (**1**) and Freundlich equation (**2**) were used to fit the adsorption isotherms data.

$$q_e = \frac{q_{\max} b c_e}{1 + b c_e} \tag{1}$$

$$q_e = k c_e^{1/n} \tag{2}$$

where q_e and c_e are the adsorption capacity (mg·g^{-1}) and the bulk concentration of As(V) (mg·L^{-1}) at equilibrium respectively, b is the Langmuir constant related to energy of adsorption (L·mg^{-1}), q_{max} is the maximum adsorption capacity (mg·g^{-1}), k and n are the Freundlich constants referring to adsorption capacity and intensity of adsorption respectively.

The parameters of fitting are summarized in Table 1. It was found that the Langmuir equation gives a satisfactory fitting to the adsorption isotherms with correlation coefficient R^2>0.99. The maximum adsorption capacities calculated by the Langmuir equation are close to those determined by experiments. Calculated by the Langmuir equation, the maximum adsorption capacity of As(V) on ZrLA is 63.38 mg·g^{-1} at 303 K, which is higher than those of activated alumina (8.99 mg·g^{-1}), Al-impregnation SBA-15 (20.99 mg·g^{-1}),[20] Fe-loaded bead cellulose (33.2 mg·g^{-1}),[29] Fe-loaded chelating resin (55.44 mg·g^{-1})[22] and Zr-loaded LDA (49.15 mg·g^{-1}).[21] In comparison with other metal containing industrial solid waste, such as Fe(III/Cr(III) hydroxide (q_{max}=11.02 mg·g^{-1}),[30] ZrLA also exhibits superior adsorption capacity for As(V). Thus, ZrLA is an effective and low-cost adsorbent for removal of As(V) from aqueous solution.

TABLE I

Langmuir and Freundlich fitting parameters of As(V) adsorption on ZrLA

Parameters	**T (303 K)**	**T(313 K)**	**T(323 K)**
q_{exp}(mg•g^{-1})	60.90	62.47	63.10
Langmuir equation			
q_{max}(mg•g^{-1})	63.83	64.61	65.51
b (L•mg^{-1})	1.730	2.402	2.667
R^2	0.9951	0.9912	0.9923
Freundlich equation			
ln$k$ (L•g^{-1})	3.466	3.603	3.682
n	2.329	2.329	2.424
R^2	0.9718	0.9628	0.9763

The Langmuir adsorption isotherm implies that adsorbates are in the state of monolayer coverage on the surface of adsorbent, and is often referred to chemical sorption mechanism. Therefore, it can be concluded that the adsorption of As(V) on ZrLA is a chemical adsorption process and can be considered as a ligand exchange reaction process.[21]

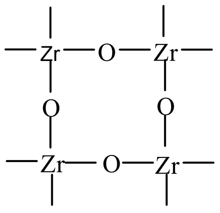
Effect of the zirconium content in ZrLA on As(V) adsorption

The adsorption capacities of As(V) on the ZrLAs with different zirconium contents were listed in Table 2. It can be observed that the adsorption capacity was increased from 42.26 mg.g^{-1} to 62.16 mg.g^{-1} when zirconium content in ZrLA was increased from 50.16 mg.g^{-1} to 92.83 mg.g^{-1}. However, the adsorption capacity was not increased as zirconium content further increased to 112.05 mg.g^{-1}. It is well known that Zr(IV) in aqueous solution will form multi-nuclear complexes through hydrolysis,[31] as shown in scheme 2 and scheme 3. This implies that not all the Zr(IV) loaded on collagen fibers can participate the adsorption of As(V). Moreover, the hindering effect may affect the adsorption of As(V) on ZrLA when the zirconium content in ZrLA was above 112.05 mg.g^{-1}. Therefore, it could be inferred that the adsorption sites are not proportionally increased with the increase of the zirconium content in ZrLA.

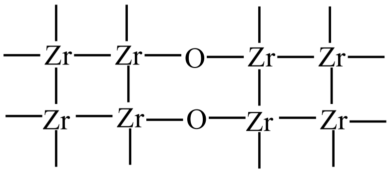
TABLE II

Influence of zirconium content in ZrLA on adsorption capacity of As(V)

Zirconium content (mgZr·g^{-1})	**Adsorption capacity (mgAs·g^{-1})**
50.16	42.26±1.48
92.83	62.16±0.98
112.05	60.60±0.79



Scheme 2



Scheme 3

Adsorption kinetics

The adsorption kinetic data of As(V) on ZrLA were illustrated in Figure 4. The adsorption equilibrium was attained around 6 h, which is nearly the same as that of Fe(III)-modified activated carbon,[32] but is faster than that of activated alumina.[33] In addition, the adsorption capacity of As(V) on ZrLA is increased with the increase of temperature, which is consistent with the results of adsorption isotherm tests.

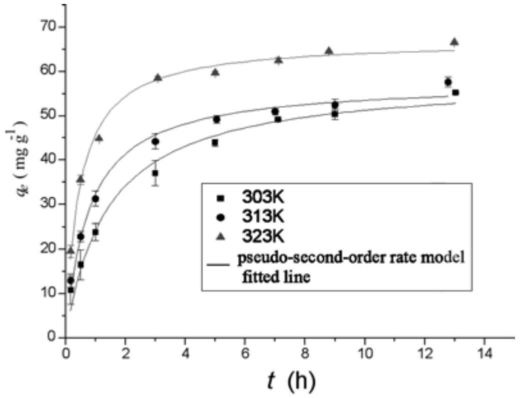


Figure 4. – Adsorption kinetics of As(V) on ZrLA (0.100 g adsorbent, initial conc. of As(V) 75.0 mg.L^{-1}, pH=4.0).

In order to further investigate the adsorption mechanism of As(V) on ZrLA, the pseudo-first-order rate model(3), the pseudo-second-order rate model(4) and intra-particle diffusion equation(5) were used to describe the adsorption kinetic data,[34, 35]

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

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

$$q_t = k_3 t^{0.5} \tag{5}$$

where q_e and q_t are the amount of As(V) adsorbed on ZrLA (mg·g^{-1}) at equilibrium and at time t(h) respectively, and k_1, k_2 and k_3 are the rate constants of pseudo-first-order-rate model (h^{-1}), pseudo-second-order rate model (g·mg^{-1}·h^{-1}) and intra-particle diffusion rate model (g·mg^{-1}·h$^{-0.5}$) respectively.

The rate parameters determined by pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model were summarized in Table 3. The value of correlation coefficient R^2 for pseudo-second–order adsorption model is comparatively higher (>0.996), and the adsorption capacities calculated by this model are close to those determined by experiments. However, the values of R^2 for pseudo-first-order model and intra-particle diffusion adsorption model are not satisfactory. Compared with other porous adsorbents, ZrLA is in fibrous state and its specific area is small, 2.835 m^2·g^{-1} determined by Surface Area and Porosity Analyzer (TriStar 300, Micromeritics, America). Therefore, the adsorption of As(V) should be mainly on the outer surface of ZrLA, leading to very rapid adsorption rate. So it can be concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of As(V) on ZrLA than other two models, and the adsorption reaction is the rate controlling step of the whole adsorption process.[35, 36] Similar phenomena had been also observed in the adsorption of As(V) on Fe-loaded bead cellulose.[29]

Moreover, the adsorption activation energy E_a was determined by Arrhenius equation (6)[37] through plotting Logk_2 against 1/T, as presented in Figure 5. The Ea determined was 32.88×10^3 J·mol^{-1}. It has been reported that the reaction can be easily processed if the reaction activation energy is lower than 42×10^3 J·mol^{-1}. [34]

$$\log k_2 = -\frac{E_a}{2.303RT} + \log A \tag{6}$$

where k_2 is the rate constant determined by pseudo-second-order rate model (g·mmol^{-1}·min^{-1}), E_a is the activation energy (J·mol^{-1}), and R is the gas constant (8.314 J·mol^{-1}·K^{-1}).

TABLE III

Adsorption kinetic model parameters of As(V) on ZrLA

Parameters	**T (303 K)**	**T(313 K)**	**T(323 K)**
$q_{e,exp}$(mg·g^{-1})	55.16	57.56	66.52
First-order rate model			
k_1(h^{-1})	0.5779	1.0018	1.526
$q_{e,cal}$(mg·g^{-1})	50.31	51.57	61.99
R^2	0.9430	0.9454	0.9426
Second-order rate model			
k_2·100 (g·mg^{-1}·h^{-1})	1.179	1.832	2.644
$q_{e,cal}$(mg·g^{-1})	59.45	59.59	68.59
R^2	0.9969	0.9981	0.9996
Intra-particle diffusion model			
k_3(g·mg^{-1}_h$^{-1/2}$)	14.27	13.33	13.39
R^2	0.9806	0.9558	0.9149

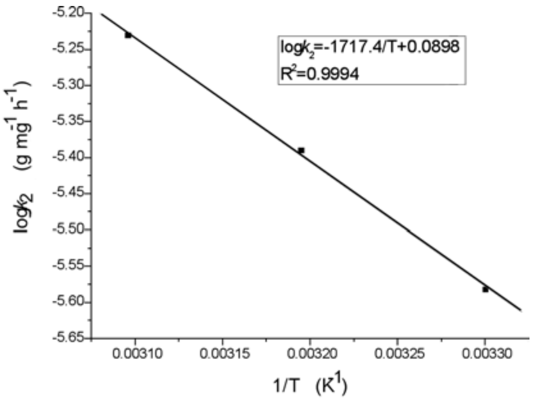


Figure 5. – Determination of activation energy of adsorption process of As(V) on ZrLA by plotting logk2 against 1/T.

CONCLUSIONS

An effective and low cost Zr(IV)-loaded adsorbent (ZrLA) can be prepared by using wet-white shavings as supporting matrix. ZrLA exhibits high adsorption capacity to As(V) in the pH range of 3.0-6.0. Ligand exchange reaction is probably the predominant mechanism for the adsorption of As(V) on ZrLA. Adsorption reaction is the rate-controlling step over the whole adsorption process. With the advantages of high adsorption capacity, fast adsorption rate and low cost, ZrLA promises to be potentially applicable in both disposal of solid wastes in tannery and removal of As(V) from aqueous solutions.

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