

# Arsenic removal by zirconium oxyhydroxide adsorbents

Kateryna Sorochkina<sup>1\*</sup>, Roman Smotraiev<sup>1</sup>, Harsha Ratnaweera<sup>2</sup>

<sup>1</sup> Department of Inorganic Substances Technology, Ukrainian State University of Chemical Technology, 49000, Gagarin av., 8, Dnipropetrovsk, Ukraine

<sup>2</sup> Norwegian University of Life Sciences, PO Box 5003-IMT, 1432 Aas, Norway

\* Corresponding author. E-mail: [kate\\_3110@mail.ru](mailto:kate_3110@mail.ru), +38 093 036 90 80

## Abstract

Composite adsorbents based on zirconium oxyhydroxide (ZOH) with adding of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  were synthesized by a sol-gel method to remove of As(V) and As(III) from drinking water. The characterization of adsorbents and their adsorption behavior are investigated. Due to the high specific surface area, from 355 to 541  $\text{m}^2/\text{g}$  and the presence of surface hydroxyl groups, adsorbents demonstrated a high efficiency for both arsenic species without pretreatment at near neutral pH. Based on adsorption experiment without stirring the most effective composition (Zr-Mn) was chosen. The equilibrium adsorption capacity of these adsorbents was achieved within 8 h with a value of arsenic removal  $R=96-98.5\%$ . The experimental data fitted pseudo-second-order model. The date of adsorption isotherms studies accorded with Langmuir isotherms due to the low arsenic concentration and suggested a high affinity of the adsorbent to As species. The influence of co-existing anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  was insufficient. More effective arsenic removal was observed at lower pH, but even at neutral pH the efficiency of treatment achieved 96-97%. The high removal efficiency, the wide range of work pH and fast treatment process make an attractive composite adsorbent based on Zr-Mn oxides to remove of both As(V) and As(III) from drinking water.

## Аннотация

С целью удалить ионы As(V) и As(III) из питьевой воды золь-гель методом были получены сорбенты на основе оксигидроксида циркония (ОГЦ) с добавками  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  и  $\text{Mn}_3\text{O}_4$ . В ходе исследований были изучены основные физико-химические и адсорбционные свойства полученных сорбентов. На основе исследований адсорбционных свойств был выбран наиболее эффективный состав сорбента, Zr-Mn. Равновесная адсорбционная емкость выбранного адсорбента достигается за 8 часов с эффективностью в 96-98,5%. Экспериментальные данные кинетики адсорбции соответствуют псевдо второму порядку. Изотермы адсорбции, в виду низких концентраций ионов As, описываются уравнением Ленгмюра. При этом присутствие дополнительных примесей ионов  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  и  $\text{CO}_3^{2-}$  практически не влияет как на механизм сорбции, так и на эффективность удаления ионов  $\text{AsO}_4^{3-}$  и  $\text{AsO}_3^{3-}$ . Изучение влияние pH на процесс адсорбции показало, что максимальное удаление примесей As достигается при низких pH, однако даже при повышении pH до нейтральных значений эффективность удаления достигает удовлетворительного уровня в 96-97%. Благодаря высокой удельной поверхности, от 355 до 541  $\text{m}^2/\text{г}$ , развитому гидроксильно-гидратному покрову, широкому диапазону рабочих pH и достаточной скорости удаления примесей предложенный сорбент на основе ОГЦ с добавкой  $\text{Mn}_3\text{O}_4$  обладает высокой эффективностью по удалению как трехвалентного так и пятивалентного мышьяка без предварительной обработки воды.

**Keywords:** arsenic, composite adsorbents, isotherm, kinetic, Zr-Mn oxide

## Introduction

Arsenic compounds are highly toxic and can be found in sources of groundwater and drinking water. In natural water they exist in two predominant forms As(V) and As(III), but trivalent arsenic is about 60 times more toxic and difficult to remove without pretreatment than oxidized pentavalent state (Jain & Ali, 2000). Many countries of the world face a health risk due to the arsenic contamination in the water, but for developing countries, such as Bangladesh, Chile, India, Argentina etc., this problem is more actual because of a lack or an insufficiency of water treatment (Mandal, 2002). While acute minimal lethal dose of arsenic in adults is estimated to be 70 to 200 mg or 1 mg/kg/day, the highest concentration of As in this region ranges from 0.1 to 3 mg/l (Dart, 2004). According to the National Academy of Sciences, even small amount of arsenic in drinking water causes different types of cancer, serious skin and heart problems (Fawell & Mascarenhas, 2011). To address health problems, the World Health Organization (WHO) and US Environmental Protection Agency (USEPA) made the maximum contamination level of As in drinking water less, from 50 to 10 µg/l. The stricter requirements have prompted a series of investigations to develop cost-effective arsenic treatment technology. Arsenic can be removed from drinking water by different treatment process as oxidation, coagulation, filtration, reverse osmosis, biological treatment, ion exchange and adsorption (Mólgora, Domínguez, Avila, Drogui, & Buelna, 2013; Mondal et al., 2014; Katsoyiannis & Zouboulis, 2004; Daus, Wennrich, & Weiss, 2004). However, many of them have significant drawbacks, such as the insufficient cleaning, a need of pretreatments, a multistage character, the high construction and service cost (Fauskrud, 2013). Adsorption technology is one of the most promising methods to remove arsenic because it can be used not only at the pilot scale, but also in households (Yang et al., 2014). At the same time, some adsorbents remove both three and pentavalent state without pretreatment that makes this technology more cost-effective (Huang, Yang, & Keller, 2014). As sorbents for arsenic removal are often used an activated carbon (Arcibar-Orozco, Josue, Rios-Hurtado, & Rangel-Mendez, 2014), metals oxides (Mohan & Pittman, 2007) and natural solids (Elizalde-González, Mattusch, Einicke, & Wennrich, 2001). Metal oxide adsorbents mainly include activated alumina, iron oxides, zirconium oxides, titanium oxides, cerium oxides, and so on. Generally, the high surface area and specific affinity for arsenic adsorption are the main factors to determine the efficiency of the treatment process (Chen et al., 2014). However, metal oxides as adsorbents are not used in their pure form due to the low chemical stability, selectivity to As (III) ions or a high price.

Zirconium oxide/oxyhydroxide always was attractive for scientist as adsorbent material. It has a unique selectivity towards multivalent anions (such as phosphates, arsenates, arsenites, etc). This behavior is explained by the presence of hydroxyl ions and water molecules in the hydrated form of zirconium, which take part in ligand substitution with arsenic (Sun, Hu, & Qu, 2013). Furthermore, zirconium oxide is non-toxic and insoluble material with unique chemical stability and good resistance to attack by acids, alkalis, oxidants and reductants (Cui, Su, Li, Gao, & Shang, 2013). However, the high cost of zirconium oxide adsorbents can cause the problem for their use in developing countries. Thus, to decrease adsorbent price and keep excellent adsorption and physicochemical properties, many scientists have proposed to synthesize the binary oxides adsorbents based on high-effective  $ZrO_2$  and low-cost  $Fe_2O_3$ ,  $Al_2O_3$  or  $Mn_3O_4$ . In the present work, composite adsorbents based on Zr-Al, Zr-Al-Fe and Zr-Mn oxides were prepared by sol-gel method, which enables to obtain a homogeneous mixture of metal hydroxides and a nanostructured material after gelation process (Chepurna, Smotraev, Kanibolotsky, & Strelko, 2011). The adsorbents were characterized and investigated for their arsenic adsorption behavior from drinking water. The results showed

high removal efficiency for both As(III) and As(V) with Zr-Mn adsorbent under stirring and medium efficiency for all adsorbents without mixing.

## **Experimental**

### **Chemicals and analysis**

The following chemicals were used in this research. Zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) was obtained from Volnogorsk Metallurgical Plant (Dnepropetrovsk region, Ukraine). Iron(III) chloride, Aluminium(III) chloride, Manganese(II) chloride and urea ( $\text{CO}(\text{NH}_2)_2$ ) were purchased from Reagent (Dnepropetrovsk, Ukraine). The arsenic solutions used were mixed at IPM laboratory to a concentration of 4 g/L. The initial arsenic solution was prepared by dissolving Sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , 98%) and Sodium arsenite ( $\text{Na}_2\text{AsO}_2$ , 100%) (VWR international, Germany) into deionized water. The working solution of As(III) and As(V) was obtained by mixing initial solutions with tap water. The pH was adjusted by Hydrochloric acid (HCl) and Sodium hydroxide (NaOH). The concentration of both arsenic forms was estimated by a laboratory technician using an Inductively Coupled Plasma Mass Spectrometer (Agilent 8800 ICP-MS in oxygen reaction mode) (IPM Department, NMBU, Norway). As(III) and As(V) were separated with strong base anion exchange resin (AER) (Dowex 21K XLT Resin). A sample (150-250 ml) passed through the AER, As (V) was adsorbed by resin, and As (III) remained in the water. Samples were taken and analyzed concentration of arsenic before (total As) and after the AER (As(III)), the difference between them – As(V).

### **Adsorbents preparation**

Adsorbents were prepared by sol-gel method during homogeneous hydrolysis of urea with mixed metal solution. Initial solutions of metal salt with concentration  $C(\text{Me}^{n+})=0,75$  mol/l were mixed at molar ratio: Zr:Al=3:1 (Zr-Al), (Zr:Al):Fe=(1:3):0,4 (Zr-Al-Fe) and Zr:Mn=10:1 (Zr-Mn). The resulted mixture was heated to 100°C in the presence of urea at molar ratio  $\text{Me}:\text{CO}(\text{NH}_2)_2=1:3$ . The obtained sol was dropped into the dual-layer solution (oil and alkali) to form the gel structure of wet adsorbents. The metal hydroxide spheres were washed with deionized water and dried at 20°C for 24 h (Sorochkina & Smotraiev, 2011).

### **Adsorbents characterization**

The elemental contents were analyzed by X-ray diffraction (XRD). Diffraction patterns were obtained on the X-ray diffractometer DRON-2 (USSR) in a monochromatic  $\text{Cu-K}_\alpha$  radiation with a wavelength  $\lambda = 1.54056 \text{ \AA}$ . Infrared spectra were collected within range of 400 and 4000  $\text{cm}^{-1}$  at room temperature on IR spectrophotometer Spektrum BX (Germany). The specific surface area and pore-size distribution were measured by water adsorption experiments using the BET method (Sorochkina & Smotraiev, 2013).

### **Batch adsorption experiments**

Arsenic solutions were freshly prepared by diluting initial As(III) and As(V) solution with tap water. The effect of composition, adsorbent dosage, a contact time and solution pH was investigated. In the experiment to investigate the effect of composition on arsenic adsorption, various amounts of adsorbents in the range of 0.2-1 g were added to 250 ml arsenic solution with concentration  $\text{As(III)}=56 \mu\text{g L}^{-1}$  and  $\text{As(V)}=54 \mu\text{g L}^{-1}$  without pH adjustment and shaken on 24 hr. For adsorbent, which showed better efficiency to remove arsenic without mixing, the optimal dosage for arsenic removal under stirring was determined. For it the amount of adsorbent from 0.05 to 0.3 g was mixed with arsenic solution during 18 hr. Kinetic

experiment was conducted to determine the contact time required to reach equilibrium. Adsorption was carried out under stirring in closed glass bottles filled 250 ml arsenic solution with predetermine mass of adsorbent ( $m=0.05$  g). The contact time was varied from 0 to 18 hr. To determine of adsorption isotherms, 250 ml of arsenic solution with initial total arsenic concentration from 100 to 350  $\mu\text{gL}^{-1}$  was shaken with 0.05 g of adsorbent during 18 hr, the pH of solution was adjusted around  $7.8\pm 0.2$  by adding HCl or NaOH. In the pH study, HCl or NaOH was added to arsenic solution of a known initial concentration to set up initial pH value in the range from 4 to 10. In order to estimate the effect of co-existing anions, the arsenic solution with total arsenic concentration  $C(\text{As})=100\text{-}350$   $\mu\text{gL}^{-1}$  and concentration of anion  $C(\text{An}^n)=1$   $\text{mmol L}^{-1}$  was shaken with 0.05 g of adsorbents during 18 hr.

## Results and Discussion

### Characterization of the synthesized adsorbents

In order to identify the crystalline structure of the sorbents, XRD studies were made. The results indicate that most of  $\text{ZrO}_2$  particles are amorphous, and crystalline structures could be observed only on  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . The presence of hydroxyl ions (OH) and water molecules on the metal oxide surface, which can act as adsorption sites, has a great effect on the adsorption properties. The stretching vibration of functional OH groups that forms wide band at  $3000\text{-}3600$   $\text{cm}^{-1}$  shows peak about  $3400$   $\text{cm}^{-1}$ , which attributes Brønsted acid centers. The band at  $\sim 1640$   $\text{cm}^{-1}$  is assigned to the hydroxyl deformation mode of water molecules and indicates the presence of physisorbed water on the binary oxides (Xu et al., 2013). Other two peaks around  $1530$  and  $1335$   $\text{cm}^{-1}$  correspond to terminal and bridging OH groups, respectively. The small wide peak at  $540$   $\text{cm}^{-1}$  shows the presence of Al-O vibration which can act as the additional adsorption center. Their specific surface area as presented in the Table 1 is higher than most Zr(IV) oxide adsorbents used in the removal of As(III) and As(V) (Zheng, Lim, & Chen, 2009; Cui, Li, Gao, & Shang, 2012; Xu et al., 2013). Most pores are micropores and their size is widely distributed from 3 to 16 Å. Thus, adsorbents created by the sol-gel synthesis have a large surface area which is beneficial for its adsorption capability.

**Table 1** Results of BET measurements for composite adsorbents based on ZOH

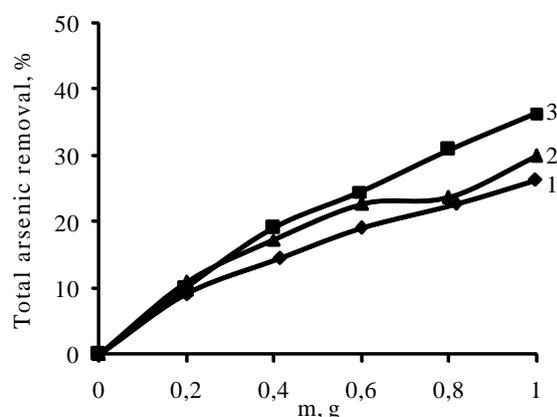
Adsorbents	S, $\text{m}^2/\text{g}$	V, $\text{cm}^3/\text{g}$	$r_{\text{dominant}}$ , Å	$r_{\text{medium}}$ , Å
Zr-Al	536.88	0.227	10.40	8.44
Zr-Al-Fe	541.46	0.225	4.00	15.99
Zr-Mn	355.70	0.113	3.40	7.85

### Determination of optimal adsorbent composition

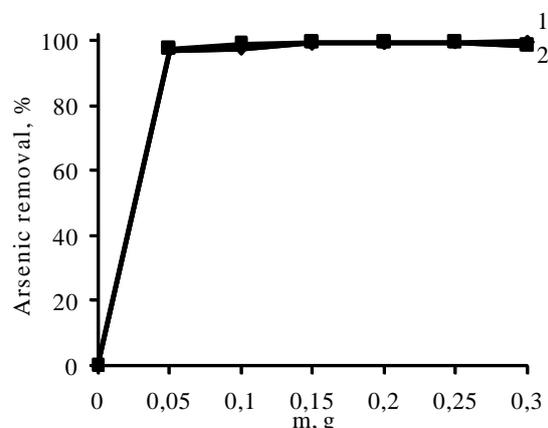
To determine the optimal composition, three different adsorbents were tested for removal of As(III) and As(V) without stirring as shown in Fig. 1. For the same initial arsenic concentration and adsorbent concentration, the Zr-Al composition has lowest removal efficiency for total As, about 25%. With Fe(III), the adsorption capacity was slightly improved to 30% for removal of total arsenic. The most effective to treat water from arsenic contaminants is Zr-Mn composition adsorbents, especially to remove As(III) state. Even without mixing it adsorbs 37% of total As, 44% of As(III) and 27% of As(V). This behavior can be explained by the fact that manganese oxides are used as the oxidizing agent (Shan & Tong, 2013). The Zr-Mn adsorbent, according to the data X-ray studies, contains  $\text{Mn}_3\text{O}_4$  ( $\text{MnO}\cdot\text{Mn}_2\text{O}_3$ ) which increase efficiency of removal As(III) due to oxidizing this state to As(V) and adsorption on the porous ZOH. Based on the adsorption study results the Zr-Mn composite adsorbent was chosen for the further experiments.

## Effect of Zr-Mn adsorbent dose

The adsorbent dose has the most significant impact on the adsorption process. To establish the optimal dosage of adsorbent for the treatment process, the removal efficiencies for both arsenic states were determined by different Zr-Mn mass under mixing (Fig. 2).



**Figure 1** Comparative study of arsenic removal by different adsorbent compositions (initial As(III)=56  $\mu\text{g L}^{-1}$  and As(V)=54  $\mu\text{g L}^{-1}$ , without stirring, 18 h): (1) Zr-Al, (2) Zr-Al-Fe, (3) Zr-Mn

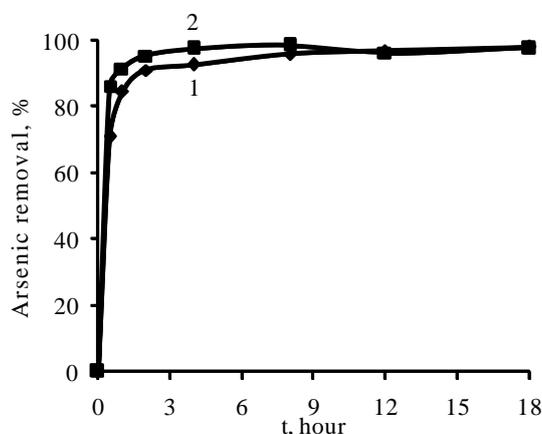


**Figure 2** Effect of adsorbent dosage on the arsenic removal efficiency by Zr-Mn adsorbents (initial As(III)=52  $\mu\text{g L}^{-1}$  and As(V)=63  $\mu\text{g L}^{-1}$ , with stirring, duration 18 h): (1) As(III), (2) As(V)

It was found that the As removal increased sharply to 97.5% with adsorbent doses 0.05 g, (compared to 37% and 1 g for previously test) and then grew insignificantly for both As(III) and As(V). Such removal rate corresponds with As concentration less than 5  $\mu\text{g/L}$ , which satisfies WHO requirements. According to this the adsorbent dosage for further study was set up as 0.05 g. The low effective dosage of adsorbents indicates the presence of a large number of active sites on the adsorbent surface that positively identifies this sorbent compared to other. The mixing process improved a diffusion of As ions to the adsorbent and into the adsorbent pore volume, thus the chemical reaction is limiting all adsorption process

## Kinetic of arsenic removal by Zr-Mn adsorbent

The kinetics of ions removal is one most important characteristic in adsorption that determines not only efficiency but also the cost of the treatment process. Hence, in the presence study, the kinetic characteristics of arsenic removal were defined to understand the adsorption behavior the Zr-Mn.



**Figure 3** Arsenic removal rate versus time by Zr-Mn (initial As(III)=55  $\mu\text{g L}^{-1}$  and As(V)=65  $\mu\text{g L}^{-1}$ , with stirring, adsorbent dosage 0.05 g, duration 18 h): (1) As(III), (2) As(V)

Figure 3 shows the adsorption data of As(III) and As(V) by Zr-Mn during 18 h. As seen from the Fig. 3 the adsorption of As(III) and As(V) was rapid in the first 30 min, when the removal efficiency achieved 70% and 86%, respectively. The removal rates for As(V) and As(III) were 95% and 91% after 2 hr that satisfies the WHO requirements. However, the adsorption equilibrium for both As(III) and As(V) was reached just after 8 hr with arsenic removal rate 96% and 98.5%, respectively. Such results are compatible with the data obtained by other researchers (Sun et al., 2013). To better describe the removal kinetics for arsenic species, the experimental data were fitted with Lagergren pseudo first-order kinetic model and the pseudo second-order kinetic model (Sun et al., 2013). The kinetic data for arsenic removal by Zr-Mn adsorbent are presented in Table 2.

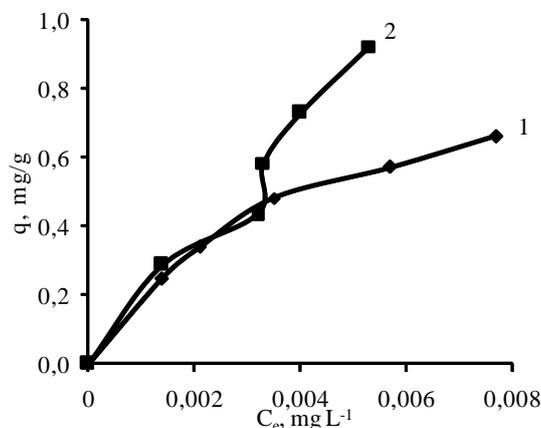
**Table 2** Coefficients for pseudo first-order and pseudo second-order kinetic models

	Pseudo first-order				Pseudo second-order		
	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	$k_1$ , ( $\text{min}^{-1}$ )	$R^2$	$q_{e,calc}$ (mg/g)	$k_2$ , (g/mg min)	$R^2$
As(III)	0.270	0.074	0.005	0.887	0.271	0.388	>0.999
As(V)	0.318	0.123	0.021	0.912	0.317	1.476	>0.999

The values of correlation coefficient  $R^2$  for the pseudo first-order model are around 89% and 91% for As(III) and As(V), respectively, and calculated equilibrium capacities are lower than determined by experiment. The  $R^2$  value for the pseudo second-order model are extremely high (>0.999) that means the experimental data of arsenic removal by Zr-Mn adsorbent fitted the pseudo second-order model and chemisorption dominated in the adsorption process. The difference between adsorption rate for As(V) and As(III) can be explained with several reasons: the difference between anion radius of As(V) and As(III) state (Sun et al., 2013); existed As(III) ions as neutral ions under the experimental conditions; and, the oxidizing As(III) state to As(V) by manganese during the initial reaction period (Kong, Wang, Hu, & Olusegun, 2014). Therefore, the application of composite adsorbents based on manganese oxide can accelerate the removal process of As from water.

### Adsorption isotherm of Zr-Mn adsorbent

The aim of adsorption isotherm studies is to define the specific relation between the equilibrium concentrations of As ions in the solution after sorption and the adsorbed by porous material as Zr-Mn. The adsorption isotherms of Zr-Mn adsorbent for As(III) and As(V) are presented in Figure 4.



**Figure 4** Adsorption isotherms of As(III) (1) and As(V) (2) on Zr-Mn (initial total As: 110-330  $\mu\text{g L}^{-1}$ , with stirring, adsorbent dosage 0.05 g, duration 18 h)

The isotherm results were analyzed using two common isotherms including the Langmuir and Freundlich and were used to represent the equilibrium data for As(III) and As(V) adsorption process (Table 3).

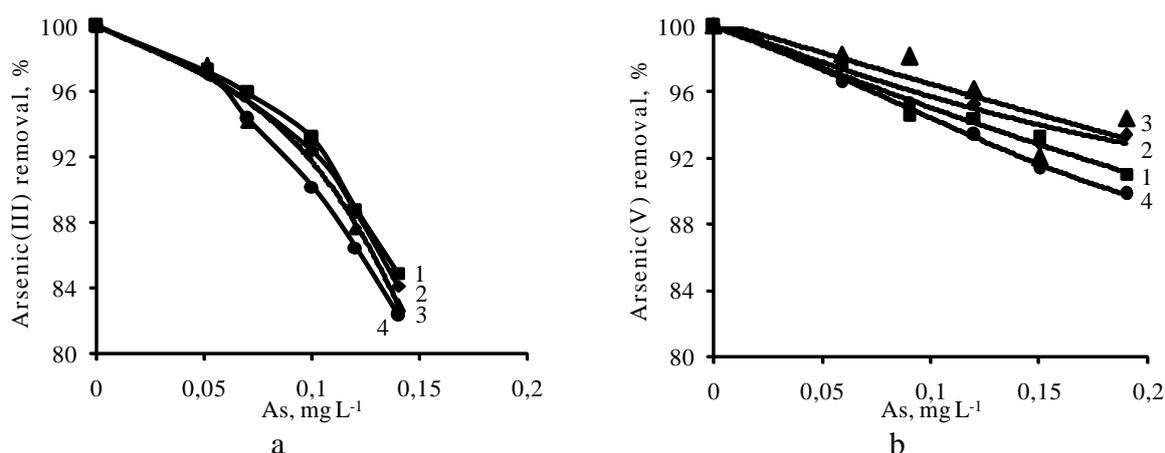
**Table 3** Isotherm parameters for As(III) and As(V) adsorption on Zr-Mn adsorbent

	Langmuir model			Freundlich model		
	$q_m$	$b$	$R^2$	$K_1$	$n$	$R^2$
As(III)	1.068	218.58	0.997	2.806	0.564	0.978
As(V)	2.224	103.35	0.911	6.807	0.871	0.907

The correlation coefficient  $R^2$  of the Langmuir isotherms for As(III) and As(V) are 0.997 and 0.911, while those for Freundlich model are 0.978 and 0.907 for As(III) and As(V), respectively. Higher regression coefficients for suggested that Langmuir model is suitable to describe the adsorption behavior of As(III) and As(V) by Zr-Mn composite adsorbents. Although most authors noted that the process of As adsorption on metal oxide adsorbents describes by Freundlich model, the obtained result is easily explained by the low initial concentration of arsenate in solution. The high value of the specific surface area of Zr-Mn adsorbent, micropores and low concentration of As ions promote the formation of a monolayer cover on the adsorbent surface. The adsorbent had high Langmuir constant ( $b$ ), which indicated the higher affinity of the adsorbent for the adsorbate, especially for As(III) in this study (Al-Anber, 2011). The Zr-Mn adsorbent had a higher adsorption capacity to As(V) than As(III), 2.224 and 1.068 mg/g, respectively. This suggested that Zr-Mn composite adsorbent is more effective for As(V) than As(III) removal, but it can be solved with oxidizing the trivalent state by manganese.

### Effect of co-existing anions

In natural or tap water in other countries, several components might exist, which can compete with arsenic anions for the same adsorption sites. In this study, anions of  $Cl^-$ ,  $SO_4^{2-}$  and  $CO_3^{2-}$  are used to test the effect of co-existing impurities. The corresponding results were illustrated in Figure 5(a and b).



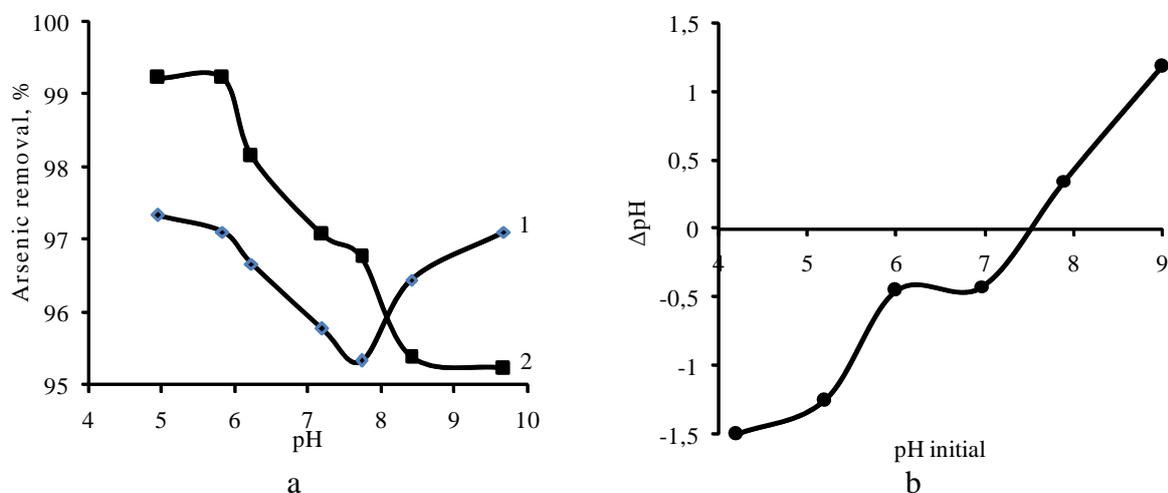
**Figure 5** The effect of co-existing anions on removal of As(III) (a) and As(V) (b) (initial As(III): 51-140  $\mu\text{g L}^{-1}$ , As(V): 59-190  $\mu\text{g L}^{-1}$ , anion concentration 1 mmol  $\text{L}^{-1}$  with stirring, adsorbent dosage 0.05 g, duration 18 h,  $\text{pH}=7.8\pm 0.2$ ): (1) without any addition anions, (2) with  $Cl^-$ , (3) with  $SO_4^{2-}$ , (4) with  $CO_3^{2-}$

The presence of co-existing anions had little or no effect on As(III) removal, especially  $Cl^-$  and  $SO_4^{2-}$ , which probably do not compete with arsenite ions. With increasing initial concentration of trivalent arsenic state,  $CO_3^{2-}$  began to effect on arsenic (III) removal, decreasing the efficiency to around 4%. The results for As(V) removal showed also little

impact of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  on the treatment efficiency with raising of the initial arsenic concentration and the negative effect of  $\text{CO}_3^{2-}$  presence. The observed negligible change in removal percentage of arsenic in the presence of with  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  and decreased arsenic removal induced by the presence of  $\text{CO}_3^{2-}$  could be explained based on the types of bonding interaction. The chloride anion could only form outer-sphere complex with metal (hydr)oxides, at the same, at  $\text{pH} > 6$ , sulfate ions would be adsorbed predominantly through this complexation. In contrast, the arsenic oxyanions form stronger bonded inner-sphere complex with the adsorbents via the ligand exchange mechanism. Therefore, chloride and sulfate anions could not obvious impact on the As removal by Zr-Mn adsorbent. The greater influence of the (bi)carbonate anion presence can be explained by not only the formation inner-sphere complex, but also the stable complex with arsenite, thus enhanced the mobilization of adsorbed As(III) (Shan & Tong, 2013). To check the influence of co-existing on the As adsorption mechanism, the isotherm adsorptions for all type of water were analyzed. The results demonstrate that Langmuir model fitted the adsorption isotherms data a little better than Freundlich.

### Effect of pH on arsenic removal

The influence of an initial solution pH (from 4 to 10) on removal of As(III) and As(V) adsorption onto Zr-Mn was studied, as shown in Figure 6a. Clearly, the arsenic removal was depending on pH, with increasing the adsorption under acid condition, however the pH impact is not too big as presented in (Sun et al., 2013), 2 and 4% for As(III) and As(V), respectively. The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of Zr-Mn adsorbent was measured as the difference between initial and final pH value (Figure 6, b).



**Figure 6** Effect of pH on the arsenic removal by Zr-Mn composite adsorbent (a) and change of pH vs initial pH for determination of ZPC of adsorbent (b) (initial As(III)=45  $\mu\text{g L}^{-1}$ , As(V)=65  $\mu\text{g L}^{-1}$ , with stirring, adsorbent dosage 0.05 g, duration 18 h): (1) As(III), (2) As(V)

According to the graph,  $\text{pH}_{\text{PZC}}=7.5$  for Zr-Mn adsorbents and, at pH is greater than this value, the surface are negatively charged and the electrostatic repulsive force between  $\text{AsO}_4^{3-}$  and adsorbent surface raised due to the more negative zeta potential of the adsorbent. Because As(III) species have a lower negative charge compared to As(V) in the range of 3-9, they do not exhibit same repulsion (Sun et al., 2013). Thereby the Zr-Mn composite adsorbent fabricated in this study with the small dosage of 0.1  $\text{g L}^{-1}$  is able to treat As contaminated water at initial concentration about 100  $\mu\text{g L}^{-1}$  to WHO required level at a wide range pH from 4 to 10.

## Conclusions

Three different types of adsorbents based on ZOH with impurities of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  have been synthesized by sol-gel method to remove arsenic from drinking water. Based on adsorption study without mixing the most effective Z-Mn composite adsorbent was chosen for further experiments with the optimal dosage 0.05 g. The removal efficiency for As(V) and As(III) achieved 95% and 91%, respectively, after 2 hr that satisfies the WHO requirements, while the adsorption equilibrium for both As(III) and As(V) was reached just after 8 hr with arsenic removal rate 96% and 98.5%. The maximum adsorption capacities for arsenite and arsenate were 1.68 and 2.24  $\text{mg g}^{-1}$  from the low concentrated solution (maximum 0.3  $\text{mg L}^{-1}$ ). The carbonate anion had the greatest effect on arsenic removal but decreased arsenic removal efficiency not bigger than on 4%. The adsorption of As(III) and As(V) by Zr-Mn was effective over a wide pH range of 4-10. These results indicated that Z-MN composite adsorbent is an attractive adsorbent for the removal both As(III) and As(V) from drinking water without any pretreatment.

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