Arsenic removal from drinking water by a zirconium–manganese composite adsorbent

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Abstract

Zirconium–manganese composite adsorbent was investigated for arsenic removal from drinking water. The batch of adsorbent optimal dosage experiments was performed. The influence of solution pH (from 4 to 10) on As removal by Zr-Mn adsorbent were investigated. The adsorption kinetics of arsenic was investigated to determine the equilibrium time for adsorption process. For both As(III) and As(V) the experimental data fitted pseudo-second-order model. The arsenic adsorption capacity of Zr-Mn adsorbent was investigated by the equilibrium adsorption isotherm study. According to the value of regression coefficients (R2) and due to low concentration of As in initial solutions Henry model is more suitable for describing the adsorption behavior of both As(V) and As(III). Maximum adsorption capacities calculated from the Langmuir equation are 16.8 mg/g for As(III), and 113.9 mg/g for As(V). The effect of presence of other anions, such as SO_4^{2-}, CO_3^{2-} and Cl^- was investigated.

Keywords: Arsenic; zirconium–manganese composite adsorbent; adsorption; drinking water.

Introduction

Arsenic pollution in natural water is a worldwide problem and has become a serious challenge for the world. Nowadays a number of countries faces this problem, among them are USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, India and others [1, 2]. Thus millions of people are exposed to a huge health risk due to arsenics toxicity.

The arsenic contents in groundwater of different countries varies and may reach hundreds (e.g. USA, Chile, Mexico) and thousands (e.g. Bangladesh, India, Argentina) μg As/l. The maximum permissible concentration of arsenic in drinking water is 50 μg l^{-1} and recommended value is 10 μg l^{-1} by Environmental Protection Agency and World Health Organisation [3].

Arsenic is listed as a hazardous material and is a suspect carcinogen, reportedly responsible for lung and skin cancers. Arsenic poisoning can lead to skin lesions, hyper-keratosis, skin cancer, liver disease, etc [2].

Arsenic exists in the environment in a number of valency states. The valency state of arsenic plays an important role for its behavior and toxicity in the aqueous system. According to National Academy of Sciences biologically, As(III) is considered more toxic than As(V). Trivalent arsenic is about 60 times more toxic than oxidized pentavalent state. Inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds [1-4].

Conventional arsenic removal technologies include coagulation, electro-coagulation, membrane filtration, and adsorption, etc. The removal of As(III) is more difficult than that of As(V). To achieve higher As(III) removal efficiency, treatment processes generally include a pre-oxidation of arsenite to arsenate.

One of the most effective ways of arsenic removal is adsorption which can be used not only in the industrial scales, but also in households. The last one is very important because mostly the problem of arsenic polluted water occurs in the areas that don't have centralized water supply systems. Moreover with help of adsorption at same time can be removed both As(III) and As(V) without pretreatment [5, 6].

As sorbents for arsenic removal are often used an activated carbon, oxides and hydrated oxides of metals. Many of them are not used in their pure form due to the low strength, low selectivity to ions of As (III) or high price. Materials based on iron and aluminum oxides are commonly used. But they have a fairly low capacitance towards arsenite and, in the case of iron, low strength and resistance to aggressive environments, which reduces their areas of application.

Hydrated zirconium oxide has a unique selectivity towards multivalent anions (such as arsenates, arsenites, phosphates, borates, carbonates, chromates, molybdates) due to hydroxyl-hydrate cover and a positive surface charge. Furthermore, hydrated zirconium oxide is steady against influence of acids, alkalis, oxidant and reductant, that favorably allocates it against the background other materials for the arsenic removal.

For improving of sorption and physico-chemical properties of the adsorbents binary compositions absorbents are used [4, 7].

1. Methods and materials

1.1 Materials

The zirconium-manganese фвыщкиуте was prepared according to the following procedure: initial solution of salts ($ZrOCl_2$, $MnCl_2$) with concentration of metal C(Me) = 1M were mixed with ions under molar ratio Zr:Mn=10:1. The mixture was heated to 100°C in the presence of urea under molar ratio Me:$CO(NH_2)_2$ =1:3. The obtained sol was dropped into the double layer solution (oil and alkali) to form a gel structure of wet adsorbents. The metal hydroxide grains were washed with deionized water and dried at 200°C for 24 h.

The arsenic solutions were prepared with concentration around of 4 g/L. $Na_2HAsO_4 \times 7H_2O$ was used to prepare Arsenic (V) solution. Na_2AsO_2 was used to prepare Arsenic (III) solution. Samples of contaminated water with different concentrations were prepared by mixing Arsenic (III) and Arsenic (V) solutions with tap water.

1.2 Adsorption experiments

The batch of adsorbent optimal dosage experiments was performed in glass bottles containing 250 mL of arsenic contaminated water and the dose of adsorbent: 0.05; 0.1; 0.15; 0.2; 0.25; 0.3 g.

The samples were mixed for 18 hours on a magnetic stirrer at room temperature.

Adsorption isotherm studies were conducted. Initial solution concentrations varied from 100 to 300 μg/L. The experiment was performed due to the following procedure. In each sample 0.05 g of adsorbent was loaded in glass bottles and 250 mL of arsenic contaminated water was added. The solutions were mixed for 18 h on a magnetic stirrer at room temperature.

To study the influence of coexisting anions to 250 mL of water samples with concentration varying from 100 to 300 μg/L such anions as SO_4^{2-}, CO_3^{2-} and Cl^- were added. The concentration of coexisting anions 1 mmol/L. The amount of adsorbent in each test was 0.05 g. The solutions were stirred for 18 h at room temperature.

The kinetic study was conducted. In each test 0.05 g of adsorbent was loaded to a glass vessel and 250 mL of water (concentration of arsenic 100 μg/L) was added. Water samples were stirred for different time from 0.5 to 18 h.

In order to study the effect of pH on adsorption process the initial pH of water samples (100 μg As/L) was adjusted by adding HCl and NaOH in interval from 4 to 10.

1.3 Analytical methods

Mass-spectrometry method was used to determine arsenic concentration in water samples. The samples were analysed on an Agilent 8800 ICP-MS mass-spectrometer.

The analysis in a mass-spectrometer gives the concentrations of total arsenic. So for determination of As(III) and As(V) the following procedure was used. The samples of analysed water (200-250 ml) were passed through an ion exchange column (Dowex 21K XLT Resin), As(V)

is adsorbed by resin, and As(III) remains in the water. Thus two samples are taken for the analysis: the sample taken before the ion exchange column gives the concentration of total arsenic in water, and the sample taken after the ion exchange column gives the concentration of As (III). The concentration of As(V) is determined by the difference between them As(tot) and As(III).

2. Results and discussion

2.1 Effect of adsorbent dose

As expected the arsenic removal efficiency grows as the amount of adsorbent increases. Although the removal efficiency doesn't change significantly: from 97.5% (m_{ads} = 0.05g) to 99.6% (m_{ads} = 0.3 g) (fig. 1). Thus even the smallest amount of sorbent m_{ads} = 0.05g gives very high efficiency and residual amount of total arsenic is 2.9 µg/L, which requires WHO standards for arsenic concentration in drinking water.

For the further experiments the chosen adsorbent dose was 0.05 g.

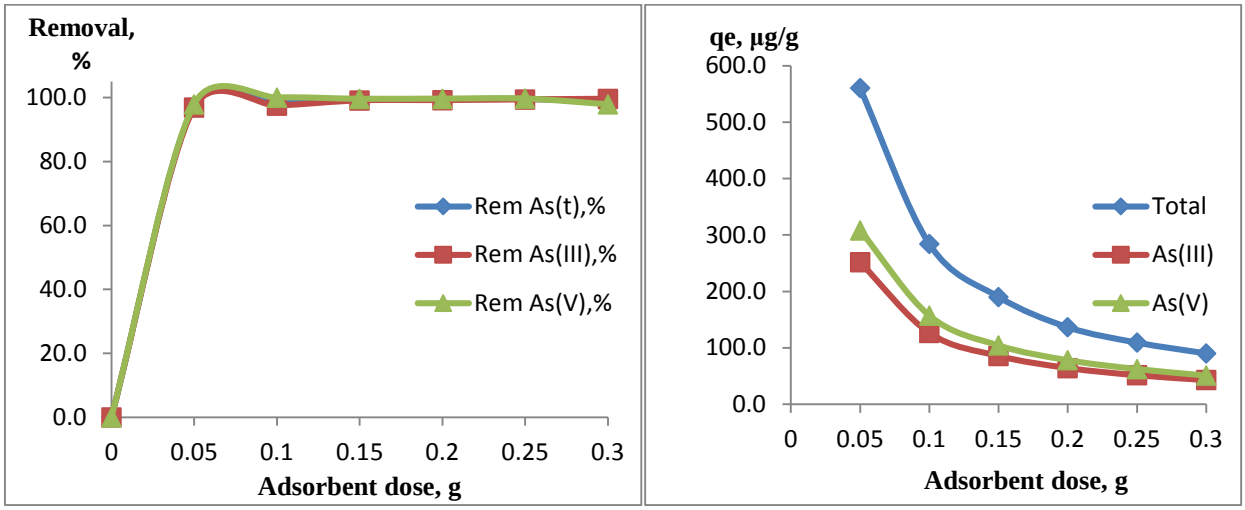


Figure 1. Effect of adsorbent dose on As removal.

2.2 Effect of pH

The influence of solution pH (from 4 to 10) on As removal by Zr-Mn adsorbent were investigated.

The effect of pH on the adsorption of As(III) and As(V) is shown in Fig. 2.

pH plays a significant role in adsorption processes, because the arsenic species and properties of the adsorbents surface strongly depend on the water pH value [5, 7, 8].

It is evident from the graph that the highest removal was reached under pH<5.

As(III) and As(V) species could coexist during whole process due to redox reaction. At pH >7.5 the adsorbent is positively charged and thus favorably attracts the dominant As(V), contributing to the higher removal efficiency at this pH range.

pH value during the process did not change significant within initial pH from 6 to 8. Removal percentage of As maintained above 95%. The residual content of total arsenic did not exceed 4.6 µg As/L

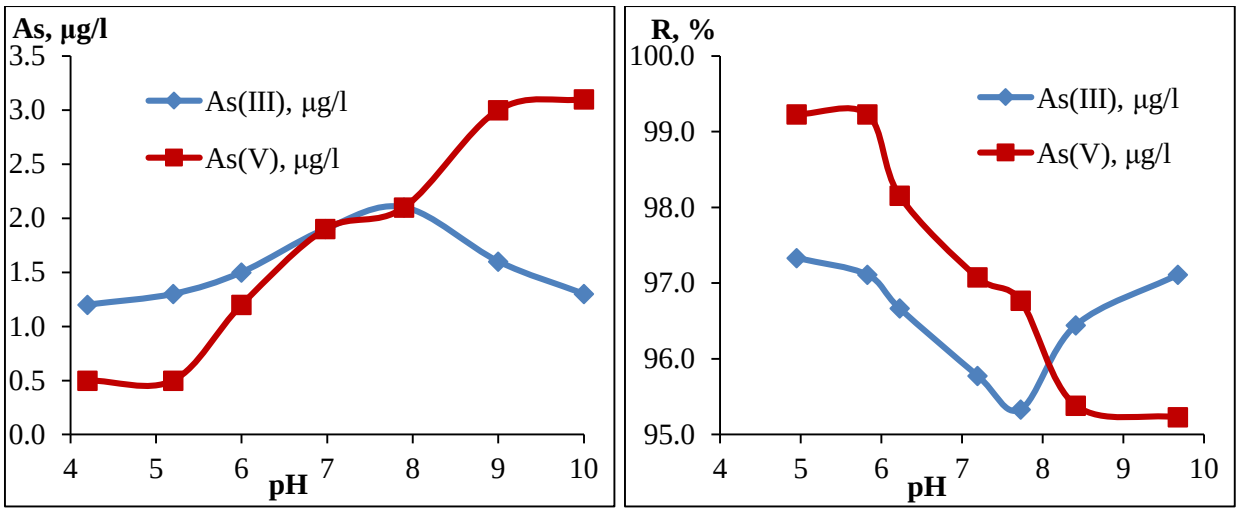


Figure 2. Effect of pH on As(V) and As(III) adsorption.

2.3 Kinetics of adsorption

The adsorption kinetics of arsenic was investigated to determine the equilibrium time for adsorption process. Fig. 3a shows the change of adsorbed arsenic as a function of contact time.

Adsorption process could be divided into two steps. In the first step, the adsorption rate was fast, and over 80% of the removal efficiency for both As(III) and As(V) was achieved within 1 hour, although the adsorption of As(V) happened more quickly than As(III).

After 12 hours removal efficiency was over 96 % for both As(III) and As(V). For both As(III) and As(V) the experimental data fitted pseudo-second-order model, which indicates that the adsorption process might be chemisorption.

Pseudo-second-order kinetic model was used to simulate the kinetics (Fig. 3b).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \qquad (1)$$

k_2 is the rate constant for pseudo-second order reaction (g/(mg min)); q_e and q_t are the amounts of solute adsorbed at equilibrium and at any time t (mg/g), respectively [8].

The kinetics parameters are summarized in Table 1. The values of regression coefficients (R2) show that the experimental data fits the pseudo-second-order model.

The value of k_2 for As(V) adsorption is higher than for As(III) adsorption under the same experimental conditions, confirming that the removal of As(V) was faster than As(III) [8].

Table 1 Kinetics parameters for As(V) and As(III) adsorption

	q_e [µg/g]	k_2 [g/(mg*min)]	R2
A(III), µg/g	271,7391	0,294483	0,9999
A(V), µg/g	317,4603	1,130125	0,9999
A(total), µg/g	588,2353	0,242653	0,9999

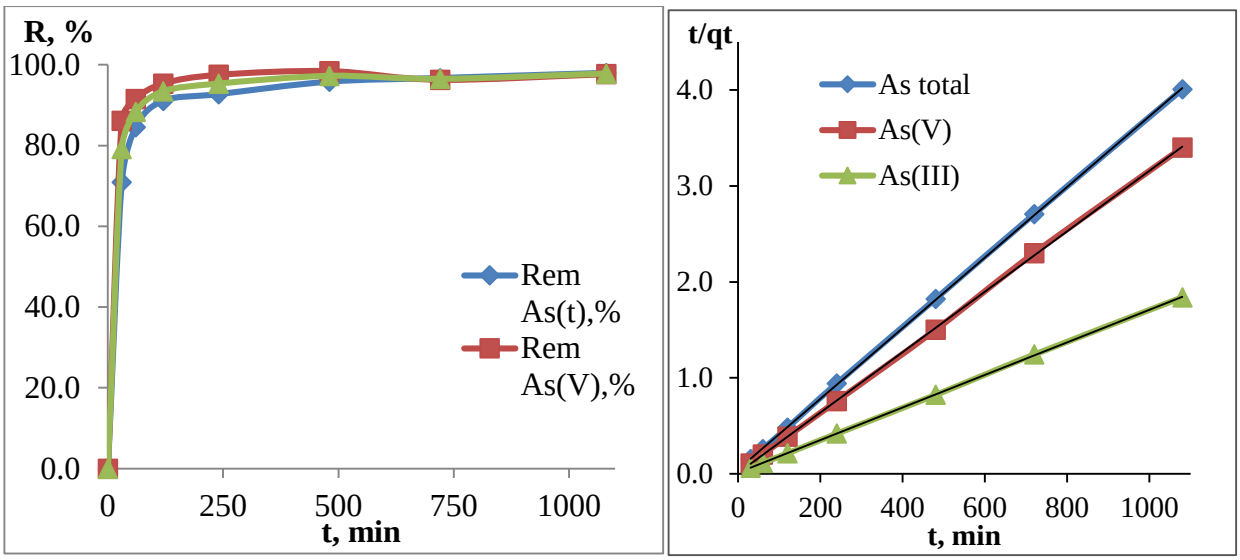


Figure 3 Kinetics of arsenic removal

2.4 Adsorption isotherm

The arsenic adsorption capacity of Zr-Mn adsorbent was investigated by the equilibrium adsorption isotherm study. Concentration of initial solution varied from 100 to 300 µg As(tot)/L.

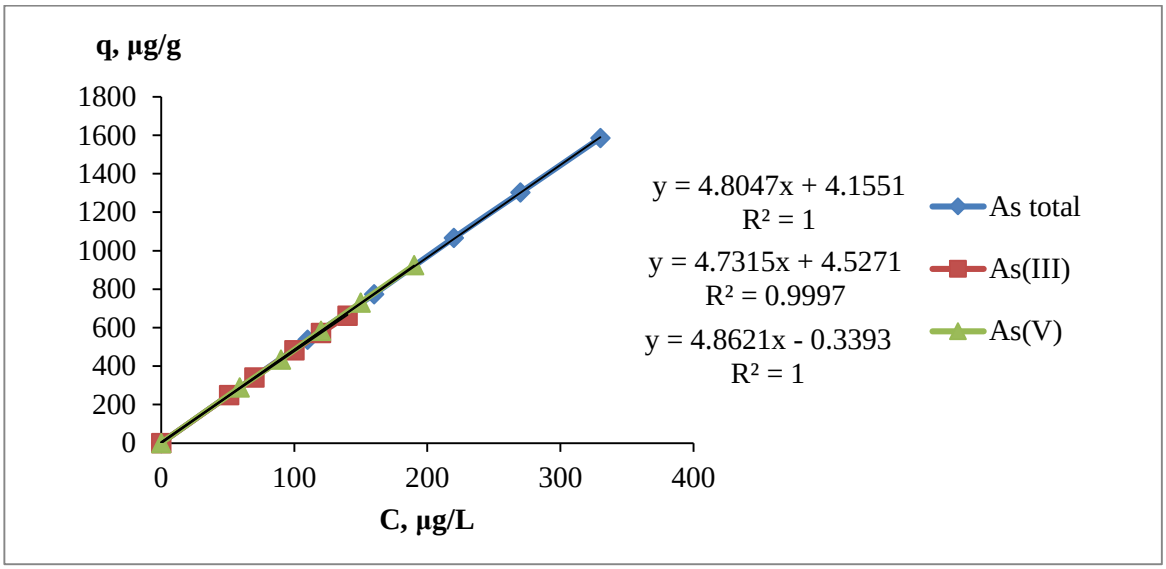
The Henry, Langmuir and Freundlich models were used to describe the adsorption isotherms (see Figs. 4 a, b, c), which are described by the following equations respectively:

$$q=KC; \qquad (2)$$

$$\frac{1}{q_e}=\frac{1}{q_m b}\cdot\frac{1}{C_e}+\frac{1}{q_m} \quad ; \qquad (3)$$

$$lnq_e=\frac{1}{n}lnC_e+lnK; \qquad (4)$$

where q_e is the amount of arsenic adsorbed at equilibrium (mg/g), C_e is the equilibrium adsorbate concentration (mg/L), q_{max} and b are maximum adsorption capacity and adsorption reaction constants, respectively, Freundlich constants K and $1/n$ are the adsorption capacity and adsorption intensity respectively [9, 10].



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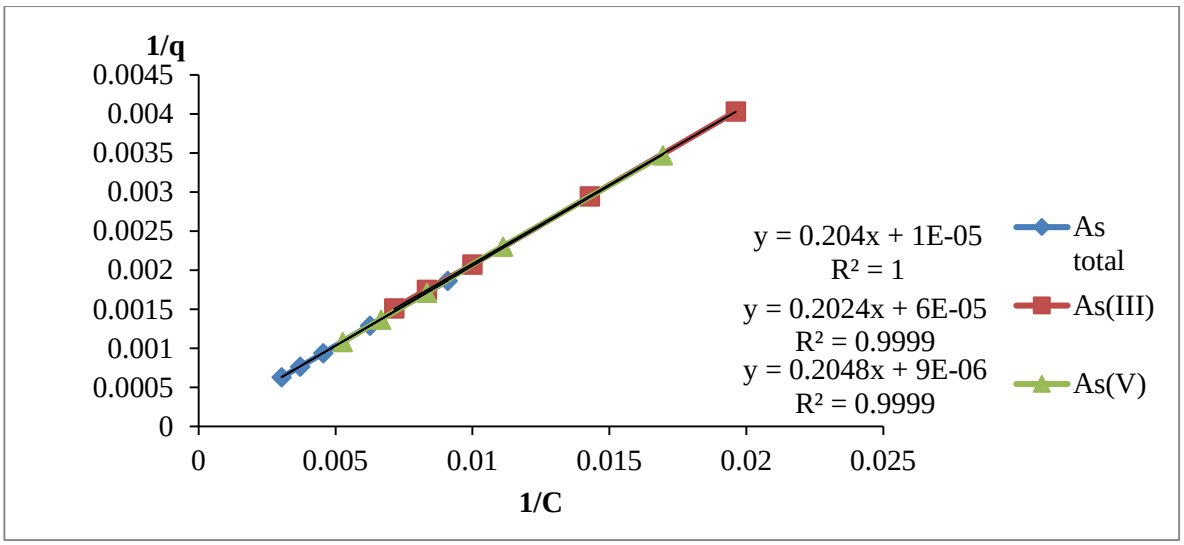

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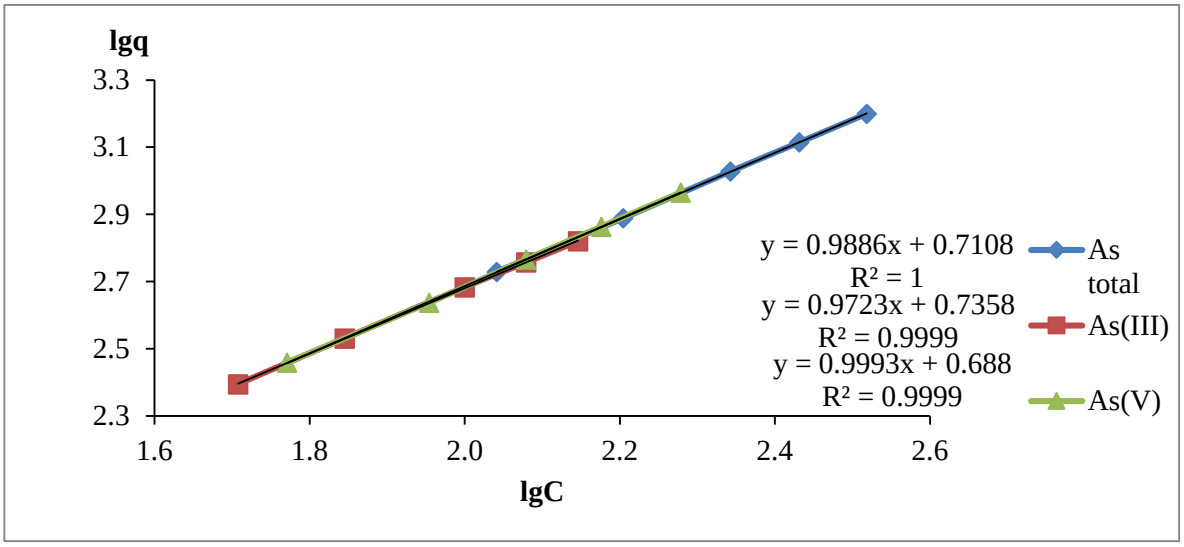

c

Figure 4 Henry (*a*), Langmuir (*b*) and Freundlich (*c*) adsorption isotherms

The adsorption parameters calculated from the isotherms are presented in Table 2. According to the value of regression coefficients (R2) and due to low concentration of As in initial solutions Henry model is more suitable for describing the adsorption behavior of both As(V) and As(III).

Constants of adsorption for As(III) and As(V) differ insufficiently, which means that for both As(III) and As(V) adsorption process runs the same way.

Maximum adsorption capacities calculated from the Langmuir equation are 16.8 mg/g for As(III), and 113.9 mg/g for As(V).

Table 2 Henry, Langmuir and Freundlich adsorption isotherm parameters

As species	Lengmuir model			Freundlich model			Henry model	
	qm, mg/g	b	R2	k	n	R2	k	R2
As(t)	76,68712	0,0639206	1	0,7108	1,01215	1	4,8047	1
As(III)	16,80672	0,2940304	0,9999	0,7357	1,02881	0,99986	4,7315	0,9997
As(V)	113,8952	0,0428613	0,9999	0,688	1,001	0,9999	4,8621	1

2.5 Effect of coexisting anions

In natural water several components might exist, which could compete with As for the available adsorption sites or interact with As itself and thus decrease the arsenic removal efficiency.

The effect of presence of other anions, such as SO_4^{2-}, CO_3^{2-} and Cl^- at concentration of anions 1 mmol/L was investigated. The results are presented at Fig. 5.

As removal efficiency decreased insufficiently. Although Carbonate anion had greater influence on adsorption process, especially adsorption of As(V) in comparison with Sulfate and Chlorine anions which might be caused by the competition between the carbonate and arsenic for the binding sites of the adsorbent [8, 11].

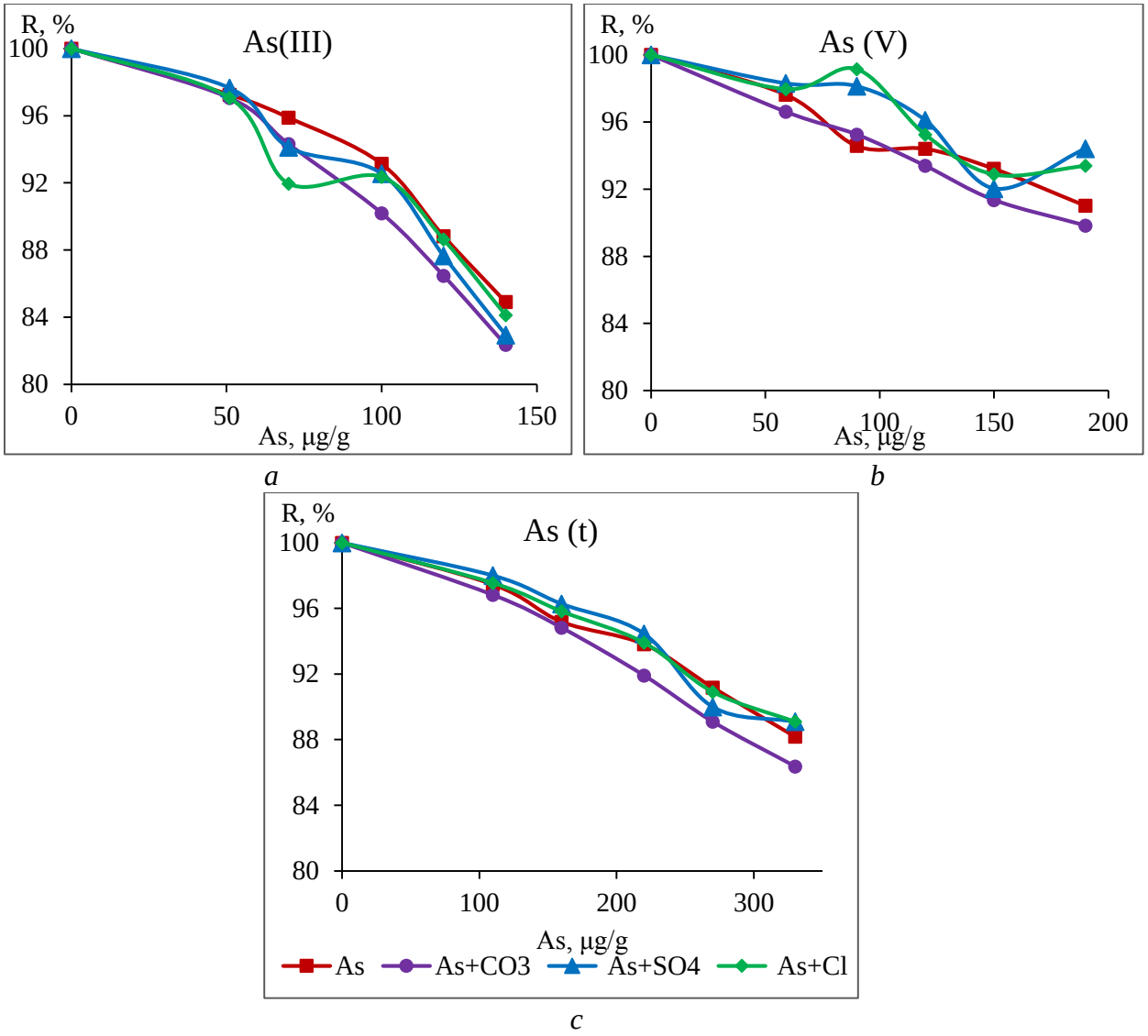

Figure 5 Effects of coexisting anions on As(V) (*a*), As(III) (*b*) and total arsenic (*c*)removal

3 Conclusions

Zirconium–manganese composite adsorbent was investigated as for arsenic removal from drinking water. Mass-spectrometry method was used to determine arsenic concentration in water samples. The samples were analysed on an Agilent 8800 ICP-MS mass-spectrometer.

The batch of adsorbent optimal dosage experiments was performed in glass bottles

The influence of solution pH (from 4 to 10) on As removal by Zr-Mn adsorbent were investigated. The highest removal was reached under pH<5. Removal percentage of As maintained above 95%. The residual content of total arsenic did not exceed 4.6 μg As/L

The adsorption kinetics of arsenic was investigated to determine the equilibrium time for adsorption process. Over 80% of the removal efficiency for both As(III) and As(V) was achieved within 1 hour, although the adsorption of As(V) happened more quickly than As(III). For both As(III) and As(V) the experimental data fitted pseudo-second-order model, which indicates that the adsorption process might be chemisorption. The value of k2 for As(V) adsorption (1,13 g/(mg*min)) is higher than for As(III) adsorption (0,29 g/(mg*min)) under the same experimental conditions, confirming that the removal of As(V) was faster than As(III).

The arsenic adsorption capacity of Zr-Mn adsorbent was investigated by the equilibrium adsorption isotherm study. The Henry, Langmuir and Freundlich models were used to describe the adsorption isotherms. According to the value of regression coefficients (R2) and due to low concentration of As in initial solutions Henry model is more suitable for describing the adsorption behavior of both As(V) and As(III).

The effect of presence of other anions, such as $SO4^{2-}$, $CO3^{2-}$ and Cl^{-} at concentration of anions 1 mmol/L was investigated. Arsenic removal efficiency decreased insufficiently. Although Carbonate anion had greater influence on adsorption process, especially adsorption of As(V) in comparison with Sulfate and Chlorine anions.

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