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## Arsenic removal from aqueous solutions by sorption onto zirconium- and titanium-modified sorbents

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**Abstract:** Arsenic reduction in drinking water can include treatment by adsorption, switching to alternative water sources, or blending with water that has a lower arsenic concentration. Commercial sorbents MTM, Greensand and BIRM (Clack Corporation) were modified with zirconium and titanium after activation. The modifications were performed with titanium tetrachloride and zirconium tetrachloride. The modified sorbents were dried at different temperatures. The sorption of arsenate and arsenite dissolved in drinking water (200 µg L<sup>-1</sup>) onto the sorbents were tested using a batch procedure. After removal of the sorbent, the concentration of arsenic was determined by hydride generation atomic absorption spectrometry (HG-AAS). Zirconium-modified BIRM showed the best performance for the removal of both arsenite and arsenate. Modification of the greensand did not affect arsenic sorption ability. Zirconium-modified BIRM diminished the concentration of total As to below 5 µg L<sup>-1</sup>.

**Keywords:** arsenic; sorption; modified sorbent; drinking water.

### INTRODUCTION

Arsenic contamination of drinking water resources is a major environmental problem in many countries of the world. As a naturally occurring toxic substance in the Earth's crust, arsenic enters into aquifers and wells through natural processes, and into the water cycle as a result of anthropogenic activities.<sup>1</sup> Arsenic pollution has been reported in the USA, Mexico, Bangladesh, China and Japan.<sup>2–6</sup> In Serbia, high concentrations of arsenic were found in some regions of the Province Vojvodina.<sup>7</sup> In January 2001, the United States Environmental Protection

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Agency (EPA) published a new standard for arsenic in drinking water, requiring public water supplies to reduce arsenic from 50 to 10 ppb by 2006.<sup>8</sup> Although many different methods, such as precipitation,<sup>9</sup> ion-exchange<sup>10</sup> and reverse osmosis,<sup>11,12</sup> have been used for arsenic removal, adsorption from solution has received more attention due to its high concentration efficiency.<sup>13,14</sup> In this paper, arsenic adsorption onto modified commercial sorbents, BIRM, GS and MTM, is presented. These commercially available sorbents were successfully used for removal iron and manganese compounds from raw water supplies.<sup>2,15</sup> Previously published results showed the efficiency of zirconium and titanium dioxide in arsenic removal.<sup>16–22</sup>

The aim of the present study was to examine influence of the modification of commercial sorbents with titanium and zirconium on their sorption characteristics. The influence of the initial pH on the sorption characteristic of the modified sorbents was also investigated.

## EXPERIMENTAL

### *Instrumentation and apparatus*

An optical emission spectrometer with inductively coupled plasma iCAP-6500 Duo (Thermo scientific, United Kingdom) was used for the measurements. The system was equipped with an integrated unit for hydride generation. The detector was a RACID86 charge injector device (CID). A SpectrAA 55-Varian (CA, USA) was also used.

Microwave digestion was performed in a pressurized microwave oven (Ethos 1, Advanced Microwave Digestion System, Milestone, Italy) equipped with a rotor holding 10 cuvettes (PTFE).

### *Sorbent materials*

BIRM (Burgess Iron Removal Media) can be used as a replacement media for manganese greensand in an iron and manganese removal filter. This media is manganese dioxide-coated alumina silicate, with the following physical properties: effective size: 0.61 mm and uniformity coefficient: 1.72. When used as an iron removal media, BIRM acts as a catalyst to enhance the reaction between dissolved oxygen (DO) and the iron compounds found in many groundwater supplies.

Manganese greensand (GS) is a zeolite mineral called glauconite processed with manganese sulfide or manganese sulfate and potassium permanganate in alternating steps to produce a black precipitate of manganese dioxide on the granules (effective size: 0.33 mm and uniformity coefficient: <1.60)

MTM is a granular manganese dioxide filtering media used for reducing iron, manganese and hydrogen sulfide from water. Its active surface coating oxidizes and precipitates soluble iron and manganese. MTM consist of a light weight granular core with a coating of manganese dioxide. MTM is an example of contact oxidation where the media itself provides the oxidizing potential (effective size: 0.43 mm and uniformity coefficient: 2.0)

*Modification of the sorbents.* For the activation of sorbents, 200 g of sorbent was mixed with 800 mL distilled water and 12 mL concentrated HCl in a 1 L glass beaker for 2 h. The sorbent was then filtered and washed with distilled water until a negative reaction for Cl ions was attained. Finally, the sorbent was dried at 105 °C for 2 h.

For the modification of the sorbents with zirconium,  $ZrCl_4$  was used. 10.79 g of  $ZrCl_4$  was placed in 1 L flask with 800 mL water and 200 g of activated sorbent. The solution was mixed for 24 h. After mixing, the sorbent was filtered and washed with distilled water until a negative reaction for Cl ions was obtained. The sorbents was dried at 105 °C for 2 h and then at 200 °C for 4 h.

For the modification of sorbents with titanium,  $TiCl_4$  was used. Into a 250 mL glass containing 100 mL distilled water with ice was added 17.21 g  $TiCl_4$  under vigorous stirring. After all the ice had melted, the solution was transferred into a 1 L flask containing 800 mL water and 200 g of activated sorbent. The solution was mixed for 24 h. After mixing, the sorbent was filtered and washed with distilled water until a negative reaction for Cl ions. The sorbent was dried at 105 °C for 2 h and then at 200 °C for 4 h.

The modified sorbents were decomposed in a Pt-crucible. 0.5 g of finely crushed sample was treated with 15 mL hydrofluoric acid (40 %) in a platinum crucible and heated on a water bath (90 °C). The hydrofluoric acid treatment was repeated. To the residue, 8–10 mL of HF (40 %) and 6 mL of 1:1  $H_2SO_4$  were added followed again by heating in a water bath, initially for 2 h, and then on a hot plate until the fumes of  $H_2SO_4$  ceased to evolve. The  $H_2SO_4$  fuming was repeated in order to completely remove fluoride as HF. The residue was then cooled, 1–2 mL concentrated  $HNO_3$  added and the heating continued.  $HNO_3$  treatment of the residue was repeated two or three times to remove any organic matter present. The residue was then dissolved in 20–30 mL of water on a water bath. The solution was transferred to a 250 mL beaker, and about 200 mL of water was added. The solution was boiled and then filtered. The filtrate was finally transferred to a 250 mL volumetric flask and made up to the mark with distilled water. The amount of Zr, respectively Ti, was determined by AAS. The amounts of Ti and Zr were also determined by ICP-OES after digestion in 5 mL 85 %  $H_3PO_4$ , 4 mL 37 % HCl and 0.5 mL 40 % HF in a pressurized microwave.

#### *Batch sorption tests*

All batch experiments were realized in 50 mL plastic flasks with drinking water spiked with 200  $\mu\text{g L}^{-1}$  As(III) or drinking water spiked with 200  $\mu\text{g L}^{-1}$  As(V). The removal of arsenite and arsenate was evaluated for the sorbents BIRM, Greensand (GS) and MTM modified with Zr and Ti and dried at different temperatures. Batch adsorption experiments were conducted by taking 40 mL of 200  $\mu\text{g L}^{-1}$  of As(III) or 40 mL of 200  $\mu\text{g L}^{-1}$  of As(V) into tightly capped 50 mL plastic flasks and adding the sorbent ( $0.3000 \pm 0.0010$  g). The plastic flasks were shaken for 1 h at room temperature. Solutions were separated by centrifugation at 3,500 rpm and the As concentrations were determined by HG-AAS.

#### *Adsorption isotherms*

Adsorption isotherms were obtained by adding different concentrations of As(III) or As(V) solution to the drinking water in 50 mL plastic flasks with 0.3000 g of MTM-Ti sorbent activated at 200 °C. The concentrations were 0.200, 0.400, 0.600, 0.800, 1.000 and 1.200 mg  $L^{-1}$ . The volume of the solution was 40 mL in all experiments. The plastic flasks were shaken for 1 h at room temperature. The solutions were separated by centrifugation at 3500 rpm and the As concentrations were determined by HG-AAS.

#### *Effect of pH on As sorption*

For the pH study, 50 mL plastic flasks were filled with 40 mL of 200  $\mu\text{g L}^{-1}$  As(III) or As(V) and 0.3000 g of modified sorbent. The correct amount of acid (HCl) or base (NaOH) solution required to adjust the pH to the target value was added. pH values of approximately 5.0; 5.5; 6.0; 6.5; 7.0 and 8.0 were used. For every pH value, the *Eh* value was measured. The

plastic flasks were shaken for 1 h at room temperature. The solutions were then separated, the pH and *Eh* values were measured and the As concentrations were determined by HG-AAS.

#### *Arsenic analysis*

Total arsenic analyses were performed using a SpectrAA 55-Varian instrument (CA, USA) equipped with an integrated unit for hydride generation. The measurements were based on the integrated absorbance using a hollow cathode lamp (Varian) at 193.7 nm.

Arsenic hydride was generated from 0.6 % NaBH<sub>4</sub> (in 0.5 % NaOH) and 6 mol L<sup>-1</sup> HCl.<sup>17</sup>

### RESULTS AND DISCUSSION

After decomposition of modified sorbents and their analysis by AAS and ICP-OES, good agreement between the two methods was obtained. The amounts of Zr and Ti were between 0.25–1.95 % (w/w) after modification of the activated sorbents (Table I).

TABLE I. Content of Zr and Ti (%) after modification of the activated sorbents

Sorbent	Ti	Zr
GS	0.6	0.85
BIRM	1.45	1.95
MTM	0.95	0.25

In the first series of experiments, the adsorption of As(III) and As(V) species on commercial sorbents and modified sorbents was examined. Greensand (GS) showed no capability for As adsorption (Table II). Modification of Greensand did not have a significant influence on the adsorption. Unmodified BIRM also did not adsorb arsenic but after modification with titanium or zirconium, good results were obtained in both cases. MTM adsorbed both species but after modification with titanium, the level of arsenic decreased by up to eight times. After modification with zirconium, inferior results were obtained.

TABLE II. Final arsenic concentrations ( $\mu\text{g L}^{-1}$ ) in solution after treatment with various sorbents dried at 200 °C. Initial As(III) and As(V) concentrations: 200  $\mu\text{g L}^{-1}$

Sorbent	As(III)	As(V)
BIRM	183.8±11.4	192.3±6.1
BIRM-Ti, 200 °C	26.4±1.4	12.2±0.8
BIRM-Zr, 200 °C	24.8±3.3	1.0±0.0
GS	174.2±22.4	191.0±1.2
GS-Ti, 200 °C	133.6±7.8	152.2±7.0
GS-Zr, 200 °C	149.4±10.0	131.4±4.2
MTM	68.8±17.8	41.7±0.7
MTM-Ti, 200 °C	20.4±9.1	9.6±2.0
MTM-Zr, 200 °C	132.7±20.4	137.2±7.8

Batch As(III) and As(V) adsorption tests were performed using activated BIRM modified with Zr and Ti and MTM modified with Ti. The effects of the

temperature employed for drying the sorbents are given in Tables II–V. Sorbents were dried at the defined temperature for 4 h.

From the results presented in Tables II–V, it could be concluded that As(III) and As(V) sorption capabilities were decreased at high drying temperatures. Heating of the sorbents at temperatures higher than 200 °C decreased the As(III) and As(V) sorption. This decrease may be due to dehydration of sorbents. Increasing the drying temperature resulted in a decrease in the number of OH<sup>-</sup> groups, which were probably the active sorption sites and responsible for the sorption of As. The maximum arsenic sorptions were achieved using sorbents dried at 200 °C.

TABLE III. Final arsenic concentrations ( $\mu\text{g L}^{-1}$ ) in solution after treatment with BIRM–Ti sorbents activated at various temperatures. Initial As(III) and As(V) concentrations: 200  $\mu\text{g L}^{-1}$

$t / ^\circ\text{C}$	As(III)	As(V)
150	3.1±1.0	3.6±1.0
200	4.4±1.8	2.4±1.4
250	15.0±4.6	10.4±2.1
300	16.4±2.4	12.8±0.6
400	38.0±3.6	26.6±2.6

TABLE IV. Final arsenic concentration ( $\mu\text{g L}^{-1}$ ) in solution after treatment with BIRM–Zr sorbents activated at various temperatures. Initial As(III) and As(V) concentrations: 200  $\mu\text{g L}^{-1}$

$t / ^\circ\text{C}$	As(III)	As(V)
150	4.3±1.0	2.4±1.4
200	9.8±3.4	2.6±1.4
250	26.2±4.2	14.6±0.1
300	29.4±10.7	26.5±8.0
400	45.6±2.8	26.8±0.4

TABLE V. Final arsenic concentrations in solution ( $\mu\text{g L}^{-1}$ ) after treatment with MTM–Ti sorbents activated at various temperatures. Initial As(III) and As(V) concentrations: 200  $\mu\text{g L}^{-1}$

$t / ^\circ\text{C}$	As(III)	As(V)
150	4.4±2.4	4.5±1.2
200	3.8±2.8	1.1±0.1
250	12.7±0.2	10.3±0.5
300	15.2±0.6	15.8±4.0
400	43.2±9.7	22.8±9.5

In order to obtain more information on the sorption by the MTM–Ti sorbent activated at 200 °C, another series of batch experiments were performed with different concentrations of As(III) and As(V). These results were used for the calculation of the constants of the Freundlich and Langmuir adsorption isotherms.<sup>23</sup> The linearized form of the Freundlich Equation was used:

$$\log (x/m) = \log K + (1/n)\log c$$

where  $x$  is the mass of adsorbed arsenic,  $m$  is the mass of sorbent,  $c$  is the equilibrium concentration of arsenic in solution after sorption,  $K$  is a constant, and  $n$  is a constant. The constant  $K$  is related primarily to the capacity of the sorbent and  $n$  is a function of the strength of the sorption (Figs. 1 and 2).

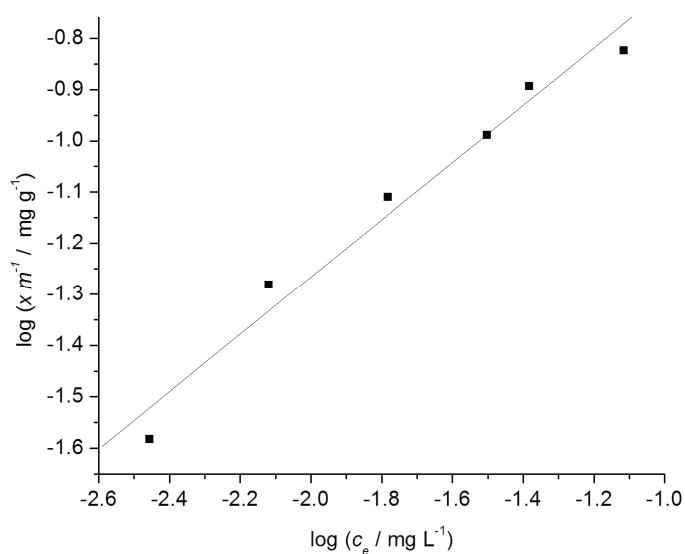


Fig. 1. Freundlich plot for As(III) sorption by MTM-Ti 200 °C.

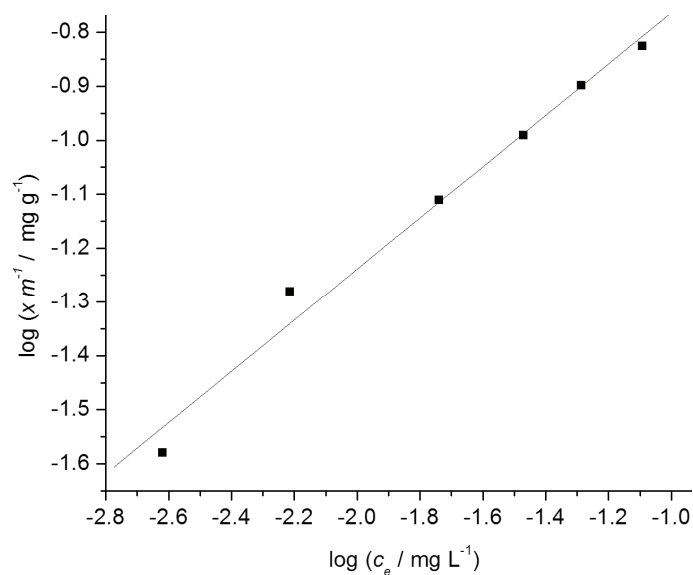


Fig. 2. Freundlich plot for As(V) sorption by MTM-Ti 200 °C.

The values of  $K$  and  $n$  obtained from adsorption isotherms are summarized in Table VI.

The Langmuir Equation is given by:

$$c_e/Q_e = 1/(bQ^0) + c_e/Q^0$$

where  $c_e$  is the equilibrium concentration,  $Q^0$  is a constant that represents the maximum adsorption density corresponding to a monolayer covering of the surface of the adsorbent,  $b$  is a constant that represents the adsorption bond energy and  $Q_e$  is the mass of arsenate sorbed per unit dry weight of adsorbent. This equation was used to describe the adsorption data presented in Figs. 3 and 4.

TABLE VI. Freundlich and Langmuir constants for the sorption of As(III) and As(V) by the MTM-Ti sorbent activated at 200 °C

Ion	Freundlich			Langmuir	
	$K / \text{mg g}^{-1}$	$n$	$R^2$	$Q^0 / \text{mg g}^{-1}$	$R^2$
As(III)	0.711	1.27	0.9718	0.193	0.9902
As(V)	0.514	2.11	0.9841	0.174	0.9757

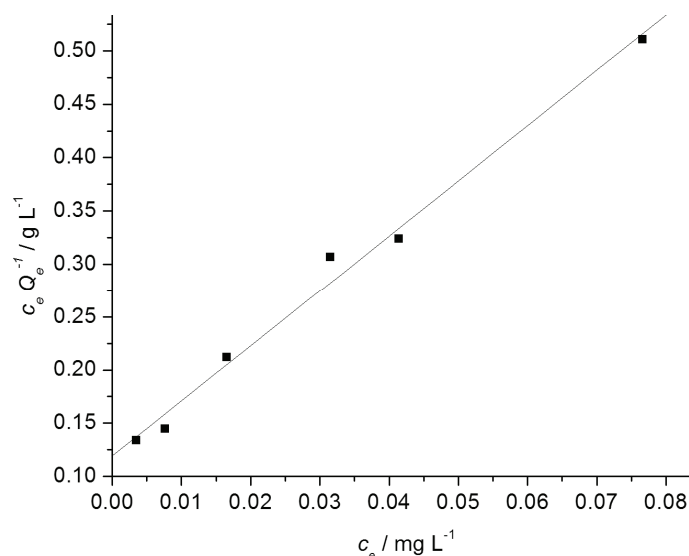


Fig. 3. Langmuir plot for As(III) sorption by MTM-Ti 200 °C.

In the case of As(III), the data fitted the Langmuir model, which assumes reversible mono-layer coverage, was better, while for As(V), a better correlation coefficient was achieved with the Freundlich Equation (Table VI).

As pH is an important parameter in adsorption processes, the effect of the initial pH of the solution on the sorption of As(III) and As(V) was investigated. In the pH range 5 to 8, there was no significant correlation between pH and the

sorption capacity. For an initial arsenic concentration of  $200 \mu\text{g L}^{-1}$ , the final arsenic concentrations were below the maximum permissible limit ( $10 \mu\text{g L}^{-1}$ ) for all the investigated pH values. The results in Table VII show that the sorbent does not have a significance influence on the pH and  $Eh$  of the solution in the pH range and experimental conditions applied in these investigations. This range of pH for adsorption of arsenic should be advantageous under real conditions.

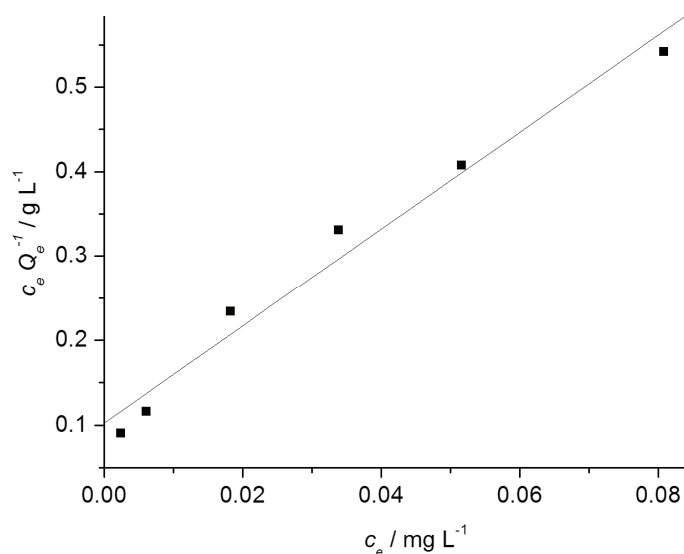


Fig. 4. Langmuir plot for As(V) sorption by MTM-Ti 200 °C.

TABLE VII. Changes in pH and  $Eh$  during the adsorption experiments (after 1 h shaking with sorbent MTM-Ti 200 °C)

Initial pH	pH	Initial $Eh$ , mV	$Eh$ / mV
5.00	5.21	404	405
5.52	5.73	385	375
6.04	6.24	361	352
6.49	6.62	346	340
6.95	6.98	336	354
7.56	7.39	293	310
8.01	7.63	280	300

#### CONCLUSIONS

After activation and modification with Zr and Ti, BIRM had higher sorption capacities. There was no improvement in the sorption capacity of GS after its activation and modification with Zr and Ti. MTM had better sorption capacities after activation and modification with Ti.

The BIRM-Zr, BIRM-Ti and MTM-Ti modified sorbents had high sorption capacities for As(III) and As(V) in the pH range of natural water. These modified



sorbents, dried at 200 °C, removed arsenic from drinking water spiked with 200  $\mu\text{g L}^{-1}$  of As(III) and As(V) to below the maximum permissible limit. With increasing drying temperature, the sorption capacities decreased. The optimal drying temperature for the modified sorbents was 200 °C.

Changing the pH of the solution in the range from 5 to 8 had no obvious effect on the sorption. In addition, the sorbents had no significant influence on the pH and *Eh* of the solution.

The obtained batch experimental results suggested that these modified sorbents could be used for As(III) and As(V) removal under real conditions.

#### ИЗВОД

#### УКЛАЊАЊЕ АРСЕНА ИЗ ВОДЕНИХ РАСТВОРА СОРПЦИЈОМ НА СОРБЕНТИМА МОДИФИКОВАНИМ ЦИРКОНИЈУМОМ И ТИТАНОМ

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Уклањање арсена из подземних вода може укључивати третман сорпцијом, прелазак на алтернативне изворе воде или мешање са водом која садржи ниске концентрације арсена. Комерцијални сорбенти МТМ, *Greensand* и BIRM су модификовани цирконијумом и титаном после активације. Модификација је урађена титан-тетрахлоридом и цирконијум-тетрахлоридом. Модификовани сорбенти су сушени на различитим температурама. Сорпција арсената и арсенита растворених у пијаћој води је тестирана *batch* поступком. После уклањања сорбента концентрација арсена је одређена HG-AAS методом. BIRM модификован цирконијумом је показао најбоље резултате у уклањању арсенита и арсената. Модификација *Greensand*-а није утицала на повећање сорпционе моћи. BIRM модификован цирконијумом је смањио концентрацију арсена испод 5  $\mu\text{g L}^{-1}$ .

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