



ORIGINAL ARTICLE

# Microwave-hydrothermal synthesis of TiO<sub>2</sub> and zirconium doped TiO<sub>2</sub> adsorbents for removal of As(III) and As(V)



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## KEYWORDS

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**Abstract** Microwave-hydrothermal method was used for the synthesis of TiO<sub>2</sub> and TiO<sub>2</sub> doped with zirconium. The method was fast and simple and adsorbents were used for removal of As(III) and As(V) from aqueous solutions. The adsorbents were characterized by BET surface area measurements and powder XRD. Experiments showed that TiO<sub>2</sub> doped with 10% of Zr using the microwave-hydrothermal method have greater specific surface area and total pore volume in comparison with TiO<sub>2</sub> synthesized using the same method. Better removal with doped adsorbent was obtained for both, As(III) and As(V). Further experiments were carried out with Zr doped TiO<sub>2</sub> sorbent in order to examine kinetic of adsorption, influence of pH and effect of common anions present in natural waters.

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## 1. Introduction

Arsenic is a ubiquitous element that ranks 20th in abundance in the earth's crust, 14th in the seawater, and 12th in the human body [1]. It was found that consumption of arsenic, even at low concentrations led to carcinogenesis. Although it was used in industrial purposes like additive to livestock, herbicide, in semiconductor industry, for preservation of wood, the greatest threat is from groundwaters that are used as a source for drinking water. The health of more than 100 million people worldwide is threatened with consumption of water

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that has elevated concentration of arsenic. In recent years elevated concentrations of arsenic in groundwater have been reported in different parts of the world, including India [2], Cambodia [3], Australia [4] and Pakistan [5].

Parallel to efforts of researchers to determine arsenic species in natural water samples [6–9] many methods have been investigated for removal of arsenic from drinking water like precipitation/coprecipitation [10], separation processes [11–13], and ion exchange [14–16]. Adsorption is considered as the best available technique for removal of arsenic from drinking water as it can be simple in operation and cost-effective. In recent years researcher investigated materials with ability to adsorb and oxidize As(III) to As(V) which are less toxic and easier to remove from water [17,18]. The application of TiO<sub>2</sub> and TiO<sub>2</sub>-based adsorbents was extensively investigated due to its physical and chemical stability, negligible toxicity as well as strong oxidizing power, easy preparation and high affinity to arsenic. It is a known fact that inorganic As(III) is more toxic and has less affinity for removal than As(V). Photocatalysis with TiO<sub>2</sub> offers a relatively inexpensive, environmentally benign way to achieve As(III) oxidation [19]. Also, in recent published papers, zirconium based sorbents showed high affinity toward arsenic adsorption [20–22].

The goal of our research was to examine the microwave-hydrothermal method for the synthesis of efficient, low-cost material for arsenic removal and the influence of doping Zr on TiO<sub>2</sub> on adsorption capabilities. Compared with conventional hydrothermal process, microwave-hydrothermal technique enables fast heating to the required temperature and extremely fast rates of crystallization. The use of microwaves for a very short time enhanced the TiO<sub>2</sub> crystallinity preventing an increase in particle size and minimized the decrease in specific surface area [23,24]. TiO<sub>2</sub> and TiO<sub>2</sub> doped with 10% of Zr materials were synthesized using this method and their efficiencies for arsenic removal were compared with commercial TiO<sub>2</sub> (Degussa P25, Germany) material. Batch experiments were conducted to examine reaction kinetics, influence of pH and presence of common anions on arsenic removal with Zr doped TiO<sub>2</sub> sorbent.

## 2. Experimental

For the synthesis of adsorbents TiCl<sub>4</sub> (Merck, Germany), ZrCl<sub>4</sub> (Merck, Germany), and NH<sub>4</sub>OH (Sigma–Aldrich, USA) chemicals of analytical grade were used. Stock solutions (1000 mg/dm<sup>3</sup>) of As(V) and As(III) were prepared by dissolving appropriate amount of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (Fluka, Spain) and NaAsO<sub>2</sub> (Fisher Scientific, USA) in deionized water, respectively. HCl (Sigma Aldrich, USA) and NaOH (Sigma Aldrich, USA) were used to adjust solution pH.

Sorbent was prepared using the microwave-hydrothermal method. In a typical preparation procedure, TiCl<sub>4</sub> was added to icy deionized water (TiCl<sub>4</sub>:H<sub>2</sub>O (v/v) ratio 1:10) and homogeneous and transparent solution was obtained. Then, the solution was subjected to precipitation by the slow addition of 30% NH<sub>4</sub>(OH) under constant stirring at room temperature. The hydrolysis was controlled with the addition of NH<sub>4</sub>(OH), until the reaction mixture attained pH between 7 and 8. The suspension was transferred into Teflon microwave closed vessels (digestion system ETHOS 1 Milestone, equipped with a High Pressure Rotor SK-10, Italy), sealed and heated by

microwave irradiation reaching a maximum temperature of 150 °C in 10 min, then kept at this temperature for 15 min more for hydrothermal treatment. The resulting product was separated by centrifugation and washed repeatedly with deionized water until the precipitate became free of chloride ion. Finally, it was dried at 80 °C for 5 h and then calcined at 500 °C for 10 h. Doped TiO<sub>2</sub> sample was prepared according to the above procedure including addition of zirconium salt in water to give 10% of dopant. Dopant concentration mentioned was expressed as the weight percent. The amount of Zr doped on TiO<sub>2</sub> was determined after total degradation of doped sorbent in MW digestion system. 0.1000 g of sorbent was treated with 5 cm<sup>3</sup> 85% H<sub>3</sub>PO<sub>4</sub> (Sigma–Aldrich, USA), 3 cm<sup>3</sup> 37% HCl and 0.5 cm<sup>3</sup> 48% HF (Sigma–Aldrich, USA) in 100 cm<sup>3</sup> PTFE. Applied MW digestion program was 15 min until 220 °C was reached and additional 20 min at 220 °C. After the degradation, the solution was transferred to a 25 cm<sup>3</sup> volumetric flask and Zr was determined on ICP-AES (iCap 6500Duo, Thermo Scientific, UK). Adsorbent TiO<sub>2</sub> doped with 10% of zirconium was labeled as 10Zr/TiO<sub>2</sub>.

X-ray powder diffraction (XRPD) was used for identification of crystalline phases, quantitative phase analysis and estimation of crystallite size and strain. XRPD patterns were collected using a Philips diffractometer PW1710 employing CuK $\alpha$  radiation. Step scanning was performed with  $2\theta$  ranging from 20° to 100°, step size of 0.10° and the fixed counting time of 5 s per step. XRPD patterns were used to refine crystallographic structure and microstructural parameters using the procedure implemented in the FullProf computer program [25].

Adsorption–desorption isotherms were obtained by nitrogen adsorption at –196 °C using a Sorptomatic 1990 Thermo Finnigan device. Prior to adsorption, the samples were degassed for 1 h at room temperature under vacuum and additionally for 16 h at 110 °C at the same residual pressure. The specific surface area of samples ( $S_{\text{BET}}$ ) was calculated by applying the Brunauer–Emmett–Teller equation, from the linear part of the adsorption isotherm [26]. Total pore volumes ( $V_{\text{tot}}$ ) were obtained from the N<sub>2</sub> adsorption, expressed in liquid form, by applying Gurevitch's rule [27]. Micropore volumes ( $V_{\text{mic}}$ ) were estimated according to the Dubinin–Radushkevich method [28]. Mesopore volumes ( $V_{\text{mes}}$ ) were estimated according to the Barrett, Joyner and Halenda method from the desorption branch of the isotherm [29].

The point of zero charge (pH<sub>pzc</sub>) was determined in accordance with procedure described by Babic et al. [30].

The sorption kinetic study was carried out at pH 7. The initial concentration of As(III) and As(V) was 10 mg/dm<sup>3</sup> in 0.01 M NaCl (Lach-ner, Czech Republic) for adjustment of ionic strength. In plastic flask 100 cm<sup>3</sup> of arsenic solution and 50 mg of adsorbent were mixed for 30, 60, 120, 240, 360, 720, 1440 and 2880 min at room temperature (20 ± 2 °C). After specified period of time samples were filtered through 0.45 μm membrane filter and pH was checked.

The effect of pH on As(III) and As(V) adsorption was examined in the range from 3 to 11. 100 cm<sup>3</sup> of 10 mg/dm<sup>3</sup> arsenic solution was adjusted to required pH value and 50 mg of adsorbent was added. Well capped plastic bottles were shaken for 1 h at room temperature and solutions were filtered using 0.45 μm membrane filter.

Adsorption isotherm experiments were conducted at room temperature and at pH 3.0 ± 0.2 by batch adsorption

procedure. Experiment was performed by adding different concentrations of As(III) and As(V) in 0.01 M NaCl solution in 100 cm<sup>3</sup> plastic flasks with 50 mg of adsorbent. The concentrations of arsenic were in the range of 1–10 mg/dm<sup>3</sup>. The volume of solution was 100 cm<sup>3</sup> in all experiments. Plastic flasks were shaken for 1 h. The samples were filtered through a 0.45 mm membrane filter.

In order to examine the influence of common anions (phosphate and sulfate) along with arsenic in water on the adsorption capabilities of adsorbents, two concentrations of anions, 1 mM and 5 mM, in 100 cm<sup>3</sup> 1 mg/dm<sup>3</sup> arsenic solution in 0.01 M NaCl at pH 3 were mixed with 50 mg of sorbent for 1 h. The quantity of adsorbed arsenic with and without these salts was compared.

All samples in experiments were analyzed within 24 h. Total arsenic concentrations were determined with ICP-AES. Instrument was equipped with pneumatic nebulizer and RACID86 detector. The parameters of analysis were: pump rate 50 rpm, nebulizer gas flow 0.5 cm<sup>3</sup>/min, auxiliary gas flow 0.5 cm<sup>3</sup>/min, coolant gas flow 12 dm<sup>3</sup>/min, and RF power 1150 W.

All experiments performed in triplicate and average values are reported. Variations between parallel experiments were less than 7%.

### 3. Results and discussions

The most intensive diffraction peaks in the powder XRD patterns of TiO<sub>2</sub> and 10Zr/TiO<sub>2</sub> (Fig. 1) can be ascribed to the anatase crystal structure (JCPDS card 78-2486). The presence of broad low-intensity diffraction peak at  $2\theta \approx 30.8^\circ$  can be ascribed to the brookite phase of TiO<sub>2</sub> (JCPDS card 29-1360). The content of brookite phase can be estimated less than 3% in TiO<sub>2</sub> sample. For 10Zr/TiO<sub>2</sub> sample there was an increase in brookite phase for 19%. Structure refinements were performed by the Rietveld method.

After total digestion of material, the percentage of Zr doped on TiO<sub>2</sub>, determined with ICP-AES, was 8.6%. Microwave-hydrothermal method was very efficient for the synthesis of doped materials as 86% of totally added Zr was incorporated in the structure of TiO<sub>2</sub>.

Determined  $\text{pH}_{\text{pzc}}$  of 10Zr/TiO<sub>2</sub> was  $6.6 \pm 0.2$ . Below this pH the surface charge of adsorbent is positive and predominantly exhibits an ability to exchange anions.

Physical parameters of TiO<sub>2</sub> and 10Zr/TiO<sub>2</sub> synthesized using the microwave-hydrothermal method are presented in

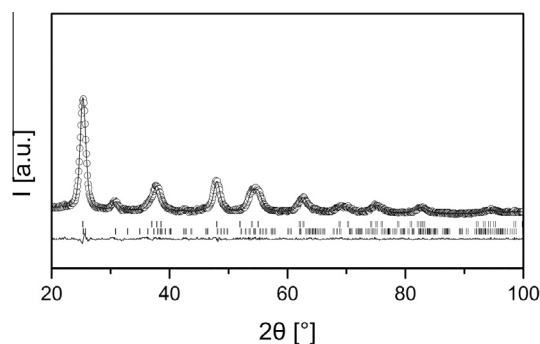


Figure 1 XRD diffractogram of 10Zr/TiO<sub>2</sub>.

Table 1. Specific surface area for TiO<sub>2</sub> was slightly higher than that reported for TiO<sub>2</sub> (Degussa P25) [19]. Comparing specific surface area, total pore volume and micropore volume of TiO<sub>2</sub> with TiO<sub>2</sub> doped with Zr we can see 3.5, 2 and 4-fold increase for doped TiO<sub>2</sub>, respectively. A large specific surface area is preferable for providing large adsorption capacity. Also, the size of micropore determines the accessibility of adsorbate molecules to the adsorption surface, so the increase in these two properties of material could be beneficial for its sorption properties.

#### 3.1. Adsorption isotherms

In order to determine adsorption capabilities of TiO<sub>2</sub> synthesized using the microwave-hydrothermal method and influence of doped zirconia on adsorption capacity of TiO<sub>2</sub>, adsorption capacities of commercially available TiO<sub>2</sub> (Degussa P25), TiO<sub>2</sub> and 10Zr/TiO<sub>2</sub> were compared. Experimental data for adsorption of As(III) and As(V) on adsorbents were fitted with Freundlich and Langmuir isotherm equations. Also, for 10Zr/TiO<sub>2</sub> adsorbent, adsorption experiments were done at two pH values, 3 and 7.

The expression for Freundlich isotherm model was given as follows:

$$Q = K_f C_e^{1/n} \quad (1)$$

where  $Q$  (mg/g) is the amount of adsorbed arsenic per unit of adsorbent,  $K_f$  is a Freundlich constant related to adsorption capacity,  $C_e$  (mg/dm<sup>3</sup>) is the equilibrium arsenic concentration, and  $n$  is a dimensionless Freundlich constant.

The Langmuir isotherm model is expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

where  $Q_e$  (mg/g) is the amount of adsorbed arsenic per unit of adsorbent,  $C_e$  (mg/dm<sup>3</sup>) is the equilibrium concentration of arsenic,  $Q_m$  (mg/g) is the amount adsorbed per unit weight of adsorbent required for monolayer capacity, and  $b$  (dm<sup>3</sup>/mg) is the Langmuir constant.

Slightly better correlation coefficients for adsorption of As(III) onto 10Zr/TiO<sub>2</sub> were obtained with Freundlich isotherm model at both pH (Table 2). At pH 7 for As(V) adsorption follows Freundlich model while for pH 3 better fit was achieved with Langmuir model. With the increase in pH from 3 to 7, adsorption capacity of As(III) increases while of As(V) decreases. Depending on whether As(III) or As(V) is dominant form of arsenic in water, the adjustment of pH can be used to achieve the maximum adsorption capacity of target species.

Commercially available TiO<sub>2</sub> (Degussa P25) was examined as a sorbent for arsenic by several researchers [31,32]. We compared Degussa P25 sorbent with our TiO<sub>2</sub> synthesized using the microwave-hydrothermal method, under identical experimental conditions. Sorption capacities, derived from Langmuir isotherm, for Degussa P25 were 3.66 and 6.61 mg/g for As(III) and As(V), respectively. Specific surface area of Degussa P25 (55 m<sup>2</sup>/g) is lower compared with our TiO<sub>2</sub> (66 m<sup>2</sup>/g) that could be the reason for smaller sorption capacity of Degussa P25.

Significant increase in 10Zr/TiO<sub>2</sub> adsorption capabilities toward both As(III) and As(V) was observed in comparison with TiO<sub>2</sub>, derived from Langmuir model. The reason for this

**Table 1** Comparison of physical properties of TiO<sub>2</sub> and 10Zr/TiO<sub>2</sub>.

Adsorbents	TiO <sub>2</sub>	10Zr/TiO <sub>2</sub>
Pore volume (Gurvich) at $p_0$ , cm <sup>3</sup> g <sup>-1</sup>	0.236	0.465
Specific surface area, m <sup>2</sup> g <sup>-1</sup>	66	231
Mesopores (B.J.H.) desorption, Stand. Lecloux, Cumulative pore volume, cm <sup>3</sup> g <sup>-1</sup>	0.306	0.357
Micropore volume (Dubinin and Raduskevich), cm <sup>3</sup> g <sup>-1</sup>	0.019	0.074

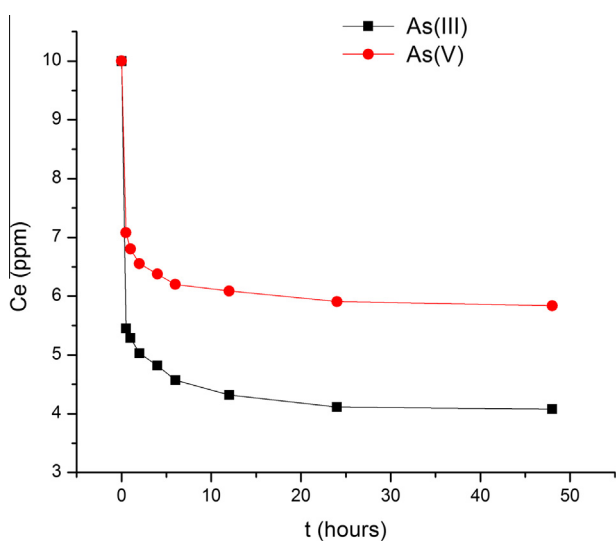
**Table 2** Freundlich and Langmuir adsorption parameters for As(III) and As(V) adsorption onto 10Zr/TiO<sub>2</sub> ( $Q_0$  (mg/g)). Experiments were conducted at room temperature. Initial arsenic concentration ranged from 1 to 10 mg/dm<sup>3</sup>. Concentration of sorbent was 0.5 g/dm<sup>3</sup>. Reaction time was 1 h.

Adsorbent	Freundlich		Langmuir	
	As(III)	As(V)	As(III)	As(V)
10Zr/TiO <sub>2</sub>				
pH 3	$R^2 = 0.9825$ $K_f = 5.04$	$R^2 = 0.9539$ $K_f = 10.91$	$R^2 = 0.9592$ $Q_0 = 8.23$	$R^2 = 0.9960$ $Q_0 = 13.72$
pH 7	$R^2 = 0.9984$ $K_f = 5.73$	$R^2 = 0.9818$ $K_f = 4.24$	$R^2 = 0.9955$ $Q_0 = 9.76$	$R^2 = 0.9731$ $Q_0 = 7.18$
TiO <sub>2</sub> pH 3	$R^2 = 0.9888$ $K_f = 3.66$	$R^2 = 0.9997$ $K_f = 5.34$	$R^2 = 0.9542$ $Q_0 = 5.52$	$R^2 = 0.9941$ $Q_0 = 7.39$
TiO <sub>2</sub> (Degussa P25) pH 3	$R^2 = 0.9757$ $K_f = 1.71$	$R^2 = 0.9737$ $K_f = 2.70$	$R^2 = 0.9739$ $Q_0 = 3.66$	$R^2 = 0.9927$ $Q_0 = 6.61$

improvement could be greater surface area and pore volume of doped adsorbent.

### 3.2. Kinetic study

Kinetic of adsorption of As(III) and As(V) at pH  $7.0 \pm 0.2$  and room temperature ( $20 \pm 2$  °C) is shown in Fig. 2. The initial rate of adsorption of both As(III) and As(V) was high. During the first 30 min for As(III) more than 70% was adsorbed of the total amount that was adsorbed in 48 h. In the same period more than 67% of As(V) was adsorbed. The time required for reaching equilibrium was 24 h for both As(III) and As(V).

**Figure 2** Adsorption kinetics of As(III) and As(V) onto 10Zr/TiO<sub>2</sub>. Initial concentration of arsenic  $c_0 = 10$  mg/dm<sup>3</sup> in 0.01 M NaCl, pH = 7, adsorbent dose 0.5 g/dm<sup>3</sup>.

Two kinetic models, pseudo-first and pseudo-second, were fitted to data from kinetic experiment.

Pseudo-first-order rate expression of Lagergren equation [33] is given as follows:

$$\log(Q_e - Q_t) = \log Q_e - k_1 t \quad (3)$$

where  $Q_e$  and  $Q_t$  are the amount of arsenate adsorbed in mg/g at equilibrium and at time  $t$  (min), respectively, and  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first-order adsorption. The adsorption rate constant can be determined from the slope of the linear plot of  $\log(Q_e - Q_t)$  versus  $t$ .

Pseudo-second-order rate expression is as follows [34]:

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e} \quad (4)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the pseudo-second-order rate constant.  $k_2$  can be calculated from the slope and intercept of the plot  $t/Q_t$  versus  $t$ .

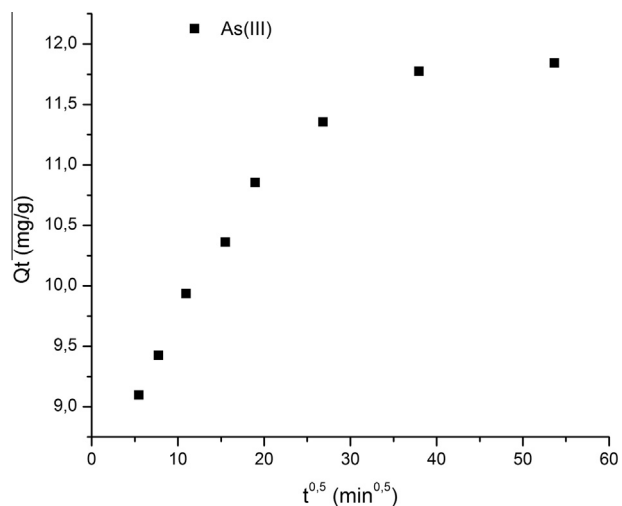
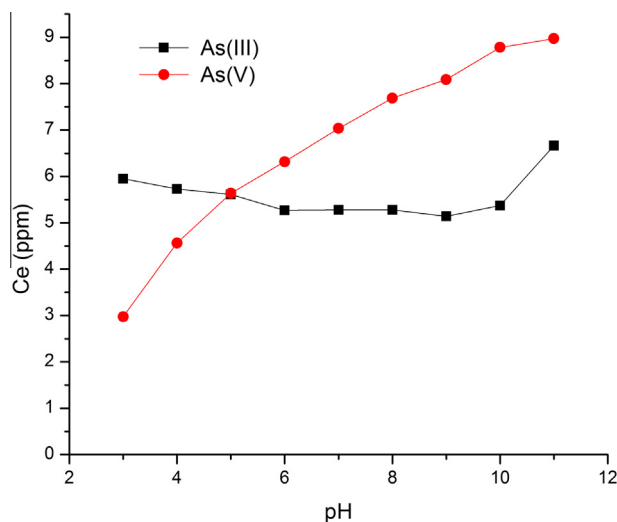
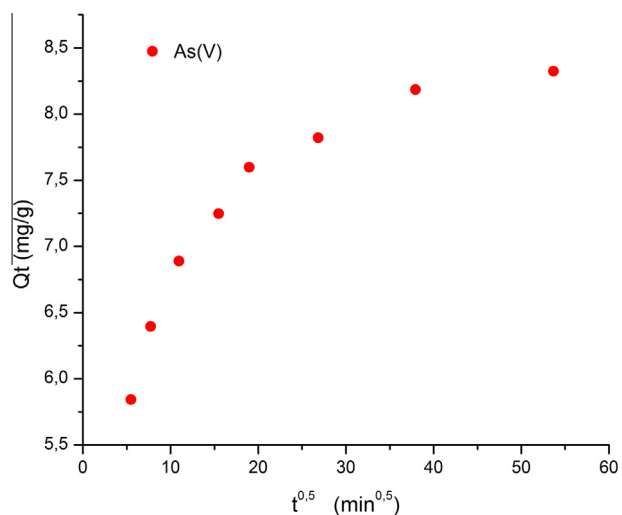
Stronger linearity was obtained with pseudo-second order model (Table 3). This indicates that the adsorption process might be chemisorption. Similar results were observed for adsorption of As(III) and As(V) on iron-zirconium binary oxide where equilibrium was achieved after 25 h and adsorption of As(III) was faster than As(V) [35]. As pseudo-second order rate model does not provide information about rate-controlling step experimental data were fitted to the Webber–Morris model [36]. If adsorption is one surface binding process and rate is limited by intra-particle diffusion, data plotted in  $Q_t$  vs.  $t^{0.5}$  should exhibit linearity and intercept at the origin. Straight lines do not pass through origin indicating that the adsorption of As(III) and As(V) is a multiple process not governed only with intraparticle diffusion (Figs. 3 and 4).

### 3.3. Effect of pH on As(III) and As(V) removal

The effect of pH on As(III) and As(V) adsorption is shown in Fig. 5. At lower initial pH the adsorbed quantity of As(III)

**Table 3** Pseudo-first and pseudo-second kinetic parameters for As(III) and As(V) onto 10Zr/TiO<sub>2</sub>. Initial concentration of arsenic  $c_0 = 10 \text{ mg/dm}^3$  in 0.01 M NaCl, pH = 7, adsorbent dose 0.5 g/dm<sup>3</sup>.

Adsorbent	Pseudo-first order		Pseudo-second order	
	$R^2$	$k_1 \text{ (min}^{-1}\text{)}$	$R^2$	$k_2 \text{ (g mg}^{-1}\text{min}^{-1}\text{)}$
10Zr/TiO <sub>2</sub> As(III)	0.9642	0.0029	0.9990	0.0041
10Zr/TiO <sub>2</sub> As(V)	0.9706	0.0025	0.9985	0.0055

**Figure 3** Intraparticle mass transfer plot for As(III) adsorption on 10Zr/TiO<sub>2</sub>. Initial concentration of arsenic  $c_0 = 10 \text{ mg/dm}^3$  in 0.01 M NaCl, pH = 7, adsorbent dose 0.5 g/dm<sup>3</sup>.**Figure 5** The effect of pH on adsorption of As(III) and As(V) onto 10Zr/TiO<sub>2</sub>. Initial concentration of arsenic  $c_0 = 10 \text{ mg/dm}^3$ , contact time 1 h, adsorbent dose 0.5 g/dm<sup>3</sup>.**Figure 4** Intraparticle mass transfer plot for As(V) adsorption on 10Zr/TiO<sub>2</sub>. Initial concentration of arsenic  $c_0 = 10 \text{ mg/dm}^3$  in 0.01 M NaCl, pH = 7, adsorbent dose 0.5 g/dm<sup>3</sup>.

slowly increased with the increase in pH to 9. With the increase in pH above 9 the decrease in adsorption occurred. This could be explained with increased electrostatic repulsion of AsO<sub>3</sub><sup>-</sup> anions, which were dominant form of As(III) above pH 9, and negative surface charge of adsorbent. For As(V) the

maximum adsorption was achieved at pH 3 and further increase in pH decreased adsorption capability almost linearly. Dominant form of As(V) at pH 3 is H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and the surface charge of adsorbent is positive. With the increase in pH, the surface charge becomes less positive up until pH<sub>pzc</sub>. After it becomes negative dominant forms of As(V) in less acidic, neutral and alkaline water are HAsO<sub>4</sub><sup>2-</sup> and/or AsO<sub>4</sub><sup>3-</sup>, resulting in increase in electrostatic repulsion of adsorbent surface and As(V) species.

#### 3.4. Effect of competing anions

PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> anions are common constituents of natural waters which have molecular structure similar to arsenic. Their influence on arsenic adsorption onto 10Zr/TiO<sub>2</sub> was investigated and results are presented in Table 4.

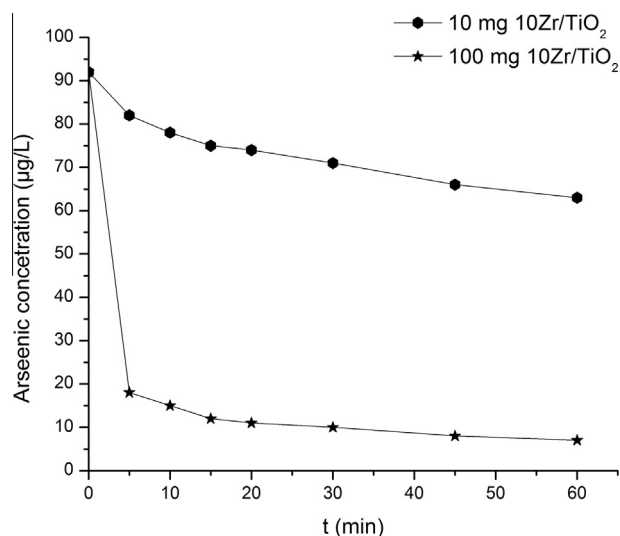
The presence of PO<sub>4</sub><sup>3-</sup> has a significant influence on As(V) adsorption on 10Zr/TiO<sub>2</sub>. With higher concentration of added anion, decrease in adsorption was more pronounced. Addition of SO<sub>4</sub><sup>2-</sup> anion did not significantly affect As(V) removal. Similar effects of PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> anions on As(V) adsorption was reported by Ren et al. [35]. As for As(III), addition of 1 mM and 5 mM PO<sub>4</sub><sup>3-</sup> achieved similar reduction in adsorption suggesting that saturation of active sites was achieved with 1 mM concentration while effect of SO<sub>4</sub><sup>2-</sup> anion was less compared with PO<sub>4</sub><sup>3-</sup>.

**Table 4** Effect of  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  anions on As(III) and As(V) adsorption onto  $10\text{Zr}/\text{TiO}_2$  adsorbent. Initial concentration of arsenic  $c_0 = 1 \text{ mg}/\text{dm}^3$ ,  $\text{pH} = 3$ , adsorbent dose  $0.5 \text{ g}/\text{dm}^3$ .

Concentration of anions	Concentration of As(V) ( $\mu\text{g}/\text{dm}^3$ ) after adsorption	Concentration of As(III) ( $\mu\text{g}/\text{dm}^3$ ) after adsorption
0	< 0.010	< 0.010
1 mM $\text{PO}_4^{3-}$	0.578	0.629
5 mM $\text{PO}_4^{3-}$	0.817	0.682
1 mM $\text{SO}_4^{2-}$	0.040	0.281
5 mM $\text{SO}_4^{2-}$	0.045	0.295

**Table 5** Chemical composition of tap water of the Zrenjanin city.

Component	Concentration ( $\text{mg}/\text{dm}^3$ )
pH	8.0
$\text{Cl}^-$	23.21
$\text{SO}_4^{2-}$	50.74
$\text{HCO}_3^-$	1705
Total P	0.67
As	0.092
Ca	14.1
Mg	10.0
K	1.4
Fe	0.61
Mn	0.027
Zn	0.26
Al	Not detected



**Figure 6** The decrease in arsenic concentration in natural water sample from the city of Zrenjanin with the increase in the contact time, for  $0.1$  and  $1.0 \text{ g}/\text{dm}^3$  adsorbent dosages (concentration of arsenic =  $92 \mu\text{g}/\text{dm}^3$ ).

### 3.5. Arsenic removal from the naturally contaminated water sample

To evaluate potential use of  $10\text{Zr}/\text{TiO}_2$  adsorbent for arsenic removal in real water samples, tap water from the city of

Zrenjanin was used (it is located in the northern part of Serbia). Groundwater was pumped from city wells and distributed to taps after the addition of chlorine. Total arsenic concentration was  $92 \mu\text{g}/\text{dm}^3$ . Other ionic species of this water sample are shown in Table 5.

Kinetic experiments with  $0.1 \text{ g}/\text{dm}^3$  and  $1.0 \text{ g}/\text{dm}^3$  loadings of  $10\text{Zr}/\text{TiO}_2$  adsorbent were carried out to investigate efficiency with natural water sample. With  $1 \text{ g}/\text{dm}^3$  adsorbent dose after 5 min of contact time the removal of arsenic was more than 80% (Fig. 6). With 30 min of contact time arsenic level in water was at the WHO recommended limit. This experiment with naturally contaminated water sample demonstrated that  $10\text{Zr}/\text{TiO}_2$  could be used to treat natural water samples with elevated concentration of arsenic.

## 4. Concluding remarks

Titanium dioxide and zirconium doped titanium dioxide, were synthesized using microwave-hydrothermal method and used for arsenic removal. XRPD patterns showed that the main phase was anatase with smaller percentage of brookite phase. Sorption capacities for As(III) and As(V) onto  $10\text{Zr}/\text{TiO}_2$  at pH 3, derived from Langmuir isotherm model, were 8.23 and 13.72 mg/g, respectively.  $\text{TiO}_2$  adsorption capacities of As(III) and As(V), at same pH (5.52 and 7.39 mg/g, respectively) were smaller compared to doped adsorbent. Compared with starting  $\text{TiO}_2$ ,  $10\text{Zr}/\text{TiO}_2$  have more developed surface area, mesopore and micropore volume as well as total pore volume which may be responsible for greater sorption capacity. In the pH range from 3 to 9 the adsorption of As(III) slightly increased, while in the same pH range substantial decrease in adsorption of As(V) was obtained. Presence of  $\text{SO}_4^{2-}$  anions affected only As(III) adsorption, while  $\text{PO}_4^{3-}$  had negative effect on both, As(III) and As(V). Initial adsorption of both arsenic species was fast. The adsorption kinetics followed the pseudo-second order rate equation for both, As(III) and As(V). Kinetic results also suggest that adsorption mechanisms were complex where both, surface adsorption and intraparticle diffusion contribute to the rate determining step. After only 30 min of treatment of natural water sample that contained  $92 \mu\text{g}/\text{dm}^3$  of total arsenic with  $1.0 \text{ g}/\text{dm}^3$   $10\text{Zr}/\text{TiO}_2$  adsorbent resulted in final arsenic concentration at the recommended WHO limit. The synthesis of zirconium doped titanium dioxide, using the microwave-hydrothermal method, provided a promising sorbent for As(III) and As(V) removal.

## References

- [1] E.A. Woolson, Arsenic: Medical and Biological Effect on Environmental Pollutants, National Academy of Sciences, Washington D.C., 1975.
- [2] M. Kumar, P. Kumar, A. Ramanathan, P. Bhattacharya, R. Thunvik, U.K. Singh, et al, Arsenic enrichment in groundwater in the middle Gangetic Plain of Ghazipur District in Uttar Pradesh, India, J. Geochem. Explor. 105 (2010) 83–94.
- [3] D.A. Polya, A.G. Gault, N. Diebe, P. Feldman, J.W. Rosenboom, E. Gilligan, et al, Arsenic hazard in shallow Cambodian groundwaters, Mineral. Mag. 69 (2005) 807–823.
- [4] S.J. Appleyard, J. Angeloni, R. Watkins, Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia, Appl. Geochem. 21 (2006) 83–97.

- [5] A. Farooqi, H. Masuda, N. Firdous, Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources, *Environ. Pollut.* 145 (2007) 839–849.
- [6] L. Elci, U. Divrikli, M. Soylak, Inorganic arsenic speciation in various water samples with GF-AAS using coprecipitation, *Int. J. Environ. Anal. Chem.* 88 (2008) 711–723.
- [7] M. Tuzen, D. Citak, D. Mendil, M. Soylak, Arsenic speciation in natural water samples by coprecipitation-hydride generation atomic absorption spectrometry combination, *Talanta* 78 (2009) 52–56.
- [8] M. Tuzen, K.O. Saygi, I. Karaman, M. Soylak, Selective speciation and determination of inorganic arsenic in water, food and biological samples, *Food Chem. Toxicol.* 48 (2010) 41–46.
- [9] O.D. Uluozlu, M. Tuzen, D. Mendil, M. Soylak, Determination of As(III) and As(V) species in some natural water and food samples by solid phase extraction on streptococcus pyogenes immobilized on sephabeads Sp 70 and hydride generation atomic absorption spectrometry, *Food Chem. Toxicol.* 48 (2010) 1393–1398.
- [10] C. Jing, G.P. Korfiatis, X. Meng, Immobilization mechanisms of arsenate in iron hydroxide sludge stabilized with cement, *Environ. Sci. Technol.* 37 (2003) 5050–5056.
- [11] J. Floch, M. Hideg, Application of ZW-1000 membranes for arsenic removal from water sources, *Desalination* 162 (2004) 75–83.
- [12] B.L. Rivas, M. Del Carmen Aguirre, E. Pereira, Cationic water-soluble polymers with the ability to remove arsenate through an ultrafiltration technique, *J. Appl. Polym. Sci.* 106 (2007) 89–94.
- [13] S. Xia, B. Dong, Q. Zhang, B. Xu, N. Gao, C. Causseranda, Study of arsenic removal by nanofiltration and its application in China, *Desalination* 204 (Spec. Iss. 1–3) (2007) 374–379.
- [14] J.E. Greenleaf, J.C. Lin, A.K. Sengupta, Two novel applications of ion exchange fibers: arsenic removal and chemical-free softening of hard water, *Environ. Prog.* 25 (2006) 300–311.
- [15] C. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 (2001) 1487–1492.
- [16] M. Tuzen, A. Sari, D. Mendil, O.D. Uluozlu, M. Soylak, M. Dogan, Characterization of biosorption process of As(III) on green algae *Ulothrix cylindricum* biomass, *J. Hazard. Mater.* 165 (2009) 566–572.
- [17] K. Wu, R.P. Liu, F.F. Chang, H.C. Qu, Arsenic species transformation and transportation in arsenic removal by Fe–Mn oxide coated diatomite: pilot-scale field study, *J. Environ. Eng.* 137 (2011) 1122–1127.
- [18] K. Wu, R.-P. Liu, H.-J. Liu, H.-C. Lan, J.-H. Qu, Enhanced arsenic removal by in situ formed Fe–Mn binary oxide in the aeration-direct filtration process, *J. Hazard. Mater.* 239–240 (2012) 308–315.
- [19] X. Guan, J. Du, X. Meng, Y. Sun, B. Sun, Q. Hu, Application of titanium dioxide in arsenic removal from water: a review, *J. Hazard. Mater.* 215–216 (2012) 1–16.
- [20] A. Bortun, M. Bortun, J. Pardini, S.A. Khainakov, J.R. Garcia, Synthesis and characterization of a mesoporous hydrous zirconium oxide used for arsenic removal from drinking water, *Mater. Res. Bull.* 45 (2010) 142–148.
- [21] Y. Ma, Y.-M. Zheng, J. Paul Chen, A zirconium based nanoparticle for significantly enhanced adsorption of arsenate: synthesis, characterization and performance, *J. Colloid Interface Sci.* 354 (2011) 785–792.
- [22] H. Cui, Q. Li, S. Gao, J.K. Shang, Strong adsorption of arsenic species by amorphous zirconium oxide nanoparticles, *J. Ind. Eng. Chem.* 18 (2012) 1418–1427.
- [23] M. Addamo, M. Bellardita, D. Carriazo, A. Di Paola, S. Milioto, L. Palmisano, et al. Inorganic gels as precursors of TiO<sub>2</sub> photocatalysts prepared by low temperature microwave or thermal treatment, *Appl. Catal., B* 84 (2008) 742–748.
- [24] G.J. Wilson, G.D. Will, R.L. Frost, S.A. Montgomery, Efficient microwave hydrothermal preparation of nanocrystalline anatase TiO<sub>2</sub> colloids, *J. Mater. Chem.* 12 (2002) 1787–1791.
- [25] J. Rodriguez-Carvajal, FullProf Suite: Crystallographic tools for Rietveld, profile matching & integrated intensity refinements of X-ray and/or neutron data. <http://www.ill.eu/sites/fullprof/>.
- [26] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids, Principles, Methodology and Applications, Academic Press, London, 1999.
- [27] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982.
- [28] M.M. Dubinin, Progress in Surface and Membrane Science, vol. 9, Academic Press, NY, 1975.
- [29] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *J. Am. Chem. Soc.* 73 (1951) 373–380.
- [30] B.M. Babic, S.K. Milonjic, M.J. Polovina, B.V. Kaludierovic, Point of zero charge and intrinsic equilibrium constants of activated carbon cloth, *Carbon* 37 (1999) 477–481.
- [31] H. Jezequel, K.H. Chu, Removal of arsenate from aqueous solution by adsorption onto titanium dioxide nanoparticles, *J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng.* 41 (2006) 1519–1528.
- [32] P.K. Dutta, A.K. Ray, V.K. Sharma, F.J. Millero, Adsorption of arsenate and arsenite on titanium dioxide suspensions, *J. Colloid Interface Sci.* 278 (2004) 270–275.
- [33] S.S. Tripathy, M.A. Raichur, Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water, *Chem. Eng. J.* 138 (2008) 179–186.
- [34] G. McKay, Y.S. Ho, Pseudo-second-order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [35] Z. Ren, G. Zhang, J. Paul Chen, Adsorptive removal of arsenic from water by an iron-zirconium binary oxide adsorbent, *J. Colloid Interface Sci.* 358 (2011) 230–237.
- [36] J.W. Weber, J.C. Morriss, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div.: Proc. Am. Soc. Civil Eng.* 89 (1963) 31–60.