

As(III) and As(V) Sorption on MnO₂ Synthesized by Mechano-chemical Reaction from Aqueous phase

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ABSTRACT: Nanoparticles of manganese-dioxide synthesized by mechano-chemical reaction were used for As(III) and As(V) sorption from water environment. The influence of a milling time of manganese-dioxide on sorption was examined with batch procedure. Sorption as a function of contact time was investigated. Kinetic of sorption, for both As(III) and As(V), was fast. The equilibrium condition for milled sorbents was achieved after one hour of mixing. Experimental data were fitted to Freundlich and Langmuir adsorption models. Both models represent experimental data well with slightly better regression coefficient for Freundlich isotherm model. With the increase of the milling time manganese-dioxide adsorption capacity for As(III) and As(V) increased. The decrease of average particle size with milling could be responsible for increase of sorption capacity. The influence of pH on sorption was also investigated. The sorption of both, As(III) and As(V), in investigated pH range (6.0-9.0) was not significantly disturbed and showed similar behaviour, what could indirectly imply oxidation of As(III) to As(V) before sorption.

Key words: Arsenite, arsenate, Removal, mechano-chemical reaction, Drinking water

INTRODUCTION

Occurrence of arsenic in the environment, its toxicity and effect on humans were examined and well documented in past three decades (Bodek et al. 1998; Jain and Ali, 2000; Bissen and Frimmel, 2003; Wang and Huang, 1994; Nriagu and Azcue, 1990). Chronic exposure causes skin, lung, bladder and kidney cancer as well as pigmentation changes like hyperkeratosis, muscular weakness, loss of appetite and nausea. Arsenic pollution has been reported in China, Chile, Canada, India, Japan and USA. One of the largest population at risk with known groundwater arsenic contamination is in Bangladesh and West Bengal (Mandal and Suzuki, 2002). In northern region of Serbia, Vojvodina, groundwaters contain elevated concentration of arsenic (Jovanovic *et al.*, 2011).

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural water and organisms. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Most environmental arsenic problems are result of

mobilization under natural conditions. However, important impact is through mining activity, combustion of fossil fuels and use of arsenical pesticides and herbicides. Arsenic occurs in environment in inorganic and organic forms. Organic species of arsenic can be found mostly in foodstuff, such as shellfish. The greatest problem is the intake of arsenic from drinking water which become the biggest threat and worldwide problem. Inorganic arsenic occurs in two valence states, arsenite (As(III)) and arsenate (As(V)). As(III) species consist primarily of arsenious acid (H₃AsO₃) in natural waters while As(V) species consist primarily of H₂AsO₄⁻ and HAsO₄²⁻ in natural waters (NRC, 1999).

Arsenic removal technologies for drinking water include: coagulation/filtration, ion exchange processes, membrane filtration and adsorption processes. Among these technologies, adsorption is considered to be one of the best because it can be simple in operation and cost-effective (Mohan and Pittman Jr., 2007). Various sorbents like granular activated carbon (Di Natale *et al.*, 2008.), activated alumina (Singh and Pant, 2004), granular ferric

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hydroxides (Driehaus et al, 1998) were commercially available and could be used as arsenic sorbents. Some low-cost sorbents were also examined including agricultural waste like coconut husk carbon (Manju et al., 1998), biosorbents like immobilised biomass (Kamala et al., 2005) and orange juice residue (Ghimire et al., 2002). However, in order to get better arsenic removal, pre-oxidation of As(III) to As(V) is required. Sorbents, known for their oxidation ability, like titanium-dioxide was also tested (Bang et al., 2005; Dutta et al., 2004). Selection of suitable sorbent media for removal of arsenic from drinking water depends on range of initial arsenic concentrations, presence of other elements and their concentrations in water, the cost of sorbent and possibility of sorbent regeneration, post treatment difficulties, etc. Therefore, the aim of this study was to investigate new sorbents which could be used to remove As(III) and As(V) from drinking water of Vojvodina below current regulation limit for arsenic in drinking water. Sorbents were synthesized with mechano-chemical treatment, a non-equilibrium solid-state process in which the final product retains a very fine, typically nanocrystalline or amorphous structure (Suryanarayana, 2001) Results obtained from the adsorption experiments like the effect of contact time on arsenic sorption, evaluation of sorption capacities form Freundlich adsorption isotherms and the influence of initial pH on sorption characteristic of sorbent were presented. Comparison of sorption capacity of our sorbent with commercially available TiO₂ (Degussa P25) was done.

MATERIALS & METHODS

MnO₂ oxide, 99 % purity (Alfa Aesar), was used as the starting material. Mechano-chemical treatment was performed in a planetary ball mill (Fritsch Pulverisette 5). A hardened-steel vial of 500 ml volume, filled with 40 hardened steel balls with a diameter of 13.4 mm, was used as the milling medium. The mass of the powder was 20 g and the balls-to-powder mass ratio was 20:1. The milling was done in air atmosphere without any additives. The angular velocity of the supporting disc and vial was 32.2 and 40.3 rad s⁻¹, respectively. The intensity of milling corresponded to an acceleration of about 10 times greater than the gravitational acceleration. MnO₂ was milled for 1, 2 and 3 hours. The characterization of sorbents was performed using scanning electron microscope (SEM), JOEL JSM-6610LV. Stock solutions containing (1000 ppm) of As(V) and As(III) were prepared by dissolving appropriate quantity of Na₂HAsO₄·7H₂O and NaAsO₂ in deionized water, respectively. Solutions of required lower concentrations were prepared by diluting the stock solutions. The effect of contact time on As(III)

and As(V) was carried out with 5000 µg/L arsenic concentration. Plastic flasks with 100 ml of arsenic solutions with 50 mg of sorbent were mixed for 1, 2, 4, 6, 8 and 12 hours. Adsorption isotherms were obtained from the results of the experiment performed by adding different concentrations of As(III) and As(V) solution in deionized water in plastic flasks with 0.0500 ± 0.0010 g of the sorbent. The concentrations were 200, 400, 600, 800, 1000 and 1500 µg/L. The volume of solution was 100 ml in all experiments. Plastic flasks were shaken 4 hours for MnO₂ at room temperature. With MnO₂ milled 1, 2 and 3 hours, shaking time was only one hour at room temperature. Sorbent was separated by centrifugation at 3500 rpm and arsenic concentration in supernatant were determined with inductively coupled plasma-atomic emission spectroscopy (iCap 6500Duo, Thermo Scientific, UK). The point of zero charge (PZC) for sorbent with highest sorption capacity was estimated by using batch equilibrium techniques (Chutia et al., 2008.). For this purpose, 0.1 g of sorbent was treated with 50 ml 0.1 M NaNO₃ solution which was used as an inert electrolyte. The initial pH values (pH_{initial}) were adjusted in a range ~3.0 to ~11.0 by adding corresponding amounts of NaOH or HNO₃ solutions. The suspensions were allowed to equilibrate 6 hours in a rotary shaker at room temperature. After completion of the equilibrium time, the mixtures were filtered and final pH values (pH_{final}) of the filtrates were measured again. For pH study, plastic flasks were filled with 100 ml of 1500 µg/L of As(III) or As(V) and 0.0500 ± 0.0010 g of MnO₂ milled for 3 hours. Correct amount of diluted acid (HCl) or diluted alkaline (NaOH) solution required to adjust the pH to a target value was added. Samples with pH values of approximately 6.0; 7.0; 8.0 and 9.0 were prepared. The plastic flasks were shaken for 1 h at room temperature. Solutions were separated; pH was checked and arsenic concentration in supernatant were determined with ICP OES.

RESULTS & DISCUSSION

The effect of contact time on removal of As(III) and As(V) was shown in fig. 1 and 2. The amount of arsenic sorbed onto corresponding oxide, Q_e (µg/g) was calculated by following equation:

$$Q_e = (C_0 - C_e) V / m$$

where C₀ (µg/L) is initial arsenic concentration, C_e (µg/L) equilibrium concentration of arsenic in solution after sorption, V (L) volume of solution and m (g) mass of sorbent.

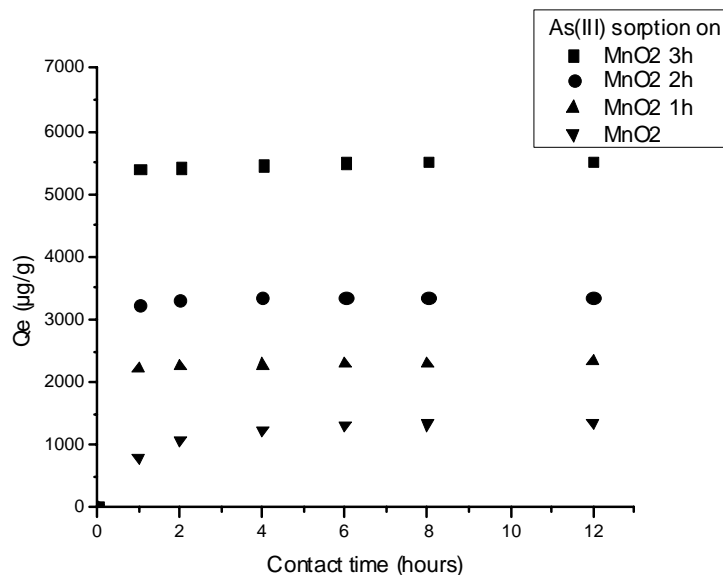


Fig. 1. The effect of contact time on As(III) adsorption on MnO₂ and milled MnO₂ (1, 2 and 3 h)

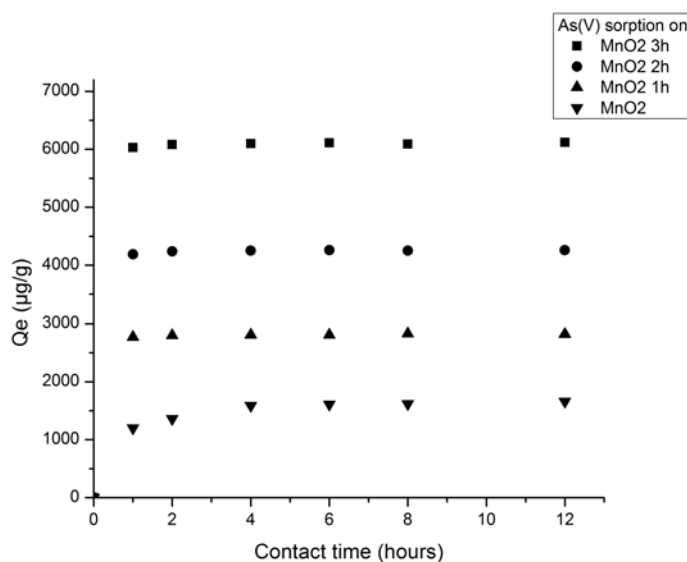


Fig. 2. The effect of contact time on As(V) adsorption on MnO₂ and milled MnO₂ (1, 2 and 3 h)

Rapid uptake of As(III) within the first hour for all four sorbents. 80% of the sorbed amount took place in first hour of batch procedure for initial MnO₂ (Fig. 1). For MnO₂ sorbents milled for 1, 2 and 3 hours, the equilibrium condition was achieved after the first hour, while for the starting MnO₂ after 4 hours. Therefore, for isotherm studies, 4 hours shaking time was used with MnO₂ and 1 hour shaking time for MnO₂ milled 1, 2 and 3 hours, respectively. Similar results were obtained for the sorption of As(V) (Fig.2). Both Freundlich and Langmuir isotherms were used for evaluation the sorption capacities of the sorbents.

Freundlich and Langmuir isotherm equations are given below. We used linearized form of Freundlich equation:

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

where x (mg) is the mass of adsorbed arsenic, m (g) is the mass of sorbent, C_e (mg/L) is the equilibrium concentration of arsenic in solution after sorption, K (mg/g) is a constant, and n is a constant. The constant K is related primarily to the capacity of the sorbent and the n is a function of the strength of sorption. The experimental data obtained from this paper were applied to linearized form of Langmuir equation:

$$C_e/q_e = 1/bQ^o + C_e/Q^o$$

where C_e is equilibrium concentration (mg/L), q_e is amount adsorbed at equilibrium (mg/g), Q^o is adsorption maxima or adsorption capacity (mg/g) and b is a isotherm constant. The sorption capacities of MnO_2 sorbents for As(III) and As(V) evaluated with Freundlich and Langmuir isotherms were presented in figs. 3, 4, 5 and 6. The values of the adsorption capacities for these two models with regression

coefficient (R^2) are listed in Table 1. High regression coefficients ($R^2 > 0.91$) suggests that both Freundlich and Langmuir models are suitable for describing adsorption of As(III) and As(V) on MnO_2 . Freundlich model gave slightly better regression coefficients suggesting multilayer sorption. Lower regression coefficient of As(III) sorption with Langmuir model was probably the consequence of the assumption that the sorption and desorption rates are identical. Oxidation of dissolved species due to reaction with surface are not included.

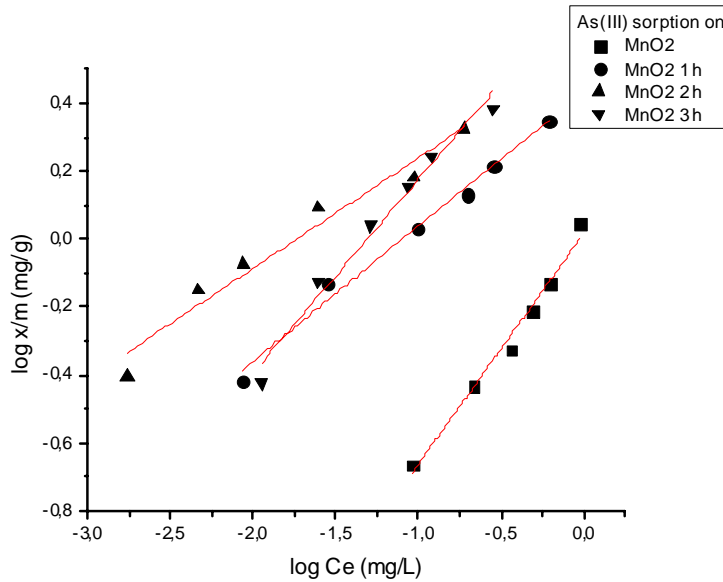


Fig. 3. Freundlich plot for the sorption of As(III) on MnO_2 and milled MnO_2 (1, 2 and 3 h)

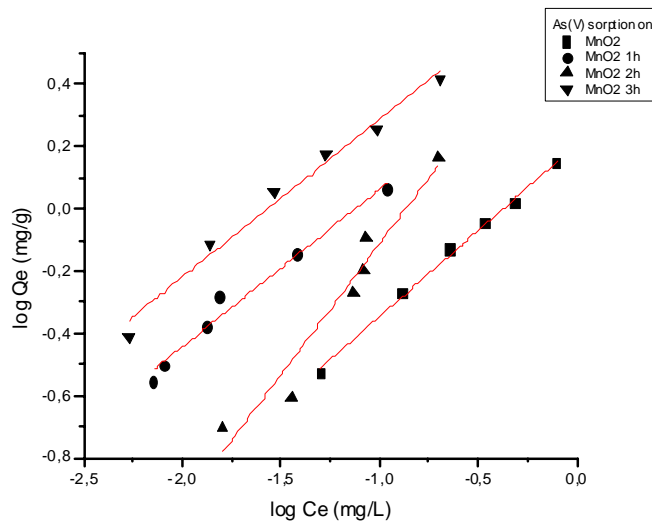


Fig. 4. Freundlich plot for the sorption of As(V) on MnO_2 and milled MnO_2 (1, 2 and 3 h)

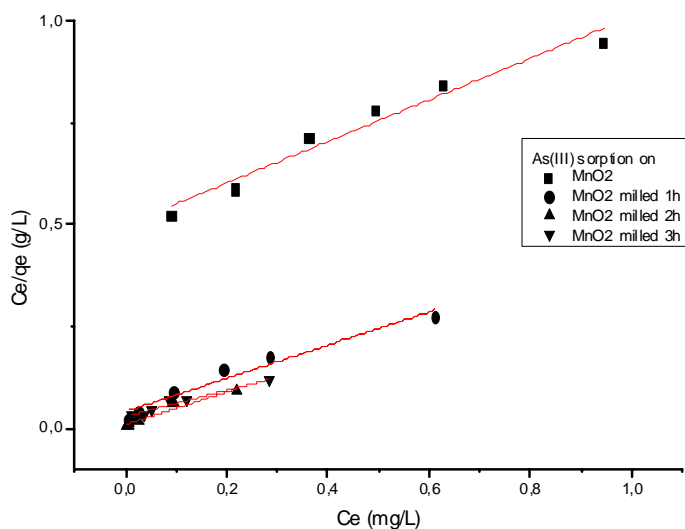


Fig. 5. Langmuir plot for the sorption of As(III) on MnO₂ and milled MnO₂ (1, 2 and 3 h)

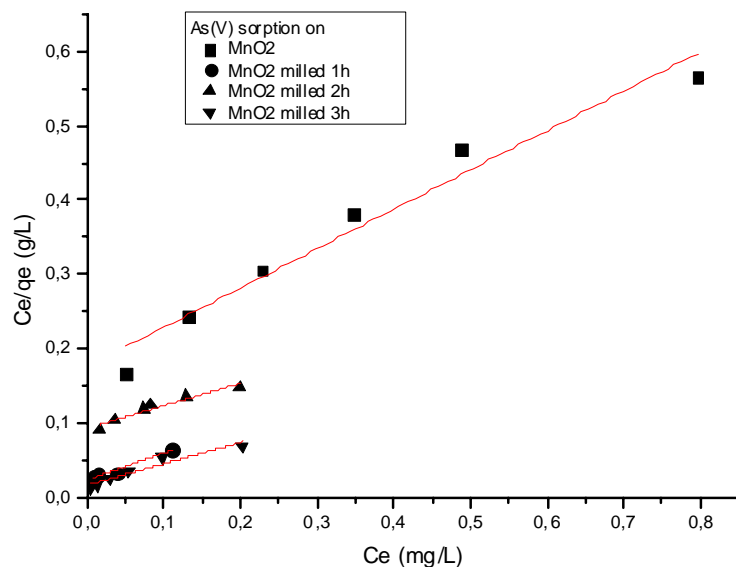


Fig. 6. Langmuir plot for the sorption of As(V) on MnO₂ and milled MnO₂ (1, 2 and 3 h)

Table 1. Freundlich and Langmuir isotherm parameters and regression coefficients for adsorption of As(III) and As(V) on MnO₂ adsorbent

milling time (h)	Freundlich isotherm parameters				Langmuir isotherm parameters			
	As(III)		As(V)		As(III)		As(V)	
	R ²	K (mg\g)	R ²	K (mg\g)	R ²	Q ⁰ (mg\g)	R ²	Q ⁰ (mg\g)
0	0.9791	1.01	0.9957	1.61	0.9536	1.86	0.9555	1.89
1	0.9859	2.69	0.9686	3.71	0.9457	2.44	0.9533	2.74
2	0.9494	3.66	0.9331	5.38	0.9322	2.50	0.9138	3,32
3	0.9719	5.56	0.9770	6.17	0.9576	3.13	0.9225	3.50

MnO₂ milled for 3 hours gave the best sorption capacities for As(III) and As(V). Therefore for this sorbent p*H*_{PZC} was determined and the effect of p*H* on sorption was examined.

SEM images of starting MnO₂ and MnO₂ milled for 3 hours are shown in figs 7 and 8. The change in surface morphology with milling and the decrease of average particle size of MnO₂ milled for 3 hours in comparison with the starting material, could be seen. They could be responsible for higher sorption capacity of milled sorbent.

The p*H* is important parameter for sorption processes as surface characteristics of the sorbent and arsenic speciation depends of it. The p*H*_{PZC} of sorbent depends of various factors like nature of crystallinity, impurity contents, temperature, degree of H⁺ and OH⁻ ions sorption. Therefore, it may vary from sorbent to sorbent (Smiciklas *et al.*, 2000). The batch experiment was carried out with 0.1 g of sorbent and result is illustrated in fig.9. A plot of p*H* values of solution after equilibrium (p*H*_{final}) as a function of initial p*H* values (p*H*_{initial}) provides p*H*_{PZC} of the sorbent by the common plateau of constant p*H* to the ordinate at around ~6.9.

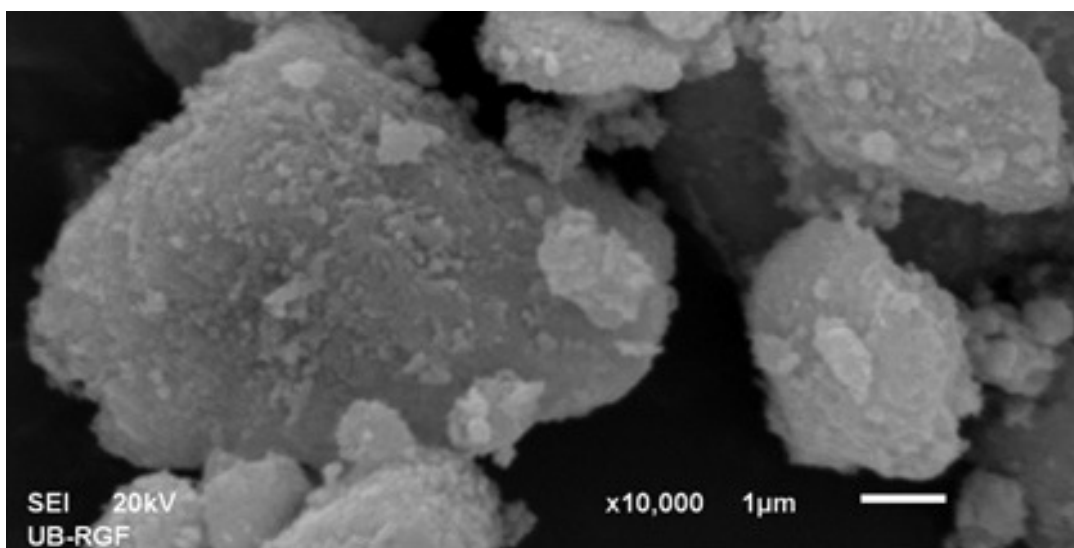


Fig. 7. SEM image of MnO₂

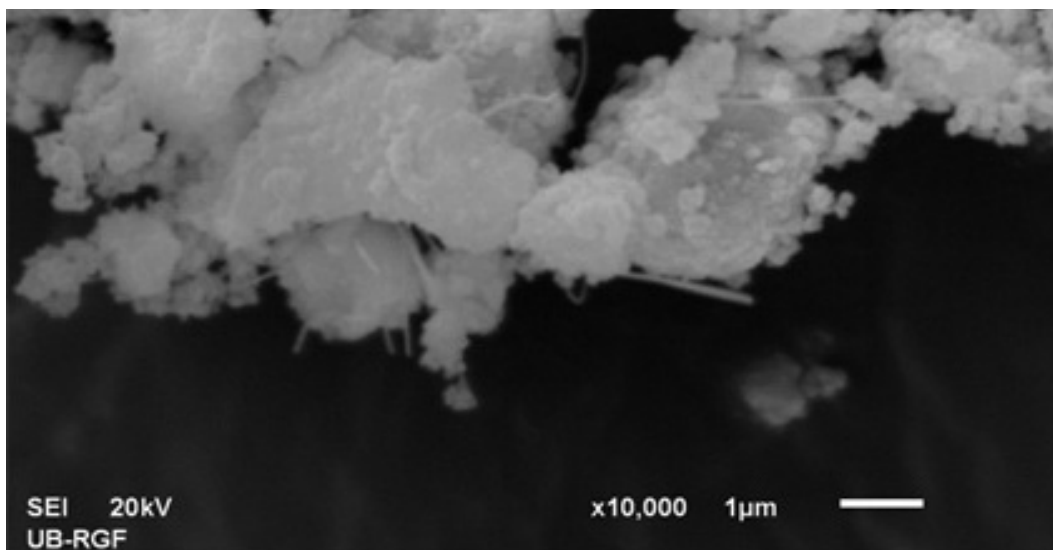


Fig. 8. SEM image of MnO₂ milled for 3 hours

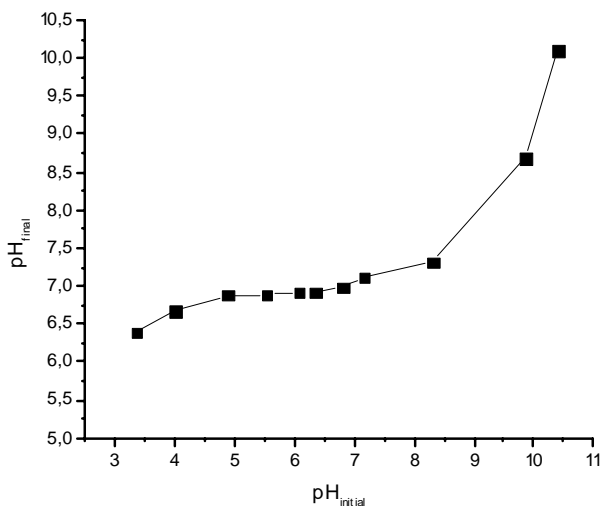


Fig. 9. Plot of pH_{final} as a function of pH_{initial} for determination of pH_{PZC}

The standard range of pH in drinking water varies from 6.5 to 8.5 (Menhage-Bena *et al.*, 2004) and therefore the sorption experiments were performed in pH range from 6.0 to 9.0. The decrease of As(V) sorption with increase of pH could be seen (fig. 10). In the investigated pH range the greatest decrease of arsenate sorption of 17% was at pH 9. The decrease of the sorption could be explained with enhanced repulsion between negative surface charge of sorbent in pH above pH_{PZC} and As(V) species, HAsO₄²⁻ and H₂AsO₄⁻

, which are dominant at pH 9 (Ferguson and Gavis, 1972). The same trend was observed with arsenite, where pH had less influence on the sorption. The similar behavior of arsenate and arsenite sorption with change of pH suggested indirectly that As(III) was oxidized into As(V) and then sorbed by the MnO₂. This small decrease of arsenate and arsenite sorption with the increase of pH indicated that this sorbent could be used for removal of arsenic species in majority of drinking water samples.

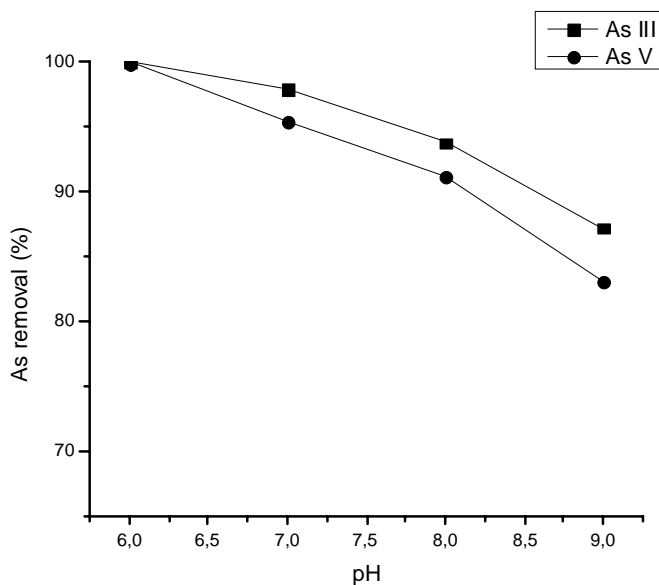


Fig. 10. Effect of pH on As(III) and As(V) sorption on MnO₂ milled for 3h

We examined sorption capacity of commercially available sorbent TiO₂ (Degussa P25) under identical experimental conditions applied for MnO₂ milled for 3h. Based on literature results TiO₂ is often used as a material for treatment arsenic, especially As(III) because of his ability to oxidize As(III) to As(V). The Freundlich isotherm constants, K, obtained from fitting the experimental data of sorption As(III) and As(V) on TiO₂ to linear Freundlich isotherm are 1.71 mg/g and 2.70 mg/g for As(III) and As(V), respectively. As we can see, sorption capacity of MnO₂ milled for 3h for As(III) is more than 3 times and for As(V) more than 2 times bigger compared to TiO₂.

CONCLUSION

Sorption capacity of MnO₂ sorbent prepared by mechano-chemical reaction was increased in comparison with the starting material. Milling MnO₂ for 3 hours increased sorption capacity of As(III) and As(V) for more than 5 and 3 times, respectively, compared to non milled MnO₂. The sorption kinetics was fast for both As(III) and As(V). The equilibrium condition and the removal of more than 90 % of sorbed arsenic was achieved within 1 hour. Experimental results indicated that As(III) could be effectively removed without pre oxidation to As(V). In the pH range typical for drinking water there were no significant decrease in sorption capacity of sorbent. MnO₂ synthesized by mechano-chemical reaction could be used for removal of arsenite and arsenate from drinking water. MnO₂ milled for 3h exhibit higher sorption capacity then commercially available TiO₂.

REFERENCES

Bang, S., Patel, M., Lippincott, L. and Meng, X. (2005). Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere*, **60**, 389-397.

Bissen, M. and Frimmel, F. H. (2003). Arsenic - a review. Part I. Occurance, toxicity, speciation, mobility. *Acta Hydrochimica et Hydrobiologica*, **31** (2), 9-18.

Bodek, I., Lyman, W. J., Reehl, W. F. and Rosenblatt, D. H. (1998). *Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods*. USA: Pergamon Press.

Chutia, P., Kato, S., Kojima, T. and Satokawa, S. (2008). Arsenic adsorption from aqueous solution on synthetic zeolites. *Journal of Hazardous Materials*, **162**, 440-447.

Di Natale, F., Erto, A., Lancia, A. and Musmarra, D. (2008). Experimental and modelling analysis of As(V) ions adsorption on granular activated carbon. *Water Research*, **42**, 2007-2016.

Driehaus, W., Jekel, M. and Hildebrandt, U. (1998). Granular ferric hydroxide-a new sorbent for the removal of arsenic from natural water. *Journal of Water Supply: Research and Technology - Aqua*, **47** (1), 30-35.

Dutta, P. K., Ray, A. K., Sharma, V. K. and Millero, F. J. (2004). Adsorption of arsenate and arsenite in titanium dioxide suspensions. *Journal of Colloid and Interface Science*, **278**, 270-275.

Ferguson, F. J. and Gavis, J. (1972). A review of the arsenic cycle in natural waters. *Water Research*, **6**, 1259-1274.

Ghimire, K.N., Inoue, K., Makino, K. and Miyajima, T. (2002). Adsorption removal of arsenic using orange juice residue. *Separation Science and Technology*, **37** (12), 2785-2799.

Jain, C.K. and Ali, I. (2000). Arsenic: occurrence, toxicity and speciation techniques. *Water Research*, **34**, 4304-4312.

Jovanovic, D., Jakovljevic, B., Rasic-Milutinovic, Z., Paunovic, K., Pekovic, G. and Knezevic, T. (2011). Arsenic occurrence in drinking water supply systems in ten municipalities in Vojvodina Region, Serbia. *Environmental Research*, **111** (2), 315-318.

Kamala, C. T., Chu, K. H., Chary, N. S., Pandey, P. K., Ramesh, S. L., Sastry, A. R. K. and Chandra Sekhar, K. (2005). Removal of arsenic(III) from aqueous solutions using fresh and immobilized plant biomass. *Water Research*, **39** (13), 2815-2826.

Mandal, B. K. and Suzuki, K. T. (2002). Arsenic round the world: a review. *Talanta*, **58**, 201-235.

Manju, G. N., Raji, C. and Anirudhan, T. S. (1998). Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Research*, **32** (10), 3062-3070.

Menhage-Bena, R., Kazemian, H., Ghazi-Khansari, M., Hosseini, M. and Shahtaheeri, S. J. (2004). Evaluation of some natural zeolites and their relevant synthetic types as sorbents for removal of arsenic from drinking water. *Iranian Journal of Public Health*, **33** (1), 36-44.

Mohan, D. and Pittman Jr., C. U. (2007). Arsenic removal from water/wastewater using adsorbents-A critical review. *Journal of Hazardous Materials*, **137** (2), 1-53.

NRC, (1999). *National Research Council, Arsenic in Drinking Water*. National Academy Press, Washington, DC.

Nriagu, J. O. and Azcue, J. M. (1990). *Arsenic in the Environment. Part 1. Cycling and Characterization*. New York: John Wiley & Sons, Inc.

Singh, T. S. and Pant, K. K. (2004). Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Separation and Purification Technology*, **36**, 139-147.

Smiciklas, I. D., Milonjic, S. K., Pfendt, P. and Raicevic, S. (2000). The point of zero charge and sorption of cadmium(II) and strontium(II) ions on synthetic hydroxyapatite. *Separation and Purification Technology*, **18**, 185-194.

Suryanarayana, C. (2001). *Mechanical alloying and milling*. *Progress in Material Science*, **46**, 1-184.

Wang, L. and Huang, J. (1994). *Arsenic in the Environment. Part II. Human Health and Ecosystem Effects*. New York: John Wiley & Sons, Inc.