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ELIMINATION OF TOXIC ELEMENTS BY NATURAL AND SYNTHETIC ADSORBENTS

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ABSTRACT

The adsorption of Zn(II) and Cu(II) onto siderite (S) and kaolin (K) and adsorption of As(V) onto bentonite (B) was studied. The chemical modification – precipitation of MnO_2 on the kaolin (KM) and siderite (SM) surface was used to improve the adsorption properties of natural materials for their application in columns. In the batch tests the higher adsorption capacity was observed for the KM sample. The binary solution of Zn(II)/Cu(II) was percolated through the columns filled with quartz sand (QS) as a bearer of KM or SM. The effect of toxic elements removal reached in average 90 % for both columns.

The adsorption of As(V) onto natural bentonite (B) and synthetic magnetic particles (MP) was studied by batch as well as column tests. Whereas the B sample did not perform good adsorption properties in batch test, in dynamic conditions its effect was comparable with MP. The effect of As(V) removal was studied in a number of series with different materials beddings and cycles repetitions. The results showed that the most effective was the column filled with QS+B+MP containing more coarse-grained fraction of bentonite. In the second cycle its removal effect reached 60 % of As(V) elimination from the solution.

Keywords: *siderite, kaolin, bentonite, toxic elements, adsorption*

INTRODUCTION

Contamination of soils by subsequent toxic elements is one of the main environmental problems of urbanization and industrialization and has recently become a serious concern in the world. The treatment of contaminated soils and sediments can be achieved by either physical or chemical methods. The stimulation of biochemical processes in decontamination is possible, if resistant bacteria are present in the soil. The biological-chemical leaching and usage of resistant bacteria was applied for Cu(II), Zn(II) and As(V) removal from the contaminated samples of soils and sediments from the Krompachy region, locality of Slovakia loaded by metallurgical industry [1,2,3,4,5]. But the obtained leachates from the remediation process also represent the environmental loads. Therefore adsorption should be the way of their regeneration.

The adsorption is considered as low-cost and effective method of toxic ions removal from the water environ. Different natural and synthetic materials, such as clays, activated carbons, metal oxides, were and are still studying as suitable adsorbents [6,7]. Iron oxides as natural compounds of soils, sediments and environment containing water, have large specific surface area and are able to adsorb significant amount of toxic ions. They represent dominant adsorbents because they could be also fine dispersed and used and surface coatings of other particles [8]. Magnetic properties allow their easier separation from water. The natural goethite a hematite were studied as adsorbents of Cu(II) and Zn(II). The synthetic oxides were more efficient, especially for Cu(II) removal, what corresponds with their better surface properties in comparison with natural materials [9]. The manganese oxides are mainly used for Pb(II) removal from the water environment [10,11]. Quartz sands are components of silicate phases, which are the results of weathering process in natural conditions. Ions of released iron, aluminum and silica are precipitated onto surface of quartz particles in forms of hematite, kaolinite and allophane. The sorption of heavy metals in these systems is the result of surface reaction [12]. From different studies follows that quartz sand is mainly used as a filler in columns as filtrate medium or as a bearer for other materials (bacteria, oxides) [13,14,15]. Siderite as representative of Fe(II) minerals, often containing manganese impurities, is also interesting natural adsorbent. The natural siderites and hematites effectively removed As spieces (arsenate, arsenite and dimethylarsenic acid) from water [16,17]. The multicomponent system (bentonite - quartz sand - MnO_2) was also used for Cd(II) adsorption [18]. The research articles are also concern with using a combination of various mentioned natural materials as column fillers for arsenic spieces adsorption. The combination of siderite-coated quartz sand and hematite-coated quartz sand greatly promoted the column performance in the process of As adsorption [19].

This research article concerns the study of adsorption properties of natural materials - siderite, kaolin and bentonite and their modified forms by synthetized MnO_2 and magnetic particles. The aim of the study is to find suitable adsorbent/combination of adsorbents for the adsorption of toxic elements present in the leachates after the biological-chemical leaching of contaminated soils loaded by the metallurgical industry. The adsorption of Cu(II), Zn(II) and As(V) by batch and column tests from the model solutions was studied.

EXPERIMENTAL

Adsorbents

The samples of natural siderite (S) from the locality Slovinky, kaolin (K) from Rudník and bentonite (B) from the deposit Jelšový potok were used for the study. For the experimental purposes the samples were dried for 24 hrs at 40 °C. The samples were sieved to obtain the fraction below 630 μm for siderite, below 100 μm for kaolin and two fractions for bentonite: 0.5 – 1 mm and below 0.5 mm. To enhance the sorption properties of S and K samples their surface was coated by MnO_2 layer. The natural samples were activated by $CaCl_2$ for 24 hrs and dried at 70 °C. 12 g of $KMnO_4$ was added into 100 ml of deionized water, the solution was heated at 90 °C for 15 min. Then 12 g of natural sample was added and the suspension was stirred for 10 min and titrated by 150 ml of 2 M HCl. The slurry was stirred for next 30 min in water bath, washed by deionized water and dried at 70 °C for 24 hrs.
Magnetic particles (MP) were prepared by precipitation method: 15.9 g $FeCl_3$ and 14.0 g $FeSO_4.7H_2O$ were diluted in deionized and heated at 60 °C under rigorous stirring. During the next heating at 90 °C, 50 ml 25 % NH_4OH was added. The slurry was heated and stirred for 1 hr to reach the complete reaction. Then the precipitate was magnetically separated, washed in 700 ml of hot deionized water and dried at room temperature.

Textural study

Textural properties of studied samples were determined by method of physical adsorption of nitrogen at -196 °C by NOVA 1200e Surface Area & Pore Size Analyzer (Quantachrome Instruments, USA). The samples were degassed at 150 °C in a vacuum oven under a pressure lower than 2 Pa for 17 hours. The measured data were processed by the BET (Brunnauer–Emmet–Teller) isotherm in the range of relative pressure 0.05-0.2 to obtain the value of specific surface area (S_{BET}). The values of external surface (S_{ext}) and volume of micropores (V_{micro}) were calculated from the *t*-plot using the Harkins-Jura standard isotherm. The value of total pore volume (V_{tot}) was estimated from the maximum adsorption at relative pressure close to saturation pressure [20].

Adsorption experiments

The batch adsorption experiments were realized by rotary shaker (30 rpm). The defined solutions with adsorbents were added into the plastic tubes. The model solutions of $CuSO_4.5H_2O$ a $Zn(NO_3)_2.6H_2O$ of initial concentrations 10 – 100 mg/L of pH 5 were used. The dose of S, K, SM, KM adsorbents was 1 g/L and the contact time 24 hrs. For the As(V) adsorption, the synthetic solution of Na_2HAsO_4 of initial concentration 10-50 mg/L of pH 4 was used. The B and MP doses were 10 g/L and 1 g/L, respectively.

In dynamic regime, the model solution of 50 mg Cu(II)/L of pH 5 was percolated through the column with mixture of S+KM and S+K adsorbents in weight ratio 32:1. The filtrate column was 110 mm high with inner diameter of 12 mm. The model solution percolated through the columns for 5 hrs (flow rate 10 ml/hr). The pH value and Cu(II) concentration in filtrates were measured continuously. The binary solution Cu(II)/Zn(II) of concentration 100 mg/L was percolated through the column filled with quartz sand (QS) and SM or QS and KM.

The MP are very fine therefore the bearer for their fixation in column is needed. QS is cheap, stable material with good permeability, proven in previous experiments. Through the glass columns with 5 g of adsorbent (QS, QS+B, QS+B+MP) percolated the solution of 30, 50 a 100 mg As(V) /L of pH 4. The adsorption effect and possibility of the column for repeated use was studied. Different combinations of adsorbents layers in column were tested. All experiments were performed duplicate.
The concentrations of toxic elements before and after the adsorption were determined by atomic absorption spectrometer 240 RS/2400 (Varian, Australia). To process the experimental data from the static regime the Langmuir isotherm was used.

RESULTS AND DISCUSSIONS

Textural properties

Adsorption/desorption isotherms of natural and modified siderite and kaolin showed hysteresis what corresponds with the presence of mesopores (pores of width 2-50 nm in diameter), Figure 1. The kaolin sample showed expressive increase of adsorbed volume at relative pressure $p/p_0 \sim 0.9$ what is characteristic for multilayered adsorption in macropores (pores of width > 50 nm in diameter). Generally, siderite and kaolin contain silicate mineral phases, whose should contribute to their porosity. The influence of their modification was presented by wider hysteresis loop. The nonhomogenous covering of their surfaces by MnO_2 particles caused the creation of new interparticle spaces of diameters corresponded with mesopores (also observed by SEM, not shown here). For the SM sample expressive increased of adsorbed gas volume was detected, following by increase of its total pore volume, Table 1. The surface modification increased the value of specific surface area of studied materials, more expressive again for the SM sample.

The natural bentonite showed wide hysteresis pointed at the presence of slit-shape pores, typical for clay minerals. The shape of the adsorption isotherm corresponds with Type I, characteristic for materials containing micropores and of relative low values of external surface. The adsorbed gas volume in the range of relative pressure 0.01-0.2 probably corresponds with the quasi-multilayer adsorption in supermicropores (larger micropores of width 1-2 nm in diameter) and in the range 0.2-0.3 adsorption in the smallest mesopores occurred. Then, in the range 0.3-0.8 the volume of adsorbed gas increased slightly, almost linearly. Also, the high volume of micropores was obtained by applying the *t*-plot method using the Harkins-Jura isotherm. For this sample, the BET method was not appropriate for the specific surface area determination (due to negative C constant value obtained from the BET isotherm), Table 1.

For the MP the volume of adsorbed gas increased regularly in the whole range of relative pressure. The present hysteresis loop corresponds with Type H1, characteristic for the materials creating agglomerates or aggregates of the spherical particles of approximately similar sizes. The hysteresis is therefore caused by the adsorption of gas into the interparticle spaces.

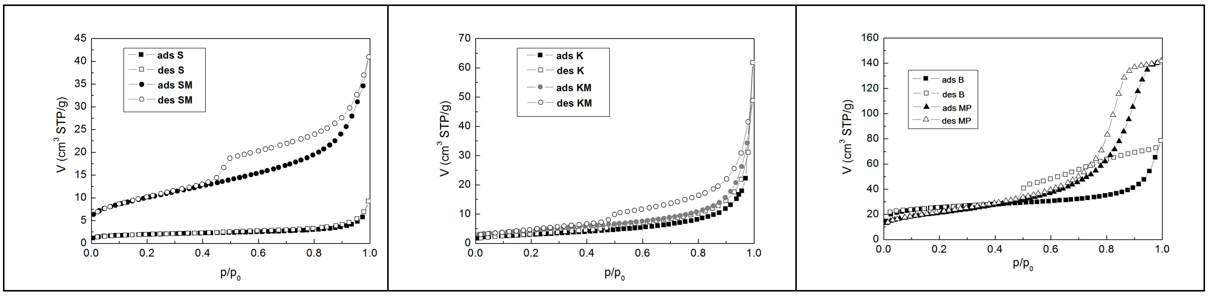

Figure 1 Low temperature nitrogen adsorption/desorption isotherms of studied materials

Table 1 Textural parameters of studied adsorbents

Sample	S_{BET} (m^2/g)	C_{BET}	S_t (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)
S	7	485.8	4	0.0143	0.0010
SM	36	134.0	31	0.0634	0.0020
K	11	77.8	10	-*	0
KM	16	87.3	15	0.0755	0
B	87	-167.7	35	0.1216	0.0239
MP	75	144.5	67	0.2192	0.0033

* The value could not be determined due to unlimited gas adsorption at high relative pressure

Adsorption of Cu(II) and Zn(II)

From the batch experiments, increasing adsorbed amounts of Cu(II) or Zn(II) ions in dependence on increasing initial metal ions concentration in the solutions can be observed, Figure 2. There was no significant difference in removed amounts of Cu(II) ions by both natural adsorbents. Comparing the affinity, higher amounts of Cu(II) were removed by all studied adsorbents.

The modification of S and K by MnO_2 enhanced their adsorption properties. Expressive difference in adsorbed amounts of Cu(II) as well as Zn(II) can be observed. Comparing the modified adsorbents, higher removal effect for both ions showed KM sample. From the solutions of lower Cu(II) initial concentrations the KM sample removed almost 100 % of Cu(II). The values of calculated maximum adsorption capacity from the Langmuir model are listed in Table 2.

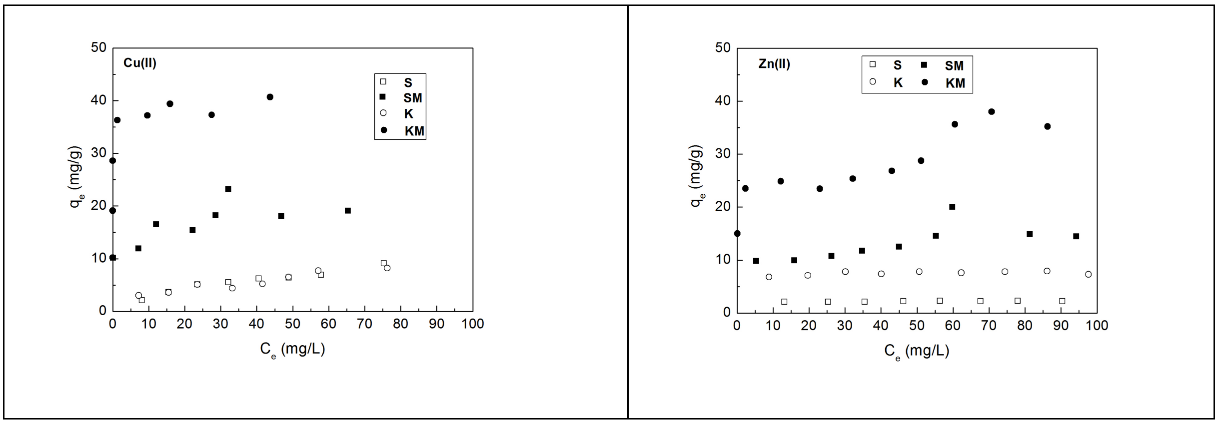

Figure 2 Adsorption isotherms for Cu(II) and Zn(II) adsorption onto siderite and kaolin and their modified forms (C_0 = 10-100 mg/L, pH 5, adsorbent dose 1 g/L)

Table 2 The value of maximum adsorption capacity of studied adsorbents for Cu(II) and Zn(II) adsorption calculated from the Langmuir model

	Cu(II)		Zn(II)	
Sample	Q_0 (mg/g)	R^2	Q_0 (mg/g)	R^2
S	12.9	0.9256	2.3	0.9973
SM	19.8	0.9754	16.9	0.9481
K	10.8	0.8255	7.6	0.9962
KM	39.8	0.9976	37.2	0.9468

On the basis of previous results only the modified forms were tested for adsorption from the binary solutions, Figure 3. For both adsorbents the removal effect was lower due to competitive ions adsorption. Similarly, higher affinity of Cu(II) appeared and expressively restrained their selectivity towards Zn(II) ions. The calculated values of maximum adsorption capacity of SM sample decreased of 20 % and 81 % for Cu(II) and Zn(II), respectively. For KM sample it was a decrease of 32 % and 84 % for Cu(II) and Zn(II), respectively.

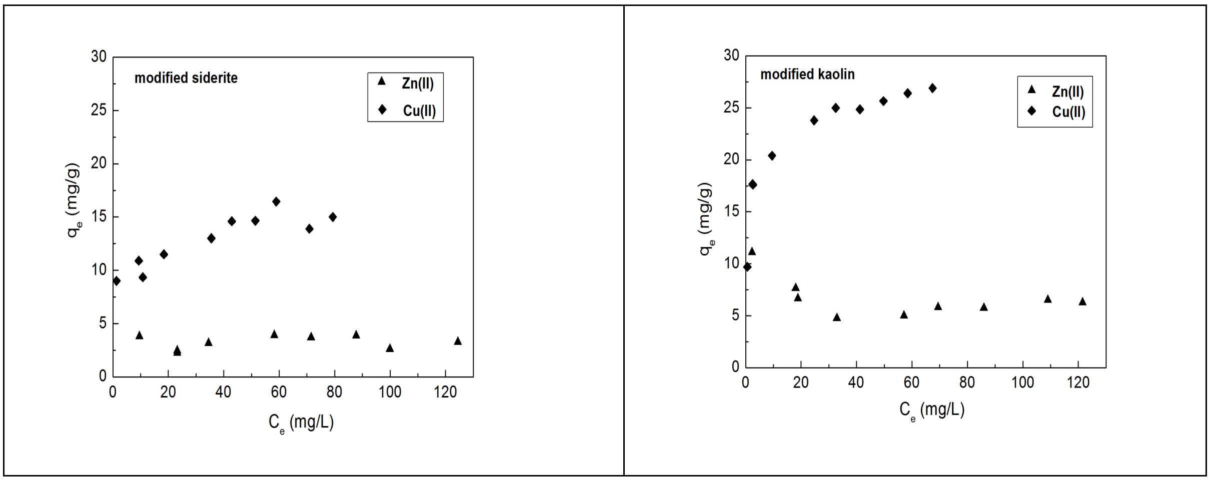

Figure 3 Adsorption isotherms for Cu(II) and Zn(II) adsorption from the binary model solutions onto modified adsorbents (C_0 = 10-200 mg/L, pH 5, adsorbent dose 1 g/L)

To verify the adsorption properties of studied materials in dynamic regime, the introductory experiments in columns were performed. The columns were filled by the mixture of S+K or S+KM. The model solution percolated through the columns. In consequence of high content of siderite in mixtures the pH of the percolated solution increased expressively what caused the Cu(II) precipitation. During first 3 hours of percolation, 100 % removal effect of columns was observed. On the end of the experiment the removal effect decreased but in average reached 85 % for both mixtures.

In next experiments the layer of QS as permeable layer as well as bearer was used. The binary solution of Cu(II)/Zn(II) percolated through the column filled with QS+SM or QS+KM, Fig. 4. During the first hour the column QS+SM removed 100 % of Cu(II) and 82 % of Zn(II), then the effect decreased for both ions. After 6 hrs it was not effective in Zn(II) removal, but still removed 50 % of Cu(II). After 11 hrs the elimination effect decreased to 20 %. For QS+KM the expressive decrease for Zn(II) removal was observed after 4 hrs, but the effect of Cu(II) removal reached 98 % also after 11 hrs of the experiment, Figure 4.

From the presented results it can be concluded that studied natural materials are cheap and easy available adsorbents of toxic elements. Their adsorption properties can be improved by simply chemical modification. The use of QS in columns is significant for the easier permeability of the layers of used adsorbents, but is also suitable as a bearer of adsorbents of finer particles, whose can not be fixed in the columns independently.

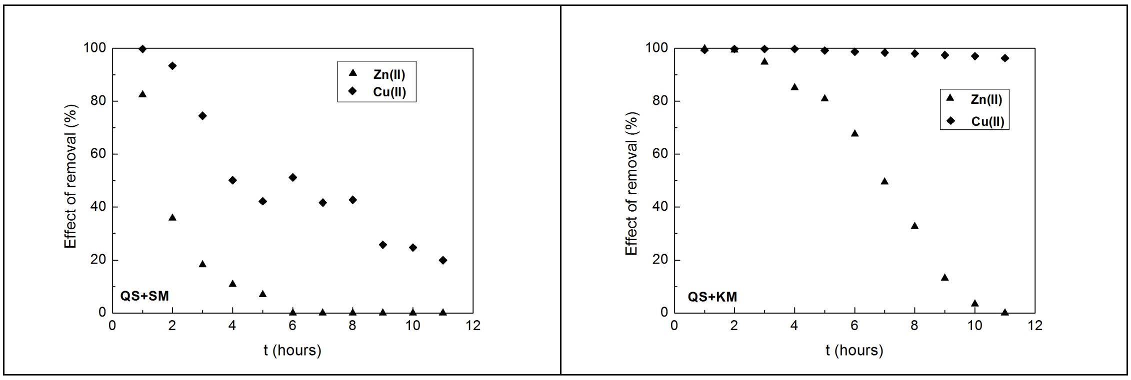

Figure 4 Adsorption of Cu(II) and Zn(II) from the binary solution in columns filled with QS+SM and QS+KM (C_0 = 100 mg/L, pH 5, m_{QS} = 4.5 g, $m_{SM\ (KM)}$= 0.5 g)

Adsorption of As(V)

In batch experiments the B sample did not perform such good adsorption properties towards As(V) as MP (not shown here). While the calculated value of maximum adsorption capacity of B sample was 3 mg As(V)/g, for the MP it was 23 mg As(V)/g. This fact should depend on the surface charge of the adsorbents in water solutions. While at pH 4 the zero point charge of B was measured for the MP the positive surface charge was obtained (not shown here), what corresponds with lower adsorption capacity of clay sample.

In dynamic regime the effect of selected parameters as arrangement/bedding of adsorbents and fraction of the adsorbents particles was tested. In the first series of experiments the columns contained natural bentonite of particle size below 0.5 mm were tested. The solution of 30 mg As(V)/L was percolated through the column twice. After the second cycle the As(V) concentration of the filtrate was still lower than 2 mg/L. However, due to the fine particles of the clay the percolation was very slow, retarded and the flow rate was not continual. In the second series the QS was used as a bearer of the MP and as a permeable layers for B columns. To better interpret the influence of the bearer on the adsorption properties of the MP or B adsorbents, the columns contained pure QS and next QS+MP, QS+B and QS+B+MP were tested. For these experiments the fraction of B sample of particle size 0.5-1 mm was used (for better permeability of the columns). The solution of 100 mg As(V)/L percolated through the columns. After the first cycle QS and QS+B column removed only 2.4 and 5.1 % of As(V), respectively. The QS+MP column removed 34.9 % of As(V) and the combination of all adsorbents reached 77.8 % of As(V) removal, Figure 5. In the second cycle only two the most effective columns were tested, Fig. 5. While the adsorption effect of QS+MP column decreased at 36 %, for the QS+B+MP column it was about 24 %. This result pointed at the fact that not only synthetic magnetic particles, but also the clay adsorbent plays important role in this process under dynamic conditions.

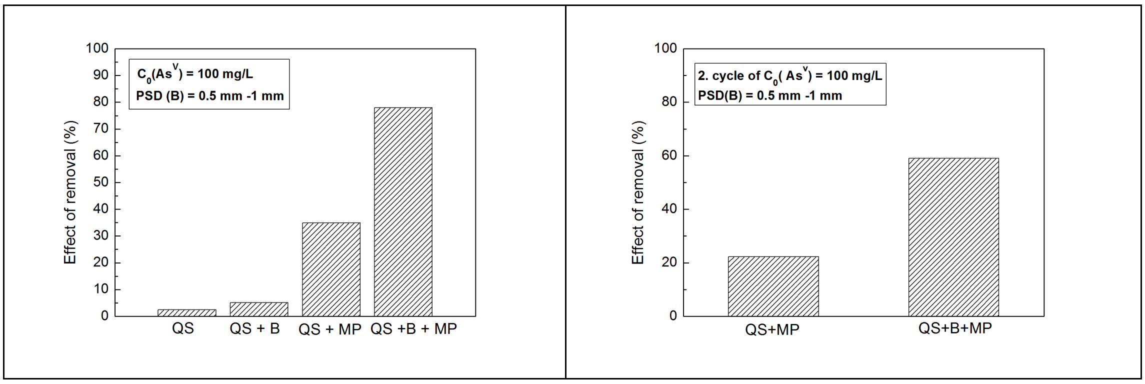

Figure 5 Comparison of As(V) removal by QS, QS+B, QS+MP and QS+B+MP columns in the 1. adsorption cycle and QS+MP, QS+B+MP columns in the 2. adsorption cycle (pH 4; layer doses - QS: 4.5 g; QS+B: 4 g + 0.5 g; QS+MP: 4 g + 0.5 g; QS+B+MP: 3.5 g + 0.5 g +0.5 g)

To evaluate the influence of particle size of clay adsorbent on the column adsorption effect the QS+B+MP column containing clay particles below 0.5 mm was tested too. In two repeated cycles the solution of 100 mg As(V)/g was used. Also after the second cycle the column reached 100 % effect of As(V) removal, but the flow was slower and the column was clogging during the experiment, Figure 6. For the practical purposes, or for further application in praxis, the use of coarser fraction of clay is suitable in spite of decrease of its removal effect at about 20 %. On the basis of obtained results it can be concluded, that by the suitable combination of layers of studied adsorbents in columns relative high concentrations of As(V) can be removed effectively

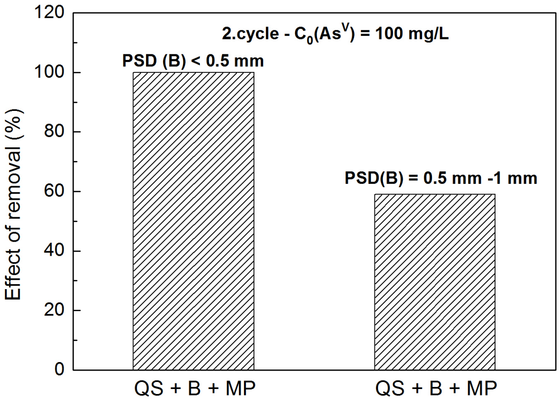

Figure 6 Influence of clay particle size on the As(V) removal by QS+B+MP column in the second adsorption cycle (pH 4; layer doses - QS+B+MP: 3.5 g + 0.5 g +0.5 g)

CONCLUSION

The aim of the study was to evaluate and compare the adsorption properties of selected natural and synthetic adsorbents in removal of toxic elements from the water solutions. The results showed that adsorption properties of natural siderite and kaolin can be enhanced by simply chemical modification by MnO_2 particles. The higher affinity towards adsorbents showed Cu(II) ions in comparison with Zn(II) ions, also in the binary solutions. In all batch experiments better adsorption properties showed KM sample than SM sample. In column experiments due to the high content of S sample in the mixtures the precipitation of Cu(II) occurred. After the replace of S by QS as a bearer, the column contained QS+KM showed higher removal effect in comparison with QS+SM column.

For the As(V) adsorption the natural bentonite and synthetic magnetic particles were tested. While in the batch experiments the clay did not perform good adsorption properties, in dynamic regime it was proved that also its presence as a layer is important and influenced the removal effect of the column. The results showed that by the suitable combination of selected adsorbents of appropriate fraction (especially in the case of clay adsorbents) the columns of high removal effect for more repeated adsorption cycles can be obtained.

For the selective removal of toxic ions for real leachates regeneration, series of columns consisted of QS+SM following by percolation through the QS+B+MP columns should be used.

List of symbols

S_{BET}	specific surface area (m^2/g)
S_t	external surface (m^2/g)
V_{tot}	total pore volume (cm^3/g)
V_{micro}	volume of micropores (cm^3/g)
C_0	initial metal ion concentration (mg/L)
C_e	equilibrium metal ion concentration (mg/L)
q_e	amount of metals adsorbed at equilibrium (mg/g)
Q_0	maximum adsorption capacity (mg/g)

R^2 coefficient of regression
t time (hrs)

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