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# COLUMN SORPTION OF TOXIC IONS IN VARIOUS QUARTZ SAND - PACKED COLUMNS

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## ABSTRACT

In this study the adsorption of As(V), Cu(II) and Zn(II) ions from multi-species model solution was tested in dynamic conditions in sand columns containing a thin layer of bentonite (B), iron-based sludge (IS) and synthetic magnetic particles (MP). Adsorption experiments were performed in order to evaluate the removal efficiency and selectivity of the individual layers in the column. The model solution with concentration of 10 mg/L Cu(II), Zn(II) and As(V) ions of each representing the real wastewater concentration was percolated through the columns of different beddings. In columns filled only with QS/B and QS/IS the removal effect for Cu(II) and Zn(II) ions was comparable while for As(V) ions more efficient column was IS bearing.

The columns with B/IS and B/MP layer showed opposite effect for removal of individual ions. While IS layer showed higher affinity towards Cu(II) and Zn(II) the MP layer enhanced the removal of As(V). The highest removal effect for all ions was obtained by QS/B/MP column. For As(V) the removal effect achieved 90 % after 4 percolation cycles. After the third percolation cycle the removal effect of QS/B/IS column decreased from 100% to 58, 90 and 77 %, for As(V), Cu(II) and Zn(II) ions, respectively. By repeating of the percolation cycles the removal of As(V) by QS/B/MP column slight decreased, up to 90 % after four runs. In spite that after the third cycle almost 100 % of As(V) was removed. For Cu(II) and Zn(II) the decrease from 100 % to 76 and 62 % was detected after four cycles, respectively.

Key words: *column sorption, copper, zinc, arsenic, iron-based sludge, synthetic magnetic particles, bentonite*

## INTRODUCTION

Water and soil pollution by heavy metals is one of the most important environmental problems today because they do not degrade into harmless products, tend to accumulate and are toxic to human beings. Unlike organic pollutants, heavy metals have the tendency to bioaccumulate and their inability to biodegrade contaminate the food chain causes detrimental health effect on the public health [1]. Some heavy metals such as copper (Cu) and zinc (Zn) play important roles in biochemical processes in the human body. However, excessive exposure to these metal ions can result in hazardous impacts. [2].
Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop

desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids [3]. The maximum allowable limit for copper, zinc and arsenic in discharged water was set by the Environmental Protection Agency (EPA) to be 1.3 mg/L, 5mg/L and 10µg/L respectively [4].
Use of natural bentonite in treating aqueous waste containing heavy metals and organic matter has been previously reported in many works. The applicability of bentonite as an adsorbent for some heavy metals - lead, cadmium, copper, and zinc was studied in [5].

Research in the preparation of magnetic particles is of great importance due to their industrial applications. They can be used for the preparation of magnetic fluids [6], in the remediation of oil spill [7] and for therapeutic or diagnostic purposes [8]. Magnetic particles can also be used to adsorb contaminants from aqueous or gaseous effluents. The authors in [9] used the nano scaled magnetic particles for batch adsorption studies of contaminants from aqueous model solutions. Magnetic property of iron oxide nanoparticles enables easy separation of adsorbents from the system and could be reused for further application.

Because almost all batch sorption experiments are conducted under ideal sorption conditions (e.g., full contact and sufficient reaction time), fix-bed adsorption experiments are often used to evaluate the sorbents as packed media in filter systems [10,11,12]. The recycling of the wastes as raw materials for various valuable products is the most desirable and environment-friendly solution to properly manage the huge amount of the waste [13,14]. Iron based sludge used in this study is a by-product of industrial waste water treatment technology. After conversion of the IS sample should be applicable adsorbent for toxic ions removal from aqueous environment.

The present study is based on previous research project dealing with the bio-chemical leaching of the soil and sediments, which are contaminated by various toxic ions and permissible limits were exceed for copper, zinc and arsenic. Obtained bioleachates contain large amounts of these toxic elements and are needed to be treated in an appropriate way. Hereby, the next step for the leachate treatment may be the adsorption in columns packed with quartz sand and adequate amount of B, IS and MP sample in form of layers to proposed simple and technologically achievable process of wastewater treatment. The various quartz-sand packed columns were tested for its selective removal of Cu(II), Zn(II) and As(V) ions from the multi-species model solution and the results were discussed.

## EXPERIMENTAL

### Materials/Adsorbents

The samples of natural bentonite (B), iron-based sludge (IS) and synthetic magnetic particles (MP) were used in this column adsorption experiments as a fillers combined with quartz sand (QS). Bentonite sample was obtained from the deposit Jelšový potok. For the experimental purposes the sample was dried for 24 hrs at 40 °C. The sample was sieved to obtain the fraction of 0.5 – 1 mm.
The iron-based sludge was formed as a side-product of industrial waste water treatment technology for AOX removal applied in a textile factory located in Czech Republic. IS sample was prepared by neutralization of acidic iron(III) sulfate solution added into industrial wastewater. After dehydration, sample was calcinated at 500°C.

Synthetic magnetic particles were synthetized by the route of chemical precipitation, where 15.9 g $FeCl_3$ and 14.0 g $FeSO_4.7H_2O$ were dissolved in 100 mL of deionized water and heated under rigorous stirring up to 60 °C. During the next heating at 90 °C, 50 ml of 25 % $NH_4OH$ was added dropwise. The precipitate was heated and stirred for 1 hour to complete the reaction. Then the precipitate was magnetically separated and washed with 700 mL of hot deionized water and dried at room temperature.

Quartz sand (QS) obtained from the deposit Šaštín-Stráže (Slovakia) was used as porous media in column experiments. Prior to use, the quartz sand was washed more times with deionized water and then dried at 40°C.

### 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 100 °C - 200 °C in a vacuum oven under a pressure lower than 2 Pa for 18 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 [15].

### Zeta potential

Zeta potential (ZP) was measured using a Zetasizer Nano ZS (Malvern, Great Britain). The Zetasizer Nano measures the electrophoretic mobility of the particles, which is converted to the zeta potential using the Helmholtz–Smoluchowski equation built into the Malvern zetasizer software. The zeta potential of samples (concentration of 2 g/L) was measured in deionized water within various pH ranges, which were adjusted by the addition of NaOH or $HNO_3$. The measurements were repeated three times for each samples.

### Scanning electron microscopy

The morphology of sample surface was observed by the field-emission scanning electron microscope (FE-SEM) of type TESCAN MIRA 3 (Czech Republic) equipped with the energy dispersive X-ray (EDX) detector (Oxford Instruments).

### Adsorption experiments

The transport studies were performed in a packed column with dimensions of 1.2 cm (inner diameter) and 11 cm (length). Different types of column were filled with appropriate amounts of quartz sand (4g) and thin layer of bentonite, iron-based sludge or synthetic magnetic particles (ca 0.5g). The scheme of the various QS packed columns is shown in Fig.1.

Then 50 ml of multi species ion solution of Cu(II)/Zn(II)/As(V) ions with concentration of 10 mg/L for each of pH 7 was percolated through the column at a constant flow rate of 6 rpm. Effluent samples were collected and the metal ion concentrations were measured with the atomic absorption spectroscopy (AAS, Varian 240 RS/2400). All treatments were tested in duplicate, and average values were reported.

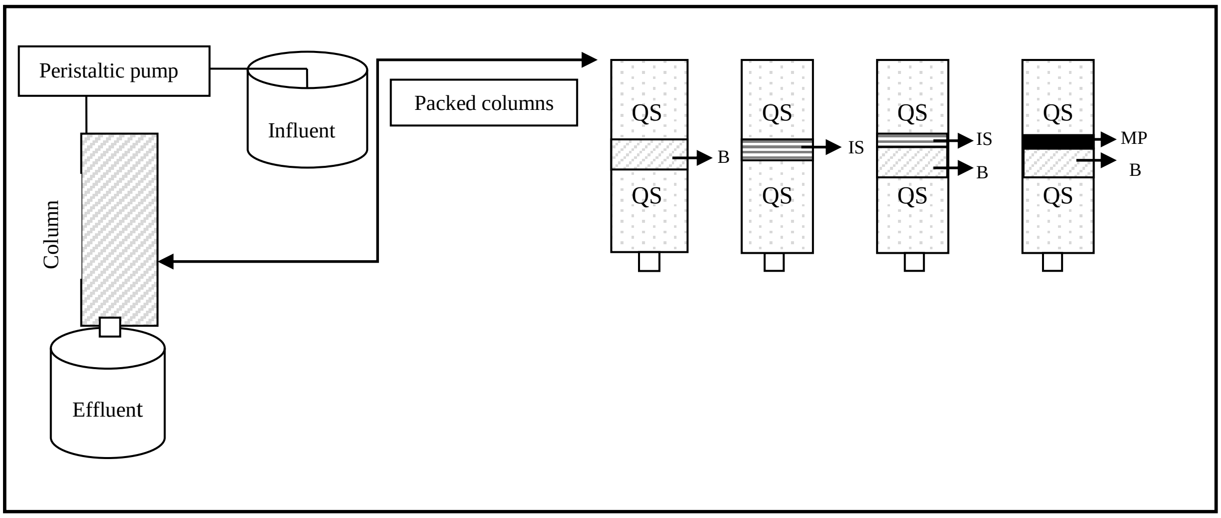

Figure 1 Scheme of various packed columns

## RESULTS AND DISCUSSION

### Textural properties

The measured isotherm of clay sample corresponds with the Type I of Brunnauer - Deming - Deming - Teller (BDDT) classification pointed at the presence of micropores [16], Fig. 2. Type I isotherms are given by microporous solids having relatively small external surfaces, the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area [17]. The adsorbed volume in the range 0.01-0.2 probably corresponded with the quasi-multilayer adsorption in supermicropores (larger micropores with diameter approx. 1-2 nm) and the range $p/p_0 = 0.2–0.3$ corresponded with lower limit of mesopores. Over the relative pressure $p/p_0 > 0.3$ the volume of the adsorbed gas increased moderately, almost linearly up to $p/p_0 = 0.8$. The B sample showed wide hysteresis loop between the adsorption and desorption branch similar to type H4, according to the IUPAC report, which relates with the presence of mesopores of slit-like shape. From the reason of negative value of intercept, as well as $C_{BET}$ constant for B sample obtained from the mathematic model (Table 1) the value of specific surface area is not of real physical meaning. But the real specific surface area, corresponding to the external surface of material particles, is only $S_{ext} = 35$ m$^2$/g. That means that about 20% of adsorbed nitrogen was concentrated in micropores.

For the magnetic particles the present hysteresis loop corresponds with type H1, according to the IUPAC report, characteristic for the materials creating agglomerates of the spherical particles of approximately similar sizes [18]. The hysteresis is therefore caused by the adsorption of gas into the interparticle spaces [17]. For the MP sample the value of $S_{BET} = 75$ m$^2$/g was very close to $S_t$ value, only a small content of micropores should be expected according to the results obtained from the *t*-plot method. This sample showed the highest value of total pore volume, what corresponds with the measured isotherm, Table 1.
For iron-based sludge sample the adsorbed gas volume increased moderate up to relative pressure $p/p_0 = 0.7$, then higher uptake was observed. Similarly than for sample MP the hysteresis loop between the adsorption and desorption branch is similar to the type H1. The value of specific surface area of IS sample, $S_{BET} = 66$ m$^2$/g, is only a bit lower than the values published for the synthetic nano-sized iron oxides (maghemite, magnetite), what pointed at the presence of higher ratio of iron oxide in the treated sludge.

The values of BET surface area calculated from the adsorption isotherm, values of external surface and pore volume are listed in Table 1.

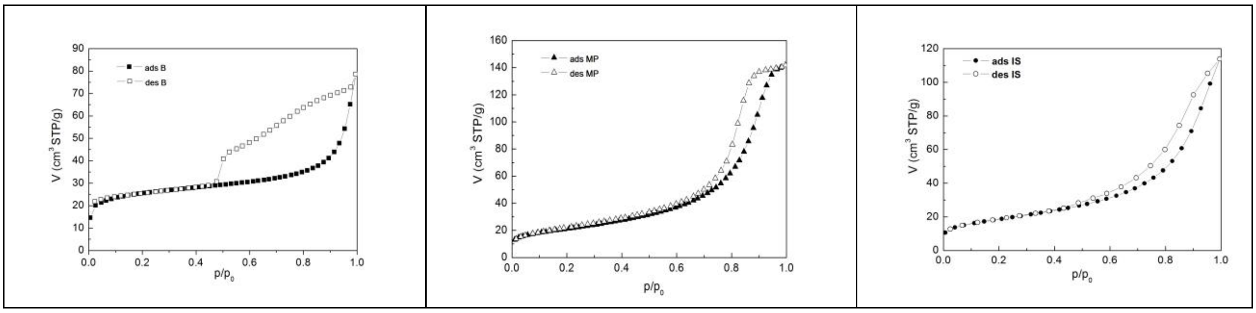

Figure 2 Low temperature nitrogen adsorption/desorption isotherms of studied materials

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) |
|---|---|---|---|---|---|
| B | 87 | -167.7 | 35.0 | 0.1216 | 0.0239 |
| MP | 75 | 144.5 | 67.3 | 0.2192 | 0.0033 |
| IS | 66 | 166 | 59,6 | 0.1761 | 0.0026 |

A detailed morphology of B, MP and IS sample observed by SEM is presented in Fig. 3. Generally, most samples of the bentonite can be summarized as follows: montmorillonite occurred either as ultrafine, thin, leaf-like crystals forming a dense agglomerates or in a more open honeycomb texture [19]. The SEM micrograph of the B sample showed its typical sheet structure corresponding with the first mentioned type, Fig. 3a. The SEM image of MP sample showed that synthesized particles presented heterogeneous morphology with no visible porosity and creating agglomerates, Fig. 3b. However, using image characterization techniques, such as SEM, is difficult to distinguish between agglomerated particles and agglomerates that were formed during the sample drying step [20].

The predominant content of maghemite and magnetite in IS sample, also detected as a high amount of iron and oxygen from the EDX analysis (not shown here), what corresponds with the results discussed above. Feasibly the iron oxides are approximately spherical particles of nanometer sizes. The IS sample in the form of agglomerated particles creating bigger shapes with different dimensions is shown in Fig. 3c.

The Zeta potential of the samples is presented in Fig. 4. The PZC (point of zero charge) of MP and B sample are measured to be pH 5.5 and 4 respectively.

The IS sample had negative charge in the whole studied pH range and did not reach the PZC, probably due to the particles agglomeration. Since the whole charge of the composite is negative, maghemite/magnetite represents positively charged sites in the composite. These parts can interact with anionic species (e.g. arsenic oxyanions). According to the measured data, the adsorbent material should be a little bit more effective in the suspensions of pH up to 7. In the solution of lower pH than 4, the dissolution of Fe ions occurs as well as for clay samples as for the magnetic particles. Column adsorption experiments were performed at pH 7 to simulate real waste water conditions.

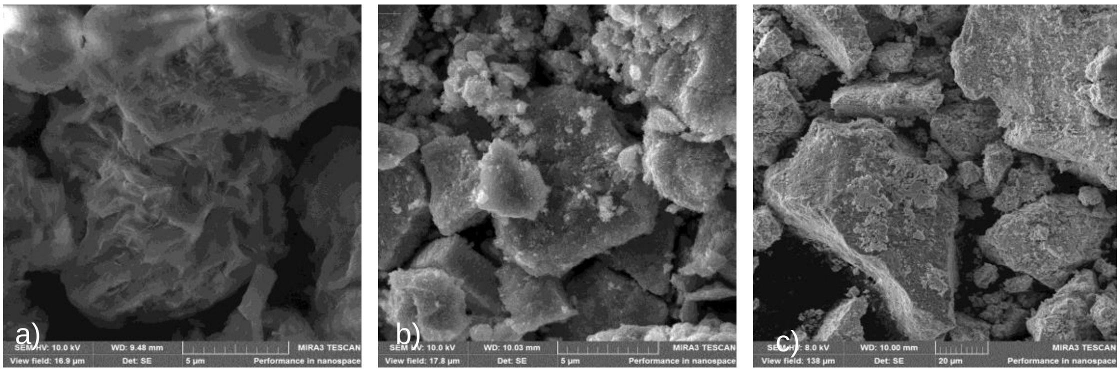

Figure 3 Morphology of the samples studied by SEM analysis;
B sample (a), MP sample (b), IS sample (c)

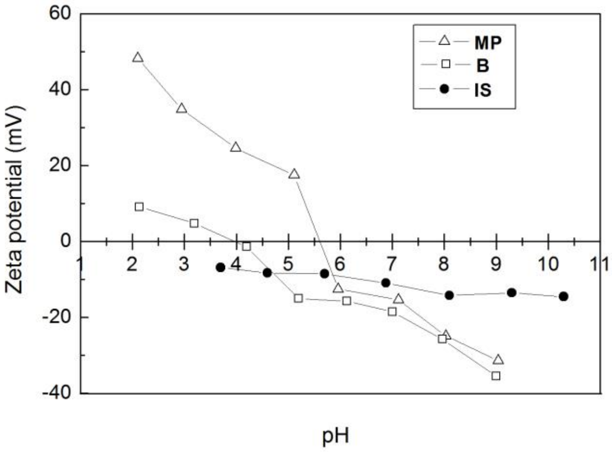

Figure 4 Zeta potential of studied samples

## Competitive adsorption

Most studies focusing on toxic ions removal by adsorbents are performed by adding this metal ion individually in experiments dealing with adsorption-desorption process. However, competence for adsorption sites in multi-metal system (which exist in wastewater) may cause the changes in adsorption process of individual ions, therefore adsorption of As(V), Cu(II) and Zn(II) ions in multi-species ion model solution has been studied.

After packing the columns, model solution with concentration of 10mg/L of each ion was percolated with the constant flow rate of 6 rpm (0.1ml/min). In the first stage, ability of IS layer in sand column to remove As(V) from single ion model solution (10mg/L) was tested, Fig. 5 (left). The removal effect decreased from 60 % to 10 % with number of percolation cycles at pH 7. At pH 5 the effect of As(V) removal was more effective (not shown here). Despite of this pH 7 was set for experiments due to above mentioned simulating of real wastewater conditions.

In the second stage, experiments with QS/B and QS/IS columns were set, where multi species ion solution was percolated and removal efficiency of bentonite with iron based sludge sample was compared. Fig.5 (right) illustrates competitive effect of ions where removal of individual ions was different. Whereas for Cu(II) and Zn(II) the removal effect was comparable in both columns, for As(V) the QS/IS column was much more effective. IS sample had a little bit lower negative charge at pH 7 compare to B sample, even if IS sample had negative charge at the whole pH range (presumably related with the agglomeration of the particles or content of some non-metallic elements (P, S, Cl) / impurity salts in the sample). Results confirmed high affinity of IS sample to As(V) ions.

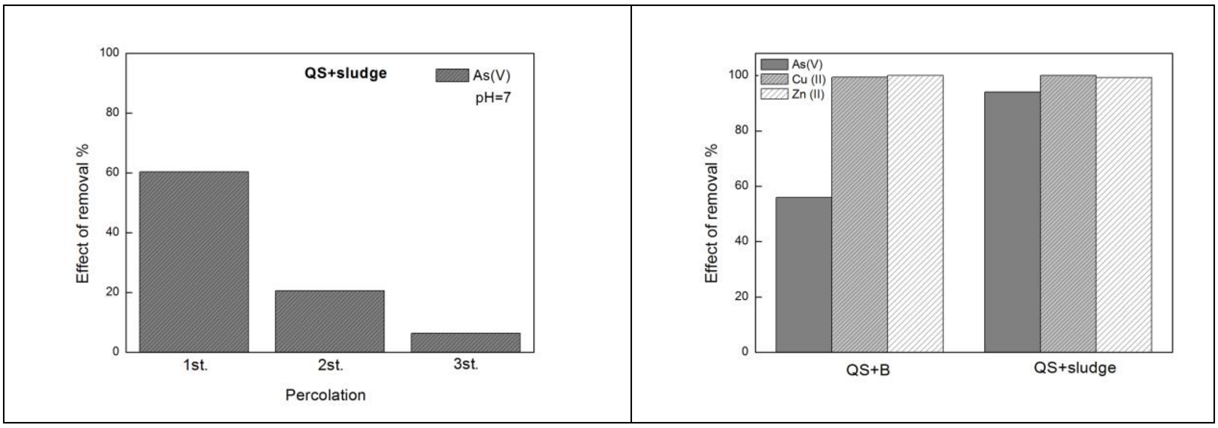

Figure 5 Adsorption of As(V) on QS/IS column after 3 percolation cycles (left);
adsorption of Cu(II), Zn(II) and As(V) ions on QS/B and QS/IS columns (1 percolation cycle) (right)

In the third stage of experiments the columns holding 4 g of QS with B/IS layer and B/MP layer were used, Fig. 6. After the first percolation the column QS/B/IS reached removal effect of 100 % for each ion. After the third flow cycle the amount of As(V) removal decreased to 58 %. For Cu(II) ions decreased slightly, while for Zn(II) ions about 20 %, Fig.6 (left). Change of IS for MP layer increased the effectivity of column especially for As(V) removal. After the fourth cycle the removal effect of As(V) decreased to 90% and the column was still efficient in ions removal. The sorption effect for Cu(II) and Zn(II) decreased to 76% and 62 %, respectively, Fig. 6 (right). The flow rate was similar during the column experiments and obtained removal effects suggest that not only iron based samples, but also the clay adsorbent plays important role in the selective removal of ions under dynamic conditions. The results also showed that the addition of IS layer to QS/B column enhanced cations removal probably due to the negative charge of the both samples at this pH value (Fig.4).

The MP layer enhanced the removal of As(V) ions in the column, which corresponds with the previous batch adsorption experiments of As(V) sorption onto IS and MP samples from the model solution. The results pointed at the maximum adsorption capacity of IS and MP sample of 0.860 and 23 mg As(V)/g, respectively [21] .

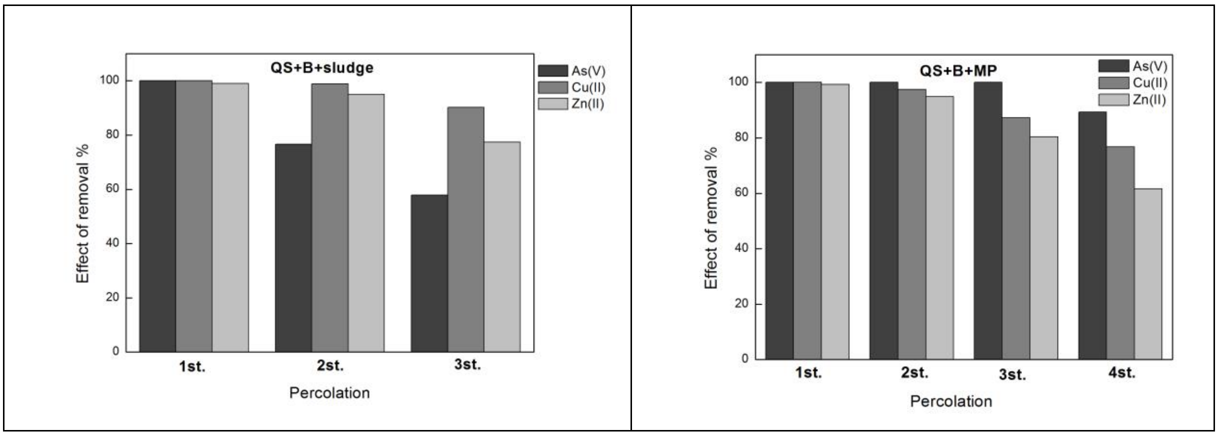

Figure 6 Adsorption of individual ions in QS/B/IS column after 3 percolation cycles (left); adsorption of ions on QS/B/MP columns after 4 percolation cycles (right).

Generally QS/B/MP column was more efficient for removal of studied toxic elements, especially for As(V) ions.

It can be concluded that QS/B/IS column is selective for studied toxic elements in following order: Cu>Zn>As, while the QS/B/MP column: As>Cu>Zn. The results showed that by the suitable combination of selected layers in the columns filled with sand which plays a role of porous media, high removal effect for number of repeated adsorption cycles can be obtained.

## CONCLUSION

Fixed-bed column experiments were used to quantitatively evaluate the removal of toxic ions dissolved in water in various quartz-sand packed columns. B, IS and MP samples were packed as a thin layer in the middle of the sand column holding approximately 4 g of quartz sand as a porous media ensure continuous flow rate. The results obtained from this study confirmed that various layer addition had different effect on individual ions removal.

The single IS layer was able to remove 60 % of As(V) from the single ion model solution.
For multi-species model solution simulating the real waste water conditions the effect of B and IS layers in Cu(II) and Zn(II) removal was comparable. For As(V) approximately 40 % higher removal effect was obtained for IS layer.

Finally the addition of B with IS or MP layer into columns was tested. An increase in flow cycles decreased the removal efficiency of ions in QS/B/IS column to 58 % for As(V). QS/B/IS column showed higher affinity to copper and zinc ions, while QS/B/MP towards arsenic.

After four percolation cycles the removal effect of QS/B/MP column decreased to 89 % for As(V), 76 % for Cu(II) and 61 % for Zn(II). It was demonstrated that the QS/B/MP column was most effective for selective ions removal, especially for As(V), and after four percolation cycles had still capacity to adsorb ions from multi-species solution.

Obtained removal efficiencies are in agreement with previous reports that the affinities of IS and MP samples for the As(V) follow the order of MP > IS in batch experiment. While the clay did not perform good adsorption properties towards As(V) in batch experiments, in dynamic regime it was proved that also its presence as a layer is important and influenced the removal effect of the column.
The small amount of B, IS and MP as a layer (0.2 g) in the sand column enabled to greatly improve the columns adsorption capacity. Based on these results studied adsorbents can be easily implemented for industrial-scale operation adsorption system designed in columns.

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