COMPARISON OF MAGNETICALLY MODIFIED MONTMORILLONITE AND SMECTA AS HEAVY METALS SORBENTS

Michaela TOKARČÍKOVÁ, Jana SEIDLEROVÁ, Oldřich MOTYKA

Nanotechnology Centre, VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU,
michaela.tokarcikova@vsb.cz, jana.seidlerova@vsb.cz, oldrich.motyka@vsb.cz

Abstract

The magnetically modified composites for Cd(II), Pb(II) and Zn(II) ions removal from aqueous solution were synthetized. Montmorillonite/Fe_xO_y composites were successfully prepared using ferrofluid. The presence of Fe_xO_y nanoparticles (NPs) on the clay surface did not influence its chemical composition and did not lead to the release of clay elements to the solution. Moreover, the Fe_xO_y NPs enhanced the sorption properties of the clays and - due to the magnetic properties of composites - they could be easily removed by external magnetic field after the sorption. The influence of initial pH of the aqueous solution containing Cd(II), Pb(II) and Zn(II) ions on sorption capacity of montmorillonite/Fe_xO_y composites was studied. The accompanying elements released from clays to final extracts were observed as well. Results show that the initial pH of aqueous solution affected the sorption capacity of the observed elements and the release of the elements from montmorillonite originated from Ivančice (M) and magnetically montmorillonite (MM). The maximum sorption capacity was determined in the acid area of pH (3-4). After the sorption, Fe_xO_y NPs were determined in final extracts at low concentrations and are, therefore, fixed onto MM strongly. However, Fe_xO_y NPs are not fixed onto magnetically modified Smecta (SM) as strongly as onto MM because they leached to the final extracts more than from MM. Due to the aforementioned results of Fe_xO_y leaching, both studied composites were still magnetic after sorption experiments. The prepared composites are functional sorbents and are stable in pH 3-7.

Keywords: Montmorillonite, magnetically composite, iron oxide nanoparticles, stability, sorption

1. INTRODUCTION

Heavy metal pollution of the environment has remained a serious problem. Its efficient removal from wastewaters eliminates the contamination and cumulation in soils, surface and underground water. Cleaning technics for heavy metals removal such as ion exchange, reverse osmosis, and electrodialysis are effective, although costly [1]. Chemical precipitation is simple and low-cost method, however, it produces large volumes of sludge and does not reduce the heavy metal content sufficiently [2]. Adsorption is, considering the criteria aforementioned, simply, low cost and quick. Biochar [3], soybean hull biosorbent [4], rice and peanut husks [5,6], zeolite, bentonite [7], montmorillonite [8] are one of the most commonly biosorbents studied for the elimination of Pb, Zn, Cd and other elements from aqueous solution. Especially clays and clay mineral have been studied as sorbents due to their large specific area, low cost, chemical stability, cation-exchange capacity, environmental safety and excellent sorption properties [9]. Potencial sorbents has been modified by various technics including treatments with steam, acids, bases, metal oxides, carbonaceous materials, clay minerals, organic compounds, and biofilms to enhance their surface area and sorption properties [10-12]. One of the best treatments is magnetic modification of sorbents using iron oxides nanoparticles (NPs). Fe_3O_4 shows paramagnetic properties therefore, it can be influenced by magnet and loses its magnetic properties after its removal from the magnetic field.

There are several methods of clay magnetization: calcination of pre-treated clay minerals [13,14], mixing clay with iron oxide particles and prepared in a microwave [15], precipitation of magnetic iron oxides from a mixture of ferrous and ferric salts by a strong hydroxide in the presence of clay [15]. The magnetization of sorbents can increase the sorption capacity and the sorbent can be removed from solution by magnet.

Smecta (S) and montmorillonite (M) were magnetized using ferrofluid. Magnetically modified Smecta (MS) and montmorillonite (MM) composites were tested as sorbents of Cd, Pb and Zn ions from aqueous solution with various initial concentration and pH (3-7). pH and elements (Fe, Si, Al, Na, K, Mg and Ca) released from composites to final extracts were determined by atomic emission spectroscopy with inductively coupled plasma (AES-ICP)

2. EXPERIMENTAL

Chemical composition (**Table 1**) of Smecta (denoted as S) and montmorillonite originated from Ivančice (M) was determined using an energy dispersive fluorescence spectrometer (XRFS) SPECTRO XLAB (SPECTRO Analytical Instruments GmbH). For this measurement, samples in powder form were pressed into tablets using wax as a binder. Magnetically modified Smecta (MS) and montmorillonite (MM) composites prepared prof. Ivo Šafařík in the Institute of Nanobiology and Structural Biology of GCRC, Academy of Sciences of the Czech Republic.

Table 1 The chemical composition of Smecta (S) and montmorillonite (M)

Element	**S (wt.%)**	**M (wt.%)**
Na_2O	< 0.005	0.093 ± 0.047
MgO	3.6 ± 1.2	3.07 ± 0.62
Al_2O_3	14.2 ± 0.5	13.9 ± 0.84
SiO_2	49.8 ± 1.0	57.47 ± 4.03
K_2O	0.168 ± 0.009	0.925 ± 0.084
CaO	1.48 ± 0.08	2.04 ± 0.63
TiO_2	0.17 ± 0.012	0.296 ± 0.030
Fe_2O_3	2.77 ± 0.09	3.40 ± 0.14
LOI	27.3 ± 0.3	17.75 ± 1.07

2.1. Adsorption experiment

$Cd(NO_3)_2.4H_2O$ (SIGMA-ALDRICH, p.a. ≥ 99.0 %), $Pb(NO_3)_2$ (LACHEMA, p.a.) and $ZnCl_2$ (Lach-Ner, s.r.o., M_r 136.29 g/mol) were used to prepare aqueous solutions with Cd(II), Pb(II) or Zn(II) ions, respectively. The initial pH was adjusted by NaOH (MACH CHEMIKÁLIE, s.r.o., p.a. M_r 40 g/mol) or HNO_3 (MACH CHEMIKÁLIE, s.r.o., p.p. 65 %) solution to range 3 - 7 pH with the initial concentration 10 mg/l of Cd(II), Pb(II) and Zn(II) ions. 0.2 g of sample was mixed with 50 ml of initial solution and was shaken in a rotating shaker at a constant speed (4.5 rpm) at laboratory temperature. The suspensions were, after 1 hour of shaking, filtered through 0.45 μm filter paper immediately after 30 minutes of centrifugation (3000 rpm). Elements leached from S, MS, M and MM samples (Al, Si, Fe, Na, K, Mg, Ca) and concentration of Cd(II), Pb(II) and Zn(II) ions were determined by AES-ICP (CIROS SPECTRO VISION) in final extracts.

The differences between the initial and final concentrations of adsorbed elements (Cd, Pb and Zn) were used to calculate the amount of sorbed metal ions. The final metal uptake capacity was calculated according to Eq. 1 [16]:

$$q = \frac{V.(c_0 - c_r)}{m}.100 \qquad (1)$$

where:

q - amount of contaminant removed from solution (%)
V - volume of the solution (l)
c_0 - concentrations of the metal ions in the initial solution (mg/l)
c_r - concentrations of the metal ions in the final solution (mg/l)
m - sorbent dose in the mixture (g)

3. RESULTS AND DISCUSSION

3.1. Effect of initial pH

Figure 1 illustrates the effect of initial pH on adsorption of metals ions from solution onto S, MS, M and MM samples. Initial concentration of metal ions in solution was 10 mg/L.

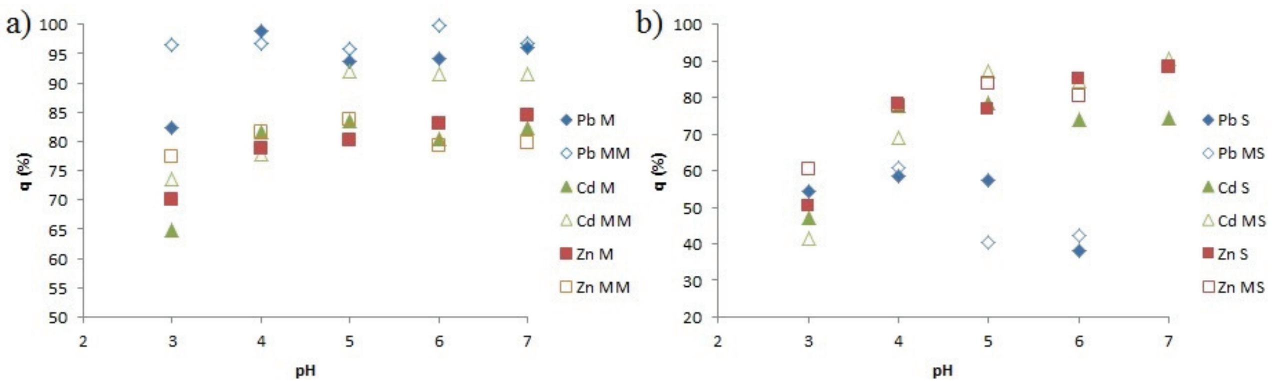

Figure 1 The amount of Pb, Cd and Zn ions removed from solution by a) original montmorillonite (M) and magnetically modified montmorillonite (MM), b) Smecta (S) and magnetically modified Smecta (MS)

The adsorbed amounts of monitoring ions increased with increasing pH of initial solution. The Cd(II), Pb(II) and Zn(II) ions uptake increased at pH ≥ 4 for original M and MM composite. Pb(II) ions show the best affinity to M and MM composite (> 95 %). The adsorption of Cd(II) and Zn(II) onto original S and MS composite increased at pH ≥ 4 as well. The removal of Cd(II), Pb(II) and Zn(II) ions from solution by the original M and MM composite was more efficient than by S or MS composite. M and MM composite removed more than 80 % of Cd(II), Pb(II) and Zn(II) from solution with pH ≥ 4. Moreover, magnetization of both clays increased their sorption capacity.

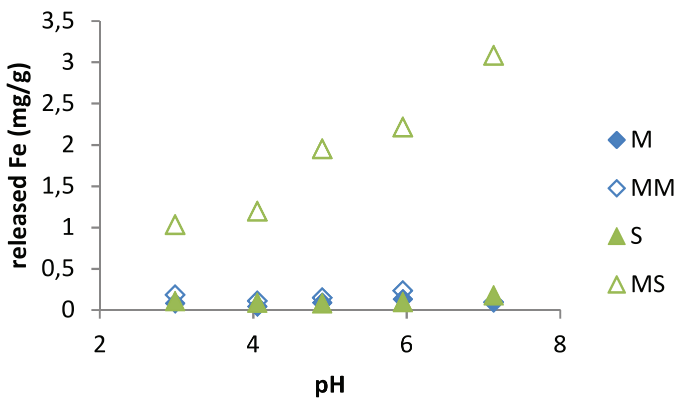

Figure 2 The amount of Fe released from original montmorillonite (M) and Smecta (S) and magnetically modified montmorillonite (MM) and Smecta (MS) to extraction agents with various initial pH

The concentration of Fe released from original M and S and from MM and MS composites after leaching test was determined as well (**Figure 2**). Fe released from MM to extraction agent is negligible in comparison to the original M. Therefore, Fe_xO_y NPs are strongly fixed onto the composite and MM composite is stable in a wide pH range. Concentration of Fe determined in final extract obtained from MS increased with increasing pH of initial solution. Amount of Fe released from MS to the final extracts did not exceed 3.5 mg/g. The after-sorption magnetic properties of MM and MS were successfully verified by magnet.

The determined concentration of Al, Si, Fe, Na, K, Mg and Ca were also evaluated using factorial analysis of mixed data (**Figure 3**).

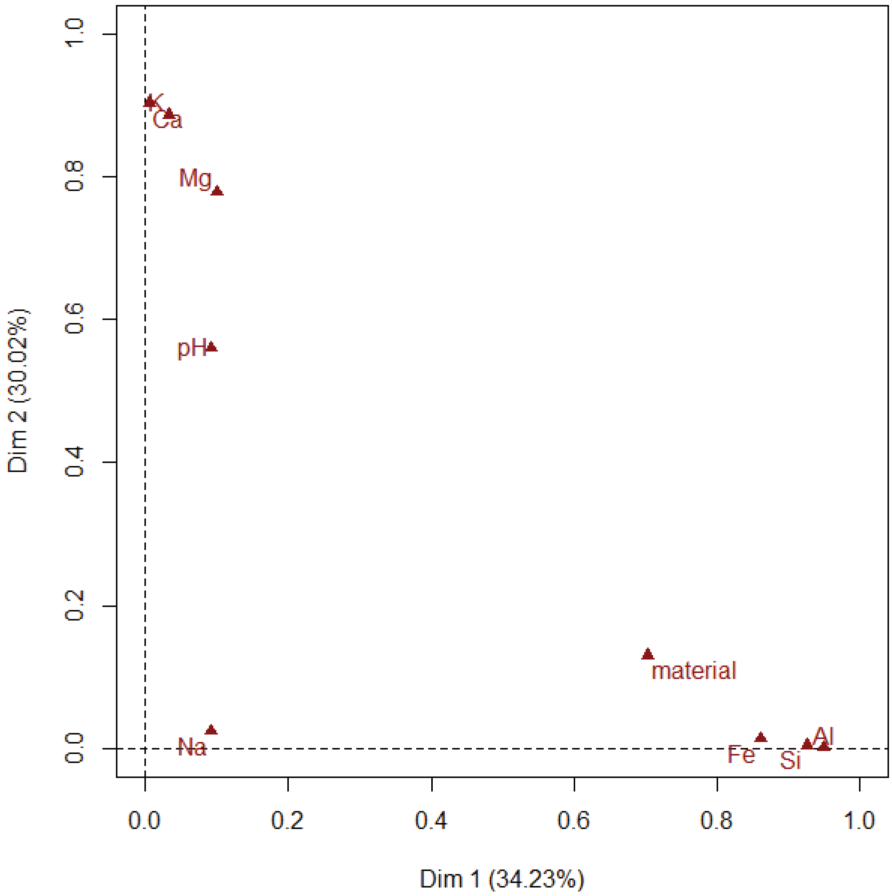

Figure 3 Factorial analysis of mixed data (FAMD)

Figure 3 shows the relation between the concentration of leached elements from samples and initial pH of extraction agents. The determined concentration of Al, Si and Fe in final extracts are display association with with materials, however seem not to be affected by the initial pH. The concentrations of K, Ca and Mg in the final extracts are not affected with tested materials, but they are related to the initial pH of extraction agents. Aforementioned relationships determined by FAMD were evaluated in more details by analysis of variance (ANOVA) and consequent Tukey HSD test.

The results of ANOVA show that the initial pH of extraction agents significantly influences the concentration of leached elements (Na, K, Mg and Ca) in final extracts ($\alpha = 0.05$). Tukey HSD test shows significant difference in released amount of Na between pH 5 and 6 as well as between pH 5 and 7. Significant difference between pH and released amount of K or Ca were observed in acidic pH area. The influence of initial pH on Mg release from materials was insignificant. Tukey HSD test proved significant difference in released amount of Al and Si between MM and MS composites and between M and MS. Significant difference to released amount of Fe was proved between S and MS, MM and MS, M and MS. This suggests that the release of Fe from composite is influenced by matrix, mainly by Smecta.

4. CONCLUSION

Magnetically modified montmorillonite (MM) and Smecta (MS) composites were successfully prepared and tested as sorbents of heavy metals ions from aqueous solution with various initial pH. Original montmorillonite and Smecta were tested as sorbents for the comparison with composites as well. The sorption properties of original montmorillonite and Smecta increased after magnetically modification. Magnetically modified Smecta removed 35-90 % of tested ions. Magnetically modified montmorillonite adsorbed up to 99 % of Pb(II), 92 % of Cd(II) and 85 % of Zn(II). Composites show the best sorption properties at pH ≥ 4. The concentration of released Fe from original clays and composites were determined in solution after sorption as well. The amount of released Fe from original montmorillonite and montmorillonite composite were similar. Therefore, the Fe_xO_y NPs are strongly fixed in montmorillonite composite in wide range of pH 3-7. The amount of released Fe from Smecta composite increased with increasing pH of solution. The released amount of Fe from magnetically modified Smecta did not exceed 3.5 mg/g and the magnetic properties were successfully verified by magnet. From the statistical point of view, the release of Fe from magnetically modified montmorillonite and magnetically modified Smecta composites was significantly influenced by the substrate.

ACKNOWLEDGEMENTS

The work was supported from ERDF/ESF New Composite Materials for Environmental Applications (No. CZ.02.1.01/0.0/0.0/17_048/0007399).

Authors also wish to thank prof. Ivo. Safarik for providing the magnetically samples and all colleagues, who participated in the measurements.

REFERENCES

[1] BHATTACHARYA, A. K., MANDAL, S. N., DAS, S. K. Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chemical Engineering Journal*. 2006. vol. 123, pp. 43-51.

[2] KANDAH, Munther Issa. Zinc and cadmium adsorption on low-grade phosphate. *Separation and Purification Technology*. 2004. vol. 35, pp. 61-70.

[3] WONGROD, Suchanya, SIMON, Stéphane, GUIBAUD, Gilles, LENS, Piet N. L., PECHAUD, Yoan, HUGUENOTA, David, D. VAN HULLEBUSCH, Eric. Lead sorption by biochar produced from digestates: Consequences of chemical modification and washing. Journal of Environmental Management. 2018. vol. 219, pp. 277-284.

[4] MÓDENES, Aparecido N., ESPINOZA-QUIÑONES, Fernando R., COLOMBO, Andréia, GERALDI, Claudinéia L., TRIGUEROS, Daniela E. G. Inhibitory effect on the uptake and diffusion of Cd^{2+} onto soybean hull sorbent in Cd-Pb binary sorption systems. *Journal of Environmental Management*. vol. 154, pp. 22-32.

[5] SAWASDEE, Suchada, JANKERD, Hathairat, WACHARABUNDIT, Prachart. Adsorption of dyestuff in household-scale dyeing onto rice husk. *Energy Procedia*. vol. 138, pp. 1159-1164.

[6] HAN, Runping, HAN, Pan, CAI, Zhaohui, ZHAO, Zhenhui, TANG, Mingsheng. Kinetics and isotherms of Neutral Red adsorption on peanut husk. *Journal of Environmental Sciences*. 2008. vol. 20, pp. 1035-1041.

[7] HAMIDPOUR, Mohsen, KALBASI, Mahmoud, AFYUNI, Majid, SHARIATMADARI, Hossein, HOLM, Peter E., HANSEN, Hans *Christian Brunn. Sorption hysteresis of Cd(II) and Pb(II) on natural zeolite and bentonite. Journal* of Hazardous Materials. 2010. vol. 181, pp. 686-691.

[8] ABDELLAOUMI, Youness, OLGUÍN, María Teresa, ABATAL, Mohamed, ALI, Bassam, MÉNDEZ, Sosimo Emmanuel Díaz, SANTIAGO, Arlette A. Comparison of the divalent heavy metals (Pb, Cu and Cd) adsorption behavior by montmorillonite-KSF and their calcium- and sodium-forms. *Superlattices and Microstructures*. 2017. In press.

[9] JIANG, Liying, YE, Qichao, CHEN, Jianmeng, CHEN, Zhong and GU, Youli. Preparation of magnetically recoverable bentonite-Fe_3O_4-MnO_2 composite particles for Cd(II) removal from aqueous solutions. *Journal of Colloid and Interface Science.* 2018. vol. 513, pp. 748-759.

[10] SIMUZ, Tom, FRESNO, Teresa, AKGUL, Gökçen, FROST, Harrison, MORENO-JIMÉNEZ, Eduardo. Biochar modification to enhance sorption of inorganics from water. *Bioresource Technology.* 2017. vol. 246, pp. 34-47.

[11] ROZUMOVÁ, Lucia, ŽIVOTSKÝ, Ondřej, SEIDLEROVÁ, Jana, MOTYKA, Oldřich, ŠAFAŘÍK, Ivo, ŠAFAŘÍKOVÁ, Mirka. Magnetically modified peanut husks as an effective sorbent of heavy metals. *Journal of Environmental Chemical Engineering*. 2016. vol. 4, pp. 549-555.

[12] NADERI, Arman, DELAVAR, Mohmmad Amir, GHORBANI, Yousef, KABOUDIN, Babak, HOSSEINI, Mehdi. Modification of nano-clays with ionic liquids for the removal of Cd (II) ion from aqueous phase. Applied Clay Science. 2018. vol. 158, pp. 236-245.

[13] BOURLINOS, A.B., KARAKASSIDES, M.A., SIMOPOULOS, A., PETRIDIS, D. Synthesis and characterization of magnetically modified clay composites. *Chemistry of Materials*. 2000. vol. 12, pp. 2640-2645

[14] GAO, Z., LI, X., WU, H., ZHAO, S., DELIGEER, W., ASUHA, S. Magnetic modification of acid-activated kaolin: Synthesis, characterization, and adsorptive properties. *Microporous and Mesoporous Materials*. 2015, pp. 1-7.

[15] SAFARIK, Ivo, HORSKA, Katerina, POSPISKOVA, Kristyna, SAFARIKOVA, Mirka. One-step magnetic modification of non-magnetic solid materials. *Powder Technology*. 2012, pp. 285-289.

[16] CORRAMI, Alessia, MIGNARDI, Silvano, FERRINI, Vincenzo. Corami, A., Mignardi, S., Ferrini, V., 2008. Cadmium removal from single- and multi-metal (Cd + Pb + Zn + Cu) solutions by sorption on hydroxyapatite. *Journal of Colloid and Interface Science*. 2008, pp. 402-408.