

## STUDY OF MAGNETICALLY MODIFIED KAOLINITE BY LEACHING TEST

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### Abstract

Magnetically modified clays are low cost materials with promising properties for using in sorption of pollutants from wastewaters. The influence of extraction agents on released of iron oxides nanoparticles (NPs) from magnetically modified kaolinite was studied in this article. Stability of mentioned new smart material was evaluated by leaching test. Characterization of prepared sample was investigated using X-ray fluorescence spectroscopy, rtg. powder diffraction spectroscopy, IR spectroscopy and SEM. Leachates were prepared according to European technical standard EN 12457-2. Material was interacted with demineralization water and extraction agents treated by solution of H<sub>2</sub>SO<sub>4</sub> on pH 2 and 4 or NaOH solution on pH 9 and 11 by discontinuous rotation container at laboratory temperature for 24 hours. The stability of magnetically modified kaolinite was evaluated on the basis of released Fe, Si, Al and accompanying elements in kaolinite structure. Elements were determined after decomposition of filtrate in HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> by atomic emission spectrometer with inductively coupled plasma.

**Key words:** Fe oxides nanoparticles, kaolinite, leaching test

### 1. INTRODUCTION

Kaolinite Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> is a natural material, it is inexpensive, commonly available, non-toxic and harmless to environment. Kaolinite can be used e.g. as sorbent of heavy metal cations [1] or for fixation of the metal particles or metal oxide NPs. Kaolinite is suitable sorption material for removal of pollutants from aqueous solutions while its sorption properties are known to increase after modification by metal oxide particles [2, 3]. Magnetic derivatization of adsorbents is a very important modification which was proven to improve the manipulation as well. Magnetic separation techniques have recently found many interesting applications in various areas of biosorption [4], for the removal of water-soluble dyes [5], in catalysis [6] and for the removal of heavy metal from water [7]. In recent years, the research effort has been devoted to preparation of low cost and efficient sorbents. Magnetically modified composites which can be prepared for example from biosorbents as peanut husks [8], and spent grain [5] or clay minerals [7] have these promising properties. In this study, magnetically modified kaolinite was prepared by fixing Fe oxides NPs on kaolinite surface by precipitation [9].

Not only positive properties of prepared composite are significant, the changes of its properties in different environments are important as well. There are lots of studies focused on NPs effect on the environment and toxicity of NPs [10, 11, 12]. The fixation of nanoparticles on the suitable substrate decreased the possible risk for environment and living organisms.

Therefore, the stability of magnetically modified kaolinite was studied before its use as a sorbent. Stability of prepared composite was investigated by leaching test according to European technical standard EN 12457-2 [13]. Leaching test is a suitable laboratory method for testing the material behaviour in various conditions. Leaching of material in modified extraction agents can approximate behaviour of material in natural conditions. This method is difficult from the point of reproducibility but still remains basis for testing strategy. Leaching tests can be carried out in varying ratio of liquid to solid or in liquid phase that can be adjusted to wide range of pH [14]. The leaching test was extended with leaching composite in extraction agents modified

by H<sub>2</sub>SO<sub>4</sub> and NaOH solutions to pH 2, 4 or 9 and 11. Fe, Al, Si and accompanying elements in kaolinite structure leached to final extracts were determined by AES-ICP.

## 2. EXPERIMENTAL

Chemical composition of original untreated kaolinite was determined using energy dispersive fluorescence spectrometer (XRFS) SPECTRO XEPOS (SPECTRO Analytical Instruments GmbH) equipped with 50 W Pd X-ray tube. The analysed sample was prepared in the form of pressed tablet (wax was used as binder). The chemical composition of original kaolinite is shown in Table 1. Magnetically modified kaolinite was prepared by precipitation and is described in details in [9]. Total amount of Fe in composite was 7.81 rel. % and it was determined after total decomposition in HF and in aqua regia by FA-AAS (UNICAM 969).

**Table 1** The chemical composition of original kaolinite, LOI – lost on ignition.

Unit	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	MgO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	SO <sub>3</sub>	LOI
rel. %	2.71	35.6	47.1	<0.02	0.14	0.05	1.38	0.10	0.10	0.004	0.02	11.7

### 2.1. Leaching test

Leachates were prepared according to European technical standard EN 12457-2. Sample was leached in deionized water and extraction agents with initial pH adjusted to 2, 4 or 9 and 11 by adding H<sub>2</sub>SO<sub>4</sub> or NaOH solutions. Mixture (solid:liquid = 1:10) was shaken in discontinuous rotation container at a constant speed (4.5 rpm) at laboratory temperature for 24 hours. Mixtures were filtered through 0.45 µm filter paper immediately after centrifugation (3000 rpm) for 15 minutes. Al, Si, Fe and accompanying elements in kaolinite structure that leached to final extracts were determined after decomposition in HNO<sub>3</sub> (65 %, pure, MACH CHEMIKÁLIE, s.r.o.) and H<sub>2</sub>O<sub>2</sub> (30 %, GR, MACH CHEMIKÁLIE, s.r.o.) by AES-ICP (CIROS SPECTRO VISION).

### 2.2. Infrared spectroscopy

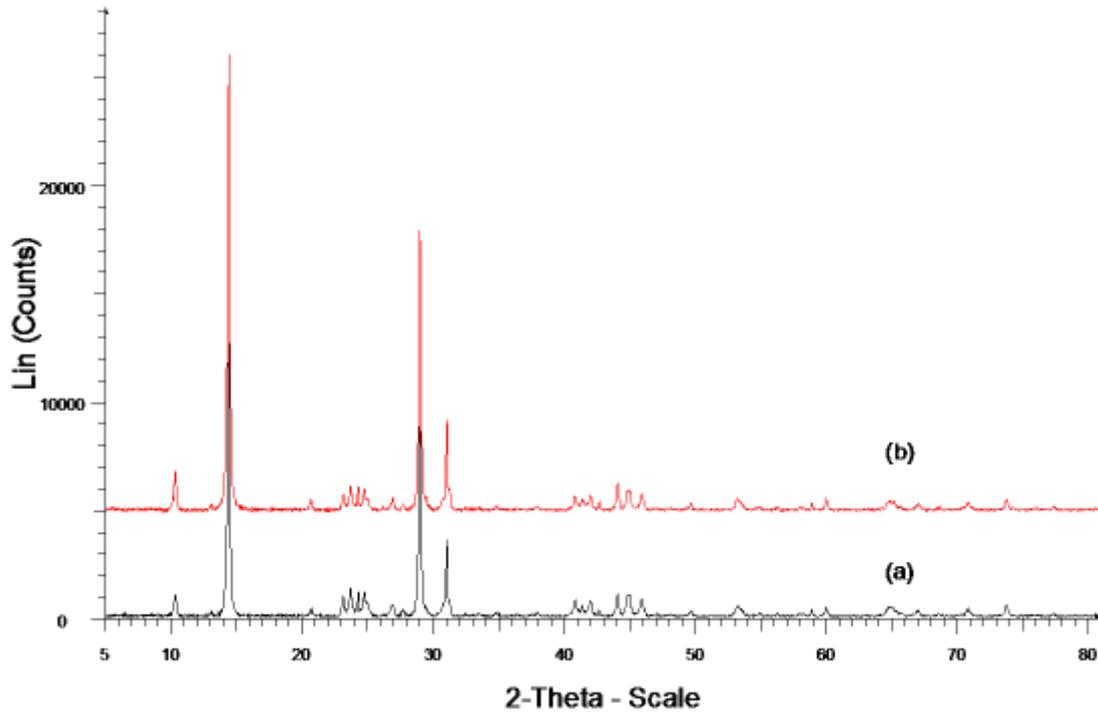
The samples were measured in the form of pellet with KBr (KBr was added to 1.5 mg of sample to final weight of 300 mg) by Perkin Elmer 2000 FT-IR spectrometer. IR spectra were recorded in mid IR region 4000 – 400 cm<sup>-1</sup>.

### 2.3. X-ray powder diffraction

The X-ray powder diffraction (XRPD) patterns were recorded under CoK $\alpha$  irradiation ( $\lambda$  = 1.789 nm) using Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with a fast position-sensitive detector VANTEC 1. Measurements were carried out in a reflection mode, powder samples were pressed in a rotational holder. Phase composition was evaluated by using database PDF 2 Release 2004 (International Centre for Diffraction Data).

## 3. RESULTS AND DISCUSSION

XRPD patterns of original kaolinite (a) and composite with Fe oxides NPs (b) are presented in Fig. 3. After magnetization of kaolinite, the crystalline domains were ordered. Magnetization of clay mineral did not influence the structure of kaolinite therefore good sorption properties of magnetically modified kaolinite can be assumed.



**Fig. 3** XRPD patterns of original kaolinite (a) and composite with Fe oxides NPs (b).

The content of selected elements leached from the composite (see equations 1 – 3) was estimated as follows.

The content ( $c_2$ ) of element per gram of sample [ $\text{mg}\cdot\text{g}^{-1}$ ] was calculated from measured concentration of element in leachate:

$$c_2 = \frac{c_1}{m_n} \cdot V_{EA} \quad (1)$$

where  $c_1$  is the concentration of an element in leachate [ $\text{mg}\cdot\text{L}^{-1}$ ],  $m_n$  is the sample weight [g], and  $V_{EA}$  represents the volume of extraction agent [L].

Content of element ( $c_3$ ) in the original sample [ $\text{mg}\cdot\text{g}^{-1}$ ]:

$$c_3 = x_1 \cdot \frac{M_r(\text{elem.})}{M_r(\text{oxide})} \quad (2)$$

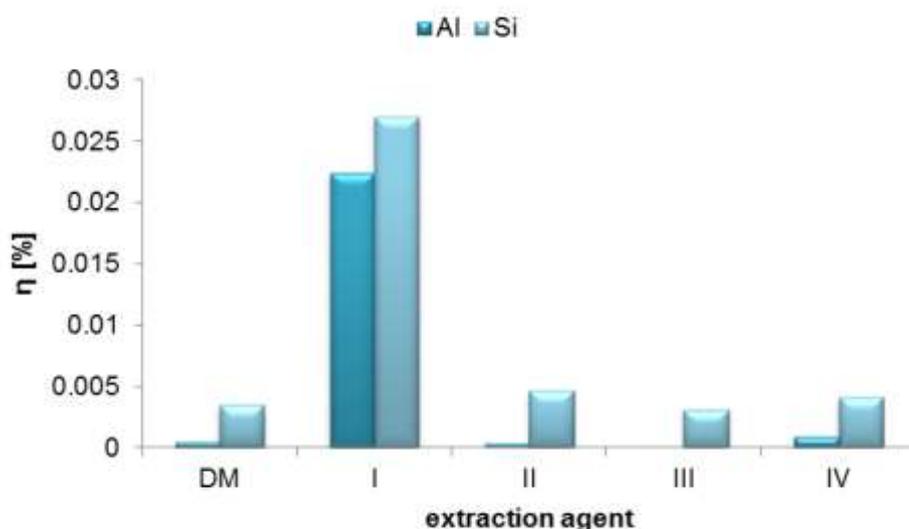
Where  $x_1$  is the quantity of element in oxide form in the original sample [ $\text{mg}\cdot\text{g}^{-1}$ ],  $M_r(\text{elem.})$  is the relative molecular mass of element [ $\text{g}\cdot\text{mol}^{-1}$ ], and  $M_r(\text{oxide})$  is the relative molecular mass of element oxide [ $\text{g}\cdot\text{mol}^{-1}$ ].

The relative portion of elements  $x$  [%] released from composite into leachate:

$$x = \frac{c_2}{c_3} \cdot 100 \quad (3)$$

Relative percent of Al and Si leached from kaolinite structure is presented in Fig. 1 and Table 2. Difference (in rel. %) between Al and Si released from composite were insignificant. Greatest rel. % of Al and Si was determined in extract obtained by leaching composite in extraction agent with pH 2 (denoted as extraction agent I). Determined concentration of Al was  $4.2 \text{ mg}\cdot\text{L}^{-1}$  and  $5.9 \text{ mg}\cdot\text{L}^{-1}$  of Si. The leached amount did not exceed 0.03 rel. %. Determined concentrations in extracts obtained from DM, extraction agents 4 (denoted as extraction agent II), 9 (denoted as extraction agent III) and 11 (denoted as extraction agent IV) were lower

than 0.1 mg·L<sup>-1</sup> of Al and Si. Therefore, determined amounts of Al and Si are negligible in comparison with original kaolinite and modification of kaolinite by Fe oxides NPs did not have impact on kaolinite structure.



**Fig. 1** The relative % of released Al and Si from composite to DM – deionized water, I - extraction agents with pH 2, II – extraction agent with pH 4, III – extraction agent with pH 9 and IV – extraction agent with pH 11.

Relative amount of Fe and accompanying elements in kaolinite released from composite are presented in Table 2. Impact of extraction agents (DM, III and IV) on release of Fe NPs from composite was insignificant. Determined concentration did not exceed 0.1·mg·L<sup>-1</sup>. Fe was released distinctively after interaction of composite with acid extraction agents, except for extraction agent adjusted on pH 2. Concentration of Fe determined in final extract with initial pH 2 achieved almost 30 mg·L<sup>-1</sup> which corresponds 3.72 rel. %.

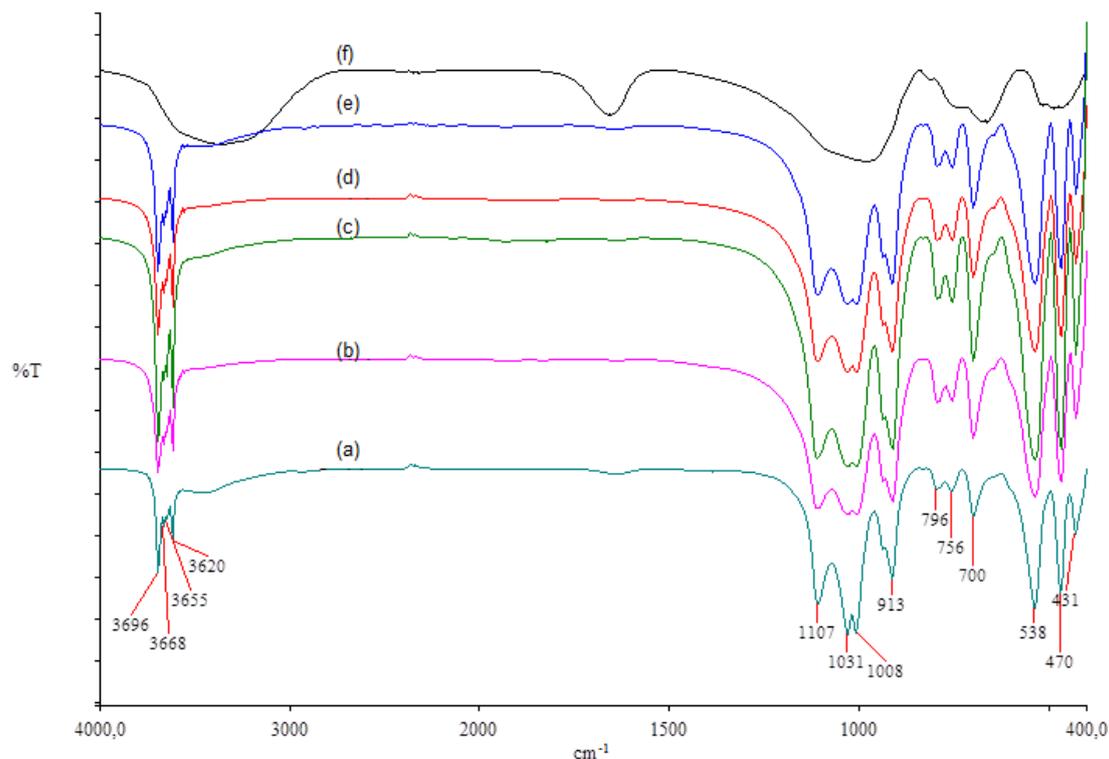
The greatest rel. % of K, Mg and Ti was determined in extract obtained by leaching composite in extraction agent with pH 2. The accompanying elements were leached from composite more easily than Al and Si (forming kaolinite structure) and added Fe oxides NPs.

**Table 2** Determined concentration and relative % of released Fe from composite. DM – deionized water, I – extraction agent with pH 2, II – extraction agent with pH 4, III – extraction agent with pH 9 and IV – extraction agent with pH 11.

Extraction agent	Al (rel. %)	Si (rel. %)	Fe (rel. %)	K (rel. %)	Mg (rel. %)	Ti (rel. %)	Ca (rel. %)
DM	0.5·10 <sup>-3</sup>	0.003	0.01	0.24	0.88	0.01	6.15
I	0.02	0.03	3.72	0.52	5.25	0.02	40.1
II	0.3·10 <sup>-3</sup>	0.005	0.06	0.29	1.13	0.05	8.33
III	-	0.003	0.01	0.25	0.76	0.01	6.13
IV	0.9·10 <sup>-3</sup>	0.004	0.01	0.22	0.35	0.01	3.07

The FT-IR spectrum of composite before and after leaching test is presented in Fig. 2. Five maximum bands at 3696, 3668, 3655 and 3620 cm<sup>-1</sup> and 913 cm<sup>-1</sup> attributed to vibration of inner and outer Al-OH bonds. Bands at 1107, 1031, 796, 470 and 431 correspond with vibrations of Si-O bonds and 1008, 756, 700, 538 belong to vibrations Si-O-Al. Although the greatest rel. % of leached elements were determined in extract

obtained by leaching composite in extraction agent with pH 2, the structural changes are apparent in composite after leaching test in extraction agent with pH 11 (f).



**Fig. 2** Infrared spectrum of composite before leaching test (a), and after leaching test in (b) – extraction agent with pH 2 or pH 4 (c), (d) – deionized water, (e) – extraction agent with pH 9 or 11 (f).

#### 4. CONCLUSION

The stability of kaolinite magnetically modified with Fe oxides nanoparticles was investigated by leaching test. The impact of extraction agent pH on release of Fe from kaolinite and kaolinite structure was studied as well. Concentrations of released elements determined in final extracts were calculated to relative percent of its content in composite to allow better comparison of the effects of extraction agent. There are differences between elements which form the structure of kaolinite and elements which are present as contaminants in the kaolinite.

The greatest amount (3.7 rel. %) of Fe was released to extraction agent with pH 2, determined concentration was almost  $30 \text{ mg}\cdot\text{L}^{-1}$  of Fe which is insignificant to its total content in the composite. In deionized water and other final extracts, determined concentration of Fe did not exceed  $0.5 \text{ mg}\cdot\text{L}^{-1}$  which corresponds to only 0.01 rel. % from the total content released to final extract. This means that the leaching test of magnetically modified kaolinite confirmed good stability of the tested composite.

The greatest concentrations of released elements were also determined in extracts obtained by leaching composite in extraction agent with pH 2. Effect of extraction agent caused easier release of K, Mg and Ca from composite than of Al and Si. Determined concentration of K did not exceed 0.6 rel. % and concentration of Mg did not exceed 5.3 rel. % in final extracts. In the mentioned agent, 40 rel. % of Ca from composite was released. In final extracts obtained by leaching composite in deionized water and extraction agents with pH 4, 9 and 11, the determined concentrations were lower than 9 rel. %.

The determined amounts of Al and Si were very similar and did not exceed 0.03 rel. % in extract obtained by leaching composite in extraction agent with pH 2. Concentrations of Al and Si determined in extract obtained from deionized water and extraction agents with pH 4, 9 and 11 were insignificant because concentrations were lower than 0.1 mg·L<sup>-1</sup>.

Modification of kaolinite by Fe oxides nanoparticles did not disrupt the kaolinite structure, the extraction agents did not have an impact on the stability of magnetically modified composite, therefore, composite is stable and suitable for future studies of sorption of pollutants from aqueous solutions.

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## LITERATURE

- [1] LI, Z., BEACHNER, R., McMANAMA, Z., HANLIE, H. Sorption of arsenic by surfactant-modified zeolite and kaolinite. *Microporous and Mesoporous Materials*, 2007, p. 291-297.
- [2] GUPTA. S. S., BHATTACHARYYA, K. G. Adsorption of Ni(II) on clays. *Colloid and Interface Science*, 2006, p. 23-32.
- [3] BHATTACHARYYA, K. G. GUPTA. S. S. Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. *Separation and Purification Technology*, 2006, p. 388-397.
- [4] ŠAFAŘÍKOVÁ, M., PTÁČKOVÁ, L., KIBRIKOVÁ, I., ŠAFAŘÍK, I. Biosorption of water-soluble dyes on magnetically modified *Saccharomyces cerevisiae* subsp. *uvarum* cells. *Chemosphere*, 2005, p. 831-835.
- [5] SAFARIK, I., HORSKA, K., SAFARIKOVA, M. Magnetically modified spent grain for dye removal. *Journal of Cereal Science*, 2011, p. 78-80.
- [6] PARRA DA SILVA, F., ROSSI, M. L. Palladium on magnetite: magnetically recoverable catalyst for selective hydrogenation of acetylenic to olefinic compounds. *Tetrahedron*, 2014, p. 3314-3318.
- [7] NAH, I. W., HWANG, K-Y., JEON, CH., CHOI, H. B. Removal of Pb ion from water by magnetically modified zeolite. *Minerals Engineering*, 2006, p. 1452-1455.
- [8] SAFARIK, I., SAFARIKOVA, M. Magnetic fluid modified peanut husks as an adsorbent for organic dyes removal. *Physics Procedia*, 2010, p. 274-278.
- [9] ŽIVOTSKÝ, O., SEIDLEROVÁ, J., ŠAFAŘÍK, I., ŠAFAŘÍKOVÁ, M. Preparation and characterization magnetically modified clay minerals – Under Review.
- [10] LIU, J., VIPULANANDAN, C. Effects of Au/Fe and Fe nanoparticles on *Serratia* bacterial growth and production of biosurfactant. *Materials Science and Engineering C*, 2013, p. 3909-3915.
- [11] WANG, D., GAO, Y., LIN, Z., YAO, Z., ZHANG, W. The joint effects on *Photobacterium phosphoreum* of metal oxide nanoparticles and their most likely coexisting chemicals in the environment. *Aquatic Toxicology*, 2014, p. 200-206.
- [12] SHINDE, S.K., GRAMPUROHIT, N.D., GAIKWAD, D.D., JADHAV, S.L., GADHAVE, M.V., SHELKE, P.K. Toxicity induced by nanoparticles. *Asian Pacific Journal of Tropical Disease*, 2012, p. 331-334.
- [13] Annex 2 to the Order 294/2005 Sb. (in Czech).
- [14] TOKARČÍKOVÁ, M., TOKARSKÝ, J., ČABANOVÁ, K., MATĚJKA, V., MAMULOVÁ KUTLÁKOVÁ, K., SEIDLEROVÁ, J. The stability of photoactive kaolinite/TiO<sub>2</sub> composite. *Composites Part B: Engineering*, 2014, p. 262-269.