

MONTMORILLONITE STABILITY AND ITS EFFECTS ON THE ENVIRONMENT

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Abstract

Montmorillonite is one of the most important groups of phyllosilicates and is an excellent sorbent. For the facilitation of the post-sorption sorbent separation from the medium (e.g.) waste water, it is convenient to use its magnetically modified form. Magnetically modified montmorillonite composites can be prepared using a simple microwave synthesis; the efficiency of this preparation method has already been proven. The aim of this study was to evaluate the effect of the microwave radiation during the preparation of its magnetic form on the structure and stability of montmorillonite. Water extracts were prepared by the batch method using deionized water. The leachate was prepared for 24 hours in different ratios of solid and liquid phase (1:10 000, 1:1 000, 1:500 and 1:100) from the montmorillonite and the magnetically modified montmorillonite. Concentrations of Al, Ca, K, Mg, Na, Si and Fe were determined using atomic emission spectrometry with inductively coupled plasma, pH of the filtrate was also determined. The results of the experiments showed that Al and Ti do not leach under the observed conditions. The assumption that the ion exchange elements (K, Na, Ca, Mg) leach to the solution was confirmed. Their amount is dependent on the leaching time and on the solid/liquid phase ratio. Silicon, a part of the fundamental layer structure also leached, however, in an amount not affecting the montmorillonite structure. The process of the microwave-assisted magnetic modification of the montmorillonite was proved not to affect the stability of the material.

Keywords: Montmorillonite, magnetic form, leaching, microwave treatment

1. INTRODUCTION

Heavy metal pollution is one of the most important environmental problems today. Various industries (e.g., mining, metallurgy, surface finishing, iron and steel production, metal surface treating, etc.) produce and discharge wastes containing numerous heavy metals and organic compounds. Such a human activity brings about serious environmental pollution, threatening both human health and ecosystems. The metals cannot be degraded to harmless products and hence persist in the environment indefinitely. Both the selected metals and organic compound have a negative effect on human health [1]. Pollution is commonly categorized according to the character of the pollutant as inorganic or organic; however, in reality, both categories of pollutants are present in various ratios.

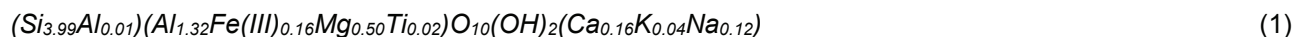
One of the most commonly applied methods for the water environment is sorption. A whole range of sorption methods are utilized in both laboratory and field and they are usually divided according to the principal, environment (gas, liquid, solid) or the characteristics of the pollutant. Frequently applied sorbent is activated carbon which, however, is a rather costly material [2,3]. Therefore, many studies were focused on the cheaper sorbent alternatives such as sheet materials - phyllosilicates [4-8], slag [9,10], ashes [11] and, finally, biomaterials, mainly various waste by-products (sawdust, orange peel, rice husks etc.) [12,13]. New sorbents are being designed continuously in order to enhance the sorption efficacy, decrease the cost of the cleaning technology and improve the functionality of the material. Introduction of new types of sorbents based on "smart" materials combines the sorption and (e.g.) catalytic characteristics of the material, and, thus, simultaneous removal of more pollutants.

In the case of the liquid environment, it is necessary to separate the sorbent from the cleansed liquid; for this purpose, filtration is used. Application of a sorbent with magnetic characteristics would allow the realization of the aforementioned separation using a magnetic field. Magnetically modified sheet materials or bio-sorbents can both be used for this purpose.

Bentonite was modified with ferrofluids by Mockovciakova et al. [4]. Sorption experiments were focused on the removal of low concentrations of Cd²⁺ and Ni²⁺ ions. Other authors describe sorption of heavy metal ions on magnetically modified zeolites [4, 5], bentonites [6,7] and montmorillonite [10]. Moreover, new composites designed by combining two or more sorbents such as magnetic nano-sorbent from the orange peel waste simultaneously precipitated with Fe₃O₂ nanoparticles and either hydroxyapatite nanoparticles [14] or zeolite [15] were successfully used for the removal of Cd²⁺ and Zn²⁺ from liquid solutions.

2. MATERIALS AND METHODS

For the purpose of this study, Montmorillonite (Mt) from the Ivančice (Czech Republic) deposit was selected. Based on the chemical composition, the crystallochemical formula of this montmorillonite was determined [16]:



Raw clay material was dried, milled, and sieved. Mt particles having size $\leq 40 \mu m$ were used for the experiments.

Chemical composition of Mt was determined using an energy dispersive fluorescence spectrometer (XRFS), SPECTRO XLAB, Spectro. For this measurement, samples in powder form were pressed into tablets using wax as a binder. Al, Ca, K, Mg, Na, Si and Fe were determined, after acid digestion, by Atomic emission spectrometry with inductively coupled plasma (AES-ICP), SPECTRO CIROS VISION, Spectro.

Two sample types were used and compared: (1) the native Mt leached in deionized water (sample denoted as M) and (2) the magnetically modified Mt prepared using microwave radiation (sample denoted as MMW). Suspension of the FeSO₄ in deionized water was treated in a microwave oven for 10 min at power 700 W, 2450 MHz. After cooling, the Mt was added into suspension. After 24 h, the Mt with Fe_xO_y was separated by filtration (pore size 0.23 μm) and dried. Both M and MMW were leached in deionized water using the batch method. The leachates were prepared for 24 hours in 1:10 000, 1:1 000, 1:500 and 1:100 ratios of solid and liquid phase from M and MMW. In the filtrate, concentrations of Al, Ca, K, Mg, Na, Si and Fe were determined using AES-ICP, the pH value was determined as well.

To determine the phases and structure of prepared samples, X-ray powder diffraction analysis (XRPD), BRUKER AXS was used. X-ray powder diffraction patterns were recorded under Co K α irradiation ($\lambda = 1.789 \text{ \AA}$) using the Bruker D8 Advance diffractometer equipped with a fast position sensitive detector VANTEC 1. Samples in powder form were pressed in a rotational holder. Reflection mode was used for all measurements. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

3. RESULTS AND DISCUSSION

The chemical composition of Mt, determined in the dried sample, revealed the high amount of Si and Al (**Table 1**).

XRPD patterns of native Mt, M and MMW shows (**Figure 1**) that the process of magnetization did not change the structure of the native Mt because the width is same. Therefore, the Fe_xO_y particles were bound on the Mt surface. The preliminary study proved, that Fe_xO_y particles prepared using the above-mention procedure are a mixture of γ -Fe₂O₃ and Fe₃O₄.

Table 1 The chemical composition of the Montmorillonite, elemental content is express as oxide

| Parameter | Content (wt. %) | Parameter | Content (wt. %) | Parameter | Content (wt. %) |
|--------------------------------|-----------------|------------------|-----------------|--------------------------------|-----------------|
| Na ₂ O | 0.093±0.047 | SiO ₂ | 57.47±4.03 | TiO ₂ | 0.296±0.030 |
| MgO | 3.07±0.62 | K ₂ O | 0.925±0.084 | Fe ₂ O ₃ | 3.40±0.14 |
| Al ₂ O ₃ | 13.9±0.84 | CaO | 2.04±0.63 | LOI | 17.75±07 |

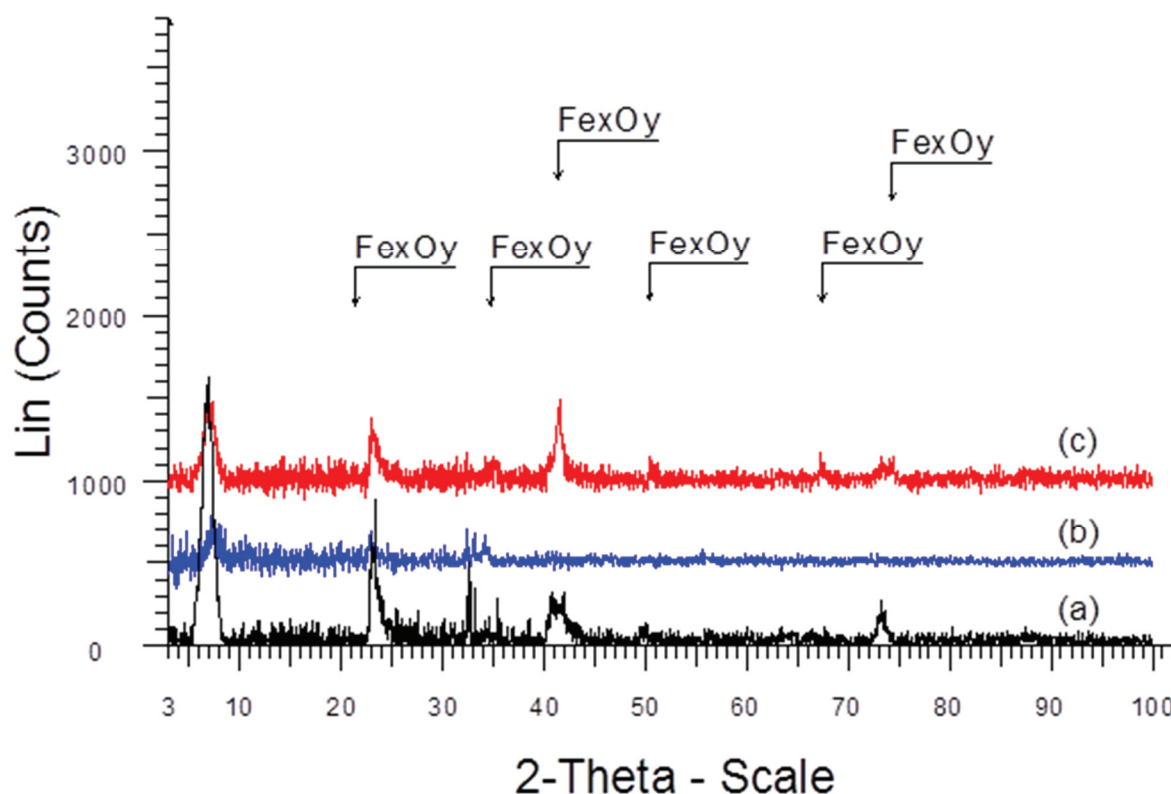


Figure 1 XRPD patterns of native Mt (a), M (b) and MMW (c) with detected Fe_xO_y phases

Iron content in Mt a MMW is presented in **Table 2**. In the magnetically modified montmorillonite, iron was found mainly in the form of FeO, Fe₂O₃ and Fe₃O₄ [13]. Magnetically modified Mt treated by microwaves contained 8.5 wt % of the total iron which is 3.5 times more than in the original Mt (2.4 wt. %). Content of ferrous oxide was six times higher in the case of MMW.

Table 2 Iron content in Mt and MMW

| Parameter | Mt (wt. %) | MMW (wt. %) |
|-----------|------------|-------------|
| Total Fe | 2.4±0.1 | 8.5±0.4 |
| FeO | 0.24±0.03 | 1.49±0.06 |

The pH values of the leachate provide important information on the two-way interaction between the solid and liquid phase. Elements present in the solid phase may dissolve into the extraction solution (deionized water) and alter the pH, as shown in the **Figure 2**. Microwave treatment of the material led to a shift of the leachate pH towards more basic values (around 7.5), while the pH was unaffected by the particular ratio of the solid and

liquid phase. The leachate pH from the native material was 6.5-7.2 which reflects the inhomogeneity of the Mt samples.

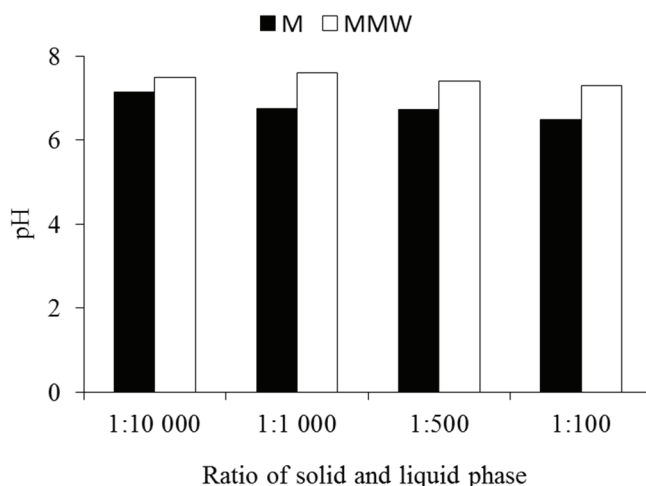


Figure 2 pH of extract solution prepared from M and MMW

Leached amounts of the observed elements in the extracts are presented in the **Figures 3 - 5**. The amounts of the leached Al and Fe were below the detection limit of the used method (< 0.01 mg/L and < 0.005 mg/L, respectively). Iron oxides are, thus, bound strongly to the Mt surface and the material is stable even after the 24-hours in contact with the water environment.

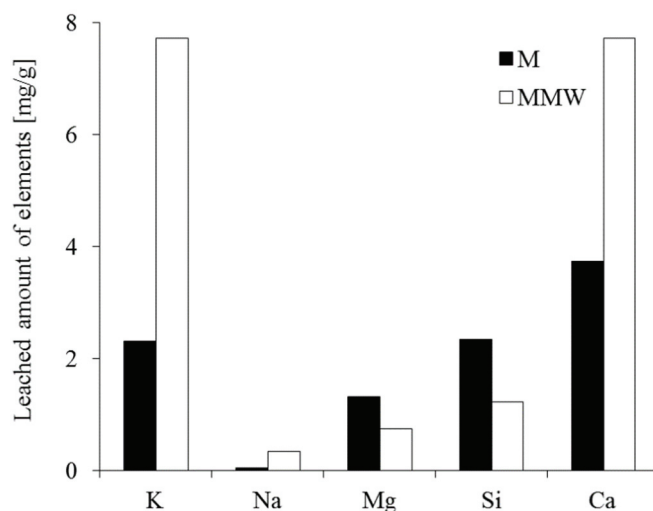


Figure 3 Leached amount of elements from M and MMW - ratio 1:10 000

Relatively highest amount of the leached elements was observed when the ratio of solid and liquid phase was 1 : 10 000 (**Figure 3**). From the MMt, K and Ca were the elements leached the most while Na, Mg and Si were leached slightly more from M. In the rest of the solid: liquid phase ratios, the same trend in the leached amount of Si was observed - this amount was also very similar in both of the samples. Hence, it can be concluded that the preparation of the magnetically modified did not alter the structure of the montmorillonite. The leached amounts of the ion-exchange elements (Na, K, Ca and Mg) differed between the materials. As expected, more K, Mg and Ca was leached from M than from MMW. This was, however, not observed in the case of Na, which was leached more from MMt than from M suggesting an alteration of the Na stability in Mt structure caused by microwave radiation. In all the elements, their amount in the leachate was affected by the solid: liquid phase ratio.

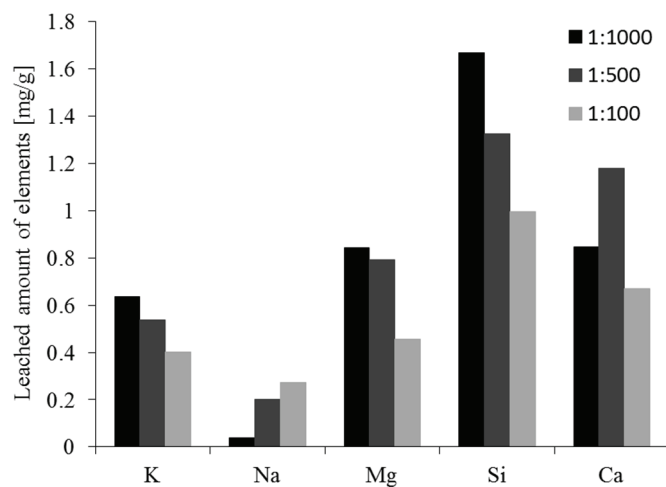


Figure 4 Leached amount of elements from M

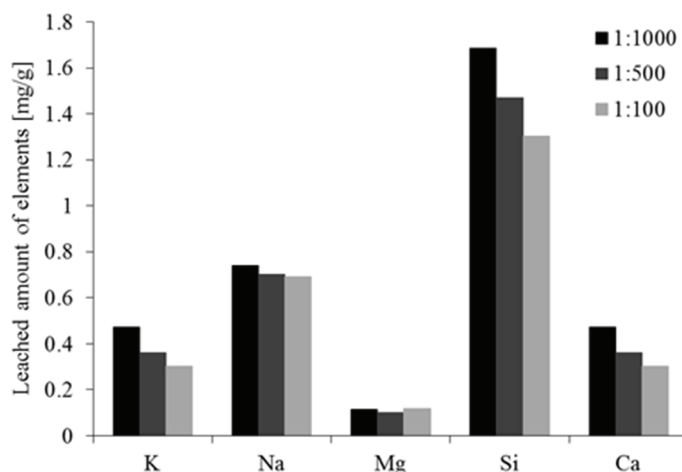


Figure 5 Leached amount of elements from MMW

4. CONCLUSION

Magnetically modified montmorillonite was prepared by a simple method using microwave radiation. The original Ivančice montmorillonite and its modified form were subjected to 24 hour leaching in deionized water applying various ratios of solid and liquid phase. It was proved that the magnetic iron oxides are bound to the Mt strongly and are, most probably, located on its surface. Microwave radiation was found not to affect the leaching of the elements of the basic structure of the montmorillonite (Al and Si). However, it seems to affect the leaching of the ion-exchange elements. Solid: liquid phase ratio affected the amount of observed elements in the leachate too.

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