

COMPARATIVE ANALYSIS OF Pb²⁺ SEPARATION USING NATURAL AND SYNTHETIC SILICATE MATERIALS

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ABSTRACT

In this study, the adsorption capacity and removal efficiency of lead using various metal-oxide materials from aqueous solution have been analyzed. Two SiO₂-based materials, natural (loam) and synthesized (metal-oxide heterostructures – MOH) were investigated. The characterization of these samples was performed using X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Adsorption tests were performed in a batch system by varying the mass of tested materials. The highest adsorption capacity for Pb²⁺ was achieved using 5 mg of MOH (166.6 μg g⁻¹), while the removal efficiency using the optimal mass (10 mg) of MOH and loam was 99.3 and 94.2 %, respectively. Based on the obtained results, it was concluded that the synthetic material has higher adsorption capacity and removal efficiency than the natural material for the selected ion.

INTRODUCTION

Water contamination with heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu) and metalloids as arsenic (As) can occur with the use of chemicals, industrial or other waste. These pollutants have long been known of their hazardous nature even in very low concentrations (ppb) and their presence deteriorate the water quality and renders it inapt for its intended uses [1]. Currently, there are several efficient methods reviewed for the removal of heavy metals such as chemical precipitation, ion exchange, coagulation, flocculation, floatation, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, etc. Adsorption as a very simple, economical, effective and versatile process has become one of the most applied methods for removal of toxic pollutants from aqueous solution [2]. Besides, there are many different materials used as adsorbents where the main distinction is according to their origin - natural and synthetic. Metal(hydr)oxides have a great potential as promising adsorbents for the separation of lead ions due to their exceptional properties, such as a high removal capacity, selectivity towards heavy metals, their high surface area to mass ratio, high surface reactivity, and unique catalytic activity [3]. The most common oxide-based materials for the adsorption process are iron (III) oxides (Fe₂O₃), zinc oxides (ZnO), titanium oxides (TiO₂), aluminum oxides (Al₂O₃), magnesium oxides (MgO), cerium oxides (CeO₂), as well as their mixtures [4]. The adsorption reaction of silicate minerals comprises the following metal–surface complex reactions: inner-sphere metal complexes (metal sorption at the surface forming bonds with oxygen atoms in the tetrahedra framework; 2) and outer-sphere metal complexes (adsorption at the surface on silanol groups, Si–OH, which are formed by the cleavage of Si–O–Si bonds) [5]. This paper presents the adsorption of Pb²⁺ onto natural and synthesized samples, which consist of several metal oxides (mainly SiO₂, Fe₂O₃, Al₂O₃, TiO₂).

METHODS

The standard solution of initial concentration of 100 μg L⁻¹ was prepared for lead ion. The singular batch experiments were conducted according to the following procedure: the different mass of the adsorbents (5, 7.5, 10 and 20 mg) were placed in flask of 10 mL containing concentration of 100 μg L⁻¹

standard solutions. The other parameters such as pH value (5), concentration ($100 \mu\text{g L}^{-1}$), contact time (24 h), and temperature ($25 \text{ }^\circ\text{C}$) were kept constant. After the adsorption process the samples were filtered through a 0.45-mm pore diameter membrane filter and analytes were acidified with nitric acid (1:1, v/v). The concentration of lead was determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500ce. Limits of quantification were quite low for the ICP-MS ($0.1\text{--}1.5 \mu\text{g L}^{-1}$), enabling analyses of very low levels of metals in drinking water.

The adsorption capacity, q , and removal efficiency, R , of the adsorbent was calculated according to the following equation:

$$q = \frac{C_i - C_f}{m} \times V \quad (1)$$

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i and C_e are initial and final metal concentrations of examined ion in the solution ($\mu\text{g L}^{-1}$), respectively, m is the dosage of the adsorbent (mg), and V is the volume of solution (mL).

In addition, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the materials, chemical structures and compositions.

RESULTS AND DISCUSSION

The structural analyses of the loam and MOH are presented in Figure 1a. The loam sample is a heterogeneous material that predominates in the content of quartz (60.9 wt. %) and kaolinite (22.6 wt. %), while diopside (84 wt. %) predominates in the MOH sample. For the loam sample, quartz (SiO_2) is the dominant phase whose diffraction peaks appear in $2\theta^\circ = 20.8, 27.2, 50.7$ and 60.1 [6]. The absorption peaks of kaolinite in loam appear at $2\theta^\circ = 12.4, 21.5, 25.0$ and 34.9 . On the other hand, in MOH sample the main constituent is diopside/diopside aluminum phase with characteristic peaks at $2\theta^\circ = 29.9, 30.4, 35.8, 39.3, 42.5, 52.3$ and 65.6 [7].

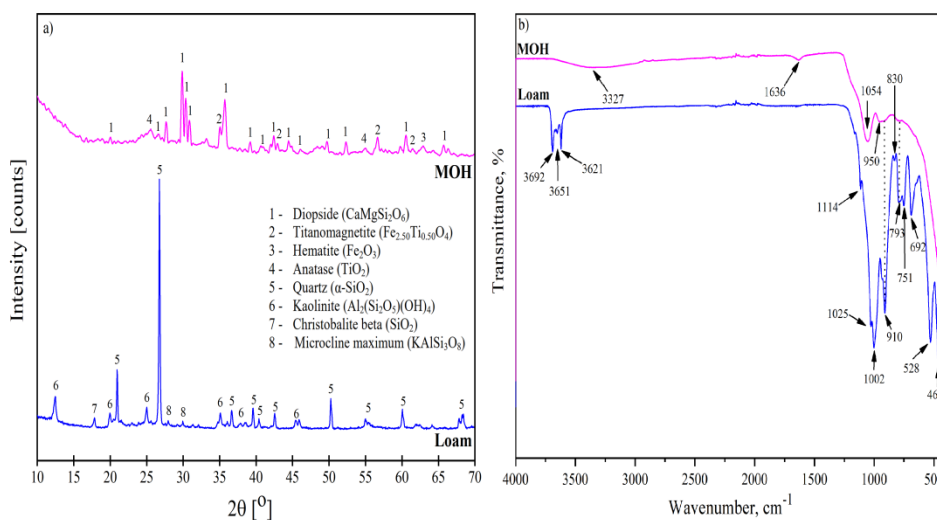


Figure 1. The characterization of MOH and loam samples by a) XRD (on the left) and b) FTIR spectra (on the right)

The FTIR spectra obtained for tested samples are showed in Figure 1b. On the IR absorption of loam material the most dominant aluminosilicate hydroxyl structural units (e.g., Si–O, Si–O–Al, Al–OH, O–H), were discovered. The Figure 1b is shown the FTIR spectra characteristic of the hydroxyl

group at: 3692, 3651, 3621 and 3327 cm^{-1} [8]. The peak of very low intensity at 1634 cm^{-1} (MOH sample) was evidence of the bending vibrational mode of absorbed H_2O . The intense bands located at 1114, 1054, 1025 and 1002 cm^{-1} are assignable to the Si–O–Si symmetric stretching vibrations [9]. The Si–O–Ti vibrations are observed only in the sample MHO at 950 cm^{-1} [10]. The absorbance at 950–600 cm^{-1} represents intensive spectra confirming the OH bending vibrations of Al–OH.

The investigations of the influence of the adsorbent mass were performed under the same experimental conditions (Figure 2). The effect of mass of adsorbent was studied with several different masses of loam and MOH in the range of 5–20 mg, while other parameters such as pH, concentration, contact time, and stirring rate were kept constant. The results showed that the removal efficiency of lead increased with the increasing the mass of adsorbents, while for the adsorption capacity it decreased (Figure 2).

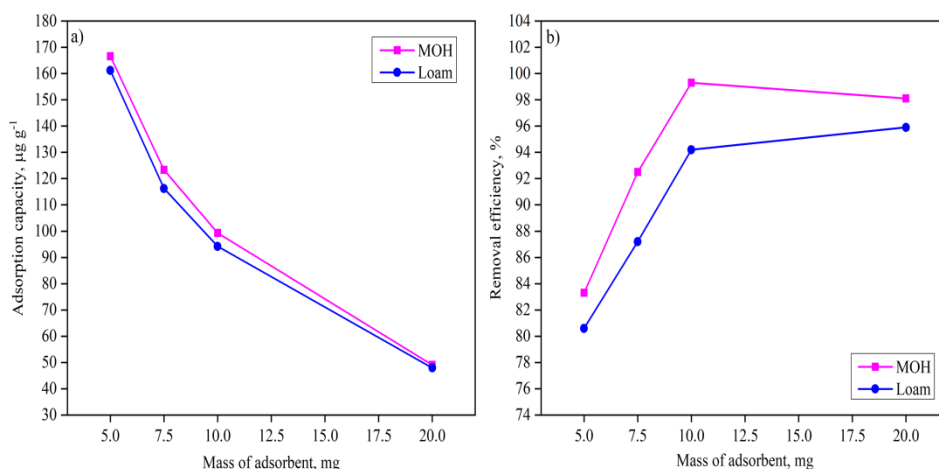


Figure 2. The effect of adsorbent mass on a) adsorption capacity and b) percentage of removal of lead onto loam and MOH

In Figure 2a, significant reduction adsorption capacity for both adsorbents can be observed. From the results, it is apparent that the quantity of adsorbent and the adsorbed amount per unit weight are inversely proportional to each other. The maximum adsorption capacity of 166 and 161.2 $\mu\text{g g}^{-1}$ was achieved using 5 mg of MOH and loam, respectively.

It was found that removal efficiency of lead increased with increasing the amount of both tested adsorbents from 5 to 10 mg (Figure 2b), which can be attributed to the availability of larger surface area and the quantity of the adsorption sites. Further increase in adsorbent mass from 10 to 20 mg showed negligible change, the adsorbent mass of 10 mg was selected as the optimal mass in further adsorption procedures. The removal efficiency of lead ions on MOH and loam was 99.3 % and 94.2 %, under the optimal conditions ($m_{\text{ads}}=10$ mg).

CONCLUSION

The separation of lead using natural and synthetic silicate materials has been investigated. Two materials were analysed, natural (loam) and synthesized (MOH), which mainly consist of different oxides such as silicon dioxide, aluminium oxide and iron (III) oxides. On one hand, the efficiency of lead removal increased with increasing the mass of tested adsorbents. The maximum removal efficiency of lead ions under optimal conditions ($C_i=100 \mu\text{g L}^{-1}$, $m_{\text{ads}}=10$ mg and pH 5) was 99.3 % and 94.2 % for MOH and loam, respectively. On the other hand, the adsorption capacity of the material decreased with increasing the mass of both adsorbents. The highest adsorption capacity was

achieved using 5 mg of MOH sample ($166.6 \mu\text{g g}^{-1}$), and for loam it was slightly lower ($161.2 \mu\text{g g}^{-1}$). Based on the results obtained, the synthesized material, MOH, was more efficient for lead ions separation from aqueous solutions. Finally, the analysed silicate materials, both natural and synthesized, can be used as effective adsorbents to remove lead ions from water systems, bearing in mind that the application of environmentally and economically acceptable materials for water purification presents a great challenge nowadays.

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