REMOVAL OF POTENTIALLY TOXIC METAL IONS FROM AQUEOUS SOLUTION BY ADSORPTION ON MECHANOCHEMICALLY ACTIVATED PYROPHYLLITE

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ABSTRACT

Pollution of the environment with heavy metals is one of the greatest contemporary problems. Pyrophyllite is a hydrous aluminum silicate, with a wide variety of applications due to its high melting point and stable chemical properties. This study aims to examine the sorption properties of the mechanochemically activated pyrophyllite for the removal of divalent heavy metal ions (Zn, Cd, Pb, Cu, and Ni). The mechanochemical-activated pyrophyllite by milling was obtained from the Parsovići mine, Konjic site, AD Harbi Ltd., Sarajevo, Bosnia and Herzegovina. Heavy metal sorption experiments were performed by the "batch" method. Results clearly showed that the sorption of Me(II) is affected by granulation and amount of pyrophyllite, and sorption time. The following results were obtained: (1) the smaller pyrophyllite particle the removal of Me(II) is more efficient and the shorter contact time is required; (2) the sorption of Me(II) on pyrophyllite decreases in the following order Cu > Pb > Cd > Zn > Ni; (3) the increase of contact time increases the removal of Me(II) from the aqueous solution; (4) mutual competition of Me(II) for pyrophyllite binding sites – significantly more efficient sorption of Cd(II), Zn(II) and Ni(II) was achieved from individual solutions compared to the mixture. Our results show the high potential of pyrophyllite as a material for the removal of heavy metals from water solutions.

1. INTRODUCTION

Pollution of the environment with potentially toxic elements is one of the world's biggest problems, and most often originates from insufficiently or untreated industrial or municipal wastewater. Potentially toxic metals (PTMs) are considered hazardous environmental pollutants because of their high stability and toxicity even at low concentrations [1]. Removal of PTMs is essential in environmental remediation and cleanup. Adsorption is one of the conventional physicochemical processes sand has been used for the removal of heavy metals from various industrial effluents due to its simplicity and cost-effectiveness [2]. In addition, partitioning reactions (sorption) to clay mineral surfaces may control metal mobility in soils [3]. The development of technology for the removal of PTMs from wastewater based on sorption on solid materials requires primarily sorbent materials of known kinetic parameters and sorption characteristics, which are non-toxic, available, chemically and mechanically stable, economically viable, and recyclable.

Pyrophyllite is a natural hydrous aluminum silicate clay mineral ($Al_2Si_4(OH)_{10}(OH)_2$) with a high melting point, stable chemical properties, and low cost. The elementary sheet of pyrophyllite is composed of an aluminium-oxygen/hydroxyl octahedral layer between two tetrahedral layers of silicon-oxygen. Pyrophyllite is hydrophobic due to the absence of hydroxyl groups on the basal surfaces of the elementary sheet [4]. The structure of pyrophyllite is similar to talc, but talc contains Mg^{2+} instead Al^{3+} in octahedral positions. The layered silicate structure of pyrophyllite crystals has natural adsorption activity [5]. Adsorption of metal cations is mainly occurred by cation exchange in the interlayers. Formation of inner-sphere metal complexes through $Si–O^-$ and $Al–O^-$ groups at both edge sites of clay particles is an additional adsorption mechanism [5]. Pyrophyllite edges are formed by the fracture of the ionic and covalent bonds and their numbers depend on the grinding procedure. Also, hydrophobic siloxane surfaces of pyrophyllite act as neutral adsorption sites and are accessible to nonpolar organic species [8]. The sorption characteristics of natural or modified pyrophyllite have been extensively studied [2,5,7,9-13].

Mechanochemical activation (MCA) is a simple method for the modification of solid materials that causes structural disorder, amorphization, and increased chemical reactivity [14]. MCA, usually performed by grinding, is an environmentally friendly process because of low energy consumption, processing temperatures, and cost.

This study aims to examine the properties of the mechanochemically activated pyrophyllite for the sorption of divalent heavy metal ions (Zn(II), Cd(II), Pb(II), Cu(II), and Ni(II)). The effect of contact time, initial metal-ion concentration, and amount of pyrophyllite on the removal of the targeted PTMs from the aqueous solution were studied.

2. EXPERIMENTAL

2.1. Chemicals

We used the following chemicals purchased from Sigma-Aldrich (St. Louis, MO, USA): zinc chloride ($ZnCl_2$), lead nitrate ($Pb(NO_3)_2$), cadmium nitrate ($Cd(NO_3)_2) 4H_2O$), copper nitrate ($Cu(NO_3)_2$ $2.5H_2O$), nickel nitrate ($Ni(NO_3)_2$ $6H_2O$), potassium chloride (KCl), sodium hydroxide ($NaOH$), nitric acid (HNO_3), sodium acetate ($NaCH_3COO$). All chemicals are p.a. purity. Deionized water was obtained using a Milli-Q water purification system (Millipore, Bedford, MA, USA). Polyethylene laboratory bottles were used to prepare and store aqueous solutions of metal salts, as well as to perform experiments. These bottles were pre-washed in 10% HNO_3 to prevent heavy metal contamination.

Heavy metal stock solutions, containing 0.16 mol dm^{-3} of a single element (Zn(II), Pb(II), Cd(II), Cu(II) or Ni(II)), were prepared separately for each metal by dissolving an adequate amount of the salt in 0.1 dm^3 of deionized water. The stock solutions were stable for months at room temperature. Working heavy metal ions solutions, with a single metal concentration of 0.16 mM (10 ppm Cu (II), 10.5 ppm Zn(II), 9.4 ppm Ni(II); 17.98 Cd(II); and 33.1 ppm Pb(II)) and total metal ions concentration of 0.8 mM, were prepared shortly before each experiment by appropriate dilution of the stock solutions with deionized water.

2.2. Adsorbents

The row natural pyrophyllite was obtained from the deposits "Parsovići" - Konjic (AD HARBI Ltd., Sarajevo, Bosnia and Herzegovina). The samples were mechanochemical modified by milling and sieving crude pyrophyllite. The granulometric composition was determined by sieving the ground pyrophyllite through standard sieves with openings of appropriate dimensions (0.1 mm and 0.045 mm). Three samples of pyrophyllite with granulation of < 0.1 mm (Pyr-0.1) and < 0.045 mm (Pyr-0.045) were used for PTMs adsorption studies.

2.3. Adsorption studies

PTMs adsorption experiments were performed by the "batch" method, i.e. direct contact of a certain amount of pyrophyllite and aqueous metal solution. Batch experiments of metal adsorption on pyrophyllite samples were carried out at room temperature by mixing mechanochemically modified pyrophyllite and working metal ions solution in closed polyethylene bottles. The samples were shaken on the laboratory shaker (Promax 2020, Heidolph, Schwabach, Germany) at the stirring speed of 200 rpm for better mass transport. After that, the liquid phases were separated by centrifugation at 1000 rpm followed by filtration through a 0.45 µmmicroporous membrane filter (Membrane Solutions LLC, TX, USA). The concentration of PTM ions in the aqueous phase was quantified by anodic stripping voltammetry with a 797 VA Computraceanalyser (Metrohm, Herisau, Switzerland) by using the Metrohm's procedure for the voltammetric determination of zinc, cadmium, lead, and copper in water samples No. 231/2.Ni(II) was determined by the addition of dimethylglyoxime as a complexing agent (Metrohm application note No. V-100).

The influence of different experimental parameters, such as the contact time (5 min - 24 h), the initial total metal ions concentration (25-600 mg dm^{-3}), the amount of adsorbent (0.5-10 g dm^{-3}), and granulation of pyrophyllite, on the removal efficiency of metal ions were investigated. The molar concentrations of Zn(II), Pb(II), Cd(II), and Cu(II) ions in a multi-metal solution were set to be equal. All experiments were carried out in duplicates and the data obtained were used for analysis.

The removal efficiency of particular metal ion (R) was evaluated using Eq. (1), respectively:

$$R(\%) = \left(\frac{C_{Me}-C_e}{C_{Me}}\right)100 \qquad (1)$$

where C_{Me} and C_e are the initial and equilibrium metal ion concentration (mg dm^{-3}).

The concentrations of alkali and alkali earth metal cations (Na(I), K(I), Ca(II), Mg(II)) were analyzed by the 861 Advanced Compact ion chromatography (IC) system (Metrohm, Herisau, Switzerland) with conductivity detector and analytical column Metrosep C2 (Metrohm, 150 mm x 4 mm). In the initial heavy metal ions solution the concentrations of Na(I), K(I), Ca(II) and Mg(II) ions were 0.1, 0.1, 0.2, and 0.5 mg dm^{-3}, respectively.

3. RESULTS AND DISCUSSION

The removal of potentially toxic divalent metal ions Me(II) from an aqueous solution is investigated in this work. The effects of contact time, MCA pyrophyllite particle size, and competitively of the targeted Me(II) for adsorption have been studied. Before the experiments of sorption of selected heavy metal ions, and considering the chemical composition of pyrophyllite, we examined whether pyrophyllite releases metal ions in equilibrium with the water. The experiments were performed by placing 200 mg of pyrophyllite in 100 cm^3 of deionized water, pH 5.0, and shaking on a laboratory shaker. The samples were taken at the following time intervals: 30 min, 1 h, 2 h, 3 h, 5 h, and 24 h and analyzed. No measurable amount of any tested metal ion was found in any of the samples, which indicates that these ions are not released (dissolved) from the pyrophyllite into deionized water.

3.1 The effect of adsorption time and particle size on Me(II) removal

Figure 1 shows the effect of contact time between pyrophyllite and the aqueous solution of the studied PTMs using two MCA pyrophyllites with different granulation: Pyr-0.1 and Pyr-0.045. The removal efficiency (R) of the studied Me(II) depends on adsorption time, the particle size of pyrophyllite, and the kind of metal ions.

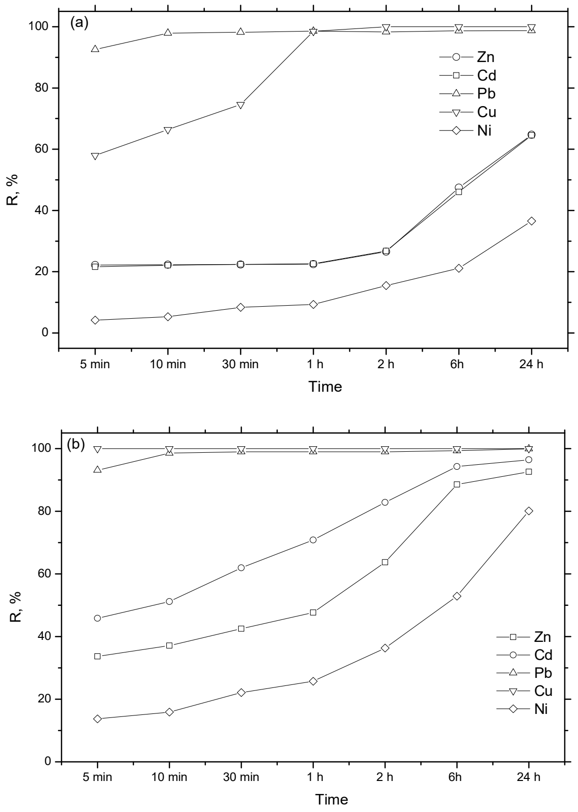

Figure 1. The effect of adsorption time on the removal of Me(II) using (a) Pyr-0.1; (b) Pyr-0.045. Experimental conditions: C_{Me} = 10 mg dm^{-3}, the volume of aqueous solution 25 cm^{3}, amount of pyrophyllite 1 g, shaking rate 200 rpm.

Removal efficiency increases with increasing adsorption time for all studied Me(II). It should be noted that pyrophyllite of smaller granulation (Pyr-0.045), due to the larger surface area, adsorbs more Me(II) for the same time compared to Pyr-0.1. The removal of Pb(II) and Cu(II) is notably higher and faster compared to Zn(II), Cd(II), and Ni(II). From Fig.1, it can be seen that Pyr-0.045 adsorbed > 98% Pb(II) and 100% Cu(II) from the aqueous solution after 10 min of contact, while it took 60 minutes to remove the same percentage of Pb(II) and Cu(II) with Pyr-0.1. The higher and faster removal of Zn(II), Cd(II), and Ni(II) was obtained using Pyr-0.045, and Zn(II) and Cd(II) reached the maximum of 95% after 24 h. Significantly lower removal (65% for Cd(II) and Zn(II), and 38% for Ni(II)) was obtained after 24h of contact with Pyr-0.1 without reaching the maximum. The results clearly show that pyrophyllite of smaller granulation removed the tested Me(II) from the aqueous solution faster and in a higher percentage: Cu(II) was completely removed after 5 min and 99% Pb(II) was removed after 30 min. The removal trend of other metal ions was similar to that of Pyr-0.1, but the removal percentage was significantly higher: 96.4%, 92.6%, and 80.1% for Cd(II), Zn(II), and Ni(II), respectively.

The initial adsorption of Cu(II) and Pb(II) at Pyr-0.045 is very fast. The adsorption is a surface phenomenon, at the beginning of the adsorption the active sites at the surface of the pyrophyllite filled up rapidly with the metal anions with high affinity towards pyrophyllite. Since Pyr-0.045 has a larger surface area, adsorption is both larger and faster compared to Pyr-0.1. Additionally, from Fig. 1 can be seen that the removal efficiency of Cd(II), Zn(II), and Ni(II) began to increase after the time when Pb(II) and Cd(II) reached the maximum removal. Adsorption of these Me(II) is much slower compared to Pb(II) and Cu(II) because Me(II) has to diffuse to the pores of pyrophyllite and inner binding sites. This also indicates competition for metal bonding sites on the pyrophyllite as well as a lower affinity for the binding sites.

From the obtained results shown in Fig. 1, it is clear that the removal of Me(II) from the solution i.e. the sorption of Me(II) on pyrophyllite is affected by the contact time, the amount of pyrophyllite and the granulation of pyrophyllite.

The following experiments aimed to determine the optimal amount of pyrophyllite for the removal of the targeted Me(II). From the results in Fig. 2, it can be seen the influence of the amount of pyrophyllite on the removal of Me(II). When the amount of pyrophyllite increases, the removal efficiency of the studied Me(II) also increases. This effect is especially pronounced in pyrophyllite with smaller particles (Pir – 0.045 μm) (Fig.2b). For example 2 g L^{-1} of Pir–0.045 is sufficient to remove 100% Cu(II) and 90% Pb(II). While, 24 g $L^{-1}$of Pir–0.045 removed 100% Cu(II), Pb(II) and Zn(II); and 97.7% Cd(II) and 93.5% Ni(II).

Comparing Figures 2 (a) and (b**)**, it can be concluded that even with the application of the triple amount of pyrophyllite with granulation of 100 μm compared to a pyrophyllite of granulation <45 μm, it is not possible to achieve such a successful removal of metal ions.

3.2 The competition of binding of tested metal ions to pyrophyllite

From obtained results shown in Figures 1 and 2, it is evident that Cu(II) and Pb(II) bind the fastest and in the highest percentage to pyrophyllite i.e. their removal from aqueous solutions is the biggest. Additionally, it is clear that the sorption of other investigated PTMs ions begins to increase when Cu(II) and Pb(II) reach equilibrium, which indicates the mutual competition of these ions for binding sites on pyrophyllite. Therefore, in the following experiments, we examined the sorption of individual PTMs ions on pyrophyllite and compared them with the results from a mixture of metals (Figure 3). To be able to follow the mutual competition Me(II), we chose the concentration pyrophyllite 8 mg dm^{-3}, because at this concentration Cu(II) achieves the maximum binding, and all the others Me(II) are less bound to pyrophyllite.

It can be concluded from Figure 3, that the sorption of Cu(II) is the same from the mixture of Me(II) and from the individual solution, which means that its binding is not affected by other metal ions, ie. Cu(II) is the most strongly bound to pyrophyllite. From a single solution of Pb(II) the sorption is 100%, while from the mixture it is 87%, and in this case, the competition of Pb(II) and Cu(II) can already be seen.

In the case of Cd(II), Zn(II), and Ni(II) of Me(II) which bind to pyrophyllite to a lower degree in the presence of Cu(II) and Pb(II), the improvement of binding from a single solution was highly pronounced. The sorption of Zn(II) was increased from 8% to 98%; from 21% to 85% for Ni(II), and slightly less for Cd(II) from 8% to 62%.

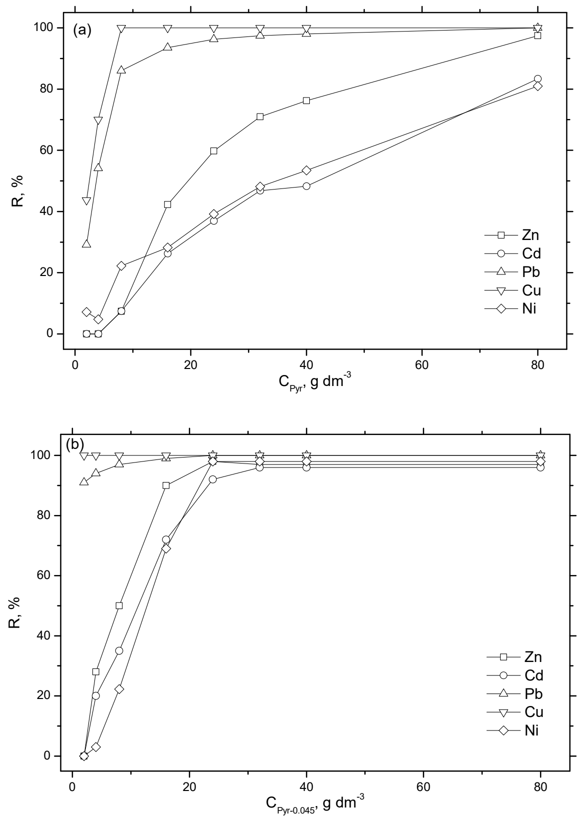

Figure 2. The effect of the amount of (a) Pyr – 0.1 and (b) Pyr – 0.045 on the removal of Me(II). Experimental conditions: C = 0.16 mM single metal, C_{tot} = 0.8 mM, the volume of aqueous solution 25 cm^3, amount of pyrophyllite 1 g, shaking rate 200 rpm, adsorption time 24h.

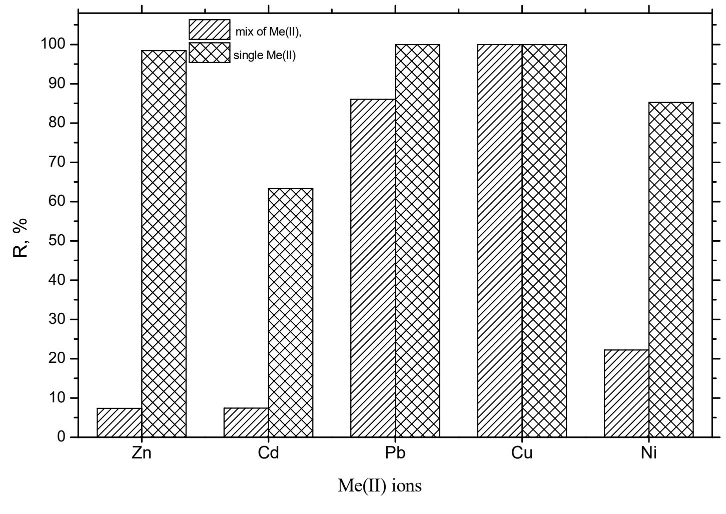

Figure 3. The removal efficiency of divalent metals from the mixture of solutions (concentration of each metal in the mixture C = 0.16 mM, total concentration of metal C_{tot} = 0.8 mM) and from single solutions (concentration of metal C = 0.16 mM)on Pyr-100.Experimental conditions: volume of aqueous solution 25 cm^3, amount of pyrophyllite 0.2 g, shaking rate 200 rpm, adsorption time 24h.

In all solutions obtained after the adsorption of metal ions on mechanically modified pyrophyllite, the concentrations of alkali and alkaline earth metals were determined (Table

2). During the adsorption of selected divalent metals from mechanically modified pyrophyllite, the release of alkali and alkaline earth metals decreased in the following sequence: Ca^{2+}> Mg^{2+}> K^{+}> Na^{+}. This indicates that divalent ions play the main role in ion exchange, primarily Ca^{2+}. The obtained results show that a smaller amount of alkali and alkaline metal ions were released by using pyrophyllites of larger granulation.

Table 1. Concentrations of alkali and alkaline earth metals released from pyrophyllite during the adsorption of heavy metals to pyrophyllite

Adsorbent	C, mM			
	Na	K	Ca	Mg
Pir -2mm	0.096	0.428	0.455	0.175
Pir - 100 μm	0.137	0.181	0.899	0.194

4. CONCLUSIONS

Contamination of water by potentially toxic metals from industrial and municipal wastewater is an acute environmental problem worldwide. This study focused on the mechanochemical activation of geopolymer - pyrophyllite and its adsorption characteristics towards heavy metals such as Cu(II), Pb(II), Ni(II), Zn(II) and Cd(II). The mechanochemical activation can be considered an ecologically friendly technique, which can contribute to reducing CO_2 emissions by replacing some thermally intensive processes. The mechanochemically modified pyrophyllite was found to be a high-potential adsorbent of metal ions fromwater through batch adsorption studies. The adsorption of the targeted metalions was evaluated as a function of experimental parameters such as pyrophyllite amount, the particle size of pyrophyllite, and contact time. The maximum removal efficiencies to the extent of 98 and 100 % for Pb(II) and Cu(II), respectively, were achieved using fine grinned pyrophyllite with particle size less than 45 μm for only 10 minutes. Additionally, the mutual competition of the studied ions for binding sites on pyrophyllite was found. The overall studies indicatet hat the mechanochemical-activated pyrophyllite could be used as an inexpensive and promising adsorbent for the removal of potentially toxic metals.

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