Minerals pretreatment for arsenic and cadmium removal from water solutions by mechanical activation

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Abstract

In this work, the sorption of As(III) and Cd(II) on mechanically activated minerals, such as magnetite Fe_3O_4 (Kiruna, Sweden), olivine $(Mg, Fe)_2SiO_4$ (Åheim, Norway) and talc $Mg_3[Si_4O_{10}](OH)_2$ (Hnúšťa, Slovakia), has been studied. Removal of heavy metals based on sorption on mineral surfaces has been suggested as an alternative approach. Activation processes based on the high-energy milling (mechanical activation) are used to modify the properties of materials and to enhance their reactivity. Sorption activity of mentioned minerals can be enhanced by the mechanical activation in high-energy mill Pulverisette 6 (Fritsch, Germany), where specific surface area (S_A) of mechanically activated magnetite increased. The increasing values of S_A of minerals relate with enhanced sorption ability to removal heavy metals from the water solution. The experimental results show that mechanically activated minerals are effective sorbents for low concentrations of heavy metals in the waste waters.

Key words: arsenic, cadmium, sorption, magnetite, olivine, talc, mechanical activation

Introduction

Arsenic and cadmium are chemical elements of significant ecological risk. Therefore a great attention is paid to them in environmental studies (Madhal and Suzuki, 2002). They are highly bioactive and toxic elements. Their presence at elevated levels in the drinking water and soils is threatening (Kang and Jin, 2004). Human beings and animals are exposed to a risk of intoxication by these elements through all components of the environment: water, air, soil, and food (Zakharova et al., 2002; Alam et al., 2003). They adversely affect biological activities as a teratogen, carcinogen or mutagen as well as having detrimental effects on the digestive system, respiratory system and immune system (Liao et al., 2005). Industrial and agricultural development has been largely responsible for the pollution of the environment with these toxic metals, although some contamination is derived from natural geological sources. Several methods have been proposed for the heavy metal removal, e.g. precipitation, membrane filtration, ion exchange and adsorption (Habashi, 1993). Many scientific works present the sorption of arsenic and cadmium onto different sorbents (Mohan et al., 2007; Yadanaparthi et al., 2009; Carrillo et al., 2006; Bhadoria et al., 2010) including magnetite (Gimenéz et al., 2007; Jönsson et al., 2009). Sorption activity can be enhanced by a pretreatment method where the solid state properties of a mineral could be changed. Mechanochemical pretreatment belongs among such methods (Baláž, 2008). Changes in the surface area as a consequence of milling can play an important role by intensification of the sorption process.

The aim of this work is to study the influence of the high-energy milling on sorption behaviour of As(III) and Cd(II) on magnetite, olivine and talc.

Experimental

Material

The investigation was carried out with the samples of magnetite (Kiruna, Sweden), olivine (Åheim, Norway) and talc (Hnúšťa, Slovakia). XRD patterns of minerals, which have been used in the sorption experiments, are shown in Fig. 1. Concentrate of olivine contains approximately 93 % of forsterite (Mg_2SiO_4) and 7 % of fayalite (Fe_2SiO_4) (Osland, 1998).

Mechanical activation

The mechanical activation of magnetite, olivine and talc was performed in a planetary mill Pulverisette 6 (Fritsch, Germany) at the following conditions: 50 balls of 10 mm diameter; material of the milling vial (V = 250 ml) and balls: tungsten carbide, ball charge: 360 g, sample charge: 10 g (magnetite), 18 g (olivine, talc); rotation speed: 500 rpm (magnetite), 450 rpm (olivine, talc), milling time in the range 1 – 120 min (magnetite), 2 – 30 min (olivine, talc).

Sorption tests

The sorption of As(III) and Cd(II) was running at various conditions (Tab. 1) in:

Tab. 1
Sorption conditions

Mineral	Amount of sample (g/L)	Sorption time and type of apparatus	
		As(III)	Cd(II)
Magnetite	8 in As(III)	0.25 – 6 hours, A	–
Olivine	8 in As(III) 5 in Cd(II)	0.25 – 6 hours, A	0.5 – 30 min, B
Talc	5 in Cd(II)	–	0.5 – 30 min, B

A. Erlenmayer´s banks placed on laboratory shaker constructed at the Institute of Geotechnics, Slovak Academy of Sciences. Initial arsenic concentration prepared from $NaAsO_2$ was 5 mg/L. During sorption tests the sorbent concentration was 8 g/L of arsenic water solution. The sorption was performed at 298 – 300 K. The sampling was made after 0.25, 0.5, 1, 2, 3, 4, 5 and 6 hours. Initial pH was 7.9. Final pH was 7.5.

B. Glass reactor (500 mL) with mechanical stirrer. Initial cadmium concentration prepared from $Cd(NO_3)_2 \cdot 4H_2O$ was 25 mg/L. The amount of cadmium solution was 200 mL. The sorption was performed at 298 – 300 K. Stirring rate of mechanical stirrer was 500 rpm. Initial pH was 5.5 and final pH was 9.5. The sampling was made after 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 25 and 30 min. All 11 samples were taken from 200 mL cadmium solution (the volume of one sample was 3 mL) and this volume (3 mL) was replanished with the initial cadmium solution.

The values of As(III) and Cd(II) in the solution after sorption on non-activated and activated samples were determined by atomic absorption spectrometry using a SPECTRAA 240FS/240Z (Varian, Australia).

Specific surface area

The specific surface area S_A was determined by the low-temperature nitrogen adsorption method. The Gemini 2360 sorption apparatus (Micromeritics, USA) has been applied.

X-ray diffractometry

The X-ray diffraction measurements were carried out using a diffractometer X´Pert (Philips, Netherlands) working in the 2Θ geometry with CuKα radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. The effect of mechanical activation was evaluated by the decrease of crystalline phase X of magnetite, olivine and talc according to formula (1):

$$X = \frac{U_0}{I_0} \cdot \frac{I_x}{U_x} \cdot 100 \ (\%) \qquad (1)$$

where U_0 and U_x denote the background of the reference and activated sample, while I_0 and I_x are integral intensities of selected diffraction lines of reference sample and activated sample, respectively (Ohlherg and Strickler, 1962).

Results and discussion

Mechanical activation

There was estimated an increase of the surface area of all above mentioned minerals with the time of mechanical activation in a planetary mill. The dependence of the specific surface area on the time of milling is shown in Fig. 2. As can be seen, the specific surface area of mechanically activated magnetite increased from the value 0.1 m²/g to 11.9 m²/g (t_M = 90 min), olivine from value 0.3 m²/g to 5.2 m²/g (t_M = 30 min) and talc from the value 4.0 m²/g to 70.7 m²/g (t_M = 15 min). The values of surface area of magnetite and talc achieved its maximum after 90 and 15 min of milling, and then this value rapidly decreased. Formation of the new surface area during mechanical activation of olivine consists of two stages. In the first stage the increase in the surface area is almost proportional to the milling time, the second stage is steady. Process of the new surface formation was accompanied by the effect of particle enlargement (aggregation and/or agglomeration).

The lattice defects deformation in the bulk of minerals can be characterized by several physico-chemical methods (Baláž, 2000; Baláž, 2008). One of them is the X-ray diffractometry method (XRD), which allows the study of the disordering of minerals crystal structure. The changes induced by mechanical activation can be observed by looking at minerals lines broadening, shift and the reduction of line intensity. The noticeable decrease of crystallinine phase X, calculated to the formula (1), is determined at mechanically activated
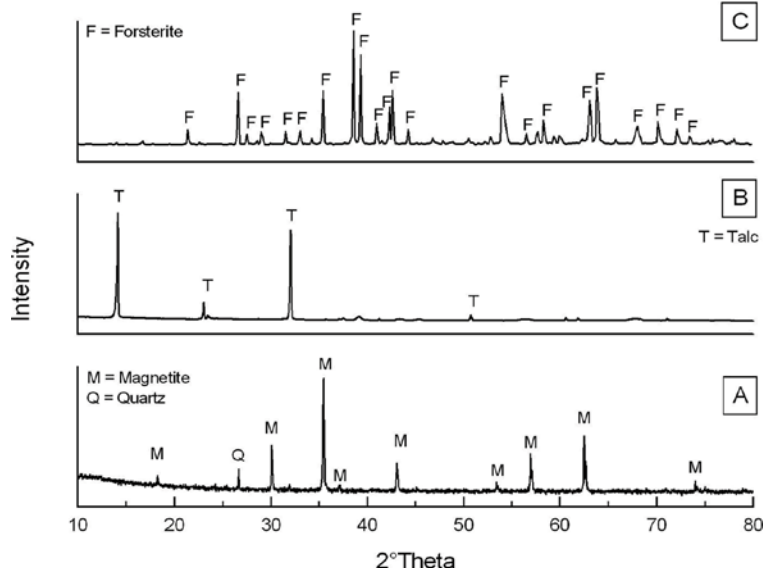
Fig. 1. XRD patterns of (A) magnetite, (B) talc and (C) olivine.

minerals (Fig. 2) and would provide complementary information about the amorphization of the process.

Sorption of As(III) and Cd(II)

Sorption experiments were done by 90 min mechanically activated magnetite, 30 min mechanically activated olivine and by 15 min mechanically activated talc, where the highest specific surface area was performed. In Fig. 3 there is a removal efficiency of arsenic E (%) from the water solutions in

dependence with the sorption time for mechanically activated magnetite and olivine. As can be seen, sorption of As(III) on mechanically activated magnetite is immediate, while on mechanically activated olivine is phased. At magnetite, the equilibrium state of sorption occurs at the beginning of sorption times and than the removal efficiency of arsenic on magnetite increases very slowly. At olivine, this state occurs later and the curve becomes sigmoid. The highest removal efficiency of arsenic was detected after 6 hours of sorption, in the case of magnetite it was 96 % and of olivine 99 %.
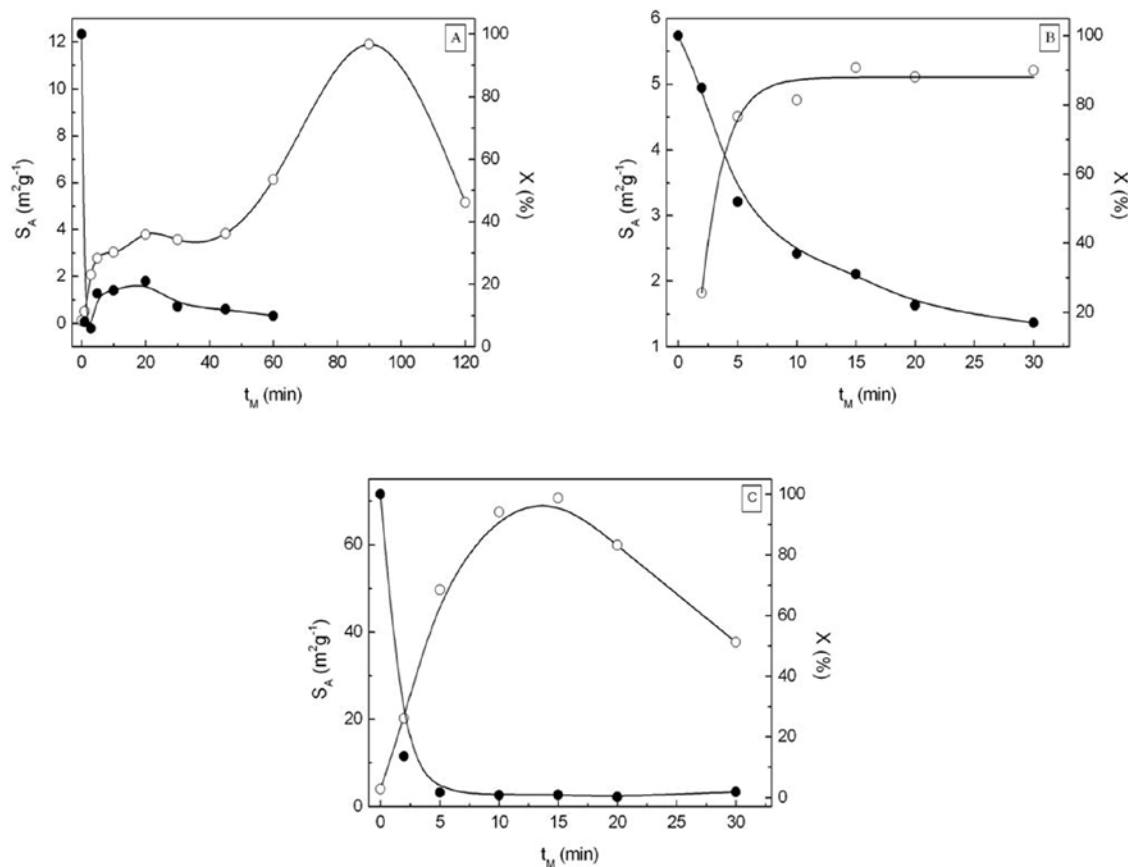

Fig. 2. Specific surface area, S_A, and content of crystalline phase, X of (A) magnetite, (B) olivine and (C) talc as a function of milling time, t_M.
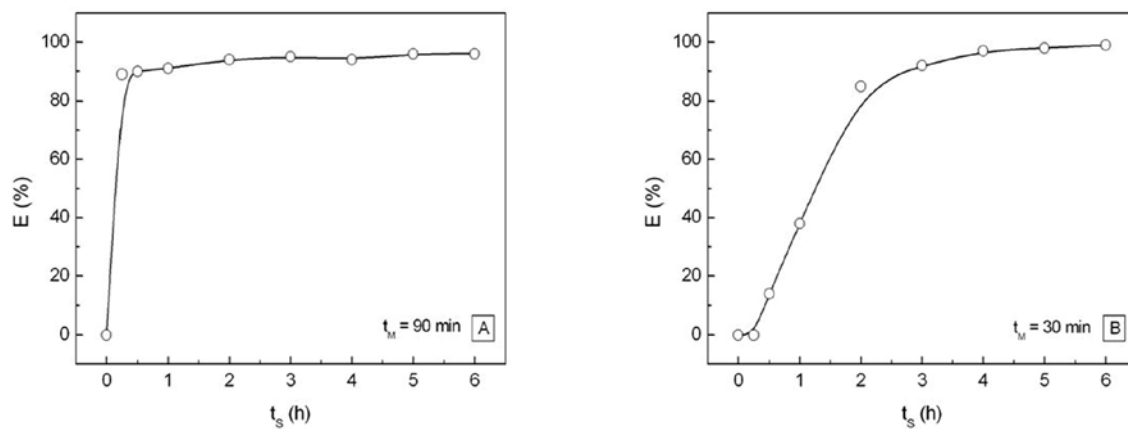

Fig. 3. Removal efficiency of arsenic, E, vs. sorption time, t_S, for (A) magnetite (t_M = 90 min) and (B) olivine (t_M = 30 min).
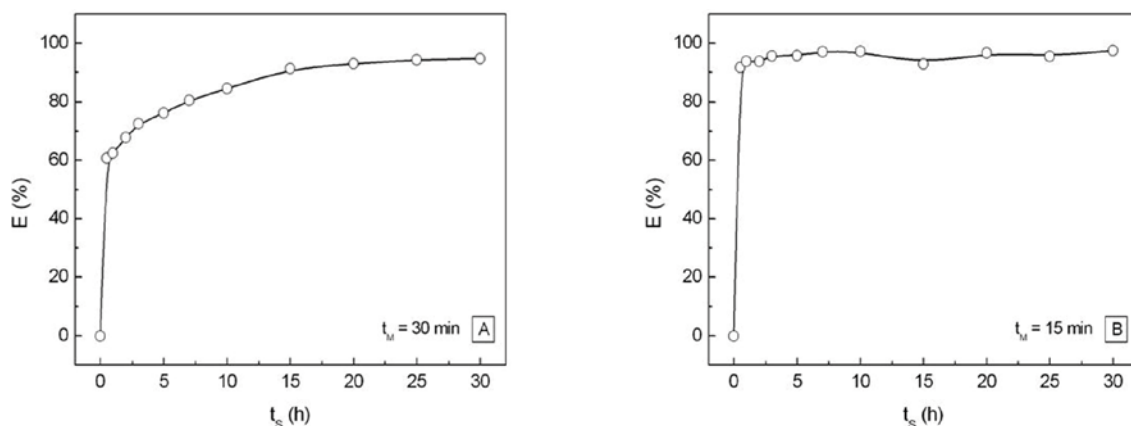
Fig. 4. Removal efficiency of cadmium, E, vs. sorption time, t_S, for (A) olivine ($t_M = 30$ min) and (B) talc ($t_M = 15$ min).

In Fig. 4 there is a removal efficiency of cadmium E (%) from the water solutions in dependence with the sorption time for mechanically activated olivine and talc.

As can be seen, sorption of Cd(II) on mechanically activated olivine is again phased, while on mechanically activated talc is immediate. The highest removal efficiency of cadmium was detected after 30 min of sorption, in the case of olivine it was 95 % and of talc 97 %.

We can conclude that mechanically activated magnetite, olivine and talc are effective minerals for removal of low concentrations of heavy metals, such as cadmium and arsenic from the waste waters. Sorption ability is in all activated samples more than 90 %, while sorption ability of non-activated samples was not detected.

Conclusion

We investigated that mechanical activation of minerals in a planetary mill causes the increase of its specific surface area with the milling time. The increasing values of S_A of minerals relate with the enhanced sorption ability to remove heavy metals from the water solution. The experimental results show that mechanically activated minerals are effective materials for removal of low heavy metal concentrations in the waste waters.

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