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The potential of ball-milled Serbian natural clay for removal of heavy metal contaminants from wastewaters: Simultaneous sorption of Ni, Cr, Cd and Pb ions

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Abstract

The influence of mechanical milling of natural Serbian clay on removal of heavy metals from an aqueous medium was investigated. The simultaneous sorption of the 4 toxic heavy metals (Ni, Cr, Cd and Pb), which are often present together in numerous polluting spills and in agrochemicals was evaluated. Microstructural and morphological changes in the ball-milled clay were characterized by X-ray diffraction (XRD), particle size distribution (PSD) and scanning electron microscopy (SEM). Induced changes in microstructure were correlated to the cation exchange capacity (CEC), determined by the EPA Method 9081. The CEC value has increased from 77 meq/100 g for the unmilled clay, to 95 meq/100 g for the milled clay. Regarding the untreated clay, the cation competition reveal some differences in their sorption: complete sorption (about 98% of the initial concentration) was achieved for Cr and Pb, while about 19% of the initial concentration of Cd and Ni still persist in the solution. The order of affinity of the metal ions is Pb $\approx$ Cr $>$ Cd $\approx$ Ni and it has not changed upon milling.

Keywords: A. Milling; D. Clays; Wastewater remediation; Heavy Metals; Sorption

1. Introduction

To reduce pollution hazards, caused by human activity, strong efforts have been made to develop remediation techniques for heavy metals contaminated water. Due to their high solubility in water, heavy metals Ni, Cr, Cd and Pb are serious environment contaminants. They are released into the aqueous system from metal plating, smelting, mining, cadmium-nickel batteries, phosphate fertilizers, paint industry, pigments and sewage. All of them are toxic causing various disorders like: problems with nervous system, lung insufficiency, bone lesions, and hypertension [1–4]. Numerous methods are available for removal of heavy metals from wastewaters like: solvent extraction, osmosis, chemical precipitation, etc., but adsorption has become preferred method for removal, recovery and recycling of toxic heavy metals from wastewaters [5]. Among various suitable adsorption materials in the focus of interest are: red mud [6], activated carbon [7], silica [8], resin [9], etc. Owing to their high cation capacity, local availability, non-toxicity, chemical and mechanical stability, BroØnsted and Lewis acidity and low cost, clays also attracted huge attention as a suitable candidate for these applications. Their layered structures and ability to accommodate water in the interlayer space facilitate the heavy metal adsorption and ion exchange.

For improvement of clay adsorption capacities, different techniques of modification of natural clay minerals were used [10–13]. Organoclays have been proven to be the technology of choice for treating oily wastewaters [13].

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Bhattacharyya and Gupta [10] demonstrated that acid activation enhances the adsorption capacity of the natural clay mineral by opening the edges of the platelets that results in the expansion of the surface area and the increase of the pore volume. They achieved the 12% increase of the CEC for montmorillonite treated with H_2SO_4. They have explained that although intercalation and calcination increase adsorption of heavy metal cations, they lead to decrease of the CEC because the large cations (ZrO^{2+}- and TBA^{+}-derivatives (tetrabutylammonium bromide)) mask some of the exchangeable cations in the interlayer space. The decrease of the CEC from 153 meq/100 g obtained for pure montmorillonite to 73.2 and 47.6 meq/100 g obtained for montmorillonite intercalated with ZrO^{2+} and TBA^{+}, respectively has been reported too [14].

Mechanical treatments typically influences microstructural and morphological properties of clay minerals, and promote transformations such as activation, amorphization, microstructural refinement, cold welding, and alloying [15]. In particular, ball milling increases the structural disorder inducing fragmentation, distortions, and decrease of the particles size, followed by increase in specific surface area, peeling off of layers, exfoliation of the particles, abrasion and amorphisation, which all could lead to the higher CEC of the clays [16–19]. For instance, peeling off of the montmorillonite particles layers, followed by exfoliation of the particles (indicated by the reduction of XRD intensities) was observed after the ball milling [7,18,20], as well as decrease of particles size, and increase of agglomeration. The ball milling method has been already used to improve clay performances for remediation of soil contaminated by heavy metals [21]. Mechanically induced reactions have been successfully used for degradation of organic pollutants such as exachlorobenzene [22], hexabromobenzene [23], PCBs [24], and more recently for degradation of sulfonic acids, also [25]. Further, ball milling has often been used for polymer clay nanocomposites processing as an alternative for exfoliation of clay mineral particles necessary for dispersing them uniformly throughout the polymer matrix [20].

Although, abounding literature exist on the effect of mechanochemical treatment on structure of montmorillonite, the consequences of microstructural changes caused by ball milling of clays on simultaneous sorption of heavy metals during the wastewater remediation have not been examined. Therefore, the aim of this paper is to investigate the microstructural and morphological changes induced by ball milling of clays and correlate this changes to CEC and the competitive sorption of the four (Ni, Cr, Cd and Pb) heavy metals.

2. Materials and methods

2.1. Clay adsorbent preparation

The adsorbent used for Ni (II), Cr(II), Cd (II) and Pb (II) uptake is a raw mineral taken from the mine of Bogovina, Serbia. 2 g of crushed and milled sample was washed several times with deionised water and dried at 105 °C in a drying oven to the constant weight. Mechanical milling was done in stainless vial of volume of 150 cm^3, using stainless balls of diameter 6 mm, for 5 h, in the air, using a Turbula Type T2C Mixer mill, at the standard milling frequency, with ball to powder ratio (BPR) equal to 4 [26].

2.2. Microstructural characterization of the clay adsorbents

Microstructure and morphology of unmilled and milled clay samples were characterized by powder X-ray diffraction analysis (XRD), particle size distribution (PSD) and scanning electron microscopy (SEM).

XRD analyses were carried out on a Siemens KRISTALLOFLEX D-500 device, with Cu-Kα Ni filtrated radiation ($\lambda = 1.5406°$) using Brag–Bretano geometry. The scan range was from $2\theta = 2°–30°$ with a scanning rate of 0.02°/s. The angular correction was performed by high quality Si standard. For a qualitative and quantitative analysis of the XRD data Powder Cell 2.4 software was used. Quantitative analysis of particles size was done using Malvern 2000SM Mastersizer which detects particles in the range from 0.02 to 2000 μm. The particles were sieved i.e. the measurement was done in air flow. SEM analysis was done using a VEGA TS 5130MM, Tescan Brno SEM equipped with the EDS detector.

2.3. The cation exchange capacity

The cation exchange capacity (CEC) was determined by saturating the unmilled and the milled clay with sodium acetate and replacing sodium with ammonium acetate [27].

2.4. Analytical techniques

The changes of the specific cation sorption produced by milling were determined as follows: sorbate solution with the concentration of 10 mg/l for each metal ion (Ni^{2+}, Cr^{2+}, Cd^{2+} and Pb^{2+} were freshly prepared in deionised water from the standard solutions for each metal (Merck, Darmstadt, Germany). Experiments were carried out by introducing 2.5 g of the clay mineral into the plastic flasks. 25 ml of the pre-selected sorbate aqueous solution was then added. The suspensions were stirred for 1 h. As heavy metals in wastewaters are usually found in a cationic form, they normally precipitate under alkaline conditions forming metal oxides and hydroxides. Large number of industrial wastewater containing heavy metals are acidic, so the adsorption studies were conducted under acidic conditions (pH = 5.5) which ensures that adsorption on clay is restricted to divalent heavy-metals ions.

Quantitative analysis of the each metal cation in aqueous solutions after adsorption on the treated and the untreated clay was carried out by Flame Atomic Absorption Spectrometry (FAAS) using an AAS Aanalyst 700/Perkin–Elmer and air and acetylene as flame gases. The results of the three replicates of the each experiment were averaged and no attempt was made to exclude air. The limit of detection (LOD) and the limit of quantification (LOQ) were determined for each heavy metal ion.

3. Results and discussion

3.1. Microstructural and morphological changes induced by milling

The XRD patterns of the unmilled raw clay (A) and milled material (B) are presented in Fig. 1. Clay belongs to phyllosilicate, consisting mostly of montmorillonite ($2\theta=6.05^\circ$; 19.82° and 34.84°) with concomitant mineral quartz ($2\theta=20.94^\circ$; 26.43°).

The changes of the clay structure upon milling are revealed in the XRD line broadening and the reduction of the diffraction intensities, suggesting the increases of structural disorder and the lattice strain. The all montmorillonite diffraction peaks, originating both from tetrahedral and octahedral sites, are affected by milling, similar to acid activation of the natural clay [10]. The inset in Fig.1 demonstrate the change of the montmorillonite (001) reflection ($2\theta=6.050^\circ$) upon milling. The basal spacing increases for 0.351 nm, from $d_{001}=14.71923$ nm for the unmilled, to $d_{001}=15.07056$ nm for the milled sample. The expansion of the basal spacing is commonly observed after different kinds of clay modification [16–19], but the modification observed in this work is smaller than the one in [19] and can be attributed to low energy of mechanical milling. At the same time, the (001) peak integral intensity is reduced for 19% indicating the increase of disorder, fragmentation and exfoliation of the clay mineral particles.

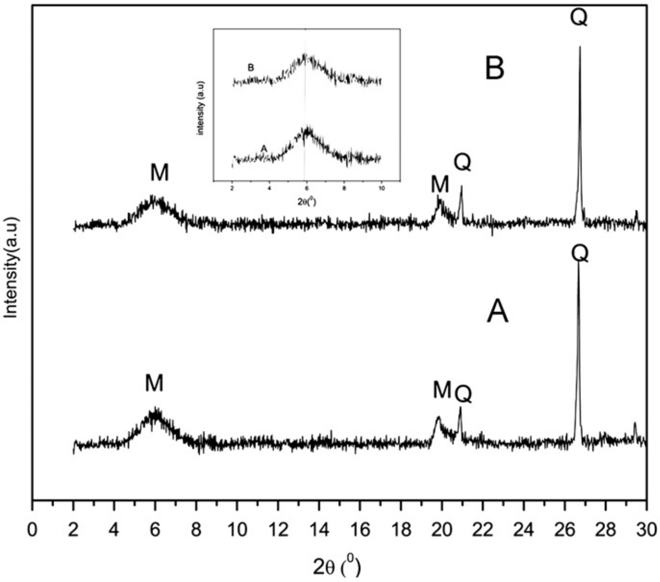

Fig. 1. XRD diffractograms of the unmilled (A), and the milled (B) clay. The change of the (001) montmorillonite reflection ($2\theta=6.050^\circ$) upon milling is presented in the inset.

The same changes in microstructure induced upon mechanochemical treatment of montmorillonite and vermiculite were observed [28–30].

The hardness of montmorillonite is 1–2 Mohs, while quartz has hardness of 7 Mohs, enabling that the majority of the energy transferred during ball impact is used to refine the crystallites of the softer (montmorillonite) phase giving the advantage of crude instead of purified clay for heavy metal adsorption (as presented below) [31].

The particle size distributions (PSD) obtained by laser diffraction measurements of the milled and the unmilled clays are shown in Fig. 2. A genereal trend of reduction of clay particles i.e. the increase of the number of small particles is present. The unmilled sample reveals the bimodal particle size distribution with mean values of particle size of 6 and 580 μm. The milling induces the shift of the main particle size for small-particles distribution peak from 6 to 2.5 μm and its increase in number of particles for 15 vol%. The number of particles in the intermediate peak, surrounding the range from 10 μm to 100 μm, increases from 9 vol% in the unmilled, to more than 30 vol% in the milled sample. The large-particles distribution peaks (shown on the right hand side of Fig. 2) describe reduction of the mean particles size from 600 μm for unmilled clay to 500 μm for milled sample and the reduction in number of these particles from 85 vol% in the unmilled, to about 50 vol% in the milled sample. As a result of the particles size reduction, the increase of the specific surface area from 0.0588 m^2/g in the unmilled, to 0.398 m^2/g in the milled clay occurs. It seems that milling opens up the edges of the platelets resulting in increase of the surface area, in a simillar way as the acid treatment [10].

Morphology of the unmilled clay can be seen in SEM images in Fig. 3, expresing the characteristic leafy structure

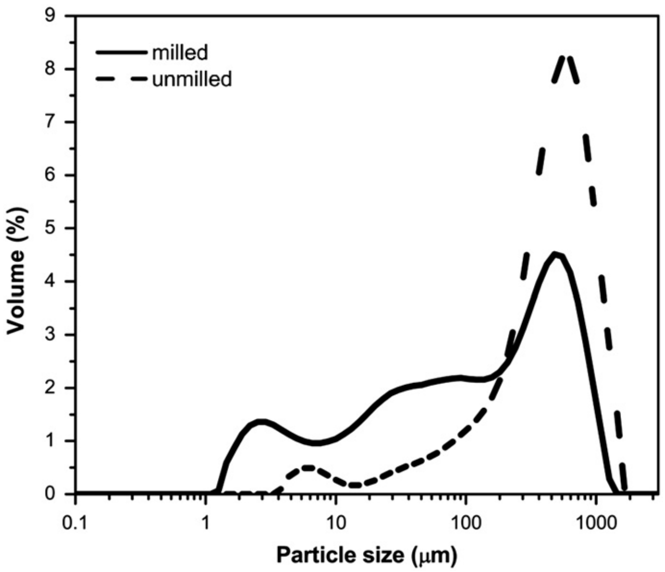

Fig. 2. Particle size distribution (PSD) of the milled (solid line) and the unmilled (dashed line) clays.

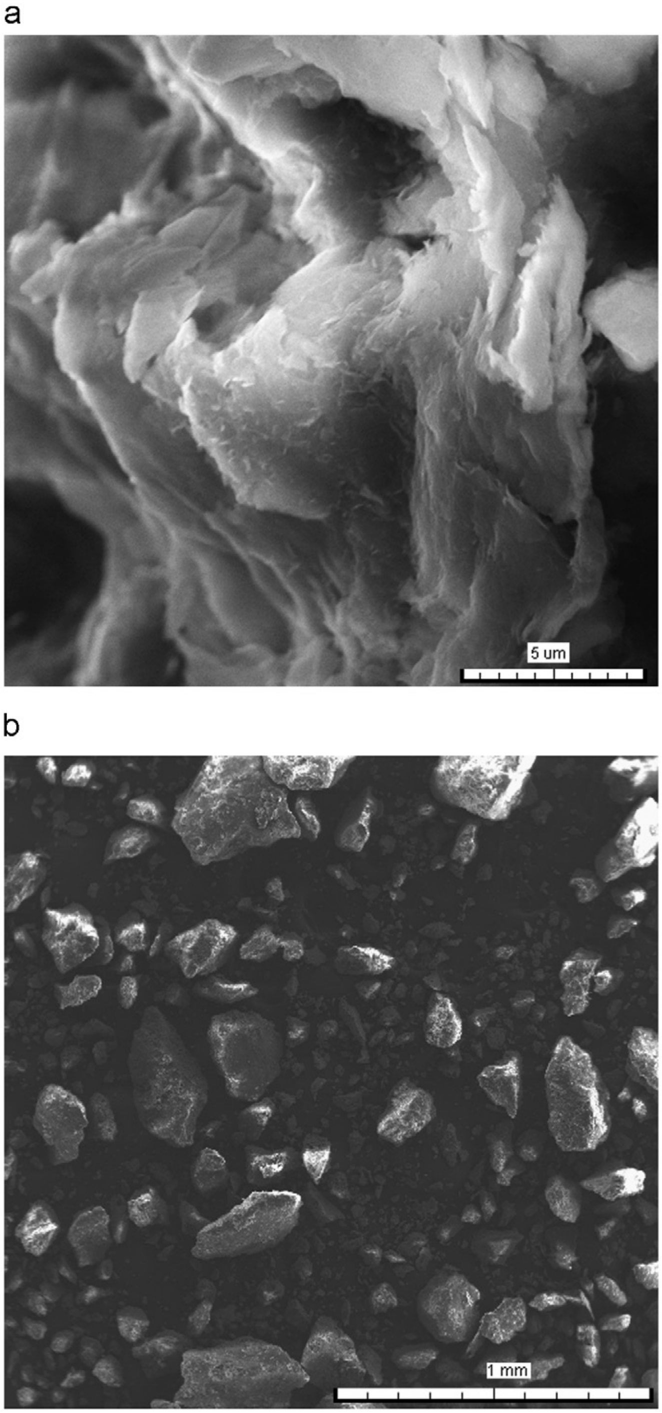

Fig. 3. SEM micrographs of the unmilled clay at magnifications: (a) 500 and (b) 65.

(Fig. 3a). The particles are of the order of micrometers and have irregular shapes with sharp edges, while their agglomerates are of the order of millimeters (Fig. 3b). This is in a good agreement with the results of PSD measurements (Fig. 2), which also reveals the bimodal distribution of particles size.

The changes of the sample morphology caused by milling are shown in Fig. 4. A partial destruction of the leafy structure is evident; the particles now resemble more welded with irregular shapes, and their size distribution is no longer a simple bimodal (see Fig. 2). It is noticeable that under performed milling conditions (milling time 5 h, BPR = 4, in air) fragmentation occurs. Anyhow, particles tend to agglomerate. This agglomeration of the mechanically milled clay minerals was observed before [20]. The formation of agglomerates can have an adverse impact on the CEC because it decreases the porosity. The first impression is that these results are not in full agreement with the PSD results, where the reduction of the particles size (i.e. agglomerates) with the average size over 100 μm was observed after the milling. This discrepancy could be a consequence of the sample preparation for PSD, as the particles of the milled sample were sieved, which could lead to separation of the weakly interacting agglomerates that are, on the other side, observed in the SEM micrographs (Fig. 4).

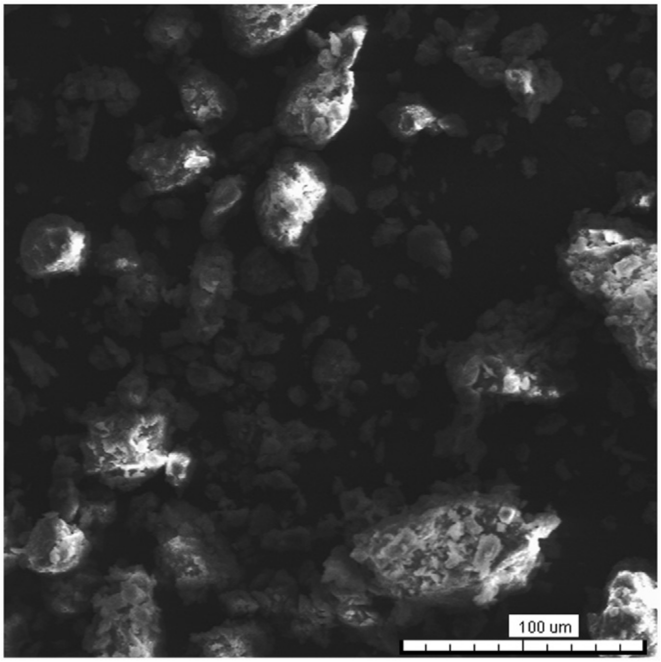

Fig. 4. SEM micrograph of the milled clay.

3.2. The CEC changes induced by milling

Modification of the clay structure and morphology (the expansion of the interlamellar space, broken bonds decrease of particles size accompanied by increase of specific surface area and agglomeration induced by milling) change the CEC from 77 meq/100 g for the unmilled, to 95 meq/100 g for the milled clay, which is an increase of 23%. This raise is of the same magnitude, or larger, than those achieved by other methods used for clays modification for waste water remediation presented in literature, e.g. acid activation, or pillaring [10,32]. Using sulfuric acidic activation and heating, Bhattacharyya and Gupta [10] achieved the montmorillonite capacity increase of 12.0%. The changes of montmorillonite structure that have led to this capacity increase are similar to those caused by mechanical milling: a decrease of the characteristic XRD peaks intensity, appearance of new peaks, and the increase the specific surface area are reported [10]. However, the heating of the samples has induced the collapse of the layered structure of montmorillonte, and thus reduction of the CEC [32]. Although pillaring leads to an increase of specific surface area, pore size and interllameral space (the same effects are produced by ball milling) the CEC values of the treated samples are smaller than that of the untreated one [33]. This implies that calcination, which leads to dehydration and dehydroxination of charged precursors of pillars and formation of neutral oxide particles, leads to irreversibility of the cation exchange. The CEC is then determined by the number of remaining exchangeable cations, which was less than in the untreated sample [34]. Vdović et al. [19] examined the changes of surface properties of montmorillonite during grinding using the technique of high-energy milling. The initial capacity of 142 cmol/kg was increased to 175 cmol/kg after 16 min of grinding. Further milling had produced a great reduction of the CEC to 10 cmol/kg. The initial increase of the CEC reported by Vdović et al. [19] after 16 min is similar to the one obtained in this work after 5 h and a more detailed investigation of the influence of energy and power deposited by milling would be of a great interest.

3.3. Changes of heavy metals ion sorption induced by milling

The concentrations (C), immobilization efficiencies (η), the limits of detection (LOD) and the limits of quantification (LOQ) of Ni (II), Cr (II), Cd (II) and Pb (II) ions before and after the sorption on the unmilled and the milled clay are presented in Table 1. As can be seen, the untreated clay almost completely absorbs Cr (II) and Pb (II): the immobilization efficiencies are $\approx 98\%$. The percentage is smaller for Cd (II) and Ni (II) ($\approx 81\%$), indicating higher affinity of sorption on raw clay for Cr (II) and Pb (II) rather then Cd (II) and Ni (II): $\mathrm{Pb} \approx \mathrm{Cr} > \mathrm{Cd} \approx \mathrm{Ni}$. The milled clay further reduces concentrations of Ni (II) and Cd (II) from the solution: the immobilization efficiencies of Ni and Cd were $\approx 81\%$ in unmilled clay and they were increased up to $\approx 87\%$ by milling. It is important to emphasize that under investigated conditions the order of affinity for sorption is not affected by milling.

Table 1
Concentrations (C), immobilization efficiencies (η), the limits of detection (LOD) and the limits of quantification (LOQ) of each heavy metal cation in mixture before and after the sorption on unmilled and milled clay.

Heavy metal ion	C_0 (mg/l)	C_{unmilled} (mg/l)	C_{milled} (mg/l)	η_{unmilled} (%)	η_{milled} (%)	LOD (mg/l)	LOQ (mg/l)
Ni(II)	10.2	1.96	1.37	80.8	86.6	0.14	0.47
Cr(II)	10.1	0.16	0.18	98.4	98.2	0.16	0.53
Cd(II)	9.45	1.81	1.20	80.8	87.3	0.01	0.03
Pb(II)	9.91	0.23	0.10	97.7	99.0	0.10	0.34

4. Conclusions

The long term, low energy milling of raw clay from Serbian Mine Bogovina has produced various structural defects: the increase of the clay interlamellar space, the decrease of the particles size accompanied by the increase of their specific surface area, and agglomeration. These changes have resulted in rise of the CEC from 77 meq/100 g to 95 meq/100 g (23%). The high affinity of sorption was achieved for all used heavy metals on the as received raw clay and it was further improved by milling: the better sorption of Ni (II) and Cd (II) has been achieved by milling. The order of affinity of the metal ions is $\mathrm{Pb} \approx \mathrm{Cr} > \mathrm{Cd} \approx \mathrm{Ni}$ and, under investigated conditions, is not changed upon milling. A combined approach, like for example acid activation or pillaring of mechanically milled clays, or milling with different kind of additives, deserves a serious consideration as a possibility for further improvement of their adsorption capacities for removal of heavy metal contaminants from wastewaters.

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