PHYSICAL CHEMISTRY 2014

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on Fundamental and Applied Aspects of
Physical Chemistry

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APPLICATION OF RAW AND MODIFIED CLAY FOR THE REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS

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ABSTRACT

This work represents a fundamental study of the simultaneous sorption of heavy metals from aqueous solutions by locally available raw and mechanochemically activated natural clay. The obtained results show that the investigated clay, as an economical and efficient sorbent, has potential for application in the treatment of heavy-metal-contaminated wastewaters.

INTRODUCTION

Wastewaters containing heavy metals as contaminants originate from a large number of metal-related industries and mines. Heavy metals are toxic and nonbiodegradable, and their presence in streams and lakes causes serious environmental problems. To avoid water pollution, treatment, that is, the removal of heavy-metal ions from industrial wastewaters, is needed before disposal. Among other conventional techniques, adsorption appears to be an attractive process in view of its efficiency and simplicity of operation, as well as the availability of a wide range of adsorbents [1 - 3].

Clay minerals are good adsorbents for metal ions from aqueous solutions owing to their high cation-exchange capacities, high abundance and local availability, nontoxicity, chemical and mechanical stability, low costs, and ability to be recycled [4]. To improve the adsorption characteristics of the clays, different techniques of modification (acid activation, intercalation and pillaring, mechanochemical activation, etc.) can be applied. In comparison with other methods, mechanochemical activation represents an environmentally friendly and inexpensive method of materials modification.

The aim of this study was to investigate the simultaneous removal of Pb(II), Cu(II), Cd(II) and Zn(II) ions using locally available raw and mechanochemically activated clay as adsorbents. The effect of the time of adsorption and the adsorbent concentration on the process efficiency was observed.

EXPERIMENTAL

The raw natural clay used as an adsorbent was obtained from the mine Bogovina (Serbia). Mechanochemical activation (milling) was performed in air in a Turbula type 2TC mixer at ball-to-powder ratio (BPR) fixed at 4:1. The milling times tested were 2 and 19 h.

Batch experiments were carried out at room temperature by mixing an adequate amount of the clay and 25 cm^3 of working multimetal ion solution in closed polyethylene bottles. Multimetal ion solution was prepared in milli-Q water using the analytical reagent grade chemicals $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $ZnCl_2$. The total metal ion concentration in the working solution was 50 mg dm^{-3} at pH 5.5. The samples were shaken at stirring speed of 200 rpm for different periods of time (ranging from 30 s to 24 h). After that, the liquid phases were separated from the solid phases by filtration. The residual concentration of heavy-metal ions in each sample was determined with a 797 VA Computrace polarography system (Metrohm, Switzerland) using the Metrohm's procedure No. 231/2 e.

The efficiency of the adsorption process was evaluated by the two parameters: (1) the removal efficiency of particular metal ion, *E*, that represents the percentage of the metal ion removed from the initial solution and (2) the adsorption capacity of the clay, q_e, that represents the amount of metal ion adsorbed per unit mass of the adsorbent.

RESULTS AND DISCUSSION

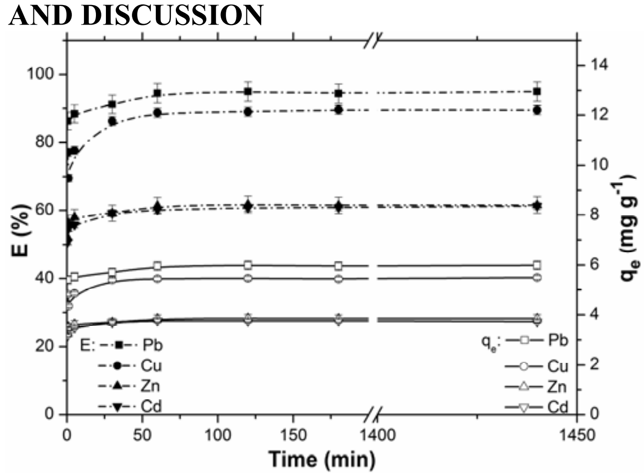

Figure 1. Effect of contact time on the adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) by the raw clay at the fixed adsorbent concentration of 2 g dm^{-3}.

Fig. 1 shows the effect of contact time on the adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) onto the raw clay. As can be seen, the equilibrium adsorption was established after 60 min of contact, and the maximum uptake on the raw clay for all investigated metals was reached: 94.7% (6.0 mg g^{-1}) for Pb(II), 89.2% (5.4 mg g^{-1}) for Cu(II), 61.6% (3.8 mg g^{-1}) for Zn(II) and 60.8% (3.7 mg g^{-1}) for Cd(II). After equilibrium was reached, the contact time had no longer influence on the metal-ion adsorption.

In addition, it is evident that, after only 5 min of adsorption, the *E* values of Pb(II), Cu(II), Cd(II) and Zn(II) exceeded 85% of their values at equilibrium. This imply that the sorption mainly took place at the surface of the sorbent during the initial stage. The adsorption time of 60 min was used for the rest of the study.

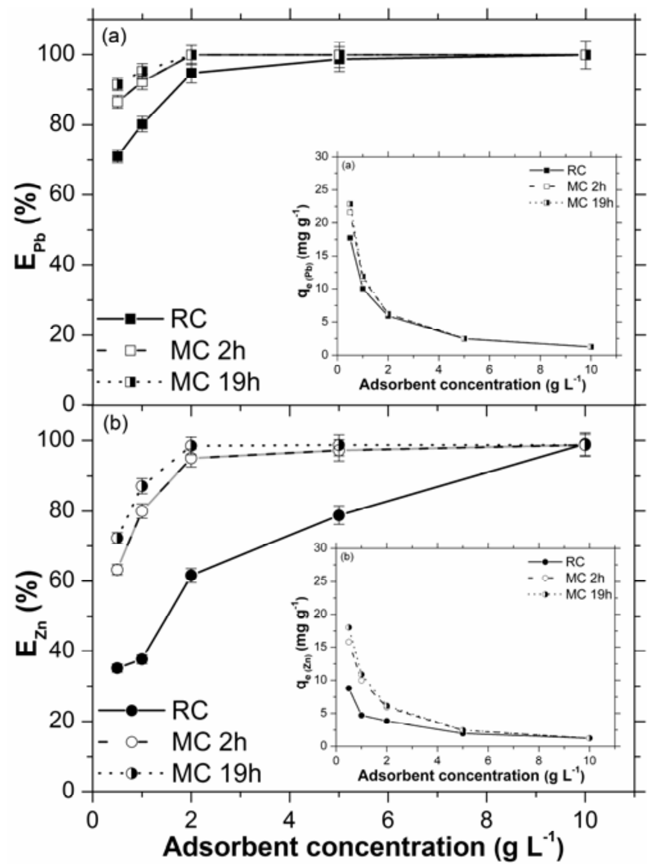

Figure 2. Effect of adsorbent concentration on the adsorption of (a) Pb(II) and (b) Zn(II) onto raw clay (RC) and 2- (MC 2h) and 19-h milled clay (MC 19h)

The effect of the adsorbent concentration was studied using raw and 2- and 19-h milled clays as adsorbents. The results obtained for Pb(II) and Zn(II)

ions are shown in panels a and b, respectively, of Fig. 2, and for the other two ions, Cu(II) and Cd(II), the obtained dependencies were similar. Obviously, upon increasing the adsorbent concentration, the amounts of adsorbed metal ions (i.e., their *E* values) increased. It can be explained by the fact that the number of available adsorption sites increased with increasing amount of clay and, hence, the *E* values of metal ions increased.
The maximum removal efficiency for the raw clay was attained at the adsorbent concentration of 10 g dm^{-3}, whereas the same removal effect, using the 2- and 19-h milled clays, was achieved at an adsorbent concentration of 2 g dm^{-3}. Thus, the modification of the used raw clay by mechanical milling not only improved the adsorption characteristics of the adsorbent, in terms of the *E* values of the investigated heavy metal ions, but also reduced, by a factor of 5, the amount of adsorbent necessary to achieve the highly efficient removal of metal ions from aqueous solutions.

CONCLUSION

Raw natural clay from the Serbian mine Bogovina is an effective adsorbent for the simultaneous removal of heavy metals from aqueous solutions. The results showed that equilibrium was established after 60 min of contact. Mechanochemical activation of the raw clay significantly improved the adsorption behavior of the adsorbent and reduced the amount of adsorbent necessary to achieve the highly efficient removal of Pb(II), Cu(II), Cd(II) and Zn(II) ions by a factor of 5.

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