INNOVATIVE MANGANESE OXIDES AND THEIR USE FOR SORPTION OF Pb, Zn AND Cd IN CONTAMINATED SOILS

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Abstract
The studied amorphous manganese oxide (AMO) has been already successfully tested as an efficient agent for decreasing the mobile fraction of risk elements in soil. However, its application is accompanied with an unsolicited phenomenon of increased dissolution of this agent related to oxidation of soil organic matter. For that reason, surface modification of the studied Mn oxide with the layer of $MnCO_3$ (Sm-AMO) has been proposed. The results of preliminary testing of the stability of both materials in demineralized water confirmed that Sm-AMO is less soluble than the original AMO. Adsorption kinetics of Cd, Pb and Zn onto AMO and Sm-AMO was performed to compare the adsorption properties of both materials. The affinity of these metals was generally higher towards AMO, but the recorded equilibrium time was similar for both sorbents. Additionally, the adsorption of the target metals increased with higher pH. Based on modelled Langmuir isotherm parameters, the Sm-AMO proved to have higher maximum adsorption capacity for the whole pH range studied and also higher affinity of Zn towards this material.

Key words:
Amorphous manganese oxide (AMO), soil contamination, metals, immobilization, adsorption

Introduction

Soil is a key component of terrestrial ecosystems and an important storage of chemical elements; however, in the last few decades, environmental problems related to its contamination have been recorded (Gil-Díaz et al., 2014). Primarily metals, i.e. Pb, Zn and Cd in this case, are known to be toxic for most organisms after exceeding a limit level. Additionally, it is very difficult to remove metals from the environment (Cao et al., 2009). The Fe and Mn oxides are important scavengers for contaminants in soils, mainly due to their high reactivity and large specific surface area. The amorphous manganese oxide (AMO) and its surface-modified form (Sm-AMO) were used in this study. An undesirable effect connected with AMO application is its increased dissolution in soil, primarily at low pH. This fact also leads to undesirable oxidation and dissolution of soil organic matter (Ettler et al., 2014; Michálková et al., 2014). A layer composed of small grains of rhodochrosite ($MnCO_3$) has been identified as secondary products on the surface of AMO particles after their incubation in contaminated soils. The formation of this layer is associated with the stabilization of the AMO particles and it reduces thus their solubility (Ettler et al., 2014). In order to optimize the material properties, surface modification of the AMO particles with $MnCO_3$ layer prior to its application was proposed. The main objective of this study was to determine the adsorption properties of the surface modified Sm-AMO and the original AMO for sorption of Pb, Zn and Cd.

Methods and materials

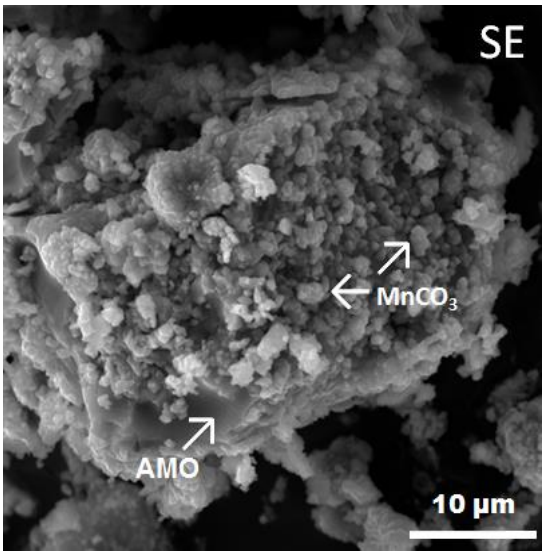
Amorphous manganese oxide (AMO) was prepared using a modified procedure for the preparation of birnessite according to Della Puppa et al. (2013). The synthesized material was then filtered, washed, dried and finely milled. In order to prepare the surface-modified particles (Sm-AMO), the AMO particles were incubated in demineralized water saturated with CO_2 for 4 days, then washed, filtered and dried again. Identification of the solid phases was performed using X-ray diffraction spectrometry (XRD; PANalytical B.V., the Netherlands) together with scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS; TESCAN Ltd., Czech Republic).

The stability of AMO/Sm-AMO was tested by agitating the particles in suspension with demineralized water at a ratio of 1/50 and 1/500 (w/v) up to 4 weeks while monitoring the chemical composition, pH

and Eh of the solution. The adsorption experiments were subsequently performed to compare the adsorption properties of the original and surface-modified AMO. The adsorption kinetics was tested in solutions of Pb, Zn and Cd of concentration 0.1 mM, at pH 5 and at the ratio of 1/1000 (w / v). The Pb, Zn and Cd adsorption isotherms corresponding to pH 4.5, 5.5 and 6.5 where subsequently constructed. Samples of AMO / Sm-AMO (1/1000, w/v) were agitated in solutions of Pb, Zn and Cd at concentrations from 0.1 to 4 mM for 60 to 80 minutes. The difference between initial and final concentrations of Pb, Zn, Cd and Mn in solution yielded the amount of metal elements adsorbed per gram of adsorbent. The obtained data were further modeled using Langmuir and Freundlich adsorption models.

Results and Discussion

The X-ray diffraction analysis together with SEM/EDS confirmed the presence newly formed phase $MnCO_3$ on the surface of Sm-AMO particles (Fig. 1). The tests evaluating the stability of AMO / Sm-AMO in demineralized water (Fig. 2) showed that the AMO is more susceptible to dissolution at both w/v ratios.



Concerning the results of adsorption kinetics (Fig. 3), the highest rate of adsorption together with the highest adsorbed amount were observed in case of Pb for both materials, which is in agreement with the previous studies focused on the adsorption properties of the original AMO (Della Puppa et al., 2013; Michálková et al., 2014). The affinity of the target metals was higher towards AMO than Sm-AMO, but the time required for reaching the equilibrium was comparable for both materials. In case of adsorption isotherms, the highest adsorbed amount of all the studied metals was recorded at the highest pH (i.e., 6.5). Based on modeled Langmuir isotherm parameters, the affinity of Cd and Pb was higher for AMO for all the pH values, yet the higher maximum adsorption capacities were observed for Sm-AMO.

Fig. 1: Scanning electron microscope image in the secondary electron mode showing the AMO surface covered by $MnCO_3$ layer.

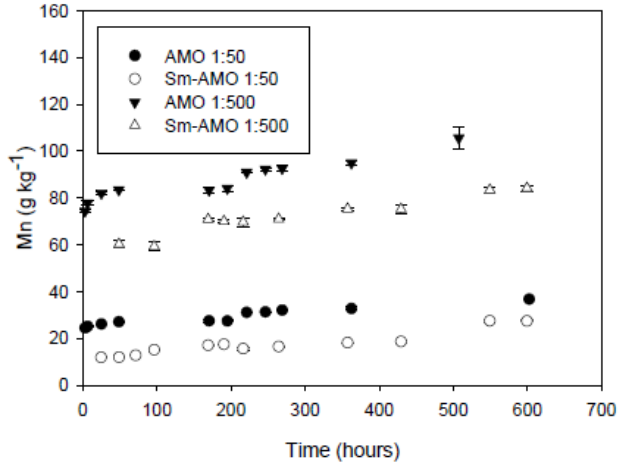


Fig. 2: Stability of AMO / Sm-AMO in demineralized water

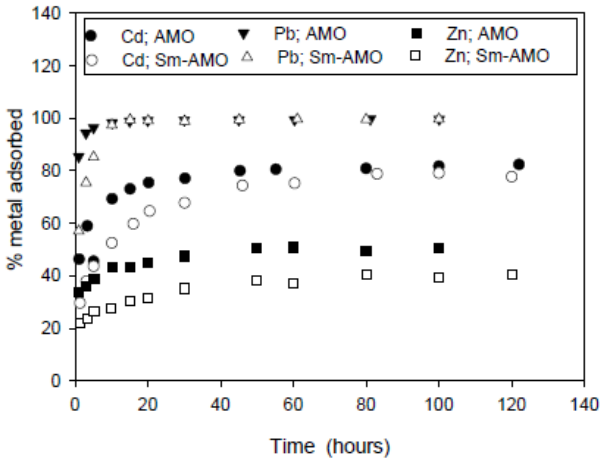


Fig. 3: Adsorption kinetics of AMO / Sm-AMO

In case of Zn, not only higher adsorption capacity but also higher affinity was observed towards Sm-AMO. In case of AMO, the maximum adsorption capacity modeled for Cd, Pb and Zn reached the values of 120, 353 and 93 mg g^{-1}, respectively, whereas the values of 179, 680 and 107 mg g^{-1} were reached in the case of Sm-AMO. Extremely high adsorption capacity of Sm-AMO recorded for Pb was probably caused by precipitation of carbonate phases in the solution during the experiment and it is thus artificially overestimated.

Conclusions

A layer of $MnCO_3$ was formed on the AMO particles as a result of proposed surface modification. Both studied materials have high adsorption capacity for Cd, Pb and Zn. Although the adsorption kinetics of these metals is lower in case of Sm-AMO, maximum adsorption capacity is comparable or higher. The results of preliminary tests of stability of both materials in demineralized water confirmed that the Sm-AMO is less soluble than the original AMO. Based on our results, the proposed surface modification appears to be efficient for improving the AMO stabilizing properties. Yet, further testing in soil conditions is necessary and is also the subject of the current work of our research group.

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