Removal of Cd(II) ions by adsorption on inorganically modified montmorillonite composite

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INTRODUCTION

Heavy metals represent significant aquatic environment contaminants whose presence in the environment is predominantly the result of anthropogenic activities. These metals such exhibit high toxicity and non-biodegradability, leading to serious consequences for both ecosystems and human health. One of the important applications of sorption properties of clay minerals, especially montmorillonite and kaolinite, and/or composite clay materials is their use in removing heavy metals from aquatic systems. For the uptake of metal cations from wastewaters, synthetic oxides/oxyhydroxides of Mn, Fe, Al, etc., with negatively charged surfaces are also suitable. MnO_2 is a type of surface acidic oxide with a pH_{pzc} (point of zero charge) of about 2.0. However, most metal oxides are only available as fine powders, which leads to practical limitations, in particular the difficulty of solid-liquid separation. A possible solution is the preparation of alternative sorbents using montmorillonite as a carrier for manganese oxides.

OBJECTIVE

- Design and preparation of novel effective composite sorbents based on clay precursors.
- Investigation the properties of manganese oxide-coated montmorillonite (Mn-Mt) as an adsorbent for the removal of Cd(II) ions from solutions in a batch laboratory system.

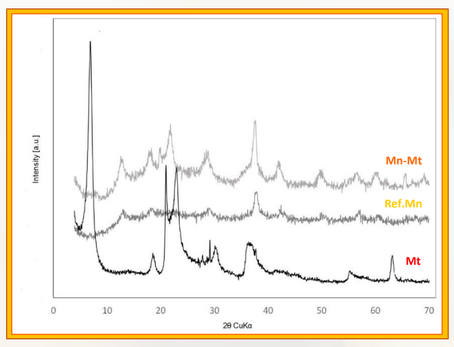
METHODOLOGY

- STx-1b (Mt) from Texas (USA) obtained from the Clay Minerals Society was used for the design and preparation of the Mn-Mt composite.
- Manganese oxide colloids were precipitated onto Mt in a 1:1 weight ratio (Mn:Mt) by a reduction procedure:

  $2KMnO_4+8HCl \rightarrow 2MnO_2+2KCl+3Cl_2+4H_2O$
- Dissolving $KMnO_4$ (27,26 g) in distilled water (30 ml), water bath 90°C, 15 min.
- Adding 15 g MMT, stirring 10 min.
- Adding 2M HCl (dropwise), color change from deep pink to black, water bath 90°C, 15 min.
- Sorption experiments: initial Cd^{2+} concentration of the model solutions in the range of 10-700 mg/l, sorbent weight 1 g/l , sorption time 24 hours.

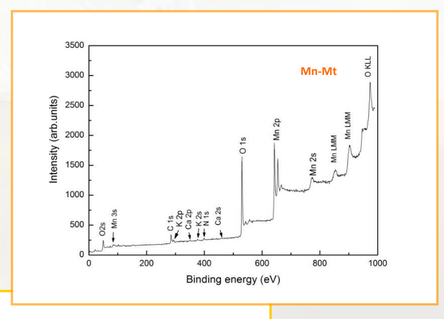
ANALYSIS

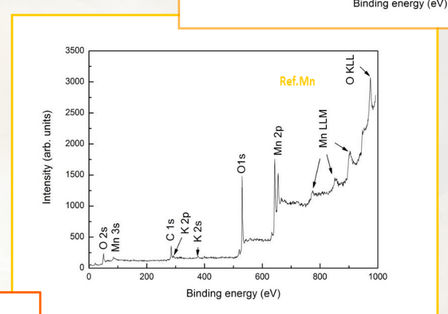
X-ray diffraction analysis

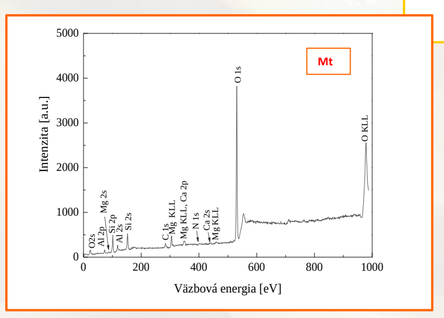


XRD patterns of Mt, Ref. Mn and Mn-Mt composite

X-ray photoelectron spectroscopy



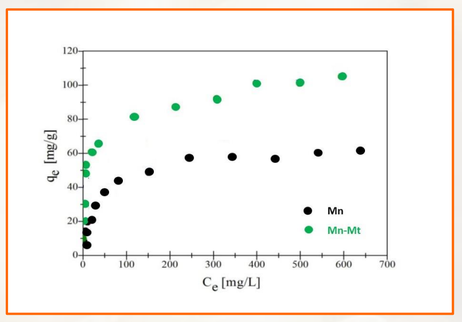




X-ray photoelectron spectrum of Mt, Ref. Mn and Mn-Mt composite

Only one oxidation number of manganese (Mn^{4+}) was determined in all studied samples

Sorption experiments



Sorption of Cd (II) on Mt and Mn-Mt

RESULTS/FINDINGS

X-ray diffraction analysis

- Synthesis procedure led to the formation of manganese oxide with the structure of cryptomelane (α-MnO_2).
- Ref.MnO_2 contains a small admixture of ε-MnO_2.

X-ray photoelectron spectroscopy

- The XPS spectrum of Mn-Mt confirm that natural montmorillonite surfactants were coated with manganese oxides because the same lines were present as in the sample Ref-Mn.
- Other calcium (Ca 2p, Ca 2s) lines from montmorillonite matrix were also used. The main aim of the detailed Mn 2p line measurements were made at high resolution in the 630 - 660 eV binding energy range.
- The presence the Mn^{4+} in the manganese-modified sample was confirmed.

Sorption experiments

- The adsorption parameters were calculated through Langmuir model due to the fact that sorption data were well fitted to the linear form of the Langmuir isotherm.
- The obtained values of maximum adsorption capacities [mg/g] were: 63.29 (Mt), 103.09 (Mn –Mt).
- The adsorption experiments with the inorganically modified forms of montmorillonite confirmed a significant improvement of the adsorption properties of the natural materials at adsorption of Cd(II) after their modification by the manganese oxides.

CONCLUSION

- The effective connection of manganese oxide with the montmorillonite was confirmed by the results of the X-ray diffraction analysis and X-ray photoelectron spectroscopy, the oxide coated on montmorillonite surface is presented mainly as cryptomelane (αMnO_2).
- XPS measurements in manganese-modified montmorillonite composites confirmed the manganese chemical status, the valence states of the precipitated manganese ions had state of Mn^{4+}.
- The sorption of Cd(II) ions by Mn-Mt composites was pH dependent and the adsorption isotherms revealed that the uptake of Cd(II) ions could be described by the Langmuir model.

ACKNOWLEDGEMENTS

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