09MECC

ZAGREB **CROATIA**
| 17 - 21 SEPTEMBER **2018** |

9th Mid-European Clay Conference

Conference Book

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9th Mid-European Clay Conference
MECC 2018

Zagreb, September 17-21, 2018

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Financed by: Croatian Science Foundation, project 2504-NanoMin "Nanominerals in sediments and soils: formation, properties and their role in biogeochemical processes"

TECHNICAL ORGANIZER:
Spektar putovanja d.o.o., Congress department, Andrije Hebranga 34, 10000 Zagreb

EDITED BY:
Darko Tibljaš, Marija Horvat, Nenad Tomašić, Marta Mileusnić & Anita Grizelj

PUBLISHED BY:
Croatian Geological Society, Croatian Geological Survey, Faculty of Mining, Geology and
Petroleum Engineering & Faculty of Science - University of Zagreb

ISBN:
978-953-6907-71-7 (Croatian Geological Survey)
978-953-6923-39-7 (Faculty of Mining, Geology and Petroleum Engineering - University of Zagreb)
978-953-6076-46-8 (Faculty of Science - University of Zagreb)

A CIP catalogue record for this book is available from the National and University Library in Zagreb under 001005359.

DESIGN OF COVER: Leitmotif kreativni biro j.d.o.o., IV. Maksimirsko naselje 21, 10000 Zagreb
LAYOUT AND PRINT: Laser Plus d.o.o., Brijunska 1a, 10000 Zagreb
ISSUED: 2018, 200 copies

SUPPORTED BY:
The Foundation of Croatian Academy of Sciences and Arts,
Kraneamus Krapina Neanderthal Museum,
Ministry of Science and Education of the Republic of Croatia,
Zagreb Tourist Board,
Croatian Geological Survey,
Faculty of Mining, Geology and Petroleum Engineering - University of Zagreb,
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Removal of chromates and arsenates by halloysite-LDH composites

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Halloysite is a natural 1:1 layered aluminosilicate clay mineral belonging to the kaolin group which exhibits a unique tubular morphology. It has active surface hydroxyl sites which allow to attract ions from aqueous solutions due to protonation/deprotonation phenomena. Industrial activity often produces wastewaters containing anionic pollutants. These are hard to remove or neutralize by most of the mineral sorbents which usually have cation exchange properties. Previous studies indicated that halloysite could be used as a very promising material especially for removing As(V) from aqueous solutions (MATUSIK, 2014; MAZIARZ & MATUSIK, 2016). Typical sorbents capable of immobilizing anionic pollutants are rare and usually based on layered double hydroxides (LDH). The composition of these anionic clays is expressed by a general formula $[(M)^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}{}_{x/n}\cdot yH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively. The isomorphous substitution in octahedral sites of the brucite-like layers results in a net positive charge, which is neutralized by the hydrated anions occupying the interlayer space. A disadvantage of using LDH as a sorbent is their limited structural stability at low pH. Therefore, the aim of this work was to synthesize halloysite-LDH composites and to examine their sorption capacity towards As(V) and Cr(VI).

For this study halloysite sample was obtained from Dunino deposit located near Legnica in Lower Silesia (Poland). In turn, LDH of Mg-Al type was synthesized in laboratory by co-precipitation method. Raw halloysite and pure LDH were used for preparation of halloysite-LDH composites containing 5, 15 and 25 wt%. of LDH. The composites were prepared by two different approaches: direct precipitation of LDH in halloysite suspension and physical mixing of the two minerals. The sorption of As(V) and Cr(VI) was conducted for initial concentration of 1 and 5 mmol/L and initial pH 5. The suspensions (solid/solution ratio: 20 g/L) were shaken for 24 h at room temperature. Afterwards the anions concentration in the supernatant solutions was measured using colorimetric methods: molybdenum blue method for As(V) and diphenylcarbazide method for Cr(VI).

The XRD pattern of the halloysite sample showed a basal peak at 7.2 Å, which confirmed the presence of dehydrated halloysite-(7 Å). The basal spacing for pure Mg-Al LDH was equal to 7.7 Å which is in agreement with other studies indicating the presence of carbonates in the interlayer space. The IR spectra of the halloysite showed bands characteristic for kaolin group minerals related to the OH-stretching (3694 cm^{-1} and 3622 cm^{-1}). Additionally, the bands associated with stretching and bending vibrations of aluminosilicate framework (1200–400 cm^{-1}) were noticed. The IR spectra of LDH showed characteristic O-H and H_2O vibrations in the range of 3600–3300 cm^{-1}. The presence of carbonates balancing the structural charge was reflected by a band in the range of 1430–1350 cm^{-1}. The absorption bands at ~670 and ~550 cm^{-1} were attributed to Al–O bond and Mg-O vibrations. The XRD patterns of halloysite composites with LDH showed peaks which could be attributed to both phases. The LDH peaks intensity increased along with its content in the composite. The same observations were made for the absorption bands in the FTIR spectra.

The sorption capacity of all samples was very high regardless of the synthesis approach and the tested concentrations were much higher than those found in industrial wastewaters. The highest uptake of As(V) and Cr(VI) was measured for the pure Mg-Al LDH in the 5 mmol/L initial solution where it reached 255 mmol As(V)/kg and 250 mmol Cr(VI)/kg. An increasing content of LDH in composites caused an increase of sorption as compared to the raw halloysite, which adsorbed only 22.7 mmol As(V)/kg and 26.6 mmol Cr(VI)/kg from 5 mmol/L solution. This proves that sorption is mainly connected with anion-exchange of As(V) and Cr(VI) for CO_3. The sorption capacity of halloysite and halloysite-based composites was lower than that calculated for the LDH. However, the use of halloysite as a support for LDH aimed at increasing pH stability of the new hybrid sorbent.

Acknowledgments
This research was supported by the National Science Centre, Poland under the project no. 2017/27/B/ST10/00898.

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