Fast, selective and ecological ion-exchange materials for hydrometallurgy (FSE-IX)

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Abstract

In this project the plan is to combine the good properties of inorganic ion-exchangers with those of ion-exchangers based on organic polymers. The resulting material will be a composite having either an inorganic ion-exchanger incorporated into an organic matrix or an inorganic matrix with organic functional groups. Furthermore, the aim is to utilize waste materials from mining industry, such as metal oxides, for the preparation of the new ion-exchangers. These synthesized materials will be tested in relevant hydrometallurgical applications.

During 2008 manganese oxides with tunnel or layered structures have been prepared and studied as selective ion exchange materials. Four manganese oxides (cryptomelane, hausmannite, birnessite and todorokite) have been prepared and their ion exchange properties for Cu, Ni, Co, Mn, Zn and Cd from hydrometallurgical process solutions have been tested. In addition the synthesized birnessite (OL-1) and todorokite (OMS-1) were supported on silica in order to have suitable particle size for column operations. In particular, attempts have been made to find an inexpensive oxidant for Mn(II) in the synthesis and to use authentic process streams as the Mn(II) source together with optimization of the cryptomelane synthesis. A novel application to use cryptomelane as sorbent/catalyst to treat complexed metal solutions has been tested with promising results.

The first syntheses of composite materials have also been made. The fine manganese oxide particles are embedded in a support material. The characterization of this polyacrylonitrile-manganese dioxide (PAN-OMS-2) hybrid material is currently in progress. The results indicate that silica supported OMS materials can be utilized as ion exchange material in hydrometallurgy. However, some limitations were observed dealing with material instability due to redox reaction and low capacity. The metal uptake in the studied materials and mass transfer in the nanoporous crystals were successfully modeled by NICA (non-ideal competitive adsorption) and Nernst-Planck equations.

Results

We have divided the project into three tasks as follows:

Task A. Preparation, Characterization and Application Testing of Cryptomelane

In our earlier studies a simulated hydrometallurgical waste water (Al 81,4; Ca 81,1; Fe 83,4; Mg 19,6; Mn 1164,0; Na 62,0 mg/L) was used as precursor for Cryptomelane-type manganese dioxide synthesis. Three out of five of the synthesised materials showed similar structural properties as a reference material synthesised from laboratory chemical. De Guzman's OMS Cryptomelane was chosen as reference material due to its well known structure and good ion exchange properties. However, the crystallinity of these three materials was very low and optimization of the synthesis procedure was attempted with good success, and materials almost identical to reference material were synthesised. Also the traces of impurities that were found in earlier synthesis were avoided with the optimised synthesis procedure (Fig. 1a). The ion exchange properties of the synthesised material were found to be good: an ion exchange capacity of 2.6 meq/g for copper uptake, and selectivity series Co>Cd>Ni for transition metals was determined.

Novel application to use the material as sorbent/catalyst in fluidised bed UV-photoreactor was tested and superb results for Co-EDTA solution was obtained. The complexes of metal─EDTA's are strong and typically neutral considering their electric charge. This makes them particularly problematic in waste water management, and at their best somewhat 90% of the complexes are destroyed or removed before their discharge. With the synthesised material 99.9 % of the chelated cobalt was removed from the solution after 4 hours of UV-radiation (Fig. 1b).

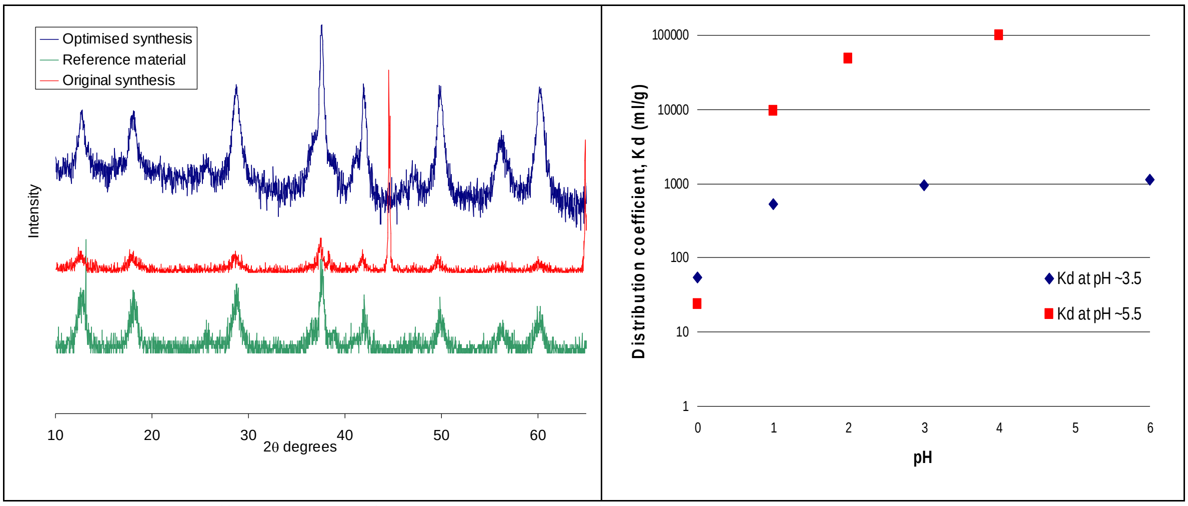

Fig. 1. a) XRD diffractograms of OMS-2 materials of: optimised synthesis (top), original synthesis and reference materials (bottom), b) distribution coefficients (ml/g) of 10 μM of cobalt from 10 μM Na-EDTA and 0.01 M $NaNO_3$ solution as a function of time and UV-radiation in photoreactor.

The possibility to make organic-inorganic hybrid materials of the synthesised OMS-2 materials was studied in co-operation with Technical University of Prague and a polyacrylonitrile-manganese dioxide (PAN-OMS-2) material was synthesised. Testing the ion exchange properties of this material is in progress.

As a result we were able to synthesize Cryptomelane structured manganese oxide material from metallurgical waste water simulant that has good ion exchange properties and potential for wide range of applications. Innovation to use the material as sorbent/catalyst in UV-photoreator for removal of complexed metals was demonstrated to be successful. The cryptomelane studies were carried out mostly at UH. A master's thesis on this topic is nearly finished and one scientific article[1] is under preparation.

Task B. Synthesis and Characterization of Other Manganese Oxides

In this work the goal was to synthesize and study the properties of a separation material, oxidation state using oxygen or even air in highly alkaline solutions. The primary product, a birnessite type (OL-1) layered manganese oxide, can be transformed by ion-exchange and hydrothermal treatments to the tunnel type cryptomelane (OMS-2) and todorokite (OMS-1). Finally, the synthesized fine materials were supported on silica gel, which was further polymerized, dried and sieved in order to have the desired particle size.

A synthetic $MnSO_4$ solution was used as the manganese source. The oxides were characterized by elemental analysis (ICP-OES, SEM-EDAX), by structural and spectral analysis (XRD, FTIR) and by physico-chemical means (pH and redox titrations). More over thermal analysis as well as particle size and pore volume measurements were done. The synthesized materials were selective to Cu over Ni, Cd and Mg, but the capacity was quite small (c.a 1 meq/g).

Task C. Hydrometallurgical separations in columns

As reference materials, we have used commercially available silica-based chelating adsorbents for the selective removal of impurity metals, notably copper, nickel and cobalt, from concentrated zinc solutions of metals. A dynamic column model has been developed to describe the loading and elution cycles and the model has been published[3].

The silica supported OMS-1 was packed in a 16-mm laboratory column with a bed height of 8 cm. The column feed was a synthetic solution. It was found that the elution of the metals was easy even with diluted (0.05 M) HNO_3 (Fig. 2). The diffusion in silica macro pores was the rate determining step, although it was only half of that inside the OMS crystals. With simplifying assumptions the metal uptake was successively modeled in OMS crystals by NICA (non-ideal competitive adsorption) and Nernst-Planck equations. A scientific article[4] is ready for submission.

Impact of the research project

The research group is in frequent contact with mining companies. This enables us to be aware of the composition of the potential process streams. The opening of the Talvivaara nickel mine in Sotkamo could be an important source of manganese and also for possible application.

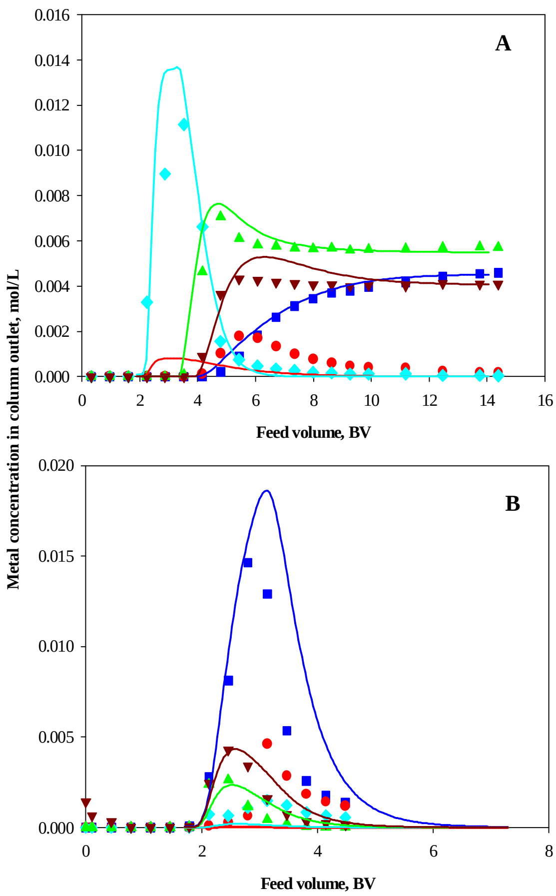

Fig. 2. Metal loading (A) and elution (B) curves with silica supported OMS-1. Feed velocities in loading and eluation were 0.32 and 16 BV/min, respectively, at 25 °C. Symbols: Cu (■), Mn (●), Ni (▲), Mg (◇) and Cd (▼). The lines were calculated with NICA-model..

Progress of the research

The project has proceeded as originally scheduled. However, some reorganization of the topics was found appropriate. More resources were allocated in preparation and characterization of the manganese oxides. Studies on functionalization of TiO_2 and other oxides have been skipped and only an extensive literary survey has been made. Based on a preliminary study on ZrO_2 as a support, it was also omitted from the plan due to its price and stability.

Publications

1. R. Koivula, J. Pakarinen, M. Sivenius, K. Sirola, R. Harjula, E. Paatero, Use of mining effluent as a precursor for the synthesis of Cryptomelane-type manganese dioxide ion exchange material, Submitted to *Hydrometallurgy*, 2008
2. K. Sirola and M. Laatikainen, *Preparation of silica-supported porous manganese oxide*, Research report, LUT, 2008, 25 pages.
3. K. Sirola, M. Laatikainen, M. Lahtinen and E. Paatero, Separation of Copper and Nickel from Concentrated $ZnSO_4$ Solutions with Silica-Supported Chelating Adsorbents, *Sep. Purif. Technol.*, **64**(1), (2008), 88-100.
4. J. Pakarinen, M.Laatikainen, K. Sirola E. Paatero, R. Koivula and R. Harjula, Behavior of Silica-Supported OMS Manganese Oxides in Hydrometallurgical Separations, manuscript ready for submission.