

Exploring the Anion-Exchange Potential of Cationic Layered Material BING-5

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*S.U.R.F. Program, 2006
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Abstract. *Using the compound BING-5 (molecular formula $Pb_3F_5NO_3$) that was originally synthesized in 2001 by Dat T. Tran et al¹, exchange of the permanganate anion in aqueous medium was investigated. It is presumed that this anion may serve as a model for the pertechnetate anion, which is a radioactive groundwater pollutant. The NO_3^- anion within the BING-5 lattice was successfully exchanged for the permanganate anion dissolved in water. Powder X-Ray Diffraction, UV-visible spectroscopy, Thermogravimetric and Mass Spectroscopy analysis were used and/or will be used for characterization of resulting exchange material and determination of the extent to which the exchange occurred and how the BING-5 structure was altered in the process.*

Introduction.

Natural and synthetic materials with the capacity to filter unwanted cations from water have been long known and utilized for water treatment. The basic requirement for water softening techniques and other methods of cation removal is an anionic substrate or resin with exchangeable cations that are electrostatically attached within the structure. While anionic substrates are abundant and inexpensive to produce, cationic substrates are currently much more difficult to synthesize, and very often not incorporated into water treatment processes.

Some examples of cationic substrates include cationic organic resins and LDHs, or layered double hydroxides. In addition to these, there is one, more recently synthesized cationic layered material known as BING-5. The formula for BING-5 is $Pb_3F_5NO_3$, making it an

inorganic substrate with completely different constituents than the LDHs, which usually contain oxygen atoms in place of the fluoride and often contain two metals.¹ A schematic of BING-5 is represented in Figure 1. The structure of BING-5 contains a rigid cationic lattice formed by lead and fluoride atoms. Nitrate molecules are present within the interlamellar spaces, and serve to quench the positive charge of the lattice. These nitrate molecules are shown here to be exchangeable for other anions, specifically the permanganate anion. BING-5 is stable in water and can sustain temperatures up to 450°C, as well as a pH range between 4 and 10.

Although anion exchange is used less frequently in water treatment than

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¹ Tran, D. T.; Zavalij, P. Y.; Oliver, S. R. J. J. Am. Chem. Soc. 2002, 124, 3966-3969.

cation exchange, there are many anionic water pollutants that pose potential environmental problems and public health risks. One such example is the oxidized form of the element technetium, or pertechnetate.² All of the isotopes of technetium are radioactive and, therefore, it is rare in nature. It is, however, a significant by-product of nuclear industry.³ The standard disposal procedure for technetium is to bury it in solid form, unfortunately, leaching of the material means that technetium is a continued threat to water systems. For this reason, an effective, cost-efficient method of removing pertechnetate and other potentially hazardous anions from water would be advantageous to society.

The research presented here was conducted in effort to develop an effective way of managing technetium waste and keeping it out of the water supply, where it might do the most damage. Since direct experimentation on pertechnetate is difficult and potentially hazardous, the permanganate anion was used as a model, where manganese is above technetium on the periodic table and expected to behave similarly. Using BING-5 as an anion exchange substrate, and the permanganate anion as a model for pertechnetate, several exchanges were performed. The resilience of BING-5's crystallinity, and its overall capacity to exchange its nitrate template

for permanganate were of particular interest. Analysis is ongoing.

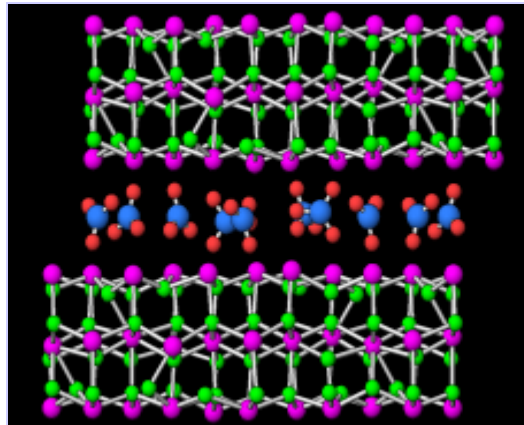


Figure 1: A crystallographic image of BING-5. Lattice has neutral, center layer PbF_4 and two positive layers $[\text{PbF}_3]^+$ on either side. Nitrate ions occupy interlamellar spaces.

Experimental.

Synthesis of BING-5.

BING-5 was synthesized by mixing lead II fluoride, nitric acid, and deionized water. Chemicals were stirred and placed in metal autoclaves with 15mL capacity Teflon interior. Autoclaves were kept in a 150°C oven for approximately 3 days to yield transparent crystals of varying size. After filtration of the crystals, any unreacted lead II fluoride was removed and recycled for future use in BING-5 synthesis.

MnO4 Exchange.

All exchanges were performed with previously synthesized and finely powdered BING-5. Potassium permanganate was purchased from Fisher Scientific and dissolved in deionized water before being measured into beakers and combined with BING-5. Exchange reactions were carried out

² Bi-Functional Resin for Removal of contaminants from groundwater. Prepared for U.S. Department of Energy. DOE/EM-0634. September 2002.

<http://apps.em.doe.gov/ost/pubs/itsrs/itsr255.pdf#search=%22pertechnetate%20groundwater%22>

³ U.S. Environmental Protection Agency. Radiation Information, Technetium-99. <http://www.epa.gov/radiation/radionuclides/technetium.htm#pagecontents>

in Nalgene beakers and were continuously stirred by stir bar. In each trial, the ratio of reactants was 1:1.5:200 for BING-5, potassium permanganate, and deionized water respectively.

Results.

Characterization of BING-5:

The characterization of BING-5's structure has already been discussed in detail in the original synthesis paper referenced above. Thermogravimetric analysis and some powder x-ray diffraction was done on the material used in the experiments here and compared to the data from the original paper in order to confirm the success of the synthesis.

MnO₄ Exchange.

Exchange samples were diluted with a 1:100 ratio of sample to deionized water before analysis with an HP UV-Visible Spectrophotometer 8452 (c. Hewlet Packard 95-98). Spectra were produced with HP UV-Visible ChemStation Software. The spectrum of the stock solution matched the expected potassium permanganate spectrum recorded in the literature.⁴ A pure permanganate spectrum was reproduced in the lab and can be found in Figure #2 along with the complete spectra of each exchange solution. Since a successful exchange would mean both leftover permanganate and nitrate ions in solution, the absorbance spectrum of pure nitrate must be considered when analyzing the spectra of exchange solutions. According to the literature, the nitrate

anion exhibits one peak in the UV-visible range at approximately 300nm⁵, which partially overlaps with the permanganate spectrum.

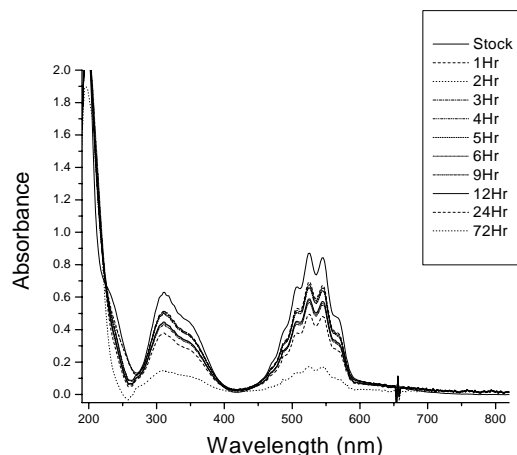


Figure 2: UV-visible spectra of permanganate stock solution and all exchange solutions obtained to date.

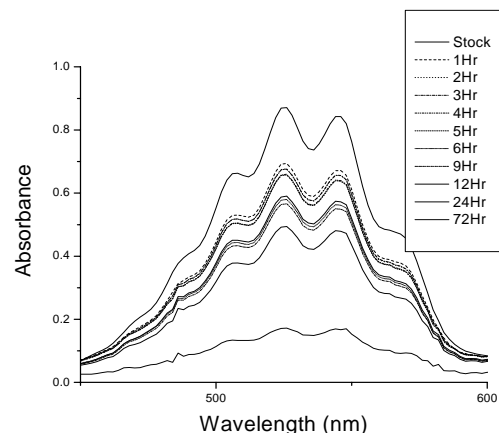


Figure 3: UV-visible spectra, zoomed in between 550nm and 600nm.

⁴ Insausti, M. J.; Mata-Perez, F.; Alvarez-Macho, M. P. *Collect. Czech. Chem. Commun.* (Vol. 59) (1994)
<http://cccc.uochb.cas.cz/Pdf/59/No03/19940528.pdf>

⁵ Skoog, D. A. *Principles of Instrumental Analysis*. Third Edition, c. 1985. Saunders College Publishing. pp. 189.

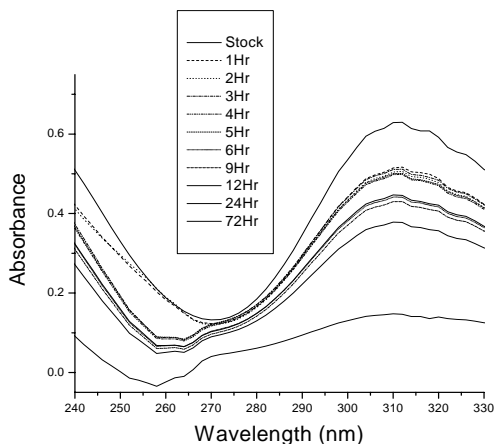


Figure 4: UV-Visible spectra; zoomed in between 240nm and 330nm.

Thermogravimetric analysis (TGA) was conducted. The data obtained using a TA Instruments TGA 2050 Thermogravimetric Analyzer. This instrument was connected to a Pfeiffer Vacuum ThermoStar Mass Spectrometer in conjunction with a ThermoStar Thermal Analysis unit. Approximately 5mg of solid sample was used for each run. Samples were heated from $\sim 25^{\circ}\text{C}$ to nearly 600°C at a ramp of 10°C per minute. Difficulties were encountered in regulating the flow of nitrogen. Samples should be rerun to confirm accuracy. It is for this reason that no TGA data is presented at this time.

Further characterization of exchange material is to be carried out in the fall of 2006 by powder X-ray diffraction. Unfortunately, analysis was delayed due to difficulties with equipment. Samples will be analyzed on a new diffraction instrument in October 2006.

Discussion.

According to the data obtained through UV-visible spectroscopy, the concentration of the permanganate ion in solution is decreasing as a function of

the duration of the exchange with BING-5. Figure #3 is an image of the sample spectra around 500nm and shows a clear decrease in permanganate absorbance. This wavelength range was chosen because there should be no interference from nitrate. Presumably, the reduction of the permanganate is observed because the anion is being incorporated into the structure of the solid BING-5 material and thereby replacing nitrate. In looking at the spectra around 300nm (Figure #4), it is more difficult to see the increase in nitrate concentrations. It does appear, however, that the spectra of the sample solutions are different than that of the stock solution between 250nm and 280nm. It is feasible that this difference denotes the presence of nitrate in solution, since the nitrate peak has a reasonably broad base.

Unlike the UV-visible analysis, the data collected by TGA did not appear to have a straightforward trend. Until powder data can be collected, it is difficult to speculate what kind of structural changes are taking place within the BING-5 structure during exchange. These structural alterations are presumed to be the cause of the distinct exchange pattern that can be seen in the UV-visible data. Analysis by mass spectroscopy is still being processed.

Future Experimentation.

In addition to performing more exchanges of different durations, and repeating exchanges already conducted, there are many other avenues of experimentation to determine if BING-5 could effectively remove the pertechnetate anion from water. Future investigations will use other anions that may serve as reasonable models for pertechnetate, such as perrhenate and

other large, single-charged anions. Tests should also be done to determine the ability of BING-5 to perform the exchange when only trace concentrations of the anion are present. Current tests have used a high anion concentration, whereas the pertechnetate anion is only present in the environment in small amounts.

Acknowledgements.

The research presented here was supported by the National Science Foundation and the Summer Undergraduate Research Program at the University of California in Santa Cruz. Thanks to the program director, Dr. Phil Crews, and all others who organized or participated in this year's program. Special thanks to Dr. Scott Oliver and the entire Oliver lab group, particularly graduate student Claudia Swanson.