Removing metals from aqueous waste streams with hydroxyfullerene

Included are a variety of main group and transition metals.

FULLERENE, WHICH IS ALSO KNOWN AS A BUCKYBALL, exhibits a hollow sphere cage structure similar to a soccer ball that contains 60-carbon atoms. This compound is prepared by vaporization of graphite and is remarkably stable.

Initial work with hydroxyfullerenes is very promising because it shows great affinity for zinc, which is a difficult metal to waste treat.

Since fullerene was discovered in 1985, this compound has been evaluated for use in such applications as solar cells and hydrogen gas storage. One area where other carbon-based materials such as graphene oxide have been evaluated is in removal of heavy metals from water through adsorption.

This application is very important because water is a precious resource and removal of metals from effluent streams generated in manufacturing plants is mandatory. In a previous TLT article, a new compound known as copper hydroxide ethanedisulfonate was found to have promise in removing anions from water though ion exchange.[1] Among the anions removed were dicarboxylates and metal oxo anions such as permanganate.

Andrew R. Barron, the Charles W. Duncan Jr.-Welch Chair of Chemistry and professor of materials science and nanoengineering at Rice University in Houston, indicates that past research has focused on looking for compounds that extract specific precious metals. He says, "There have been lots of studies on nanomaterials to evaluate their ability to extract specific precious metals. One material that has shown promise is graphene oxide, which has been found in the literature to remove transition metals, lanthanides and actinides from water."

None of these nanomaterials have the ability to extract all of the metals that may be present in a specific effluent stream. Barron says, "Based on the work conducted with carbon nanomaterials, we decided to look at hydroxyfullerenes. Our initial work showed that hydroxyfullerenes chelate ferric ions (Fe^{3+}) to form a water insoluble complex."

The other attractive reason for working with hydroxyfullerenes is that they function in a similar manner to the phenolic derivative, catechol in forming cross-linked complexes with metals. A catechol derivative known as 3,4-dihydroxyphenylalanine is used by marine mussel proteins to chelate metals. Barron says, "Hydroxyfullerenes are a larger version of the phenolic ligands seen in biological systems."

Hydroxylation of fullerene takes place through reaction with sodium hydroxide in the presence of tetrabutylammonium hydroxide. Barron says, "Depending upon the reaction conditions, over 20 hydroxyl groups can be placed on a single fullerene molecule. Some of the groups are alkoxides that are neutralized with sodium cations."

A recently completed study has now shown that hydroxyfullerenes can extract

KEY CONCEPTS

- Hydroxyfullerenes, a derivative of the 60-carbon atom buckyball structure known as fullerene, exhibit promise in removing metals from aqueous waste streams.
- A wide range of metals can be extracted, but the ones preferred are +2 charge cations with small atomic radii and +3 charge cations with large atomic radii.
- The reason for this preference is that hydroxyfullerenes are mixtures of different molecules with hydroxyl groups placed in multiple orientations.

 The Apollo 11 spacecraft consisted of the command module, Columbia, and the lunar module, Eagle.

a variety of main group and transition metals from an aqueous environment.

NANOAGGREGATES

Barron and his associates evaluated the ability of hydroxyfullerenes to cross-link a series of metal salts. The process used is to mix solutions of the metal salts and the hydroxyfullerenes at room temperature, observe the formation of a precipitate, isolate the solid and then analyze the metal ligand through the use of ultraviolet-visible spectroscopy.

Experiments were done using individual salts and then comparing a specific metal salt with ferric nitrate in a series of competitive cross-linking reactions. The researchers evaluated salts of aluminum, cadmium, calcium, cobalt, copper, manganese, nickel, silver and zinc.

Barron says, "We found that hydroxyfullerenes prefer to bind with +2 charge cations that have small atomic radii and with +3 charge cations that have large atomic radii. For our experiments, hydroxyfullerenes have the most affinity for zinc of the +2 charge cations followed by cobalt, manganese, nickel, cadmium and copper. The +3 charge cation that has most affinity to hydroxyfullerenes is lanthanide followed by iron and aluminum."

The reason for this effect was at first puzzling for Barron and his colleagues because they did a computational study assuming that the hydroxyfullerenes doing the binding mainly had diols adjacent to each other in the 1,2 position. He says, "We initially did *ab initio* calculations on catechols and found that binding is based on size as expected and not on charge. For hydroxyfullerenes, the computational studies were not consistent with the empirical results."

The reason for the discrepancy is that hydroxyl groups attached to the fullerene cage are not only in the 1,2 orientation but also in the 1,3 and 1,3,5 orientations. Barron says, "Fullerene is functioning as a mixture of different molecules and this explains the binding behavior for +2 and +3 charged cations."

Transmission electron microscope images of the cross-linked hydroxyfullerene metal samples show nanoaggregates that contain a series of metals and fullerenes. Barron says, "In dilute solutions, we found that these nanoaggregates are dozens of nanometers long because chains initially made from one hydroxyfullerene molecule tend to aggregate to other chains. The aggregates can contain as many as 20-30 hydroxyfullerene molecules."

Figure 2 shows an image of a nanoaggregate formed from the cross-linking of hydroxyfullerenes with nickel and iron salts. The choice of the anion appears to have no effect on the ability of the hydroxyfullerene to bind to the metal. Barron says, "We tried a series of anions that included acetates, carbonates, citrates, nitrates and sulfates. None of these anions impacted the cross-linking process."

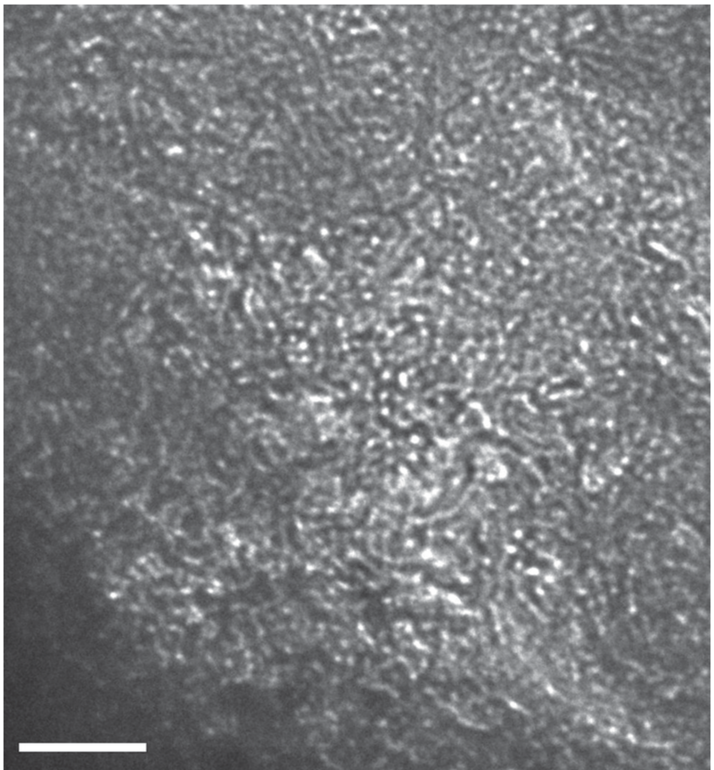

Figure 2 | **Nanoaggregates formed from the cross-linking of hydroxyfullerenes with metals (the example shown is with iron and nickel) explain how this fullerene derivative is effective in extracting metals from aqueous streams.** *(Figure courtesy of Rice University.)*

Future work will involve trying to boost the metal: hydroxyfullerene ration used and to work with carbon nanotubes. Barron says, "Our objective is to determine if carbon nanotubes bound to a membrane filter can act as tentacles to bind metals in the effluent stream."

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REFERENCES

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2. Heimann, J., Morrow, L., Anderson, R. and Barron, A. (2015), "Understanding the relative binding ability of hydroxyfullerene to divalent and trivalent metals," *Dalton Transactions*, **44**, pp. 4380-4388.

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