



Written and Published by

Jennifer, Washington DC

Grade 8

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Electrowinning: New Technology for Removing Heavy Metals from Wastewater

Metals are found naturally in the environment. They are present in animals, plants, soil, and rocks. Metals can be present in the environment as ions dissolved in water, vapors, or salts or minerals in rock, sand, and soil. They also can be found bounded in organic or inorganic molecules, or attached to particles in the air.

While metals have many beneficial effects, they also can be harmful in excessive doses or through repeated exposure. Health risks associated with a specific set of metals, known as heavy metals, are one of the major health and environmental concerns worldwide.

Once metals enter the environment, they remain for hundreds of years. So the best thing to do is to try to keep excessive, harmful quantities metals out of the environment. My science project researches the effects of heavy metals on the health of living things. My experiments test a new technology—electrowinning—that has the potential to capture raw metals from wastewater. This will allow companies to recycle or sell the raw metals, and will keep the metals out of streams and groundwater and reduce the amount of toxic materials put in landfills.

Heavy Metals

Scientists have identified fourteen metals and metalloids, each with a high molecular weight, which they include in this list of heavy metals:

Arsenic (As)	Copper (Cu)	Silver (Ag)
Antimony (Sb)	Indium (In)	Thallium (Tl)
Bismuth (Bi)	Lead (Pb)	Tin (Sn)
Cadmium (Cd)	Mercury (Hg)	Zinc (Zn)
Chromium (Cr)	Selenium (Se)	

These heavy metals are relatively abundant in the Earth's crust, are frequently used in industrial processes or agriculture, are emitted in places where the public comes in contact with them, are toxic to humans, and can make significant alterations to the biochemical cycles of living things.

Heavy metals occur naturally in several different chemical forms. For example, mercury can be present as liquid elemental mercury ($\text{Hg}_{(l)}$), vapor elemental mercury ($\text{Hg}_{(g)}$), monomethyl-mercury (HgCH_3), dimethyl-mercury ($\text{Hg}(\text{CH}_3)_2$), or mercury chloride (HgCl_2). These forms are called species. The species of heavy metals are determined by the solubility of the compounds, the environmental conditions, and the availability of complexing agents.

The absorption rate of the material and its effect on the biochemical process also determine the toxicity of heavy metals. Metals that can enter the biological membranes that protect the brain or blood cells are the most dangerous. For example, liquid mercury is not very toxic, but vapors of mercury are very dangerous because they can be inhaled and enter the bloodstream.

Heavy metals also can bond easily with the sulfhydryl (sulfur-hydrogen-related) group of enzymes. These are the enzymes that control the speed of metabolic reactions

in living things. This is another reason why heavy metals are harmful to plants, animals, and humans.

A third reason why heavy metals are toxic is because of bioaccumulation. Heavy metals tend to accumulate in living things. This means that as you move up the food chain the concentration of heavy metals increases. For example, in mid-March, health experts in Maryland issued a warning to residents not to eat fish caught in a Baltimore reservoir more than four times a month. The fish are contaminated with mercury, which they have absorbed from the water. Scientists estimate that the amount of mercury in the reservoir, if added together, would be approximately the size of a quarter. Scientists fear that people who eat many fish from the reservoir will build up a highly toxic amount of mercury in their systems.

Pollution Sources

There are two categories of sources of heavy metals emissions into the environment: natural and anthropogenic.

The natural sources of heavy metal emission are the erosion and alteration of rocks. This makes heavy metals available to plants and animals in soil and water. The concentration of heavy metals in a rock depends on the rock. Rocks that contain metallic ores have much higher concentrations than rocks that do not. They can easily be dissolved by rain or surface waters, because their metal ore deposits are made up of oxides and sulphurous minerals, which react easily with water. Because of this, they can contaminate underground and surface waters.

Anthropogenic sources are not natural. Instead, they are sources of pollution from industry and other processes. The two types of emissions are diffuse sources and stationary sources.

Diffuse sources are most common in urban areas. The concentration of heavy metals in street dust is very high due to the heavy traffic in highly populated, urban areas. The usual inner city amount of lead in street dust is estimated to be 1,000-10,000 mg/kg; in rural areas the amount of lead in street dust is between 300 and 500 mg/kg. The main heavy metals in urban street dust are lead, from automobile emissions, and cadmium, from the rubber used to make tires.

Most of the stationary sources of heavy metal pollutants are industrial. Industries, such as mining, metal processing, and those that burn fossil fuels let out heavy metals into wastewater or the air. The heavy metals are then transported by wind or runoff water, and contaminate air and water sources miles from the industrial site. Other industry categories that are monitored by the Environmental Protection Agency (EPA) for heavy metals pollutants include: the rubber and miscellaneous plastic products industry (zinc and lead compounds); the metal casting industry (copper, zinc, and lead, copper, and chromium compounds); the lumber and wood products industry (chromium, copper, and arsenic); the iron and steel industry (lead, chromium, copper, zinc, and their related compounds); the electronics and computers industry (lead, chromium, copper, and zinc compounds, and copper); the fabricated metals industry (lead, chromium, copper, zinc, and their related compounds); and the nonferrous

metals industry (lead, chromium, copper, zinc, arsenic, cadmium, and all their related compounds).

Heavy metals in consumer goods and industrial processes also enter the environment when we burn or dump wastes. Because these heavy metals are elements, they do not degrade. They can only change their form.

The production of heavy metals, especially lead, zinc, and copper, has increased ten times since the Industrial Revolution. As the health and environmental impact of heavy metals becomes more known, the use of these elements is being controlled. For example, lead pipes are no longer used for plumbing, and arsenic is no longer used to control insects in apple orchards. Recently, the lumber industry also agreed to stop using arsenic to treat lumber that will be used inside homes and buildings. The list of heavy metals also may expand as technology begins to use new metals. For example, the level of platinum pollutants has increased because the metal is a component in catalytic converters required on all vehicles.

Health Effects

Many of the heavy metals are "essential metals" and are necessary for good health. Chromium, cobalt, copper, iron, manganese, selenium, tin, and zinc are needed by the body to create and build enzymes and proteins. They become toxic when the amount in the body is excessive. This is known as the threshold of toxicity. The threshold of toxicity depends on the metallic element, the type of organism, the individual, and environmental factors.

There are two types of intoxication: acute intoxication, which is caused by a short-time exposure to a large amount of toxic material and causes rapid and intense effects; and chronic intoxication. Chronic intoxication occurs when a person is exposed to a smaller amount of toxic material over a longer period.

Humans are exposed to heavy metals through the inhalation of air pollutants, consumption of contaminated drinking water, exposure to contaminated soils or industrial waste, or the consumption of contaminated food. Fish, vegetables, and other animals that we commonly eat can become contaminated when they eat or absorb heavy metals in the water or in the soil.

The ingestion of heavy metals through food and water is the most common way that people are exposed to heavy metals, with inhaling and absorbing heavy metals through the skin other common ways that metals enter the body. Many Japanese women became sick in the 1950s when they ate rice that was poisoned with cadmium. The women suffered kidney and skeletal damage from what they called Itai-itai disease.

Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and sometimes even death. Exposure to some metals, such as mercury and lead, can also cause the development of autoimmunity. Autoimmunity is when a person's immune system attacks its own cells. This can later lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system.

Infants and young children exposed to heavy metals when they are young can have learning difficulties, memory impairment, damage to the nervous system, and

behavioral problems, including aggressiveness and hyperactivity. Sometimes metals can even cause brain damage. Children are more likely to be exposed to higher doses of heavy metals than adults because the amount of food they eat for their body weight is greater than adults. They also absorb metals more readily through their intestinal tract than adults.

Electrowinning Technology

Electrowinning is a new technology that industry is using to try to recapture some heavy metals from industrial wastewater.

The Environmental Protection Agency (EPA), which monitors the industrial discharge and emissions of more than 600 pollutants, including all 14 of the heavy metals, also requires industry to treat its wastewater and attempt to recover and recycle as many products as possible. Because heavy metals have value, industry has been trying to find a way to capture these metals instead of just disposing of them.

In the past, many industries have shipped their wastewater off to decontamination plants for treatment. The water is evaporated and the acid and other chemicals are neutralized. This creates a sludge-like material. Using various chemical processes, metals in different forms are captured, and the rest of the sludge has been placed into secure containers and disposed of as hazardous waste. The chemical treatment process is expensive and the metals that have been recaptured usually can be reused only in limited ways because they are not pure.

Electrowinning is different from most other water treatment processes because elemental metal is recovered during the process. Some scientists describe electrowinning as a process for mining wastewater because it produces the raw metal, which can be sent to scrap dealers and reused just like the raw metal mined from the ground.

The heavy metals that can be removed from plating wastes are copper, cyanide, cadmium, zinc, brass, tin-head, silver, and nickel. The easiest metals to capture are gold, silver, copper, cadmium, and zinc.

Electrowinning's main objective is to recover metals from concentrated sources such as ion exchange regenerate acid solutions, highly concentrated rinse waters, or spent plating solutions. The factors that determine how much metal is recovered include the:

- Size of the cathode area
- Amount of electrical current applied
- Species of metal being recovered

Electroplating Principals

Electrowinning is based on the principals of electroplating. During the electroplating process an electrical current is completed within a container filled with a liquid solution. This is done by attaching the cathode, which is the metal piece to be plated, to the negative side of the battery, giving it a negative charge. The metal plate called the anode then is attached to the positive side of the battery, giving it a positive charge. The positively charged anode excites the particles to move through the solution to the negatively charged cathode. Through electro-magnetism, the particles are bonded to the cathode, creating a plate of new material over the surface of the cathode.

The process was discovered by Michael Faraday, a British scientist, in the mid-1800s. From his experiments, Faraday proposed that electricity was a force that could be passed from one particle of matter to another. Based on this, he introduced a theory that electricity could be used to create chemical reactions. Faraday's Laws of Electrolysis, explain that the amount of electricity applied is extremely important because it determines two things, the:

- Elements that will combine, which determines the metal to be used for the cathode
- Metals that will be captured during the electrowinning process because the amount of electricity is directly proportional to the metal's atomic mass

This is important because wastewater can contain many heavy metals. To collect these different metals, the wastewater is run through different tanks with anodes and cathodes charged with different electrical currents. In each tank, a different metal is collected because a low electrical current will attract metals with low atomic masses, and high electrical currents attract metals with high atomic masses.

A simple electrowinning chamber includes metal-bearing wastewater or a spent plating bath solution, or another solution from an industrial process. The chamber has alternating anode and cathode contacts that have an electrical charge. The solution passes through the chamber at a rate that is slow enough to allow the metals in the solution to become attracted to and deposited onto the cathode contacts.

Schematic of the electrowinning system; <http://www.micromagazine.com/archive/99/09/maeda.html>

The arrangement of the anodes and cathodes within the solution create an electro-chemical cell in the tank, helping to keep the level of electricity in proportion to the metal being captured or plated and the cathode. Sulfuric acid often is used to increase the conductivity of the solution.

Just like electroplating, electrowinning depends on three things:

1. Movement of the particles inside the solution
2. Attraction to the negatively charged cathode
3. Bonding by the metal to the cathode through an electro-chemical reaction

Experiments

To conduct my experiments, I used a Plug N' Plate kit for copper and nickel from Caswell Plating. The kit included the following materials:

- Power source: power pack 4.5v DC @ 300ma
- Wands: copper for copper plating and stainless steel for nickel plating
- 8 ounces of solution: copper for the copper plating and nickel for nickel plating
- Four strips of gauze, approximately 1.5 inches wide by 10 inches long

I added a number of pieces of stainless steel and copper that were used for the cathodes and sometimes for the anodes.

Methodology

Wearing rubber gloves and safety glasses, I followed the set-up below:

1. I poured 4 ounces of each solution into a clean plastic container and set it aside. This solution was not used in the brush plating (#1) or dip plating (#2) experiments.
2. I prepared each of the anodes by wrapping them each with two of the gauze strips, so that the metal did not show, and secured the gauze with rubber bands.
3. At the beginning of each experiment, I soaked the anode in the 4 ounces of the appropriate solution so that the gauze was saturated.

Experiment #1: Brush Plating

Brush plating is a technique that allows you to plate a small area on a piece of metal without immersing it in a tank. To brush plate, I gently brushed the cathode with the gauze-covered anode, dipping the anode in the solution when it began to dry out.

I used the brush plating to see how it worked and also as part of the electrowinning experiment to see if additional metal was deposited into the solution during the brush plating process.

Hypothesis: There is a relationship between temperature and the effectiveness of the plating process.

Setup #1: Plate two-square inches of the stainless steel cathode with nickel; copper will not adhere to stainless steel directly.
Plate one square-inch area with copper with solution at room temperature.
Plate one square-inch area with copper with solution heated in microwave for 45 seconds.

Setup #2: Plate one square-inch area with nickel with solution at room temperature.
Plate one square-inch area with nickel with solution heated in microwave for 45 seconds.

Record: Observations about quality of plating after 5 minutes.

A minute amount of copper was plated on an area 2x2 inches and 2 x 1/5 inches. Only a slight copper sheen can be seen.

A thin layer of nickel, enough to turn the copper cathode silver, was plated on the following surfaces: 2 x 2 inches and 2 x 1.5 inches (providing a layer on which to plate the copper); 1x1.5 inches and 1x1.125 inches.

Observations:

It is easier to plate with the heated solution than when the solution is at room temperature. The nickel plated to the copper cathode easily. At both room temperature and heated, I had a hard time plating the copper to the nickel-plated surface on the stainless steel cathode. There was not enough copper plated to measure at either temperature.

Conclusion: My conclusion is that when the solution is heated, both the copper and nickel plate easier and faster than when the solution is at room temperature. I think the reason for this is that the particles in the solution are already moving because it is heated, so they move faster and have a greater attraction when the electricity is on.

Experiment #2: Dip Plating

To dip plate something, you put both the anode and the cathode in the solution. I used dip plating to see how it worked, to compare results with brush plating, and to see if it left metals in the solution.

Hypothesis: The distance between the anode and cathode affects the quality and quantity of the plating.

Setup #1: Plate nickel to copper with the anode and cathode far apart.
Plate nickel to copper with the anode and cathode close together.

Setup #2: Plate copper to stainless steel with anode and cathode far apart.
Plate copper to stainless steel with anode and cathode close together.

Record: Observations about the quality and quantity of the plating after 5 minutes.

Copper plated on the front and back of stainless steel cathodes approximately 1x1.25 inches and .875x1.5 inches. The copper sheen was smoothest at the bottom and darker and blacker higher up.

Nickel plated to the front and back of copper cathodes approximately 1.5x.875 inches and 1.125 x 1.5 inches. The nickel sheen was smoothest

at the bottom, though the nickel covered smoothly and uniformly as higher up as well.

Observations:

When I plated the nickel to the copper with the anode and the cathode close together, I felt a strong attraction between the anode and the cathode, and about halfway through the experiment, I noticed that I could see nickel floating through the liquid and attaching itself to the copper. This plated very nicely and thoroughly, with the best adhesion at the bottom of the cathode, even though the anode and the cathode did not touch the bottom. The back of the cathode also plated cleanly.

When I plated the nickel to the copper with the anode and cathode far apart, I did not feel as strong an attraction and I could see very little nickel solution floating to the copper cathode. The cathode did not plate as thoroughly as when it was close to the anode.

When I plated the copper to the stainless with the anode and cathode close together, the copper plating was not as clean. It had dark marks through it. The back also didn't plate well. Like the nickel to copper experiment, the plating was best at the bottom of the cathode.

When I plated the copper to the stainless steel with the anode and cathode far apart, the plating was not as clean and did not plate as thoroughly as when the anode and cathode were close together. The best plating was at the bottom of the cathode.

Conclusion: My conclusion is that the solution plates better if the anode and the cathode are positioned close together, rather than far away. I think this helps strengthen the attraction of the particles to the cathode. I also think it shows that the current is the strongest at the bottom, because the bottom on all the cathodes plated better than the top.

Experiment #3: Electrowinning

In this experiment I wanted to see two things:

- Will electrowinning really pull raw metal from the solution?
- Did the brush plating and dip plating experiments increase the amount of metal in the solutions?

Both copper and nickel can be recovered using electrowinning, but copper is supposed to be easier than nickel. Nickel solutions have a higher acid content, so the pH level must be controlled. I did not have a way to do this, so I performed the electrowinning experiment the same way for both metals.

Hypothesis: Using electrowinning, trace copper can be removed from the copper solution and nickel from the nickel solution, which is substituted for "wastewater."

Setup #1: Place stainless steel anode and stainless steel cathode in "used" copper solution, used to brush plate and dip plate in experiments #1 and #2.

Place stainless steel anode and stainless steel cathode in "unused" copper solution, which was set aside in the beginning.
Leave each setup in the solution for 6.5 hours.

Setup #2: Place stainless steel anode and stainless steel cathode in "used" nickel solution, used to brush plate and dip plate in experiments #1 and #2. (Within an hour, the stainless steel anode had been "eaten" so it was replaced with a copper anode. I also replaced the stainless steel cathode with a copper cathode, because the original one didn't seem to be collecting any metal. See observations for what happened.)

Place stainless steel anode and copper cathode in "unused" nickel solution, which was set aside in the beginning.
Leave each setup in the solution for 6.5 hours.

Record: The quantity of raw metal recovered from each solution by noting the weight of the cathode before and after the experiment. Also note the weight before and after of the anode to see if it was affected by the process.

Used Copper Solution			
	Before Electrowinning	After Electrowinning	Difference
Anode (stainless steel)	4.0 g	3.2 g	- 0.8 g
Cathode (stainless steel)	3.4 g	7.5 g	+ 4.1 g

Unused Copper Solution			
	Before Electrowinning	After Electrowinning	Difference
Anode (stainless steel)	5.0 g	3.2 g	- 1.8 g
Cathode (stainless steel)	4.9 g	9.9 g	+ 5.0 g

Used Nickel Solution			
	Before Electrowinning	After Electrowinning	Difference
Anode (stainless steel)	5.5 g	4.4 g	- 1.0 g
Cathode (stainless steel)	4.6 g	6.2 g	+ 1.6 g

Used Nickel Solution			
	Before Electrowinning	After Electrowinning	Difference
Anode (copper)	3.2 g	0.0 g	- 3.2 g
Cathode (copper)	4.4 g	8.5 g	+ 4.1 g

Unused Nickel Solution			
	Before Electrowinning	After Electrowinning	Difference
Anode (stainless steel)	6.2 g	0.0 g	- 6.2 g
Cathode (copper)	6.5 g	13.7 g	+ 7.2 g

Observations:

Used Copper: Before the experiment, the copper solution was a light blue color. Half an hour into the experiment, the liquid changed from its original light blue color to a dark green color. Immediately after I put in the cathode and the anode, copper began to collect on the cathode. It did not fizz and it did not foam. The cathode and anode were left in for 6 ½ hours. The anode looked like it had been very finely sandpapered and then polished. The anode weighed slightly less than it did before the experiment.

Unused Copper: Before the experiment, the copper solution was a light blue color. Half an hour into the experiment, the liquid changed from its original light blue color to a dark green color. Immediately after I put in the cathode and the anode, copper began to collect on the cathode. It did not fizz and it did not foam. The cathode and anode were left in for 6 ½ hours. The anode looked like it had been very finely sandpapered and then polished. The anode weighed slightly less than it did before the experiment.

Used Nickel: In this experiment, I used two pieces of stainless steel. The solution fizzed around the anode. The solution did not fizz around the cathode. The fizzing was hydrogen gas created by a chemical reaction between the acid in the solution and the stainless steel anode accelerated by the positive charge in the anode. The cathode and the anode were left in the used nickel solution for 1 ½ hours, then taken out because it was eating the anode. When the cathode came out of the solution, it looked like it had been thinly plated with copper with nickel streaks. The anode had been eaten away, and had holes all through it.

Used Nickel: After the stainless steel anode was eaten, I put in a copper anode and a copper cathode. The solution fizzed around the anode. The fizzing was hydrogen gas created by a chemical reaction between the acid in the solution and the copper anode accelerated by the positive charge in the anode. About halfway through the experiment, I noticed that the copper anode was being eaten away and that all of the copper that had been eaten away from it lay in a big pile right under the anode. The cathode, halfway through the experiment, was already heavily covered in a very dark substance that easily broke off if you moved the cathode. The nickel solution turned a very dark green, even darker than it had started out. The copper anode and copper cathode were left in the used nickel solution for 6 ½ hours. When I took the anode out, it had been eaten up halfway. A third of what was left had been covered with a light blue powdery substance. It looks like copper after it has been oxidized. When I took out the cathode, it was covered very thoroughly with a very dark substance that looked

almost like a combination of copper and nickel. After the experiment, the copper that lay on the bottom settled out and some of the copper rose to the surface of the container.

Unused Nickel: For this experiment, I used a stainless steel anode wrapped in gauze, and a copper cathode. Hydrogen gas was still created. I left the anode and the cathode in the solution for 6 ½ hours. When I took out the anode and unwrapped the gauze, there was nothing left of the anode, only a few little shreds of metal. The cathode was thoroughly covered with a dull silvery-like material, that won't flake off like the copper would. It also looks like a piece of the anode got loose from the gauze and attached itself to the cathode.

Conclusion: My experiment proved that electrowinning will pull the raw materials from the solutions. I don't think that the brush plating and dip plating experiments added significant amounts of metal to the solutions.

Conclusion

Electrowinning is a process that has the potential to keep certain heavy metals out of the environment. It also offers industry a way to get rid of certain harmful metals that they otherwise would have to pay to dispose of. For certain metals, they also could earn income through the resale of the raw material.

Resources

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