

## Removal of Copper, Chromium, and Arsenic by Water Hyacinths

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The removal of different concentrations of toxic metals by water hyacinths (*Eichhornia crassipes*) from a simulated aqueous environment was studied in an outdoor experiment. The hyacinth's tissues were analyzed to evaluate the removal of copper (Cu), hexavalent chromium (Cr VI), and arsenic (As) from CCA (Chromated Copper Arsenate) contaminated water (5, 10, and 20 mg/L arsenic content, 7, 14, and 28 mg/L chromium concentration, and 2.5, 5, and 10 mg/L copper concentration) over a 17 day period. The vigor of the plants was also recorded during this period. The results showed that the hyacinth was not a suitable plant to remediate arsenic and copper. Arsenic removal for 5, 10, and 20 mg/L concentrations were 4.8, 4.7, and 0% respectively and copper removal for 2.5, 5, and 10 mg/L showed 53, 0, and 0% respectively. However, water hyacinth did show promising results as a hyper-accumulator of chromium. Percent chromium removal for 7, 14, and 28 mg/L contaminated water was 72.3, 21, and 19% respectively. The amount of copper in the containers with water hyacinths present was higher than the containers without plants (controls) indicating that the water hyacinth exudates might cause copper to stay in aqueous solution longer. As for the vigor of the plants, 5 and 10 mg/L arsenic concentrations damaged the plants somewhat over the 17 day period but overall these plants remained alive for the duration. Plants that were treated with 20 mg/L arsenic began to wilt and change color after day 1 and by the end were lifeless.

**Keywords:** *Treatment, Toxic metals, Water quality*

### Introduction

One of the major problems the public faces is contamination of drinking water. There are many industries that may or have contributed to the contamination of waterways by discharging toxic metals into rivers and streams.

One wood preservative that is used in the Forest Products industry is CCA (Chromated Copper Arsenate). During the spring of 2001, Florida newspapers began to report that arsenic was leaching from playground equipment made of CCA treated wood (Hauserman, 2001). In Dec. 2003, CCA treated wood was voluntarily taken off the residential market by the wood-treating industry.

Of the three metals in CCA, only two are extremely toxic: hexavalent chromium and arsenic. Chromium is a naturally occurring element found in rocks, animals, and plants. It is usually present in several different forms, the most common of which are hexavalent chromium (extremely toxic) and chromium III (nontoxic). Chromium III is essential for breaking down sugar, fat, and protein inside an animal's body, thus making it vital for good health. In contrast, hexavalent chromium can be detrimental to the health of anyone exposed over long periods of time. Inhaling or ingesting hexavalent chromium over time can cause nosebleeds, ulcers, convulsions, kidney and liver damage, various cancers, and/or death (ATSDR online).

Chromium can also contaminate soil, sediment, and groundwater (Mei et al., 2002). It is because of this pollution that scientists seek new methods to clean up waterways that contain chromium. In one study, water-hyacinths (*Eichhornia crassipes*) were used to

accumulate hexavalent chromium from contaminated water. As the plants were put under an x-ray spectroscope, the plants had converted hexavalent chromium to chromium III in the lateral roots of the plant, thus detoxifying the water significantly (Lytle et al., 1998).

Arsenic is the 20th most abundant element found naturally in the Earth's crust. In very small quantities, it plays an essential role in animal metabolism but in large amounts it is damaging due to its carcinogenicity (Pickering et al., 2000). Arsenic is a heavy metal that can cause significant health problems by primarily attacking the immune system (Huang et al., 2004). When arsenic is ingested, it also increases the risk of bladder and prostate cancers. It can also cause other health disorders such as a decrease in hearing ability, skin thickening, and disturbances to the nervous system.

Because of the health risks involved with arsenic contamination in the drinking water in the US, the Environmental Protection Agency (EPA) had set a maximum arsenic contaminant level standard for drinking water at 50 ppb. Due to growing concerns from the general public and government officials the EPA considered dropping the standard to 10 ppb (EPA online, 7/13/04).

Copper, a metal that occurs naturally in rocks, soil, water, and air throughout the environment, is an essential element in plants and animals (including humans). Therefore, plants and animals must absorb some copper from eating, drinking, and breathing (ATSDR online). Although copper is not as toxic as hexavalent chromium or arsenic, it can be potentially serious if high levels are present in drinking water. The most common symptoms of copper toxicity are

injury to red blood cells and lungs, as well as damage to liver and pancreatic functions (OR Online, 3/19/06). Long-term exposure to copper can also cause irritation of the nose, mouth and eyes, as well as headaches, stomachaches, dizziness, vomiting and diarrhea (Lenntech Online, 3/22/06).

At the present time, the most common way to clean water contaminated with heavy metals is a coagulation/filtration method that involves removing pollutants by chemically conditioning particles to agglomerate into larger particles that can be separated and settled, followed by running the contaminated water through various filters that trap the pollutants and hold them for disposal. One of the major problems with this method is the sludge-like by-product that is produced as a result of the settled and trapped contaminants (Huang et al., 2004). Use of these methods for cleanup/disposal of contaminated water is very expensive and disruptive to the habitats that surround the water (Tu and Ma, 2002). Scientists are searching for new and economic ways to alleviate this contamination problem.

One new and promising method that has been drawing interest for many years is called phytoremediation or phytoextraction. Simply put, phytoextraction is the use of plants to remove contaminants from water by pulling the contaminants out of the water through the root system and into the plant body (Huang et al., 2004). This makes disposal easier and much less expensive because properly destroying the plants and the contaminants held within is a relatively simple process. The major contaminants that are removed from water by plants are various carcinogenic metals such as copper, chromium, arsenic, mercury, etc.

One aquatic plant that has been studied is the water-hyacinth (*Eichhornia crassipes*). It is a floater plant with large, glossy leaves and a small blue or yellow flower in the center of its vegetative mat (USGS online, 8/22/03). It is native to the southeastern US and California and one of the most invasive aquatic plant species ever introduced into the US (USGS online, 8/22/03).

The objectives of this study were: 1) to evaluate the removal of arsenic, chromium, and copper by water-hyacinths in water contaminated with different CCA concentrations and 2) to observe the effects of these metals on the health and vigor of the plants.

## Methods and Materials

### Plant Preparation

A mat of water-hyacinths were purchased and placed in a plastic container filled with de-ionized water. The water hyacinth mat was then separated into individual plants.

### Preparation of CCA Solution

A CCA solution consisting of 17% arsenic, 24% chromium, and 9% copper was obtained from the Mississippi State University Forest

Products Laboratory. A stock solution was prepared by adding de-ionized water to the CCA until desired metal concentrations were obtained.

### Project Setup

Twenty-four quart size mason jars were filled with 450 ml of water and 50 ml of Miracle-Grow solution (prepared according to label). After the solution was added, a black line was drawn on the jars so a 500ml water level could be kept constant. Plants were placed into jars three days prior to the application of the different concentrations of stock solution so the plants could establish themselves inside the jars. The jars were then sorted into three treatments with six jars in each treatment and a control group with the last six jars. Each group had three jars with plants and three jars without plants (figure 1).



Figure 1. Photo taken of water-hyacinths in different treatments and their controls.

For group 1 treatments (5 ppm arsenic, 7 ppm chromium, and 2.5 ppm copper), the water-hyacinths were removed temporarily from the jars and 1 ml of the above concentration the stock solution was added to the water/Miracle grow solution in each of the six jars. The solutions were then mixed and the plants were placed back into the jars. For Group 2 (10 ppm arsenic, 14 ppm chromium, and 5 ppm copper) and group 3 (20 ppm arsenic, 28 ppm chromium, and 10 ppm copper) treatments, 2 or 4 ml of stock solution was added to each jar in the same manner. The solutions were mixed and the plants were placed back into the jars. In the fourth group, the water-hyacinths were placed into the three plant jars and no stock solution was added to these six jars (controls). All 24 jars were then placed in an area outdoors and observed for 17 days.

### Project Upkeep

Every 1-2 days, the plants were checked and de-ionized water was added to each jar so the 500 ml water level line remained constant. Pictures were taken also to document the health and vigor of the plants.

### Preparation of Samples for Analysis

The mason jars were assorted into eight groups with three jars representing the respective arsenic concentration. For each of the eight groups, a 30 ml composite sample was generated by placing a 10 ml aliquote from each of the three jars and combining them in glass bottles. The eight composites were logged into the lab notebook and transported to the Mississippi State University Diagnostic Instrumentation & Analysis Laboratory for metal analysis. Also, plant and root tissues were dried, crushed, and digested with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. The digested solution was filtered and then analyzed for As, Cr and Cu by atomic absorption analysis (Sridhar et al., 2002).

### Results

Table 1 shows the levels of arsenic in the water after 17 days of observation. The plants appeared to have little remediatory affect on arsenic contaminated water. The levels of arsenic in the water after analysis remained around the same concentration (5 ppm) as the initial levels at the beginning of the experiment.

The greatest change in concentration occurred with chromium levels in the water samples. The data in Table 2 show that a significant amount of chromium was removed from the water.

Results from copper treatements show a different outcome in the data values in Table 3. In the water samples that contained plants, the copper values were higher than samples that without plant. One explanation could be that exudates on the roots of the plants may have kept copper in suspension.

The health and vigor of the plants were observed over the 17 days of this experiment. At the end, the plants that were treated with 5 mg/L arsenic stock solution were affected by a slight wilting of the stems and a rusty coloration on parts of the leaves (figure 2). The same results occurred at 10 mg/L arsenic treatment, except that there were more rust coloration present on the leaves (figure 3).

Table 1. Arsenic uptake by water-hyacinths during a period of 17 days.

Sample ID	Arsenic	% Removal vs. control
Ctrl. w/ plant	0.056	0
Ctrl. w/o plant	0.03	
5 ppm w/plant	5.4	4.8
5 ppm w/o plant	5.67	
10 ppm w/plant	10.2	4.7
10 ppm w/o plant	10.7	
20 ppm w/plant	20.4	0
20 ppm w/o plant	19.6	

The plants in the 20 mg/L arsenic treatment were near death after the first week as the leaves totally wilted and became completely covered with rust. In group three (20 ppm treatment), two of the three plants were found dead in the first week due to root damage from the higher metal concentrations. After 17 days, these plants were the only plants in the experiment to die (figure 4). Plant injuries could have attributed to much lower chromium uptake for 10 and 20 mg/L treatments.



Figure 2. Photo taken shows the health and vigor of the water-hyacinth at a treatment of 5ppm.

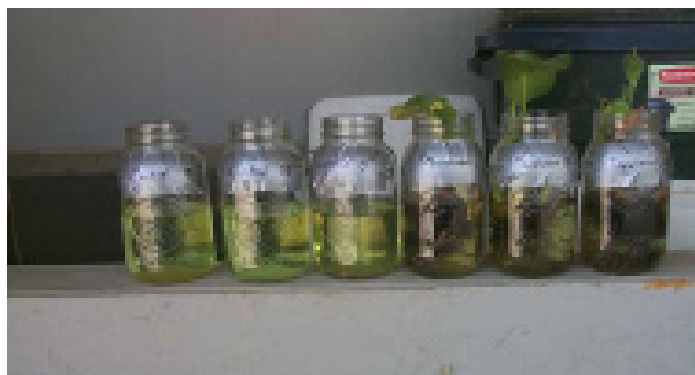


Figure 3. Photo taken shows the health and vigor of the water-hyacinth at a treatment of 10ppm.



Figure 4. This photo shows the health and vigor of the water-hyacinth at a treatment of 20ppm.

Table 2. Chromium uptake by water-hyacinths during a period of 17 days.

Sample ID	Chromium	% Removal vs. control
Ctrl. w/ plant	0.067	0
Ctrl. w/o plant	0.014	
7 ppm w/plant	1.98	72.3
7 ppm w/o plant	7.16	
14 ppm w/plant	10.4	21
14 ppm w/o plant	13.1	
28 ppm w/plant	20.7	19.1
28 ppm w/o plant	25.6	

### Discussion

The results show how arsenic, chromium, and copper are affected by a floater plant like water-hyacinth. Water-hyacinths do not seem to remove large amounts of arsenic or copper from contaminated water. Post-analysis levels of arsenic were close to the beginning levels of arsenic, and it was concluded that water-hyacinth will not remediate arsenic contaminated water.

The water-hyacinth appeared to be a good choice for removing chromium from polluted water. At low concentrations, the plant removed about 70% of the chromium in the water (Table 2). As the concentrations increased, the plant appeared not to be able to take up as much percent chromium, but the amount the plant was able to take up was still significant (around 25%). This reduction could be attributed to plant tissue injuries caused by high arsenic levels.

The copper data showed directly opposite results when compared to chromium and arsenic. It seems that when a plant such as a water-hyacinth is in the presence of large amounts of copper, levels of copper in water are greater than when copper is present without any plants. With no plants present, copper is much more likely to precipitate out of an aqueous solution (Tucker and Hargreaves, 2003). Water samples for this study were collected from the center of the jars, if this copper had precipitated out, the analysis would show that levels were low in the jars that had no plants. The samples that had plants present had the higher values because of how plants and copper react with each other. Root exudates from the water hyacinth could have kept copper soluble or suspended in water, thus showing higher amount of copper in the samples with plants.

In conclusion, if a body of water is polluted with CCA and phytoremediation is the choice to clean it, water hyacinths are not the plants to be used for copper and arsenic removal. Although they

Table 3. Copper uptake by water-hyacinths during a period of 17 days.

Sample ID	Copper	% Removal vs. control
Ctrl. w/ plant	0.567	0
Ctrl. w/o plant	0.266	
2.5 ppm w/plant	0.949	53
2.5 ppm w/o plant	2.02	
5 ppm w/plant	3.45	0
5 ppm w/o plant	2.9	
10 ppm w/plant	5.38	0
10 ppm w/o plant	2.39	

might be effective against chromium, they do little to control an arsenic or copper contamination. To remedy this situation, use of more than one plant species could be the answer. More experiments on other aquatic plants are needed to determine which plants are the best to uptake arsenic or copper, then the two could be combined to help remediate the problem.

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