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Passive Removal of Copper Ions and Salts from Water for Potable Use

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Authors' Summary: South Korea is a water stressed nation. Thus, we sought out low cost methods to provide potable water. We tested materials for chloride removal from artificial seawater. We found that of the materials tested, the sweet sagewort plant performed best. The addition of sweet sagewart to seawater can be a low-cost passive pretreatment prior to filtration by reverse osmosis. South Korea is also a major semiconductor producer where copper is released into water supplies in large quantities. Thus we tested various materials for copper removal and found the indigenous Korean melon to be successful at removing copper from water.

Abstract

Eleven different organic materials were tested for their ability to remove chloride ions from an artificial seawater solution. The sweet sagewort (*Artemesia annua*) was found to have the highest absorption capacity and was further tested in order to determine the optimum conditions for chloride removal. Sweet sagewort is from the same Asteraceae family as the *Parthenium sp*. which has been shown to remove high percentages of chloride ions from artificial seawater, possibly due to its abundance of amine binding sites. An FT-IR test (Fourier Transform Infrared Spectroscopy) showed that amine groups were also present in the sweet sagewort. The sweet sagewort was able to remove 27.1% of the chloride ions at a ratio of sagewort to artificial seawater of 7 g per liter. Although Korean melon was unsuccessful at removing chloride ions, it removed copper (II) ions from water. The Korean melon was able to achieve 95% removal at a ratio of 2.5 g/L (melon/water) at pH of 7.

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Introduction

South Korea, a peninsular nation, has difficulty securing a stable water supply. It has been listed as a "water-stressed" nation by the U.S.-based Population Action International [1]. The process of desalination is viewed as a solution to this problem. Chloride ions constitute a large proportion of seawater and its removal is a necessary process in desalination. However, processes used to remove chloride ions, including reverse osmosis, distillation, and MSF (Multi-Stage Flash) are energy consuming and cost ineffective [2]. As an alternative to these methods, a collaboration between students from Bugil and Hwachong schools tested numerous organic materials under varied conditions for the optimum removal of chloride ions from artificial seawaters.

Copper (II) ions are by-products of many industrial processes and are released in large quantities into rivers. It is one of the main heavy metals released from the semiconductor and plating industries, which are booming industries in Korea [3]. The conventional methods of removing copper from water include reverse osmosis and electrokinesis, which are impractical and costly [4]. As an alternative to these methods, Bugil tested the Korean melon for copper (II) ion removal under various conditions in order to achieve the maximum removal of copper ions from water.

Chloride Removal

Previous studies have shown that dendrimers containing primary amine groups were able to adsorb chloride ions [5]. *Parthenium sp*, a weed from the Asteracae family, has also been tested and found to remove chloride ions from wastewater [6]. This gives rise to the possibility that biomass containing amino acids and other organic materials from the Asteracae family can also remove chloride ions. Eleven kinds of plant matter (sweet sagwart, laver seaweed, enoki mushroom, soybean, onion, chestnut, shitake, cranberry, crown daisy, rice husk, and Korean melon) were chosen to investigate their ability to remove chloride ions.

Copper Removal

In a previous study, Honeydew melon was tested for its ability to remove iron and manganese from groundwater, possibly due to amine binding sites [7]. The Korean melon was chosen as the adsorbant for copper removal, as it is from the same cucumis family as the Honeydew melon. Melons are also known to have porous, rigid surfaces that are ideal for heavy metal removal [8].

Methods

Organic materials for all experiments (chloride and copper removal) were prepared in the following manner. The materials were washed and placed in distilled water for 1 hour to remove any impurities. The materials were dried to a consistent mass in an oven at 100°C. The contents were then ground to a fine powder using a mixer and sieved to ensure uniformity of particle size. The contents were stored in an airtight container to prevent dampness due to moisture.

Each experiment was repeated for a total of three trials.

Chloride Removal

Artificial seawater (ASW) was prepared using the major ion composition and concentration of typical seawater accurate to 0.001 grams. The molarity of chloride in the ASW was 0.408M [9].

Each organic material was measured to the desired mass and placed inside a beaker with 100 ml ASW. The mixture was stirred using a magnetic stirrer at room temperature (25°C). After mixing for up to an hour, the organic material was filtered from the solution.

The remaining chloride in the solution was determined through Volhard's titration method [10]. A 0.1M silver nitrate solution (10 ml) was added to 5 ml of the treated ASW and saturated ferric ammonium sulfate solution (1 ml) was added as the indicator. The white precipitate was filtered. The resulting solution was titrated with 0.04M potassium thiocyanate until red.

An FT-IR (Transform Infrared Spectroscopy) analysis was conducted in order to find out whether the suspected functional groups for chloride removal (N-H ties) were present in the Sweet Sagewort.

After the most suitable organic material was found, the selected plant material was heated at 500°C for 15 minutes in an oven in order to create char. Charring an organic material expands the plant's surface area and increases porosity (the percentage of biochar particle volume not filled with solid), generally enabling a higher adsorption capacity [11].

Copper II Ion Removal

The copper (II) solutions were prepared by dissolving copper (II) chloride ($CuCl_2$) in distilled water (19 mg/L). The pH of the copper solution was adjusted to 5.5, 7.0, and 9.0 using a 0.01 M NaOH solution. In all tests the concentration of copper was set to 300 μM.

Table 1. Organic Materials Tested for Chloride Removal.

Porphyra umbilicalis (Laver seaweed)	*Flammulina velutipes* (Enoki Mushroom)	*Artemisia annua* (Sweet Sagewort)
Castanea mollissima (Chestnut)	*Chrysanthemum coronaries L.* (Crown Daisy)	*Glycine max* (Soybean)
Allium cepa L. (Onion)	*Lentinula edodes* (Shiitake)	*Vaccinium oxycoccos* (Cranberry)
Oryza Sativa (Rice Husk)	*Cucumis melo L.* (Korean Melon Rind)	

For each trial, 80 ml of 300 μM copper was placed in a beaker with the ground melon rind. The mixture was stirred using a magnetic stirrer at a medium-low speed at room temperature. Afterwards, the melon rind was filtered from the solution.

The amount of copper that was remaining in the solution was determined through the Iodometric titration of copper [12]. Potassium iodide (3–5 g) was added to 50 mL of the solution as the indicator and 5 mL of a starch solution (10%) was added to obtain a dark purple color to facilitate determination of the end-point (when the solution turns white).

We repeated procedures above with variations in contact times (0 – 60 min), the ratio of mass of organic materials to volume of water (0.125 g/L to 2.5 g/L), and the pH (5.5 – 9).

Results & Discussion

Chloride Ion (Cl^-) Removal

Of the 11 different types of organic materials tested, the most effective material for chloride removal was the sweet sagewort. The sweet sagewort was able to remove 19% of the chloride from ASW using 1g/L ratio of sagewort per ASW when the other materials were only able to remove 13% chloride or below (Figure 1).

As the contact time between sagewart and ASW increased, the percentage removal of chloride ions also increased, as there was more time for the chloride ions to bind to the binding sites on the sweet sagewort (Figure 2). After 20 minutes, however, the binding sites became saturated and were not able to remove more chloride ions. Thus, the optimal contact time for 1g/L (sagewort /ASW) of sagewort in ASW was 20 min.

The ratio of mass of sweet sagewort to ASW was also varied. Each trial was conducted for 20 minutes, as 20 minutes was found to be the optimum contact time for 1g/L ratio of sagewort per ASW in the previous test. As the mass of sweet sagewort in ASW increased, the percentage of chloride removal also increased until 7g/L (sagewort /ASW). The increase in mass of sweet sagewort increases the amount of chloride ion binding sites. Above 7g/L however, time became a limiting factor, reaching a maximum chloride removal of 27% (Figure 3).

3.1.4 Treating (Ashing) Sweet sagewort

Charring an organic material widens its pores and increases binding sites available for removal [11, 13]. However, creating

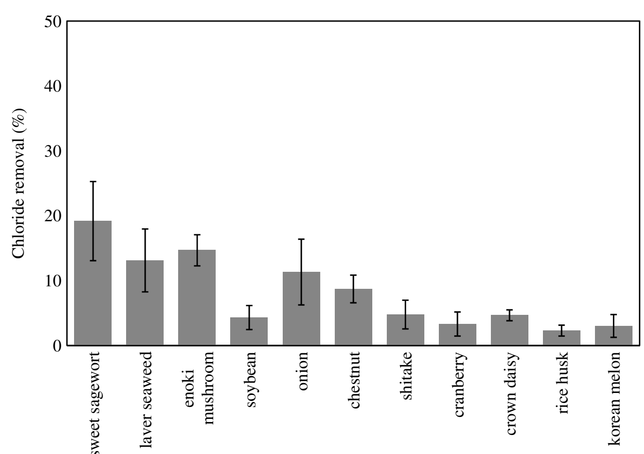

Figure 1. Chloride removal by various organic materials. Error bars represent the standard deviation of three replicates.

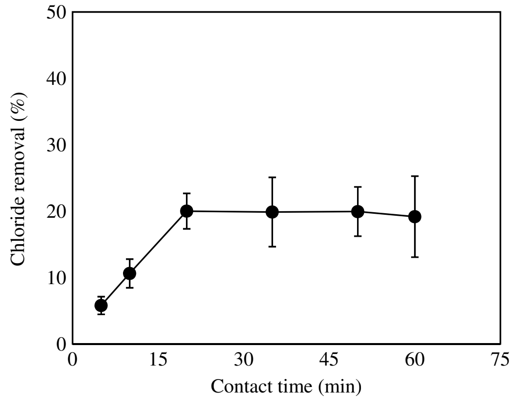

Figure 2. Changes in removal of chloride ions with increased contact times. Error bars represent the standard deviation of three replicates.

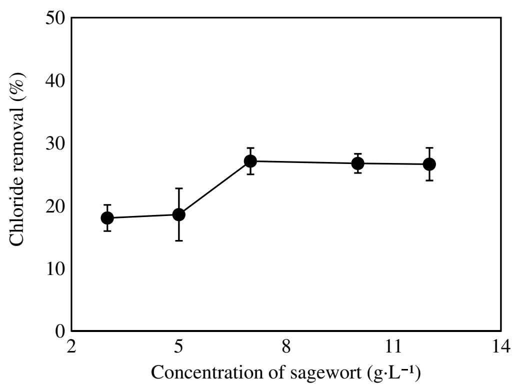

Figure 3. Changes in removal of chloride ions with different ratios of sagewort to artificial seawater. Error bars represent the standard deviation of three replicates.

biochar requires high heating at an oxygen free environment. These conditions could not be fulfilled in the current experiment and ashed sweet sagewort, rather than charred sweet sagewort, was acquired. Merely ashing, not charring, the sweet sagewort was unable to enhance the adsorption capacity. Ashed sweet sagewort removed a lower percentage of chloride, only 15.8% compared to the initial 19%.

There were a few limitations to this experiment. First, natural coloring and scent from the various organic materials leached onto the ASW. This coloration may be removed by pretreatments with formaldehyde in acidic medium [14], although further research and experimentation will have to be conducted to determine if this is feasible. Second, it was difficult to determine the optimum conditions for chloride removal as only one variable was altered for each trial. Time was a limiting factor when testing for the optimum concentration of mass of sweet sagewort to ASW. A 7g/L ratio of sagewort per ASW may not have been the optimum levels had the experiment been conducted for a contact time of more than 20 minutes, as 20 minutes was only the optimum contact time for 1g/L (sagewort /ASW).

The sweet sagewort was able to achieve a maximum chloride removal of 27% from ASW using a 7g/L ratio of sagewort per ASW. Amine groups shown in the FT-IR spectrum may be responsible for chloride removal (Figure 4). Although the adsorption capacity of the sweet sagewort was less than that of the *Parthenium sp.*, which achieved 40% chloride removal, the required contact time for the *Parthenium sp.* was longer (120 min) compared to the sweet sagewort (20 min) [6]. The sagewort also achieved less chloride removal compared to a study in which 55% removal of chloride ions was achieved using electrochemical methods [15]. However, using a bio-adsorbent like the sagewort is more environmentally friendly. In the future, other methods, such as varying the pH and the temperature of the ASW solution and properly charring the Sweet sagewort could be tested in order to enhance the adsorption capacity of the sagewort for chloride removal. Varied contact times along with different ratios of mass of organic material to volume of ASW solution can be tested in order to find more accurate optimum conditions for removal. The capacity of organic materials to remove other ions from water, such as sodium ions, can also be tested.

Copper II Ion (Cu^{2+}) Removal

For this experiment, Korean melon rind was mixed with water containing 9 mg/L copper ion solution at a ratio of 2.5g melon per liter. A large percentage of copper was adsorbed by the melon rind instantly, as 1 minute of contact resulted in around 77% removal of copper. As the contact time increased, the percent removal of copper increased until the 30 minute mark. At thirty minutes, the copper ion binding sites on the melon rind became saturated and were unable to further remove copper ions (Figure 5)

As the ratio of melon rind to copper solution increased, the percentage copper removed also increased. With a 0.125g/L ratio of melon rind to copper solution, only 27% removal of copper was achieved. As the mass of adsorbent increased, the percentage removal of copper steeply increased and reached 89% removal with 1.25g/L melon rind to copper solution. Between 1.25g/L and 2.25g/L of melon rind to copper solution however, only 5% more removal took place (Figure 6). Thus, the removal of copper using Korean melon is most effective using smaller melon rind to copper solution ratios, although for higher percentages of copper removal, larger amounts of melon rind is preferred.

The percentage removal of copper increased significantly as the pH of the copper solution was increased to 7. At pH 5.5, a 0.625g/L ratio of melon rind to copper solution achieved a 56.1% removal but at pH 7 achieved a 96.4% removal. The removal of copper receded to 90% at pH 9. Therefore, the optimum removal of copper occurs around pH 7 (Figure 7). Lower pH may have caused less removal due to protonation of amine groups at binding sites as the NH_2 ions in the amino acids prefer to bind with the available H^+ ions, forming NH_3^+ ions, decreasing the binding sites available for copper removal [16].

As with the chloride experiment, the color of the melon leached onto the treated water. Because the endpoint of the titration is white, charred Korean melon could not be tested, as the black coloration from the char would leach into the copper solution and make it difficult to distinguish the endpoint of the titration. In order to test this method in the future, further research needs to be done to prevent the leaching of the char.

The Korean melon was able to achieve 95% removal (29.4mg/g, copper/melon) at a pH of 7. The adsorption capacity of the Korean melon was nearly 6 times as great as the honeydew melon, which removed a maximum of 4.98mg/g (copper/melon) [7]. The adsorption rate of the Korean melon was also very fast, as the test to find the optimum contact time showed that after 1 minute of contact time, 2.25g/L (melon/copper solution) achieved 77% adsorption of the 19 mg/L copper solution. This shows that the Korean melon is very time efficient and suitable for use in a filtration system. In the future, the Korean melon can be tested for its

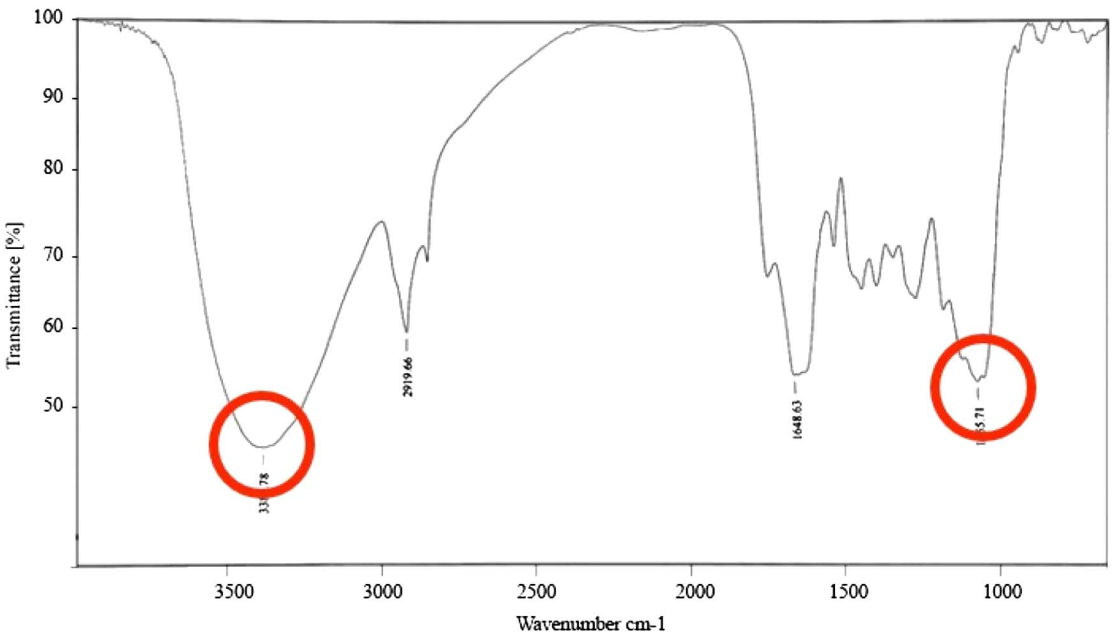

Figure 4. An FT-IR spectrum of *Artemisia annua* shows a N-H stretch between 3300 and 3500. An absorption between 1080 and 1360 is a C-N stretch. These two stretches suggest the presence of amine groups.

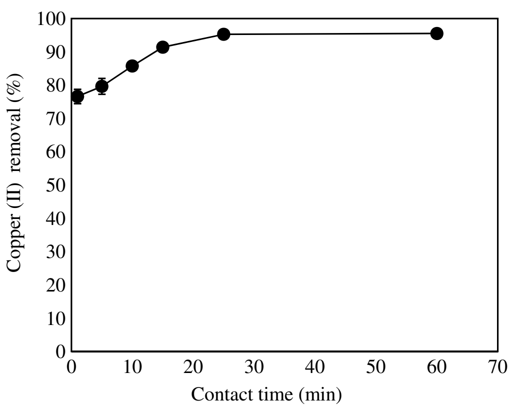

Figure 5. Changes in removal of copper with increased contact times. Error bars represent the standard deviation of three replicates.

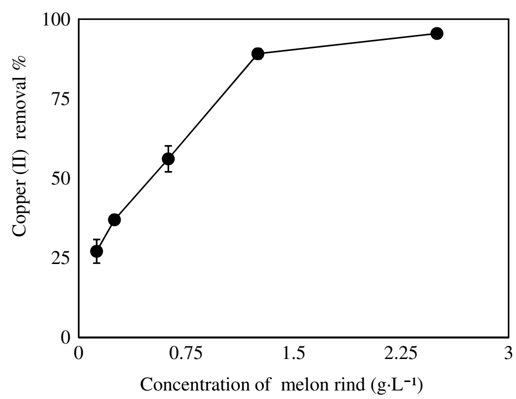

Figure 6. Changes in removal of copper ions with different ratios of melon to water. Error bars represent the standard deviation of three replicates.

capacity to remove other heavy metals, such as iron, from wastewater. Although it is suspected that amine groups are responsible for the absorption of copper ions, an FT-IR analysis can be conducted to accurately find the components of the Korean melon rind responsible for removal of copper (II) ions.

Conclusions

Chloride Ion (Cl^-) Removal

The sweet sagewort was able to achieve a maximum chloride removal of 27% from ASW using 7g/L (sagewort/ASW) within 20 minutes. Ashing the sweet sagewort reduced its chloride removal capacity. This study proved the efficiency of the sweet sagewort at removing chloride ions from ASW and showed potential in removing chloride ions using biomass. Although 27% removal is smaller compared to other studies using electrical and electrochemical methods, the passive treatment method using sweet sagewort costs less energy and can be enhanced through further experimentation. Sweet sagewort may be used in desalination plants in order to remove a portion of the chloride ions before desalination is carried out, reducing energy consumption and costs.

Copper II Ion (Cu^{2+}) Removal

The melon rind is a waste material from food processing industries in Korea and can easily be recycled. The maximum adsorption capacity of the Korean melon rind in removing copper (II) ions from water was 29mg/g at the optimum pH of 7. These results were significantly higher than the amount of copper (II) removed by the Honeydew melon in a similar study. The rate of metal uptake was also very rapid. After one minute of mixing, 76 % of copper (II) ions were removed. The high adsorption capacity and

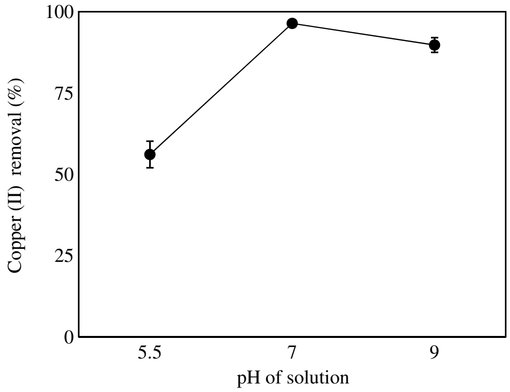

Figure 7. Changes in removal of copper ions at different pHs. Error bars represent the standard deviation of three replicates.

time efficiency of the Korean melon rind implies that it can be used as inexpensive and energy friendly alternative to costly adsorbents such as activated carbon and resins.

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