Heavy Metal Adsorption Using Renewable Adsorbents

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Senior Design CPE 472 – Spring 2012

Submitted: April 27, 2012

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Abstract

The purpose of this project was to investigate the heavy metal adsorption capabilities of biomass. The overall goal was to design a process that will replace current nonrenewable water treatment technologies with a cheap and biodegradable alternative. In this case, the research team tested the ability of orange peels to uptake cadmium and nickel from solutions created in the lab. From previous research done to test heavy metal adsorption, the team developed a method of testing using mainly a peel-packed glass column. The column was used to run metal solutions through the peels and then ICP-MS testing was used to evaluate metal concentrations in the effluent liquid. The team's results proved promising, as the orange peels reduced the concentration of a 90ppm nickel solution by 54.2%. A sample of cadmium solution was reduced in concentration by 33.9% under normal conditions and 48.2% under acidic conditions. However, the team has strong recommendations for future work. The experimental techniques can be improved with some procedural adjustments, and the results can be reproduced to assess service life of the peels and verify results.

Introduction

At this time, there is no commonly used method for extracting metals from water with biodegradable sources. Current technology is expensive, with many treatment plans using carbon filtration to remove heavy metals from water. The research team investigated the feasibility of adsorbing heavy metals from water using renewable absorbents. This would ideally be a less expensive and more environmentally friendly alternative to the current technology while not compromising the effectiveness of heavy metal removal. Previous studies performed on alternative technology only evaluated the amount of metals that could be removed using cellulosic materials. The approach was aimed to go beyond these previous studies and apply this technology to natural sources: fruit peels. Since previous research of adsorption of heavy metals using biomass had only been done on a small, laboratory scale, this research project may lay the foundation for large scale applications of this technology.

The team measured the ability of orange peels to remove nickel and cadmium from water. Based on technology researched during the group's literature review, they planned to create packed columns composed of ground, dried fruit peel. The contaminated water samples would then run through the columns over a designated time period (i.e., until equilibrium occurs). The metals were to be used at various concentrations with varying pH to determine the most effective means of metal adsorption. After the metal solutions were treated by the fruit peel column, each water sample was evaluated using ICP-MS at Central State University.

Background

The United States Environmental Protection Agency has a great interest in heavy metals in the water supply and has many regulations for metals in water (6, 7, 8, 9). This focus on water treatment has already led to research and patents focused on this topic (2, 4, 5). Orange peels are partially composed of cellulose and pectin (3). Therefore, if cellulose and pectin function as biosorbents under heavily modified conditions, they should be able to perform the same process under natural conditions. Thus, using an orange peel as a natural biosorbent, with minimal modification, should allow heavy metals to be removed from water.

Experimental Methods

Safety Procedures

Because this experiment dealt with heavy metals, some precautionary measures were taken while performing the procedure. All work with the metals was done in the fume hood, since both the Nickel reference solution and Cadmium Acetate cause respiratory irritation upon inhalation. Proper eye and hand protection was necessary while handling the samples, as well. After the samples were collected, all peel and effluents samples not in use were disposed of in a waste container. All procedures were done in a safe manner, with the well-being of everyone using the lab carefully considered. There were no injuries and the lab facilities were cleaned and organized promptly after usage.

Equipment and Materials

In order to conduct the desired experiments, the team required the following laboratory equipment:

- Graduated cylinders
- Various sized glass beakers
- 2L glass containers with lids (for waste collection)
- Ring Stand Apparatus
- Glass Adsorption Column
- 20 mL vials with lids
- pH meter
- Paper towels
- Clay crucibles
- Scale
- Oven
- Tin foil
- Masking tape (labels)

- Sharpie Marker
- Kitchen knife

The team also required the following materials:

- Cadmium Acetate
- Nickel Reference Standard
- Sulfuric Acid
- Oranges
- Deionized water
- Dawn dish detergent

Orange Peeling and Drying

Each orange was washed in DI water and dried. Then, the peel was cut off of the oranges in strips. Then, the peels were cut into small, square-shaped pieces and put into clay crucibles. See the figure 1 below for an example.

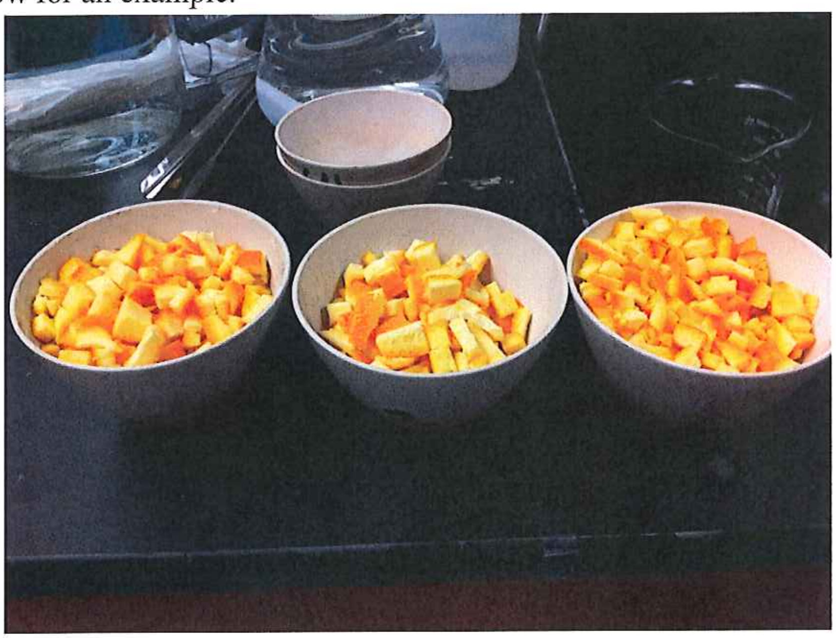

Figure 1. Sliced orange peels before oven drying

The peels were kept at 50 °C in the oven for approximately 24 hours. If they were not fully dried, the temperature was raised to about 75 °C and the peels were dried for about 2 more hours.

This initial procedure for the peels yielded unstable peels and samples that had molded. The procedure was changed based upon literature to include bone drying based on charring research that had suggested would yield better results (10).

The same slicing and cutting procedure as before was followed. Then the peels were kept at 100 °C in the oven for approximately 24 hours. If the peels were not bone dry, the temperature was raised to around 150 °C and the peels were dried for about 2 more hours.

20g of dried peel was measured out and then blended until ground into very small pieces, see figure 2 below. This additional step was based on prior research (1).

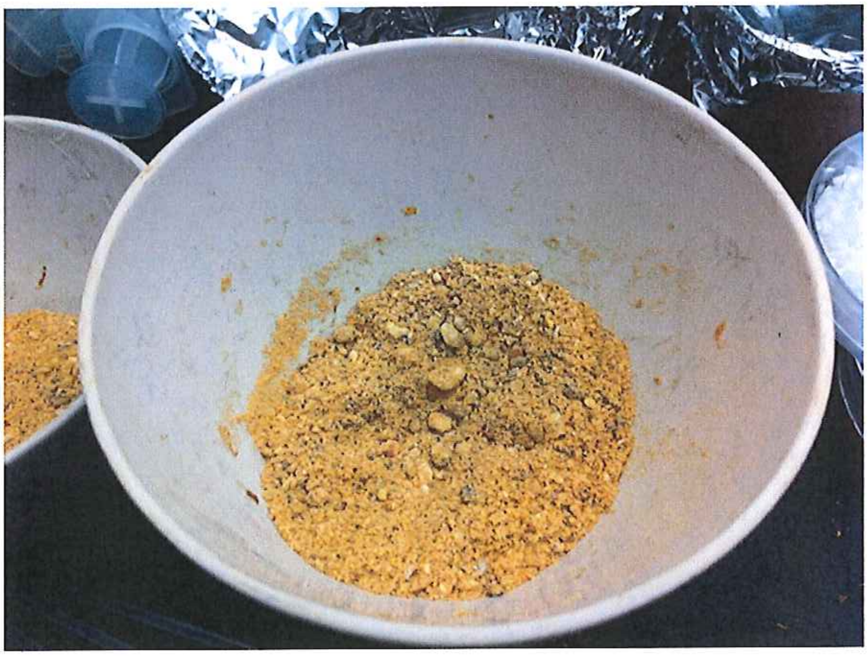

Figure 2. Charred and grounded orange peels before use in the column

Preparing the Adsorption Column

The adsorption column was cleaned by using hot water and Dawn detergent. Then DI water was run through the column. This initial setup is shown in figure 3. This setup was used for both blanks and orange peel trials.

Figure 3. Absorption column setup

When orange peels were used, the 20g of peels were packed into the bottom of the column. This is seen in figure 4.

Figure 4. Column setup with orange peels

Preparing the Sample Solutions

Cadmium Acetate and Nickel Reference Standard were the metals tested. The cadmium was in a powdered form while the nickel was in solution.

The methods for preparing each kind of sample are discussed below:

The Cadmium Acetate used by the team was 42.18% Cadmium by weight/mass fraction. Therefore, Equation 1 was used to find the amount of Cadmium Acetate that was needed to reach a desired concentration of solution after solution volume was selected.

$$\frac{.4218 * Mass\ of\ CdAc}{Volume\ of\ solution\ made} = Desired\ concentration \tag{1}$$

The Nickel Reference Standard was at 1000 ppm Nickel. Serial dilutions were made using DI water to reach the desired concentrations.

Sulfuric acid was added to change the pH when necessary with the pH meter used to determine acidity.

Trial Runs through the Column

20 mL blanks were run of the metal to be tested to determine how the frit would affect the trial and collected for analysis. Then peels were placed in the column and 100 mL of the selected metal solution was allowed to pass through the apparatus. This resulted in 20 mL samples. One set of orange peels was used for each metal solution and then discarded.

Preparing Samples for Testing

20 mL of sample was collected for 100 mL of metal solution. The collection vial was labeled with blank or peel and pH. Initial samples were not secondarily filtered. A later sample can be seen in figure 5. Too much particulate was observed during ICP analysis and a 0.45μm syringe filter was used to filter the sample to remove this. An example can be seen in figure 6.

Figure 5. Labeled sample vial to the left and blank vial to the right

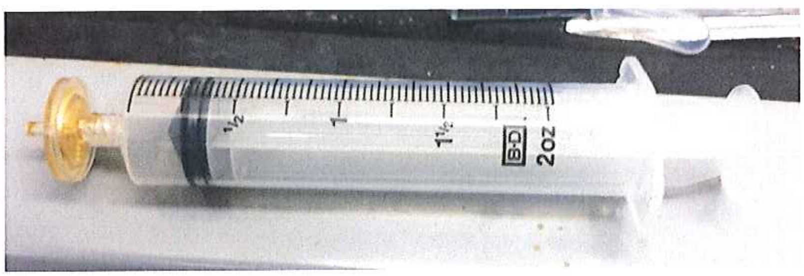

Figure 6. 0.45μm filter with syringe

Post-Experimental Cleaning

The column and associated materials were cleaned with Dawn detergent after each trial.

Waste Disposal

Any hazardous or toxic material that remained after an experimental trial was deposited into a labeled waste container, this included; waste peels, extra sample solution, metal solutions, syringes, and filters. The Miami University Office of Environmental Health and Safety was contacted for final disposition of the waste.

Sample Analysis

The ICP-MS at Central State was used to perform analysis of the samples.

Adsorption Experimental Procedure

Initial cadmium solutions were made at 100 ppm but a higher concentration of 1000 ppm was made after initial results were undetectable. pH of the solution was around 7 without addition of acid. Sulfuric acid was later added to lower the pH to around 4.2.

Nickel solutions were made at 100 and 500 ppm from the Reference Standard. The pH of the reference standard was at 2.1 so the pH was not modified.

The final trials were run as a maximum adsorption run to determine how much metal the peels can adsorb.

Results and Discussion

The full results reported from Central State's ICP-MS tests on the team's samples are in Appendix D.

No results were obtained from the samples in trials 1-5 or 8-9 because of experimental error and detection limits on the ICP-MS. Trials 6-7 and 10-13 produced valid results. A summary of the results can be seen in Table 1.

Table 1. Valid trial results

Trial	Metal	Conditions (blank or run through peels)	pH	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Reduction (%)
6	Ni	Blank	2.1	100	89.87	
7	Ni	Peels	2.1	100	41.13	54.2
10	Cd	Blank	7	1000	1119.65	
11	Cd	Peels	7	1000	739.60	33.9
12	Cd	Blank	4.18	1000	1129.52	
13	Cd	Peels	4.18	1000	584.87	48.2

These results confirm the team's hypothesis that orange peels can significantly reduce heavy metals concentration in solution by adsorption. Each valid result showed a percent reduction in metal of over 30%. Also, these results indicate that lower pH has a positive effect on adsorption as Cd adsorption increased by approximately 14%.

Error Analysis

An initial source of error comes from the fruit particles that got stuck in the frit of the adsorption column after each trial. There was no way to easily measure the residual amounts of peel left in the column frit and therefore it is unknown how much the residual matter affected the next trial's results.

An additional source of error comes from the outside testing of the samples at Central State. It is unknown how accurate their tests and testing procedure are.

Finally, complete confirmation of the hypothesis cannot be done due to the lack of reproduced results.

Conclusions

This experiment showed promising results. With reductions of at least 30% in metal content in the filtered samples, the developed method appears to be a viable way to remove heavy metal from water. However, the hypothesis cannot be confirmed due to the results not being reproduced. The method of running a standard before each sample allowed for a much better idea of initial, non-filtered concentration of metal that showed us much better data than if standards were not used before testing samples through peels. Overall, the valid results were positive and indicate that future work should be done to reproduce and expand upon these results.

Recommendations for Future Work

Throughout the course of this project, the team came up with a couple of ways that the project could be improved as well as future work that would need to be done to improve the knowledge gained from this project.

Improvements in Procedure

The primary method for improvement was a way to remove the orange color, likely imparted by the citrus oil, from the water. Additionally, some initial samples had material that passed through the frit and needed to be filtered out. A method for filtering out the citrus oil and materials in one step would be ideal in an application setting. This could result from additional charring of the peels, such that only the carbonaceous material is left behind. This carbon could be activated with a strong base like sodium hydroxide, which will increase the porosity of the peels.

Another way to improve the experimental procedures would be to have multiple setups as frit saturation became an issue. This way the solutions can be tested in a timelier manner to get results and data more quickly.

Additional Possible Procedures

In terms of future work, more heavy metals should be tested via this method of adsorption to see how effective the orange peels can be at removing a variety of metals and not just Cadmium or Nickel. Other fruit peels should also be tested in a similar manner. If the results are viable then this can provide a variety of low water treatment cost options. Additionally, if some peels are found to adsorb certain metals better than others, special combinations of peels could be used to treat water in locations that have specific water standards. However, the team also recognizes that this is all based on the availability of peels in those areas as well.

This procedure may also benefit from the addition of isotherm development. An isotherm will model the comparison between adsorbate concentration and amount of adsorbate at a constant temperature. The temperature could also be altered to increase the pore size of the cellulose, allowing more metal to be trapped within the fibers. There were promising results shown in the literature review when the temperature of the samples was increased.

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Appendix A: First Semester Budget Request

Table 1. Budget Requested during Fall semester

Equipment/Item Needed	Purpose	Cost
1000 Translucent polypropylene test tubes (Fisher Scientific)	To hold our samples after performing adsorption experiments, then used in the imaging equipment *The test tubes that are already purchased by the university are glass test tubes, which we have been the equipment advisor in the chemistry department informed us will affect the results of imaging our samples. There are metals in the glass in those test tubes, and the imaging equipment could therefore detect those along with the metals in our samples. This would skew our results by showing a higher metal content in our samples than there actually is.	$129.62
Cadmium Chloride, 100g	Used as the heavy metal contaminant in 1/3 of the experiments	$84.36
Lead Chloride, 250g	Used as the heavy metal contaminant in 1/3 of the experiments	$66.85
Nickel (II) Chloride, 250g	Used as the heavy metal contaminant in 1/3 of the experiments *We would like to purchase our own metals from Fisher Scientific instead of purchasing them from the university because we will be using a large quantity of the metals in our samples and we believe the cost is cheaper from a company outside the university.	$125. 04
Apples, oranges, bananas	Fruit peels used as the adsorbent in the glass column	$100.00
Hourly fee to use the imaging equipment in the Chemistry Department (ICP-MS)	9.5 hours of testing*$15.00/hr	$142.50
Glass adsorption column and accessories	Used to hold the experimental adsorbents and heavy metal solutions *There is currently no glass adsorption column in the chemical engineering department's labs, so we would need to purchase a new column.	$350.00
TOTAL		**$998.37**

Appendix B: First Semester Test Matrix

Table 2. First semester's Experimental Test Matrix

Test Matrix Note: All low values are equivalent to present EPA Drinking Water Standards
Note: Volumes of Fruit Peels are given as mass will be determined from average densities found when lab work is begun

Fruit Peel(s)	Metal(s)	Amount of Fruit Peel	Initial Amount of Metal	Final Amount of Metal
Apple	Cadmium	8 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	8 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	8 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	8 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	8 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	8 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	8 mL	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	
Banana	Cadmium	8 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	8 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	

	Nickel	8 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	8 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	8 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	8 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	8 mL	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	
Orange	Cadmium	8 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	8 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	8 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	8 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	8 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	8 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel,	8 mL	H: Cd 0.015ppm, Ni	

	Lead		0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	
Apple and Banana	Cadmium	4 mL and 4 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	4 mL and 4 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	4 mL and 4 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	4 mL and 4 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	4 mL and 4 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	
Apple and Orange	Cadmium	4 mL and 4 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	4 mL and 4 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	4 mL and 4 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	4 mL and 4 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	

			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	4 mL and 4 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	
Banana and Orange	Cadmium	4 mL and 4 mL	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	4 mL and 4 mL	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	4 mL and 4 mL	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	4 mL and 4 mL	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	4 mL and 4 mL	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	4 mL and 4 mL	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	

Apple, Banana, and Orange	Cadmium	3 mL each	H: 0.015ppm	
			M: 0.010ppm	
			L: 0.005ppm	
	Lead	3 mL each	H: 0.045ppm	
			M: 0.030ppm	
			L: 0.015ppm	
	Nickel	3 mL each	H: 0.0015ppm	
			M: 0.0010ppm	
			L: 0.0005ppm	
	Cadmium and Lead	3 mL each	H: Cd 0.015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm, Pb 0.015ppm	
	Cadmium and Nickel	3 mL each	H: Cd 0.015ppm, Ni 0.0015ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm	
	Lead and Nickel	3 mL each	H: Pb 0.045ppm, Ni 0.0015ppm	
			M: Pb 0.030ppm, Ni 0.0010ppm	
			L: Pb 0.015 ppm, Ni 0.0005ppm	
	Cadmium, Nickel, Lead	3 mL each	H: Cd 0.015ppm, Ni 0.0015ppm, Pb 0.045ppm	
			M: Cd 0.010ppm, Ni 0.0010ppm, Pb 0.030ppm	
			L: Cd 0.005ppm,Ni 0.0005ppm, Pb 0.015ppm	

Appendix C: Samples Tested

Trial	Date	Metal	Metal Concentration	Blank (without peel) or with peel?	Peel Amount	pH	Comments about trial
1	2/20/12	Ni	100 ppm	Blank	0 g	-	This sample was discarded because the corresponding sample (trial 2) was unusable.
2	2/20/12	Ni	100 ppm	With peel	52.8 g	-	This was the sample that molded and therefore was unable to be sent out for testing.
3	2/28/12	Cd	100 ppm	Blank	0 g	-	This sample was discarded because there was not enough time to test it before students left for Spring Break.
4	3/15/12	Cd	100 ppm	Blank	0 g	-	
5	3/15/12	Cd	100 ppm	With peel	20.117 g	-	
6	3/19/12	Ni	100 ppm	Blank	0 g	-	
7	3/19/12	Ni	100 ppm	With peel	20.058 g	-	
8	3/19/12	Cd	100 ppm	Blank	0 g	4.26	
9	3/19/12	Cd	100 ppm	With peel	20.042 g	4.26	
10	4/2/12	Cd	1000 ppm	Blank	0 g	-	
11	4/2/12	Cd	1000 ppm	With peel	20.061 g	-	
12	4/2/12	Cd	1000 ppm	Blank	0 g	4.18	
13	4/2/12	Cd	1000 ppm	With peel	21.623 g	4.18	
14	4/2/12	Ni	500 ppm	Blank	0 g	2.1	No sulfuric acid was added to this sample; the Nickel Reference Standard is already very acidic.
15	4/2/12	Ni	500 ppm	With peel	20.004 g	2.1	No sulfuric acid was added to this sample; the Nickel Reference Standard is already very acidic.
16	4/12/12	Ni	500 ppm	Blank	0 g	-	Attempt at maximum adsorption tests
17	4/12/12	Ni	500 ppm	With	20.006 g	-	Attempt at maximum

				peel			adsorption tests – 9 vials of this solution were collected for the same 20.006 g

Appendix D: ICP-MS Results of Samples Tested

Trial	Date	Metal	Metal Concentration	Blank (without peel) or with peel?	Peel Amount	pH	Comments about trial	**Results from ICP-MS**
1	2/20/12	Ni	100 ppm	Blank	0 g	-	This sample was discarded because the corresponding sample (trial 2) was unusable.	none
2	2/20/12	Ni	100 ppm	With peel	52.8 g	-	This was the sample that molded and therefore was unable to be sent out for testing.	None
Table 1. Samples Tested 3	2/28/12	Cd	100 ppm	Blank	0 g	-	This sample was discarded because there was not enough time to test it before students left for Spring Break.	None
4	3/15/12	Cd	100 ppm	Blank	0 g	-		Undetectable
5	3/15/12	Cd	100 ppm	With peel	20.117 g	-		Undetectable
6	**3/19/12**	**Ni**	**100 ppm**	**Blank**	**0 g**	**-**		**89.87 ppm**
7	**3/19/12**	**Ni**	**100 ppm**	**With peel**	**20.058 g**	**-**		**41.13 ppm**
8	3/19/12	Cd	100 ppm	Blank	0 g	4.26		Undetectable
9	3/19/12	Cd	100 ppm	With peel	20.042 g	4.26		Undetectable
10	**4/2/12**	**Cd**	**1000 ppm**	**Blank**	**0 g**	-		**1119.65 ppm**
11	**4/2/12**	**Cd**	**1000 ppm**	**With peel**	**20.061 g**	-		**739.60 ppm**
12	**4/2/12**	**Cd**	**1000 ppm**	**Blank**	**0 g**	**4.18**		**1129.52 ppm**
13	**4/2/12**	**Cd**	**1000 ppm**	**With peel**	**21.623 g**	**4.18**		**584.87 ppm**
14	4/2/12	Ni	500 ppm	Blank	0 g	2.1	No sulfuric acid was added to	73 ppm

							this sample; the Nickel Reference Standard is already very acidic.	
15	4/2/12	Ni	500 ppm	With peel	20.004 g	2.1	No sulfuric acid was added to this sample; the Nickel Reference Standard is already very acidic.	Not tested yet
16	4/12/12	Ni	500 ppm	Blank	0 g	-	Attempt at maximum adsorption tests	Not tested yet
17	4/12/12	Ni	500 ppm	With peel	20.006 g	-	Attempt at maximum adsorption tests – 9 vials of this solution were collected for the same 20.006 g	Not tested yet

Appendix E: Overall Project Timeline

Task	Type of Task	Status of Completion	Date of Completion
Conduct Literature Review	Research	Completed	September – October 2011
Apply for Funding	Application/paper	Completed	October 16, 2011
Water Treatment Plant Tours	Research	Completed	November 2011
Final First Semester Proposal	Paper	Completed	December 4, 2011
Reserve imaging technology at Central State	Meeting/schedulin g	Completed	January 30, 2012
Collect fruit peels	Materials collection	Completed	March 30, 2012
Scale down test matrix	Experimental Design	Completed	April 12, 2012
Research properties of fruit peels	Research	Completed	January 30, 2012
Locate sources of funding/materials	Materials collection	Completed	January 30, 2012
Set up testing area and ensure safety protocol	Experiments	Completed	February 10, 2012
Build column/materials	Experiments	Completed	February 10, 2012
Conduct experiments with metal standard solutions (without using fruit peel)	Experiments	In progress	April 12, 2012
Conduct experiments with fruit peel	Experiments	In progress	April 12, 2012
Evaluate results on ICP-MS	Evaluation	In progress	-
If time permits: Adjust experimental design based on results	Experimental Design	Not started	-
Conduct new experiments	Experiments	Not started	-

Heavy Metal Adsorption using Renewable Adsorbents

With Honors Thesis Addendum: A global look at where this work can be applied

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University Honors Program

Heavy Metal Adsorption using Novel Adsorbents

Honors Thesis Addendum: A global look at where this work can be applied

By: Daniel Dolan

Introduction

The main body of this paper examined the science of using biomass to remove heavy metals from water, specifically orange peels. The experiments were a success. The purpose of this addendum is to discuss and examine how this research can be applied to individual's lives. Too often science is done without developing the application of the research to the society that needs that information. Therefore, this paper will be an examination of some citrus producing countries that also suffer from heavy metal problems and a brief method on how to set up a water cleaning apparatus on an individual basis in a low socioeconomic status environment.

Examination

By far the largest producer of oranges in the world is Brazil with production in 2009-2010 of 17,750 metric tons. The US comes in second at 7,444 MT. Then the EU-27, China, Mexico, South Africa, Egypt, and Turkey are next and all produce over 1,000 MT as well. The countries that produce the least are Vietnam, Morocco, Mozambique, Malaysia, Japan, Israel, Guatemala, Costa Rica, Australia, and Argentina ("Citrus: World markets," 2010). Many of those countries have heavy metal issues. Mexico, Brazil, and Egypt are the three focuses for this discussion. The US will not be examined due to the high scrutiny that is placed upon the water system by both the government and individuals.

Mexico

Mexico currently has over 51% of its population below the poverty line. Of its total rural population, 91% have access to an improved water source. Access to an improved water source refers to the percentage of the population with reasonable access to an adequate amount of water from an improved source, such as a household connection, public standpipe, borehole, protected well or spring, and rainwater collection. Unimproved sources include vendors, tanker trucks, and unprotected wells and springs. Reasonable access is defined as the availability of at least 20 liters a person a day from a source within one kilometer of the dwelling ("Data by country," 2012).

Mexico also happens to produce 65,000 metric tons of oranges per year ("Citrus: World markets," 2010). Though the population has a high level of access to improved sources, it is hard to collect data on the quality of these sources. It would be an enormous undertaking to test every source of water for a population.

Also, Mexico has proven issues with water quality. Many indigenous populations use traditional sources such as lakes and rivers to collect water. Even though the population has access to improved sources of water, that does not always mean they use them. As recently as 2008 the San Pedro River was deemed to have heavy metal contamination (Gutierrez, Rubio-Arias, Quintana, Ortega & Gutierrez, 2008). The San Pedro flows into the Conchos and then down the Rio Grande. Therefore this issue becomes one that affects not just some other nation but the US as well.

However, this is not an isolated event. The Lerma river is the second longest river and is known for its pollution. Its course winds its way through central-west Mexico and empties into Lake Chapala, the largest lake in Mexico. It too shows a high level of contamination (Avila-Perez, Balcazar, Zarazua-Ortega, Barcelo-Quintal & Diaz-Delgado, 1999). This river is undoubtedly a source for drinking water.

With the simple knowledge that the people can improve their health by using fruit peels, these people can live better lives. This is the point of research like this.

Brazil

As a nation, Brazil has 21.4% poverty with 85% access to improved water sources ("Data by country," 2012). Undoubtedly there are native tribes that help to constitute the remaining sum of those who do not have access to water. The Tapacura River Basin in Northeastern Brazil is one such site that could be aided. It flows through both industrial and agricultural areas as well as cities. Though the levels of heavy metals are below the EPA, they still show a high degree of contamination (Aprile & Bouvy, 2008).

Yet, this is not just an issue in northern Brazil. Sao Carlos sits in the south of Brazil and has been shown to have seasonal variation of metal contamination (Chiba, Passerini, Baio, Torres & Tundisi, 2010). Even here, a simple method of cleaning water would be a boon. If you put a fruit in your glass of water this is only barely different.

Egypt

The point should be quite evident now that this method is easily applicable in many places both expected and not so expected. Egypt, for example, has a poverty level of 22%, while 99% of the population has access to improved water source ("Data by country," 2012). Though the levels are within supposed standards, there still exists contamination (Saeed and Shaker 2008). Simple measures here could have massive impact.

Potential Methods for Water Cleaning

From the research an easy guide as to how to utilize this information follows. However, it should be noted that the focus of this is on an individual basis. Scaling this up to an industrial size process would take much more research and the design of these steps would allow an individual, in an impoverished Third World nation, to take advantage of this process.

1. Acquire waste peel from citrus growers or juice producers.
2. Clean and divide the peel into small pieces less than 0.5cm wide and 1cm long.
3. Dry the peel by placing it close to a heat source, a campfire or something similar.
    a. Close enough to take away water but not close enough to burn or touch the flames.

4. Take a clean piece of cloth and place the dried peel in it.
5. Pass water over the dried peel and through the cloth while collecting it at the bottom.
6. Carefully dispose of waste peels where it will not be disturbed by humans or come in contact with the water supply.
    a. For example, bury the material high above the water table in a water proof wrapper or container of some sort.

These 6 steps are low cost, easy to use and require only a heat source, a piece of clean cloth, a way to collect the water, and a way to properly dispose of the used peels. This technique could be used anywhere. The key is to make sure that none of the peel is consumed by the drinker. In this manner, people with low socioeconomic status have the ability to have clean water. The cost of this process is staggeringly low. The largest burden would most likely be a heat source capable of fully drying the peels. Also, there is the issue of the color and potential taste. Because of the drying and division processes it is possible for some of the peel to enter the water. This would cause the water to take on the taste of the fruit peel used. But, the benefits of clean water outweigh the fact that the water is not 100% pure and possibly tasting of the fruit peel. Further work would need to be done to refine the technique and ensure that the color of the water is clear and no residue from the peel enters solution.

This process is only slightly different than putting fruit in water to drink. Instead, drying the peel first and allowing the water to be filtered before it is consumed.

Ideally, the World Health Organization (WHO) and the Peace Corps would be able to distribute this information. They already have a broad reach in many of the areas that could benefit from this work. Therefore, after some process refinement and testing of minimalist ways to perform the 6 steps, the information should be given to those organizations and deployed across the globe.

Conclusion

All over the world, the idea that using fruit peels to clean water could be taken advantage of. By allowing people to empower themselves and get access to clean water we can improve the health of populations. This improves the ability of people to work and be productive and contribute to society. While this method is not the end all be all for societal improvement, it is certainly a method for societal improvement. Five simple steps can lead to better, safer water. All that needs to happen is to tell people how to do it.

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