Entry to the Stockholm Junior Water Prize 2013

Eggshells: Simple, Practical, Cost Efficient Remedy to Address Cadmium Pollution

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2a. Abstract

This paper presents the results of studies carried out in order to determine which of six breeds of chicken eggshells filters cadmium out of drinking water the most efficiently, to ultimately develop a filtration device for those in developing countries where cadmium pollution has become a major cause for concern. The wastewater solution was passed over the eggshells 5 times, with each pass through lasting the duration of one minute. This procedure was repeated 5 times for the eggshells of each breed of chicken. It was found that Hungarian Yellow was significantly better then Barred Rock, Shaver White, and Bovans, and all breeds of chicken eggshells were extremely efficient at filtering cadmium out of the wastewater solution. Results showed that with each filtration the eggshell was continuing to remove cadmium. The statistics showed that there was not a significant interaction between the replicate and the breed, which in turn meant that the eggshells had not reached their saturation level for filtering cadmium out of the drinking water. If more filtrations would have been done, more cadmium would have been removed; this leads to the ultimate conclusion that eggshells are extremely relevant for real world application.

2b.Table of Contents

2c. Key Words

Cadmium ·Heavy Metal ·Saturation Level ·Barred Rock ·Hungarian Yellow ·Heritage Line ·Lohmann Lite ·Lohmann Brown ·Shaver White ·Bovans ·Commercial Breed ·Eggshells ·Cadmium absorption ·Low cost ·Efficient ·Differences among differing breeds of chickens; efficiency of cadmium absorption

2d. Abbreviations and Acronyms

HY-Hungarian Yellow; BR-Barred Rock; BV-Bovans; SH-Shaver White; LB- Lohmann Brown; LL-Lohmann Lite; WHO-World Health Organization; Cd-Cadmium

2e. Acknowledgements

Dr. Bruce Rathgeber Ph.D., Dalhousie University Agricultural Campus, provided me with space, time, equipment, eggshells and expertise

Margie Tate, Laboratory Instructor, Dalhousie University Agricultural Campus, provided expertise and use of the Atomic Absorbency Spectrophotometer

2f. Short Biography

My name is Hannah Landry and I am a grade 12 student at Hants East Rural High in Milford, Nova Scotia, Canada. Next year I am attending the University of Ottawa and will be majoring in Biomedical Science, and am hoping to minor in neuroscience. My plans for the future include medical school, studying and volunteering abroad and ultimately becoming a psychiatrist with a specialization in eating disorders. It is my hope that next year I will get the opportunity to volunteer at the University of Ottawa's eating disorder clinic, to get more hands on experience. I am extremely passionate about helping other people and science which inspired me to do this exact study. I combined both of these passions to come up with an idea addressing not only cadmium pollution but the deprivation of a basic human right in developing nations.

3. Introduction

One of the most important and troublesome environmental issue arises from the toxic contamination of the world's water streams/sources [1]. With the human population on the rise, various industries have had to increase production in order to meet demands. With this increase comes an increase in the pollutants these industries are letting off which in turn contributes to the ever deteriorating state of the world's water supply [1]. In developing nations in particular cadmium pollution has become a great cause for concern as a direct result of industrial processes; with the battery industry being the biggest contributing factor to cadmium pollution. It is known that the 4 main heavy metals that pose a threat to human health are lead, arsenic, mercury and CADMIUM.

Cadmium pollution has become an epidemic. In India studies show that surface water pollution has increased drastically to 20 times the currently accepted "safe level" in more than 22 critically polluted areas within the country [4]. This does not include the areas of the country that are still polluted above acceptable levels but do not have the status of "critically polluted". Developing nations do not have the money to buy expensive filtration systems for heavy metals, such as activated carbon, ion exchange, precipitation, reverse osmosis, electro-dialysis, and adsorption [1]. Therefore many people have to ingest drinking water with concentrations of cadmium much higher than the standards set out by the World Health Organization (0.003ppm).

Cadmium is a confirmed carcinogen and can cause lung tumors, can be poisonous if ingested, can affect the respiratory tract and kidneys, and even brief exposure to cadmium in high concentrations can result in pulmonary edema and death [3]. So it is important to have as little cadmium present in your drinking water as possible.

On July 28th, 2010 the United Nations General Assembly passed resolution 64/292 which recognized that clean drinking water and sanitation are basic human rights and that clean drinking water and sanitation are essential to the realization of all human rights [5]. Those in developing nations are being deprived of their right to clean drinking water because there is currently no low cost cadmium filtration device readily available to them.

The world currently has a chicken population of approximately 15.8 billion. Eggs are one of the world's most largely produced food products; the consumption of eggs has in turn meant the

large presence of waste eggshells in landfills across the globe. If these eggshells could be utilized for filtering the cadmium out of the drinking water, there is potential to raise the quality of the drinking water in developing nations with a relatively inexpensive filtration device (the eggshell).

Using the eggshells of 6 different breeds of chickens, the goal was to determine which was the most efficient at filtering cadmium out of drinking water; to ultimately design a cadmium filtration device for those in developing nations. It was my belief that the heritage chicken line (Hungarian yellow) would filter out the most cadmium. Prior research performed on the treatment of wastewater using eggshells is limited to commercial eggshells. These experiments successfully demonstrated that eggshells from commercial hens filtered out the "pollutant" in the water after significant time periods. The eggshells of different breeds of chickens have different properties; one of the characteristics of a Hungarian Yellow is that it has a thicker shell. Through various research papers it was found that the reason the eggshells were so efficient at filtering cadmium out of drinking water was because the cadmium was binding to the calcium carbonate which in turn removed the cadmium from the drinking water. An eggshell is made up of 85-95% calcium carbonate and I thought that because the eggshell of the Hungarian Yellow was thicker it might have more calcium carbonate readily available to bind with the cadmium.

4. Materials and Methods

4.a Pretreatment

The eggshells were collected from hens housed at Dalhousie University, Agricultural Campus in Truro, NS. The eggshells collected came from 6 breeds of chicken. Four commercial breeds included; Lohmann Brown (LB), Lohmann Lite (LL), Shaver White (SH) and Bovans (BV). There were two heritage line breeds that included Hungarian Yellow (HY) chickens maintained as an unselected line and Barred Plymouth Rock (BR) which was generated by hatching eggs at the University of Guelph from a line that were selected for increased egg production. The shells were washed with deionized water, to remove imperfections such as dirt. The shell membranes were left on the eggshells. After the eggs had been dried at room temperature for identical periods of time, they were crushed and ground in a coffee grinder. They were then sifted through a No. 16 sieve (1.18mm), followed by a No. 25 (0.71mm) sieve to get a

consistent size of eggshell particle. There were no further physical or chemical treatments done to the eggshells.

4.b Structural Characteristics of the eggshells

In order to prepare the synthetic wastewater solution, a 75ppm cadmium solution prepared from cadmium nitrate in deionized water was used. In all repetitions with all breeds of chickens, 2.5g of eggshell was used as filter material to filter 40ml of the 75ppm Cd wastewater solution into a 250ml filter flask. Whatman #114 (size: 4.25cm) filter paper was placed into a 50ml filter funnel, which was wet with 3ml of wastewater solution at the start of all repetitions in order to ensure no eggshell was getting under the filter paper. For each repetition the cadmium solution was passed/filtered through the eggshells a total of 5 times, with each filtration lasting the duration of one minute. At the end of each one minute interval a vacuum was applied to draw through any water still left in the filter. The filtered solution was then poured into a 125ml flask where, using a 5ml pipette, 5ml of cadmium solution was taken and put into a scintillation vial to later be analyzed. Between changing eggshell breed the tip of the pipette was discarded and replaced. This was repeated for all 5 filtrations for each of 5 replicate samples of eggshell. All replications were conducted at a controlled temperature of 25˚C. A control sample was taken using the same process but without eggshells in the filter. This was done to determine if the filter paper was a contributing factor to the eggshells efficiency at filtering cadmium out of the drinking water.

4.c Adsorption Measurement

The equation used to calculate the amount of cadmium absorbed by the eggshells was as follows:

% adsorption= $(C_i-C_f)/C_i \times 100$

C_i= initial cadmium concentration

C_f = final cadmium concentration

4.d Atomic Absorption Spectrophotometer Analysis

All 150 samples were analyzed using a Varian Atomic Absorption Spectrophotometer insturment. The instrument was calibrated with a 2.00ppm cadmium standard. Because the samples were highly concentrated they had to be diluted, by ratios of 1:4, 1:11, 1:20 and finally the most consistently used dilution factor of 1:15. To read each sample, a tube connected to the instrument was taken out of deionized water cleaned with a sterile wipe to prevent cross-contamination and then placed in the resulting cadmium solution of the first sample. The instrument then detected the amount of cadmium left in the solution in ppm by comparing the amount of light absorbed by the sample to the amount of light absorbed by the standard. The tube was taken out of the first sample, cleansed with a sterile wipe (to prevent cross contamination) and put back into the deionized water. The result was then recorded. This process was repeated for all 150 samples plus 10 control samples.

5. Results

Table 1. Statistical significance of difference between reps, between breeds and interaction between rep and breed

Type 3 Tests of Fixed Effects				
Effect	**Num DF**	**Den DF**	**F Value**	**Pr>F**
Rep	4	120	58.56	<.0001***
Breed	5	120	5.49	0.0001
rep*breed	20	120	0.43	0.9839

(*- HIGHLY significant)**

Table 3. Statistics comparing the breeds' cadmium removal efficiency to one another

Analysis of Variance				
Breed	**Breed**	**Estimate**	**T Value**	**Adj P**
BR	HY	3.9942	3.34	0.0138
BV	HY	4.9664	4.16	0.0008
HY	SH	-5.552	-4.65	0.0001

*Used the conventional cut off point of 0.05 for P

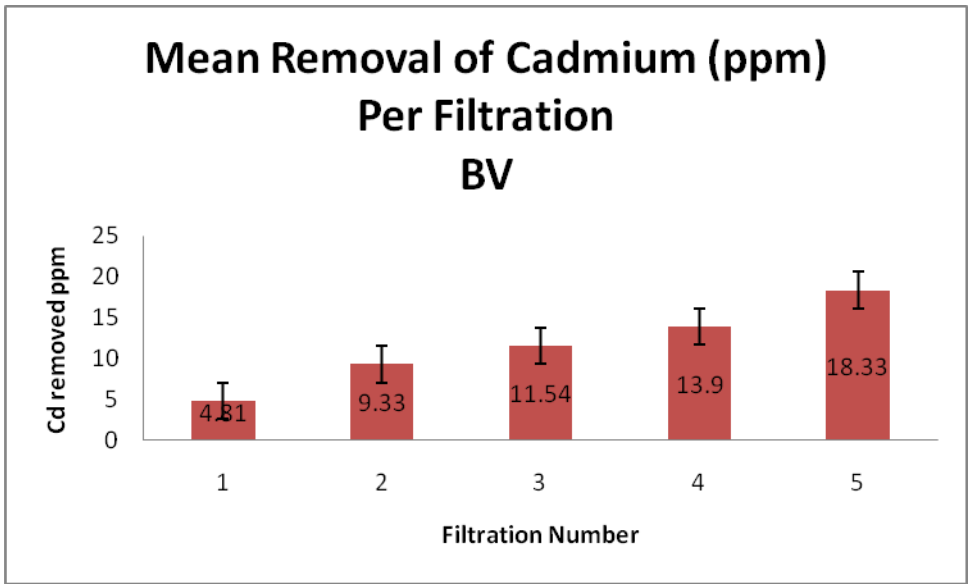

Figure 1. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Bovans)

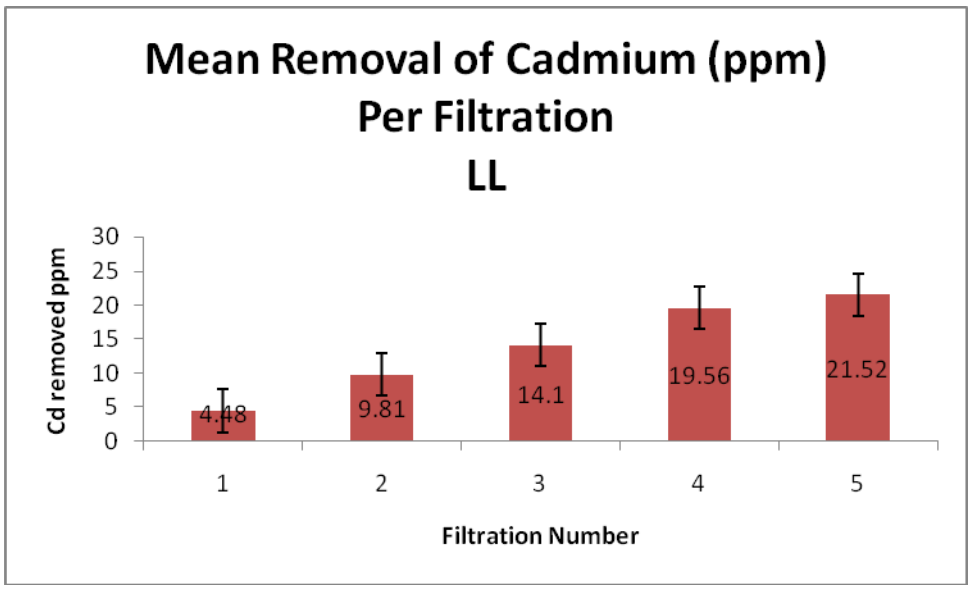

Figure 2. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Lohmann Lite)

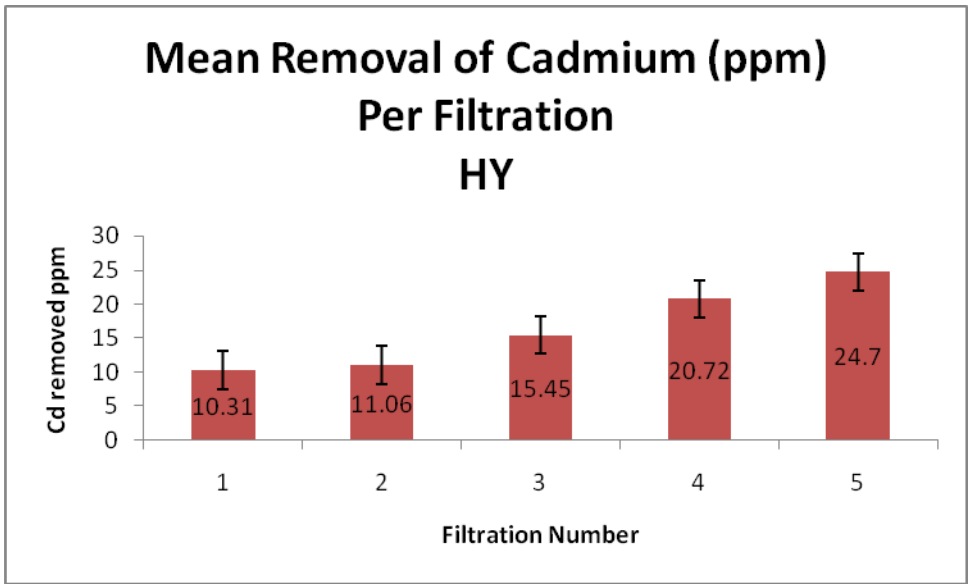

Figure 3. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Hungarian Yellow)

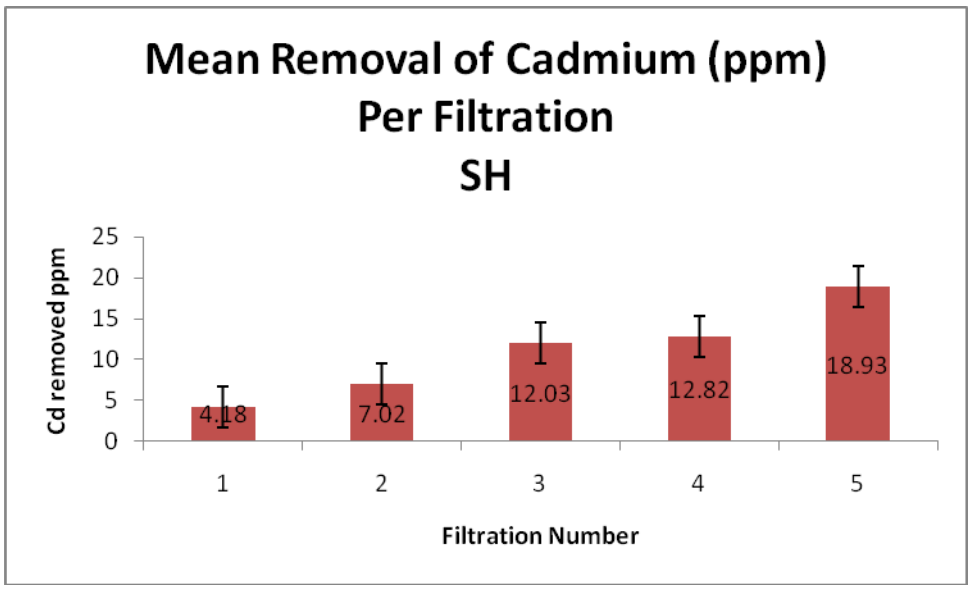

Figure 4. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Shaver)

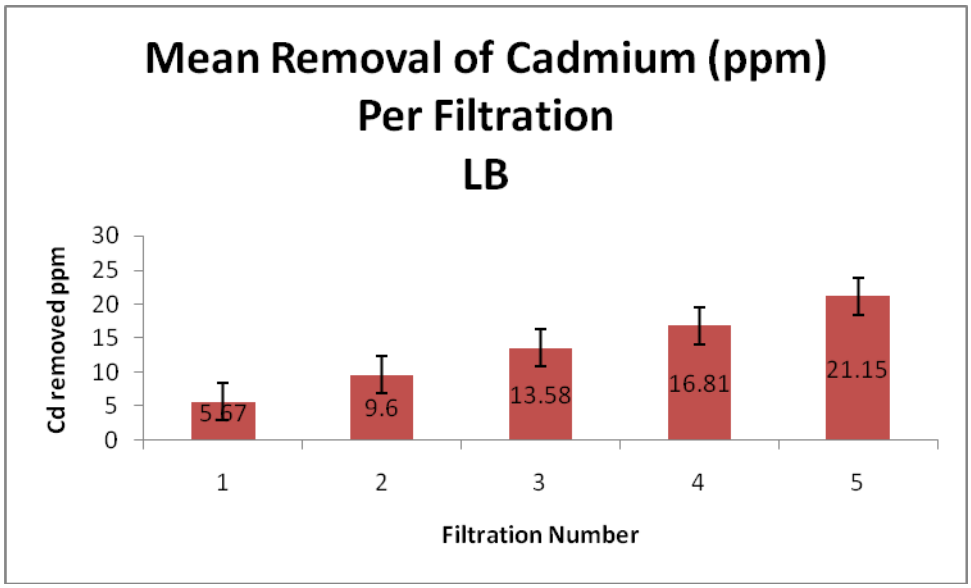

Figure 5. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Lohmann Brown)

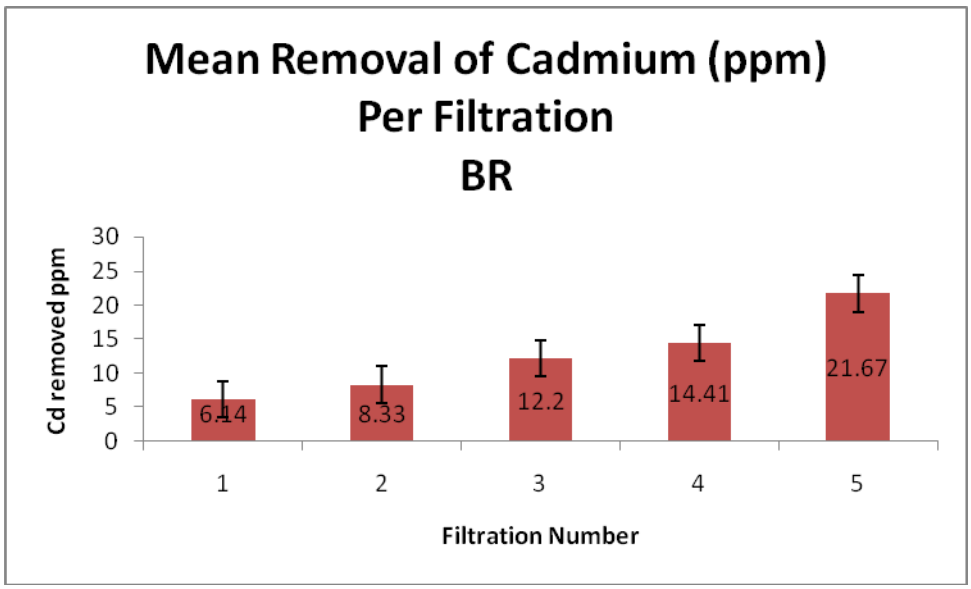

Figure 6. Mean taken from each filtration within each repetition (5 repetitions of 5 filtrations) (Barred Rock)

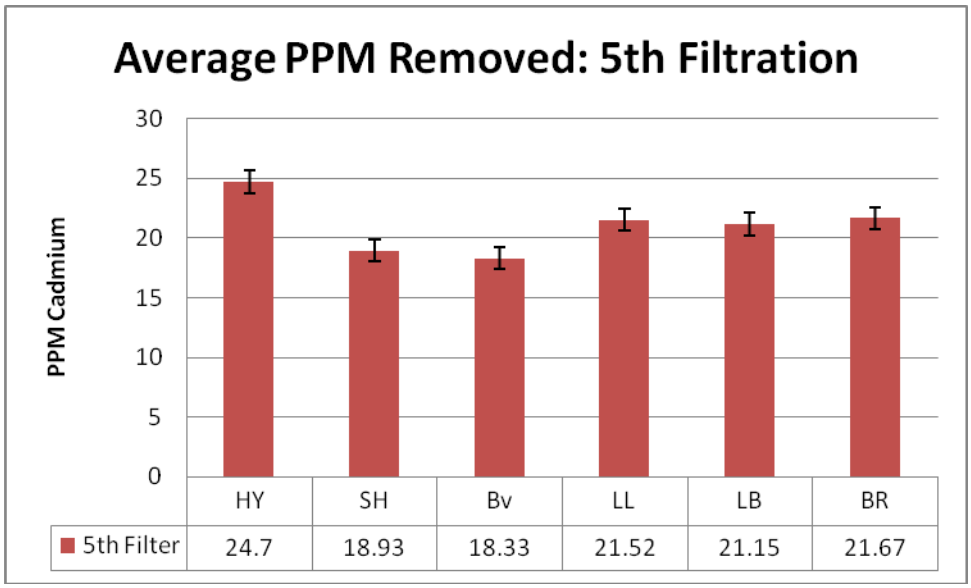

Figure 7. Average ppm removed after the 5th filtration for each of the breeds

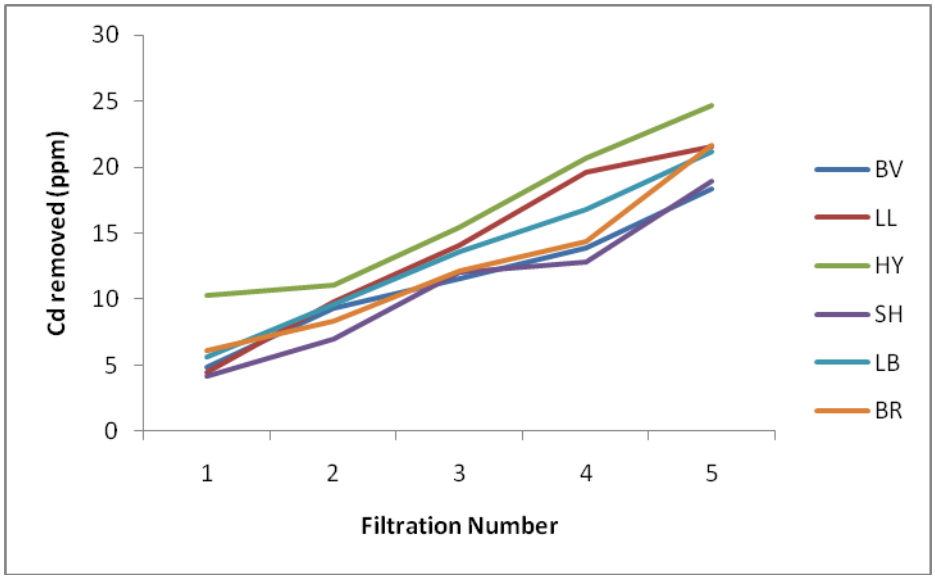

Figure 8. Comparison of breed's efficiency, mean cadmium removal (ppm) by breed per filtration

6. Discussion

It was the hypothesized in this study that the Hungarian Yellow's eggshells would work the most efficiently at filtering the cadmium out of the drinking water. After testing 150 samples, the statistics showed that the Hungarian Yellow was in fact significantly different from BR, SH, BV (see Table 3). LL and LB were slightly better than BR, SH, and BV but did not prove to be significantly different from HY. This begs the question as to why the Hungarian Yellow was the most efficient at filtering the cadmium from the drinking water. My hypothesis to explain this is that an eggshell is made up of three primary layers; the shell membrane, the mammillary layer (or spongy layer) and the palisade layer. The palisade layer is the outer protective barrier for the shell. In eggs where the chick is allowed to hatch, the palisade layer has to be thick enough so that the eggshell doesn't break but thin enough that the chick can still break through. With this being said, in the commercial production of eggs the farmer's have no need to concern themselves with a chick trying to break through the eggshell. So over the years the producers of these eggs have wanted to make the transportation of their produce as efficient as possible, so the palisade layer has become much thicker. However, the palisade layer of the eggshell has gotten thicker at the expense of the mammillary layer, which is the source of calcium for a developing chick. As previously stated research done surrounding this topic came to the conclusion that it was the calcium carbonate in the eggshells that were binding with the cadmium to remove the pollutant from the water. Because Hungarian Yellow is a heritage line chicken their eggs are not mass produced so their mammillary layer is considerably thicker than that of the commercial breeds. This leads me to believe that the heritage line chickens (specifically the HY) had more calcium carbonate readily available to bind with the cadmium, due to its thicker mammillary layer, which made it more efficient then the other breeds eggshells.

As seen in Figure 1- Figure 6, as more filtrations were performed the concentration on average of cadmium removed from the wastewater solution was increasing. There was a generally linear relationship of cadmium removed per filtration (see Figure 8.) which could mean the eggshells had not reached their saturation level. After running the statistics it was found that there was in fact no significant interaction between the rep and the breed (see Table 2.). This does in fact prove that the eggshells had not reached their saturation level, so in theory (as shown by the statistics) as more and more filtrations continue to be done, the eggshells will continue to remove

the cadmium from the wastewater solution until the eggshells reach their saturation level or plateau at 0ppm cadmium left in the solution. The saturation level of the eggshell refers to the maximum concentration of cadmium the eggshell has the ability to remove from the wastewater solution.

On average HY removed approximately 24.7ppm cadmium from the wastewater solution, and this was after the eggshells had been in direct contact with the cadmium wastewater for only five minutes (a total of five filtrations). Even in the most concentrated of all polluted areas, the highest concentration that has been reported to date is between 30-35ppm cadmium. Comparing the experiment to this real world situation, after only five minutes of being in contact with cadmium wastewater solution, the eggshells removed 80.7% of all cadmium that would be found even in the most highly polluted areas. This figure in itself proves the relevance and efficiency of the eggshells in a real world setting. And to add to that, the eggshells had not reached their saturation level (as proved by the statistics) so with more filtrations that percentage would get higher, until again it could theoretically reach 100% cadmium removed. With this figure one could confidently say that there is a very viable remedy to cadmium pollution; which ultimately will improve upon the quality of drinking water in developing nations and may also serve as a cost efficient solution for the governments of developed nations.

7. Conclusion

There are many filtration devices currently available that serve the purpose of filtering cadmium out of water. However, these devices may exist but they are not universally accessible; developing nations do not have the money nor the time to invest in proper filtration techniques. But should this mean that the citizens inhabiting these countries have a basic human right revoked - the right to clean drinking water? The answer is no, and with the help of this study these citizens may no longer have to drink contaminated water.

In conclusion, the hypothesis was proven correct, the Hungarian Yellow would work the most efficiently at removing cadmium from water. Although the Hungarian Yellow worked the best, the other breeds of chickens also worked extremely well. After 5 filtrations, the eggshells removed anywhere from 18.3 ppm to 24.70 ppm. The eggshells had been in contact with the wastewater solution for a total of 5 minutes. The results showed that the eggs had not reached

their saturation level, which means that with more passes through the eggshell filter more cadmium would be removed.

75ppm is not a level of cadmium that you would see even in the most polluted areas, the highest concentrations that have been reported being 30-35ppm. The Hungarian Yellow, after 5 filtrations, filtered out on average approximately 24.70ppm. This means that the eggshells can be considered extremely efficient in the sense of real world application, removing 80.7% of the amount of cadmium that would be found in an extremely polluted environment. It is noted that levels are typically well below 30ppm however the health effects even at low levels can be serious with prolonged exposure leading to death.

With a worldwide chicken population of approximately 15.8 billion, chickens can be found almost anywhere except for Antarctica and the high Arctic. Wherever there are humans you will find chickens. This increases the practicality of the study even further, given that there are 15.8 billion chickens in the world, eggshells are first and foremost one of the world's largest waste products. Eggshells are readily available and because they are a waste product will, in most cases, cost little to no money.

Eggshells are the simple, practical and a cost efficient remedy to cadmium pollution. This study has shown that eggshells have the potential to improve the quality of living in developing nations as well as developed nations.

8. References

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10. Future Plans

The next step in the study would be to conduct an experiment based solely on determining the saturation level of the eggshells. Through this it could be determined when/if eggshells can be used to filter out all cadmium using only one set of eggshells or if multiple sets of eggshells are needed to reduce the concentration of cadmium below the World Health Organization's standards. It must be known that if one set of eggshells is not sufficient to get the drinking water to meet WHO standards, the eggshells can still be considered extremely efficient as they are able to remove a high percentage of the cadmium concentration.

A beneficial addition to the study would be to determine the chemistry behind why the eggshells are so efficient at filtering cadmium.

Finally, having the study expanded to not only include cadmium, but experimenting with other heavy metals as well; to see if the eggshells are as efficient with these metals as they are with cadmium.