

Chemical Engineering for Good Challenge

2016 Competition Submission

How Chemical Engineering Can Be Applied to Solve World Problems on a Micro Scale

University Name & Location: Miami University, Oxford, Ohio

☒ EWB-USA Student Chapter: or ☐ AIChE Student Chapter (outside USA)

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List all team AIChE members; identify as student or professional (at least one AIChE member per team is required) Note: *membership in an AIChE student chapter is not sufficient, must be a member of AIChE with a membership ID number.*

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Title of Submission: Keratin-based Adsorbents for the Removal of Heavy Metals from Water

Submission Type: ☒ underutilized technology ☐ technology toolkit

Option 1: Recommendation of the application of a specific technology, available today, that is not currently utilized in IDP projects.

A. Define the specific community problem being addressed

The shortage of clean water has become a major crisis. In many third world countries, people do not have access to clean water. Currently 884 million people do not have access to safe water supplies.¹ These people are forced to settle for any water that is available to them. This often leads to a lack of clean drinking water, poor hygiene practices, and little to no sewage systems. As a result of this people often defecate in the open which in turn can further contaminate the surrounding water.² Approximately 840,000 people die each year due to a lack clean water.¹

Toxins and heavy metals, such as mercury, lead, cadmium, and copper can be found in our drinking water in trace amounts. The most common of metals found in water are lead and copper. Our water sources can easily be contaminated through rain water as they percolate through rocks and other materials. Although the EPA regulates our water to meet a set standard, other countries do not have this benefit.³

In addition to the benefits clean water has on people's lifestyles, having clean water also has positive economic impacts. Benefits stem from many areas. The amount of health services needed would be reduced as people no longer contract diseases related to contaminants in drinking water. The amount of productive work time in countries would increase, as people would no longer be sick as often, and they would not die as early. In the United States, for every dollar spent on clean water, a two dollar economic return can be expected.³ Figure 1 below shows the benefit to cost ratios in different regions when improving sanitation. All of the benefit to cost ratios are greater than one, which indicates that the benefit of having access to clean water is greater than the cost of obtaining it.

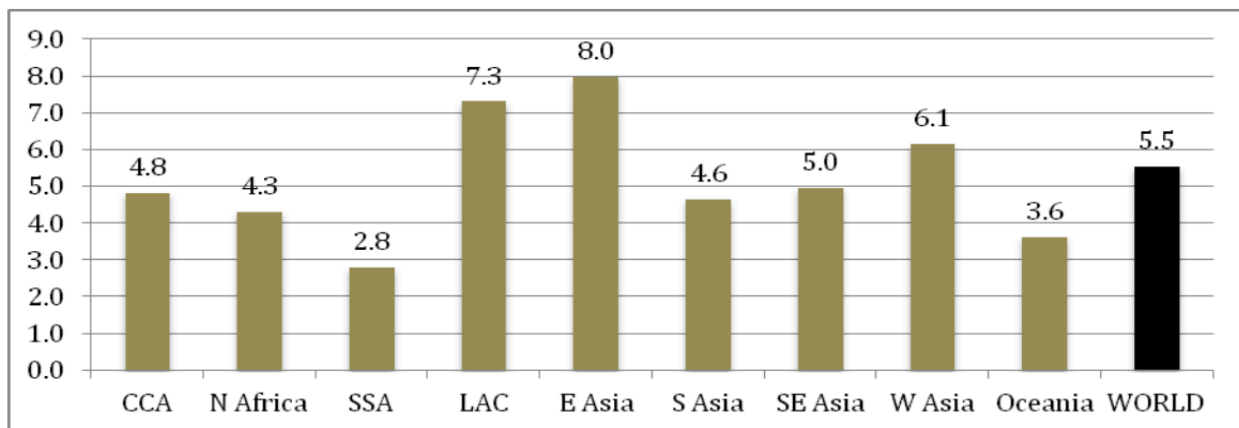


Figure 1. Benefit-cost ratios of interventions to attain universal access of improved sanitation, by region (2010).²

Many of the procedures used to filter water into clean drinkable water are either very expensive or require materials that an average person cannot easily obtain. Keratin can be easily found in cheap materials such as chicken feathers, hair, or wool from sheep or unwanted clothing.⁴ Over 5 million tons of keratin wastes are generated annually worldwide.⁷ It's binding properties allow it to extract metals, such as lead and copper, from unclean water.⁵ This extraction works because of the presence of several functional groups on the keratin protein, most notably the ionisable groups found on beta-keratins found in the structure of chicken feathers.⁶

The keratin that will be used for this project is a "hard keratin" or a keratin extracted from the structural parts of feathers. This species of keratin is rich in cysteine, and is "characterized by high levels of protein cross-linking."⁶ This increased cross-linking will promote the formation of an aerogel, which is the primary keratin structure that will be used in this project. Our goal is to produce a high porosity, high surface area keratin material to extract harmful metals from contaminated water in a practical and affordable way.

Chicken feathers are produced in large amounts in poultry processing, and are often disposed of in environmentally and economically inefficient ways. These feathers are high in proteins including keratin, which could be turned into a valuable product.⁴ If keratin were extracted from the chicken feathers before their disposal and used to remove metals from water, it could be turned into an environmentally and economically practical product.

B. Describe the specific technology and how it is based on chemical engineering principles; provide electronic copies of or links to references (papers, descriptions of commercial applications & offerings, patents, other supporting material)

The technology used for this project is adsorption on a novel adsorbent, a keratin aerogel. Therefore, both adsorption and materials science are used in this project. An aerogel is a highly porous material prepared by removing the liquid phase from a gel. One physical advantage of aerogels is their porosity. Large porosity allows aerogels to be potentially great water filters; aerogels will enhance accessibility of heavy metals to bonding sites on the protein, and they are able to filter out larger contaminants.⁸

Keratin has been found, via literature, to have the capacity to adsorb heavy metals from water.⁵ Its capacity to remove metals is due to its nanostructure and metal binding capacity protein sites. The protein is also stable over a range in pH and has good tensile strength which is beneficial for design. Compared to other protein fibers, keratin fibers are greater in strength and absorbability. A study at the University of Nevada Reno, keratin can successfully adsorb Copper as well as other metals such as Hg, U, Cr, Ni, Sr & Cs.¹⁴ The protein is insoluble in water which is a necessity for our project goal. It also has a

high surface area, which is an advantage in reactivity. Another study at Tohoku University has shown that keratin is able to remove precious metals (gold and platinum) in a high yield and short contact time.¹⁵

Keratin aerogels can be made by preparing a 15 wt% solution of keratin in water. This solution is frozen overnight at -80 Celsius, and is then put into a lyophilizer for several days to dehydrate the gel. Aerogels can also be made using supercritical drying. Rather than freezing the samples, they would be heated and pressurized until it reaches its critical point. At this temperature and pressure, the surface tension of the liquid disappears. This allows the liquid to be removed from the gel. Once only solid material remains, the system is depressurized and returned to ambient pressure.⁹

Keratin can be extracted from a variety of sources including chicken feathers, wool, and hair. For our research, we will primarily focus on chicken feathers as a resource. Once the chicken feathers have been collected, they are cleaned with ether and water. From there there a number of methods in the literature that could be used or modified. Different chemicals may be used for this process, but the main methodology involves a reducing agent to break chemical bonds, and another agent to form the protein precipitate.

C. Describe what kind of data would be required to design / customize this technology for ISP projects

The data required to design and customize this technology includes both thermodynamic adsorption capacity and kinetic adsorption capacity of keratin for heavy metals. Adsorption isotherms will be used to assess the thermodynamic adsorption capacity of keratin at various temperatures. The sand filtration process with a keratin layer in the sand bed will be used to assess the kinetic or working capacity of keratin for metals. Both processes are explained in more detail below. Ground water would also need to be tested to assess whether naturally occurring minerals will impact the effectiveness of the keratin aerogel.

Adsorption Isotherms

Adsorption isotherms relate the mass of pollutant (metal ion) adsorbed per unit mass of adsorbent (keratin aerogel). Adsorption isotherms show how effective keratin is as an adsorbing material for metal pollutants. In our study, we have used copper ion as a representative metal contaminant. To make an isotherm, batch solutions of varied copper solutions were contacted with a measured mass of keratin aerogel for a given period of time, and then the copper ion concentrations were re-measured. The mass of copper adsorbed was calculated by the difference between initial and final copper concentrations and the volume of the sample. The adsorption capacity is the mass of metal adsorbed per mass of keratin aerogel in the sample.

We are currently in progress of collecting adsorption isotherm data. Our progress is shown in Figure 2 below. Noted is that our keratin aerogel can adsorb approximately 20 mg Cu / g keratin.

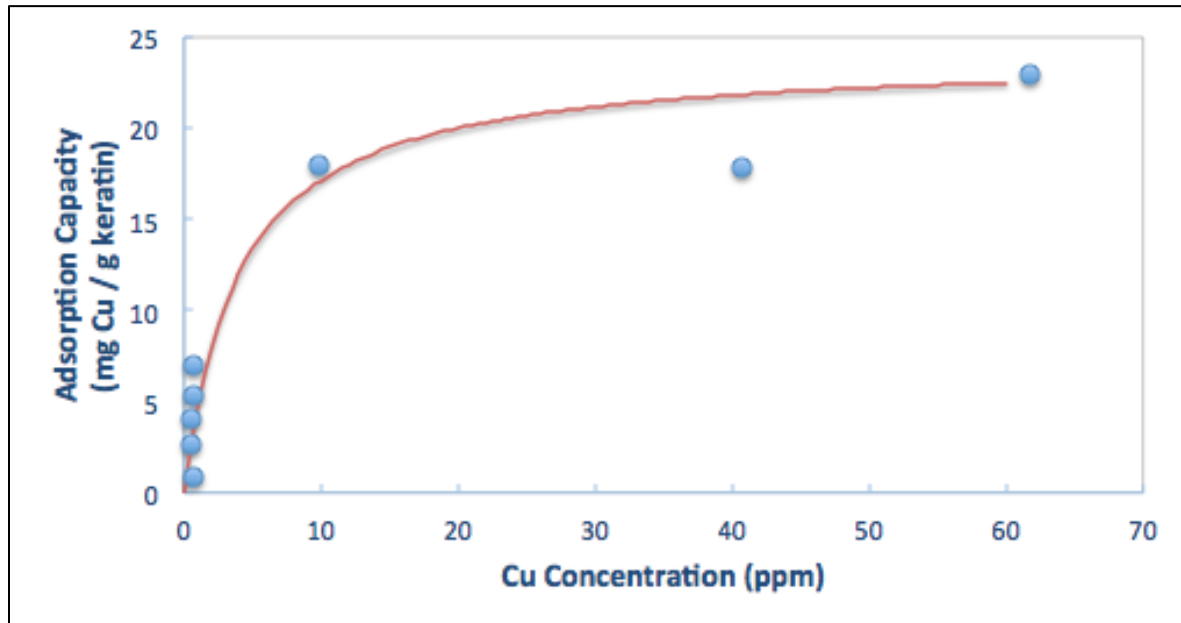


Figure 2. Adsorption Capacity versus equilibrium Copper Concentration.

The copper concentration was measured using an Ion Selective Electrode (ISE). Solutions of varied copper ion concentrations were used to calibrate the ISE, according to the operating procedures of the ISE. It was observed that the obtained values changed with time from the addition of the Ionic Strength Solution. To account for this variation, a standard calibration curve was made each time measurements were taken.

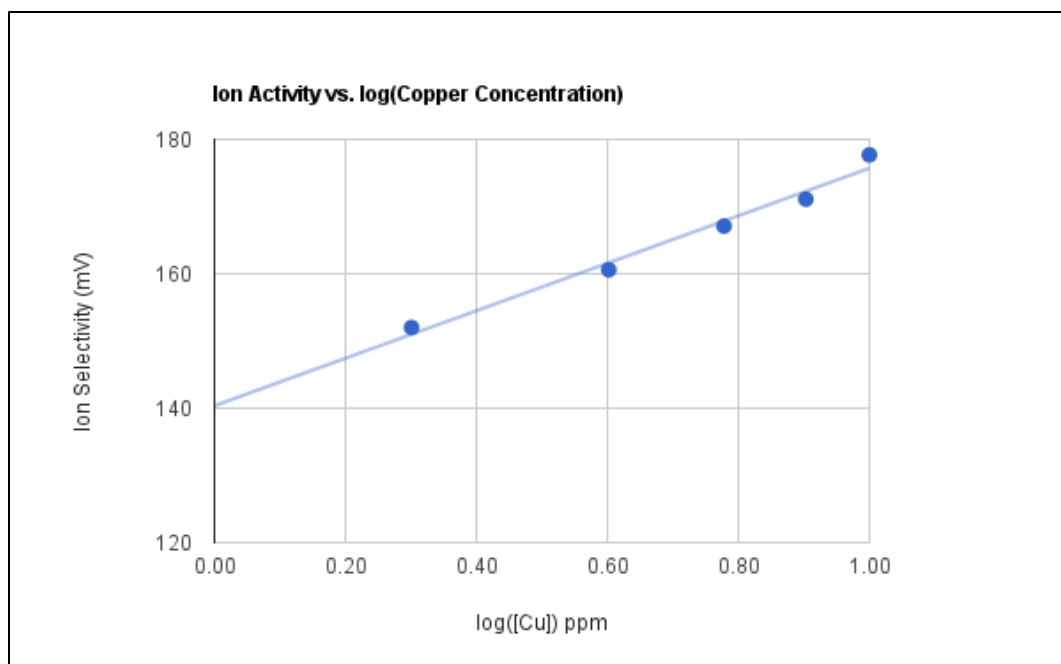


Figure 3. Calibration Curve for Ion Selective Electrode.

Trials were also conducted to determine the minimum volume of sample required to run the Ion Selective Electrode effectively. Because the amount of keratin available is limited it will be necessary to use the minimum volume required in the batch tests. Although it was determined that for batch trials the volume used should ideally be between 75 and 100 mL to get the most accurate results with the ISE, we are limited with the amount of keratin available to us. Therefore, we used 15 mL copper ion solution sample with 20 mg of keratin in each batch adsorption test with copper ion solution. The ISE was also calibrated, then, using 15 mL standard solutions of copper ion in water. From the initial tests we were able to generate a calibration curve and an initial adsorption isotherm.

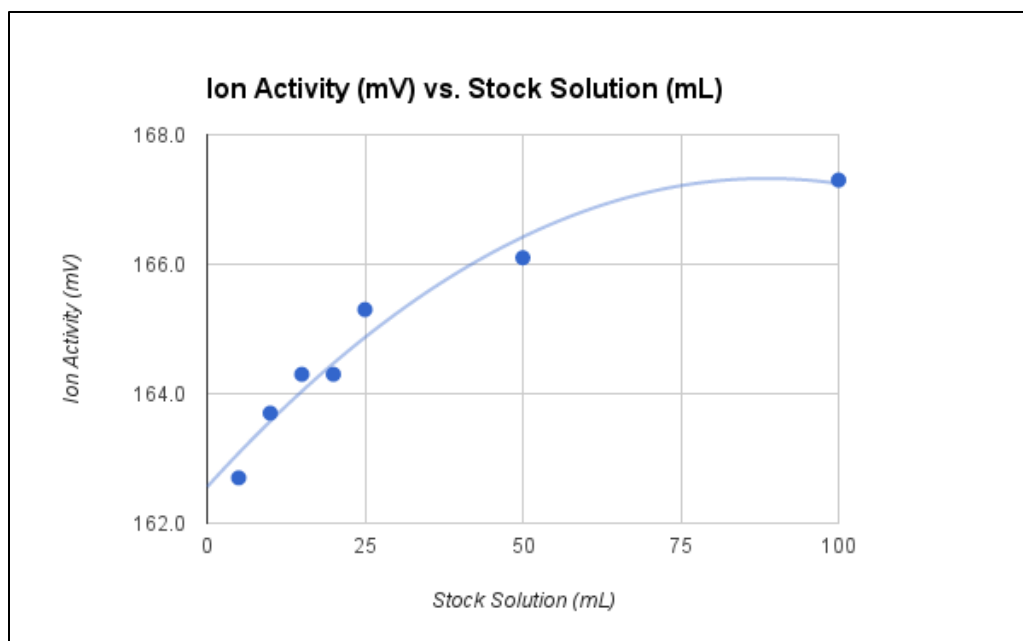


Figure 4. Minimum volume required for Ion Selective Electrode.

The effect of the ionic strength stabilizing solution (HI 4000) on the ISE measurement of copper was also investigated. The operating manual for the ISE recommends 2 mL of ionic strength solution is added per 100 mL of sample. Since our experiments will use smaller samples sizes (15 mL), we will scale the amount of ionic strength accordingly. However, we assessed the ISE output to a constant copper ion concentration as a function of ionic strength solution added, and we found that 3 mL ionic strength solution per 100 mL would give us the most consistent results with the ISE.

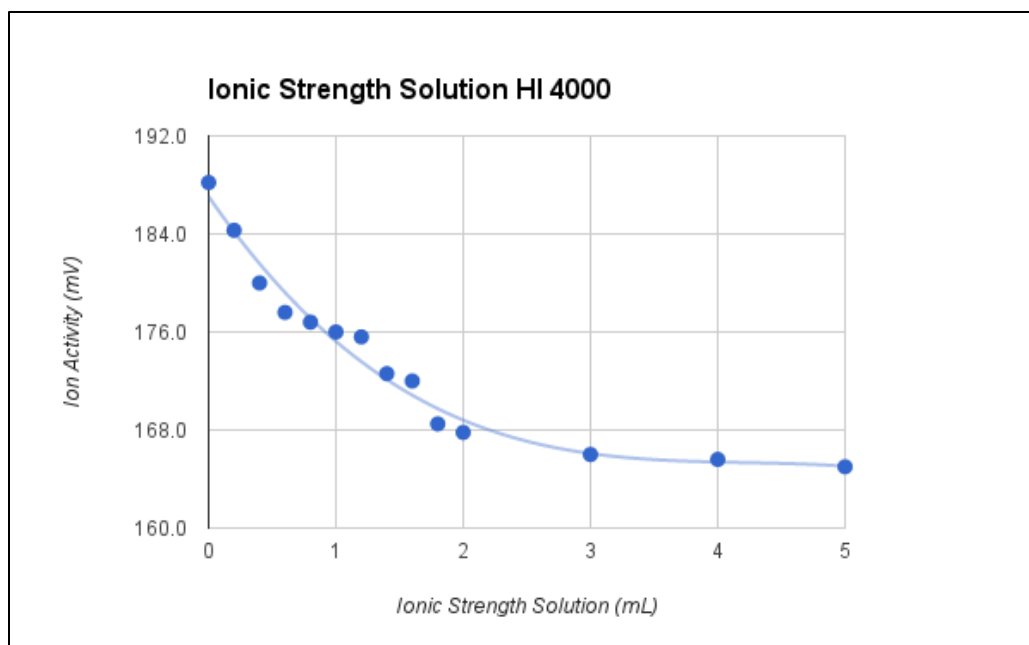


Figure 5. Effect of volume of ionic strength solution HI 4000 on ion selectivity.

Sand Filtration System

A sand filtration process will be constructed with a keratin aerogel layer for filtering drinking water. Sand filters are often used to remove particulate matter from drinking water, and so the added layer of keratin adsorbent will also remove metals from drinking water. Flow through the sand bed will be characterized as a function of pressure head, and this data and Darcy's law will be used to determine the permeability of play sand. Our results will form a basis on which we can design and construct a slow sand filter that will filter approximately 25 liters per day and can be implemented affordably in developing communities. The sand filter would contain an amount of the keratin aerogel suitable to the size of the sand bed, the amount of water to be filtered, and the concentration of copper in the water sample. Our keratin-based sand bed performance will be tested and assessed using pond water spiked with selected metals. Success will be measured by the extent of metal removal and particulate removal from the water at a water treatment rate of 25 liters per day.

Keratin Extraction

After demonstrating the feasibility of utilizing a keratin-based sand filtration system for treating drinking water, we will demonstrate that the keratin extracted from a common waste material, such as chicken feathers, can also be used as an adsorbent for metals in water. Washed and dried feathers will be cut into small pieces and soaked in 100 mL of a solution containing 8M urea, 0.5 M sodium metabisulfite, and NaOH to bring the pH up to 6.5. The entire solution will then be placed in a cellulose tube for dialysis with distilled water for three days. The keratin aqueous solution is then filtered with a 5 micrometer pore

size and cast onto a polyester plate for drying. This results in a solid keratin that will be converted to an aerogel and used for adsorption of heavy metals.⁷

Since keratin is not readily available and easily accessible to other countries, our goal is to extract keratin in a procedure that can be easily replicated by others, with materials that are more likely to be accessible to other countries. For this study, we are planning to extract keratin from chicken feathers since they are easily accessible and in abundance.

Keratin Characterization

The keratin materials will be characterized using several methods, including Thermogravimetric Analysis (TGA) (TA Instruments, Q500), Differential Scanning Calorimetry (DSC) (TA Instruments, Q2000), Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM).

TGA measures the mass of a sample as a function of temperature. As temperature increases from room temperature to 800 C, the sample degrades, and mass is lost. The mass lost vs temperature profile can give us information on how processing keratin can affect various bond strengths.

DSC measures the flow of heat energy to and from a sample as its structure changes with temperature. These results provide insight into changes in bonding or structure as the keratin is converted to an aerogel. The temperature range of our DSC is -80 C to 300 C, giving us a large range of temperatures in which to characterize our keratin aerogels.

FTIR can be used to assess the functional groups within keratin, and changes of functional groups due to raw materials and processing of the keratin. We plan to use FTIR to help us understand the roles of each processing step with respect to structural changes of the keratin adsorbent.

SEM will be used to visualize the keratin powder (both purchased and extracted from chicken feathers) before and after it is processed and converted into an aerogel. With SEM, we will be able to better assess the porosity and morphology of the keratin adsorbent.

Prototype Design, Construction, and Demonstration

A prototype keratin-based sand filtration system will be designed, constructed, and demonstrated. Based upon the demonstration and effectiveness of the keratin-based sand bed for removing particulate matter and metal contaminants, modifications to the design will be made in an iterative manner. Once the required effectiveness of the process for treating water is demonstrated, a scaled up model will be

designed. The scale up model will be considered the commercial model that would be used by the clientele.

D. Describe why this technology would be appropriate for implementation in partner communities. Include consideration of technical, maintenance, financial, and cultural sustainability. Provide estimated typical costs for initial installation, maintenance, and operation.

From the "Review of Heavy Metals in the African Aquatic Environment" it is clear that there are regions in Africa that have dangerous amounts of heavy metals. Specifically the Sasha Str region of Lagos, Nigeria had a lead concentration of 0.1 ppm.¹¹ The EPA declared that the maximum contaminant level (MCL) for lead is 0.015 ppm and the maximum contaminant level goal (MCLG) is 0 ppm.¹² This is one extreme case; however, cross referencing the article written by Biney and the EPA recommendations heavy metal exposure in African water sources is a problem.

The goal of this project is to use simple methods to extract keratin from chicken feathers, and then implement a keratin layer into slow sand filters. Sand filtration is already a viable water sanitation method due to the widespread access to the necessary supplies. Preliminary results suggest that keratin has the ability to adsorb heavy metals on small scale levels. The goal moving forward is to attempt to recreate keratin extraction methods from literature, and scale up this process. The current project scope is for filtration of 25 liters per day.

Technical and maintenance sustainability would be addressed through extensive education. By training operators in the community to extract keratin from the normally wasted chicken feathers and implementing into a sand filter. This could be implemented into existing water systems or built from the round up if no distribution network existed in the community. Assuming that all supplies, especially chicken feathers, are readily available to the community this project should be affordable and sustainable. By developing community relationships with the same methods as Engineers Without Borders it should be possible to begin implementing these filters as early as June 2018.

Financial and cultural sustainability would be ensured through involving the community in each step of the process. An assessment would first be done to identify which partner communities would be prime candidates for implementation. This would address the availability of supplies in or around the community, If a community met the necessary criteria, the project would be owned and driven by the community. If done through Engineers Without Borders there would be other stipulations that ensure ownership on all sides. The community would be required to contribute a minimum 5% cash contribution. All parties involved (EWB chapter, community, local NGO, local government) would sign partnership

agreements laying out the specific roles and responsibilities of each party. The EWB chapter would agree to a five year commitment to the community partner to allow for long term project planning, as well as conducting regular monitoring, evaluation and lessons learned to improve current and future work.

The CDC estimates that average sand filters lasting for 10 years will cost \$100 or 0.068 cents per liter.¹³ The initial cost is estimated at \$15-\$60, but by using locally sourced materials we would aim to be in the lower end of this range. Adding the batch keratin adsorption will increase the maintenance costs, as compared to a typical sand filter. The specific costs would vary based on water use, contamination levels, and the source of the keratin; but based the market price of keratin in the US the expected cost is approximately 5 cents per liter. We expect that through continued work this price could be slashed 10 fold as new extraction methods are explored. The current extraction methods are expensive, but also produce a final product that is likely more pure than what is needed. As we continue this research a main goal is to simplify this process to make it more accessible to developing communities.

Works Cited

1. "11 Facts About Water in the Developing World." *DoSomething.org*. N.p., n.d. Web. 12 Oct. 2016.
2. Hutton, Guy. *Global Costs and Benefits of Drinking-water Supply and Sanitation Interventions to Reach the MDG Target and Universal Coverage*. Geneva, Switzerland: World Health Organization, 2012. Print.
3. Pedersen, T. L. "Metals In Your Drinking Water." *Metals In Your Drinking Water*. N.p., June 1997. Web. 12 Oct. 2016.
4. Gupta, A.; Perumal, R. & Yunus, R.B.M. Extraction of Keratin Protein from Chicken Feathers. Universiti Malaysia Pahang, Faculty of Chemical and Natural Resources Engineering.
5. Kar, P., & Misra, M. (2004). Use of keratin fiber for separation of heavy metals from water. *Journal of Chemical Technology and Biotechnology*, 79, 1313-1319.
6. Ghosh, A., & Collie, S. (2014). Keratinous Materials as Novel Absorbent Systems for Toxic Pollutants. *Defence Science Journal DSJ*, 64(3), 209-221. doi:10.14429/dsj.64.7319
7. Aluigi, A.; Tonetti, C; Vineis, C; Tonin, C. & Mazzuchetti, G. Adsorption of copper (II) ions by keratin/PA6 blend nanofibres. *Euro. Pol. J.*, 2011, 47(9), 1756-1764.
8. Hariharan, S., Heom, K., Quien, M., and Shukla, S. (2015) Nanotechnology of Foam: Water Filtration 1–11. (<http://soe.rutgers.edu>) (Hariharan 2015)
9. How is Aerogel Made? *Aerogel.org RSS*. WordPress. (<http://www.aerogel.org>)
10. Baek, D.H., Ki, C.S., Um, I.C., and Park, Y.H. (2007). Metal ion absorbability of electrospun wool keratose/silk fibroin blend nanofiber mats. *Fibers and Polymers*, 8(3), pp. 271-277.
11. C. Biney, A.T. Amuzu, D. Calamari, N. Kaba, I.L. Mbome, H. Naeve, P.B.O. Ochumba, O. Osibanjo, V. Radegonde, M.A.H. Saad. (1994). Review of Heavy Metals in the African Aquatic Environment. *Ecotoxicology and Environmental Safety*. 28(2), pp. 134-159.
12. Table of Regulated Drinking Water Contaminants. (n.d.). Retrieved November 13, 2016, from (<https://www.epa.gov>).
13. Slow Sand Filtration. (2014). Retrieved November 16, 2016, from (<http://www.cdc.gov>).
14. Misra, M., Kar, P., Priyadarshan, G. and Licata, C. (2001) 'Keratin Protein Nano-fiber for Removal of Heavy Metals and Contaminants', *MRS Proceedings*, 702. doi: 10.1557/PROC-702-U2.1.1.
15. K. Suyama , Y. Fukzawa and H. Suzumara , "Biosorption of Precious Metal Ions by Chicken Feathers", *Applied Biochemistry and Biotechnology*, Vol. 57/58, 1996, pp. 67–74.