

# **Removal of Arsenic from Water**

## **Using Ground Clam Shells**

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### **ABSTRACT**

Arsenic is a toxic chemical that is known to cause cancer. This metalloid is soluble in water and exists as arsenite or As (III) and arsenate or As (V). As (III) is more difficult to remove from water than As (V) and is most commonly found in groundwater.

Groundwater contaminated with arsenic is a major health problem in many countries, especially in Bangladesh, where it is pumped from wells and is used as drinking water. The current methods for arsenic removal are costly and not easily applicable to small household facilities.

This study examined whether pulverized clam shells would be effective in removing arsenic from water for potential use as a filter medium in households. The parameters that were tested were amount of clam shells to As (III) in solution ratio, clam shell particle size, and type of clam shell used. Nearly 70% removal of arsenic was achieved. Removal increased with smaller clam shell particle size and with higher clam shell to arsenic ratio. Non-pigmented clam shells had higher rates of removal than pigmented ones.

Future research would determine the optimum particle size, the optimum clam shell to initial As (III) ratio, and the best preparation methods for non-pigmented types of clam shells. Optimization of these parameters could result in even higher removal of arsenic from water.

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### **1. INTRODUCTION**

Arsenic is a semi-metallic element that is naturally occurring in various geological formations. It is mainly found in shale rock, which points to arsenic's preferential adsorption on clays, and in sulfide minerals (such as pyrite) that are prevalent in the earth's crust. When water comes into contact with these rocks and minerals on the earth's surface and in the subsurface, a fraction of the arsenic dissolves in the water provided the chemical conditions are appropriate for dissolution to take place. Arsenic in surface water and in groundwater occurs mainly in the following two ionic forms: As (III) or arsenite and As (V) or arsenate. Under reducing conditions, which usually occur in deep groundwater, arsenic is encountered in the form of As (III). In oxidizing environments, the As (V) form prevails. Besides its natural occurrence,

arsenic is also introduced into groundwater as a result of industrial processes (for example, metal mining) and as waste following the use of arsenic containing products, such as herbicides, insecticides, and wood preservatives (1).

Arsenic is toxic and it is a human carcinogen. Chronic exposure to arsenic at very low concentrations is known to increase the risk for developing various forms of cancer, such as bladder, lung, and skin cancer (3). Exposure to higher concentrations may result in various skin ailments, such as blackfoot disease. Although it is not yet known which form of arsenic is mostly responsible for inducing cancer, recent research indicates that As (III) is probably the most toxic, carcinogenic form of arsenic (2). The maximum allowable concentration of total arsenic in drinking water, as set by the World Health Organization, is 10 parts per billion (ppb) (3).

Groundwater that is contaminated with arsenic is of concern in countries such as Chile, Taiwan, Mexico, and the United States (in states such as Arizona, California, Oregon, Minnesota, Massachusetts, Maine, and New Hampshire). Groundwater contaminated with naturally occurring arsenic is a major health problem in Bangladesh where approximately 3 million wells (more than half of the country's existing wells) are contaminated. An estimated 70 million people are at risk of arsenic poisoning. The arsenic concentrations detected in the groundwater in the Bangladesh wells range from 100 to 300 ppb (4).

There are several known methods for the removal of arsenic from water. They include precipitation (as arsenic sulfide, calcium arsenates, ferric arsenate and other insoluble compounds of arsenic); co-precipitation with iron salts and adsorption onto the iron hydroxides formed; cementation (where metals such as zinc or iron replace arsenic in solution to form arsenic metal); precipitation by lime, in the presence of other metals such as iron, aluminum, and magnesium; membrane filtration; anion exchange using anion exchange resins, and activated alumina (3).

The most conventional method for the treatment of arsenic-contaminated water is precipitation with iron. This method can achieve up to 98% arsenic removal. However, prior to precipitation, the arsenic has to be oxidized to As (V) using an oxidizing agent. Similarly, in all other precipitation or co-precipitation methods, arsenic has to be oxidized to the more easily removable As (V). Also, depending on the precipitating agent, the pH of the solution has to be adjusted to the optimum precipitating conditions (3).

The present methods of removing arsenic from water either require special chemical know-how or they are complex and expensive to maintain. As a result, they are only suitable for industrial environments and large water treatment facilities. They are not suitable for household use, such as in the case of the private wells in Bangladesh. A household system devised for use in Bangladesh utilized ferric chloride co-precipitation and was field-tested in April 2000. Chemicals were pre-mixed in small plastic packets and were added to 20-liter containers containing water contaminated with arsenic. The water was then filtered through another bucket containing a sand filter. The system was able to reduce arsenic "from approximately 300  $\mu\text{g/l}$  in the well water to less than 50  $\mu\text{g/l}$ " (4). Despite the significant arsenic removal, such a system would still be cumbersome to operate in a household.

Recent research for the removal of heavy metals from water has focused on the use of waste products of biological origin to provide sorption surfaces for the metals in solution. It has been reported that, in certain cases, this process can be efficient and cost-effective because most of these materials are waste products. In one case, chemically and thermally treated crab shells were tested for the removal of anion metal complexes, including arsenic, from contaminated water (5). Cocoa shells were also used in very acidic conditions to remove lead from solution (6). Finally, activated carbon filters from pecan shells were used to remove organic pollutants, such as acetone and toluene, from industrial wastewater (7).

The use of ground, calcium-rich marine shells for the removal of heavy metal ions from aqueous solution has been studied recently at Columbia University. It has been reported that ground Quahog and oyster clam shells are capable of removing up to 98% of lead and zinc from an aqueous solution. It was also reported that the rates of removal are much higher for the calcium-rich marine shells than for limestone, which was used as a control material. The limited data collected for As (III) indicated that up to 40% of arsenic was removed after 24 hours from a 100 ppm As (III) solution (8).

The main constituent of sea-clam shells is  $\text{CaCO}_3$ . Evaluation of the content of two types of clams, the ocean quahog and the surf clam, revealed calcium content in the range of 35%-40%. The clams also contained small amounts of silicon (less than 5%) (9).

The shell material of sea clams comprises nearly 83% of the solid waste generated by the sea clam processing industry. This waste material has been used as fill material in road construction and, in its ground form, it has been investigated for use as a calcium supplement for lactating cows (9). It would be beneficial to find additional uses for the sea-clam shells given the large quantities of clams harvested and processed every year.

The purpose of this study was to examine the effectiveness of ground clam shells in removing As (III) from water, and their potential use as a filter medium in households.

## **2. MATERIALS AND METHODS**

The experiments were designed to study the suitability of ground clam shells as a medium for the removal of As (III) from water and to investigate the effect of several parameters. The parameters studied included the ground clam shell to arsenic ratio, the particle size of the ground shells, and the initial concentration of As (III) in the solution.

Two types of shells were used in this study. One type consisted of clam shells collected from seafood restaurants in New York City by a former graduate engineering student at Columbia University. The shells were originally from the Atlantic Ocean coast and were stored in tightly capped glass jars for several years. The second type of shell was collected from a beach located in the Corinthian Gulf, in southern Greece, in August 2006. These clam shells were mostly white with an elliptical shape. Both types of clam shells were manually ground using a mortar and the powder was sieved using a No. 120 standard U.S. sieve with sieve openings of  $125\mu\text{m}$  and a No. 60 standard U.S. sieve with sieve openings of  $250\mu\text{m}$ . The particles that were used in this study had a particle size of  $<125\mu\text{m}$  and between  $125$  and  $250\mu\text{m}$ .

A stock solution of 1,000 ppm As (III) was prepared by adding solid  $\text{As}_2\text{O}_3$  (Fisher Scientific) to DI water, and the pH was raised to 12.8 with the addition of concentrated NaOH (Amend Drug and Chemical Company) until complete dissolution. The pH was then adjusted to 3 with concentrated sulfuric acid (Fisher Scientific) and the solution brought to 1 liter with DI water. Solutions of different arsenic concentrations were prepared by diluting the stock solution.

400 ml of the prepared As (III) solution was placed in a 500 ml beaker and stirred at a speed level 4 with a 1 in. teflon coated magnetic stirrer. The measured amount of clam shell powder was then gradually added to ensure good mixing. The pH of the initial and final solution was measured and recorded.

For each experiment, samples were taken at pre-determined time intervals using syringes with filters of  $0.45$  and  $0.20\mu\text{m}$  pore size (much smaller than the shell size). All samples were stored in glass vials that were tightly capped. They were then analyzed for soluble arsenic content using a Buck Scientific Graphite Furnace Atomic Absorption Spectrophotometer (Autosampler model 220-AS, Furnace model 220-GF, AA Spectrophotometer model 210 VGP). The GFAAS used in this study had a detection limit of 1 ppb and a working range of 5-5000 ppb.

### 3. RESULTS

The first set of experiments examined the effect of the amount of clam shell material added to the solution on the removal of arsenic. Figure 1 shows the results for the removal of arsenic from a solution of about 500 ppb of As (III) using approximately 8 g of ground Atlantic clam shells of particle size <125  $\mu\text{m}$ . The highest removal in this experiment, with over 68 % of arsenic removed from solution, was achieved after 27 hours of mixing. The total concentration of arsenic was reduced from 523 ppb to 164 ppb. However, after 54 hours, the concentration of arsenic in solution increased to 353 ppb most likely due to re-dissolution of the arsenic adsorbed on the clam shell particles.

**Figure 1: Removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 8 g. of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$**

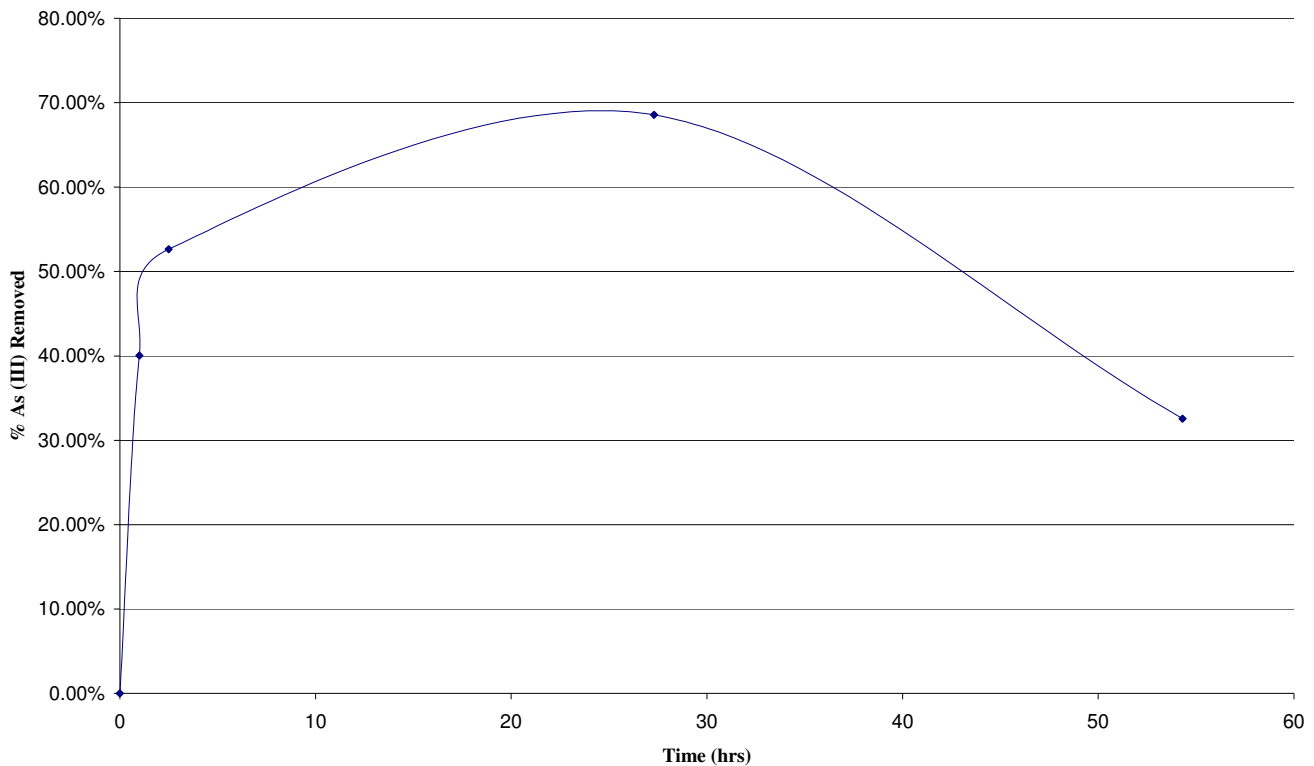
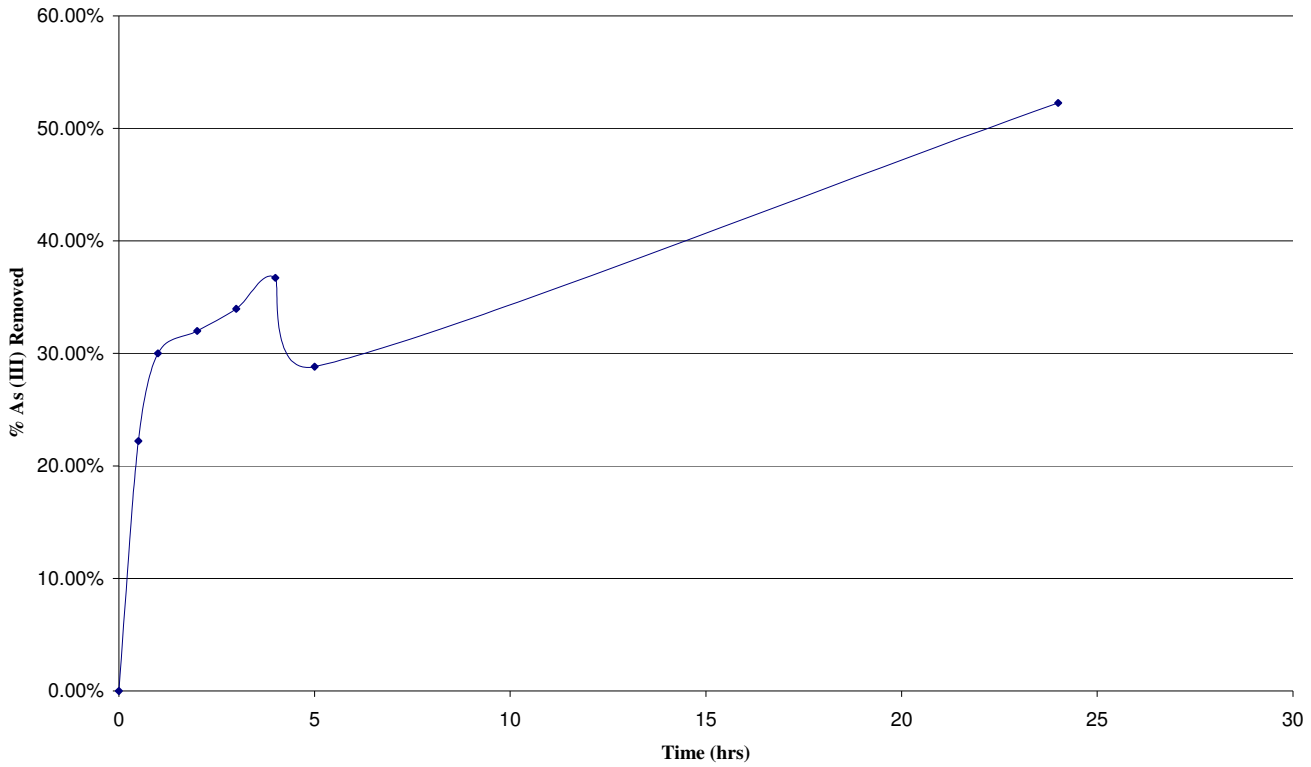


Figure 2 shows the results of the removal of arsenic from a solution of about 500 ppb of As (III) using approximately 8 g. of ground Atlantic clam shells of particle size <125  $\mu\text{m}$ , as in the experiment above. In this experiment, though, samples were taken at more frequent time intervals than in the first experiment. The removal of arsenic from this solution reached a maximum of 52 % of arsenic removed after 24 hours of continuous stirring. The total arsenic concentration in the water was reduced from 521 ppb to 249 ppb.

Figure 3 shows the results for the removal of arsenic from a solution of about 500 ppb of As (III) using approximately 16 g. of ground Atlantic clam shells of particle size <125  $\mu\text{m}$ . The removal of arsenic from this solution reached a maximum of 57 % of arsenic removed after 24 hours of continuous stirring. The total arsenic concentration in the water was reduced from 416 ppb to 178 ppb.

**Figure 2: Removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 8 g. of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$ .**



**Figure 3: Removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 16 g. of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$ .**

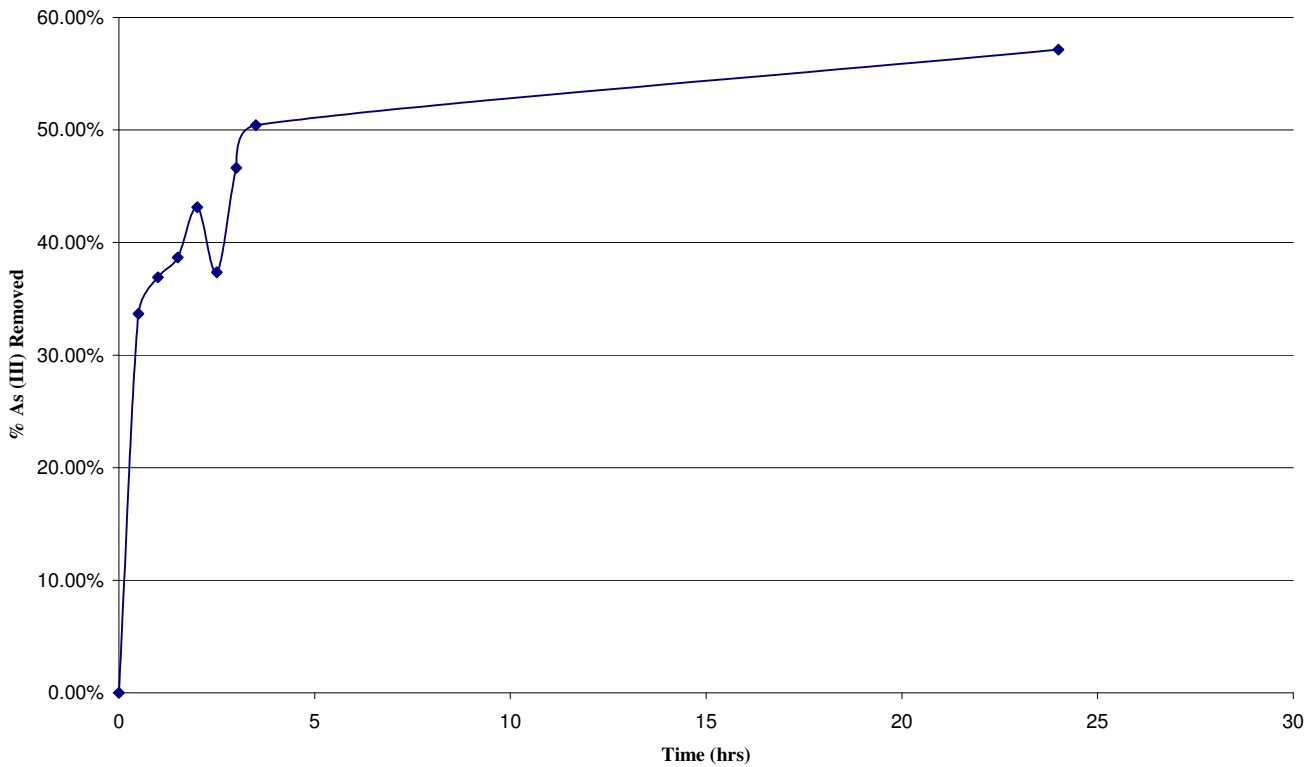


Figure 4 shows a comparison between the rates of removal of arsenic from the 8 g. and 16 g. clam shell solutions. Initially, the 16 g. clam shell solution has a higher rate of removal of arsenic than the 8 g. solution. Although the difference in the arsenic removal percentages, for samples taken at the same time intervals, was never large between the 8 g. experiments and the 16 g. experiment, the difference between these values increased at a greater rate as time progressed.

Experiments were also designed to examine the effect of the particle size of the ground clam shells on the removal of arsenic. Figure 5 shows the results for the removal of arsenic from a solution of about 500 ppb of As (III) using approximately 16 g. of ground Atlantic clam shells of particle size between 125 and 250  $\mu\text{m}$ . In this experiment, the removal of arsenic from the solution reached a maximum of 23 % after 3.5 hours of continuous stirring. The total arsenic concentration in solution was reduced from 406 ppb to 313 ppb. However, after 48 hours, the concentration of arsenic in solution had increased to 359 ppb, probably as a result of re-dissolution.

Figure 4: Comparing the removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 16 g. of ground Atlantic clam shells and 8 g., with particle size of <125  $\mu\text{m}$ .

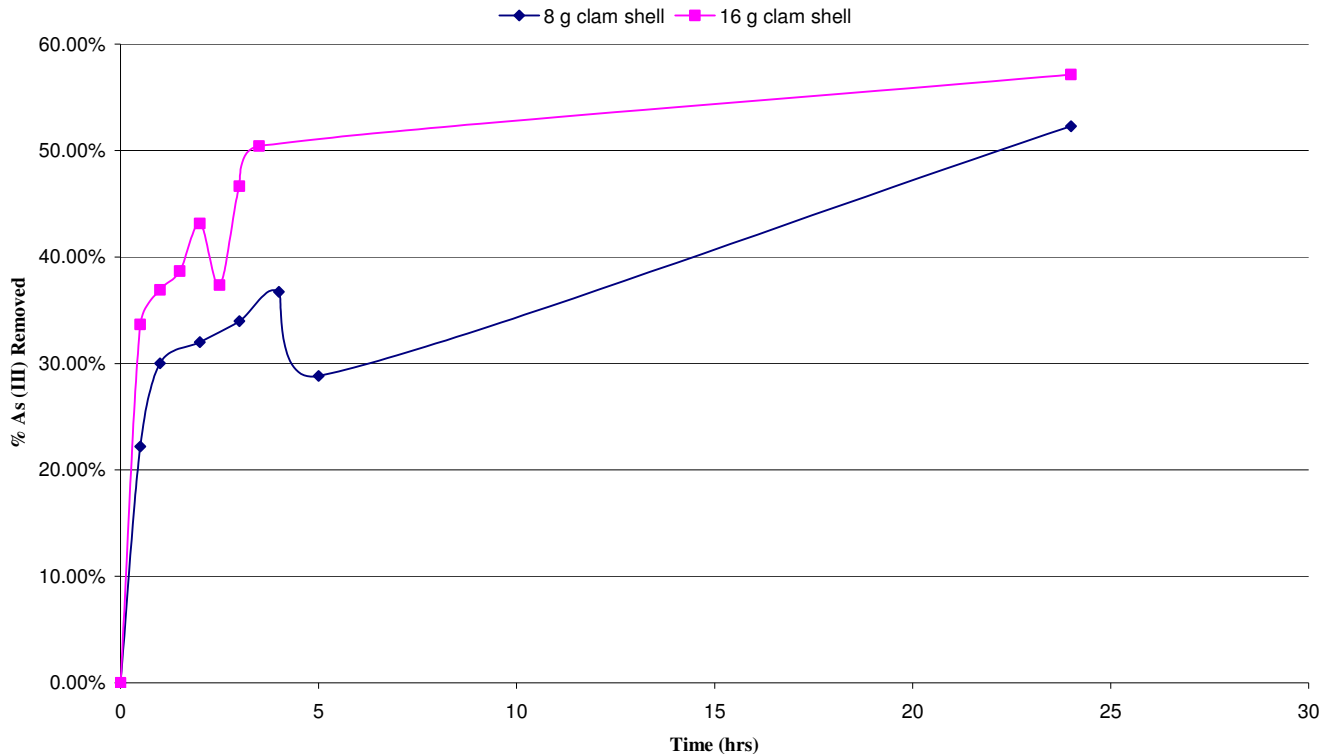


Figure 5: Removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 16 g. of ground Atlantic clam shells with particle size btwn. 125 and 250  $\mu\text{m}$ .

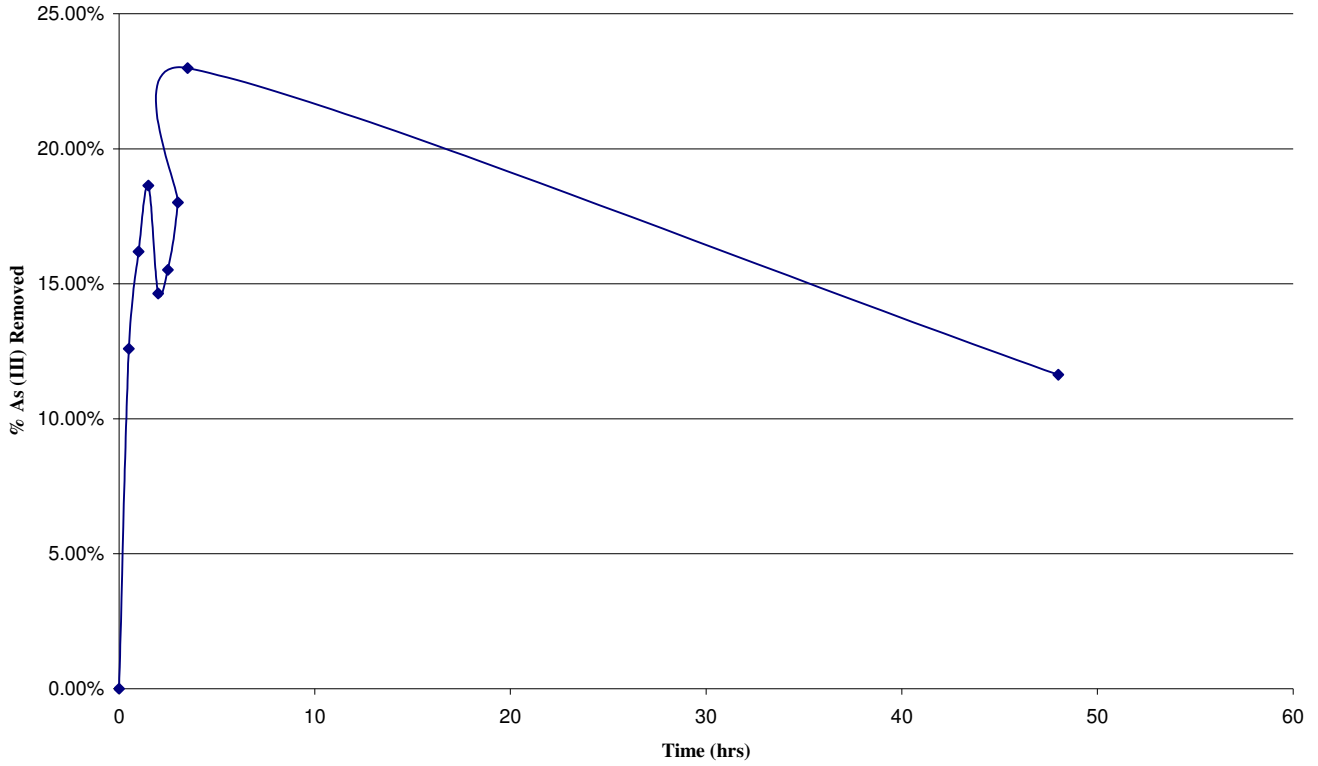


Figure 6: Comparing removal of arsenic from a solution containing about 500 ppb of As (III) using approx. 16 g. of ground Atlantic clam shells with particle size btwn. 125 and 250  $\mu\text{m}$  and <125  $\mu\text{m}$ .

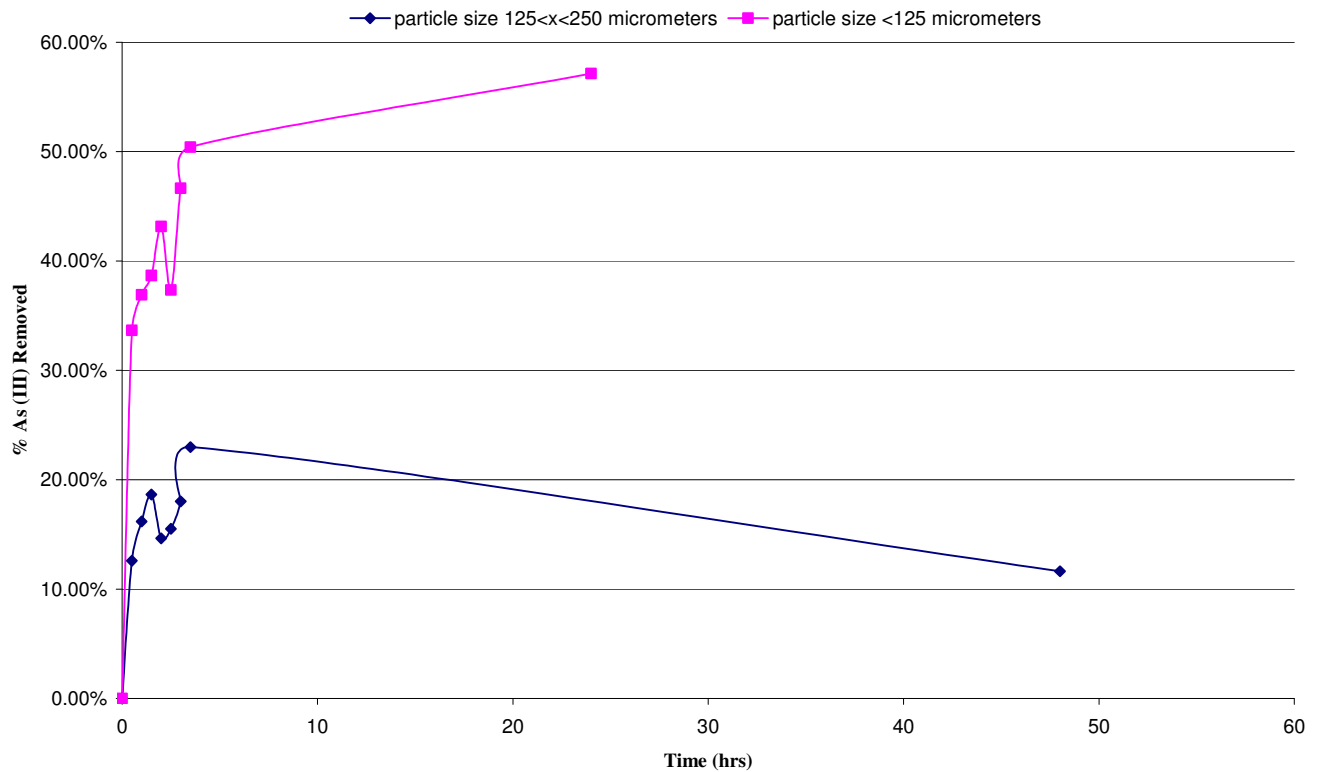


Figure 6 shows a comparison between the rates of removal of arsenic from solution using 125-250  $\mu\text{m}$  and <125  $\mu\text{m}$  particle size Atlantic clam shells. The smaller particle size achieves a much higher rate of removal in the initial half-hour and a much higher overall removal of arsenic after 3.5 hours (approximately 50 % versus 23 %) compared to the larger particle size.

Table 5 shows the results for the removal of arsenic from solution of about 125 ppb As (III) using approximately 16 g. of ground Atlantic clam shells of particle size <125  $\mu\text{m}$ . After 3.5 hours of continuous stirring, the removal of arsenic from solution reached a maximum of 43 % and the total arsenic concentration in the water was reduced from 125 ppb to 71 ppb.

**Table 5: Removal of arsenic from a solution containing about 125 ppb of As (III) using approx. 16 g. of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$ .**

Sample	Time (hrs)	Concentration of Arsenic remaining (ppb)	Percent of Arsenic removed
1	0	124.89	
2	0.5	96.43	22.29 %
3	1	79.84	36.07 %
4	1.5	75.67	39.41 %
5	2	72.36	42.06 %
6	2.5	82.89	33.63 %
7	3	71.78	42.53 %
8	3.5	71.03	43.13 %

Table 6 shows the results for the removal of arsenic from a solution of about 50 ppb As (III) using approximately 16 g. of ground Atlantic clam shells of particle size <125  $\mu\text{m}$ . The highest arsenic removal, with 55% of arsenic removed from solution, was achieved after 1.75 hours of continuous stirring.

**Table 6: Removal of Arsenic from a solution containing about 50 ppb of As (III) using approx. 16 g of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$ .**

Sample	Time (hrs)	Concentration of Arsenic remaining (ppb)	Percent of Arsenic removed
1	0	42.918	
2	0.25	41.769	2.68 %
3	0.5	39.803	7.26 %
4	0.75	33.026	23.05 %
5	1	36.931	13.95 %
6	1.25	31.846	25.80 %
7	1.5	28.505	33.58 %
8	1.75	19.215	55.23 %
9	2	30.529	28.87 %
10	2.25	21.739	49.35 %
11	2.5	25.182	41.33 %
12	2.75	34.435	19.77 %
13	3	23.449	45.36 %
14	3.25	37.606	12.38 %
15	3.5	24.437	43.06 %
16	3.75	28.762	32.98 %
17	4	30.516	28.90 %



Figure 7 shows a comparison between the rates of removal of arsenic from initial solutions with As (III) concentrations of 50, 125, and 500 ppb. The initial removal and the overall removal of arsenic from water decrease with decreasing initial As (III) concentration.

**Figure 7: Removal of arsenic from a solution containing about 50 ppb of As (III), about 125 ppb As (III), and about 500 ppb As (III), using approx. 16 g. of ground Atlantic clam shells with particle size of <125  $\mu\text{m}$ .**

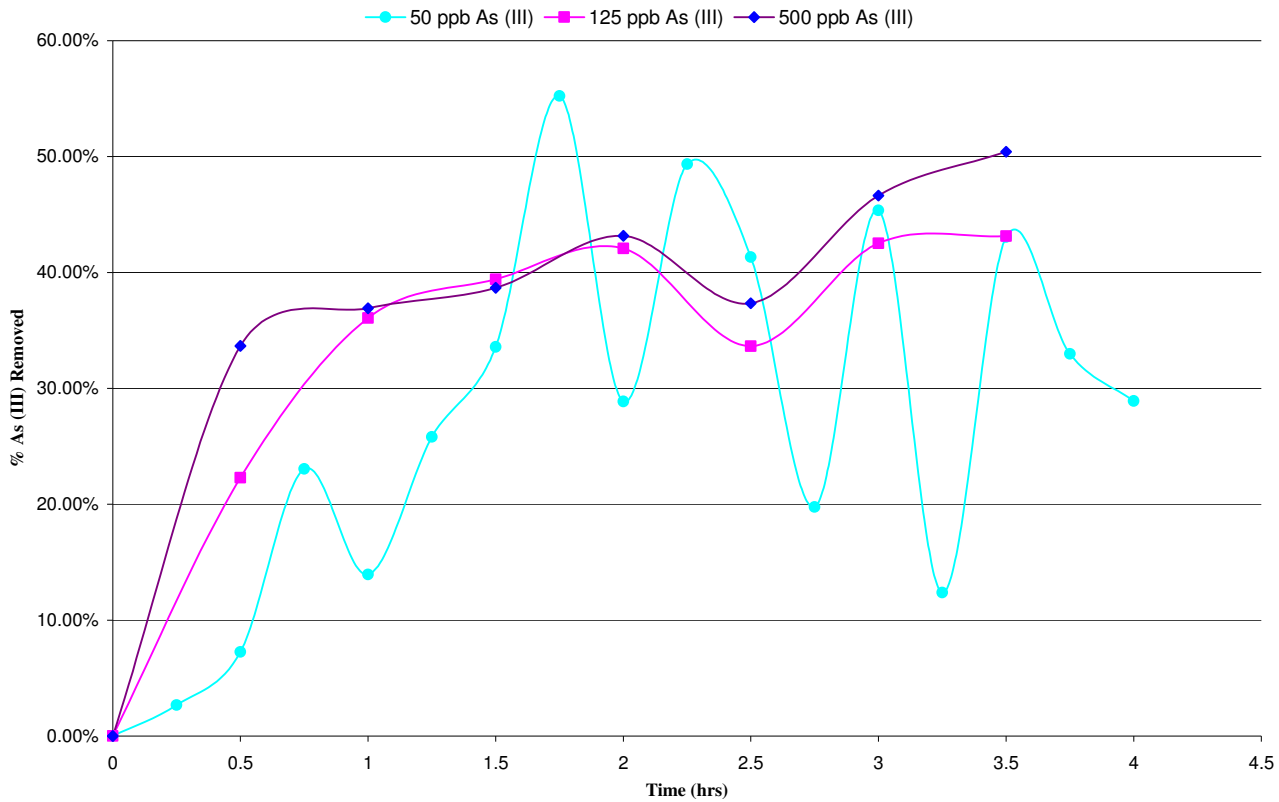


Figure 8 show the results for the removal of arsenic from a 300 ml solution of about 41 ppb As (III) using approximately 12 g. of Greek clam shells of particle size <125  $\mu\text{m}$ . The removal of arsenic from solution reached a maximum of 48% of arsenic removed after 2.5 hours of continuous stirring. The total arsenic concentration in solution was reduced from 41 ppb to 21 ppb.

Figure 8: Removal of arsenic from a solution containing about 41 ppb As (III) using approx. 12 g. of ground Greek clam shells with particle size of <math><125 \mu\text{m}</math>.

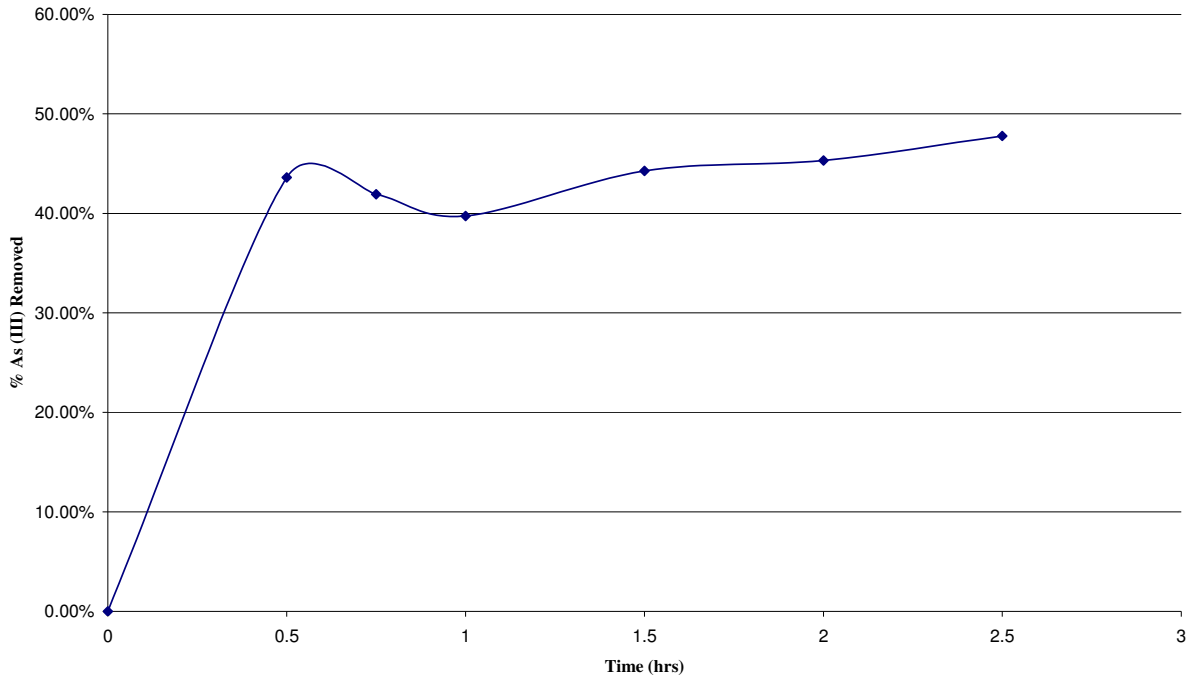


Figure 9: Comparing the removal of arsenic from a solution containing As (III) using approx. 16 g. Atlantic clam shells (400 ml solution) and approx. 12 g. of Greek clam shells (300 ml solution) with particle size of <math><125 \mu\text{m}</math>.

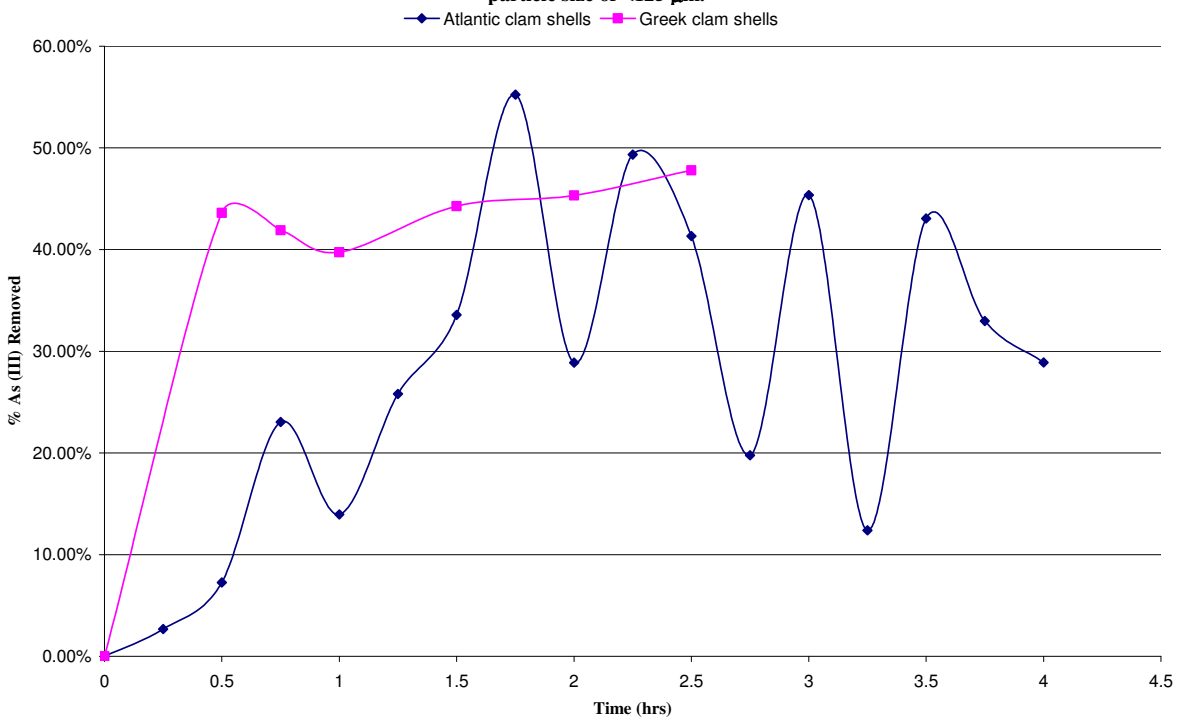


Figure 9 shows a comparison between the rates of removal of arsenic from solutions using Greek clam shells and Atlantic clam shells.

#### 4. DISCUSSION

In the first set of experiments, which examined the effect of the amount of clam shell material added to the solution on the removal of arsenic (Figure 1), re-dissolution of absorbed arsenic was observed after 54 hours of stirring. The re-dissolution could have occurred as a result of number of factors: a change in pH beyond a critical value, a change in temperature due to heating from the continuous operation of the stirrer, or a change in the crystal structure of the formed calcium/arsenic compound following sorption.

In comparing the removal of arsenic from two solutions containing 8 g and 16 g of clam shells of particle size  $<125\ \mu\text{m}$  (Figure 4), it was observed that, although initially the difference in the arsenic removal was not large between the two solutions, the removal of arsenic became much higher in the 16 g solution as time progressed. Such a pattern suggests that when using a larger amount of clam shells, more time is needed for the shells to mix in the solution before they can fully react with the arsenic ions.

A set of experiments was designed to investigate the effect of the initial As (III) concentration on the removal of arsenic from a water solution (Tables 5 and 6, Figure 7). It was found that the initial removal of arsenic decreased with decreasing initial arsenic concentration. However, the results of the experiment for the 50 ppb initial arsenic concentration differ from the results of all the other experiments in that there is a great deal of fluctuation, from sample to sample, in the concentration of arsenic in solution. Such a pattern indicates that removal occurs, then re-dissolution, then removal again and so on. This pattern becomes more pronounced after the maximum 55 % removal is achieved at 1.75 hours. It is not certain whether this is the result of error or whether this points to a certain mechanism of sorption and re-dissolution, in quick succession, when a limited concentration of As (III) in solution is reached. It should be noted, though, that the maximum percent removal is achieved at 1.75 hours and within the next 2.25 hours the arsenic removal has declined to 29 %, approximately half the maximum removal.

Finally, an experiment was run using ground clam shells that were collected in Greece and the results were compared to a similar experiment with Atlantic clam shells in order to investigate the effect of the type of clam shell on the removal of arsenic (Figures 8 and 9). In the experiment with the ground Greek clam shells, approximately 44 % of the arsenic content had been removed from the solution in the first half-hour. This was significantly higher than the 7 % arsenic removal achieved in the same time interval from a solution of similar initial As (III) concentration using Atlantic clam shells. The arsenic removal rate achieved with the Greek clam shells in the first half-hour was the highest removal rate achieved after half-hour among all the experiments that were performed. This indicates that although the basic material of the clam shells is the same, calcium carbonate, the manner in which this material crystallizes to form the clam shell might be of importance in the mechanism of the removal of arsenic from water by the clam shell powder. Although 44 % of arsenic had been removed in the first half-hour by the ground Greek clam shells, very little additional arsenic was removed in the next two hours.

The pH of the As (III) solutions prior to the addition of the clam shell material ranged from pH 5 to pH 6.5. The pH of the solutions measured 24 hours after the ground clam shells had been added, under continuous stirring, ranged from pH 8 to pH 8.5.

A qualitative difference that was observed when performing the experiments with the ground Atlantic clam shells and the ground Greek clam shells was that, upon mixing, the solutions were strikingly different in appearance. Upon mixing, the Atlantic clam shells formed a dark purple and frothy solution, and the shell powder tended to agglomerate. The Greek clam

shell solution, on the other hand, formed a fine, chalky white suspension. The difference in the two solutions' appearance could possibly explain the rapid removal that was achieved with the Greek clam shells. In a Columbia University Ph.D. thesis, it was concluded that the mechanism of the removal of heavy metal ions is rapid sorption of the metal and exchange of calcium ions of the shell with metal ions from the aqueous solution. The thesis also reported that strongly pigmented areas of the oyster shell surface were found to have low concentrations of calcium (8). Therefore, it can be speculated that, because of the presence of pigment (purple solutions) in the Atlantic coast clam shells, the calcium sites are fewer on the surface of the shell particle and the As (III) ion has to travel to the interior before the ion exchange takes place. Meanwhile, ion exchange takes place rapidly on the surface of the Greek clam shell particles due to the absence of pigment, as was observed in the solutions of the Greek clam shells.

## 5. CONCLUSIONS

- The results of this study show that ground clam shells are a suitable material for the removal of As (III) from water. Maximum arsenic removal of approximately 70% was achieved.
- Parameters affecting the arsenic removal included the amount of clam shell material used, its particle size, the initial arsenic concentration, and the type of clam shells.
- Increasing the clam shell amount resulted in a higher percent removal and in a higher rate of removal, at least during the first hour. A smaller particle size of ground clam shells resulted in a higher percent removal of arsenic from water and at a higher rate, possibly as a result of the increased surface area of the clam shell material.
- Increasing the initial concentration of As (III) in solution resulted in a higher rate of arsenic removal.
- Different types of clam shells had distinctly different arsenic removal characteristics. At low As (III) concentrations, Greek clam shells had a much higher rate of removal than Atlantic clam shells. The lower removal rate of the Atlantic clam shells was attributed to the presence of surface pigmentation, which resulted in fewer calcium sites available for ion exchange at the surface.
- Finally, it was found that the arsenic removed by the ground clam shells might not be stable when adsorbed to the clam shell material and could, therefore, re-dissolve back into the water under certain favorable conditions (such as an increase in the pH.)
- Future research would determine the optimum particle size, the optimum clam shell to initial As (III) ratio, and the best preparation methods for non-pigmented types of clam shells. Optimization of these parameters could result in even higher removal of arsenic from water.

## 6. ABBREVIATIONS AND ACRONYMS

**As (III):** arsenite

**As (V):** arsenate

**ppb:** parts per billion

**µg/L:** micrograms per liter

**ppm:** parts per million

**µm:** micrometers

**DI:** deionized

**GFAAS:** Graphite Furnace Atomic Absorption Spectrophotometer

**g:** grams

## 7. ACKNOWLEDGEMENTS

### Credits

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### Author

Demetra Tsiamis is a senior at the Bronx High School of Science and is an active member of her high school community. In addition to taking challenging honors and A.P. courses in both science and the arts, Demetra plays for her high school's basketball team. Demetra has been a member of her school's basketball team since she was a freshman. She has been playing at the Varsity level these past two years and this past season, she was appointed co-captain. In addition to the basketball team, Demetra is also a member of her school's Hellenic Cultural Society where she has been elected as the club's Secretary for the last two years.

Environmental science is an area of special interest to Demetra. Demetra has always been made aware of the environmental issues that face modern society as a result of her father's work at the U.S. Environmental Protection Agency. When she was younger, her father, who manages the clean up of polluted sites, would often explain to her the methods that engineers use to remediate contaminated water and soil. Demetra pursued her interest in improving the environment in her research where she addressed the pressing international problem of arsenic contamination in groundwater.

Demetra will be attending The Cooper Union in the fall of 2007 where she will study as a chemical engineering major. As a result of her research, Demetra has become more aware of how science provides the answers to the most pressing problems of the world, from conservation of resources to fighting diseases. As an engineer, Demetra hopes to contribute to solving some of these problems.

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