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Reducing Lead and Selenium from Drinking Water Using Limestone-based Material

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REDUCING LEAD AND SELENIUM FROM DRINKING WATER USING LIMESTONE-BASED MATERIAL

A Thesis
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Western Kentucky University
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Of the Requirements for the Degree
Master of Science

By
Sindhu Tumati

May 2012

REDUCING LEAD AND SELENIUM FROM DRINKING WATER USING
LIMESTONE-BASED MATERIAL

Date Recommended 5-3-2012

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Dean, Graduate Studies and Research Date

I dedicate this thesis to my parents, Prabhakar Reddy and Veerabhadra who are a great inspiration to me. I also dedicate this work to my behalf Sandeep Cheekati, who helped me greatly in everything to complete my Masters.

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Finally, I dedicate my thesis to my parents for their continuous support throughout my life.

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LIST OF ABBREVIATIONS AND SYMBOLS

MCLG	Maximum Contaminant Level Goal
ppb	Parts Per Billion
ppm	Parts Per Million
ICP	Inductively Coupled Plasma
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

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Sindhu Tumati May 2012 56 pages

Directed by: Dr. Cathleen Webb, Dr. Bangbo Yann, Dr. Rui Zhang

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Contamination of drinking water with metals is a major problem facing many areas of United States and the World. There is a need for an inexpensive remediation technology for the removal of metals in drinking water that can be applied to small rural water systems. This research will focus on the development of a process for removal of select metals from drinking water by limestone-based material. Metals in drinking water considered for this research include lead and selenium. Limestone-based material has demonstrated the potential to reduce select metals (lead, cadmium and arsenic) in drinking water, with the additional benefit of low-cost disposal of a stable waste product in ordinary landfills.

Earlier research by the principal investigators using limestone-based material for drinking water treatment has clearly shown that this material can achieve metals removal of greater than 90 percent. This project will investigate techniques to improve removal efficiency of limestone-based material through adsorption and precipitation. This research will assist in the development of a granular adsorbent product that will remove metals and that can be manufactured and sold for use at the drinking water source, at point-of use, or at point-of entry.

Limestone was coated with Iron and its removal efficiency is compared with the uncoated limestone. Uncoated limestone was effective in removing lead completely from drinking water and iron-coated limestone was effective in removing selenium completely from drinking water. Effect of pH on removal of metals was also studied. Limestone is readily available and its use for metals removal is relatively inexpensive. The technology can be applied to small, rural water systems. Benefits of this research will include a low-cost treatment technology for source reduction that will reduce select metals to below drinking water standards.

I. INTRODUCTION

"Numerous metals have received attention as both environmental contaminants and potential toxicological hazards. For example, heavy metals like arsenic, cadmium, and lead are extensively distributed in the environment" (Chappell, et al, **1997**). Human activities have altered the natural distribution of these metals in the environment, which leads to the elevated concentration levels of these metals in drinking water. "The occurrence of arsenic, cadmium and lead and other metals in drinking water is an important pathway of potential exposure for citizens of the United States and many other nations in the world" (Barry Ryan, et al, **2000**). This research will focus on the removal of lead and selenium from drinking water.

As trace elements, some heavy metals (copper, selenium, zinc) are essential to the human body to maintain a healthy metabolism. However, at high concentrations, they lead to poisoning (Lobinski, et al, **1997**). To a small extent they can enter the human body through drinking water, food and air. In high concentrations, they tend to bioaccumulate in the body. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the concentration of the chemical in the environment. Heavy metals can enter into water supplies by industrial and consumer wastes.

For this reason the US-EPA (United States Environmental Protection Agency) has established standard values for the contaminants allowed in drinking water as shown in table 1. Below this level, these contaminants are not considered harmful.

Table 1. Drinking water standards for some common heavy metals

Contaminant	**MCLG (mg/L)**
Arsenic	0.010
Lead	0.015
Selenium	0.05
Cadmium	0.005
Zinc	5
Copper	1.3

A. Lead:

"Lead is the commonest of the heavy elements and accounts for 13 mg/kg of the earth's crust. Lead is used in industries the production of lead acid batteries, solders, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes, plastic stabilizers and many more" (*Lead—environmental aspects*. Geneva, World Health Organization, 1989 (Environmental Health Criteria, No. 85)). Lead is present in smaller quantities in tap water as a result of its dissolution from natural sources like household plumbing systems in which the pipes, solders and fittings contains lead. PVC pipes also contain some lead compounds that can be leached from them and result in higher concentrations of lead in drinking-water.

The amount of lead leached and dissolved in water from the plumbing system depends on different factors, including the presence of chloride and dissolved oxygen, pH, temperature, water softness, and standing time of the water. Acidic water is most suitable for lead as a solvent (Schock, et al, **1989**). The concentrations of lead in drinking water can be reduced by adding lime and also by adjusting the pH from <7 to 8-9 (Sherlock, et al, **1984**).

Prepared food in containers also contains small but a significant amount of lead. Lead content is increased when the water used for cooking or the cooking utensils contain lead, or the food, especially if acidic, has been stored in lead-soldered cans. The intake of lead from lead-soldered cans has been reduced as the use of lead-free solders became more widespread in the food processing industry (Galal-Gorchev, et al, **1991**).

A.1. Effect in humans:

Lead is a cumulative general poison. Infants, children up to 6 years of age, the fetus, and pregnant women are the most susceptible to lead and will have adverse health effects. It will mainly affect the central nervous system. Signs of acute intoxication include dullness, restlessness, irritability, headaches, muscle tremor, abdominal cramps, kidney damage, hallucinations, and loss of memory. “Encephalopathy occurs at blood levels of 100–120 μg/dl lead in adults and 80 – 100 μg/dl lead in children. After 1–2 years of exposure, muscle weakness, gastrointestinal symptoms, lower scores on psychometric tests, disturbances in mood, and symptoms of peripheral neuropathy were observed in occupationally exposed populations at blood lead levels of 40–60 μg/dl” (Campbell, et al, **1977**).

The pE-pH diagram represents the Nernst equation as a function of pH. The pE-pH diagram for lead is shown in figure 1 (Brookins, et al, **1988**). The upper dotted line represents the oxidation boundary of water and the bottom dotted line represents the reducing boundary of water. Drinking water has a pH range from 6-8. In this range, lead mainly exists as Pb[2+] ion. When the pH is increased to 7-9, lead forms lead hydroxide (PbOH[+]) and eventually precipitates as $Pb(OH)_2$.

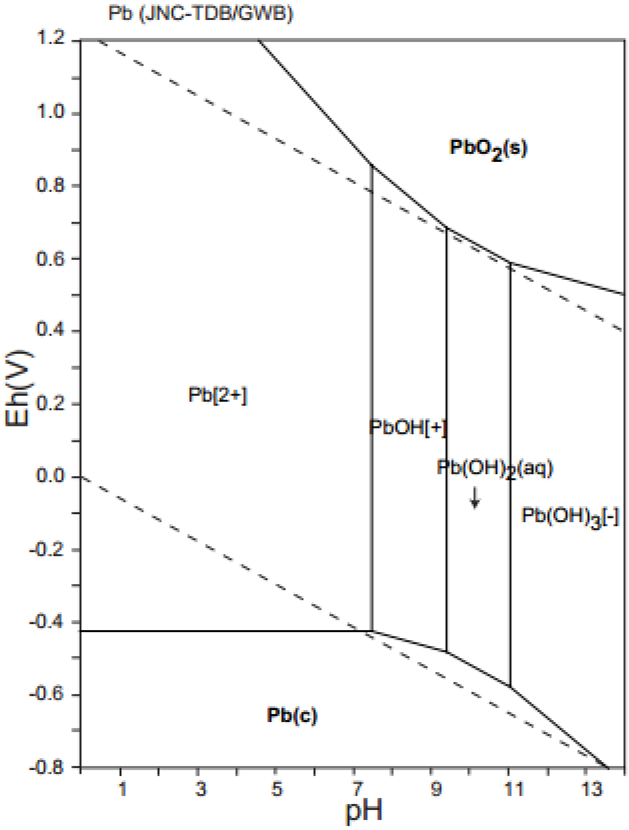

Figure 1. pE-pH diagram for lead (Brookins, et al, **1988**)

B. Selenium:

“Selenium is present in the earth's crust, sometimes in association with sulfur-containing minerals. The levels of selenium in groundwater and surface water ranges from 0.06 to about 400 μg/litre” (Smith, et al, **1937**). Selenium (Se) is recognized as an essential micronutrient in most species, including humans. It is an important integral component of glutathione peroxidase (GSH-Px) and also has a function in detoxification of peroxides. Selenium also exhibits some inhibitory effect on carcinogenesis. Different health problems can arise with excess levels of selenium and as well as with a deficiency of selenium with a narrow margin between its essential and toxic actions.

“Foodstuffs constitute the main source of selenium for the general population. Daily dietary intake of selenium varies according to geographical area, food supplies, and the dietary habits. Recommended daily intakes have been set at 1.7 µg/kg of body weight in infants and 0.9 µg/kg of body weight in adults” (National Research Council. *Recommended dietary allowances*, 10th ed. Washington, DC, National Academy Press, 1989). Most of the drinking-water contains much less than 10 µg/litre, except in certain seleniferous areas. Total Selenium levels in the environment range from 0.1-400 µg/L in natural waters, to 0.06-1.8 ng/g in soils and a few nanograms per cubic meter in the atmosphere. The accumulation of total selenium depends on the environmental factors, and it is affected by pH (Selenium Concentrations in Natural and Environmental Waters, *Chem. Rev*. **1997,** 97, 1979-2003).

B.1. Effects in humans:

In humans, few reports of signs of selenium deficiency are available. It can be a factor in endemic cardiomyopathia (Keshan disease) and also possibly in joint and muscle disease (*Selenium.* Geneva, World Health Organization, 1987 (Environmental Health Criteria, No.58)). Acute oral doses of selenium compounds cause symptoms like nausea, diarrhoea, abdominal pain, chills, tremor, numbness in limbs, irregular menstrual bleeding, and marked hair loss (Sioris, et al, **1980**).

The pE-pH diagram for selenium is shown in figure 2 (Brookins, et al, **1988**). It shows the Nernst equation as a function of pH. From this diagram we can determine that, in typical drinking water, selenium will exist as a mixture of anions, $HSeO_3$[-] and/or SeO_4[2-]. When the pH is increased, it will still exist as an anion (SeO_4 [2-]) or possibly as SeO_3[2-]. These anions can chemisorb to the iron on the surface of the limestone through oxygen; hence it should be more easily removed with the iron-coated limestone than uncoated limestone.

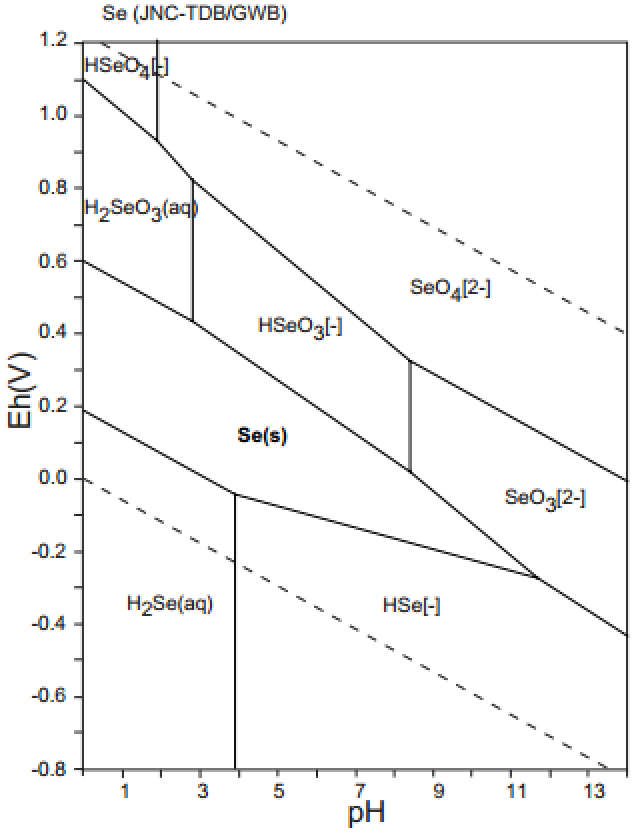

Figure 2. pE-pH diagram for selenium (Brookins, et al, **1988**)

A variety of treatment processes have been examined for heavy metal removal. Major technologies include coagulation/precipitation (McNeill, et al, **1997**), membrane separation (Waypa, et al, **1997**), ion exchange, and adsorption (Dambies, et al, **2004**), reverse osmosis. Most of these techniques are expensive and have their own disadvantages. Among all these techniques adsorption is cost-effective and advantageous. Effectiveness of adsorption-based methods depends primarily on the adsorbent (granular media) used.

Different granular media can be used for removal of heavy metals from drinking water. Methods include granular activated alumina and granular activated carbon (Pattanayak, et al, **2000**) and limestone. These materials are less effective than iron oxides for arsenic adsorption. Limestone is used to remove many heavy metals like arsenic, selenium and lead (Mercedesdiaz-Somano, et al, **2004**). Several iron-based granular materials have been developed for the removal of heavy metals. They include iron oxide coated sand, sulfur-modified iron and granular ferric hydroxide (Zhimang, et al, **2005**).

Heavy metal adsorption or precipitation onto plain limestone is generally considered to be minimal, so it is not typically applied for water treatment. Literature has already shown that the adsorption on to the limestone can be increased significantly by treatment with various iron compounds (Reed, et al, **2000**). It is likely that some iron compounds produced by the treatment increase the surface area of the limestone, resulting in the enhanced removal.

Limestone properties:

Limestone has a very heterogeneous surface and has good buffering capacity. Uncoated limestone is shown in figure 3. Pretreatment of the sample pH is not necessary with the use of limestone. There is no need to recycle the limestone as disposal is also easy. Limestone can be disposed in cement and is not leachable. Consequently, we propose to reduce heavy metals in drinking water using limestone as the base material.

Figure 3. Uncoated Limestone

The objective of this study is to develop and characterize a granular material that can be used for effective drinking water treatment. The heavy metals we are focusing on include lead and selenium. The base material used is limestone. We will also compare the effectiveness of iron-coated limestone and plain (uncoated) limestone to reduce heavy metals in drinking water. Here, the iron acts to increase the surface area of the limestone and, thereby, increases the capacity to remove metals. After treatment with limestone, water samples were analyzed with Inductively Coupled Plasma (ICP). This material was characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) technique. The ability of the media to remove heavy metals was evaluated through both batch and kinetic studies. The effect of pH on the removal was also studied in batch experiments.

II. EXPERIMENTAL SECTION

A. Chemicals and Materials:

Deionized water, obtained from a Nano Pure system was used throughout this work. Commercially available limestone (#16/60 limestone, Pete Lien and Sons, LaPorte, CO) was used on-site. Earlier studies were conducted with limestone that was ground and sieved. The commercially available limestone, commonly used in chicken feed, was found to be quite efficient.

A.1. Preparation of Iron-coated limestone:

A sample of 100g of limestone was placed into a round bottom flask. A 100mL solution of 0.1M iron (III) chloride ($FeCl_3$) was then placed in the flask. The flask was placed on a shaker. After 24 hours, a few drops of concentrated sodium hydroxide is added to the solution to help precipitate iron. The granules were then rinsed with deionized water and air dried. Iron-coated limestone after drying is shown in figure 4.

Figure 4. Iron-coated Limestone

A.2. Preparation of solutions:

Standard solutions (1000 ppm) of lead and selenium were purchased from Inorganic Ventures. All other solutions were prepared from these standards.

Preparation of 10ppm lead solution:

An aliquot of 1mL of the standard lead solution was place in a 100mL volumetric flask and the volume is made up to 100mL with deionized water.

Preparation of 50ppb lead solution:

An aliquot of 5mL of the 10ppm lead solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

Preparation of 100ppb lead solution:

An aliquot of 10mL of the 10ppm lead solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

Preparation of 200ppb lead solution:

An aliquot of 20mL of the 10ppm lead solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

Preparation of 10ppm selenium solution:

An aliquot of 1mL of the standard selenium solution is taken into a 100mL volumetric flask and the volume is made up to 100mL with deionized water.

Preparation of 50ppb selenium solution:

An aliquot of 5mL of the 10ppm selenium solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

Preparation of 100ppb selenium solution:

An aliquot of 10mL of the 10ppm selenium solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

Preparation of 200ppb selenium solution:

An aliquot of 20mL of the 10ppm selenium solution is taken into a 1000mL volumetric flask and the volume is made up to 1000mL with deionized water.

B. Apparatus:

A Burrell Wrist action shaker (model 75) was used to stir the solutions. The shaker is shown in figure 5. The shaker was kept on a speed of 1 cycle/sec and the solutions were stirred along with the limestone. Whatman cellulose nitrate membrane filters (0.45micron) were used to filter the solutions using a micro filtration syringe apparatus. A Fisher Scientific AB 15 pH meter was used to measure the pH of all the solutions. The pH meter is shown in figure 6. All the glassware is made of Pyrex glass.

Figure 5. Burrell Wrist Action Shaker

All the samples were analyzed using Inductively Coupled Plasma (ICP). Microscopic studies of the limestone are done using Scanning Electron Microscopy and X-ray Diffraction. The ICP instrument is located at the Advanced Material Institute (AMI) lab, which is located in the Center for Research and Development, Western Kentucky University.

Figure 6. Fisher scientific AB 15 pH meter

C. Methods:

C.1. Kinetics:

Kinetic tests are conducted using a fixed amount of limestone (5g) and standard solution volumes (100mL) using different time intervals (30min, 1hr, 1.5hrs, 2hrs, 4hrs, 10hrs and 24hrs). Different concentrations of standard solutions (50, 100 and 200ppb) are used for this experiment. A volume of 100mL of each standard solution is placed in the round bottomed flask and kept in contact with coated and uncoated limestone (5g) for the different intervals of time.

C.2. Batch tests:

Batch tests are conducted using different amounts of limestone (5, 10, 20, 50 and 100g) with 100mL of the prepared standard solutions for both Lead and Selenium. The limestone and the solution are placed in the round bottomed flask and stirred for 5hours for Selenium and 30 minutes for Lead.

C.3. pH studies:

The effect of pH on the removal of the heavy metals is also studied by using solutions of different initial pH. Standard solutions of lead (100ppb) and selenium (100ppb) with varying initial pH (pH 5, 6, 7, 8 and 9) were placed and kept in contact with the limestone on the shaker. The initial pH of the standard solutions was adjusted with 1M sodium hydroxide. The final pH of the solutions after treatment with the limestone was also measured.

C.4. Sample collection and analysis:

After treatment with the limestone, the solutions are filtered using 0.45 micron Whatman cellulose nitrate membrane filters. All the samples are collected in glass bottles and analyzed using Inductively Coupled Plasma (ICP).

C.5. Calibration:

Samples are analyzed by ICP using the 1000ppm standard solutions of lead and selenium for the calibration of the instrument. Different concentrations of standard solutions (blank, 5, 10, 20, 30, 40 and 50ppb) are prepared with deionized water. The instrument is calibrated and the samples are loaded onto the auto sampler tray.

C.6. Sample introduction:

The nebulizer is used in ICP to inject the samples. This converts liquids into an aerosol, and the aerosol is swept into the plasma to create the ions. The plasma used in an ICP is made by using argon gas.

C.7. Auto session:

Flush time is kept for 80 seconds. The wavelength used for lead is 220.353nm and the wavelength for selenium is 196.026. To analyze the samples, first the water flow is started and the plasma is turned on. Auto session is turned on and calibration of the instrument is done first. As the instrument consists of an auto sampler, it will run automatically. It takes 3 minutes for each sample to run and analyze.

C.8. Microscopic studies

Microscopic studies of the limestone are done by using SEM (Scanning Electron Microscopy) and XRD (X-Ray Diffraction). Scanning electron microscopy uses beams of electrons and gives the information about the sample's surface topography and composition. SEM studies are done for the uncoated limestone, iron-coated limestone, uncoated limestone after the treatment with 100ppb lead solution and iron-coated limestone after the treatment with 100ppb selenium solution.

Scanning electron microscope consists of a sample holder, an electron column and an electron detector. Samples are held on cylindrical stubs using a carbon tape. An excess sample is removed by blowing compressed air on it. Stubs are placed in the sample holder and analyzed using SEM. The sample holder contains four cylindrical mounts to hold the stubs.

X-Ray diffraction provides information about the crystal structure, chemical composition and physical properties of materials. The uncoated and the iron-coated limestone is ground, homogenized and analyzed to determine their composition using XRD. X-ray diffractometer consists of an X-ray tube, a sample holder and an X-ray detector.

III. RESULTS AND DISCUSSIONS

A. Effect of contact time:

The effect of contact time on the removal of lead and selenium was examined using a fixed amount of limestone (5g) and different time intervals. Different concentrations of standard solutions (50, 100 and 200ppb) were used to study the kinetics. Plain and iron-coated limestones are used for the comparison of their removal capacity.

The calibration curve for lead is shown in figure 7. The graph is plotted between concentration on X-axis and Intensity on Y-axis. Calibration is done with different concentrations (5, 10, 20, 30, 40 and 50) of lead standard solution. The R^2 value for the calibration curve is 0.999.

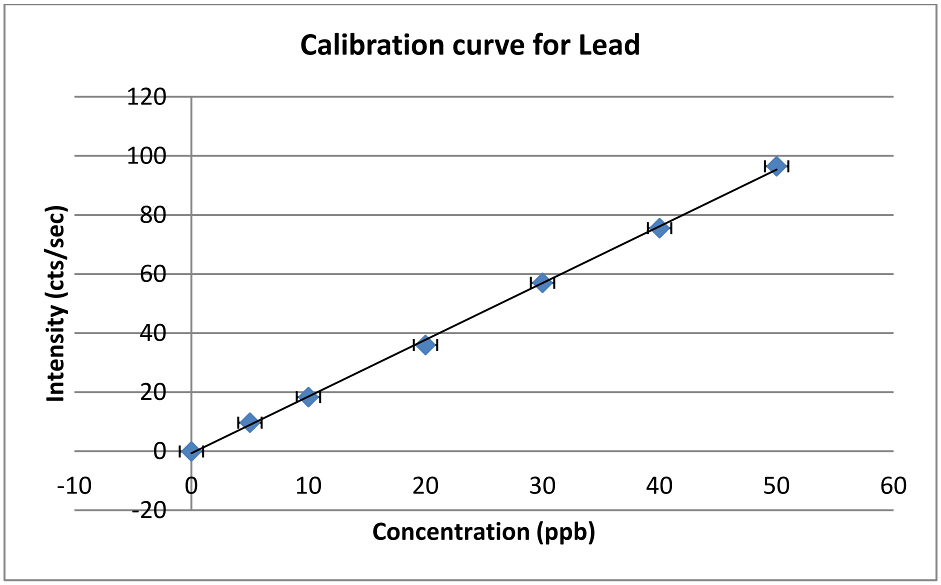

Figure 7. Calibration curve for Lead

The effect of time on removal of lead was studied through kinetic studies. The results for the kinetics experiment for 50ppb lead solution with 5 grams uncoated limestone is shown in table 2 and figure 8.

Table 2. Kinetics experiment with 50ppb lead solution using 5g uncoated limestone

Time (in minutes)	**Concentration (in ppb) (±0.05)**
2	ND
5	3.23
10	ND
15	4.55
20	4.37
25	2.36
30	4.87

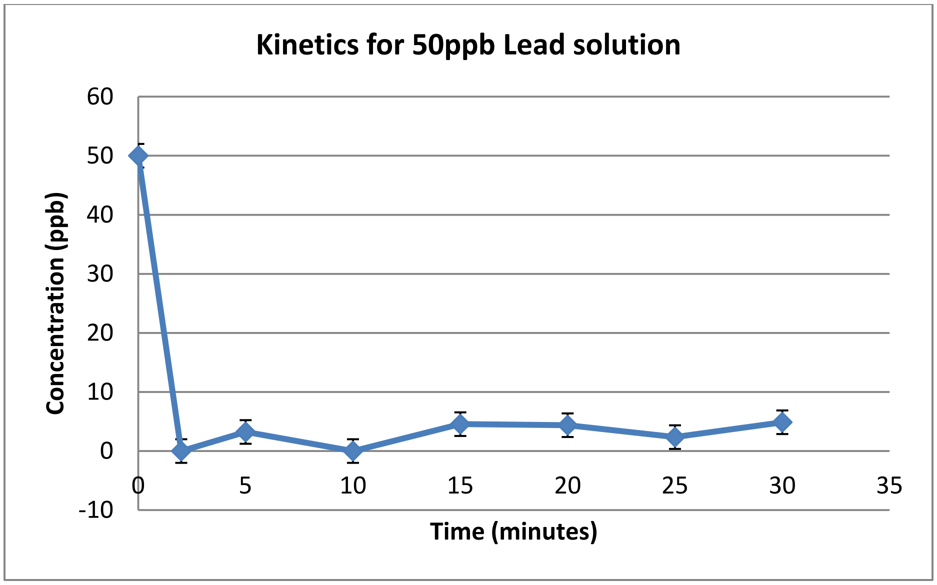

Figure 8. Kinetics experiment with 50ppb lead solution using 5g uncoated limestone

Lead has been reduced to below the drinking water standard of 15ppb within 3 minutes from an initial concentration of 50ppb, when treated with 5 grams of uncoated limestone.

The results for the kinetics experiment for 100ppb lead solution with 5 grams uncoated limestone is shown in table 3 and figure 9.

Table 3. Kinetics experiment with 100ppb lead solution using 5g uncoated limestone

Time (in minutes)	**Concentration (in ppb) (±0.05)**
2	0.59
5	0.42
10	0.43
15	0.10
20	0.21
25	0.13
30	0.13

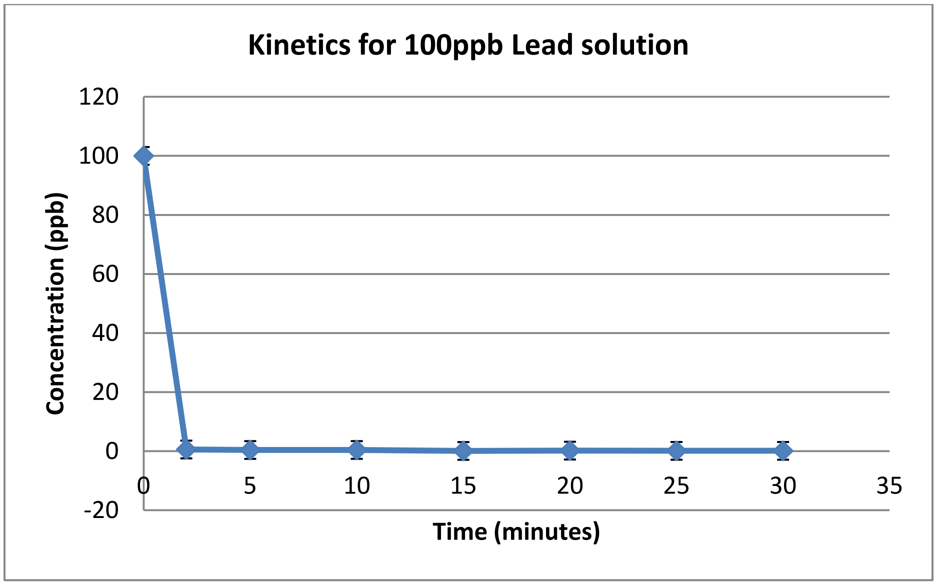

Figure 9. Kinetics experiment with 100ppb lead solution using 5g uncoated limestone

Lead has been reduced to below the drinking water standards within 30 minutes from an initial concentration of 100ppb, when treated with 5grams of uncoated limestone.

The results for the kinetics experiment for 200ppb lead solution with 5 grams uncoated limestone is shown in table 4 and figure 10.

Table 4. Kinetics experiment with 200ppb lead solution using 5g uncoated limestone

Time (in minutes)	**Concentration (in ppb) (±0.05)**
2	0.25
5	0.49
10	0.32
15	0.18
20	0.01
25	0.59
30	0.09

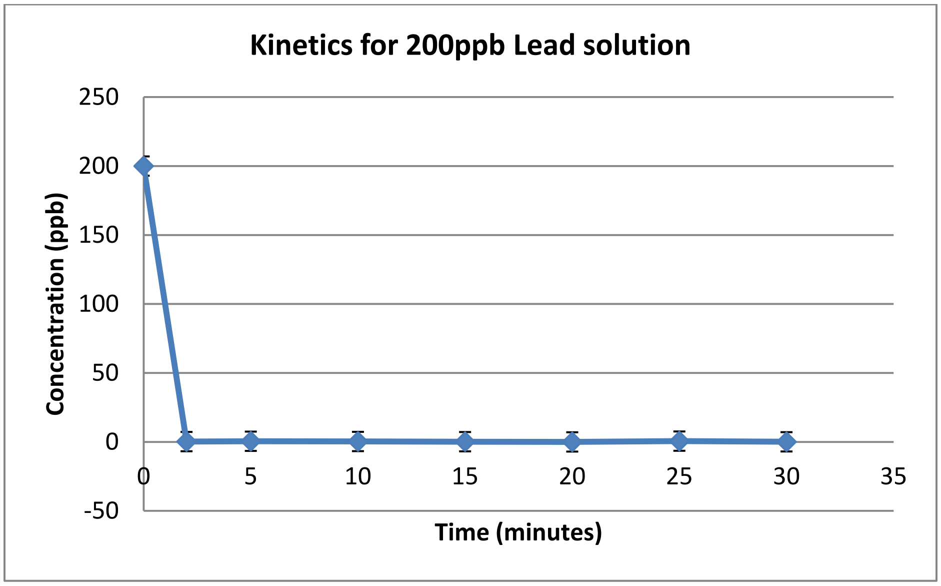

Figure 10. Kinetics experiment with 200ppb lead solution using 5g uncoated limestone

Lead has been reduced to below the drinking water standards within 10 minutes from an initial concentration of 200ppb, when treated with 5 grams of uncoated limestone.

The results for the kinetics experiment for 50ppb lead solution with 5 grams Iron-coated limestone is shown in table 5 and figure 11.

Table 5. Kinetics experiment with 50ppb lead solution using 5g iron coated limestone

Time (in hours)	**Concentration (in ppb) (±0.05)**
0.5	3.74
1	1.62
1.5	0.21
2	3.15
4	4.46
10	ND
24	ND

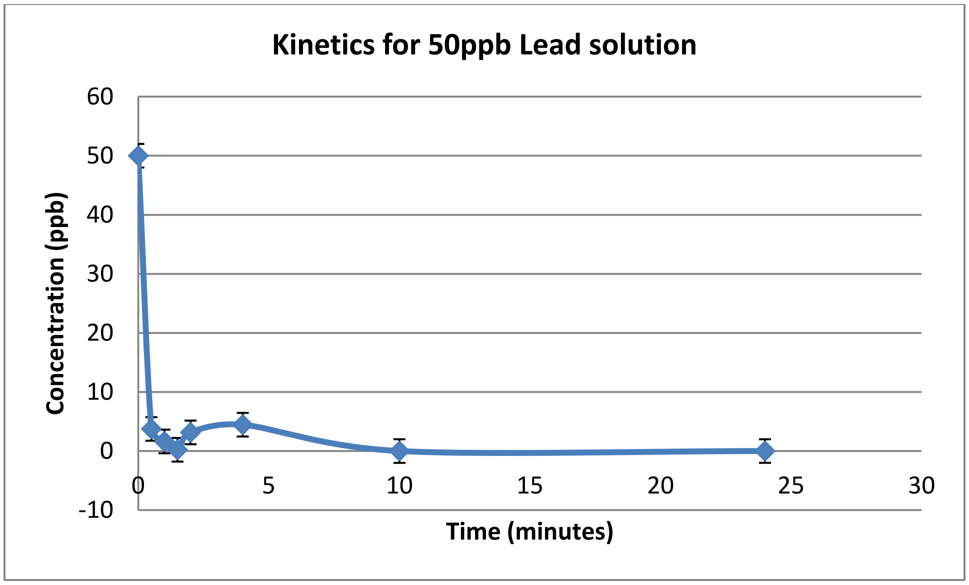

Figure 11. Kinetics experiment with 50ppb lead solution using 5g iron-coated limestone

Lead has been reduced to non-detect levels within 10 hours from an initial concentration of 50ppb, when treated with 5 grams of uncoated limestone. The uncoated limestone is more effective than the iron-coated limestone, because uncoated limestone removes lead completely within 30 minutes.

The calibration curve for selenium is shown in figure 12. The R^2 value for the calibration of selenium is 0.999. The graph is plotted between concentration on X-axis and intensity on Y-axis. Calibration is done with different concentrations (10, 20, 30, 40 and 50) of selenium standard solution. The R^2 value for the calibration curve is 0.998.

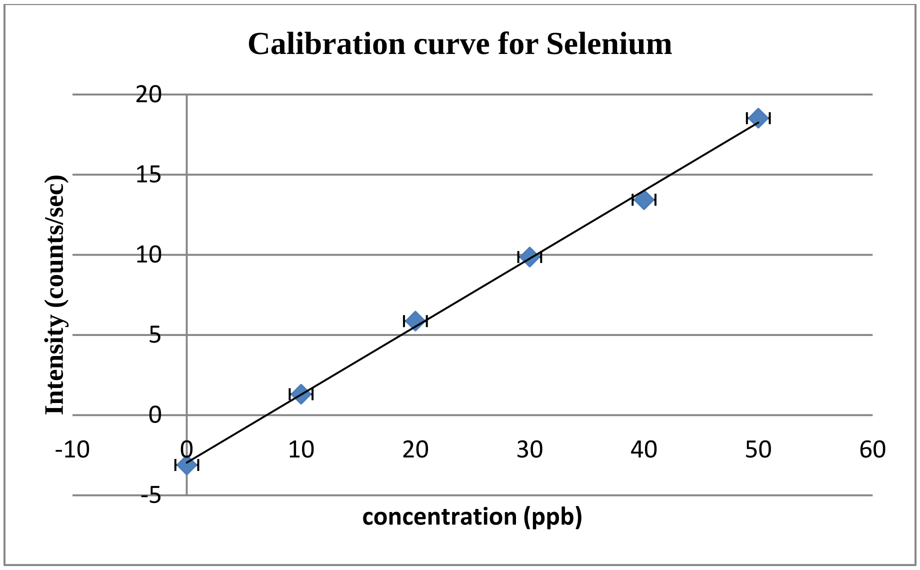

Figure 12. Calibration curve for selenium

The effect of time on removal of selenium was studied through kinetic studies. The results for the kinetics experiment for 50ppb selenium solution with 5 grams Iron-coated limestone is shown in table 6 and figure 13.

Table 6. Kinetics experiment with 50ppb selenium solution using 5g iron-coated limestone

Time (in hours)	**Concentration (in ppb) (±0.05)**
0.5	0.30
1	1.06
1.5	0.76
2	1.03
4	0.80
10	0.12
24	2.57

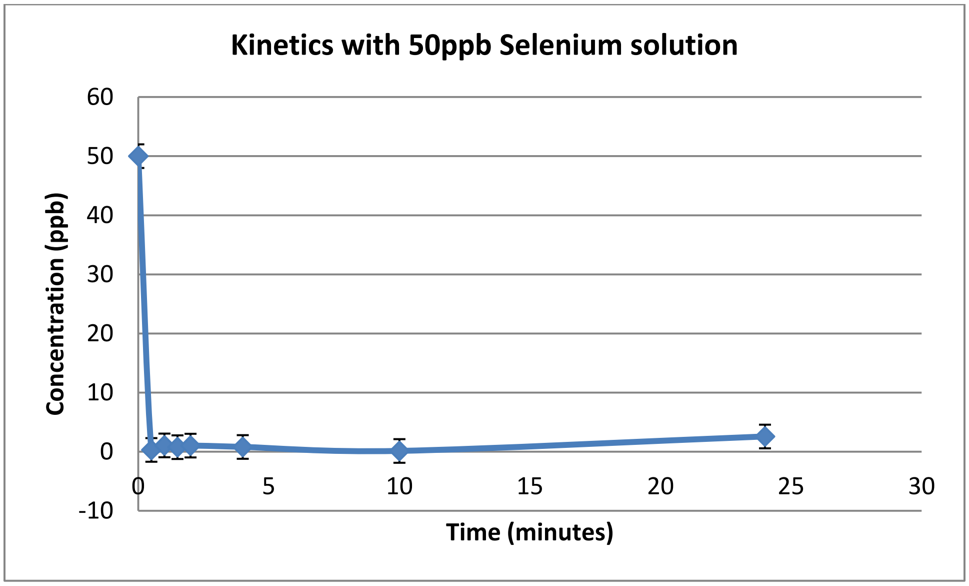

Figure 13. Kinetics experiment with 50ppb selenium solution using 5g iron-coated limestone

Selenium has been removed to less than the drinking water standard of 50ppb within 5 hours only. Removal of 99.4% of the selenium after treatment with 100mL solution of 50ppb concentration and 5 grams of iron-coated limestone occurred in 5 hours.

The results for the kinetics experiment for 100ppb selenium solution with 5 grams iron-coated limestone is shown in table 7 and figure 14.

Table 7. Kinetics experiment with 100ppb selenium solution using 5g iron-coated limestone

Time (in hours)	**Concentration (in ppb) (±0.05)**
0.5	9.63
1	10.0
1.5	9.56
2	10.5
3	8.96
4	7.48
5	12.0

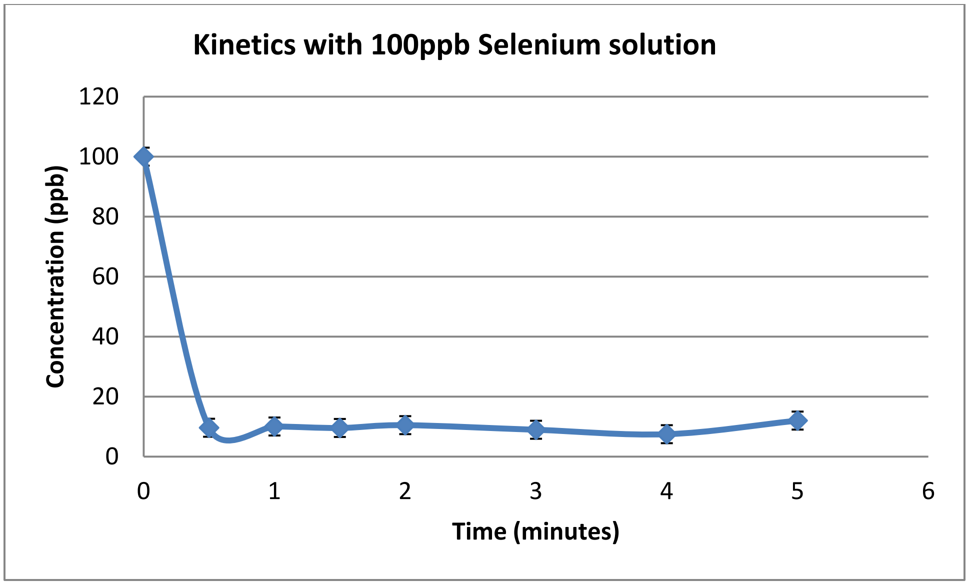

Figure 14. Kinetics experiment with 100ppb selenium solution using 5g iron-coated limestone

Selenium has been removed to less than its drinking water standard within 4 hours. It can be seen that 92.5% of the selenium was removed after treatment with 100mL solution of 100ppb concentration and 5grams of iron-coated solution.

The results for the kinetics experiment for 200ppb selenium solution with 5 grams iron-coated limestone is shown in table 8 and figure 15.

Table 8. Kinetics experiment with 200ppb selenium solution using 5g iron-coated limestone

Time (in hours)	**Concentration (in ppb) (±0.05)**
0.5	19.99
1	16.71
1.5	14.86
2	18.15
3	10.86
4	14.97
5	23.35

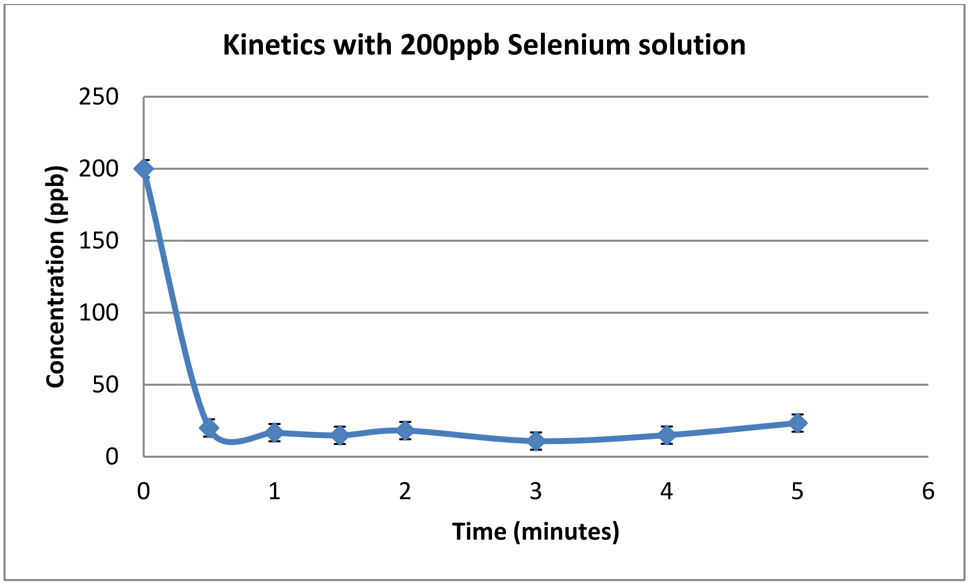

Figure 15. Kinetics experiment with 200ppb selenium solution using 5g iron-coated limestone

Selenium has been removed to less than its drinking water standard within 3 hours with 94.6% of the selenium removed after treatment with 100mL solution of 200ppb concentration and 5grams of iron-coated solution.

The results for the kinetics experiment for 50ppb selenium solution with 5 grams uncoated limestone is shown in table 9 and figure 16.

Table 9. Kinetics experiment with 50ppb selenium solution using 5g uncoated limestone

Time (in hours)	**Concentration (in ppb) (±0.05)**
0.5	13.07
1	40.15
1.5	37.62
2	38.26
4	37.31
10	33.23
24	10.19

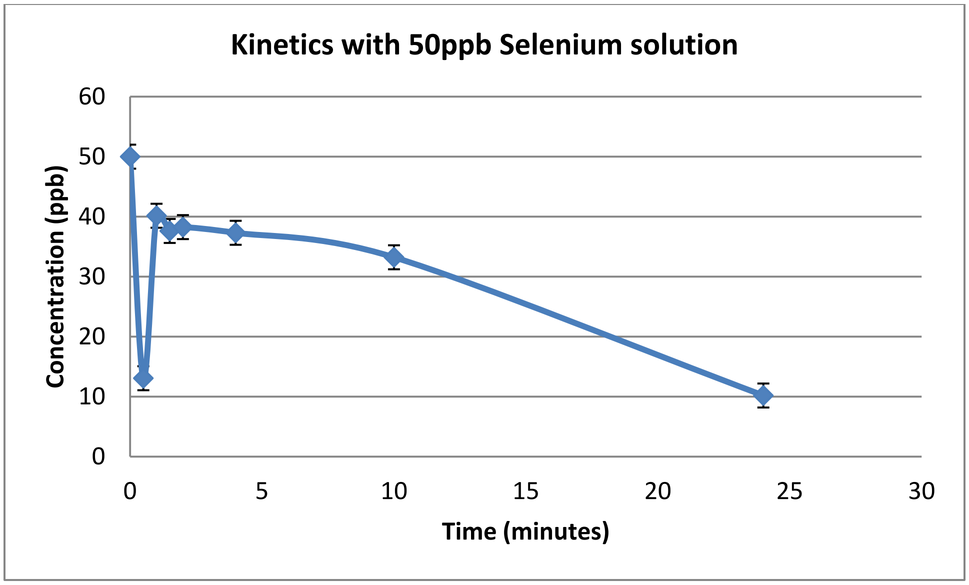

Figure 16. Kinetics experiment with 50ppb selenium solution using 5g uncoated limestone

In this experiment 5 grams of uncoated limestone removes 79.6% of the selenium from a 100mL solution of 50ppb concentration in 24 hours.

B. Effect of limestone amount:

The effect of limestone on the removal capacity was studied using different amounts of limestone (5, 10, 20, 50 and 100g) while the contact time is kept the same for all samples. The results are also compared with different concentrations (50, 100 and 200ppb) of lead and selenium standard solutions.

The effect of limestone on the removal of lead was studied using batch tests. The results for the batch test with 50ppb lead solution using uncoated limestone are shown in table 10 and figure 17.

Table 10. Batch test with 50ppb lead solution using uncoated limestone

Weight of limestone (grams)	**Concentration (ppb) (±0.05)**
5	4.87
10	ND
20	2.58
50	0.36
100	0.72

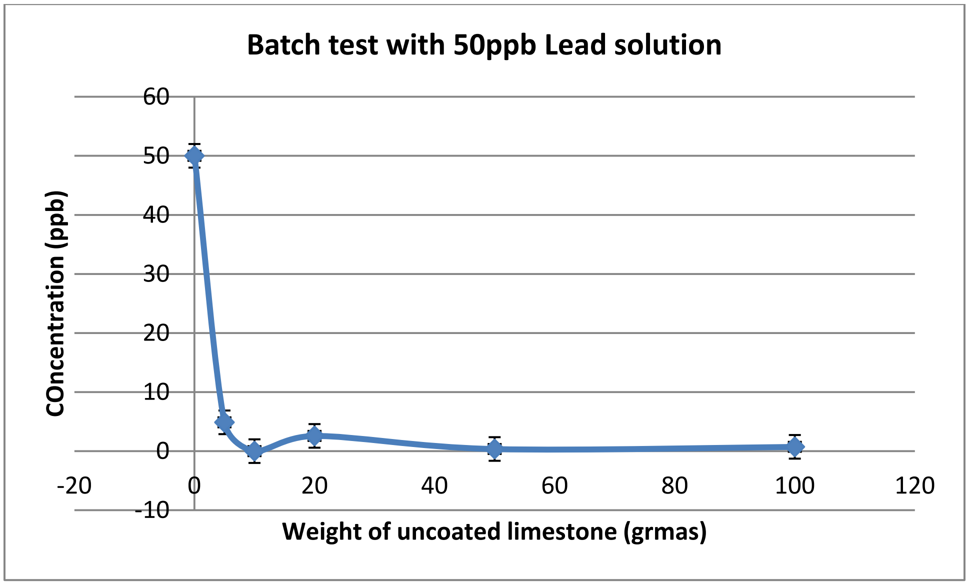

Figure 17. Batch test with 50ppb lead solution using uncoated limestone

Different amounts of plain limestone (5, 10, 20, 50 and 100g) are used to remove lead. A sample of 10grams of uncoated limestone efficiently removes lead completely from a solution of 50ppb concentration to non-detectable levels.

The results for the batch test with 100ppb lead solution using uncoated limestone is shown in table 11 and figure 18.

Table 11. Batch test with 100ppb lead solution using uncoated limestone

Weight of limestone (grams)	**Concentration (ppb) (±0.05)**
5	0.13
10	0.76
20	0.10
50	0.25
100	0.12

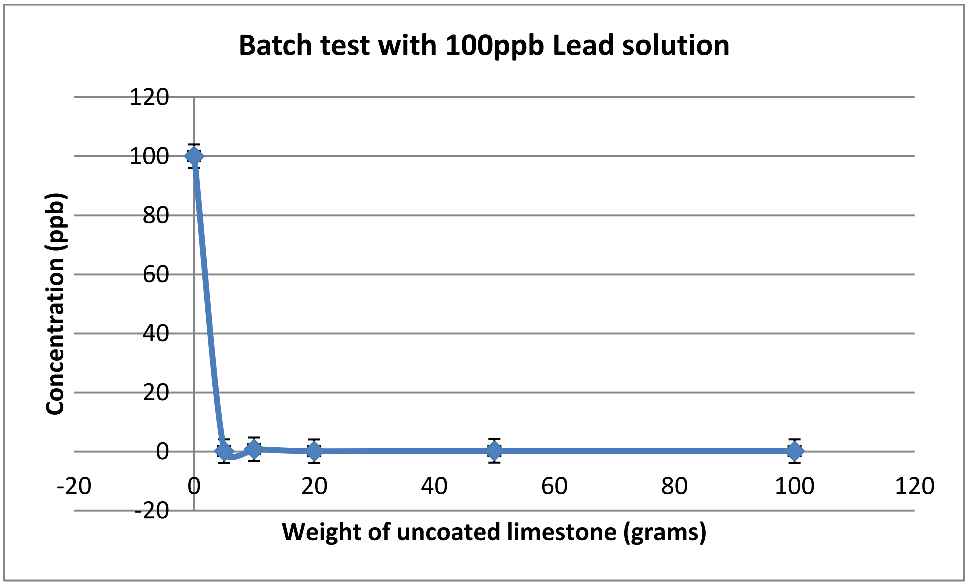

Figure 18. Batch test with 100ppb lead solution using uncoated limestone

Uncoated limestone efficiently removes lead from 100ppb solution. Twenty grams limestone is more efficient than the other amounts removing up to 99.8% of the lead from a 100mL solution of 100ppb concentration.

The results for the batch test with 200ppb lead solution using uncoated limestone is shown in table 12 and figure 19.

Table 12. Batch test with 200ppb lead solution using uncoated limestone

Weight of limestone (grams)	**Concentration (ppb) (±0.05)**
5	0.09
10	0.25
20	0.30
50	0.00
100	0.01

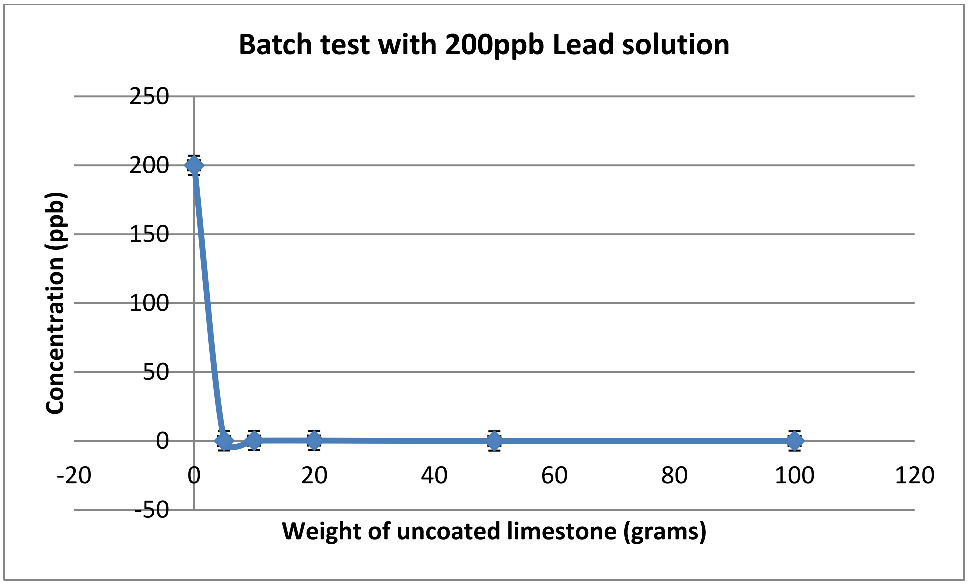

Figure 19. Batch test with 200ppb lead solution using uncoated limestone

In this experiment 50 grams of limestone removes 99.99% of lead efficiently from a 100mL solution of 200ppb concentration.

The effect of limestone on the removal of selenium was studied using batch tests. The results for the batch test with 100ppb selenium solution using uncoated limestone is shown in table 13 and figure 20.

Table 13. Batch test with 100ppb selenium solution using iron-coated limestone

Weight of limestone (grams)	**Concentration (in ppb) (±0.05)**
5	12.02
10	6.02
20	4.07
50	4.86

100	5.12

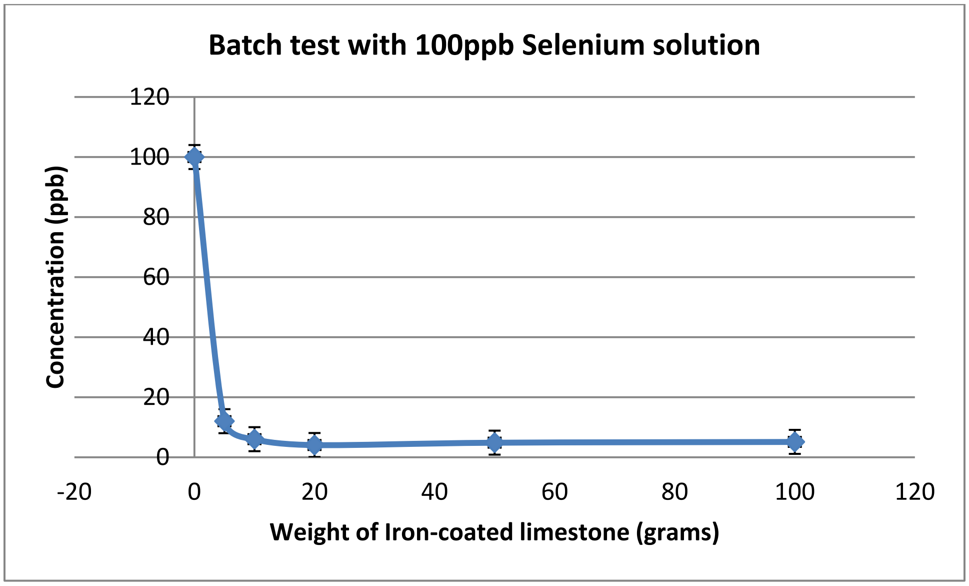

Figure 20. Batch test with 100ppb selenium solution using iron-coated limestone

Batch tests with limestone are very effective with all the amounts. It was found that 20 grams of iron-coated limestone is more effective for removal of selenium from a 100mL solution of 100ppb concentration, since this level removes 95.92% of the selenium from the solution.

The results for the batch test with 200ppb selenium solution using uncoated limestone is shown in table 14 and figure 21.

Table 14. Batch test with 200ppb selenium using Iron-coated limestone

Weight of limestone (grams)	**Concentration (in ppb) (±0.05)**
5	23.3
10	10.5
20	5.99
50	5.01
100	4.20

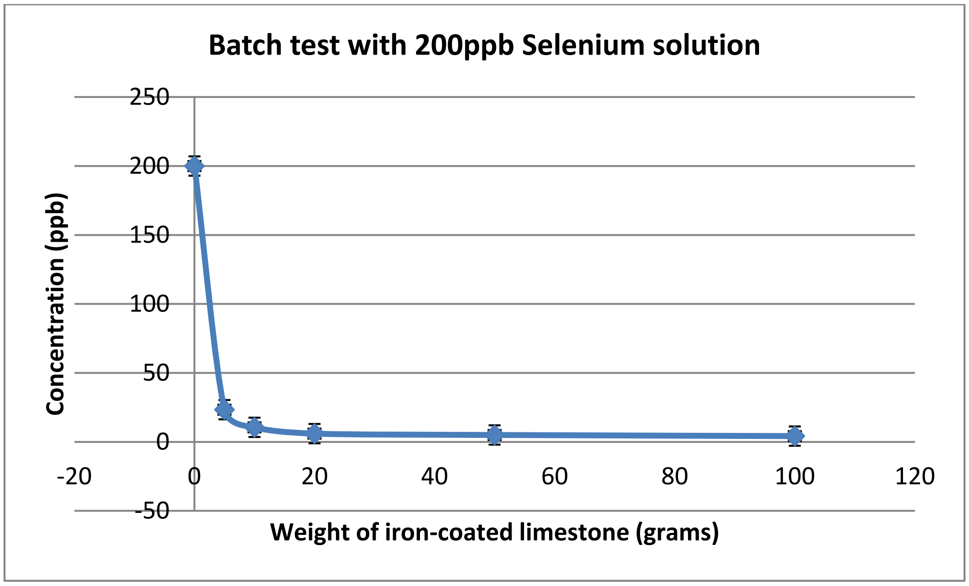

Figure 21. Batch test with 200ppb selenium solution using iron coated limestone

All the amounts of limestone are effective and removes selenium below its drinking water standard. A sample of 100 grams iron-coated limestone is most effective because it removes 97.9% of the selenium from the solution.

C. Effect of pH on Adsorption Capacity:

The effect of pH on the removal of metals is studied by adjusting the pH of the standard solutions. The pH was adjusted by using 1M sodium hydroxide (NaOH). The effect of pH on removal of lead is shown in table 15 and figure 18. The effect of pH on the removal of selenium is shown in table 16 and figure 19.

Table 15. Effect of pH using 100ppb lead solution with 5g uncoated limestone

Initial pH	**% removal (±0.05)**	**Final pH**
5	33.2	8.1
6	73.0	8.2
7	40.8	8.2
8	64.2	8.5
9	3.00	8.7

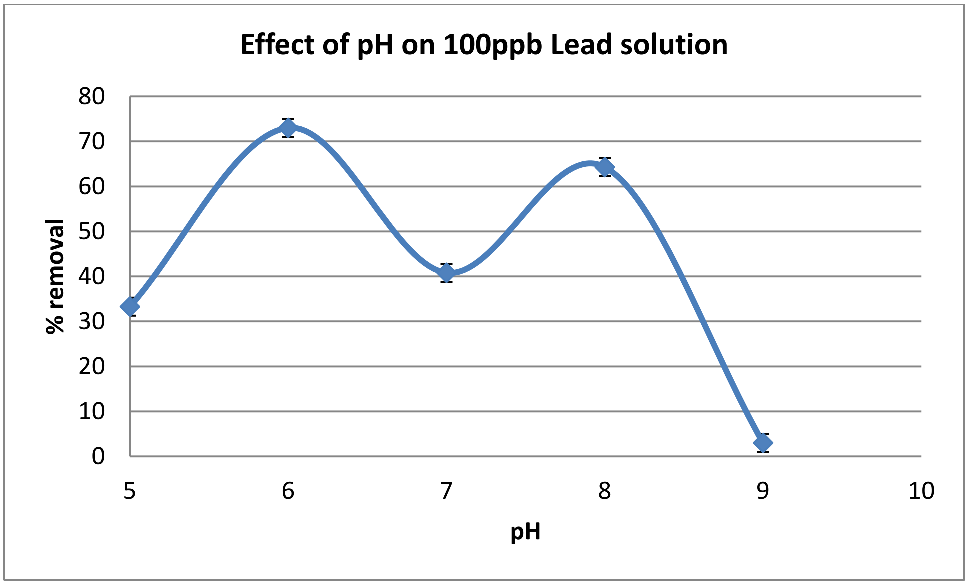

Figure 22. Effect of pH using 100ppb lead solution with 5g uncoated limestone

The pH 6 is most efficient at removing lead from a 100mL solution of 100ppb concentration with 73.0% of the lead removed when the pH was adjusted to 6. The initial pH of the 100ppb lead solution is 2.6. Final pH of the solutions after the treatment with uncoated limestone were measured and are shown in table 14. This buffering is expected as limestone is the base material.

Table 16. Effect of pH using 100ppb selenium solution with 5g iron-coated limestone

Initial pH	**% removal (±0.05)**	**Final pH**
5	85.5	8.3
6	94.6	8.3
7	90.1	8.4
8	90.4	8.6
9	89.4	9.0

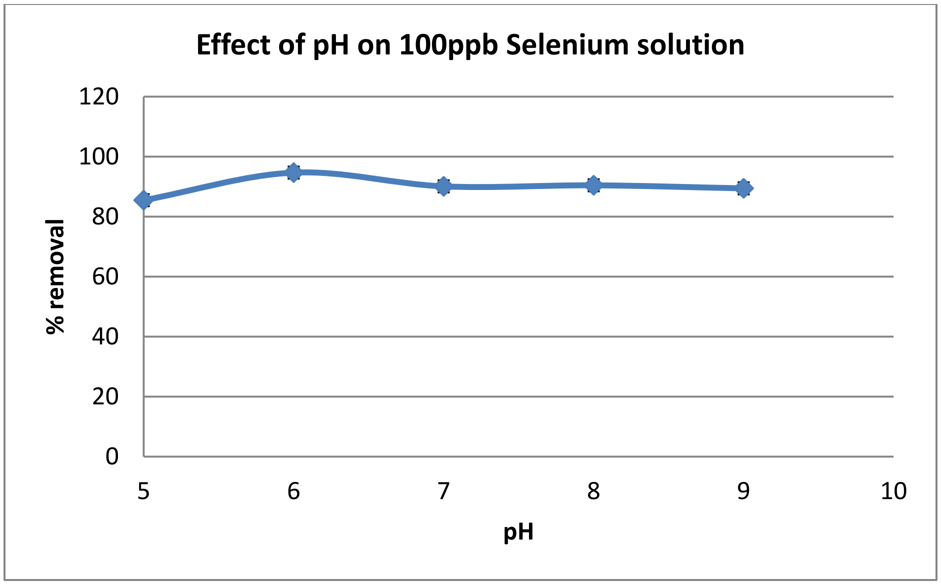

Figure 23. Effect of pH using 100ppb selenium solution with 5g iron-coated limestone

A pH 6 is most effective to remove selenium from a 100mL solution of 100ppb concentration. However, all tested pH conditions are also effective at removing selenium to below the drinking water standard. When the pH is adjusted to 6, selenium has a 94.7% removal.

D. Microscopic studies:

D.1. Scanning Electron Microscopy:

Scanning Electron Microscopic (SEM) images of the plain (uncoated) limestone, iron-coated limestone, plain limestone after treatment with 100ppb of lead solution and coated limestone after treatment with 100ppb of selenium solution are taken using Scanning Electron Microscopy. SEM images are shown in figures 24, 25, 26 and 27.

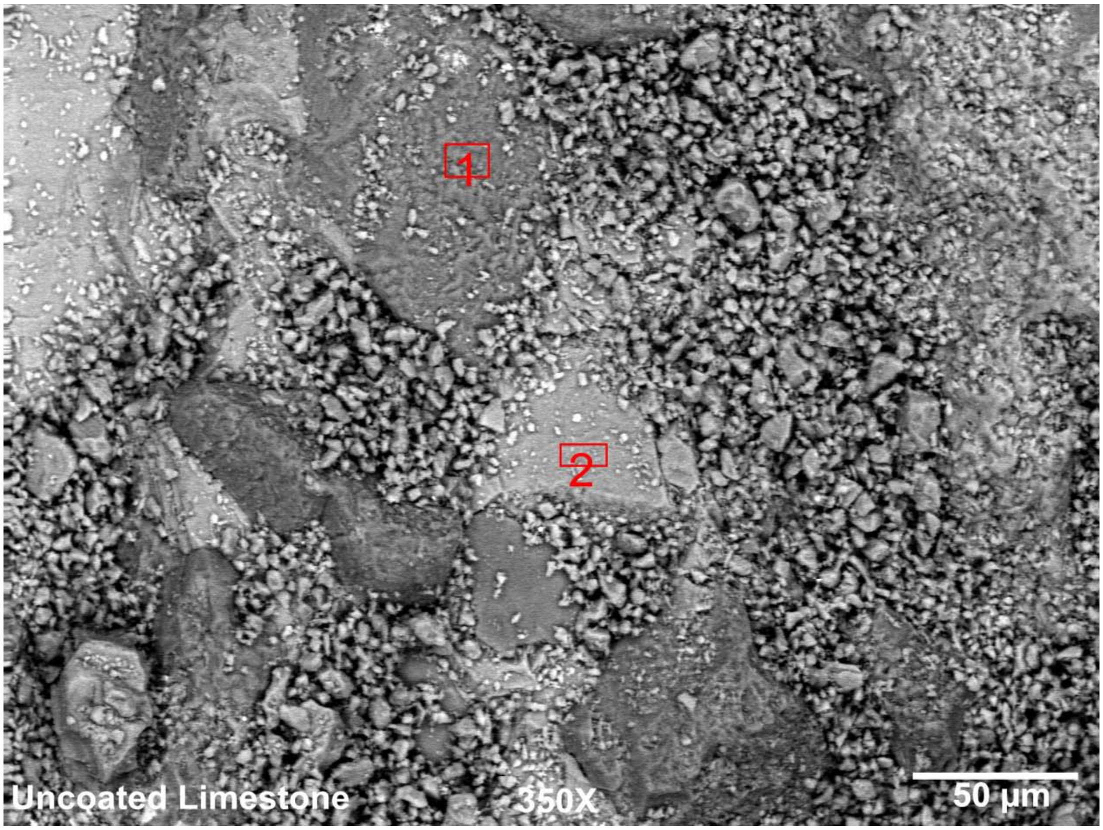

Figure 24. SEM image of uncoated limestone

Analysis Report:

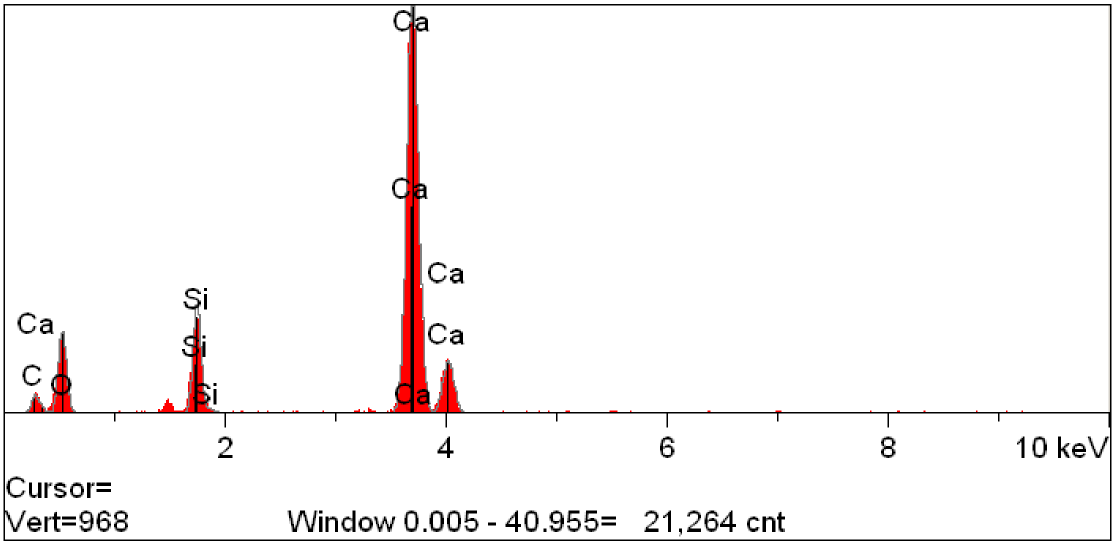

Table 17. SEM analysis of uncoated limestone

	Image-1		**Image-2**	
Elt.	**Atomic %**	**Conc Wt%**	**Atomic %**	**Conc Wt%**
C	5.07	3.03	9.88	5.71
O	66.35	52.80	66.43	51.13
Si	21.47	30.00	4.38	5.92
Ca	7.11	14.18	19.31	37.24
Total	100.00	100.00	100.00	100.00

The analysis of the SEM images of the uncoated limestone indicates that it is primarily $CaCO_3$ with small amounts of silicon (SiO_2).

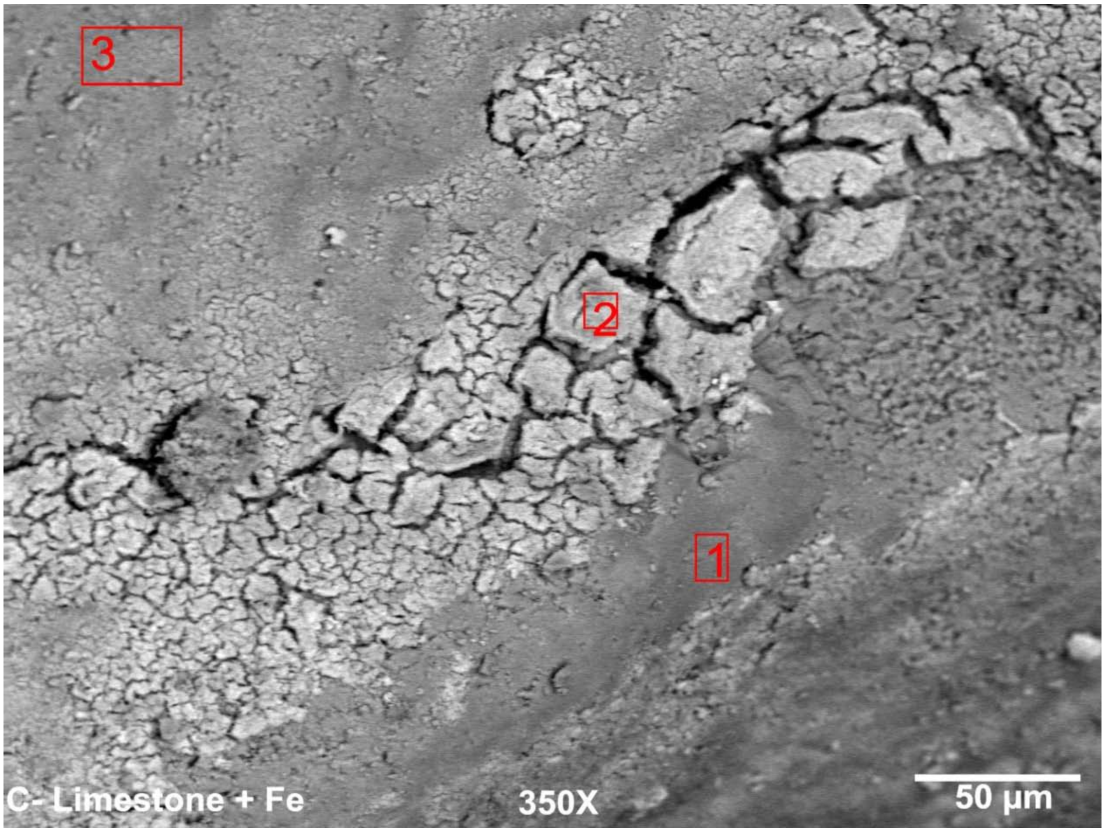

Figure 25. SEM image of iron-coated limestone

Analysis Report:

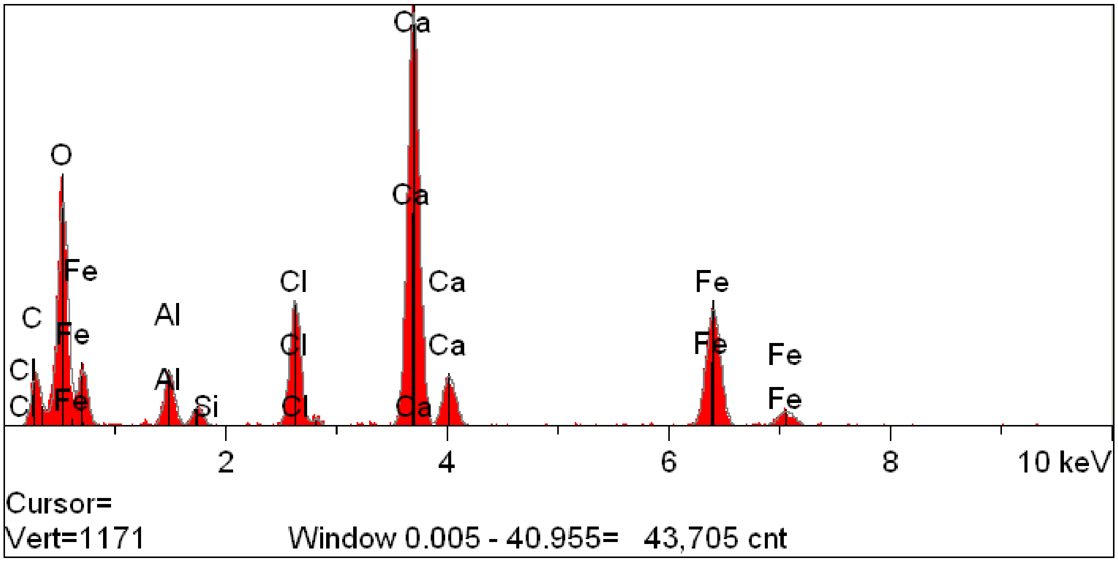

Table 18. SEM analysis of iron-coated limestone

	Image-1		Image-2		Image-3	
Elt.	**Atomic %**	**Conc (wt.%)**	**Atomic %**	**Conc (wt.%)**	**Atomic %**	**Conc (wt.%)**
C	20.01	13.01	18.17	10.89	16.34	10.23
O	65.46	56.67	63.38	50.58	67.36	56.17
Al	2.95	4.30	1.89	2.55	2.07	2.91
Si	0	0	0.55	0.77	0.29	0.42
Cl	0.47	0.91	2.41	4.27	0.72	1.33
Ca	9.90	21.46	8.80	17.59	11.61	24.24
Fe	1.21	3.65	4.80	13.37	1.61	4.70
Total	100.00	100.00	100.00	100.00	100.00	100.00

The analysis of SEM images of the iron-coated limestone indicates that iron is not distributed uniformly and is clearly on the surface of the limestone. The bands where iron is accumulated can be observed directly. The limestone particles also have some chloride probably due to the use of the iron chloride solution to prepare the iron-coated limestone.

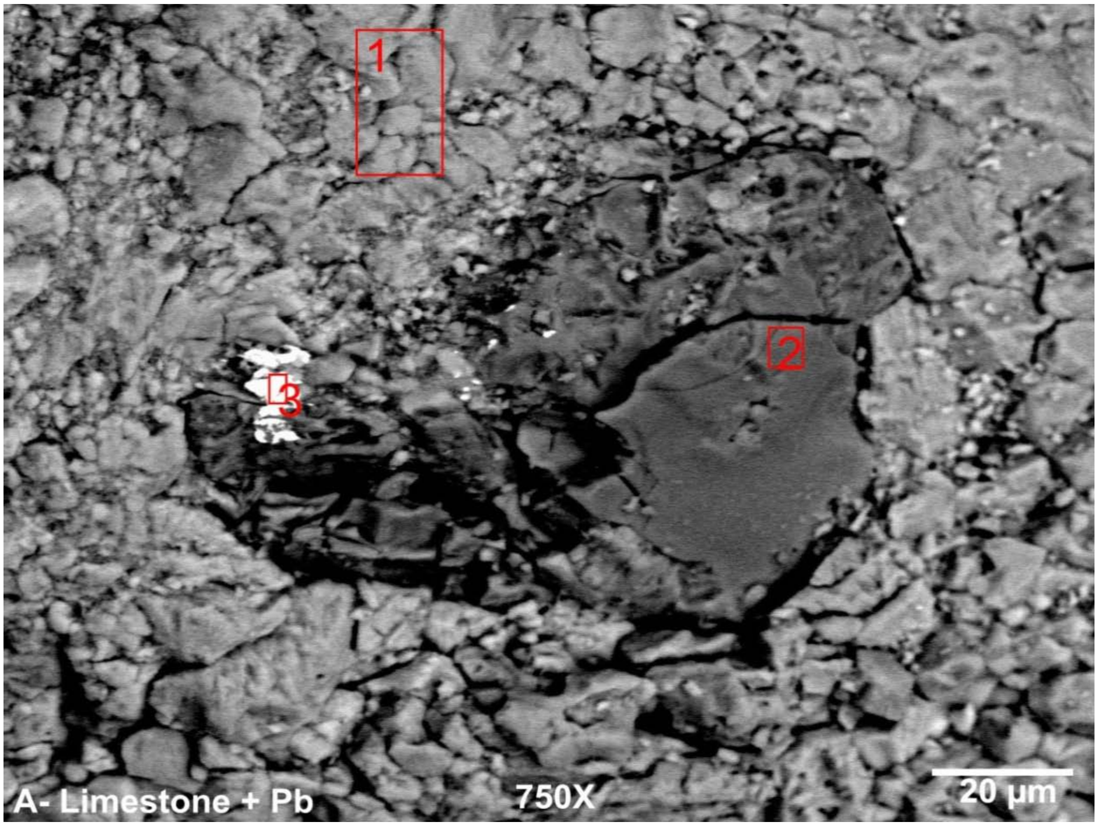

Figure 26. SEM image of the uncoated limestone after the treatment with 100ppb lead solution

Analysis Report:

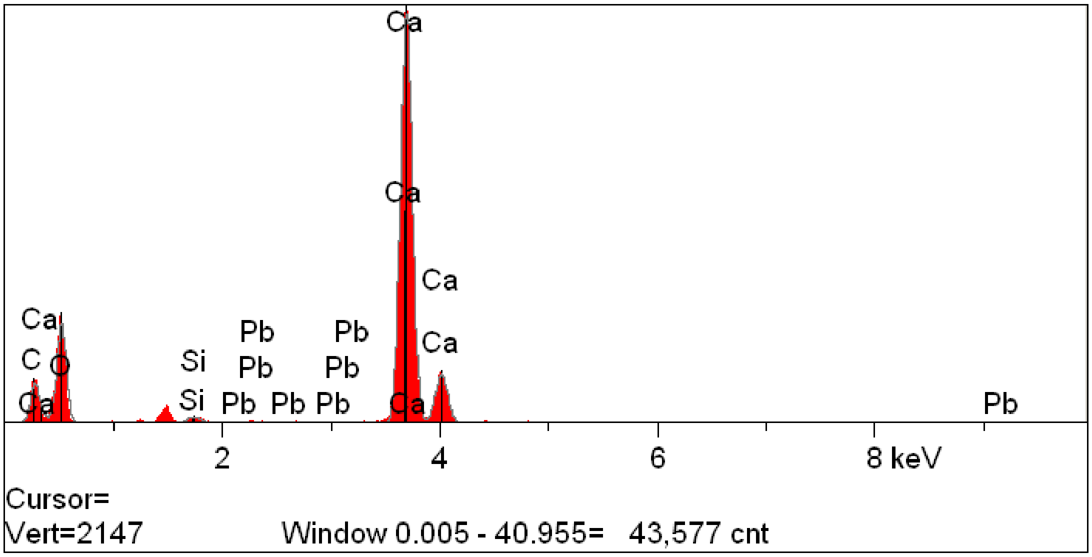

Table 19. SEM analysis of uncoated limestone after treatment with 100ppb lead solution

	Image-1		Image-2		Image-3	
Elt.	**Atomic %**	**Conc Wt%**	**Atomic %**	**Conc Wt%**	**Atomic %**	**Conc Wt%**
C	13.63	8.21	8.71	5.50	14.29	8.87
O	67.15	53.89	67.26	56.55	69.39	57.37
Si	1.25	1.77	20.08	29.64	0.38	0.56
Ca	17.97	36.13	3.95	8.32	15.91	32.95
Pb	0.00	0.00	0.00	0.00	0.02	0.26
Total	100.00	100.00	100.00	100.00	100.00	100.00

The analysis of the SEM image of the plain limestone after treatment with 100ppb lead solution indicates that the material does have small amounts of lead precipitated on the surface which actually can be seen as bright spots in image-3 in table 19 and figure 26.

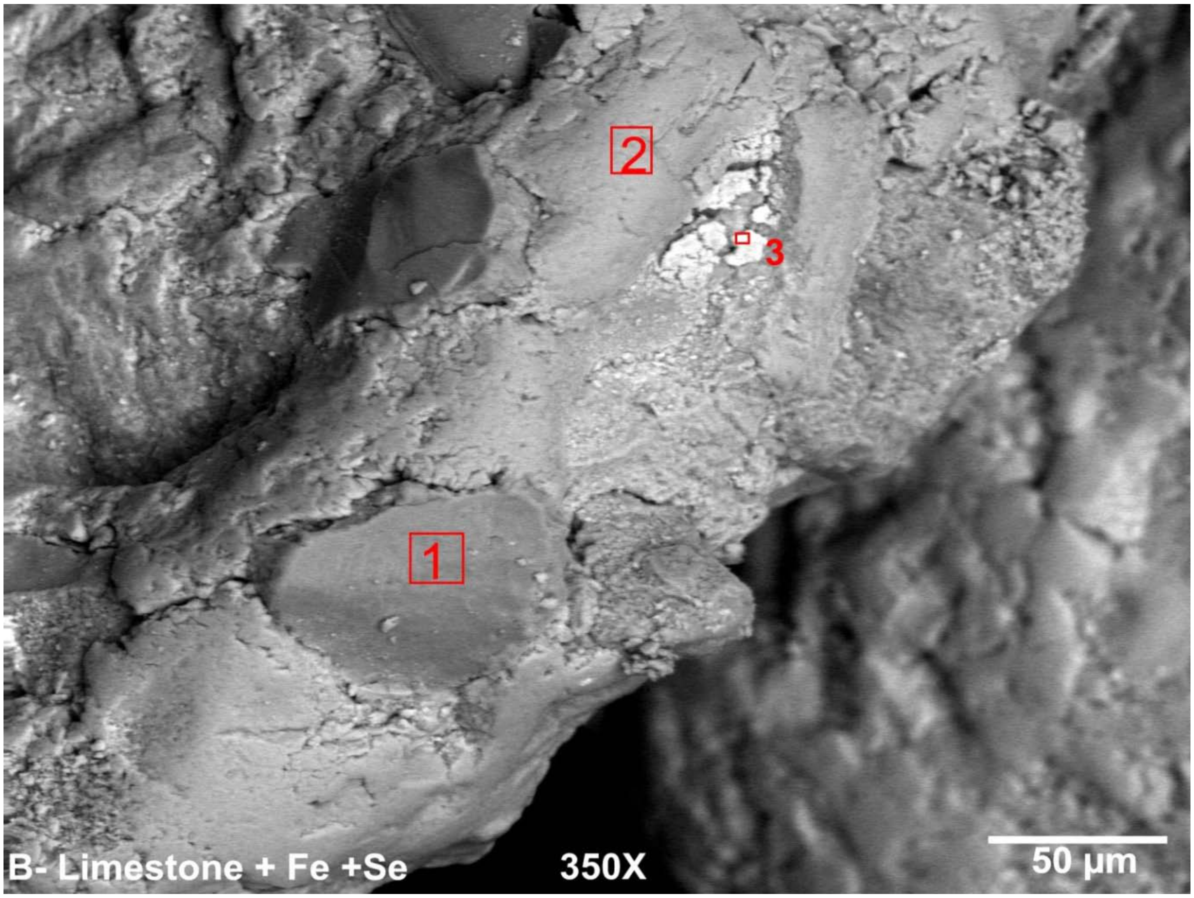

Figure 27. SEM image of the iron-coated limestone after the treatment with 100ppb selenium solution

Analysis report:

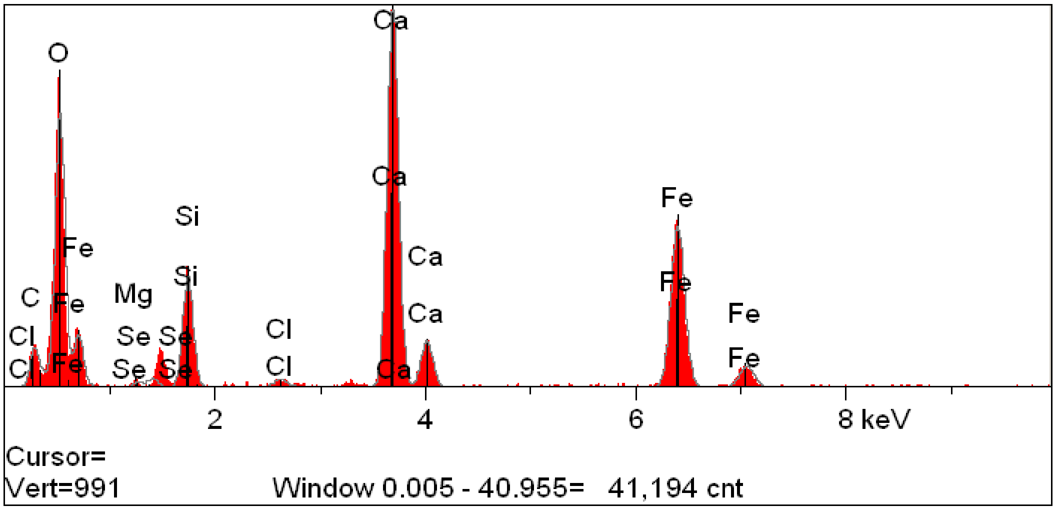

Table 20. SEM analysis of iron-coated limestone after the treatment with 100ppb selenium solution

	Image-1		Image-2		Image-3	
Elt.	**Atomic %**	**Conc wt%**	**Atomic %**	**Conc wt%**	**Atomic %**	**Conc wt%**
C	0.00	0.00	16.24	10.18	11.43	6.55
O	68.18	53.34	66.75	55.70	69.04	52.73
Mg	0.00	0.00	0.72	0.91	0.12	0.14
Si	27.28	37.47	1.84	2.69	3.41	4.57
Cl	0.00	0.00	0.00	0.00	0.21	0.36
Ca	4.16	8.15	14.09	29.46	8.59	16.43
Fe	0.38	1.05	0.36	1.06	7.18	19.13
Se	0.00	0.00	0.00	0.00	0.02	0.07
Total	100.00	100.00	100.00	100.00	100.00	100.00

The analysis of SEM images of the iron-coated limestone after the treatment with 100ppb selenium solution indicates that the limestone has a very small amount of selenium on the surface associated with higher iron levels. No specific images of a selenium mineral can be observed. It is probably chemisorbed to iron hydroxide and is diffusely distributed with iron.

D.2. X-Ray Diffraction technique:

X-Ray diffraction provides information about the crystal structure, chemical composition and physical properties of materials. Uncoated and the iron-coated limestone is ground, homogenized and analyzed to determine their composition using XRD.

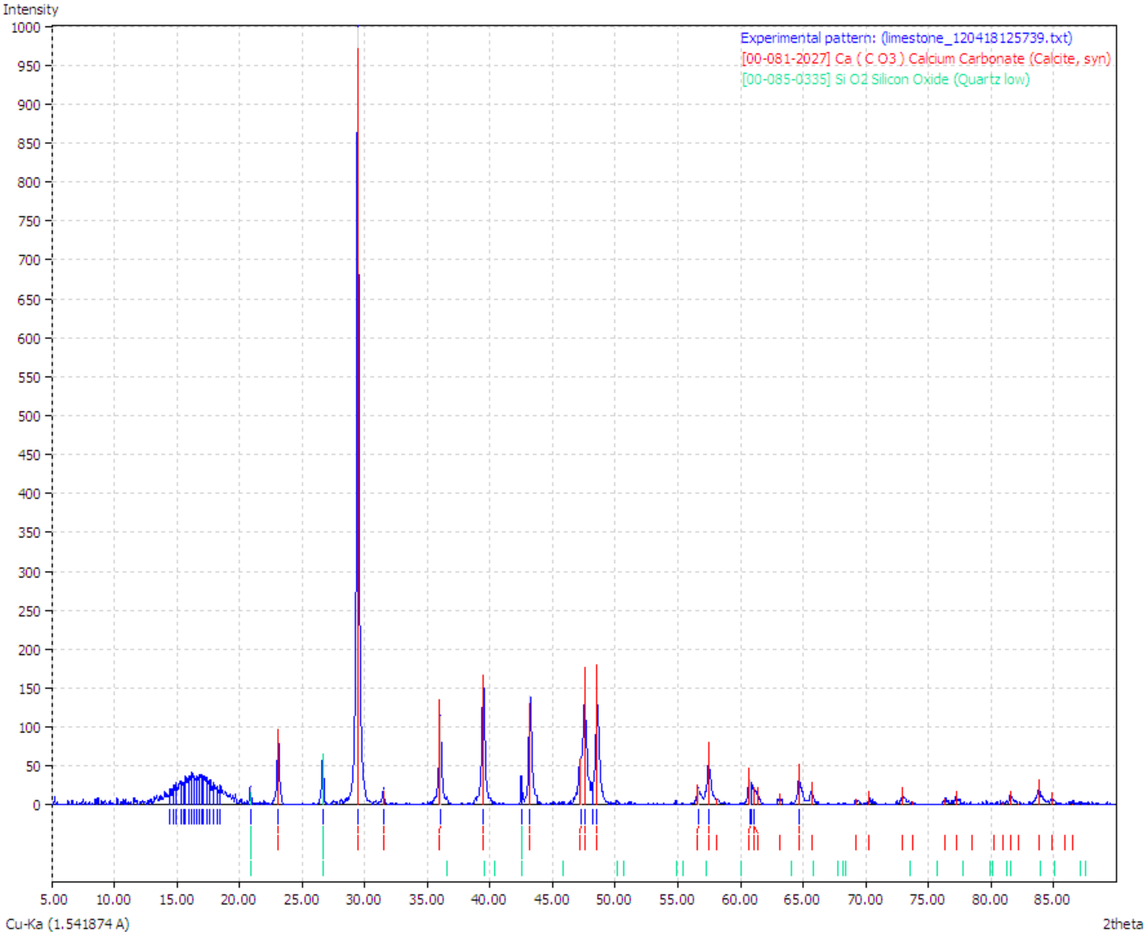

Figure 28. XRD pattern of uncoated limestone and $CaCO_3$

The XRD pattern of the uncoated limestone matches with the known reference peaks of $CaCO_3$.

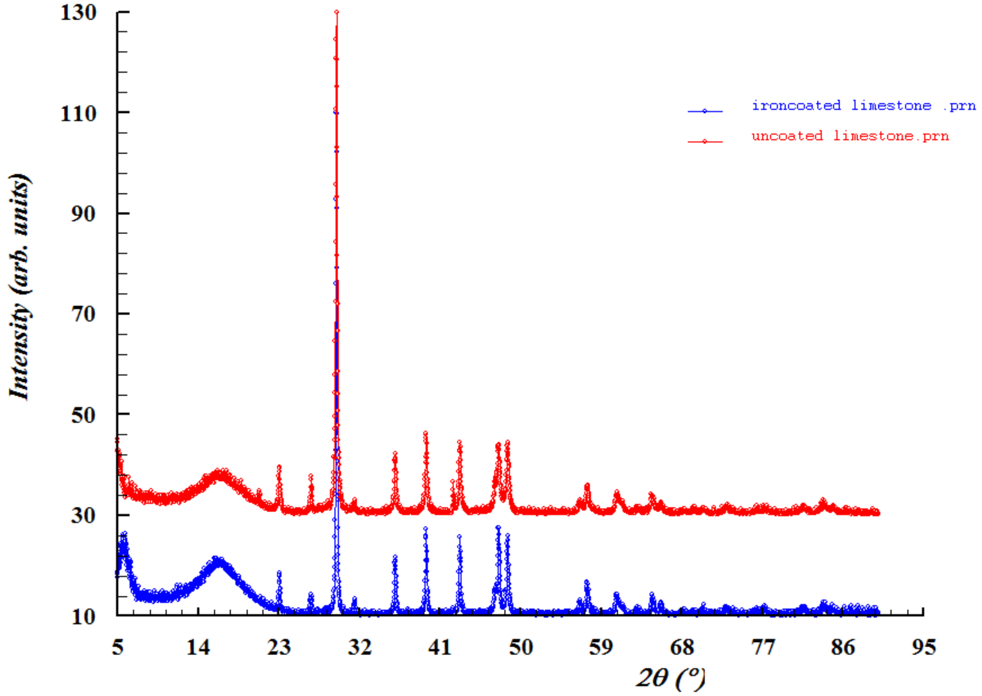

Figure 29. XRD pattern of uncoated and Iron-coated limestone

Little difference can be seen between the uncoated and iron-coated limestone. Iron hydroxide is amorphous and finely distributed. It cannot be directly observed at this level using XRD.

IV. CONCLUSIONS

Limestone is successfully used as a base material for the removal of the selected heavy metals. Plain limestone is coated with iron using iron (III) chloride solution and the efficiency of iron-coated and plain limestones were compared using batch and kinetic experiments. The effect of pH on the removal capacity of limestone was also studied.

The effect of contact time was studied in kinetics studies. It was found that 5 grams of the uncoated limestone removes the lead from a solution of 50ppb concentration within 10 minutes to below the drinking water standard. Over 99% of the lead from a 100mL solution of 100ppb concentration and a 100mL solution of 200ppb concentration was also removed quickly. A level of 5 grams iron-coated limestone removes lead completely from a solution of 50ppb concentration in 10 hours, however the drinking water standard was met within minutes. The uncoated limestone is more effective than the iron-coated limestone, because uncoated limestone removes lead completely in 30 minutes.

Selenium has also been quickly reduced to less than its drinking water standard. Within 5 hours, 99.4% of the selenium was removed after the treatment of 100mL solution of 50ppb concentration with 5grams of iron-coated limestone. It was also found that 92.5% of the selenium was removed in 4 hours after the treatment of 100mL solution of 100ppb concentration with 5 grams of iron-coated solution and 94.6% of the selenium was removed in 3 hours after the treatment of 100mL solution of 200ppb concentration with 5 grams of iron-coated solution. However, the drinking water standard was achieved much sooner. Uncoated limestone removes 79.62% of the selenium from a 100mL solution of 50ppb concentration in 24 hours and was less effective than iron-coated limestone because it removes lead to below the drinking water standard in 30 minutes.

The effect of different amounts of uncoated limestone (5, 10, 20, 50 and 100g) to remove lead was studied. A sample of 10 grams of uncoated limestone efficiently removes lead completely from a 100mL solution of 50ppb. Additionally, 20 grams of uncoated limestone removes 99.8% of the lead from a 100mL solution of 100ppb and 50 grams of limestone efficiently removes 99.9% of lead from a 100mL solution of 200ppb concentration. However, drinking water standards were easily met with 5 grams of uncoated limestone.

Batch tests with limestone are very effective with all amounts. However, 20 grams of iron-coated limestone is most effective at removing selenium from a 100mL solution of 100ppb concentration, with 95.9% of selenium from the solution. Iron-coated limestone worked better for selenium because it removes selenium to below the drinking water standards in less than 4 hours.

The effect of pH on the efficiency of limestone to remove lead was studied. A pH of 6 is most efficient for removing lead from a 100mL solution of 100ppb. At pH 6, 73% of the lead has been removed. Results were widely varied over pH, however, which indicates the need for further study.

The effect of pH on the efficiency of iron-coated limestone to remove selenium was also studied. A pH 6 is more effective to remove selenium from a 100mL solution of

100ppb concentration. However, all other pH conditions tested were also effective to remove selenium below the drinking water standard.

Efficiencies of the uncoated and iron-coated limestones to remove heavy metals from drinking water were compared through batch and kinetic tests. Uncoated limestone was found to be more effective to remove lead. The mechanism for the removal of lead is probably precipitation as lead hydroxide. Iron-coated limestone was found to be more effective to remove selenium and is probably chemisorbed to iron hydroxide. This can be considered as chemisorption.

V. FUTURE WORK

Limestone is readily available and is relatively inexpensive for heavy metal removal. This technology can be adapted to small, rural water supply systems to reduce the heavy metals below their drinking water standards. Different time intervals can be used to study the effect on removal of metals. The effect of pH needs further studies. The mechanism for the removal of lead could be precipitation and needs to be studied further. selenium is removed by binding with iron through oxygen, this is considered as adsorption and further research need to be done to study this mechanism.

Different concentrations of iron (III) chloride can be used to coat the limestone and their effect to remove heavy metals can be compared. We can apply this method to remove combinations of metals.

VI. PERSPECTIVE

Drinking water is polluted with metals that are harmful for people due to waste from industries. There are ways to remove the metals from drinking water, but they are hard and costly. We came up with an idea to remove lead and selenium with a really simple cheap material. Our material is limestone. Limestone is available everywhere. Metals are attracted to the surface of the limestone and can be removed easily. Plain limestone worked very well for lead, but not for selenium. So, we just coated the limestone with a small amount of iron and this removed all the selenium. After the limestone is full, we can just take the limestone to a cement plant to be used in cement because the metals won’t come off.

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