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Removal of Heavy Metals from Drinking Water by Adsorption onto Limestone with a Focus on Copper and Aluminum Applications

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REMOVAL OF HEAVY METALS FROM DRINKING WATER BY ADSORPTION ONTO LIMESTONE WITH A FOCUS ON COPPER AND ALUMINUM APPLICATIONS

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Master of Science

By
Swarna Latha Somasani

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REMOVAL OF HEAVY METALS FROM DRINKING WATER BY ADSORPTION ONTO LIMESTONE WITH A FOCUS ON COPPER AND ALUMINUM APPLICATIONS

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8/27/12

Dean, Graduate Studies and Research Date

I dedicate this thesis to my mother, father and brothers for their love and support. Also, I dedicate this thesis to my research advisor, Dr. Cathleen Webb, for her help and support throughout my research. Also, dedication goes to all my friends at Western Kentucky University.

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Elevated levels of arsenic and other heavy metals like copper, aluminum, zinc, and selenium in drinking water are found to have deleterious effects on human health. Hence, finding methods for reducing their levels is critical. Iron-coated limestone is used as an adsorption material for the removal of heavy metals from drinking water. Removal of heavy metals by native or uncoated limestone was also observed and used for comparison to and evaluation of the improvement in removal efficiency from the iron-coated material. The removal efficiency with limestone was studied for different concentrations of heavy metals. Kinetic studies were done to determine the decrease in heavy metal concentration as a function of time using limestone. Inductively coupled plasma spectroscopy was used for metal analysis. The effective removal rate of copper and aluminum was found to be four hours and one hour, respectively. This method of removal by using limestone is cost effective, eco-friendly, and hence, of great potential importance for heavy metal removal.

Iron-coated limestone is used as an adsorption material for the removal of heavy metals from drinking water. This project will investigate techniques to improve removal efficiency of heavy metals using limestone-based material through adsorption. 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 is readily available and its use for metals removal is relatively inexpensive. The technology can be adapted to small, rural water supply 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

Heavy metals are a class of metallic elements which are abundant in earth’s crust. Heavy metal contamination has been a serious concern throughout the world (Romero, et al, **2001**). Humans may require trace amounts of heavy metals such as copper, and zinc. Unfortunately, these metals can be dangerous at high levels. Heavy metal accumulation at higher levels can result even in death. Heavy metal toxins contribute to a variety of adverse health effects (Romero, et al, **2001**). Around twenty different known heavy metals were identified that can impact human health. Accumulation of heavy metals within the body can lead to a decline in the mental, cognitive, and physical health of the individual (Aziz, et al, **2005**). Global environmental changes have dramatically increased the overall environmental 'load' of heavy metals (Lee, et al, **2005**). Today, heavy metals are abundant in our air, soil, and even drinking water. They are present in virtually every area of modern life (Chen, et al, **2008**). Heavy metal concentration in drinking water in the United States is regulated by the United States Environmental Protection Agency (U.S. EPA), under the Safe Drinking Water Act. Several international organizations and national organizations like United Nations International Children’s Emergency Fund (UNICEF), World Health Organization (WHO), World Bank and National Government Organizations (NGOs) have initiated steps to control heavy metal levels in drinking water, especially in Asian countries (Hossain, et al, **2005**).

Heavy metals may cause chronic poisoning with some considered to be a human carcinogen. Copper and aluminum have been found in ground water in many parts of the world like India, Bangladesh, Inner Mangolia and Taiwan (Ferguson, et al, **2007**). Higher levels of copper and aluminum were found to cause skin, lung, and bladder cancer (Le, et al, **2000**). Heavy metals in ground water tend to be mostly in a reduced state which can be inferred from the lower redox potentials. Geochemical conditions may also lead to naturally occurring higher levels of heavy metals in ground water (Kim, et al, **2000**). The maximum contaminant level (MCL) is referred to as maximum level of heavy metals in water that can cause potential effects on human body.

<u>Copper</u>**:** Copper is a transition element with atomic number 29 and atomic weight 63.55 amu. In solution copper (II) has a blue color. It may exist in both the cuprous (+1) and cupric (+2) forms. Melting and boiling points of copper are 1357 K and 2835 K, respectively. Copper exhibits malleable and ductile properties. Hence, it has wide applications in electrical wiring, utensils, pipes, building materials, alloys, electroplating, petroleum refining, and the azo dye manufacture (Landner & Lindestrom, **1999**). Copper compounds are also used in fungicides, insecticides, and in fertilizers as a nutrient to support growth.

Copper is essential for proper functioning of enzymes such as superoxide dismutase, ceruloplasmin, cytochrome-c oxidase, tyrosinase, monoamine oxidase. Copper is found in various parts of the body such as the lungs, liver, kidney, and brain (Linder, et al, **1996**). Adsorption of copper occurs in the upper gastrointestinal tract. Copper is removed from the body through bile, sweat, and urine (Luza, et al, **1996**; Cox, **1999**).

Copper enters into humans through food, water and air. Food and water are the major source of copper ingestion into the body. The lethal dose of copper lies between 4 and 400 mg of copper (II) per kg body weight (Chuttani, et al, **1965**). Copper exposure can lead to headaches, diarrhoea, nausea and vomiting at low doses. Increased doses of copper can result in gastrointestinal bleeding, hepatocellular toxicity, renal failure and oligouria (Agarwal, et al, **1993**).

Figure 1 shows the speciation diagram of copper in water. Copper exists in both the free state and in hydroxyl forms. Among all the forms free copper (II) ion and monohydroxy copper (II) are considered to be highly toxic. While the anionic complexes such as carbonate complexes are less toxic. The particulate copper is not toxic unless it is solubilized in water or within the fluids of organism (Cuppett, et al, **2006**).

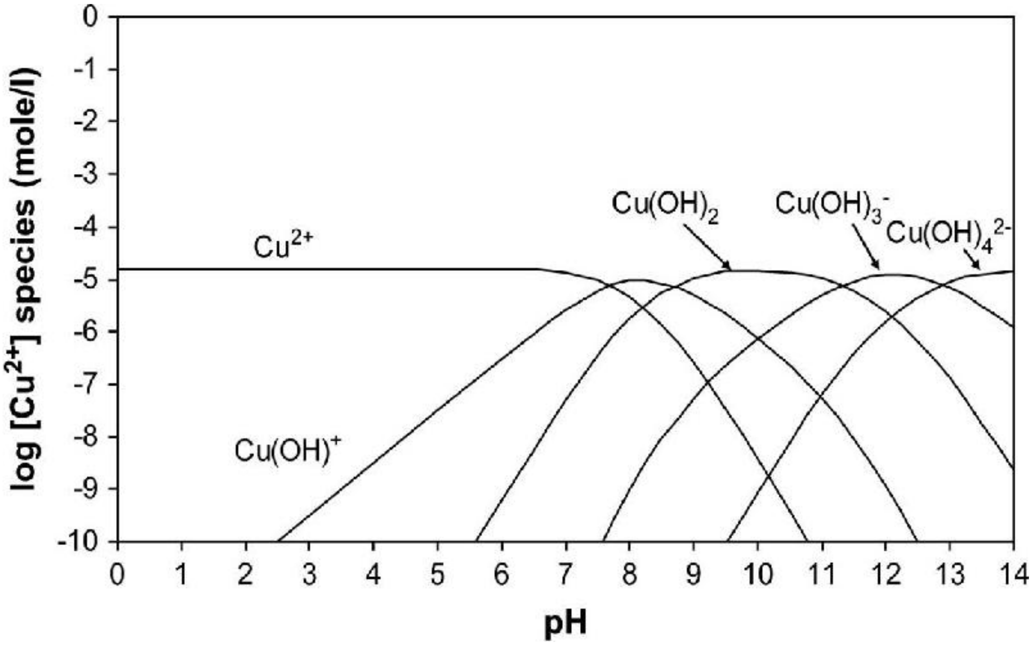

Figure 1: Copper Speciation in water (Cuppett, et al, **2006**)

In pure water, copper has a minimal solubility around pH 5. Copper in drinking water is analyzed by inductively coupled plasma spectroscopy (ICP) and the detection limits for copper are given as 3.6 µg/L (ISO, **1996**).

Aluminum: Aluminum is a metallic element with atomic number 13 and atomic mass of 26.98 amu. It is colorless and typically exists in +3 oxidation state. It is available in earth's crust as silicates, oxides and hydroxides along with other metals such as sodium and fluorides. The melting and boiling points are found to be 933 K and 2740 K respectively.

Aluminum is widely used in automotive, aircraft, construction, electric industries and in alloys. It is also used in cooking utensils and in food packaging. It is also used in water treatment process to reduce the level of microbes, organic matter, color and turbidity. It serves as a coagulant in the water treatment process. It is commonly used in pharmaceutical industries such as in the preparation of antacids. It is also used in antiperspirants and food additives (ATSDR, **1992**).

The most common source of ingestion of aluminum in humans is by air, water and food. Aluminum is present in water in different forms and its existence is influenced by pH. In pure water, aluminum has a minimal solubility in the pH range of 5.5-6.0. Aluminum in drinking water is analyzed by inductively coupled plasma spectroscopy (ICP) and the detection limits for aluminum are given as 30 µg/L (ISO, **1996**). Aluminum in lethal doses was found to cause skin rashes, arthritis, mouth ulcers, skin ulcers, nausea and vomiting (WHO, **1997**).

Figure 2 represents the speciation diagram of aluminum in water at 25^0C. Aluminum exists mostly in the +3 oxidation state up to pH 4. Many transitions occur between pH 5 and 6. Aluminum in the +3 oxidation state is transformed to the hydrated form around pH 5.

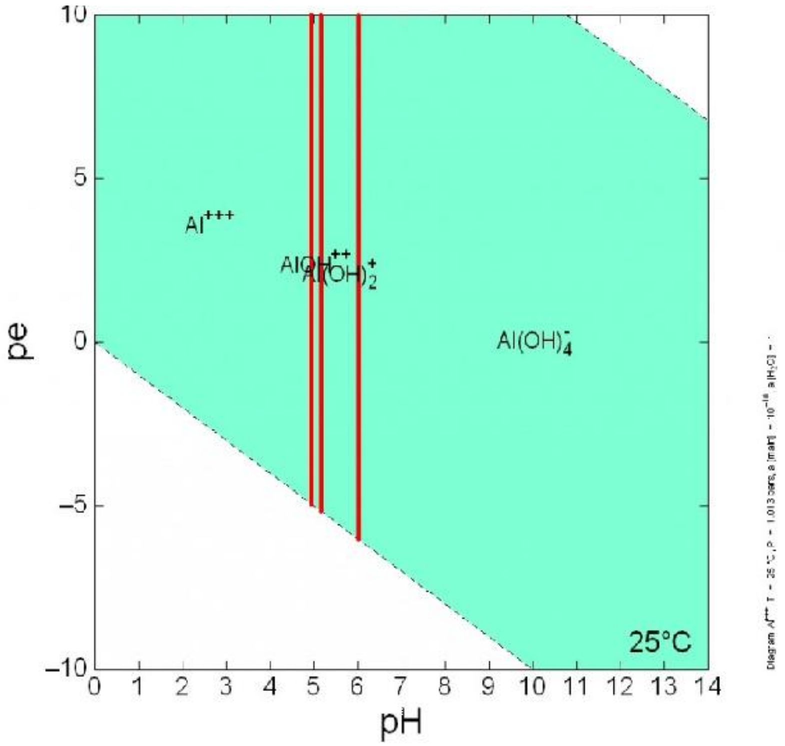

Figure 2: Aluminum Speciation in water

In recent years, heavy metal contamination in ground water has been found to be alarming in ground water in Asian countries like Bangladesh, India and China (Hossain, et al, **2005**). Specific rock types, geochemical conditions, proximity to hydrologic and landscape variables are found to be the reasons of higher content of heavy metals in ground water (Joseph, et al, **2006**).

Techniques for heavy metal removal: Several techniques are well established and have been in use for the removal of heavy metals from drinking water including coagulation, ion exchange, reverse osmosis, nano filtration, adsorption and usage of activated alumina.

Coagulation/ Flocculation: Iron chloride is used as a coagulant to remove heavy metals from drinking water at certain pH conditions. The presence of sulfates and other organic matter affected the removal efficiency. Alum can also be used as coagulant. Alum is chemically hydrated aluminum potassium sulfate (Janet, et al, **1997**).

Activated Alumina: Activated alumina is efficient in removing total dissolved solids and is effective for arsenic. However, it is difficult to regenerate activated alumina (Nurul, et al, **2006**).

Ion exchange: Ion exchange removal occurs by the exchange of heavy metal ions with other species in a column. This process may be efficient in removal but there is competition among the heavy metals for the exchange sites. Pores often get clogged with suspended solids, and other matter (Nurul, et al, **2006**).

Reverse Osmosis: Cellulose triacetate membranes are generally used for separation. This is an efficient method for removal but often the membranes get degraded by chlorine and they are difficult to clean or regenerate (Mina, et al, **2009**).

Nanofiltration: Nano filters act by the principle of charge exclusion and retain certain ions. Pore distribution and membrane size also influences the separation of uncharged organic species. Since it is an expensive technique, the usage is limited (Nurul, et al, **2006**).

Adsorption Techniques: Several materials such as limestone, hematite and feldspar, activated carbon, and activated alumina have been used as adsorbents (Silva, et al, **2010**).

Limestone: Limestone acts as an adsorbent in heavy metal removal. The most commonly used limestone is calcite and dolomite. Limestone in a pulverized form is typically used. Commercially available limestone is pulverized and then sieved so that smaller particles with enhanced surface area are produced (Silva, et al, **2010**). Earlier research by using limestone as an adsorbent for removal of heavy metals from drinking water has showed the removal efficiency of 90%. Adsorption using limestone is found to be economic, efficient and eco-friendly since it produced no harmful products.

Bio techniques such as use of bacterial sensors and ferns, which are inexpensive and nontoxic, can help in removing heavy metals from drinking water. Unfortunately, these techniques are labor and resource intensive.

Earlier, extensive research was done on arsenic removal from drinking water since it poses severe health problems. Arsenic sources can be categorized as either anthropogenic or natural. Anthropogenic sources include agriculture chemicals and wood preservatives, forest fires. Natural sources of arsenic include arsenopyrite (FeAsS), pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$), piment (As_2S_3). Arsenic in ground water can also be obtained by the dissolution of arsenic bearing iron oxides (Peters, et al, **1999**). Arsenic is also introduced by volcanoes, and erosion (Islam, et al, **2007**).

Elevated levels of arsenic and other heavy metals like copper, aluminum, zinc, selenium in drinking water are found to have deleterious effects on human health. The US EPA set the drinking water standards for arsenic at 0.01 ppm, copper at 1.3 ppm, aluminum at 0.2 ppm, zinc at 3 ppm, cadmium 0.003 ppm, selenium at 0.01 ppm, and lead at 0.01 ppm. Higher levels of arsenic in drinking water cause numbness in hands and feet, blindness, and cancers of lung, liver and prostate. Various techniques are used to reduce the levels of arsenic from drinking water. Sorption and desorption process were studied in arsenic removal from water using limestone, rice husk and granular activated carbon (GAC). Limestone is coated with a layer of porous Si-Ca-As containing iron oxide with some manganese oxide. Water with low levels of As (III) was obtained after passing through the filter using limestone. Adsorption studies using rice husk also showed reduced arsenic levels in water. Column tests with granular activated carbon showed removal of As (III) and As (V) from drinking water. Sorption and desorption of arsenic were found to depend upon aqueous concentration of arsenic, pH and aqueous concentration of other heavy metals. After the removal of arsenic from drinking water different instrumental methods are used to detect and measure the levels of arsenic. Arsenic interferes with cellular activity by inhibiting cellular enzymes, thus causing cell death, lactic acidosis and other health problems (Janet, et al, **1997**; Stocker, et al, **2003**).

Arsenic occurs in two oxidation states: arsenate and arsenite. In surface waters it is present in the form of arsenate, As (V). In ground waters it is mostly present in the form of arsenite, As (III). Combinations of As (III) and As (V) are also present. As (V) is easily removed when compared to As (III). Most methods require As (III) to be converted into As (V) for efficient removal (Nurul, et al, **2006**). Arsenite is oxidized by free chlorine, potassium permanganate, ozone, chloramines, chlorine dioxide and UV radiation (Sorlini, et al, **2010**). Oxidation by using chlorine, potassium permanganate, ozone is more effective in comparison to chloramines, UV radiation, and chlorine dioxide. The adsorption process is often carried out through column tests. Various factors such as particle size, flow rate and amount of adsorbate affect the adsorption process. As the particle size decreases the removal efficiency increases because of the greater surface area when compared to larger particles (Nurul, et al, **2006**).

Adsorption occurs by two ways: affinity adsorption and anion exchange. Affinity adsorption is related to the surface behavior of the rice husk. Anion exchange is between arsenic in the water and the carbon surface of adsorbent material. Recovery add substantially to cost, waste disposal, technical difficulty and safety (Nurul, et al, **2006**).

Anion exchange mechanism can be explained electrochemically. Hydroxyl groups are created on the surface of adsorbent. Carbon present on the surface of adsorbent in contact with water reduces oxygen to hydroxyl ions. Carbon loses electrons and becomes positively charged. Electrical neutrality is maintained with the help of hydroxyl ions, which results in their adsorption. The hydroxyl ions are deposited on the surface of the adsorbent. When a solution containing anions with greater affinity towards carbon than hydroxyl ions is passed through, then the hydroxyl ions are exchanged for anionic species (Nurul, et al, **2006**).

Desorption process is a method for recovery of the adsorbent, which is typically expensive. Recovery is done by hydrochloric acid, sulfuric and nitric acid and base solution such as sodium hydroxide and potassium hydroxide (Nurul, et al, **2006**).

Limestone is used as the adsorbent in the proposed research. The structure of limestone was investigated from the experiments such as helium gas infiltration where the porosity was found to be 17.6%. Nitrogen adsorption experiments indicate that limestone exhibits two kinds of pores. Most of the surface area of limestone is found to possess micro pores which are responsible for increase in surface area thus resulting in enhanced adsorption (Leith, et al, **1996**). Limestone is so inexpensive it does not need to be recovered. It can be safely disposed of in cement or concrete.

Instruments for analyzing heavy metal content: For detection of heavy metals in drinking water various instrumental methods have been designed such as Inductively Coupled Plasma Mass Spectrometry (ICPMS), High Performance Liquid Chromatography (HPLC), and Graphite Furnace Atomic Absorption Spectrometry (GFAA), and Flow Injection Hydride Generation Atomic Absorption Spectrophotometer (FI-HG-AA).

II. Experimental Section

Chemicals and Materials: Table 1 shows chemical names and their manufacturers.

Table 1: Materials

Chemical Name	Manufacturer
Nanopure water	Barnstead Nano Pure II
Limestone (#16/60)	Pete Lien and Sons, LaPorte, CO
Ferric chloride ($FeCl_3$. $6H_2O$)	Mallinckrodt
Whatman cellulose nitrate membrane filters (0.45 µm, 25 mm)	Fisher Scientific
Millipore Swinnex Filter Holder	Fischer Scientific
Sodium hydroxide (NaOH)	Fischer Scientific
Buffers (pH 4 and pH 7)	Fischer Scientific
Copper (1000 ppm)	Inorganic Ventures
Aluminum (1000 ppm)	Inorganic Ventures
Nitric acid (Concentrated, Trace metal grade)	Fischer Scientific

Preparation of stock solutions

Preparation of 0.1M iron chloride solution: A sample of 27 grams of $FeCl_3 \cdot 6H_2O$ was dissolved in 10 mL of nanopure water and transferred to a 1000 mL volumetric flask. The volume is made to 1000 mL with nanopure water.

Preparation of iron-coated limestone: A sample of 100 grams of limestone was placed into a round bottom flask. A solution of 100 ml 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 1M sodium hydroxide were added to shock the solution. The granules were rinsed with nanopure water and then air dried.

Preparation of 1M sodium hydroxide solution: A sample of four grams of sodium hydroxide was dissolved in 10 mL of nanopure water which was then transferred to a 100 mL volumetric flask. The volume is made to 100 mL with nanopure water.

Standard solutions 1000 ppm of copper and aluminum were purchased from Inorganic Ventures. All other solutions were prepared from these standards.

Preparation of 20 ppm copper solution: An aliquot of 20 mL of 1000 ppm standard copper solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Preparation of 40 ppm copper solution: An aliquot of 40 mL of 1000 ppm standard copper solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Preparation of 100 ppm copper solution: An aliquot of 100 mL of 1000 ppm standard copper solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Preparation of 2 ppm aluminum solution: An aliquot of 2 mL of 1000 ppm standard aluminum solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Preparation of 4 ppm aluminum solution: An aliquot of 4 mL of 1000 ppm standard aluminum solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Preparation of 6 ppm aluminum solution: An aliquot of 6 mL of 1000 ppm standard aluminum solution was placed in a 1000 mL volumetric flask and the volume is made up to 1000 mL with nanopure water.

Instrumentation

Inductively Coupled Plasma (ICP-ES): Inductively coupled plasma emission spectroscopy provides for the multi-element analysis. An instrument of ICP is shown in Figure 3. It usually consists of a torch which carries argon gas through it. The torch is connected to a water cooled induction coil. The coil is in turn, connected to a radio-frequency generator. A spark from the Tesla causes ionization of the argon gas, producing ions and electrons and resulting in the formation of high temperature plasma. The sample to be analyzed is introduced into the torch. Usually a nebulizer converts the sample into fine droplets and introduces the sample into the plasma. The elements converted into ions. They recombine in the plasma remitting radiation at the characteristic wavelengths of the elements involved. Hence, a particular element is detected. (Skoog, et al, **1998**).

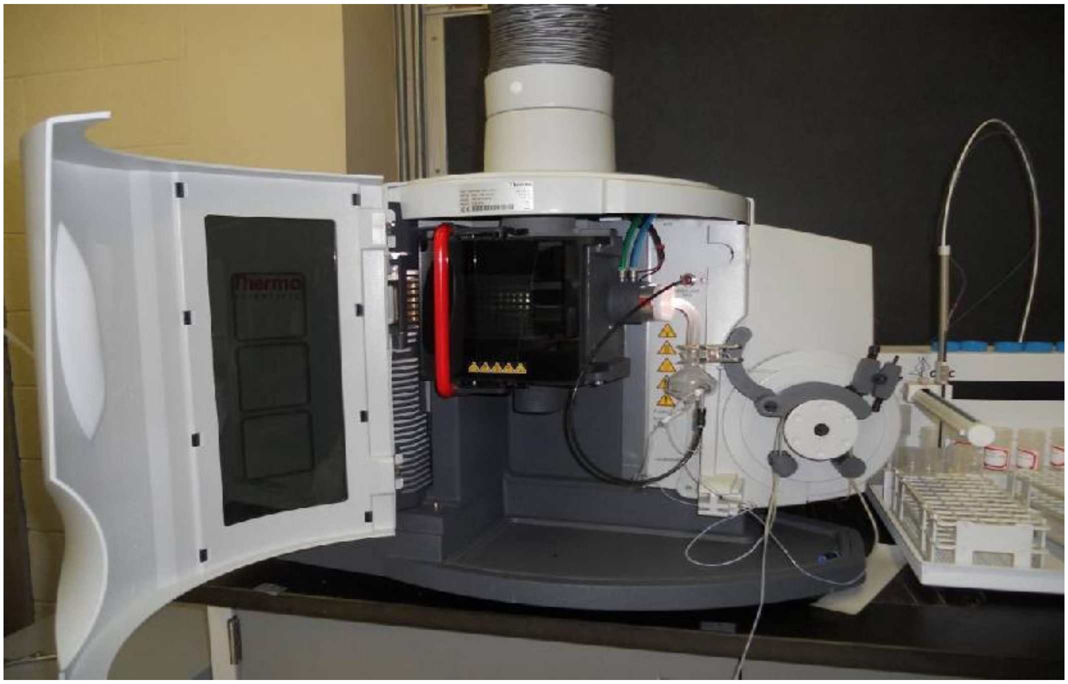

Figure 3: Inductively coupled plasma

Wrist action shaker: A wrist action shaker is used for the purpose of stirring. The Burrell wrist action shaker (model 75) shown in Figure 4 was used. The shaker is designed in such a way that it can hold eight flasks at a time. The desired time and speed can be setup on the shaker. This is used to coat the limestone material and also for stirring of the solutions.

Figure 4: Burrell wrist action shaker

pH meter: An Accumet basic AB15 pH meter shown in Figure 5 was used for the purpose of pH measurement of all the solutions. It consists of a glass electrode. The instrument is calibrated with pH buffers 4 and 7. After calibration it is used for pH measurement.

Figure 5: Accumet pH meter

Scanning electron microscope: The JEOL JSM-5400 LV SEM was the used to analyze the samples.

Sample preparation for SEM:

Mounting: SEM samples are generally mounted on metal holders called stubs. The stubs are generally made of aluminum. The sample is generally fastened on to the stub by a mounting material such as tape. The mounting material should be stable upon the bombardment of electrons with minimal release of solvents, and should have good electrical conductivity.

X-ray diffraction methods (XRD): X-ray diffraction is used for the qualitative and quantitative determination of solid samples. It works on the principle that X-ray diffraction pattern is unique for each sample. This pattern from XRD is compared with a known compound and the chemical compound is identified.

Experimental Methods

Kinetic studies

Copper

Kinetic studies: Kinetic studies were done to study the effect of time on heavy metal removal rate. These experiments were conducted with iron-coated limestone and uncoated limestone. For kinetic studies, the same amount of limestone was used and kept in contact with the standard solution for different time intervals (0.25, 0.5, 1, 1.5, 2, 4, 10 and 24 hours). A 100 mL volume of 20 ppm of copper solution was taken in round bottom flask. To each flask ten grams of iron coated limestone was added and kept in contact with the copper solution for the stated time intervals. Kinetic studies were done using both coated and uncoated limestone. The speed of the shaker is set to 1-2 cycles per sec. The pH of the copper solution was measured before and after the kinetic experiments. The same experiments were done with uncoated limestone and an initial copper solution of 20 ppm.

Aluminum

Kinetic studies: Kinetic studies for aluminum were done to study the effect of time on heavy metal removal rate. These experiments were conducted with both iron-coated limestone and uncoated limestone. For kinetic studies, the same amount of limestone was used and kept in contact with the standard solution for different time intervals (0.25, 0.5, 1, 1.5, 2, 4, 10 and 24 hours). A 100 mL volume of 2 ppm of aluminum solution was placed in a round bottom flask. To each flask, ten grams of coated limestone was added and kept in contact with the aluminum solution for stated time intervals. Kinetic studies were done using both coated and uncoated limestone. The speed of the shaker is set to 1-2 cycles per sec. The pH of the aluminum solution was measured before and after the kinetic experiments. The same experiments were done with uncoated limestone and an initial aluminum solution of 2 ppm.

Batch tests

Copper

Batch tests: These experiments were conducted with both iron-coated limestone and uncoated limestone. Different amounts of iron coated limestone (5, 10, 20 and 100 grams) are used. A duplicate of ten grams was also prepared for quality control and assurance. Different amounts of limestone were placed into separate round bottom flasks and 100 mL of 20 ppm copper solution was introduced into each of the flasks. The speed of the shaker is set at 2 cycles per sec for four hours.

The same experimental procedure was followed for uncoated limestone with copper solution of 20 ppm for time period of four hours. All the samples, once they are removed from the shaker, were microfiltered and analyzed on ICP.

Aluminum

Batch tests: These experiments were conducted with both iron-coated limestone and uncoated limestone. Different amounts of iron coated limestone (5, 10, 20 and 100 gms) are used. A duplicate of ten grams was also prepared for quality control and assurance. Different amounts of limestone were weighed into separate round bottom flasks and 100 mL of 2 ppm aluminum was introduced into each of the flasks. The speed of the shaker is set at 1-2 cycles per sec for a time period of one hour.

The same experimental procedure was followed for uncoated limestone with initial aluminum solution of 20 ppm for a time period of one hour. All the samples once they are removed from the shaker are microfiltered and analyzed on ICP.

pH studies: The effect of pH on heavy metal removal was studied for both aluminum and copper heavy metals. For this purpose, stock solutions of copper (40 ppm) and aluminum (4 ppm) of varying pH 5, 6, 7, 8 and 9 prepared. The desired pH is achieved with addition of small amounts of sodium hydroxide solution (1M). The solutions kept in contact with iron coated limestone on the shaker for a time period of four hours for copper and one hour for aluminum solution. Then, the solutions are microfiltered and analyzed on ICP.

Limestone and water interactions: In order to study if there are any interactions of water with limestone, limestone was kept in contact with water for 24 hours and then analyzed on ICP and SEM.

Sample analysis: The samples were collected into separate vials with 25 µ Whatman cellulose nitrate membrane filters. ICP is used for the sample analysis. ICP is calibrated using standard solution of the heavy metal that is being analyzed. Flush time of 60 seconds and 80 seconds are used for copper and aluminum solutions respectively. Wavelengths of 324.754 nm and 308.2 nm are used in ICP for copper and aluminum samples respectively.

Microscopic studies: Microscope studies are done to study the surface behavior of limestone. They are done both by scanning electron microscopy (SEM) and X-ray diffraction studies (XRD). SEM and XRD studies are done to study the surface nature of both iron-coated and uncoated limestone. SEM studies are also done for iron coated limestone after the treatment with copper and aluminum solutions.

III. Results and Discussions

Kinetic Studies: The effect of contact time on the removal rate of aluminum and copper was determined by kinetic experiments. For kinetic studies, fixed amount of limestone (ten grams) is kept in contact with limestone for different time intervals. The kinetic experiments were done using both coated and uncoated limestone and compared for their removal efficiency. The calibration data for copper after the analysis on ICP-ES is shown in Table 2 and Figure 6.

Table 2: Calibration data for copper

Copper concentration (ppm)	Signal intensity (324.7 nm)	Signal intensity (327.3 nm)
0	241.4	138
0.5	18566	10198
1	39675	21931
2.5	95179	52151
5	187120	103409
10	365045	205641
15	531312	298638
20	724002	407667

Figure 6 shows the calibration curve for copper. The graph is plotted for concentration on the X-axis and signal intensity on the Y-axis. Calibration is done at different concentrations (0.5 ppm, 1 ppm, 2.5 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm) of copper standard solution. The wavelengths used for copper analysis are 324.7 nm and 327.3 nm. The calibration curve has a correlation value of 0.999 at both wavelengths.

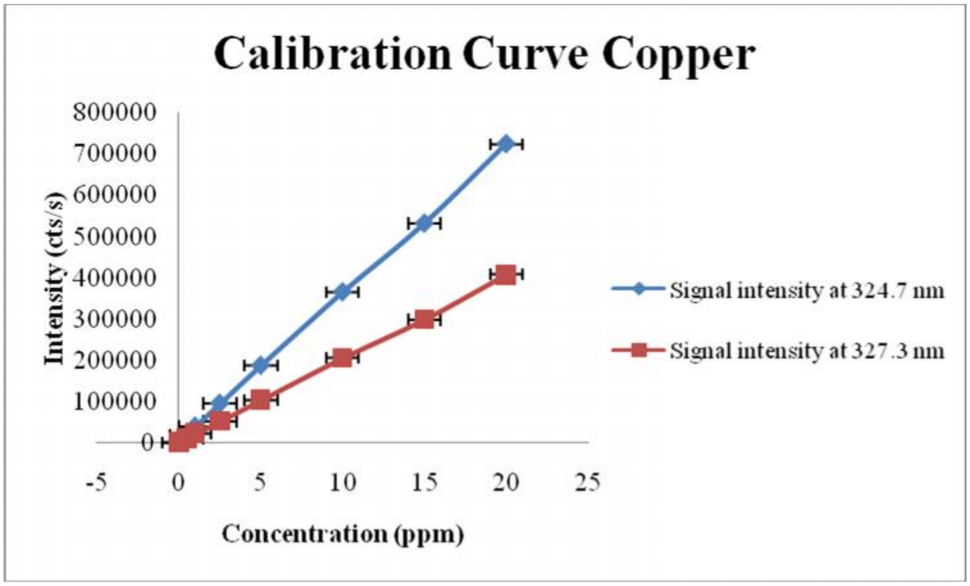

Figure 6: Calibration curve for copper

Table 3 shows the the data obtained for kinetics experiment with 20 ppm copper using uncoated limestone after the analysis on ICP-ES. Figure 7 shows the kinetics experiment with an initial concentration of 20 ppm copper solution on uncoated limestone.

Table 3: Kinetics experiment with 20 ppm copper solution using ten grams uncoated limestone

Time (hours)	Copper concentration (ppm) at 324.7 nm (± 0.15 ppm)	Copper concentration (ppm) at 327.3 nm (± 0.15 ppm)
0	20.00	20.00
0.5	10.95	10.87
1	18.13	17.99
1.5	17.42	17.24
2	16.09	15.94
4	0.541	0.519
10	6.643	6.605
24	0.667	0.650

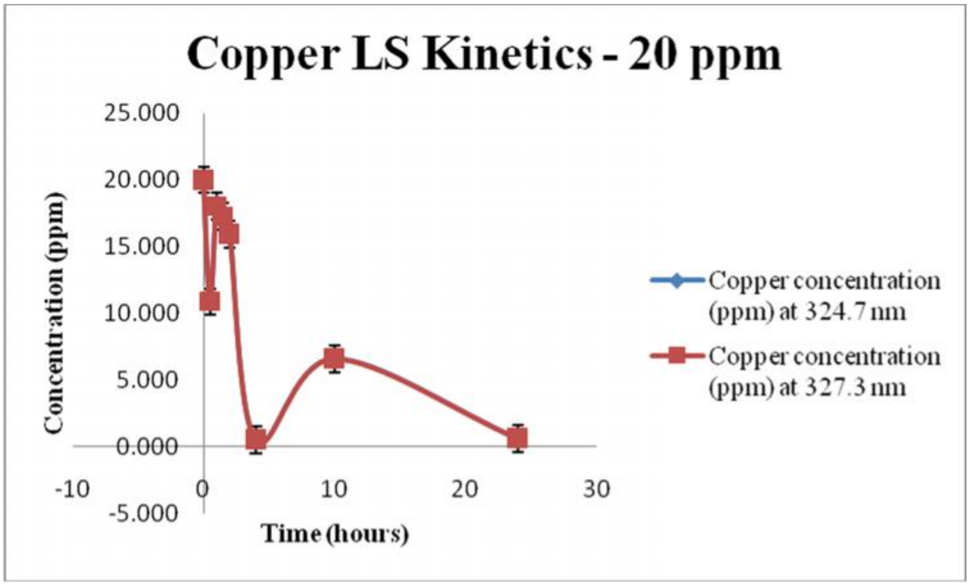

Figure 7: Kinetics experiment with 20 ppm copper solution using ten grams uncoated limestone

In Figure 7, the X-axis represents the time in hours and the Y-axis represents the residual concentration of the copper metal after treatment with plain limestone. The two series represent the concentrations of copper at wavelengths 324.7 nm and 327.3 nm. It showed the maximum removal within four hours. An amount of ten grams of uncoated limestone could remove 97 percent of the copper from the solution. However, the drinking water standard of 1.3 ppm for copper was achieved within four hours.

Table 4 shows the the data obtained for kinetics experiment with 20 ppm copper using iron-coated limestone after the analysis on ICP-ES. Figure 8 shows the kinetics experiment with an initial concentration of 20 ppm copper solution on iron-coated limestone.

Table 4: Kinetics experiment with 20 ppm copper solution using ten grams iron-coated limestone

Time (hours)	Copper concentration (ppm) at 324.7 nm (± 0.15 ppm)	Copper concentration (ppm) at 327.3 nm (± 0.15 ppm)
0	20.00	20.00
0.5	8.591	8.478
1	5.149	5.086
1.5	4.120	4.071
2	4.418	4.336
4	0.598	0.581
10	0.377	0.353
24	1.273	1.245

In Figure 8, the X-axis represents the time in hours and the Y-axis represents the residual concentration of the copper metal after treatment with iron-coated limestone. The two series represent the concentrations of copper measured at wavelengths 324.7 nm and 327.3 nm. Maximum removal is within four hours. An amount of only ten grams of iron-coated limestone could remove 97 percent of the copper from the solution within four hours. However, the drinking water standard of 1.3 ppm for copper was achieved within four hours.

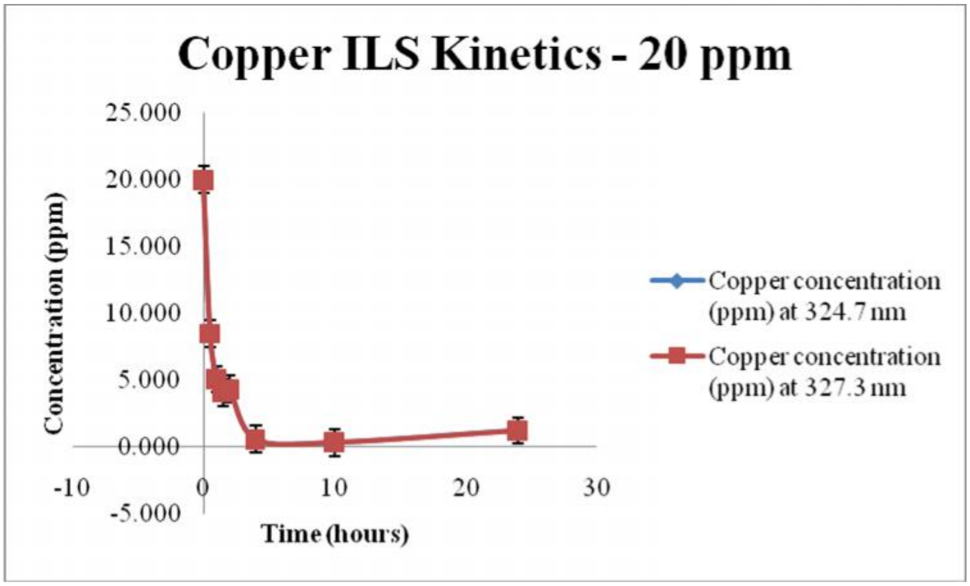

Figure 8: Kinetics experiment with 20 ppm copper solution using ten grams iron-coated limestone

The effect of limestone on removal rate was also studied using batch tests. Batch tests are typically done with varying amounts of limestone (5, 10, 20, 50 and 100 grams) with a fixed contact time of four hours since maximum removal rate is achieved within four hours.

Table 5 shows the batch experiment with an initial concentration of 20 ppm copper solution on iron-coated limestone. Figure 9 shows the batch experiment with an initial concentration of 20 ppm copper solution on iron-coated limestone.

Table 5: Batch test with 20 ppm copper solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Copper concentration (ppm) at 324.7 nm (±0.015 ppm)	Copper concentration (ppm) at 327.3 nm (±0.015 ppm)
0	20.00	20.00
5	0.195	0.177
10	0.373	0.357
10	0.363	0.355
20	0.026	0.011
50	0.028	0.016
100	0.045	0.033

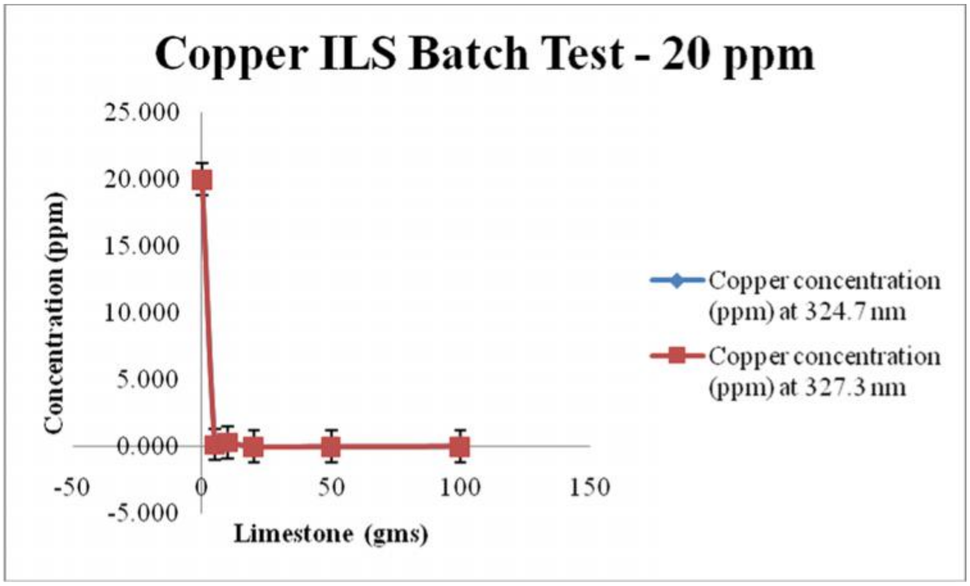

Figure 9: Batch experiment with 20 ppm copper solution using iron-coated limestone

In Figure 9, the X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the copper metal after treatment with iron-coated limestone. The two series represent the concentrations of copper at wavelengths 324.7 nm and 327.3 nm. An amount of 20 grams of iron-coated limestone could effectively remove 99.8 percent of the copper from the solution within four hours. The concentration of copper was found to be 0.02617 ppm after treatment with 20 grams of iron-coated limestone. However, the drinking water standard of 1.3 ppm for copper was achieved with five grams of iron-coated limestone.

Table 6 shows the batch experiment with an initial concentration of 40 ppm copper solution on iron-coated limestone. Figure 10 shows the batch experiment with an initial concentration of 40 ppm copper solution on iron-coated limestone.

Table 6: Batch experiment with 40 ppm copper solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Copper concentration (ppm) at 324.7 nm (± 0.015 ppm)	Copper concentration (ppm) at 327.3 nm (± 0.015 ppm)
0	40.00	40.00
5	0.174	0.198
10	1.765	1.762
10	1.065	1.079
20	0.674	0.696
50	0.275	0.282

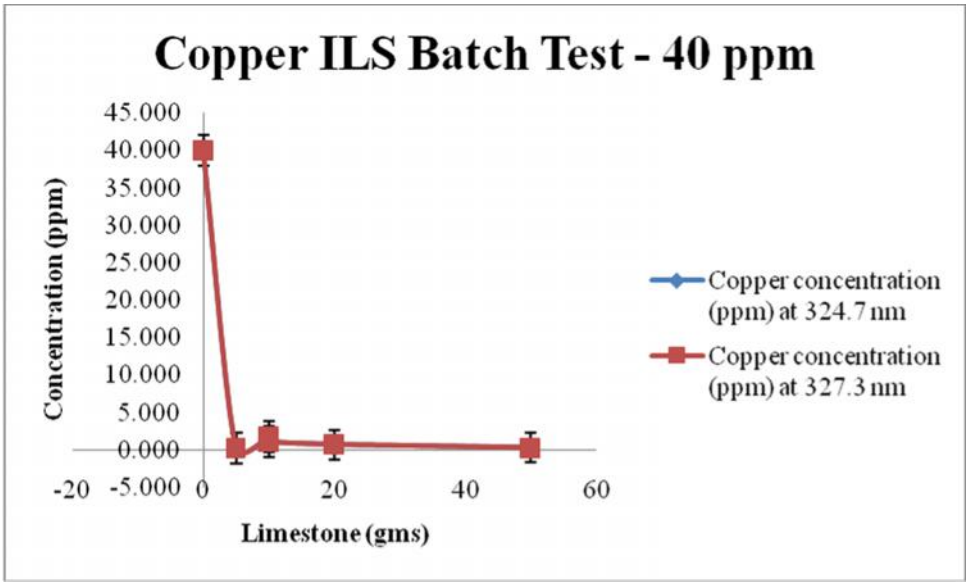

Figure 10: Batch experiment with 40 ppm copper solution using iron-coated limestone

In Figure 10, the X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the copper metal after treatment with iron-coated limestone. The two series represent the concentrations of copper at wavelengths 324.7 nm and 327.3 nm. An amount of 20 grams of iron-coated limestone could effectively remove 99.3 percent of the copper from the solution within four hours. The concentration of copper was found to be 0.6744 ppm after treatment with 20 grams of iron-coated limestone. However, the drinking water standard of 1.3 ppm for copper was achieved with five grams of iron-coated limestone.

Table 7 shows the batch experiment with an initial concentration of 1000 ppm copper solution on iron-coated limestone. Figure 11 shows the batch experiment with an initial concentration of 100 ppm copper solution on iron-coated limestone.

Table 7: Batch experiment with 100 ppm copper solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Copper concentration (ppm) at 324.7 nm (± 0.015 ppm)	Copper concentration (ppm) at 327.3 nm (± 0.015 ppm)
0	100.0	100.0
5	ND	ND
10	0.002	0.010
10	ND	ND
20	0.017	0.013
50	ND	0.006

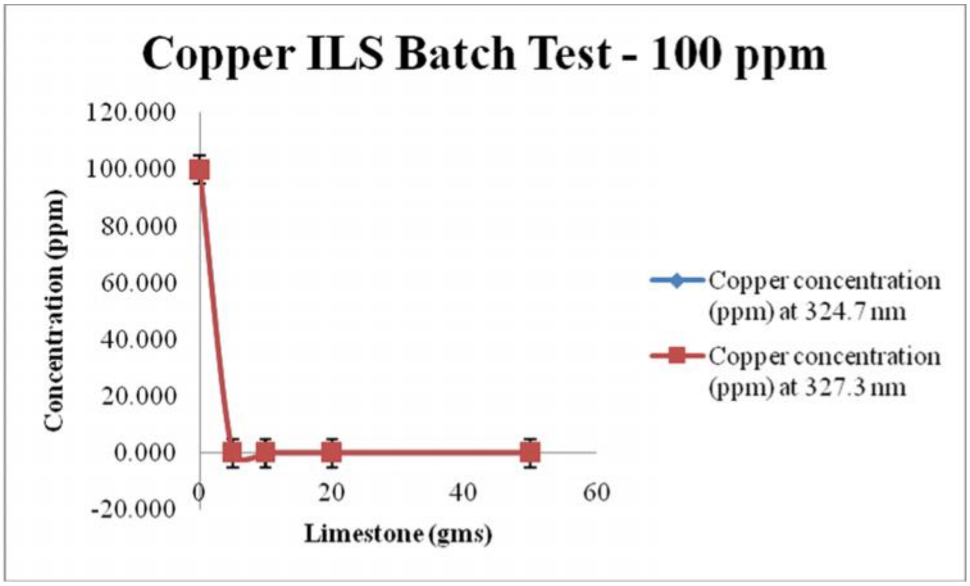

Figure 11: Batch experiment with 100 ppm copper solution using iron-coated limestone

Figure 11 shows the batch experiment with an initial concentration of 100 ppm copper solution on iron-coated limestone. The X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the copper metal after treatment with iron-coated limestone. The two series represent the concentrations of copper at wavelengths 324.7 nm and 327.3 nm. An amount of five grams of iron-coated limestone could effectively remove 100 percent of the copper from the solution within four hours. The concentration of copper was found below the detection limits after treatment with five grams of iron coated limestone. However, the drinking water standard of 1.3 ppm for copper was achieved with five grams of iron-coated limestone.

The effect of pH on removal efficiency was studied for copper solution at different pH values 5, 6, 7, 8 and 9. The desired pH was adjusted using smaller amounts of 1M sodium hydroxide solution.

Table 8 shows the data for effect of pH on removal efficiency for copper solution using iron-coated limestone. Figure 12 shows the effect of pH on removal efficiency for copper solution using iron-coated limestone.

Table 8: Effect of pH using ten grams iron-coated limestone with 40 ppm copper solution

Initial pH (± 0.1)	Percentage removal measured at 324.7 nm (±2%)	Percentage removal measured at 327.3 nm (±2%)
5	99	99
6	100	100
7	100	100
8	98	98
9	99	99

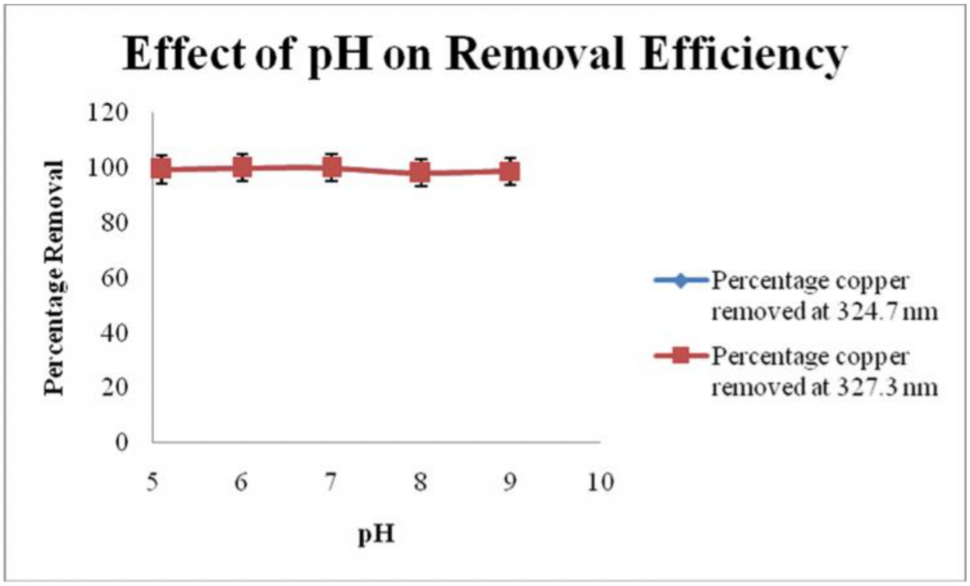

Figure 12: Effect of pH using ten grams iron-coated limestone with 40 ppm copper solution

In Figure 12, the X-axis represents initial pH of copper solution before treatment with iron-coated limestone and the Y-axis represents the percentage of copper removed after treatment with iron-coated limestone. The two series represent the percentage of copper removed at wavelengths 324.7 nm and 327.3 nm. At pH 7 copper was completely removed from the solution, i.e., 100 percent removal efficiency was achieved. The concentration of copper was below the detection limits at pH value of 7 for an initial concentration of 40 ppm copper solution using iron-coated limestone. Since the removal efficiency did not vary with pH the removal efficiency is insensitive to pH.

The calibration data for aluminum after the analysis on ICP-ES is shown in Table 9 and Figure13.

Table 9: Calibration data for aluminum

Aluminum concentration (ppm)	Signal intensity (308.2 nm)	Signal intensity (309.2 nm)
0	273.6	ND
0.25	595.1	ND
0.5	1277	1252
1	2348	3630
2.5	5651	10940
5	11110	23030
7.5	16650	35370
10	22150	47560

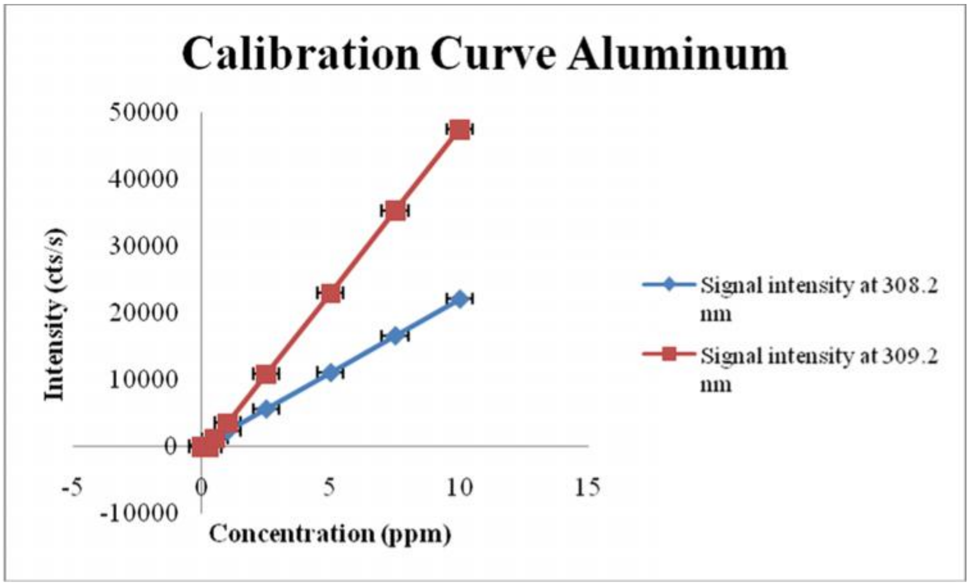

Figure 13: Calibration curve for aluminum

Figure 13 shows calibration curve for aluminum. The graph is plotted for concentration on X-axis and signal intensity on Y-axis. Calibration is done at different concentrations (0.5 ppm, 1 ppm, 2.5 ppm, 5 ppm, 7.5 ppm, and10 ppm) of aluminum standard solution. The wavelengths used for aluminum analysis are 308.2 nm and 309.2 nm. The calibration curves have good correlation values of 0.999 at both wavelengths.

Table 10 shows the data for kinetics experiment with an initial concentration of 2 ppm aluminum solution with uncoated limestone. Figure 14 shows the kinetics experiment with an initial concentration of 2 ppm aluminum solution with uncoated limestone.

Table 10: Kinetics Experiment with 2 ppm aluminum solution using ten grams uncoated limestone

Time (hours)	Aluminum concentration (ppm) at 308.2 nm (±0.015 ppm)	Aluminum concentration (ppm) at 309.2 nm (±0.015 ppm)
0	ND	0.003
0.25	0.290	0.260
0.5	0.617	0.580
1	0.572	0.535
1.5	0.651	0.619
2	0.595	0.564
4	0.627	0.592
10	0.383	0.349
24	0.525	0.486

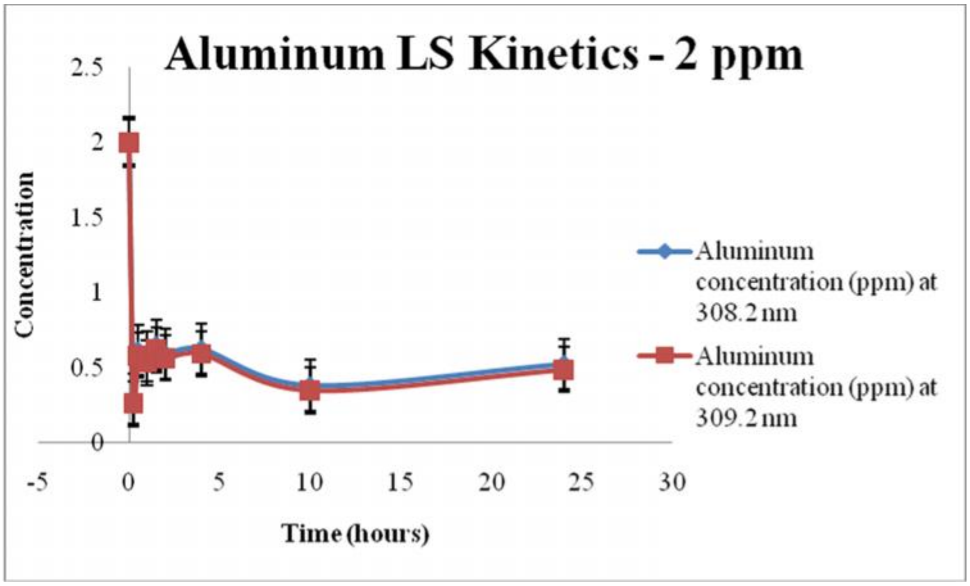

Figure 14: Kinetics experiment with 2 ppm aluminum solution using ten grams uncoated limestone

In Figure 14, the X-axis represents the time in hours and the Y-axis represents the residual concentration of the aluminum metal after treatment with uncoated limestone. The two series represent the concentrations of aluminum measured at wavelengths 308.2 nm and 309.2 nm. Maximum removal is achieved within fifteen minutes. An amount of only ten grams of iron-coated limestone could remove 85.4 percent of the aluminum from the solution within fifteen minutes. However, the drinking water standard of 0.2 ppm for aluminum was achieved within thirty minutes using uncoated limestone.

Table 11 shows the data for kinetics experiment with an initial concentration of 2 ppm aluminum solution with iron-coated limestone. Figure 15 shows the kinetics experiment with an initial concentration of 2 ppm aluminum solution with iron-coated limestone.

Table 11: Kinetics experiment with 2 ppm aluminum solution using ten grams iron-coated limestone

Time (hours)	Aluminum concentration (ppm) at 308.2 nm (±0.015 ppm)	Aluminum concentration (ppm) at 309.2 nm (±0.015 ppm)
0	2.000	2.000
0.25	0.062	0.032
0.5	0.012	ND
1	0.004	ND
1.5	0.010	ND
2	0.031	0.002
4	0.046	0.013
10	0.049	0.019
24	0.045	0.018

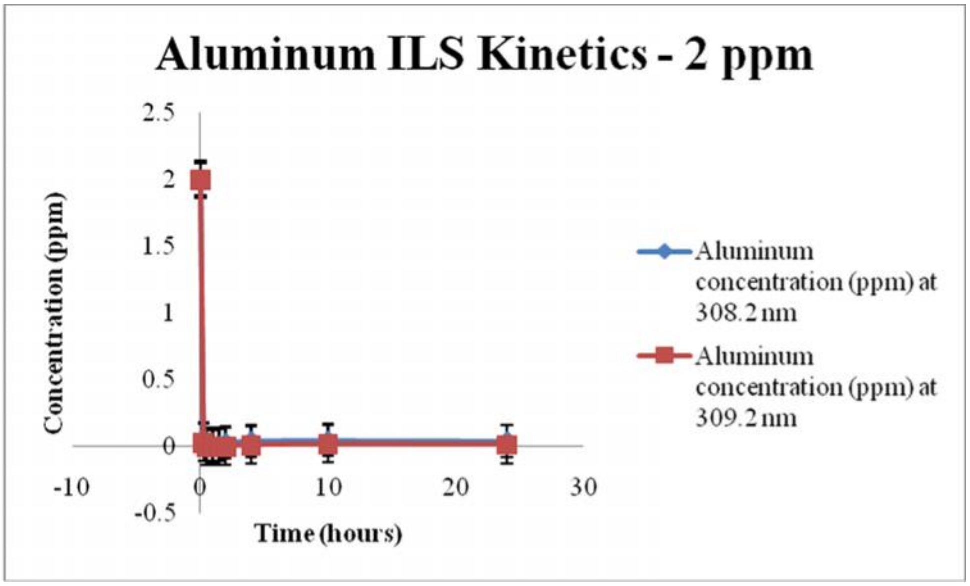

Figure 15: Kinetics Experiment with 2 ppm aluminum solution using ten grams iron-coated limestone

Figure 15 shows the kinetics experiment with an initial concentration of 2 ppm aluminum solution on iron-coated limestone. The X-axis represents the time in hours and the Y-axis represents the residual concentration of the aluminum metal after treatment with iron-coated limestone. The two series represent the concentrations of aluminum measured at wavelengths 308.2 nm and 309.2 nm. Maximum removal is achieved within one hour. An amount of only ten grams of iron-coated limestone could remove 99.8 percent of the aluminum from the solution within one hour. Iron-coated limestone could more effectively remove aluminum than uncoated limestone. Hence iron-coated limestone is used in further experiments for aluminum removal. However, the drinking water standard of 0.2 ppm for aluminum was achieved within fifteen minutes using iron-coated limestone.

Table 12 shows data for batch experiment with an initial concentration of 2 ppm aluminum solution on iron-coated limestone. Figure 16 shows the batch experiment with an initial concentration of 2 ppm aluminum solution on iron-coated limestone.

Table 12: Batch experiment with 2 ppm aluminum solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Aluminum concentration (ppm) at 308.2 nm (±0.015 ppm)	Aluminum concentration (ppm) at 309.2 nm (±0.015 ppm)
5	0.023	0.003
10	0.018	0.012
10	0.019	0.023
20	0.019	0.031
50	0.010	0.026
100	0.012	0.031

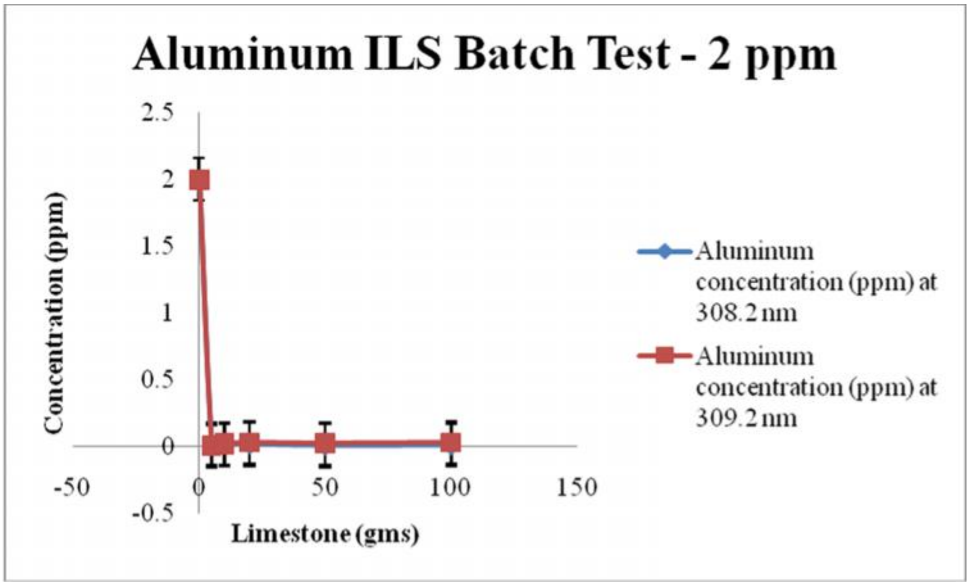

Figure 16: Batch experiment with 2 ppm aluminum solution using iron-coated limestone

In Figure 16, the X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the aluminum metal after treatment with iron-coated limestone. The two series represent the concentrations of aluminum at wavelengths 308.2 nm and 309.2 nm. An amount of 50 grams of iron-coated limestone could effectively remove 99.5 percent of the aluminum from the solution within one hour. The concentration of aluminum was found to be 0.009531 ppm after treatment with 50 grams of iron coated limestone. However, the drinking water standard of 0.2 ppm for aluminum was achieved with five grams of iron-coated limestone.

Table 13 shows data for batch experiment with an initial concentration of 4 ppm aluminum solution on iron-coated limestone. Figure 17 shows the batch experiment with an initial concentration of 4 ppm aluminum solution on iron-coated limestone.

Table 13: Batch experiment with 4 ppm aluminum solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Aluminum concentration (ppm) at 308.2 nm (±0.015 ppm)	Aluminum concentration (ppm) at 309.2 nm (±0.015 ppm)
5	0.041	0.086
10	0.011	0.066
10	0.007	0.055
20	0.005	0.061
50	ND	0.049
100	ND	0.053

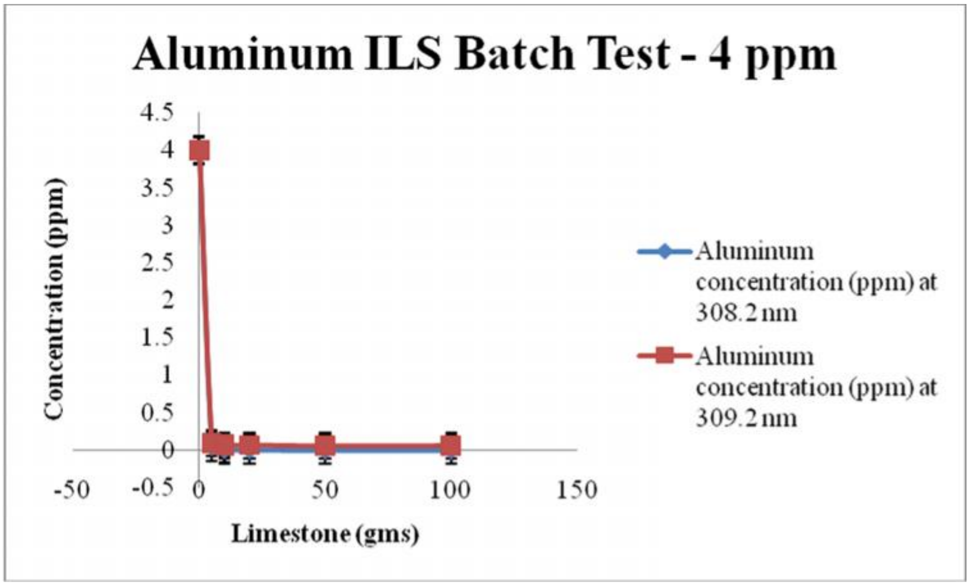

Figure 17: Batch experiment with 4 ppm aluminum solution using iron-coated limestone

Figure 17 shows the batch experiment with an initial concentration of 4 ppm aluminum solution on iron-coated limestone. The X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the aluminum metal after treatment with iron-coated limestone. The two series represent the concentrations of aluminum at wavelengths 308.2 nm and 309.2 nm. An amount of 50 grams of iron-coated limestone could effectively remove 100 percent of the aluminum from the solution within one hour. The concentration of aluminum was below the detection limits after treatment with 50 grams of iron coated limestone. However, the drinking water standard of 0.2 ppm for aluminum was achieved with five grams of iron-coated limestone.

Table 14 shows data for batch experiment with an initial concentration of 10 ppm aluminum solution on iron-coated limestone. Figure 17 shows the batch experiment with an initial concentration of 10 ppm aluminum solution on iron-coated limestone.

Table 14: Batch experiment with 10 ppm aluminum solution using iron-coated limestone

Weight of iron-coated limestone (grams)	Aluminum concentration (ppm) at 308.2 nm (±0.015 ppm)	Aluminum concentration (ppm) at 309.2 nm (±0.015 ppm)
5	0.037	0.103
10	0.006	0.078
10	0.049	0.012
20	ND	0.057
50	ND	0.059
100	ND	0.064

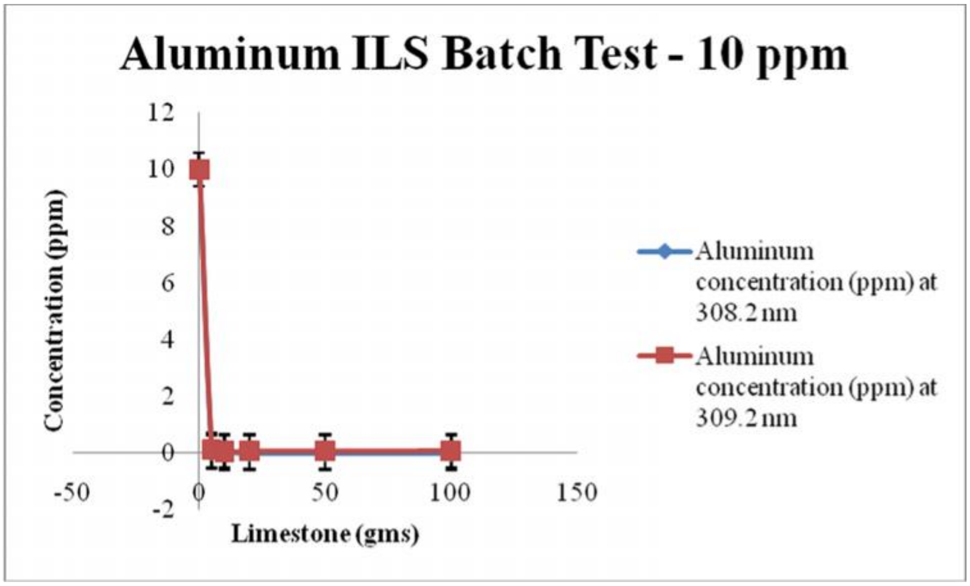

Figure 18: Batch experiment with 10 ppm aluminum solution using iron-coated limestone

Figure 18 shows the batch experiment with an initial concentration of 10 ppm aluminum solution on iron-coated limestone. The X-axis represents the amount of limestone (grams) and the Y-axis represents the residual concentration of the aluminum metal after treatment with iron-coated limestone. The two series represent the concentrations of aluminum at wavelengths 308.2 nm and 309.2 nm. An amount of 20 grams of iron-coated limestone effectively removes 100 percent of the aluminum from the solution within one hour. The concentration of aluminum was below the detection limits after treatment with 20 grams of iron-coated limestone. However, the drinking water standard of 0.2 ppm for aluminum was achieved with five grams of iron-coated limestone.

Table 15 shows the experimental data obtained for effect of pH using 4 ppm aluminum solution with ten grams of iron-coated limestone. Figure 19 shows the effect of pH on removal efficiency for aluminum solution using iron-coated limestone

Table 15: Effect of pH using 4 ppm aluminum solution with ten grams iron-coated limestone

Initial pH (±0.1)	Percentage aluminum removal measured at 308.2 nm (±3 %)	Percentage aluminum removal measured at 309.2 nm (±3 %)
5	96	94
6	86	85
7	98	97
8	93	91
9	94	94

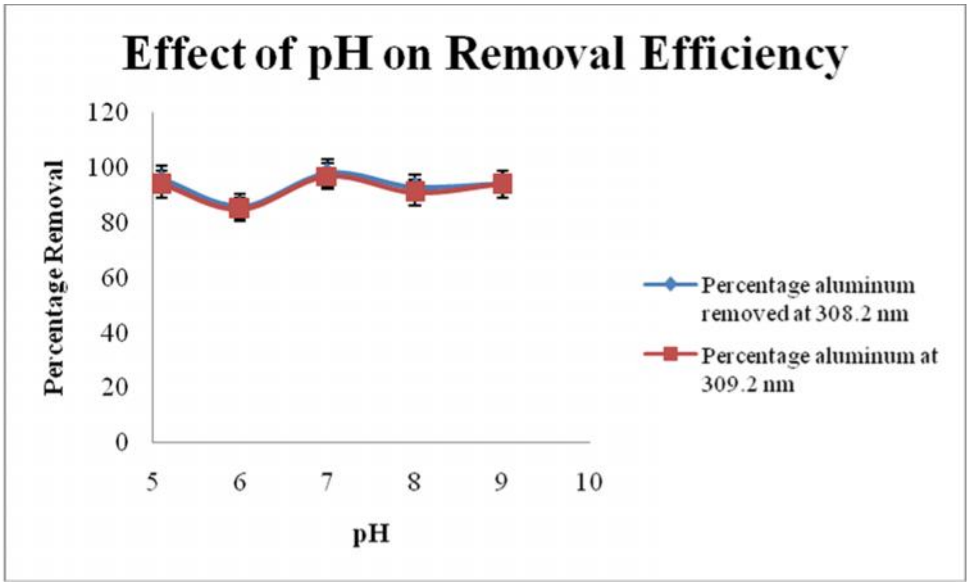

Figure 19: Effect of pH using 4 ppm aluminum solution with ten grams iron-coated limestone

Figure 19 shows the effect of pH on removal rate for aluminum solution using iron-coated limestone. The X-axis represents initial pH of aluminum solution before treatment with iron-coated limestone and the Y-axis represents the percentage of aluminum removed after treatment with iron-coated limestone. The two series represent the percentage of aluminum removed at wavelengths 308.2 nm and 309.2 nm. At pH 7, aluminum had a removed to maximum extent of 98.41 percent. The concentration of aluminum was found to be 0.06327 ppm at a pH value of 7 for an initial concentration of 4 ppm aluminum solution using iron-coated limestone. The removal efficiency did not vary much with pH change. Hence, removal mechanism is generally independent of pH.

XRD Results: X-ray diffraction technologies gives information about the crystal structure and physical properties and chemical composition of solid substances. The chemical composition of iron-coated and uncoated limestone was studied by XRD and compared with that of known substances. The samples were ground, homogenized and then the XRD studies were conducted. Figure 20 represents the XRD peaks obtained for uncoated limestone with that of the known compound calcium carbonate

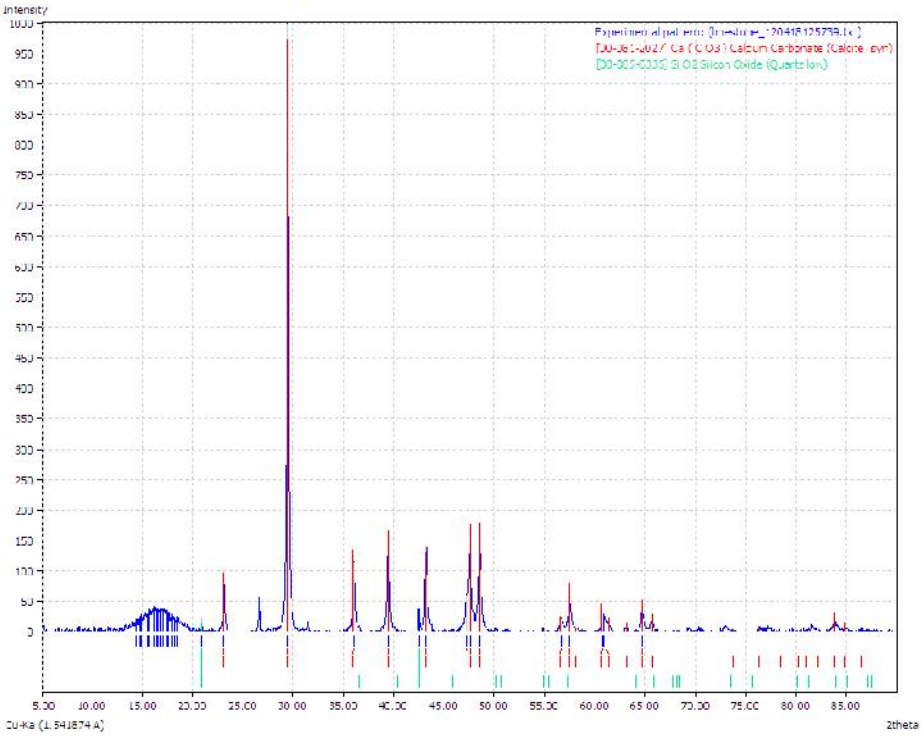

Figure 20: XRD pattern comparing uncoated limestone with calcium carbonate.

Upon comparing XRD peaks of uncoated limestone with calcium carbonate, almost all the peaks matched, confirming the base material to be composed of calcium carbonate. Minor differences could be due to presence of sand and carbon in limestone.

Figure 21 shows the XRD pattern of iron-coated limestone and uncoated limestone. The two peaks looks similar except for few differences which is attributed to the deposition of iron hydroxide on iron-coated limestone.

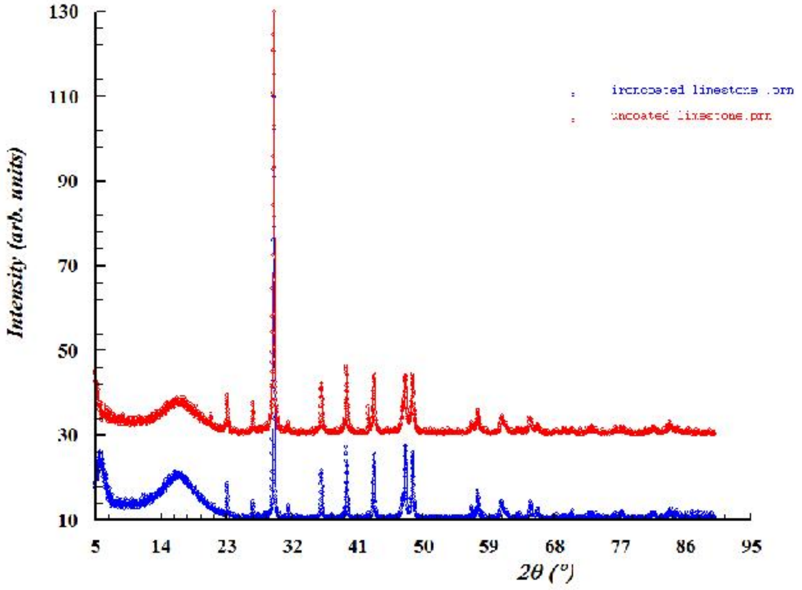

Figure 21: XRD pattern of uncoated limestone and iron-coated limestone

SEM Results: Figure 22 shows the SEM images for uncoated limestone. Figure 23 shows the analysis report of uncoated limestone. Table 16 shows the analysis data for uncoated limestone.

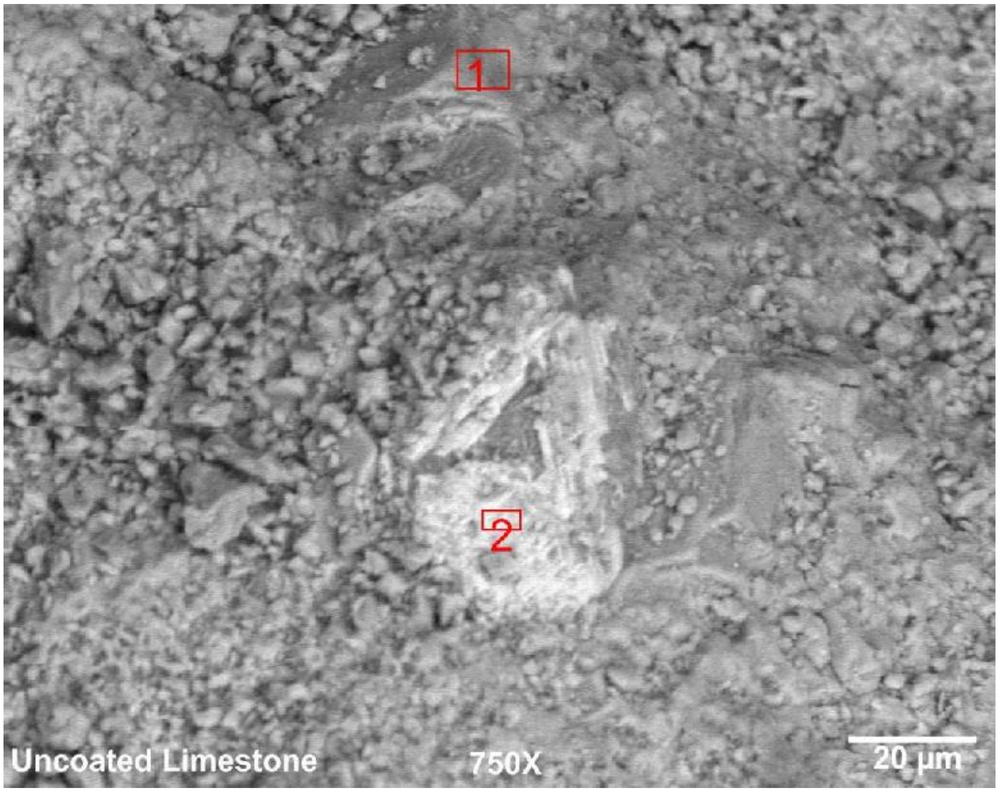

Figure 22: SEM image of uncoated limestone

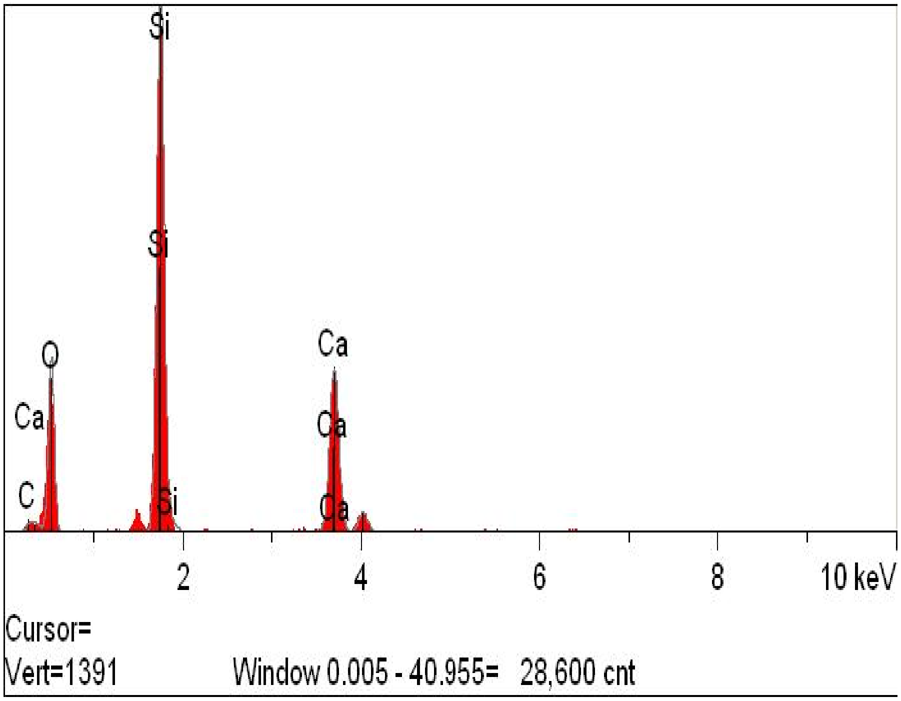

Figure 23: SEM analysis report for uncoated limestone

Table 16: SEM analysis data for uncoated limestone

	Location-1		Location-2	
Element	Atomic %	Concentration Wt %	Atomic %	Concentration 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 SEM image of the uncoated limestone indicates that it has calcium carbonate and small amounts of silicon and sand (SiO_2).

Figure 24 shows the SEM image for iron-coated limestone and Figure 25 gives the analysis report of iron-coated limestone. Table 17 shows the analysis data for iron-coated limestone obtained using SEM.

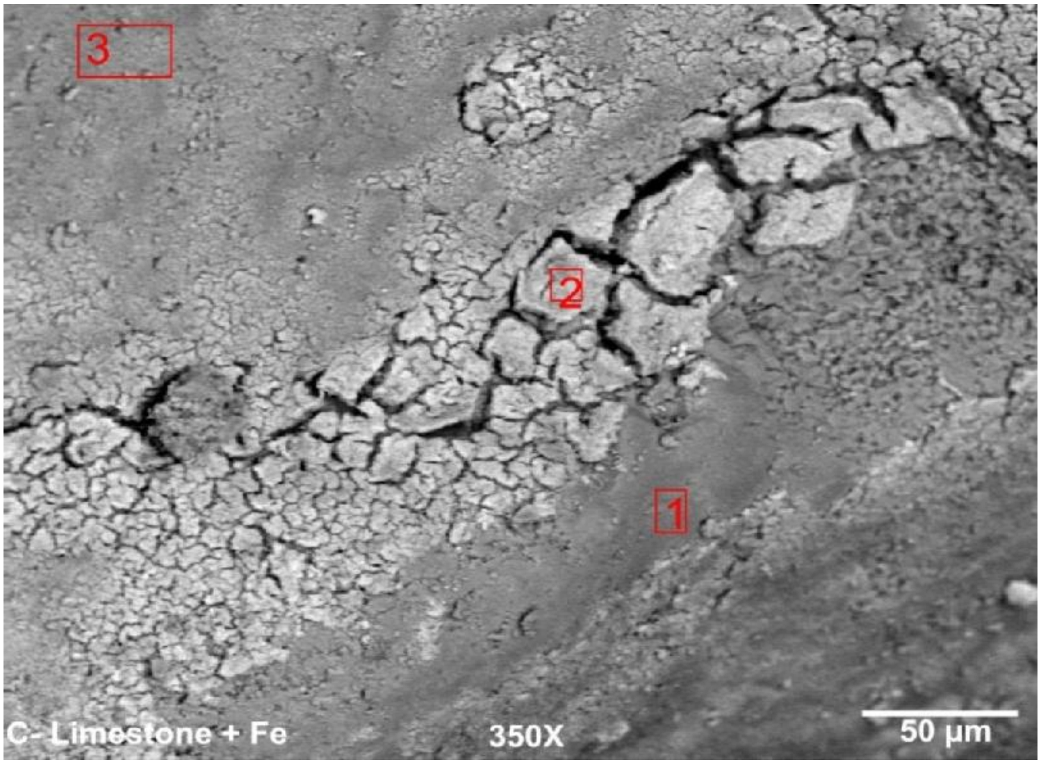

Figure 24: SEM image of iron-coated limestone

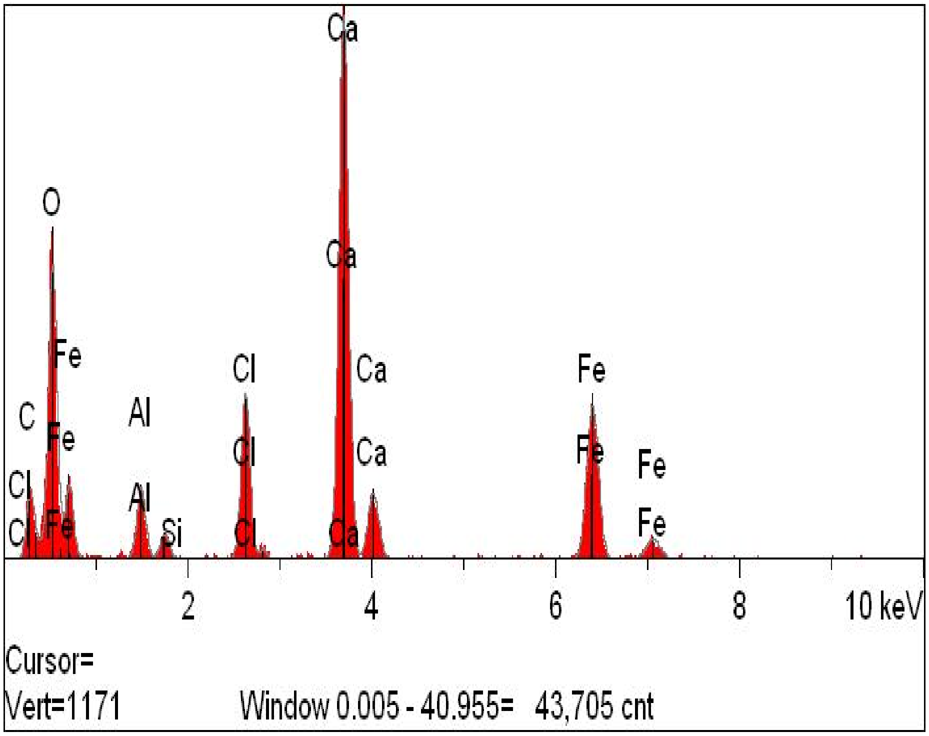

Figure 25: SEM analysis report of iron-coated limestone

Table 17: SEM analysis data for iron-coated limestone

	Location 1		Location 2		Location 3	
Element	Atomic %	Concentration (Wt %)	Atomic %	Concentration (Wt %)	Atomic %	Concentration (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 images for iron-coated limestone showed the uneven distribution of iron indicating the heterogeneous nature of the iron coated limestone. The acidic effect of iron chloride can be seen from the Figure 24. The increase in the surface area could be attributed to the precipitation of iron hydroxide on limestone from iron chloride solution.

Figure 26 shows SEM image of iron-coated limestone after treatment with 10 ppm aluminum solution. Figure 27 gives the analysis report of iron-coated limestone after treatment with 10 ppm aluminum solution. Table 18 shows the data for iron-coated limestone after treatment with 10 ppm aluminum.

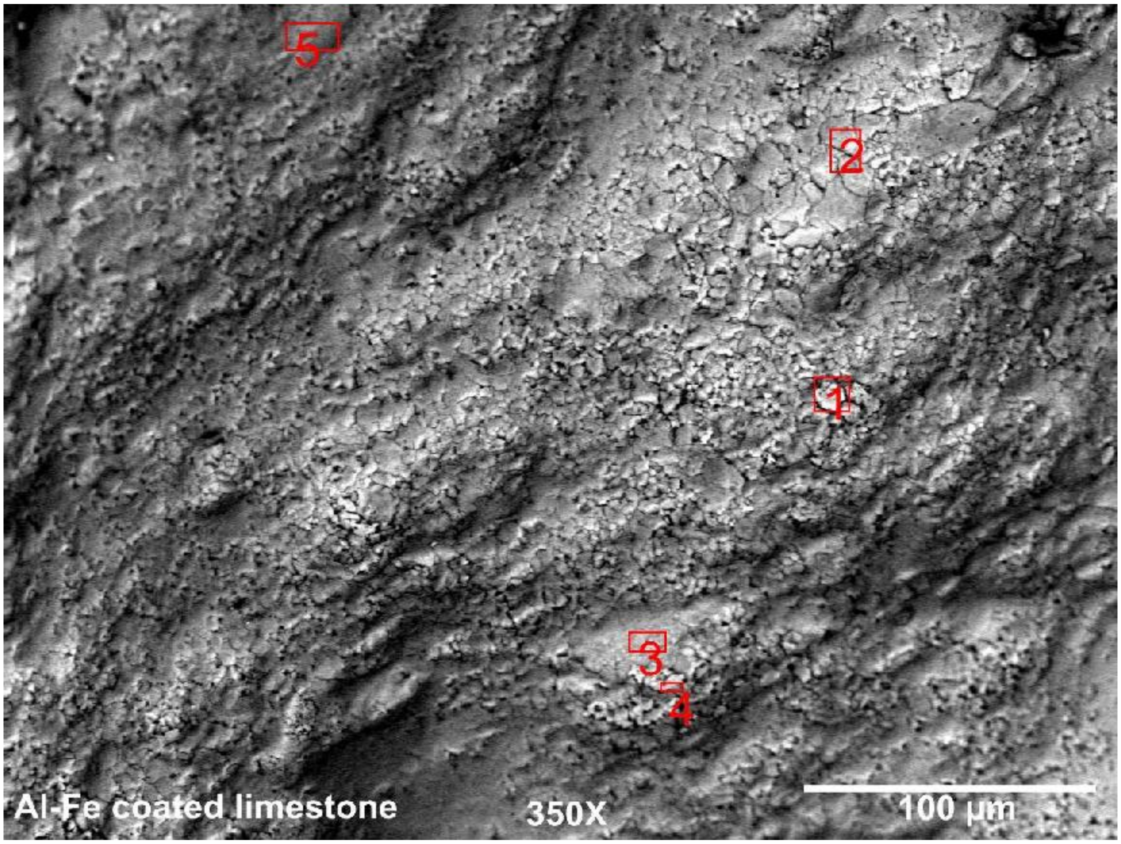

Figure 26: SEM image of iron-coated limestone after treatment with 10 ppm aluminum solution

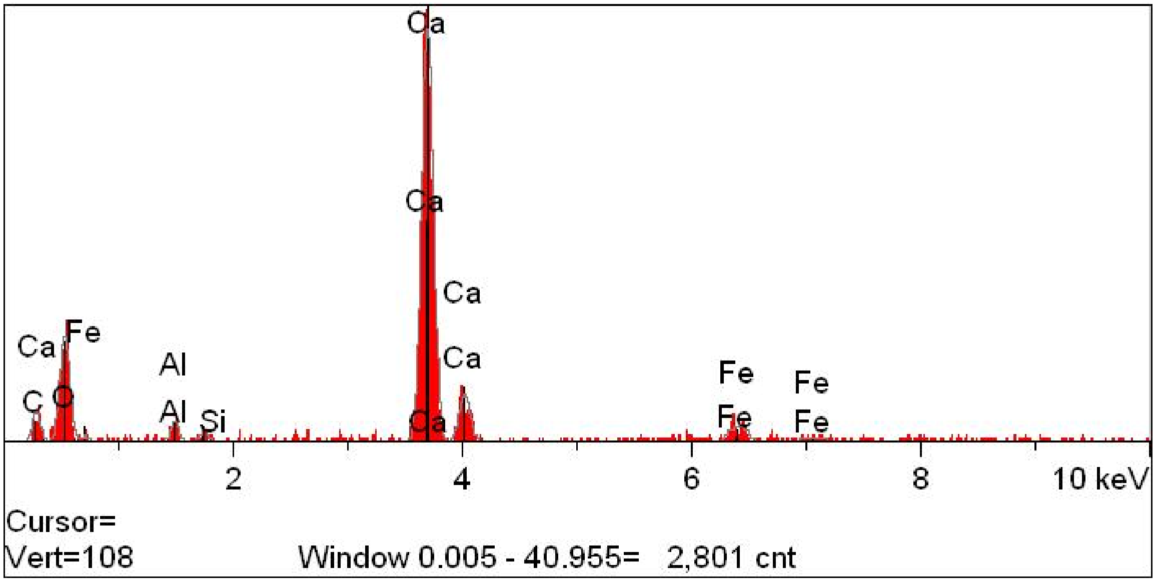

Figure 27: SEM analysis report for iron-coated limestone after treatment with 10 ppm aluminum solution

Table 18: SEM analysis data for iron- coated limestone after treatment with 10 ppm aluminum solution

	Location-1		Location-2		Location-3	
Element	Atomic %	Concentration (Wt %)	Atomic %	Concentration (Wt %)	Atomic %	Concentration (Wt %)
C	12.61	5.94	10.06	5.64	13.23	8.06
O	69.22	50.93	65.47	48.89	68.99	55.97
Al	1.04	1.21	0.6	0.75	0.3	0.41
Si	0.43	0.31	0.13	0.17	0.52	0.74
Ca	15.15	0.61	23.46	43.89	16.53	33.59
Fe	1.55	33.63	0.21	0.56	0.44	1.24
Total	100.00	100.00	100.00	100.00	100.00	100.00

Limestone treated with aluminum showed the presence of the aluminum on the surface while confirming its removal.

Figure 28 shows SEM image of iron-coated limestone after treatment with 100 ppm copper solution. Figure 29 gives the analysis report of iron-coated limestone after treatment with 100 ppm copper solution. Table 18 shows the data for iron-coated limestone after treatment with 100 ppm copper.

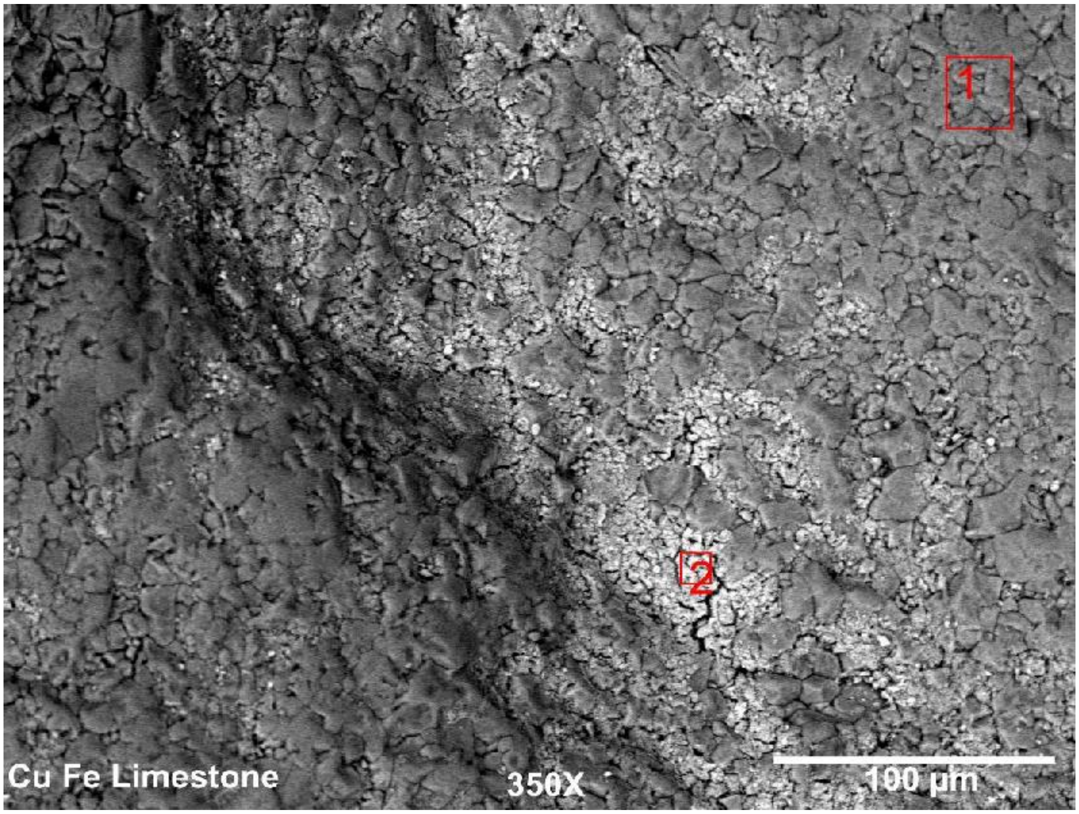

Figure 28: SEM analysis image for iron-coated limestone after treatment with 100 ppm copper solution

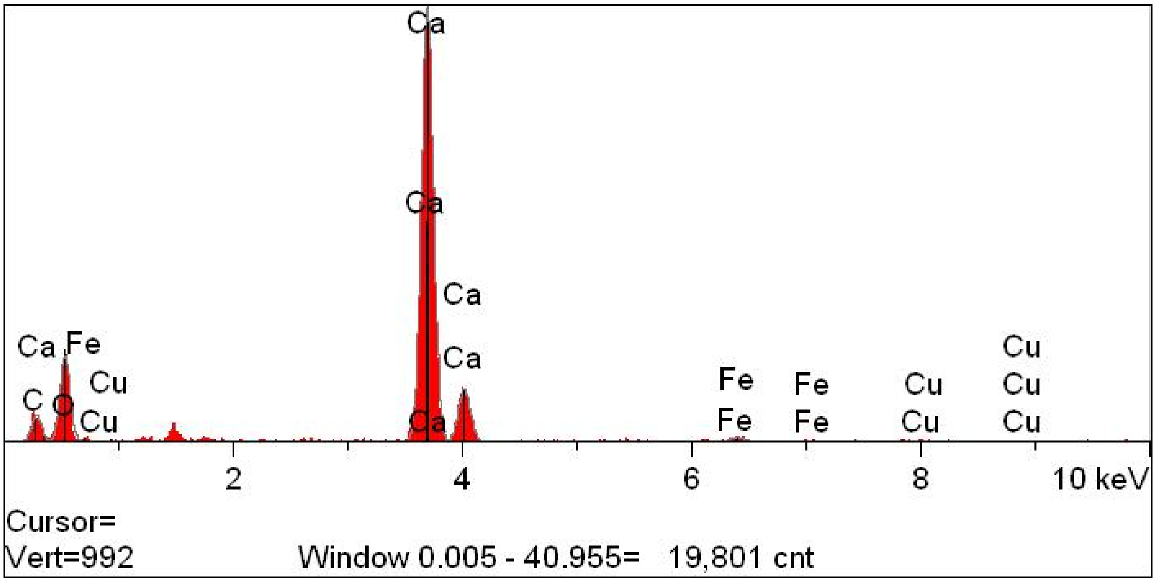

Figure 29: SEM analysis report for iron-coated limestone after treatment with 100 ppm copper solution

Table 19: SEM analysis data for iron- coated limestone after treatment with 100 ppm copper solution

	Location 1		Location 2	
Element	Atomic %	Concentration (Wt %)	Atomic %	Concentration (Wt %)
C	10.25	6.04	12.99	7.80
O	72.38	56.88	68.78	55.02
Si	0.54	0.75	ND	ND
Cl	0.22	0.38	ND	ND
Ca	12.80	25.19	17.54	38.15
Fe	3.11	8.52	0.41	1.14
Cu	0.72	2.24	0.28	0.9
Total	100.00	100.00	100.00	100.00

Limestone treated with copper showed the presence of the copper on the surface while confirming its removal.

Figure 30 shows SEM image of iron-coated limestone after treatment with water. Figure 31 gives the analysis report of iron-coated limestone after treatment water for four hours. Table 18 shows the data for iron-coated limestone after treatment with water.

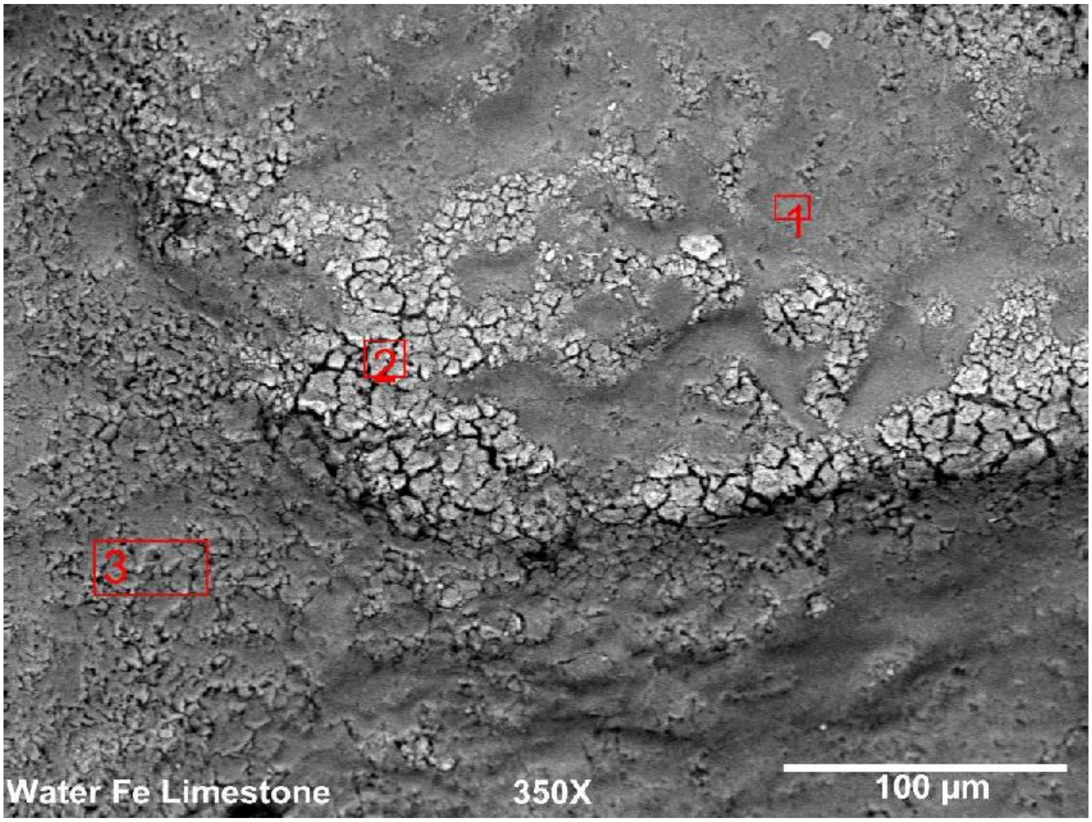

Figure 29: SEM image for iron-coated limestone after treatment with water

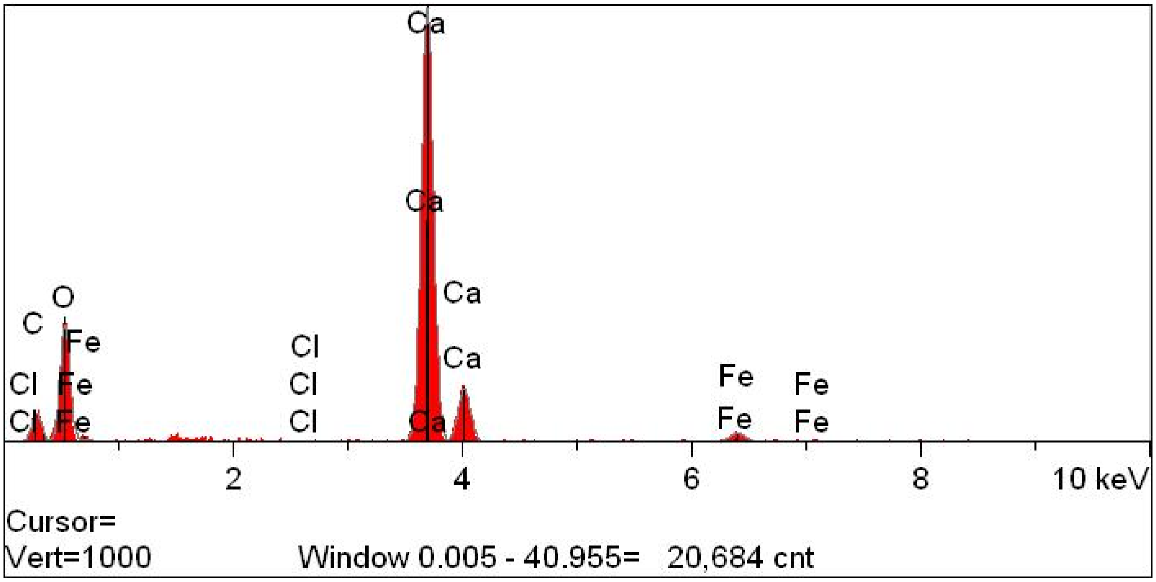

Figure 30: SEM analysis report for iron-coated limestone after treatment with water

Table 20: SEM analysis data for iron-coated limestone after treatment with water

	Location 1		Location 2	
Element	Atomic %	Concentration (Wt. %)	Atomic %	Concentration (Wt. %)
C	12.12	7.47	13.40	8.26
O	71.82	58.96	71.44	58.66
Cl	0.03	0.05	0.07	0.13
Ca	15.33	31.53	12.09	28.46
Fe	0.7	2.00	2.65	7.58
Si	ND	ND	0.36	0.51
Total	100.00	100.00	100.00	100.00

The results from SEM indicate that there are no significant changes with exposure to water.

IV. Conclusions

Heavy metal contamination has been a serious problem throughout the world because of the hazardous effects on the health of humans. Even though there are well established techniques for the heavy metal removal from drinking water, their usage can be limited by cost. Hence, there exists a need to develop a method for heavy metal removal from drinking water which is cost effective, efficient and eco-friendly. We propose a novel method of using limestone to remove heavy metals from drinking water. The U.S. EPA has set the drinking water standards for copper and aluminum as 1.3 ppm and 0.2 ppm, respectively. This research is primarily focused on reducing heavy metal levels to below the drinking water standards set by U.S. EPA.

Both uncoated and iron coated limestone are used for heavy metal removal. The time required for the removal of heavy metal was determined by kinetic studies. Uncoated limestone using a sample size of ten grams could remove 97 percent of copper from a solution with an initial concentration of 20 ppm within four hours. Kinetics studies were also done with iron-coated limestone. The removal efficiency was found to be 97 percent for copper solution with an initial concentration of 20 ppm. The removal rate of 97 percent was also achieved within four hours. For copper, both iron-coated limestone and uncoated limestone removed the metal nearly to the same extent when the contact time was four hours. However, the removal rate did not remain the same at other contact times. Iron-coated limestone was more efficient for short time intervals for copper. Further experiments with copper were solely conducted with iron-coated limestone keeping the contact time for four hours.

Batch experiments for copper were conducted with iron-coated limestone. For a 20 ppm copper solution, an iron-coated limestone of 20 grams could remove 99.8 percent of copper from the solution. For a 40 ppm copper solution with 20 grams of iron-coated limestone 99.3 percent of copper was removed from the solution. For a 100 ppm copper solution using iron-coated limestone of five grams could remove 100 percent of copper from the solution. For the batch tests using iron coated limestone (5, 10, 20, 50 and 100 grams) for copper solutions of 20 ppm, 40 ppm, 100 ppm, drinking water standards was achieved for all challenge concentrations. The pH studies indicated that copper was completely removed from 40 ppm copper solution using iron coated limestone with a contact time of four hours. The removal of copper is not sensitive to pH.

For aluminum, uncoated limestone with sample size of ten grams could remove 85.4 percent of aluminum from a solution with an initial concentration of 2 ppm within fifteen minutes. Kinetics studies were also done with iron-coated limestone. The removal efficiency was found to be 99.79 percent for aluminum solution with an initial concentration of 2 ppm. The removal rate of 99.79 percent was achieved within one hour. Iron-coated limestone was more efficient in comparison to uncoated limestone. Hence, further experiments were solely conducted with iron-coated limestone for aluminum.

Batch experiments for aluminum were conducted with iron-coated limestone. For a 2 ppm aluminum solution, an iron-coated limestone of 50 grams could remove 99.5 percent of aluminum from the solution. For a 4 ppm aluminum solution with 50 grams of iron-coated limestone, 100 percent of aluminum from the solution was removed. For 10 ppm aluminum solution using iron-coated limestone of 20 grams could remove 100 percent of aluminum from the solution. For the batch tests using iron coated limestone (5, 10, 20, 50 and 100 grams) for aluminum solutions of 2 ppm, 4 ppm, and 10 ppm, drinking water standards was also achieved for all challenge concentrations. The pH studies indicated that aluminum was removed to a maximum extent of 98.4 percent from 4 ppm aluminum solution using iron-coated limestone with a contact time of one hour. However, not much significant difference in removal efficiency was found for different pH values. The removal efficiency is not sensitive to pH.

V. Future Work

The work can be extended for further investigations of other heavy metals which poses risk to the health of humans. Application of the technique to real water samples from different parts of the world is important. The method should be studied for a mixture of two or more heavy metals in combination could be reduced by using limestone. Further investigation of the kinetics is warranted.

The nature of limestone after the treatment with heavy metals like copper and aluminum should also be studied to determine the mechanisms involved in the heavy metal removal by limestone. Application of this technique to small and rural water systems for heavy metal removal should be a long term goal.

VI. Perspective

Drinking water is contaminated with several pollutants that affect the health of humans. Heavy metals are one of the type of pollutants that cause severe health problems. We thought of reducing these heavy metals in drinking water to those levels where they are not harmful.

In our proposed method we use limestone to reduce the heavy metal content. Water with heavy metals was taken and kept in contact with limestone for a certain period of time. The amount of heavy metals after contact with limestone were found to be reduced to safe levels. The treated limestone can be easily disposed off without causing any harm to the environment. The treated limestone is mixed with concrete and disposed of. This method is affordable and easily available.

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