

REMOVAL OF ARSENIC FROM WATER **USING HYBRID MATERIAL**

A dissertation submitted in the fulfillment of the
requirement for award of the degree of

MASTER OF TECHNOLOGY
IN
ENVIRONMENTAL ENGINEERING
BY

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CERTIFICATE

This is to certify that MR. RAJAT GUPTA, an M. Tech. student in the Department of Environmental Engineering has submitted a project report “REMOVAL OF ARSENIC FROM WATER USING HYBRID MATERIAL” in partial fulfillment of the requirement for award of degree of Master of Technology in Environmental Engineering, during the academic year 2016-17.

It is a record of the student’s research work prepared under my/our supervision and guidance.

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Declaration of Originality

I hereby undertake that Rajat Gupta, the sole author of this report. I undertake that this report neither infringes upon anyone's copyright nor violates any proprietary rights to the best of my knowledge. Any ideas, techniques, quotations, or any other material form of work of other people included in this report, published or otherwise, are fully acknowledged in accordance with the standard referencing practices.

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M.Tech (ENVIRONMENTAL ENGINEERING)

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PREFACE

It is the requirement of the M.Tech (Environmental Engg.) degree that a student has to undergo project training at the fourth semester of two year course. In this time period he has to acquire the work experience in any organization in public sector, private sector or government departments. Along with working exposure the student has to develop an application or model of it.

I underwent my project training at Environment laboratory (Dept. of Env. Engg.) in DTU campus. During project training I have analyzed the methods to remove Arsenic under project named “REMOVAL OF ARSENIC FROM WATER USING HYBRID MATERIAL” at Env. Lab. This project is developed for scientific analysis. This report briefly describes the systematic approach taken to develop this project. The project development report contains information about objective, material & methods required, analysis and result discussion.

ACKNOWLEDGEMENT

Any accomplishment requires the efforts of many people and this work is no exception. I appreciate the contribution and support which various individuals have provided for the successful completion of this study. It may not be possible to mention all by name but the following were singled out for their exceptional help.

First and foremost, I would like to express my deepest gratitude to my project supervisor **Dr. A.K Gupta**, Department of Environmental Engineering, Delhi Technological University, for his valuable guidance, support, motivation and encouragement during the project work, without which the completion of the work would have been impossible.

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I would like to thank my family members for supporting and helping me at every step of life. Their sincere blessings and wishes have enabled me to complete my work successfully. I am also thankful to all my friends for their unconditional support and motivation during this work. Above all thanks to the God, for the blessings that has been bestowed upon me in all my endeavors.

Rajat Gupta

ABSTRACT

Contamination due to heavy metals in water has caused a major concern. It is not only confined to our country, but it is also a serious concern globally. One of among such heavy metals is Arsenic, which is most commonly found in water, especially sub-surface water. The various routes through which these heavy metals can interact with living beings is through water and air. Hence removal of heavy metals is a big necessity for us.

In this study, physical methods are used for removal of arsenic. Basically, adsorption technique with Hybrid materials is used. Water sample is prepared by using salt of sodium arsenate. Batch studies were conducted to conclude the optimum pH, optimum concentration and optimum period of hydrolysis.

To detect the amount of arsenic, a special instrument called Atomic Absorption Spectrometer (AAS) is used.

pH is the measure of acidity or alkalinity of aqueous samples which is measured using pH meter.

Hydrolysis can be defined as a phenomenon in which chemical breakdown of a compound occurs with the help of reaction with water.

Keywords:

Adsorption, Hybrid Material, Coarse calcite, hydrated ferrous sulfate, AAS.

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CHAPTER NO. 1

INTRODUCTION

Heavy metals can be defined as metals having relatively high density or they also incorporate high relative atomic weight. Billions of people across the world suffer only because they are exposed to heavy metals through their daily needs. It is mainly due to anthropogenic activities like waste water disposal from both domestic and industrial sectors that raise the arsenic level to an alarming extent.

More than 70% of Delhi's water supply is under Yamuna. Yamuna is also a great source of irrigation for neighboring territories surrounding Delhi. Delhi is a major centre for industrial development due to which it is attracting a lot of manufacturers and hence population is increasing in haphazard manner. In Delhi Yamuna is stretched till Okhla barrage where water is heavily polluted with biological wastes and possess dark color. The canals originating from Yamuna in Haryana contain Heavy Metals which have crossed the permissible limits suitable for drinking. They are very lethal to crops when they enter the food chain through aquatic system.

Heavy metals have nature of being persistent and bio-accumulative. In aquatic system heavy metals are removed by settlement of particles. Pesticides and fertilizers are also a great source of arsenic in agricultural fields which enter the aquatic system by runoff.

1.1 Brief points regarding Arsenic

Arsenic is distributed throughout the crust of the earth in the form of minerals, ores and pure crystals. Naturally, arsenic enters the water bodies through weathering of mountains and rocks containing ores and minerals of arsenic which gets dissolved into the bodies. However, major contribution in raising arsenic level are anthropogenic activities.

There are various forms in which arsenic can be found . In India, it is mainly found in two forms: As(III) and As(V). But As(III) is considered to lethal than As(V). It is due to the inert nature of As(III) that it remains unaffected towards any treatment . Hence As(III) is first oxidized prior to any treatment.

Arsenic exists in organic and inorganic form. Organic arsenic are less lethal and are removed from body from time to time. But inorganic arsenic is more lethal and can be found in various natural water sources with high concentration. As per Environmental Protection Agency (EPA), the maximum permissible limit of arsenic in drinking water is 10ug/l or 10pp

1.2 Consequences of arsenic exposure and its toxicity

Exposure of arsenic for a long period of time pose various threats. Some of them are change in skin color, weakening of muscles, cancer in lungs, kidney and urinary bladder.

Arsenic is also responsible for infection in blood vessels leading to formation of Gangrene, which is also known as Blackfoot Disease.

Its toxicity is not only limited to humans but it also affects plants to a greater extent. Symptoms observed in plants exposed to arsenic are:

- Decrease in growth of plant
- wilting of leaf tips
- decrease of photosynthetic capacity of plants.

1.3 Conventional Treatment methods for Arsenic removal

There are certain methods which are employed for removal of arsenic from water. Some of them are listed below:

- Adsorption
- Coagulation
- Ion-exchange
- Precipitation
- Oxidation and reduction
- Reverse osmosis

In the present study, adsorption method is used for removal of arsenic. As adsorption is a surface phenomenon, hybrid materials are used for implementing treatment.

1.4 OBJECTIVE

- The primary aim of this study is to generalize the purpose of hybrid materials.
- To perform batch study and find out the optimum conditions which are suitable for removal.
- To produce water suitable for drinking by reducing the concentration of Arsenic.
- To use methods which are economic and effective.

CHAPTER NO. 2

LITERATURE REVIEW

2.1 Methods for removing heavy metals

- **Coagulation**

Coagulation process is traditionally realized by adding ferric or aluminium ions (Hering et al. , 1996). In this process fine particles in water first aggregate into coagulates because added ferric or aluminium ions strongly reduce the absolute values of zeta potential of the particles.

Coagulation with ferric ions for arsenic removal can be traced back to the late 1960s in Taiwan to treat deep-well water with naturally elevated arsenic concentrations (Shen, 1973).

Gulledge and O'Connor (1973) also reported that arsenic could be readily removed from water to a higher degree by conventional water treatment using ferric or aluminium ions as coagulents.

The effective pH for arsenic removal was reported to be 5-7 for aluminium ions , and 5-8 for ferric ions (Sorg and Logsdon, 1978).

Besides iron and aluminium compounds, manganese, calcium and magnesium compounds are also effective coagulents for removing arsenic from water in neutral medium (Raje and Swain, 2002; Jijang, 2001).

Recently it was reported that modified coagulation/ filtration could give a residual arsenic concentration of 2µg/l or less for treated well water (Han et al., 2003).

The arsenic removal is also dependent on the pore size of the membrane filter disks used for coagulation process (Han et al., 2003), since coagulates smaller than the pore can pass through the filter and remain in water.

Usually coagulations are enhanced by adjusting pH and electrolyte concentration to reduce the absolute values of zeta potentials of particles, and by optimizing coagulation kinetics (S. Song et al., 2004).

Coagulation process is considered to be the most cost effective and documented methods using FeCl₃ for large scale system (Mondal et al., 2008). In this process arsenic and chromium can be controlled through strict control over pH, coagulant type and dosage. The process involves addition of coagulant to the contaminated water under efficient stirring whereby flocculation occurs. Negatively charged particles and micro particles are attached to the flocs by electrostatic force of attraction that can be removed by partial sedimentation and filtration for complete removal of flocs (Qin et al., 2005).

Advantage and disadvantage of coagulation technique

Though coagulation is an easy and simple process with handy operation but it also has some disadvantages (Alexander et al., 2012; Golbaz et al., 2014). The main disadvantages of coagulation is settling/filtration of the coagulated which require the direct addition of the coagulant to water, thus leading to undesirable residual levels of iron or aluminium. Secondly the process is highly sensitive to pH therefore appropriate reagents is often added to adjust the pH which increases the risk of secondary contamination (Fuerstenau et al., 1979).

- **Adsorption**

The attachment of particles to a surface is called adsorption. The substance that adsorbs is the adsorbate and the underlying material is the adsorbent desorption is the reverse process of adsorption. In words of chemical engineering, adsorption is called the separation process during which specific components of one phase of a fluid are transferred onto the surface of solid adsorbent (Deng et al., 2004). The adsorption of various substances on solids is due to the increased free surface energy of the solids due to their extensive surface area (Brum et al., 2010).

The main advantage of this technique are the reusability of the material upto many cycles of adsorption, low capital cost, selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time. Molecules and atoms can attach to surfaces in three different ways:

1. Physical adsorption: In this, vanderwall interaction between the adsorbate and substrate takes place for long time but are weak in nature. Moreover the energy released during particle adsorption is of the same magnitude as the enthalpy of condensation. This small enthalpy change is sufficient to lead to bond breaking, so a physisorbed molecule retains its identity, although it might be distorted by the presence of surface molecules.
2. Chemical adsorption: In this, the molecules stick to the surface by forming a chemical bond usually a covalent bond, and tend to find sites that maximize their coordination number with the substrate.
3. Electrostatic sorption: In ion exchange, solid material takes up charged ions from a solution and release an equivalent amount of other ions into the solution (Inamuddin et al., 2007). The ability to exchange ions is due to the structural properties of the materials. The exchanger consists of a matrix, with positive or negative excess charge. This excess charge is localized in specific locations in the solid structure or in functional groups. The charge of the matrix is compensated by the counter ions, which can move within the free space of the matrix and can be replaced by other ions of equal charge sign (Helfferich, 1962). Ion-exchange resins after saturation can be easily regenerated using acid or alkali. These resins

are applicable for selective ions only. However, in presence of large quantities of competing mono and divalent ions, efficiency of ion-exchange process decreases.

Ion removal by solids could involve more phenomenon like ion exchange and adsorption processes (Inglezakis et al., 2004) simultaneously. Inglezakis et al., (2004) reported the effects of competitive cations and co-anions on ion-exchange of heavy metals on clinoptilolite and found the selectivity of clinoptilolite for heavy metals. Baciaocchi et al. (2005) reported ion exchange equilibrium of arsenic in the presence of high sulfate and nitrate concentrations.

- **Solvent extraction**

The aqueous solution containing the metal of interest is mixed very well with the appropriate organic solvent and the metal passes into the organic phase (Li et al., 2014). The extraction efficiency is affected by concentration of heavy metal, initial pH and phase ratio (solvent to water) (Roh et al., 2000). The extractant used are alcohols, glycols, polyphenols, hydroamic acids, esters, of phosphinic and phosphoric acids etc., but they are phased out due to high aqueous solubility.

Advantage and disadvantage of solvent extraction

This method is simple, convenient and rapid to perform the separation. However, this method is not as effective for metal separation from dilute solutions due to loss of extractant, additional phase formation, long separation time, emulsion formation, co-extraction of mineral acids and high concentration of extractant requirement and also use of inflammable solvents (Huang et al., 2009).

- **Membrane separation**

A membrane is a thin layer of semi permeable material that separates substances when a driving force is applied across the membrane. Membrane filtration processes are progressively used for removal of bacteria, micro-organisms, natural organic material and toxic ions (Guo et al., 2011). The membrane processes can be classified as :

(a) Microfiltration : It is used with a membrane having pore size of approximately 0.03 to 10 microns. Similarly in ultrafiltration, membrane has a pore size of approximately 0.002 to 0.1 microns. Nanofiltration membranes have a nominal pore size of approximately 0.001 microns. Filtering water through these small membrane pores requires a higher operation pressure than microfiltration or ultrafiltration technique.

The above methods are suitable for micro-organism removal. RO can effectively remove nearly all inorganic contaminants, heavy metals, toxic ions, and natural organic substances from water (Chen et al., 2012; Nataraj et al., 2009).

2.2 Global scenario of arsenic contamination

More than 100 million people are exposed to heavy metal pollution above the permissible limit (Vineis et al., 2009). Many nations of the world are facing the ill consequences of excess arsenic and chromium exposure (USEPA, 1999; Smith et al., 2009). In India, Bangladesh and China over 20 million people are suffering from arsenicosis and skin diseases due to consumption of arsenic and chromium contaminated drinking water (USEPA, 1999; Smith et al., 2009). In the year 1993, arsenic polluted water was first detected in Bangladesh (Smith et al., 2009; WHO, 2010). Today 1.04 million of tubewells out of 4.07 million tubewells are found to contain arsenic above permissible limit of 50 ppb (Smith et al., 2009; Choong et al., 2007).



In Taiwan, Blackfoot disease, a form of Gangerene occurs due to cardiovascular complications because of arsenic poisoning (Smith et al., 2009; Andrade et al., 2013). Near 13 million people in the US are exposed daily to drinking water with arsenic levels greater than 10 $\mu\text{g}/\text{l}$ (Smith et al., 2009). Many countries like Mongolia, South Africa, Zimbabwe, and former Soviet Russia are also facing the problems of arsenic contamination in drinking water (Smith et al., 2009).

2.3 Local Scenario of Arsenic contamination

Source: The Hindu

A study conducted by The Energy and Resources Institute (TERI) indicates the presence of heavy metals in the vegetables that are grown with water from the Yamuna, making them potentially hazardous to health.

Yet another recent study conducted by the Department of Geology at Delhi University has pointed to the presence of arsenic in ground water from around the Yamuna floodplains. “The level of arsenic in some places like Geeta Colony, Shastri Park was very high. Near the Rajghat Power Plant it was as high as 40-45 ppm (parts per million).

During the course of the study from 2007-09, samples were collected from the Yamuna floodplains, considered a crucial ground water recharge zone.

The contamination of ground water has also been acknowledged by the Union Water Resources Ministry. In a report to Parliament the Ministry admitted that groundwater in several areas of the city has excess fluoride, nitrates, **arsenic** and iron.

Arsenic removal from water is an important subject worldwide, which has recently attracted great attentions. A variety of treatment processes has been developed for arsenic elimination from water, including coagulation (precipitation) (Wickramasinghe et al., 2004; Hering et al., 1997), adsorption (Wang et al., 2002; Zhang et al., 2003; Katsoyiannis and Zouboulis, 2002), ion exchange (Korngold et al., 2001), membrane filtration (Sato et al., 2002), electrocoagulation (Kumar et al., 2004; Arienzo et al., 2002), biological process (Katsoyiannis and Zouboulis, 2004), iron oxide-coated sand (Thirunavukkarasu et al., 2003), high gradient magnetic separation (Chiba et al., 2002) and natural iron ores (Zhang et al., 2004), manganese green sand (Thirunavukkarasu et al., 2005), etc.

There are numerous review papers for the arsenic removal technologies, some of which were recently made by Jiang (2001), Bissen and Frimmel (2003), Dambies (2004) and USEPA (2000).

Coagulation and adsorption processes are most promising for arsenic removal from high-arsenic water because of the low cost and high efficiency, and are widely used in the developing world. But, they have not been shown to deeply eliminate arsenic from water and to produce cleaned water with a very low arsenic concentration, say 10 mg/l. However, membrane filtration process could lower arsenic concentration in water from 48 to 1–2 mg/l (Bissen and Frimmel, 2003), and ion exchange process could remove arsenic to levels lower than 5 mg/L for water with initial

arsenic concentration of 87 mg/L (Wang et al., 2002), which are currently used in the developed world. The other processes are still at a laboratory or pilot scale.

More than 13 districts of Bihar have been reported to have As contamination level above the Indian standards. The reason being all these districts are located nearby large rivers like The Ganga and The Gandak [Biharprabha News, 25 September 2013].

Natural dumping phenomenon such as earthquakes, volcanos, storms, algae blooms, etc. causes major changes in the ecologic status of water and water quality. Statistics exemplify the scale of problem that adulterated water like chemicals discharged from factories or washed down drains can cause [D. Mohan et al (2007)]. About half of the ocean pollution is due to the dumping of sewage and polluted water. Every single year, the world produces beyond 40, 00,000 lakh tons of industrial sludge, whose maximum proportion is dumped directly into oceans, rivers and other waterways. In India only, around 4, 00,000 factories take fresh water from streams and rivers and polluted waters are pumped back in their place. However, major improvements have been carried out in waste water treatment recently [C. Su et al (2001)].

As(III) is the reduced form of inorganic arsenic, which is a extremely poisonous [Mandal et.al (1997)]. It is highly toxic, soluble and mobilized than inorganic arsenic (As-V). The disadvantageous presence of As in the environment is of great concern. Arsenic forms 0.0006% of the entire mass of the earth's crust. Consumption of adulterated water, whose arsenic concentration is above 0.05ppm, is detrimental for human health. In West Bengal, arsenic poisoning by drinking tube well water was first reported in the year 1980[Kundu et. al (2002)].

Long-term intake of arsenic adulterated water may cause pigmentation, hyperkeratosis on the palms and soles of the feet. Black foot disease, skin cancer, bone marrow depression, cardiovascular disorder and cirrhosis are instigated by long term exposure of arsenic. In view of the catastrophic effects within Asia due to As intake, Bangladesh is at the top tailed by West Bengal (India), Cambodia and Vietnam, where more than 15 crores people are at danger in West Bengal and Bangladesh alone. In all these areas, arsenic happens to be in deltaic soil deposits constituting shoal aquifers [J. Pattanayak et. al (2000)].

Duration and dosage of exposure are two crucial parameters of the severity of arsenic effect. It starts with change in pigmentation; hyperkeratosis and following to horrendous diseases like cancer of the skin, lungs, etc. In India, the unwellness due to arsenic consumption is mostly common in the rural areas where groundwater is used directly for drinking, bathing, cleaning and various other household works without its proper treatment. This is most likely due to the absence of services from the government [Chowdhury U.K., Biswas B.K., Chowdhary T. R. (2000)].

CHAPTER NO. 3

MATERIALS AND METHODOLOGY

3.1 Coarse Calcite as Adsorbent (Peng et. al. (2004))

Materials

Around 100 g of sodium arsenate salt is used so as to prepare the arsenic solution. Fused calcite is taken as adsorbent. Sieve of 400 mesh size is used, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (Ferric Sulfate). To ensure thorough mixing, mechanical shaker is used. To measure the acidity or alkalinity of the samples, pH meter is used. Whatman no. 41 filter is used to filter the solutions. To quantify the heavy metals, Atomic Absorption Spectrometer is used. Precision balance is used for weighing the samples.

Methodology

- Sodium arsenate salt of 100 g was taken in a 200 ml of distilled water sample.
- Calcite was crushed to size $< 38\mu\text{m}$ with the help of 400 mesh size.
- Calcite was added to prepared arsenic sample at different densities of 2, 5, 7.5, 10g/l, i.e, of weight 0.4, 1, 1.5, 2g in 200 ml arsenic solution.
- Now hydrated ferric sulfate { $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ } is added to the above prepared solution.
- Calcite along with $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ was used as coagulant.
- Now the solutions were subjected to magnetic stirrer where they are stirred for 30 minutes at 150 rpm and then passed through $2.5\mu\text{m}$ filter paper.
- NaOH and HCl were added to adjust the pH of the solutions in the range of 4-8.
- The solution is now left for agitation at 240 rpm at 40 degrees Celsius for 30 minutes.
- Whatman filter paper no. 41 was used to filter all solutions prepared above.
- Now the batch analysis was carried out by varying the pH of samples.
- Concentration of As for individual pH was measured using AAS

($\lambda = 193.7\text{nm}$, silt = 0.7, argon flow= 50ml/m and pump velocity =120 rpm) by taking 15 ml each time for analysis.

- Mean of the 2 values are reported for individual sample.

3.2 Activated carbon as an adsorbent (V. Fierro et. Al. (2008)

Materials required

Around 100 g of sodium arsenate salt is used so as to prepare the arsenic solution. Granular activated carbon is taken as adsorbent. Ferric chloride is used for iron- doping, sieve of 400 mesh size, Nitric acid of 1M, Hydrochloric acid and Potassium Iodide. Hot air oven is used for drying. To neutralize the samples, HCl and NaOH are used. To ensure thorough mixing, mechanical shaker is used. Whatman no. 2 filter is used to filter the solutions. Precision balance is used for weighing the samples. To quantify the heavy metals, Atomic Absorption Spectrometer is used.

Methodology

- Sodium arsenate salt of 100 g was taken in a 500 ml of distilled water sample.
- Granular Activated carbon weighing 22g is passed through sieve of 400 mesh size, of which 4 - 4.5 g retained.
- 0.05M FeCl_3 measuring 650ml was prepared in acidic medium by taking pH = 4 .
- The retained activated carbon approximately 17-17.5 g was taken and boiled in 1M HNO_3 for 2 hours at 100 degree Celsius.
- The above solution is now oven dried for a day.
- The oven dried mass weighs 14.5g.
- Four samples, each containing 3.5 g of activated carbon along with 150 ml of 0.05M FeCl_3 were taken.
- Each of four samples were then subjected to forced hydrolysis in which they were heated to 100 degree Celsius.

- Then pH of all samples was set to 7 i.e., neutral by adding Hydrochloric acid and sodium hydroxide.
- The samples were then subjected to overnight oven drying at 80 degree Celsius.
- 3g of Activated Carbon was taken from each sample and added to each 100mL of 0.05 ppm Arsenic solution.
- KI (10% v/v) and HCl(10% v/v) were added in each samples.
- Each sample was subjected to mechanical shaking for 40 minutes at 35 degree Celsius at 240 rpm.
- The samples are passed through Whatman No. 2 filter paper.
- Concentration of As was measured using AAS ($\lambda = 193.7\text{nm}$, slit = 0.7, argon flow= 50ml/m and pump velocity =120 rpm).
- Mean of the 2 values are reported for individual sample.

3.3 HPPC as an Adsorbent (Kundu S. et. al., 2004)

Materials required

Around 100 g of sodium arsenate salt is used so as to prepare the arsenic solution. Ordinary portland cement of grade 43 is used to prepare the required adsorbent. To measure the acidity or alkalinity of the slurry, pH meter is used. Distilled water is used to prepare the slurry and washing purposes. To ensure thorough mixing, mechanical shaker is used. Whatman no. 41 filter is used to filter the solutions. Hot air oven is used for drying. To quantify the heavy metals, Atomic Absorption Spectrometer is used. Precision balance is used for weighing the samples.

Methodology

- A sample of Arsenic solution of 0.2mg/l was prepared using Sodium Arsenate salt by taking 100g of sodium arsenate in 500 ml of distilled water.
- Take half kilogram of OPC and prepare slurry of w/c = 0.45.
- Measure the pH of slurry.
- The slurry was kept for drying naturally for 72 hours.
- Then the dried pieces are broken down and kept for 96 hours in water.
- The fine particles then obtained are oven dried at 100-110 degree Celsius for 72 hour.
- The oven dried particles were then put in bottles and arsenate solution of 100ml was added.
- Adsorbent quantity was taken from 2-25g/l.
- The bottles were then shaken for 7h at speed of 200 rpm.
- The samples are passed through Whatman No. 2 filter paper.
- Concentration of As was measured using AAS ($\lambda = 193.7\text{nm}$, slit = 0.7, argon flow= 50ml/m and pump velocity =120 rpm).
- Batch analysis such as variation of pH , adsorption time and concentration was carried out.

CHAPTER NO. 4

RESULTS AND DISCUSSIONS

4.1 COARSE CALCITE

4.1.1 Efficiency of arsenic removal on varying pH of samples

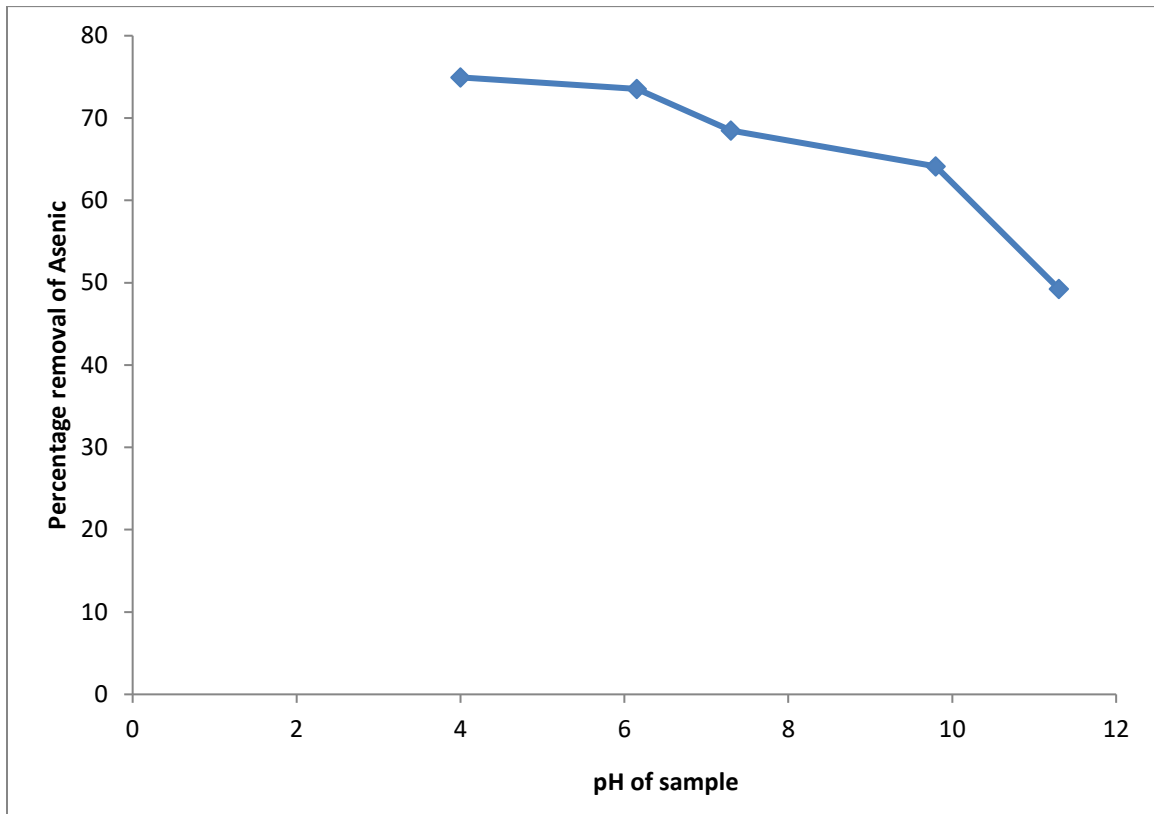
Initially, pH of the sample was 3.70. pH of the sample is varied to check if the removal efficiency is better in acidic or basic medium. pH of the sample is varied by adding Sodium Hydroxide and Hydrochloric acid.

- Calcite concentration = 7.5 g/l
- Stirring Time = 30 minutes

Table 1 : Removal of As by coarse calcite on variation of pH

pH of sample	Initial concentration of As (ppm)	Final concentration of As (ppm)	% Removal of Arsenic
4	5	1.253	74.94
6.15	5	1.323	73.54
7.30	5	1.576	68.48
9.8	5	1.793	64.14
11.30	5	2.537	49.26

Graph 1 : Percentage removal of Arsenic v/s pH of sample using Coarse Calcite



At pH = 4, the efficiency was quite good enough but as NaOH is added, the pH rises and the efficiency reduces. From the graph it can be observed that percentage removal of arsenic decreases with the increase in pH of sample and therefore pH should be kept minimum for higher efficiency.

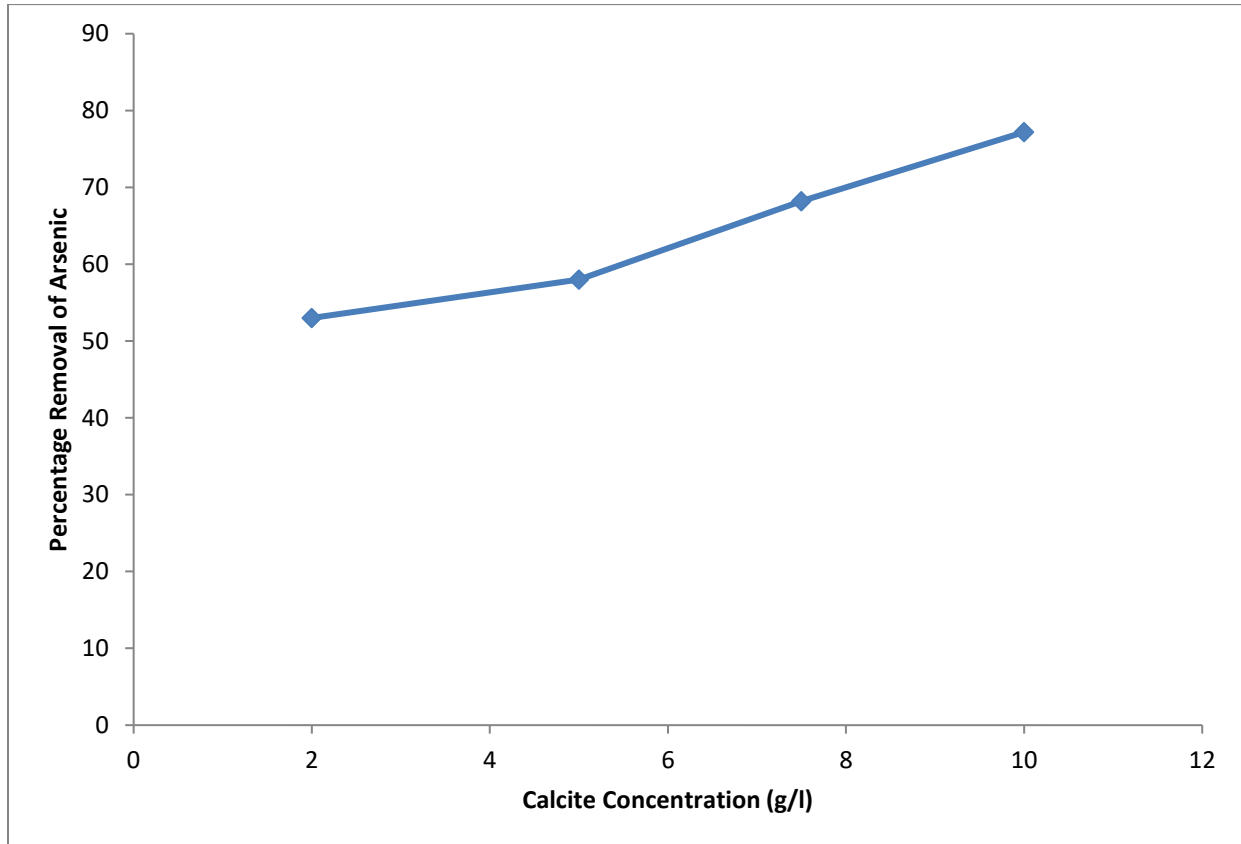
4.1.2 Efficiency of arsenic removal on variation of calcite concentration

- pH of sample = 5.2
- Stirring time = 30 minutes

Table 2 : Arsenic removal percentage on variation of calcite concentration

Calcite concentration (g/l)	Initial Concentration of Arsenic (ppm)	Final concentration of Arsenic (ppm)	% removal of Arsenic
2.0	5	2.35	53.0
5.0	5	2.10	58.0
7.5	5	1.59	68.20
10.0	5	1.14	77.2

Graph 2: Percentage removal of Arsenic v/s Calcite Concentration



From the graph it can be observed that calcite concentration favours the removal of arsenic, as the efficiency drastically increases with the increase in concentration.

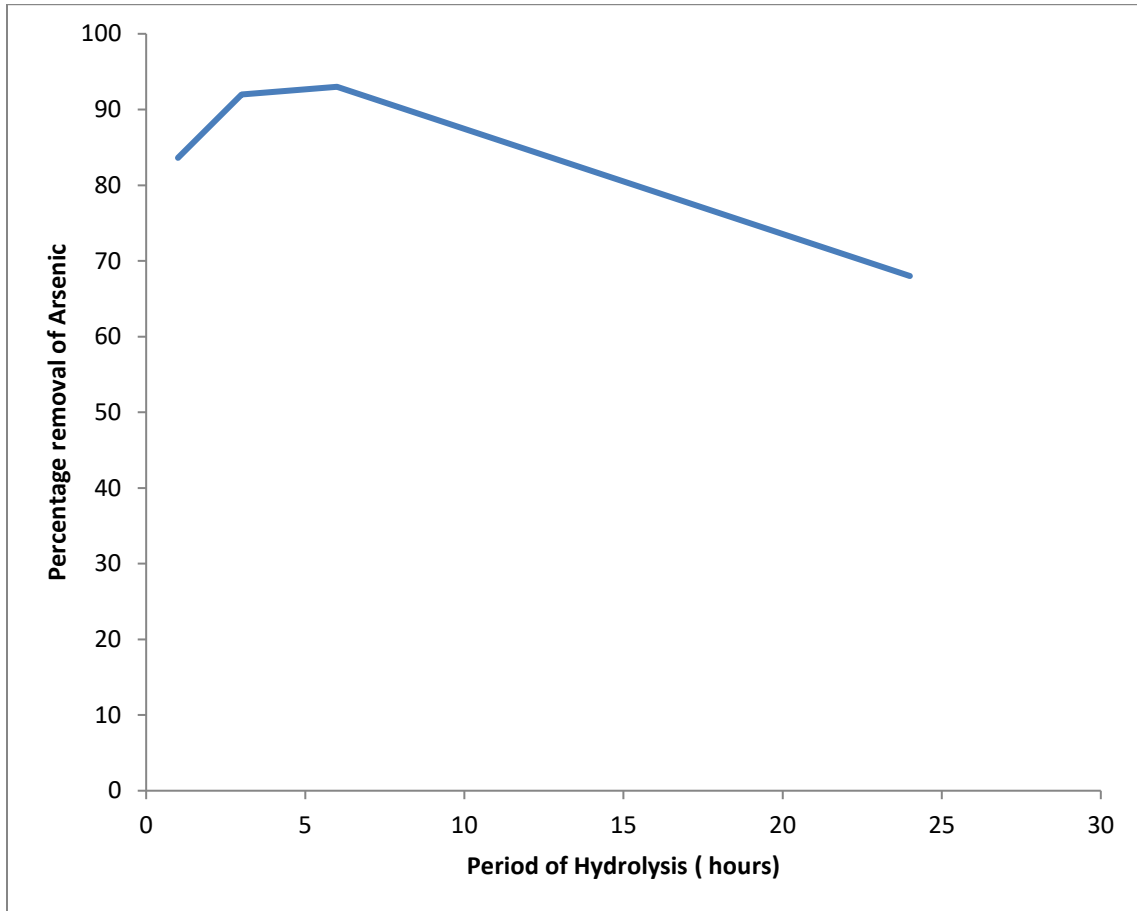
4.2 ACTIVATED CARBON

4.2.1 Efficiency of As removal on variation of period of Hydrolysis

Table 3 : Percentage Removal of Arsenic by Activated Carbon on variation of Hydrolysis Period.

Forced hydrolysis period (hrs)	Content of Iron in Activated Carbon (% by weight)	Initial Concentration of Arsenic (ppb)	Final concentration of Arsenic (ppb)	Percentage removal of Arsenic
1	1.1	50	8.2	83.6
3	1.8	50	4.0	92.0
6	2.1	50	3.5	93.0
24	8.6	50	16	68

Graph 3 : Percentage Removal by Activated carbon v/s Hydrolysis Period



Doping the activated carbon with iron is dependent on the period of hydrolysis. More the hydrolysis period, more will be the doping. But after a certain hydrolysis period, the efficiency reduces significantly. This might be due to the doping capability of the Activated carbon.

4.3 HPPC

4.3.1 Efficiency of Arsenic removal on variation of pH of sample

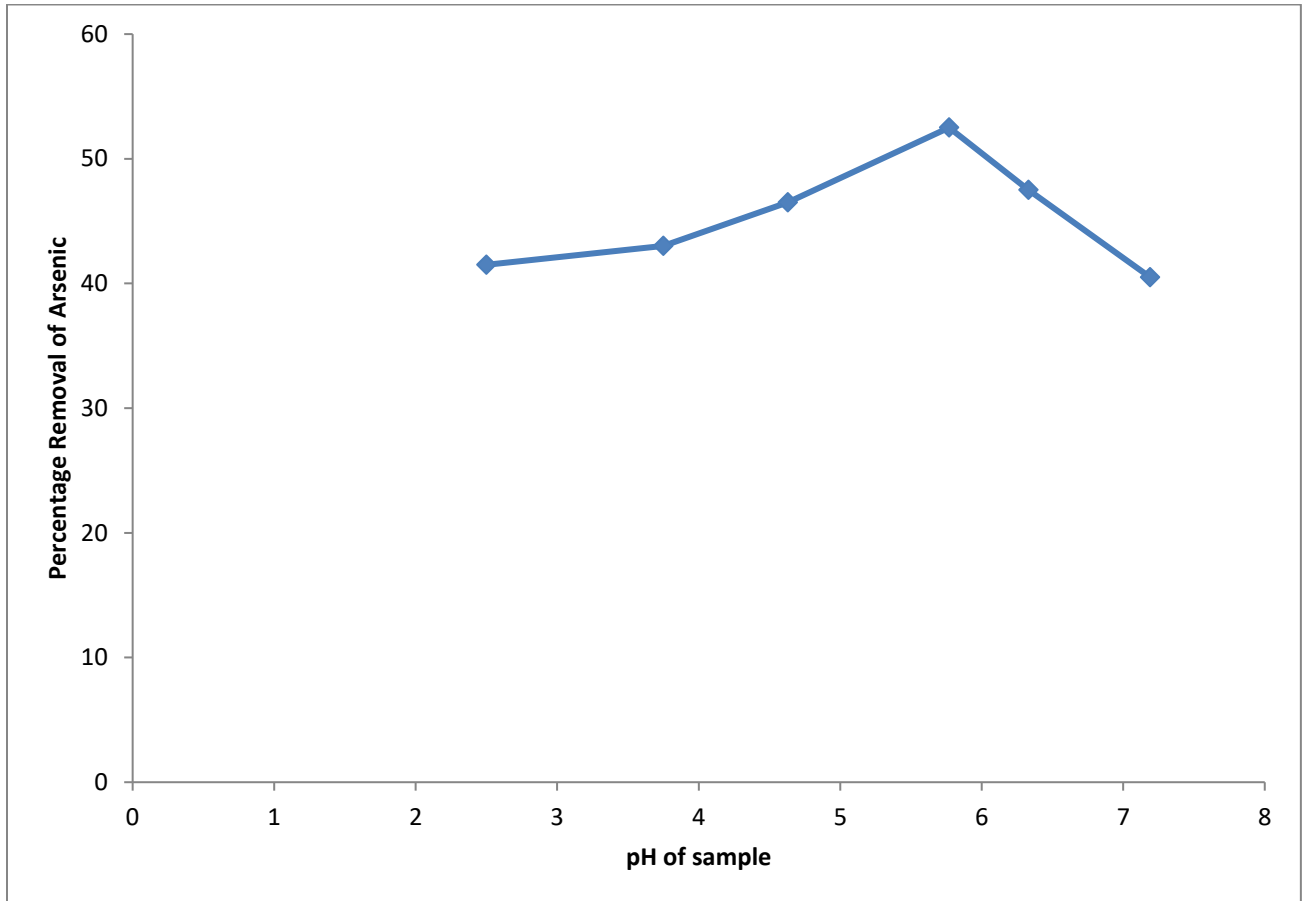
Initially pH of the sample was 6.33. pH of the sample is varied to check if the removal efficiency is better in acidic or basic medium. pH of the samples are varied by adding Sodium Hydroxide and Hydrochloric acid.

- Concentration of cement : 15 g/l.
- Adsorption time : 8 h

Table 4: Percentage Removal of Arsenic on variation of pH of sample using HPPC

pH of sample	Initial concentration of Arsenic (ppm)	Final concentration of Arsenic (ppm)	% Removal of Arsenic
2.50	0.2	0.117	41.5
3.75	0.2	0.114	43
4.63	0.2	0.107	46.5
5.77	0.2	0.095	52.5
6.33	0.2	0.105	49.50
7.19	0.2	0.119	40.50

Graph 4 : Percentage Removal of Arsenic v/s pH of sample of Arsenic sample using HPPC



After pH = 2.5 when sodium hydroxide is added, there is an increase in efficiency of removal but it is upto pH = 5.77. But on further addition of sodium hydroxide, the removal efficiency decreases.

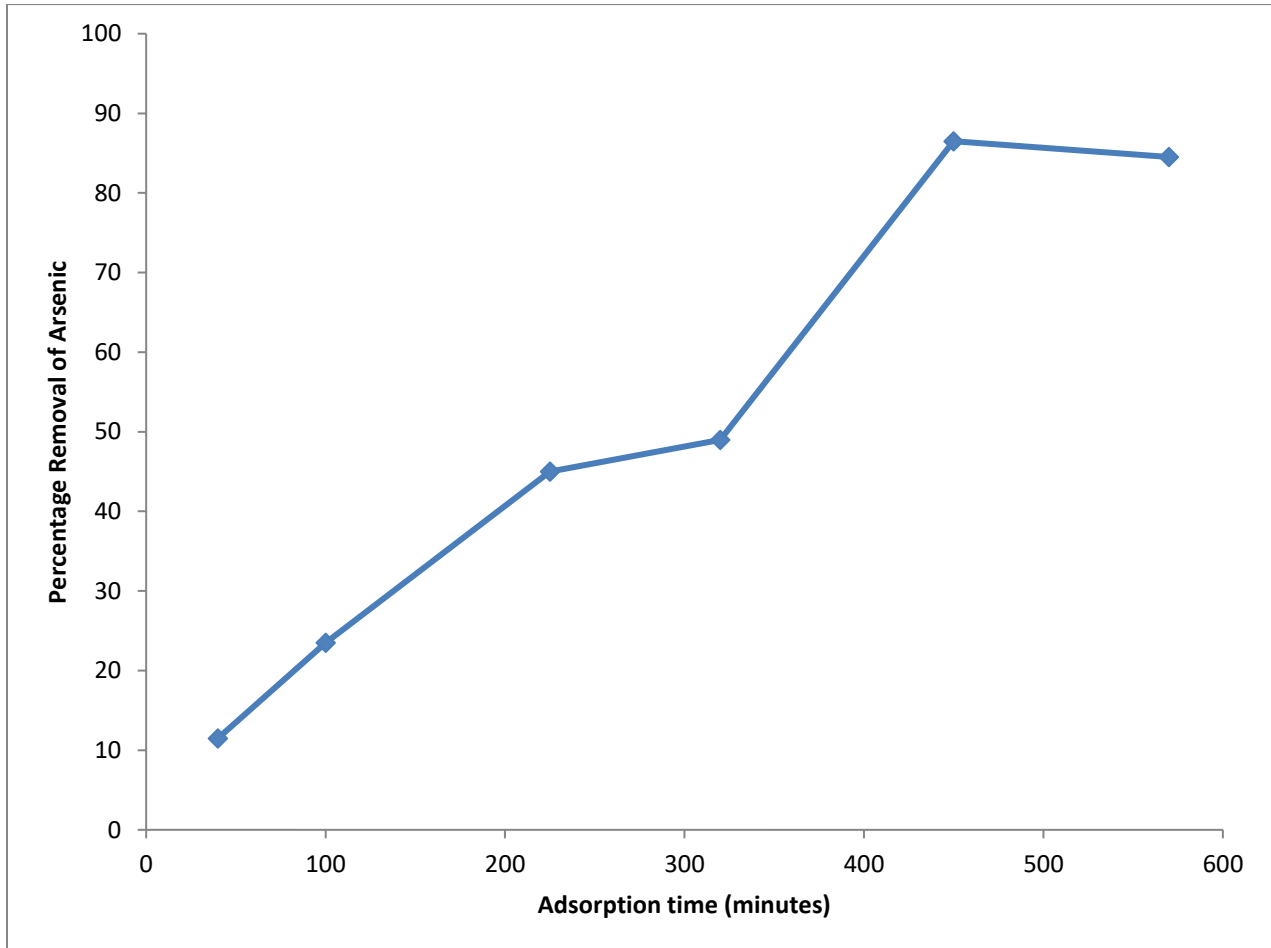
4.3.2 Efficiency of Arsenic removal on variation of time of adsorption

- Concentration of cement: 20g/l
- pH of Arsenic sample: 6.0

Table 5: Percentage Removal of arsenic on variation of adsorption time using HPPC

Adsorption time (minutes)	Initial concentration of Arsenic (ppm)	Final concentration of Arsenic (ppm)	% removal of Arsenic
40	0.2	0.177	11.5
100	0.2	0.153	23.5
225	0.2	0.110	45.0
320	0.2	0.102	49.0
450	0.2	0.027	86.50
570	0.2	0.031	84.50

Graph 5: Percentage Removal of arsenic v/s adsorption time using HPPC



From the graph, it is clearly observed that as the adsorption time increases, removal of Arsenic is increased upto a certain extent and then decreases. This might be due to the saturation capacity of the adsorbent which is observed after a period of 450 minutes.

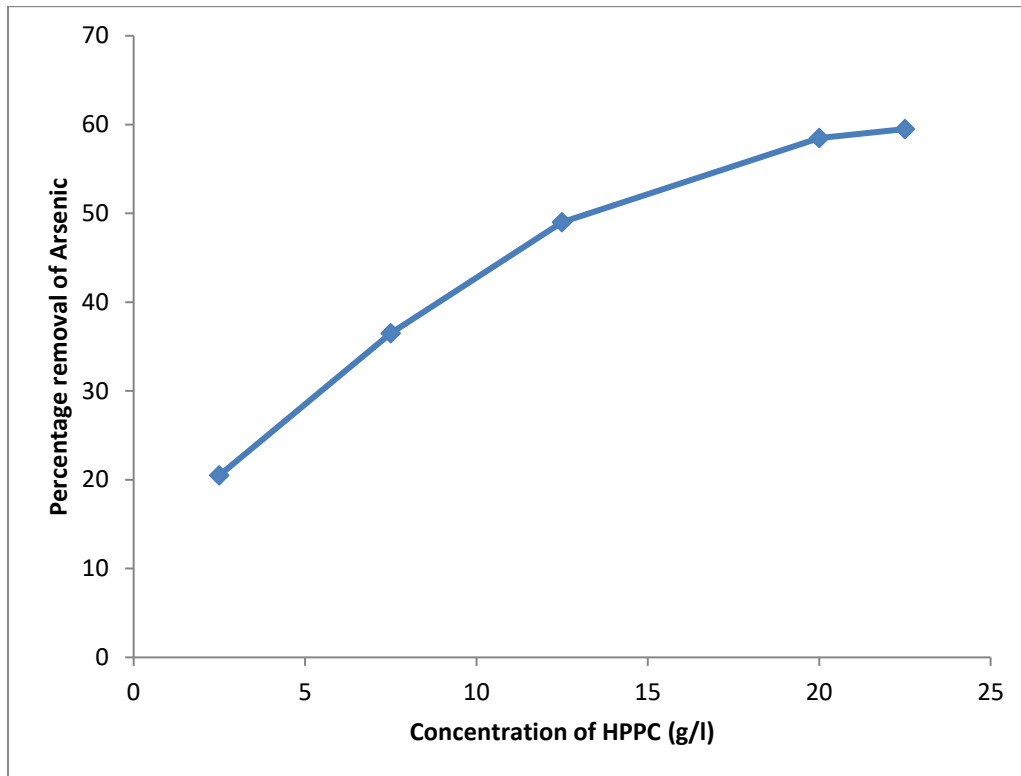
4.3.3 Efficiency of Arsenic removal on variation of concentration of HPPC

- pH of Arsenic sample= 6
- Shaking time = 8 hours

Table 6: Arsenic removal percentage on variation of concentration of HPPC

Concentration (g/l)	Initial concentration of Arsenic (ppm)	Final concentration of Arsenic (ppm)	% removal of Arsenic
2.5	0.2	0.159	20.5
7.5	0.2	0.127	36.5
12.5	0.2	0.102	49
20.0	0.2	0.083	58.50
22.5	0.2	0.081	59.5

Graph 6 : Percentage removal v/s concentration of HPPC



It can be seen that for a particular pH and shaking time the removal efficiency of adsorbent increases with the increase the increase in its concentration.

CHAPTER NO. 5

CONCLUSIONS

A) Activated carbon

When hydrolysis period = 1 hr , removal efficiency was 83.6%. As the hydrolysis period is increased to 6 hr, the removal efficiency is 93%. On further increasing the hydrolysis period to 24 hr, the removal efficiency is dropped to 68%. This might be due to the doping capability of the Activated carbon.

B) Coarse calcite

At pH = 4, the percentage removal efficiency is 74.94. On taking the pH to near neutral level, i.e, at pH= 7.3, removal efficiency is 68.48%. And in basic medium, i.e., at pH = 11.30, the removal efficiency is 49.26%. This indicates that coarse calcite shows greater efficiency in acidic medium.

Coarse calcite of concentration 2g/l shows efficiency of 53% and when the concentration is gradually increased to 10g/l, it shows efficiency of 77.2%.

C) HPPC

At pH = 2.5, percentage removal of arsenic is 41.5. On further increasing pH, removal efficiency remains maximum upto pH = 5.77. At pH = 7.19, removal efficiency reduces to 40.5%. This might be due to the fact that in basic medium, adsorption capacity of HPPC reduces.

The removal efficiency is 86.5% upto adsorption time of 450 minutes. At adsorption time of 570 minutes, removal efficiency is 84.5%. This is caused as HPPC cannot adsorb beyond a certain adsorption time due to its saturation capacity.

HPPC at concentration of 2.5g/l shows efficiency of 20.5%. And as the concentration is gradually increased to 22.5g/l, the removal efficiency is 59.5%.

REFERENCES

- Alexander J. T., Hai F. I. & Al-aboud (2012). Chemical coagulation-based processes for trace organic contaminant removal: Current state and future potential. *Journal of Environmental Management* , 195-207.
- Daus B, Wennrich R, Weiss H.(2004). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes. *J. Geochem.Explor* , 109–131.
- Driehaus W., Jekel M., Hildebrandt J. (1998). Granular ferric hydroxide—a new adsorbant for the removal of arsenic from natural water, *J. Water Supply Res. Technol.-Aqua* 47, 30–35.
- Fierro V., Gonzalez-Sánchez G. (2009): Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis , *Journal of Hazardous Materials* 168 430-437.
- Mohan D. (2007). Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142 , 1–53.
- Geological Survey of India: Arsenic Pollution in Ground Water of the Deltaic Alluvial Plain of West Bengal – A Case Study of Malda District.
- Gullledge J.H., O'Connor J.T.(1973). Removal of arsenic (V) from water by adsorption on aluminum and ferric hydroxides. *J. AWWA* 65 (8), 543.
- Gu Z., Fan J., Deng B. (2005). Preparation and evaluation of GAC-Based iron containing adsorbents for arsenic removal, *Environ. Sci. Technol.* ,39, 3833–3843.
- Han B., Zimbron, J., Runnells, T.R., Shen, Z., Wickramasinghe S.R. (2003). New arsenic standard spurs search for costeffective removal techniques. *J. AWWA* 95 (10), 109–118.

- Hering J.G., Chen P.Y., Wilkie J.A., Elimelech M., Liang S.(1996). Arsenic removal by ferric chloride. *J. AWWA* 88 (4), 155–167.
- Jekel MR. (1994) Removal of arsenic in drinking water treatment Part I: Cycling and Characterisation; Willey and Sons Inc New York, 26, 119-132.
- Kundu S., Kavalak S.S, Pal A., Ghosh S.K. (2004): Removal of arsenic using hardened paste of Portland cement *Water Research*, 38 (17), 3780-3790.
- Mandal B.K., Chowdhury T., Samanta G. (1997)- Chronic arsenic toxicity in West Bengal, *Current Science*, 72(2), 114 117.
- Mondal K., Pattanayak J., Mathew S., Lalvani S.B. (2000). A parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents, *Carbon* 38, 589–596.
- Mondal P., Majumder C.B., Mohanty B. (2006). Laboratory based approaches for arsenic remediation from contaminated water: Recent developments. *Journal of Hazardous Materials* ,137, Issue 1, 2006, 464-479.
- Murshidabad—One of the Nine Groundwater Arsenic-Affected Districts of West Bengal (2005), India. Part I: Magnitude of Contamination and Population at Risk , 43(7) , 823-834.
- Pal T., Jana N.R. (1996). Polarity dependent positional shift of probe in a micellar environment. *Langmuir* 12, 3114–3121.
- Raje N., Swain K.K. (2002). Purification of arsenic contaminated ground water using hydrated manganese dioxide. *J. Radioanal. Nucl. Chem.* 253, 77–80.
- Samanth G. (2001)- Preservation and Field Speciation of Inorganic Arsenic Species in Groundwater, 473-476.

- Shen Y.S. (1973). Study of arsenic removal from drinking water. *J. AWWA* 65 (8), 543.
- Song S., Lopez-Valdivieso A., Hernandez-Campos D.J, Peng C., Monroy-Fernandez M.G., Razo-Soto I. (2006). *Water Research* 40 (2) , 364-372.
- Sorg J.T., Logsdon, G.S.(1978). Treatment technology to meet the interim primary drinking water regulations for inorganics. Part 2. *J. AWWA* 70 (7), 379–392.
- Su C., Puls R.W. (2001) Arsenate and arsenite removal by zero valent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 , 1487–1492.
- Vineis P. & Xun W. (2009). The emerging epidemic of environmental cancers in developing countries, *Annals of Oncology* 20: 205–212.
- WHO (1993). *Guidelines for Drinking Water Quality*. World Health Organization, Geneva.