ARSENIC ADSORPTION FROM GROUND WATER USING NON-TOXIC WASTE AS ADSORBENTS

BY

DIKSHYA DHAKAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
(ENGINEERING AND TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
THAMMASAT UNIVERSITY
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A Thesis Presented

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Abstract

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Master of Science in Engineering and Technology, Sirindhorn International Institute of Technology, 2018

Groundwater sources contaminated by arsenic pose a great threat to the environment and the living organism including human. Exposure to arsenic at low concentration for a long period or high concentration for a short period, would create a lot of problem on the health and environment. Treatment of water containing soluble arsenic ions is a must and if possible, followed by recovery or secure disposal of it. Various conventional techniques are being applied to treat arsenic contaminated water which are either expensive or less efficient. Adsorption is the most cost effective, simple and easy way to treat water containing heavy metals. The energy requirement to carry out adsorption process is minimal and could be more economic if we are able to use low cost adsorbents. In an effort to treat arsenic contaminated water in an economic way, this study attempts to find locally available and non-toxic adsorbent so that arsenic could be removed via the process of adsorption. Egg shell (ES) and banana peel (BP) were selected and their arsenic removal capacity were investigated.

Some physical and chemical properties of ES and BP were studied using techniques such as FTIR to find the functional group present in the adsorbents, BET surface area analysis, SEM to observe the surface morphology of the adsorbents and EDX to know the chemical composition of the adsorbents. The results of FTIR analysis showed the involvement of calcium carbonate of ES and hydroxyl group of BP for arsenic adsorption. BET surface area analysis revealed that the surface area of ES and BP was 0.77 m^2/g and 0. $4m^2/g$. Lower surface area in both adsorbents was due to the flat surface as seen in the SEM images. EDX analysis showed increment or decrement in weight percentage of element in adsorbents before and after adsorption. This suggests the involvement of the ions during adsorption process and confirmed the adsorption process being held.

Adsorption experiments were carried out to optimize the influencing parameters such as adsorbent dose, pH, agitation speed, contact time and initial concentration on both the arsenite [As(III)] and arsenate [As(V)] forms of arsenic. Arsenic removal capacity of ES is greater than the arsenic removal capacity of BP under same experimental conditions. As(V) removal capacity of adsorbents is greater than As(III) removal capacity even in short period of time. As(III) and As(V) adsorption were more sensitive to pH of the solution. As(III) removal was maximum at pH 9 and As(V) removal was maximum at pH 6. Moreover, pHzpc of BP was found at pH 7.06 and of ES was found at 8.03. At optimum conditions, As(III) and As(V) removal efficiency of ES is 68.54 % and 72.01 %, respectively. Likewise As(III) and As(V) removal efficiency of BP is 63.77 % and 67.12 %, respectively. Effect of competing ion such as phosphate and nitrate were also studied. These ions have a great influence on arsenic removal efficiency. As the concentration of these ions increases, arsenic removal efficiency of the adsorbents decreases. Modification of adsorbents were done in order to improve the removal efficiency. Carbonization at 700℃ slightly increased the removal efficiency but acid modification was not favourable.

Carbonized banana peel (CBP) and carbonized egg shell (CES) along with BP and ES were further used for experiments at pH 7 to model the adsorption data using different isotherm and kinetic equation. The best isotherm and kinetic equation were chosen with the help of some error analysis tools. As(III) uptake by all adsorbent and As(V) uptake by CBP are best fitted to Langmuir isotherm indicating formation of monolayer during adsorption process. But, As(V) adsorption on BP, ES and CES followed the Freundlich isotherm model indicating multilayer adsorption. Adsorption of As(III) and As(V) on BP, CBP and CES followed pseudo-second order kinetic equation and adsorption of As(III) and As(V) on ES followed Elovich kinetic equation indicating that the adsorption process is controlled by chemisorption process. In addition, adsorption rate on ES decreases exponentially with an increase in quantity of adsorbed ions. Comparison of evaluating suitable isotherm and kinetic model based on R^2 and error values revealed that R^2 values may not be true representative of the model. Overall result of the study concluded that BP and ES are promising alternate to the toxic and expensive adsorbents for the removal of arsenic from groundwater.

Keywords: Arsenite, Arsenate, Adsorption, Low-cost adsorbents, Isotherm, Kinetics

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Chapter 1

Introduction

1.1 Background

Water pollution has been a major environmental problem since the start of industrial revolution. Rapid urbanization and population growth triggered to an increase in water consumption and wastewater generation. Households, institutions and industries are disposing untreated wastewater haphazardly that causes severe deterioration of the water bodies in the developing world. Huge quantities of the wastewater generated are being disposed into the water bodies without any proper treatment. This trend of disposal leads to the accumulation of harmful materials including pathogens, toxic substances, biodegradable organic matter, and chemicals in water streams and rivers. The ultimate consequence is the shortage of clean water and the water borne diseases. This, in turn obligated people to rely upon groundwater.

Groundwater is an important source of water for a wide range of purposes. Groundwater use has been increased progressively as an alternative to polluted surface water. The major source of water used for irrigation and livestock purposes is groundwater. People in some regions also depends upon groundwater for drinking and cooking purposes. However, groundwater is also not a secure option. Groundwater contaminated with arsenic is a globally recognized environmental problem. Countries like Bangladesh and India (West Bengal) use groundwater as the main source of drinking water. But groundwater in those countries is severely contaminated with arsenic due to the release of arsenic from arsenic contaminated sediments in groundwater aquifers and recharge areas (Murugesan, Sathishkumar, & Swaminathan, 2006). Groundwater also gets contaminated through infiltration of arsenic from contaminated soil. Arsenic accumulation in soil may be attributed to the use of arsenical pesticides to increase cultivation, application of fertilizers to improve the quality of soil. Dust particles released from the burning fossil fuels, and disposal of industrial and animal wastes in the land also increases arsenic level in soil. After certain time, arsenic accumulated in soil could infiltrate to the water bodies and some of them can also enter the air through volatilization. Higher concentration in arsenic could also be due to mining activities, burning of coal, fuels and wastes, smelter operations and volcanic emissions. Hence, the concentration of arsenic in water bodies is increasing day by day as a consequence of the up-growing industrialization and urbanization of the world.

At present, 70 countries are affected with water contaminated by arsenic (Rehman, Yusoff, Ahmmad, & Alias, 2015). About 150 million people around the world are affected by arsenic contaminated water among which 110 million people live in South and South-east Asia (Singh, Singh, Parihar, Singh, & Prasad, 2015). Exposure to inorganic arsenic at lower level would cause irritation in the stomach and lungs, but if exposed at higher level may cause serious health hazards like infertility, miscarriage in women and retarded development in children. It will affect the respiratory track, cause cardiovascular abnormalities, gastrointestinal effects, brain damage, and even lower the immunity power against some infections (Abernathy et al., 1999). Long term exposure to high arsenic concentration would cause diseases such as skin lesions and cancers that include hyper-pigmentation (excess skin pigmentation), hyperkeratosis, gangrene in the limb, skin cancer, lung cancer and bladder cancer (Joshi & Sahu, 2014). Arsenic also gets accumulated in soil if the land is irrigated by water contaminated with arsenic. One of the studies done in Bangladesh showed that if soil is irrigated by arsenic contaminated water then the arsenic will be accumulated in the soil layers (Bhattacharya et al., 2007). Once the soil is contaminated it would decrease the crop quality and crop yields. It is reported that 25 mg/kg arsenic is accumulated in soil because of the irrigation done with arsenic contaminated water due to which 10% of the rice yield has been decreased (Bhattacharya et al., 2007). It is also stated that if 0.1μg/g of arsenic is released from solid phase then it may increase the groundwater arsenic concentration in the 200 μg/L (Pokhrel, Bhandari, & Viraraghavan, 2009).

1.2 Statement of the Problem

Groundwater containing arsenic is one of the major environmental problem. If human or other organism are exposed to arsenic contaminated water, it will cause severe health issues. Unlike organic pollutants, the majority of which are susceptible to biological degradation, arsenic will not degrade into harmless end products. Thus, treatment of aqueous wastes containing arsenic ions requires major attention followed by recovery or secure disposal. There are several treatment methods for the removal of arsenic from groundwater and wastewater. Some of them includes: oxidation techniques, coagulation and flocculation, ion-exchange method, phytoremediation, membrane separation approach, adsorption by activated carbon, etc (Dadwal & Mishra, 2016). But these processes are either expensive or are inefficient or toxic to be used for drinking water treatment. In this regard arsenic discharging industries and people relying on groundwater would not prefer to treat the water with high cost for the treatment. In comparison to the available treatment methods, adsorption technique provides an efficient and economical way of arsenic ion removal. Adsorption techniques are widely used in the uptake of arsenic ions from water and wastewater using different adsorbents such as siderite (Guo, Stüben, & Berner, 2007), hematite (Dickson, Liu, & Cai, 2017), zeolite (Chutia, Kato, Kojima, & Satokawa, 2009), brick powder (De Gisi, Lofrano, Grassi, & Notarnicola, 2016), tea waste (Murugesan et al., 2006), fish scale (Rahaman, Basu, & Islam, 2008), $FeCl_3$ treated lemon peel (Marín-Rangel, Cortés-Martínez, Cuevas Villanueva, Garnica-Romo, & Martínez-Flores, 2012), $FeCl_3$ treated pomegranate peel (Thapa & Pokhrel, 2013) etc. Although various adsorbents have been studied for arsenic removal, yet there are only few studies that have determined the possibility of using biomass without any chemical treatment for arsenic removal. Hence, there is a need to obtain inexpensive, easily available and non-toxic adsorbents that could be used in developing countries for remediation of arsenic contaminated groundwater.

1.3 Purpose of the Study

Locally available non-toxic biomass i.e. egg shell and banana peel is selected as adsorbent in this study. The purpose of this study is listed as follows:

- To investigate the efficiencies of locally available and non-toxic biomass for the removal of arsenic(III) and arsenic(V) from water.
- To optimize the influencing parameters such as adsorbent dose, pH, contact time, agitation speed, initial concentration and co-existing minerals that affects the adsorption capacity for banana peel and egg shell.
- To model the experimental results with suitable isotherm and investigate the adsorption mechanisms using appropriate kinetic models.

1.4 Scope of the Study

In this study, the adsorption capacity of locally available adsorbents for the removal of arsenic is investigated. Synthetic water with known concentration based upon the groundwater concentration of arsenic in different countries. Suitable locally available substances such as egg shell and banana peel were collected from the market and were used as adsorbents for the removal of arsenic. Some physical and chemical properties of the adsorbents were studied using the techniques like BET surface area analysis, Fourier Transform Infrared Spectroscopy (FTIR) analysis to identify the functional groups and Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) to determine the surface characteristics and elemental composition of the adsorbents. After that the adsorption efficiency based on the different experimental parameters was investigated and optimal conditions for adsorption were defined. The parameters include adsorbent dose from 2 g/L to 10 g/L, pH from 4 to 11, contact time from 40 min to 240 min, agitation speed from 50 to 250 rpm and initial analyte concentration from 0.1 to 10 mg/L. The effect of co-existing ions such as phosphate and nitrate were also studied. Three isotherm model namely the Langmuir, Freundlich and Elovich isotherm models were studied to ascertain the feasibility of adsorption process and also to find the maximum adsorption capacity of the adsorbents. Likewise, adsorption kinetics process was studied using pseudo-first order reaction models, pseudo-second order reaction model and Elovich equation. Finally, in order to select the suitable model and kinetics that represents arsenic adsorption on the adsorbents, some error analysis tools were applied. These tools included the chi-square test, root mean square error and average percentage error analysis.

Chapter 2

Literature Review

This chapter provides the overview of arsenic, its forms, impacts and worldwide distribution in groundwater especially in the countries like Bangladesh, India and Nepal. Different treatment methods used for arsenic removal are reviewed with a well description of adsorption process. Adsorption Isotherm and kinetics are also reviewed. Various types of adsorbent used for arsenic removal are listed with their optimum conditions.

2.1 Heavy Metals

Heavy metals are those chemical species whose density is greater than 5 g/cm^3 (Barakat, 2011). These chemical species include transition metals, a few metalloids, lanthanides and actinides. Industries, leaded petrol, gasoline, motor oils, cigarette, etc are the main root of origin of heavy metal which causes environmental degradation. Some of the examples of heavy metal are chromium, lead, nickel, copper, zinc, cadmium, mercury, etc. Heavy metals could be a severe hazard to man and aquatic plants and animals if its concentration exceeds beyond the maximum limits. Heavy metal concentration in the effluent that is discharged to the environment is increasing day by day. The major reason for the increment of level of heavy metal is the manmade activities. Industries like mining and ore processing, alloys industry, leather tanning industry, glass industry, paint industry, chemical fertilizer industry etc are resulting in increased levels of heavy metal in water resources. Some heavy metals like iron, zinc and copper are essential in trace amounts in our body while other heavy metals like nickel, cadmium, lead, mercury etc are toxic. Excess amount of any metal would result in serious health effects. Heavy metals are those substances which cannot be degraded as harmless end products. During the present context, people are also aware about the greater effects of harmful metals in the environment. As a result, lot of studies are being done to treat heavy metal contaminated water, for metal recovery and also for the safe disposal. Moreover, many innovative technologies have developed over decades, most of which are either expensive or energy consuming.

Heavy metals are introduced the food chain via soil and water. Once the heavy metal enters the human bodies, they will start to accumulate in tissues of bodies and start causing health effects to the body. Individual metal has its own toxicity and effects in the environment. Heavy metals have the potential of affecting different organs of human body. Some of the heavy metals are carcinogenic to man while some of them are required by our body. The heavy metals required by our body are zinc (adults need 15 mg and for pregnant and lactating women about 20 to 25 mg), copper for the formation of enzyme (adults need 2 to 3 mg and for children about 1 to 3 mg), manganese (adults need 2.5 to 5.0 mg), iron, etc. But if the same metal intake is in high concentration then it will give rise to different health problem. One of the heavy metals, chromium has no adverse effect in the form of pure metal. But if the concentration is very high and exposure to chromium is for long time then it can cause some toxic effects (Baruthio, 1992). Chromium(VI) are corrosive and irritants, they are easily adsorbed by lungs, skin and by digestive track (Baruthio, 1992). Respiratory track is the major target organ for chromium (VI) toxicity. It can cause nasal irritation, lung cancer, nasal ulcer and asthma (Shrivastava, Upreti, Seth, & Chaturvedi, 2002). Some of the heavy metal with their health effects is listed below (Duruibe, Ogwuegbu, & Egwurugwu, 2007; Martin & Griswold, 2009):

- Zinc: Intake of zinc at low concentration or short time causes some mild effects such as vomiting, abdominal pain, dehydration, drowsiness, nausea and lack of muscular coordination. But excess intake of zinc may cause body system dysfunction which results in impairment of growth and reproduction. It may cause anaemia, may damage the pancreas, HDL cholesterol levels may lower down and LDL cholesterol levels may increase in level and finally it may cause a risk of Alzheimer's disease.

- Lead: Lead contamination can lead to inhibition of the haemoglobin synthesis; dysfunctions and damage in the kidneys, joints and reproductive systems, cardiovascular system. It may cause indirect effect on heart, reproductive problems, renal tubular damage, and it may cause acute and chronic damage to the central and peripheral nervous system. Kidney and liver are the most targeted organ of lead and chronic exposure may lead to serious and permanent damage of brain.

- Copper: Large dose of copper has the potential to wide spread capillary damage, renal and hepatic damage and irritation in central nervous system which is followed by depression. Other effects of copper include blue green diarrhoea stool and saliva, acute haemolysis and abnormalities and damage of kidney functions.

- Cadmium: Cadmium even at low concentration can cause cardiovascular diseases and cancer if exposed for long term. It gets accumulated in the kidney and liver for long time and affects the renal tube which results in the dysfunction of tube to absorb protein, sugar and amino acid. High exposure could lead to obstructive lung disease, cadmium pneumonitis, sometimes even pulmonary oedema and death. Depending on the level of exposure to cadmium, the symptoms of effects of cadmium include abdominal cramps, nausea, vomiting, muscular weakness and dyspnoea.

- Nickel: Nickel has the potential to damage lung and can cause lung fibrosis and make the person difficult to breathe and sometimes cancer in respiratory tract. It can cause allergies in skin, inflammation of conjunctiva, eosinophilic pneumonitis and also asthma.

- Manganese: When compared to other heavy metals, manganese has the less effect on human. It only causes acute effects at higher concentrations. The occupational workers who are exposed to dust fumes of manganese may be the victim of neurological disorder known as manganism.

- Mercury: Mercury is not needed by human body but it exerts many toxic effects if someone is exposed to it. Mercury intake would lead to fatigue, cortical blindness, loss of concentration and memory, tremors constriction of visual field, etc in combined called as Minamata disease. Inorganic forms of mercury may be more harmful and can cause spontaneous abortion, congenital malformation and gastro-intestinal disorder.

2.2 Introduction to Arsenic

Arsenic is a universal element which can be found in atmosphere, living organism, rocks, soil and in water bodies (Smedley & Kinniburgh, 2002). Arsenic is commonly known as a hazardous heavy metal but actually it is a semi-metal (Barakat, 2011). Some of the facts about arsenic are given below:

- Arsenic is the 20th most abundant element found in earth's crust and it is the 33th element in the periodic table (Lenntech, 2011; Mandal & Suzuki, 2002).
- Arsenic has an atomic weight of 75gm/mol and density 5.7gm/cm^3 (Lenntech, 2011).
- The boiling point and melting point of arsenic is 615℃ and 814℃ respectively (Lenntech, 2011).
- Arsenic has various oxidation state such as -3,0,+3 and +5 among which trivalent oxidation state and pentavalent oxidation state are the most common states found in natural water (Smedley & Kinniburgh, 2002).
- There is a wide range of arsenic concentration found in natural waters which ranges from 0.5 μg/L and may exceed more than 5000 μg/L (Smedley & Kinniburgh, 2002).
- One of the applications of arsenic compounds is that they are used for making special types of glass, used as a preservative of woods (sodium arsenate and zinc arsenate) and in some semiconductors to generate laser light from electric current (Lenntech, 2011).
- WHO stated that the maximum concentration of arsenic that can be in drinking water without causing any effect is 10 µg/L (World Health, 2004).

Arsenic is universally distributed in the solid form as minerals and are found in very small amounts in all organisms. There are around 150 species of minerals which contains arsenic among which some of them are considered as arsenic ore (Akinbile & Haque, 2012). Arsenic occurs in environment combined with oxygen, chlorine, carbon, mercury, lead, sulphur, hydrogen, gold, etc. The condition of accumulation of arsenic is due to the natural processes such as volcanic eruption, weathering reactions and some biological and anthropogenic activities. However, in present days arsenic is accumulated in soil due to human activities due to the use of arsenical pesticides to increase cultivation, application of fertilizers to improve the quality of soil and use of arsenic as an additive to livestock feed (Smedley & Kinniburgh, 2002). Smelting of non-ferrous material along with the production of fossil fuels are the major reason due to which arsenic is transferred from ground state to the air and water resources. Combustion of coal in electrical power generating plants and in boiler are the major causes of arsenic mobilization in the environment. Likewise, mining operations is also a means of arsenic mobilization. Arsenic may have been released from the soil and sediments to the water bodies. It is stated that if 0.1µg/g of arsenic is released from solid phase then it may increase the groundwater arsenic concentration in the 200 µg/L (Pokhrel et al., 2009). Figure 2.1 represents the arsenic cycle and the transfer of arsenic from one phase to another. Humans will mainly come in contact with arsenic through water and also through food and air.

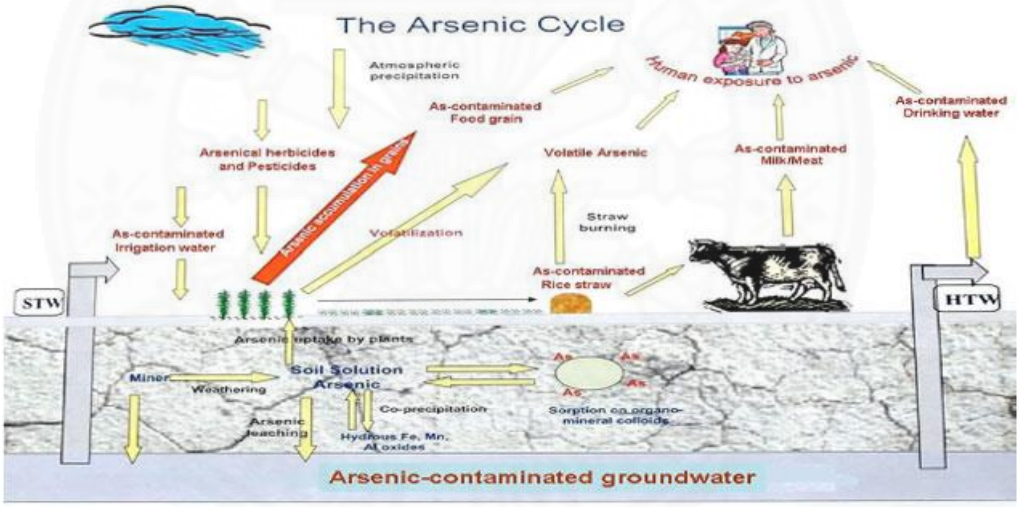


Figure 2.1: The arsenic cycle (Akinbile & Haque, 2012).

2.3 Forms of Arsenic

The oxidation state of arsenic is dependent on the environmental temperature, pH, associated ionic species, and oxidation reduction conditions and a relative change in the oxidation state occurs with the change in these environmental parameters. It may be possible that arsenic changes from less toxic state to more toxic state with the change in these parameters (Rehman et al., 2015). Compared to other oxyanion forms of elements, oxyanion form of arsenic causes most of the problems due to its potential of relative movement in a wide range of redox conditions (Smedley & Kinniburgh, 2002).

In groundwater, inorganic arsenic is the predominant form which exists in two oxidation states arsenate [As(V)] and arsenite [As(III)] (Marín-Rangel et al., 2012). As(III) is highly toxic and mobile in comparison with As(V). Arsenate is a thermodynamically stable form of arsenic and arsenite favours reducing condition and hence found in anaerobic ground waters. These inorganic forms of arsenic has greater toxicity compared to the organic forms and arsenite is more toxic than arsenate in biological systems (Katsoyiannis & Zouboulis, 2002). It is also stated that the conventional treatment process of arsenic has the efficiency to remove arsenate greater than that to remove arsenite. Hence, a preoxidation step is to be carried out for the treatment of arsenite (Katsoyiannis & Zouboulis, 2002).

The most important parameter that controls arsenic speciation is pH and redox potential condition. The As(V) species remain in the form of oxyanions ($H_2AsO_4^-$ and $HAsO_4^{--}$) throughout the pH range and under oxidising conditions. $H_2AsO_4^-$ is present at lower value of pH whereas $HAsO_4^{2-}$ is present at higher value of pH. Other forms such as $H_3AsO_4^0$ and AsO_4^{3-} are present in highly acidic and highly basic conditions respectively. Similarly, in case of As(III), its species exists in protonated form as $H_3AsO_3^0$ under reducing conditions and pH below 9.2 (Kanel, Greneche, & Choi, 2006). At higher pH, negatively charged arsenite species ($H_2AsO_3^-$ and $HAsO_3^{--}$) becomes dominant (Liu, Ao, Xiong, Xiao, & Liu, 2012). The existence of arsenic species as a function of pH can be clearly understood in Figure 2.2.

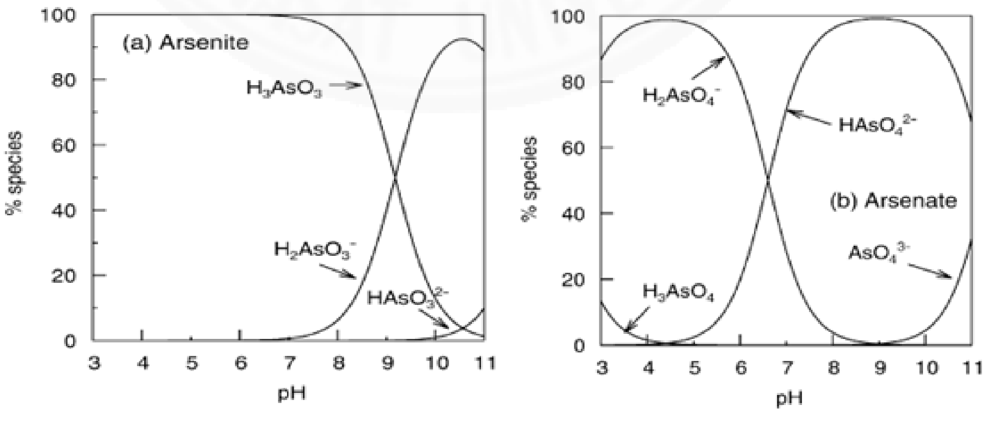


Figure 2.2: (a) Arsenite and (b) arsenate speciation as a function of pH (Smedley & Kinniburgh, 2002).

2.4 Worldwide distribution of Arsenic in Groundwater

There is wide range of region where the groundwater is contaminated by arsenic. In unpolluted natural water, arsenic concentration is found from 1-10 µg/L that may be increased to 100-5000 µg/L in the region where mining and sulphide mineralization is done (Mandal & Suzuki, 2002). The concentration of arsenic is increasing in natural water resources all over the world due to these mining activities. In present context, 70 countries are being affected and more than 100 million people are facing problem of clean drinking water and polluted fresh water resource (Rehman et al., 2015). The concentration of arsenic is reported in a wide broad from 0.5 µg/l to 5000µg/l in more than 70 countries (Singh et al., 2015). Table 2.1 shows the concentration of arsenic in groundwater samples in different countries. People who are affected by arsenic, groundwater is the main cause however in some cases people are also affected by arsenic through the foods and crops grown in the arsenic contaminated soil. The high concentration of arsenic were found in groundwater of New Zealand, Bangladesh, China, Mexico, Chile, Germany, Vietnam, Japan, Argentina, India Hungary, Taiwan, and US due to the presence of arsenic in the sediments of the aquifer (Singh et al., 2015). Around 150 million of people around the world are affected by arsenic contaminated water among which 110 million people live in the countries of South and South-east Asia (Singh et al., 2015). Contamination of aquifers of drinking water is the world's largest issue for arsenic related health problems especially in the countries like Bangladesh and West Bengal, India, which is affecting millions of people (Thakur, Thakur, Ramanathan, Kumar, & Singh, 2010). Most of the developing countries like Bangladesh, India, China, Nepal, and Vietnam depend upon the groundwater for irrigation and in some places for drinking water as well. In this way arsenic from water enters the soil through irrigation and the soil also gets contaminated.

Table 2.1: Arsenic concentration in groundwater of different countries.

Location	Sampling time	Arsenic source	Concentration (µg/L)	References
Nawalparasi, Nepal	2017	Hand pumps	41.04 - 745.2	(Mueller, 2018)
West Bengal, India	-	Groundwater	1186 (maximum)	(Chatterjee et al., 2018)

Punjab, Pakistan	2012	Tube well	12 - 448.5	(Rasool et al., 2017)
Jianghan Plain, China	May 2012 to December 2013	Groundwater	0.71 - 1081	(Li et al., 2018)
Datong Basin, China (83 sample)	October 2016	Groundwater	0.31 - 452	(Huq et al., 2018)
Kushtia District, Bangladesh (49 sample)	September 2015	Groundwater	6.04 - 590	
Nakhon Si Thammarat province, Thailand	1996	Shallow groundwater	1.25 - 5114	(Rujiralai, Juansai, & Cheewasedtham, 2018)

Unlike the natural sources of drinking water contamination, man-made activities are also increasing arsenic concentration. Industrial processes such as burning of fuels and wastes and mining and smelting release arsenic to the environment. Industries that produce pulp and paper, and which manufacture glass and cement also release arsenic to the environment. Industrial and sewage influence are the main reason which increases arsenic concentration in the surrounding. Higher concentration in arsenic is also due to coal burning, smelter operations and volcanic emissions. Mining activities is another reason for arsenic contamination. Due to the mining activities the arsenic present in the sulphide minerals gets oxidised and gets released. The concentrations of arsenic in water around the areas where mining operations are carried out sometimes reach in mg/L level. Many countries around the globe, are being afflicted by arsenic contamination due to mining activities such as Thailand, USA, Ghana and Greece (Smedley & Kinniburgh, 2002). The worst case of Arsenic poisoning due to mining activities is reported in southern Thailand. The maximal concentration of arsenic of 5 mg/L was found in groundwater due to mining operation and around 1000 people were affected due to arsenic related problems in the nearby area (Smedley & Kinniburgh, 2002). In New Zealand, the maxima arsenic concentration of 8.5 mg/L was found in the areas where thermal activities are carried out (Mandal & Suzuki, 2002). High level arsenic concentration up to 48 mg/L and 12 mg/L was reported in well water of US due to the mining activities (Smedley & Kinniburgh, 2002). Figure 2.3 represents the countries that are at a danger of arsenic poisoning due to arsenic contaminated drinking water.

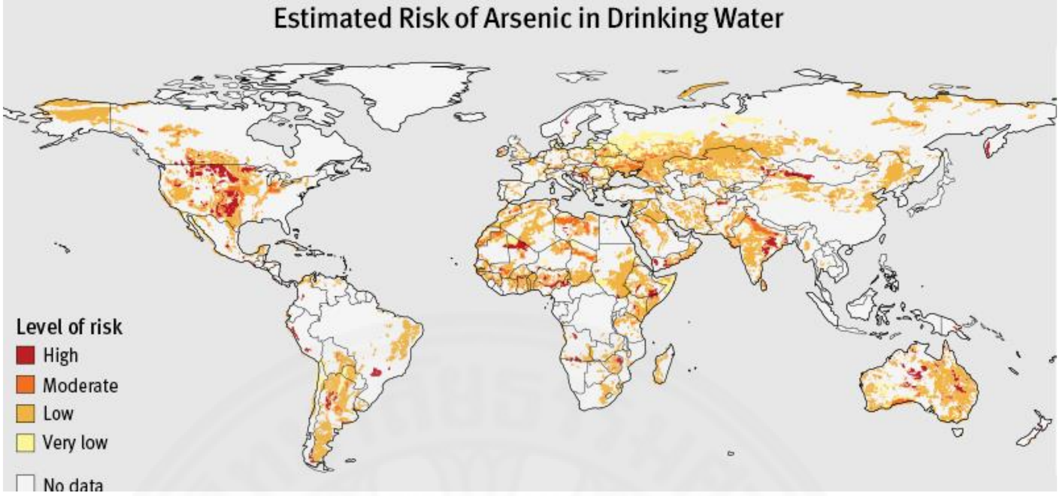


Figure 2.3: Map showing estimated risk of arsenic in drinking water around the world (Schwarzenbach, Egli, Hofstetter, von Gunten, & Wehrli, 2010).

The standard of arsenic is different depending upon different countries. In 1993, WHO set a guideline for drinking water having arsenic concentration value of 10µg/L. But a lot of developing countries like Bangladesh, China, Nepal, India, Philippines and Vietnam limit the standard of arsenic concentration to 50µg/L. In opposition to that, in Australia, arsenic concentration in drinking water is set to 7µg/L (Pokhrel et al., 2009). In the European countries, they follow the WHO guidelines as arsenic concentration greater than 10µg/L has never been detected so that is not a matter of concern to them. However in some countries they follow strict arsenic guideline such as 5µg/L is the standard of arsenic concentration in Denmark (Van Halem, Bakker, Amy, & Van Dijk, 2009).

2.4.1 Bangladesh

Bangladesh is a country which depends heavily upon groundwater. Even the government wants the public to use groundwater as an alternative to polluted surface water so that there is reduction in water-borne diseases. In the past the surface water of Bangladesh had been contaminated by microorganisms which caused death of many infants and children. So, for the alternative to the surface water many shallow surface wells were made and people started using groundwater tremendously. During that time arsenic contamination was not identified but in 1993 arsenic contamination was first detected in Nawabganj district (Smith, Lingas, & Rahman, 2000). In the present context, looking at the global scenario, people of Bangladesh along with West Bengal are mostly affected due to arsenic contamination in groundwater (Smedley & Kinniburgh, 2002). The aquifer in this region consists of the sand, silt and clay deposited by the river systems namely the Ganges, Brahmaputra and Meghna river. Due to the upland Himalayan catchments and also the basement areas of the northern and western parts of West Bengal, generation of sediments occurs and gets collected with the deposited layer of clay and silt. This finally restricts the entry of air in the aquifer creating a reducing environment favourable for arsenic. Hence arsenic concentration increases and groundwater gets contaminated which is a major problem along this area.

In Bangladesh, a wide range of arsenic concentration could be found in groundwater of contaminated areas that is from 0.5 µg/L to 3200 µg/L (Smedley & Kinniburgh, 2002). It is studied that out of the 120 million populations in Bangladesh, more than 100 million people are at the risk of arsenic poisoning and out of the total area of 148393 sq.km, around 118,849 sq.km area has the risk due to arsenic contamination (Mukherjee et al., 2006). It is reported that 52 districts out of the 64 districts in Bangladesh had arsenic concentration in groundwater higher than 10 µg/L (standard limit set by WHO) and 42 districts had higher than 50 µg/L (standard limit set by Bangladesh) (Chowdhury et al., 2000). Around 27% of shallow wells has more than 50µg/L of arsenic concentration and about 30-35 million people are being exposed to arsenic contaminated water of concentration more than 50µg/L (Smedley & Kinniburgh, 2002). In one of the study in Jessore district, especially the Samta village, it was found that around 91% of the wells in the village had arsenic contaminated water of concentration more than 50 µg/L (Smith et al., 2000). In a British Geological Survey around the southern, eastern and western parts of Bangladesh, they tested 2,000 hand tube-well water samples and resulted that around 21 million people were drinking water having arsenic concentration higher than 50 µg/L (Chowdhury et al., 2000). Figure 2.4 shows the level of arsenic contamination in different parts of Bangladesh.

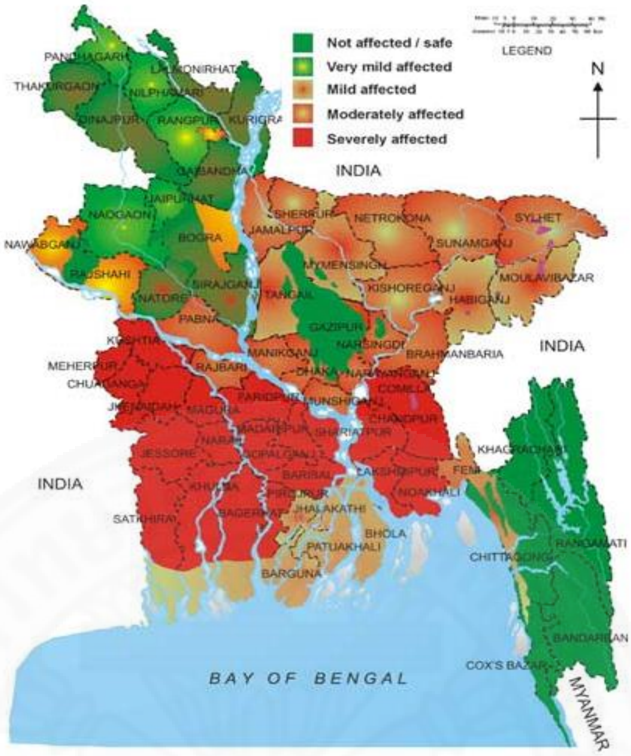


Figure 2.4: Arsenic distribution in groundwater of Bangladesh (Chakraborti et al., 2003).

2.4.2 India (West Bengal)

People of West Bengal also heavily rely upon groundwater for household purposes and drinking water as well. In the global scenario, people of West Bengal are also the mostly affected people due to arsenic contamination in groundwater along with Bangladesh (Smedley & Kinniburgh, 2002). Like in Bangladesh, groundwater use has been actively encouraged in this region by government and other agencies. There is practise of using private tube wells in high rate however there are large number of public tube wells as well. This indicates how deeply people rely upon the groundwater. Presence of arsenic in the groundwater in the region of West Bengal is due to the same reason as mentioned above in case of Bangladesh. The Arsenic affected ground waters in the Bengal Basin are because of the arsenic contaminated sediments in the range from 2 to 20 mg/kg of arsenic (Smedley & Kinniburgh, 2002). These sediments are carried by the three rivers Ganges, Meghna and Brahmaputra.

West Bengal has a total area of 88,750km² among which around 38,861km² area is affected by the arsenic contamination. These places include Nadia, North and South

Parganas, Murshidabad and Kolkata districts. Out of the total population in West Bengal, around 6 million people are in the exposure of arsenic contaminated water (Smedley & Kinniburgh, 2002). In one survey in 18 districts of West Bengal it was found that 9 districts have arsenic levels higher than 50 µg/L in groundwater and people from 7 districts were suffering from arsenical skin lesions (Chowdhury et al., 2000). In other survey reported by Mukherjee et al. (2006), 140150 water sample from tube wells were analysed and found that 48.2% had arsenic concentration higher than 10 µg/L and 23.9% had higher than 50µg/L. Health problems regarding arsenic contamination among the people first came into notice of government in 1978 (Mandal & Suzuki, 2002). 5000 patient having health problems such as the skin problem have already been identified in this region due to arsenic groundwater contamination and more than 200,000 people are suffering from arsenic poisoning or arsenicosis (Smedley & Kinniburgh, 2002). Some test of hair, nail and urine of the people who were living in the arsenic affected area were done and found that around 77% of the sample of people contained arsenic above the normal/toxic level. Figure 2.5 shows the level of arsenic contamination in different parts of West Bengal.

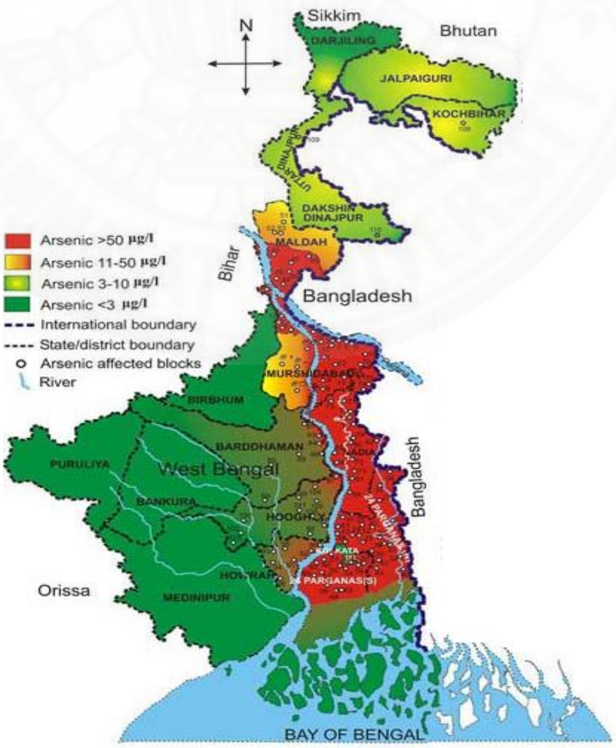


Figure 2.5: The area of arsenic-contaminated groundwater in West Bengal (Chakraborti et al., 2003).

2.4.3 Nepal

In Nepal about 47% of the total population live in the terai region (Mukherjee et al., 2006). The terai region covers 33,998.8 km^2 areas out of the total 147,181 km^2 area of Nepal. The terai region is somehow similar to that of Bengal Delta Plain, and the sedimentary layer comprises the Holocene thick sand and gravel deposits. They are interlocked along the alluvium flood plains which are carried by rivers from Siwalik Hills. The major sources of arsenic in the groundwater of terai region are the dissolution of arsenic bearing rock, minerals and sediments. In this region around 90% of the population is dependent on groundwater as a major source of drinking water and for other domestic purposes (Mukherjee et al., 2006). Investigations of arsenic contaminated water began in 1999 and found out that the total arsenic was between 1.7 and 404 μg/L with As(III) as the dominant form (Pokhrel et al., 2009). WHO has set the standard value of arsenic in drinking water as 10 µg/L but for a developing country like Nepal the standard was not feasible to apply so Nepal government limit the standard to 50 µg/L (Thakur et al., 2010).

Different study and report shows that an arsenic concentration average of 9 mg/L was found in the sediments of Nawalparasi district while the groundwater concentration was found to be 0.01 to 0.74 mg/L. Maximum arsenic concentration of 2.62 mg/L was found in drinking water in Rupandehi district and maximum level of arsenic found in tube wells of Bara, Nawalparasi, Rautahat, Parsa, Rupandehi, and Kapilvastu districts were 254, 571, 324, 456, and 2620 μg/L, respectively (Pokhrel et al., 2009; Thakur et al., 2010). The population at risk in the terai region for arsenic poisoning was estimated to be around 3.5 million. One study also reported that in Nawalparasi district, arsenic was found in food materials because of the arsenic contaminated water use for irrigation. Some of the examples of food were onion (0.45 mg/kg); potato (0.01 mg/kg); brinjal (0.09 mg/kg); cauliflower (0.33 mg/kg); and rice(0.18 mg/kg) (Pokhrel et al., 2009). Figure 2.6 shows the areas affected by arsenic and the concentration of arsenic in that area. In conclusion, in Nepal a maximum number that is 89.8% of samples has the arsenic concentration below 10 μg/L, 7.9% of samples has arsenic concentration in the range of 10–50 μg/L and 2.3% of the sample has arsenic concentration higher than 50 μg/L. The results showed that south western to south eastern regions are extremely affected by arsenic contamination with concentration greater than 50 μg/L (Thakur et al., 2010).

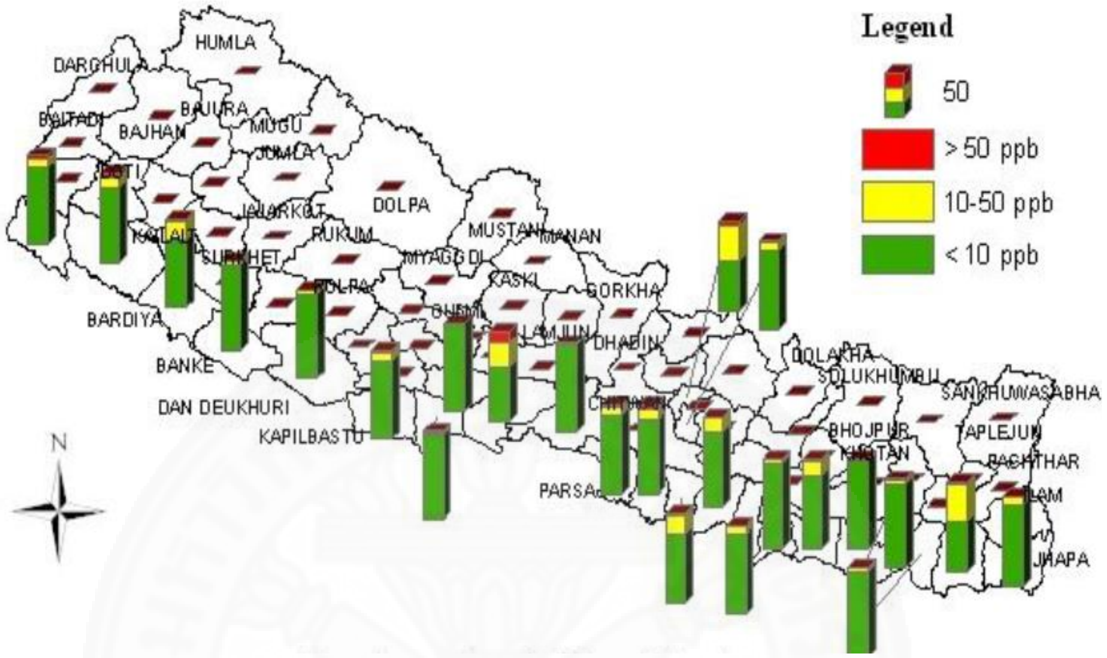


Figure 2.6: Arsenic contaminated groundwater samples found in various districts of Nepal (Thakur et al., 2010).

2.5 Impacts of Arsenic

Arsenic is one of the major toxic compounds. Impacts of arsenic depend upon the dose, exposure and contact time between the victim and arsenic.

2.5.1 Effects on Human Health

Arsenic is severely poisonous to human. IARC (International Agency for Research on Cancer, 2004) has categorized arsenic as a human carcinogenic substance (Van Halem et al., 2009). There are two main ways from which people come in contact with arsenic: one from drinking arsenic contaminated water and the other is eating arsenic contaminated foods. This may lead to the accumulation of inorganic arsenic in our body. In mammal arsenic has a special affinity in ectodermic tissue, specifically the nails and hair and moreover inorganic arsenic generally accumulates in keratin-rich tissues like hair. In human body, arsenic content is less than 0.3 mg/g on a wet weight basis; arsenic concentration in hair, nail and urine is about 0.08–0.25 mg/g, 0.3490.25 mg/g, 5-40 mg/day urine respectively (Mandal & Suzuki, 2002). However there also occurs excretion of arsenic through urine and faeces as the minor route and skin, hair and nails are the other routes for excretion. It is stated that organic arsenic is excreted faster than inorganic arsenic and pentavalent arsenic is excreted faster than trivalent arsenic.

Exposure to inorganic arsenic at lower levels would cause irritation in the stomach, lungs and also intestines decrease the production of red and white blood cells. But if exposed to inorganic arsenic at higher levels, it may cause serious health hazards. It may cause infertility, miscarriage in women and retarded development in children could also be the symptom arsenic poisoning. It will affect the respiratory track, cause cardiovascular abnormalities, gastrointestinal effects, brain damage, and even lower the immunity power against some infections (Abernathy et al., 1999) . The organic arsenic will not harm as much as the inorganic arsenic do. Long term exposure to high arsenic concentration would cause diseases such as skin lesions and cancers that include hyper-pigmentation (excess skin pigmentation), hyperkeratosis, gangrene, skin cancer, lung cancer and bladder cancer (Joshi & Sahu, 2014). Hyper-pigmentation is the first symptom seen in patient who is highly exposed to arsenic. The severe effect that arsenic poisoning can cause is the possibility of having cancer in various organs especially the skin, lung, and bladder.

Chronic exposure to high concentration levels of arsenic in drinking water caused Black Foot Disease (BFD) in Taiwan and the people also had increased risk of diabetes who were exposed to arsenic either occupationally or through contaminated water (Ng, Wang, & Shraim, 2003). A study done in Bangladesh revealed that the children who were exposed to higher arsenic level have less intellectual function compared to those exposed to lower arsenic levels (Pokhrel et al., 2009). One of the survey revealed that 25 districts out of 27 studied in Bangladesh and 7 out of 9 districts studied in West Bengal, had people suffering from arsenical skin lesions (Chowdhury et al., 2000). Usually the arsenic disease such as skin lesions and keratosis of the hands and feet start to appear only after 5–15 years of arsenic exposure. Figure 2.7 shows the harmful effects of arsenic seen on different parts of the body.

a) Skin disease b) Ear c) Foots d) Hands

e) Cancer f) Keratosis of feet g) Cancer in hand

Figure 2.7: The harmful effect of arsenic on different parts of the body (Joshi & Sahu, 2014; Panda, 2015).

2.5.2 Effects on Environment

Arsenic is non-biodegradable but it keeps on changing its phase from one state to another. The major effect of arsenic is in cultivation if the soil gets contaminated. Arsenic may be accumulated in soil due to the use of arsenical pesticides to increase cultivation, application of fertilizers to improve the quality of soil, dust particles released from the burning fossil fuels, and disposal of industrial and animal wastes in the land. Arsenic in the soil after some time could infiltrate to the water bodies and some of them can also enter the air through volatilization. In this way arsenic keeps on rotating in the environment. On top of that arsenic also accumulates in soil if the land is irrigated by water contaminated with arsenic. Arsenic is generally available as inorganic form in the soil but it has the ability to bind other organic material present in the soil (Mandal & Suzuki, 2002). Arsenic is commonly found in the tissue of living organism. Transfer of arsenic from one organism to other is a slow process. If plants get contaminated by arsenic then it is very rare case that the arsenic gets transferred from the plant to other organism because plants would die or get injured if it is exposed to arsenic. Thus, if the soil is contaminated by arsenic it will reduce the crop yields but it is rare that it gets transferred to other animals.

One of the studies done in Bangladesh showed that if soil is irrigated by arsenic contaminated water then the arsenic will be accumulated in the soil layers. Soil layers of 12 rice fields in Bangladesh were tested for arsenic out of which 4 were arsenic affected area and 2 were unaffected areas. The results showed that the top soil of the rice fields irrigated by arsenic contaminated water had arsenic concentration of 79–436 μg/L while the top soil of rice fields irrigated by less contaminated water had arsenic concentration less than 1μg/L (Bhattacharya et al., 2007). Bhattacharya et al. (2007) clearly showed the effects of arsenic contaminated soil on the crop quality and crop yields. It is reported that 10% of the rice yield has been decreased due to accumulation of arsenic in soil at a concentration of 25 mg/kg. Arsenic accumulation was due to irrigation done with arsenic contaminated water.

If arsenic enters the sea or marine water, the aquatic animals would also get affected. However, marine animals have some capacity to bind inorganic arsenic from solution. They accumulate arsenate from seawater and convert it to arseno-sugars that they utilize replacing the arseno-sugars from other foods. Marine animals store arsenic in tissues in the form of nontoxic arsenobetaine. Arsenobetaine and other organoarsenic compounds are the compounds which can be excreted rapidly and easily by mammals. Hence if humans or other animals feed these marine animals then there would not be any effect. But if there is high concentration of inorganic arsenic in water, these animals will store arsenic in their body particularly in some tissues of gills and digestive glands. These tissues would not be consumed by human so there is less effect of arsenic in human due to marine animals contaminated with arsenic but it will affect those individual animals (Neff, 1997).

2.6 Methods for Arsenic Removal

2.6.1 Coagulation and flocculation

Coagulation and flocculation is the most common and widely used treatment process for drinking water and wastewater in order to remove suspended particles from the water. There are suspended particles in the water containing some charges most of which carry negative charges. The negative charges cause repulsion between the particles which prevents them from agglomerating and they remain suspended. Coagulation and flocculation is a successive process to destabilize and agglomerate these particles into a big mass and settle them to separate from the water. For the process an external chemical reagent named as coagulant is used.

Coagulation and flocculation is also the most common method for arsenic removal as it is relatively simple and less expensive compared to other techniques. For the removal of arsenic, mostly used coagulants are iron(Fe) and aluminium(Al) based coagulants such as aluminium sulfate, ferric chloride, or ferric sulphate. Ferric chloride and alum was used as a coagulant to treat water containing arsenic in the form of arsenite and arsenate and the result was significant (Hering, Chen, Wilkie, & Elimelech, 1997). They are easily available at low cost and also easy to use. The coagulants consist of positive charge that neutralizes the negative charge present in the colloidal particles and forms larger particles called flocs. Arsenic is also adsorbed in the coagulated flocs and hence removed by sedimentation and filtration. It is reported that coagulants containing iron are more efficient than aluminium based coagulants for removal of arsenic (Dadwal & Mishra, 2016). Kartinen and Martin (1995) studied the removal efficiency of alum and ferric sulphate for the removal of arsenic in water with a concentration of 300µg/l. Alum dose of 30 mg/L removed about 10% of arsenic while same amount of ferric sulphate removed about 50% of arsenic. With addition of chlorine the removal efficiency increases to 90% and 95% respectively.

For the greater efficiency of arsenic removal, the coagulant is generated in situ by electrolytic oxidation technique and the process is called electrocoagulation. In electrocoagulation process for arsenic removal, iron electrodes are used and current is developed in the solution so that metallic cations of iron are generated and that would agglomerate the arsenic ions present in water. Metallic cations and hydroxides formed are responsible for the neutralization of the negatively charged colloids that allows them to coagulate. The electro coagulation process is based on the principle that the cations produced through electrolytical process from iron and/or aluminium anodes is responsible for the enhancement of the coagulation of arsenic ions present in the contaminated water.

It is easy to remove arsenic(V) compared to the arsenic(III) as trivalent arsenic occurs in non-ionised form. Therefore it is recommended to oxidise As(III) to As(V) at first as a pre-treatment process (Ahmed, 2001). Oxidation can be done by the addition of bleaching powder (chlorine), manganese dioxide, potassium permanganate (Ahmed, 2001; Ng, Ujang, & Le-Clech, 2004). The rate of coagulation depends upon pH of the solution and also the presence of other chemicals like phosphate and silicate. For the efficient removal of arsenic, the aluminium based coagulant should be used at pH value around 6-7 and the iron based coagulant could be used in a wider pH range usually between 6.0 and 8 (Ahmed, 2001; Ng et al., 2004). The main problem after the process is to handle and manage the resultant sludge. Sludge is produced in huge quantity containing the concentration of arsenic.

2.6.2 Membrane filtration

Membrane separation is a process that removes materials via minute pores or gaps present in a membrane. A membrane is a thin layer of semi-permeable material consisting of billions of pores and microscopic holes. Dadwal and Mishra (2016) stated that “Membranes are normally made of synthetic materials with pores that act as a selective barrier, which permits specific solutes to pass through while others are partially or completely excluded”. Membrane filtration is commonly divided into four categories based on the size of the pore: micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and hyper-filtration or reverse osmosis (RO). Generally, separation is accomplished by MF membranes and UF membranes via mechanical sieving and in NF membranes and RO membranes, capillary flow or solution diffusion is the cause of separation. The most effective method for arsenic removal at household level is the reverse osmosis method which is capable of removing about 90-99% of the dissolved mineral salts from water (Kumar, Namdeo, Mehta, & Agrawala, 2015). In RO, the membrane contains microscopic pores with size of 0.0001 micron that allows only molecules smaller than that to pass through it and generally dissolved minerals and salts have size larger than that of the microscopic pores.

When a solution containing some charged particles comes in contact with the membrane then the charge particles retain in the membrane and efficiency of membrane would be more if the membrane contains the same charge. The membrane with fewer negative charge should be selected to increase the arsenic removal efficiency from drinking water so membrane as arsenic is present in the form of anions (Kumar et al., 2015). In membrane separation the removal efficiency does not depend upon the chemical composition and pH of the feed. But in the case of As(III) and As(V), removal efficiency using the membrane filtration method show high efficiency when pH value was from 7 to 10 and from 3 to 5 respectively for As(III) and As(V) (Ng et al., 2004). Membrane filtration technology can reduce As concentrations to less than 50 mg/L and even below 10 mg/L in some of the cases (Singh et al., 2015). This process of filtration cost high due to which it is not practiced commonly (Amarasinghe & Williams, 2007).

2.6.3 Ion Exchange

Ion exchange is a physical process in which exchange of ions occurs between an electrolyte solution and a complex or between two electrolytes. This process is the result of the variation in affinity of an ion for the resin material. In this process an ion with a high affinity towards the resin material present in the ion exchange column replaces an ion with a lower affinity that was previously bound to the column resin. New ion having high affinity replaces the ion already present in the column resin. Once the resins are saturated, it needs to be regenerated with either an acid or alkaline medium. The main disadvantage of this process is high operational and maintenance costs and also secondary pollutant containing heavy metals would be produced.

For arsenic removal using the ion exchange method, the ion exchange resin is commonly loaded with chloride ions and is placed in vessel (Kartinen & Martin, 1995). Arsenic contaminated water is passed through the vessel. Previously attached chlorine ion is now replaced by the arsenic ion present in the water and the concentration of arsenic lowers in the water while concentration of chlorine increases. Once all the chlorine ions in the resin get replaced by the arsenic ion in the water, resin become exhausted and requires a process of regeneration. The reaction which occurs in the resin and during the regeneration is given below (Ahmed, 2001):

Arsenic exchange: $2\mathrm{R}-\mathrm{Cl} + \mathrm{HAsO_4}^{--} = \mathrm{R_2HAsO_4} + 2\mathrm{Cl}^-$

Regeneration: $\mathrm{R_2HAsO_4} + 2\mathrm{N}^+ + 2\mathrm{Cl}^- = 2\mathrm{R}-\mathrm{Cl} + \mathrm{HAsO_4}^{--} + 2\mathrm{Na}^+$

Here R: Ion exchange resin

Normally the ion exchange process does not depends upon the pH of the solution but in the case of arsenic pH should be at least 7.5 and the arsenic oxidation state should be pentavalent for greater efficiency (Kartinen & Martin, 1995). While oxidising trivalent arsenic to pentavalent arsenic the excess oxidant needs to be removed as it may cause damage to the resin (Ahmed, 2001). The arsenic removal capacity also depends upon the existing co-ion. For example if the solution contain some ions of sulphate and nitrate then these ions will be exchanged before arsenic and decrease the efficiency of arsenic removal (Ahmed, 2001).

2.6.4 Phytoremediation

Phytoremediation is a natural process in which plants are used directly for the removal of metal ions from contaminated water. It is an in-situ and eco-friendly process for the treatment of water based on the concept that nature cleans nature. Plants could remove heavy metals by certain processes like accumulation, translocation or absorption by different parts of the plants. Phytoremediation include several processes such as rhizofiltration, phytoextraction, phytovolatilization, phytodegradation, and phytostabilization. The main route for the uptake of the contaminants is from the root. Plants while absorbing or taking nutrients and water from the root also take the contaminated ions. Therefore, we can say that this process is a natural process of plants which is used to remove metals from contaminated sources. Hence the main advantages of phytoremediation process are environment friendliness, cost effectiveness and in situ application. But the main disadvantage is that the arsenic taken up by the plant would again come to the environment after the decay of the plant (Dadwal & Mishra, 2016).

The Chinese brake fern (*Pteris vittata L.)* was the first identified as arsenic hyperaccumulating plant(Singh et al., 2015). It is well stated that some of the tropical and sub-tropical species of plant can tolerate and uptake various inorganic and organic forms of As (Bhattacharya et al., 2007). Other plants which are suitable for phytoremediation and used for the uptake of arsenic are *Dryopteris filix-mas, Blumea lacera, Mikania cordata, and Ageratum conyzoides, Clerodendrum trichotomum and Ricinus communis* (Mahmud, Inoue, Kasajima, & Shaheen, 2008). Presently there are many plants both terrestrial and aquatic that have the capacity to remediate arsenic.

2.6.5 Oxidation

Oxidation generally refers to a process in which an element combines with oxygen. In wastewater treatment one way to oxidise the ion or molecules present in it is through natural oxygen and the other way is by adding some chemicals reagent (oxidising agent). However, the second way may produce some toxic by-products. Solar Oxidation, the photochemical oxidation process, is the other way applied to treat small quantities in individual units. Advanced oxidation could also be done to remove the toxic by-products through processes such as air stripping, steam stripping, or activated carbon adsorption. Chemical oxidation and advanced oxidation are normally used as a pre-treatment process of heavy metal wastewater containing organic compounds.

In groundwater, inorganic arsenic is the predominant form which exist in two oxidation state arsenite [As(III)] and arsenate [As(V)] (Marín-Rangel et al., 2012). Most of the treatment methods for arsenic shows high efficiency in removal of As(V) compared to As(III). Thus, the oxidation of As(III) to As(V) is recommended as a pre-treatment process to get higher efficiency in arsenic removal. As(III) can be oxidized via oxygen, free chlorine, hydrogen peroxide, hypochlorite, ozone, permanganate, and Fulton’s reagent. In developing countries the most common oxidising agents are atmospheric oxygen, hypo chloride and permanganate (Ahmed, 2001). 54–57% of As(III) can be oxidized to As(V) by using air or pure oxygen but for complete oxidation of As(III), ozone can be used(Singh et al., 2015). Arsenic if oxidised with air could take longer period of time but if some chemicals like chlorine and permanganate are added then they can rapidly oxidise arsenic.

Some equations for the oxidation process is given below (Ahmed, 2001):

Oxygen: $\mathrm{H_3AsO_3} + \frac{1}{2}\mathrm{O_2} = \mathrm{H_2AsO_4}^{-} + 2\mathrm{H}^{+}$

Chlorine: $\mathrm{H_3AsO_3} + \mathrm{HClO} = \mathrm{HAsO_4}^{--} + \mathrm{Cl}^{-} + 3\mathrm{H}^{+}$

Ozone: $\mathrm{As(OH)_3} + \mathrm{O_3} = \mathrm{AsO_4}^{3-} + \mathrm{O_2} + 3\mathrm{H}^{+}$

Permanganate: $\mathrm{H_3AsO_3} + 2\mathrm{KMnO_4} = 3\mathrm{HAsO_4}^{--} + 2\mathrm{MnO_2}^{+} + 2\mathrm{K}^{+} + 4\mathrm{H}^{+} + \mathrm{H_2O}$

Table 2.2: Comparison of different methods of arsenic removal.

Methods of Arsenic Removal	**Advantages**	**Disadvantages**
Coagulation and Flocculation	-Relatively simple and less expensive	-Huge amount of sludge is produced
Membrane Separation	-Highly efficient even at low concentration -Less amount of sludge is produced	-Cost of operation is high -Relatively slow process
Ion Exchange	-Regeneration of materials	-High operational and maintenance cost -Less number of metal ion is removed
Phytoremediation	-Cost effective -In situ application -Environment friendly	-Re-entering of arsenic into the environment as plant degrades
Oxidation	-Low cost of operation	-Less efficient -Slow process hence takes a lot of time

2.7 Adsorption

Adsorption is a process with simple mechanism for the removal of organic and inorganic pollutants. When a solution that contains absorbable solute comes in contact with some external particles which have the tendency to attract the absorbable solute then liquid-solid forces of interaction causes the absorbable solute to be deposited on the surface of external particle. This accumulation of absorbable solute into the surface of another particle is called adsorption. The absorbed solute is called adsorbate and the particle which absorbed solute in it is called adsorbent. In the other way, adsorption is also known as a mass transfer process in which mass from liquid phase is transferred to the external solid phase added in it.

Adsorption techniques are widely used in the uptake of toxic heavy metal ions from water and wastewater. This technique provides an efficient and economic means of metal ion removal as compared to expensive, conventional methods such as ion-exchange, activated carbon etc. It has advantage over the conventional methods because of its simple design and requires low investment both in terms of initial cost and land area. In this process, the metal ions present in the solution are adsorbed onto the surface of the adsorbents until a saturation limit is reached, beyond which the adsorption process starts to become inefficient. This is due to the complete loading of the active adsorption sites on the surface of the adsorbents. Actually, adsorption by some material is possible due to the presence of protein, carbohydrates and phenolic compound present in it. The compounds consist of functional groups such as carboxyl, arsenate, hydroxyl, sulphate and amino groups which binds the heavy metals (Chiban, Zerbet, Carja, & Sinan, 2012). Chemical modification of the adsorbents leads to further increase in the efficiency of adsorbents to remove metal ions. Adsorption process depends upon the parameters such as pH, contact time, dosage of adsorbent, metal ion concentration and temperature. The adsorption process can be batch, semi batch or continuous batch operations (Seniunaite, Vaiskunaite, & Bolutiene, 2014).

There are two types of adsorption (Rashed, 2013):

- Physical adsorption: It occurs due to the intermolecular forces of attraction between the molecules of adsorbate and adsorbent. The force of attraction is a physical force called the Vander Walls force. Multilayer adsorption could occur in adsorbent and could easily be disrupted with increase in temperature.
- Chemical adsorption: It occurs due to the chemical interaction between the molecules of adsorbate and adsorbent. In chemical adsorption either transfer or sharing of electron occurs or the formation of chemical bonds between the molecules occurs. Hence monolayer adsorption takes place.

The amount of adsorption of the molecule at the equilibrium phase can be determined using the given formula:

$$q_e = \frac{V * (C_i - C_f)}{M}$$

where,

q_e: Adsorption amount (mg/g)

V: Volume of solution (L)

M: Mass of adsorbents (g)

C_i: Initial adsorbate concentrations

C_f: Equilibrium adsorbate concentrations.

The percent adsorption (%) is calculated using the given equation (Erdem, Karapinar, & Donat, 2004):

$$Percent\ Adsorption = \frac{C_i - C_f}{C_i} * 100$$

where,

C_i: Initial adsorbate concentrations

C_f: Equilibrium adsorbate concentrations.

2.8 Adsorption Isotherms

Adsorption isotherm describes the distribution of adsorbed molecules of the liquid phase to the surface of the solid phase at equilibrium state. Adsorption isotherms represent the equilibrium relationship that describes interaction between adsorbate ions and adsorbent's surface. The process of adsorption is generally studied on the basis of graphs or curves known as adsorption isotherm obtained at a constant pH and temperature (Foo & Hameed, 2010). It is a graphical representation between the amounts of adsorbate that is adhered to the surface of the adsorbent. The graph describes the phenomenon which governs either the retention or the mobility of some substance from a liquid phase a solid phase at constant pH and constant temperature (Foo & Hameed, 2010). Adsorption equilibrium occurs when an adsorbate in any phase comes in contact with the adsorbent for a sufficient period of time. Some of the widely used isotherms in adsorption processes include the Langmuir, Freundlich and Elovich isotherm. According to Langmuir and Freundlich theory of adsorption, adsorption processes can take place either forming a homogenous layer or a heterogeneous layer. It depends upon the number of active sites present on the surface of the adsorbents.

2.8.1 Langmuir Adsorption Isotherm

The Langmuir isotherm assumes that a fixed number of adsorption sites is present on the adsorbent's surface, and that all those vacant sites are of equal size and shape. It also states that each vacant site can hold one molecule and a constant amount of heat is released in the process. Due to these reasons Langmuir isotherm is also called the homogenous adsorption. This isotherm best describes the chemisorption type of adsorption. The adsorbed molecules and the free molecules are in dynamic equilibrium with one another. This means that the adsorption and desorption processes are in equilibrium during the entire mechanism. The most underlying assumption of this isotherm model is that adsorption forms a solitary layer of adsorbed molecules and there is no transmigration of adsorbate in surface plane. According to theory of Langmuir isotherm, when the distance between the molecules increases, the intermolecular attractive force between them decreases (Foo & Hameed, 2010). Langmuir adsorption parameters are determined from the following non- linear equation (Foo & Hameed, 2010):

$$q_e = \frac{Q_o b C_e}{1 + b C_e}$$

where:

C_e: equilibrium arsenic concentration (mg/L)
q_e: the amount of arsenic uptake per gram of the adsorbent at equilibrium (mg/g)
Q_o: Langmuir constant indicating measures of monolayer adsorption capacity (mg/g)
b: Langmuir constant indicating adsorption rate (L/mg)
Other linear forms of equations are:

i. $\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$, here plot is between $\frac{C_e}{q_e}$ vs C_e

ii. $\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e}$, here plot is between $\frac{1}{q_e}$ vs $\frac{1}{C_e}$

iii. $q_e = Q_o - \frac{q_e}{bC_e}$, here plot is between q_e vs $\frac{q_e}{bC_e}$

iv. $\frac{q_e}{C_e} = bQ_o - bq_e$, here plot is between $\frac{q_e}{C_e}$ vs q_e

A dimensionless factor called the separation factor (R_L) that determines the nature of adsorption process is given by (Foo & Hameed, 2010).

$$R_L = \frac{1}{1 + \mathrm{b}C_i}$$

where:

C_i: Initial concentration of metal ions (mg/L)
b: Langmuir constant indicating adsorption rate (L/mg)

The lower value of R_L reflects that the adsorption is more favourable. Actually, the value of R_L indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Foo & Hameed, 2010).

2.8.2 Freundlich Adsorption Isotherm

Unlike the Langmuir isotherm model which limits in monolayer adsorption, Freundlich isotherm can be applied to multilayer adsorption and it describes the non-ideal and reversible adsorption. It states that the adsorption process results in a heterogeneous adsorbate layer, rather than a homogeneous monolayer. According to theory of Freundlich isotherm, "the stronger binding sites are occupied first and adsorption energy decreases exponentially until the adsorption process completes" (Foo & Hameed, 2010). The parameters of the Freundlich adsorption isotherms are obtained from the following non-linear equation (Foo & Hameed, 2010):

$$q_e = k_f C_e^{\frac{1}{n}}$$

where:

k_f and n: Freundlich constants that indicate the adsorption capacity and intensity

C_e: equilibrium arsenic concentration (mg/L)

q_e: amount of arsenic adsorbed per gram of the adsorbent (mg/g)

The logarithmic form of this equation can be represented as,

$log\, q_e = \log k_f + \frac{1}{n} logC_e$, here plot is between log q_e vs log C_e

The slope of the curve (1/n) represents the measure of surface heterogeneity or adsorption intensity. The value of 1/n represents to be either the heterogenous adsorption (1/n tends to 0), chemisorption type of adsorption (1/n tends to 1) and cooperative adsorption (1/n>1) (Foo & Hameed, 2010). In other words, the value n = 1 describes the adsorption to be linear leading to equal adsorption energies for all the sites (Mishra & Chandra, 2017). Values of n between 2 and 10 represents good adsorption, between 1 and 2 represents moderately difficult adsorption and below 1 represents poor adsorption characteristics (Ahamad, Singh, Baruah, Choudhury, & Sharma, 2018; Motsi, Rowson, & Simmons, 2009). Table 2.3 shows values of the Langmuir and Freundlich isotherm constants for different heavy metal adsorption using various adsorbents.

Table 2.3: Isotherm constants for the adsorption of arsenic using different adsorbents.

Heavy Metals	**Adsorbents**	**Langmuir**		**Freundlich**		**Reference**
		b (L/mg)	**Q_o (mg/g)**	**K_f**	**n**	
Arsenic (As(III))	Basic Oxygen furnace slag (steel industry)	1.10	1.40	0.502	1.71	(Kanel & Choi, 2016)
	Pomegranate Peel ($FeCl_3$ treated)	0.873	50	2.51	1.79	(Thapa & Pokhrel, 2013)
	Fish Scale	5.2	0.025	0.685	1.64	(Rahaman et al., 2008)
	Siderite	1.9	1.040	0.013	0.59	(Guo et al., 2007)
Arsenic (As(V))	Fish Scale	8.8	0.027	0.396	1.54	(Rahaman et al., 2008)
	synthetic zeolites (H-MFI-24)	0.009	35.8	3.52	1.11	(Chutia et al., 2009)
	synthetic zeolites (H-MFI-90)	0.011	34.8	4.21	1.12	(Chutia et al., 2009)
	Siderite	6.6	0.516	0.064	0.28	(Guo et al., 2007)
	Orange Peel	483	0.036	0.42	0.72	(Khaskheli, Memon, Siyal, & Khuhawar, 2011)
	Oat hulls	44.2	2.04	0.42	2.48	(Chuang et al., 2005)

2.8.3 Elovich Adsorption Isotherm

Elovich isotherm model is also based on the multilayer adsorption as the Freundlich isotherm model. Elovich isotherm model states "the adsorption sites increase exponentially with adsorption resulting in a multilayer adsorption" (Ahamad et al., 2018). Elovich isotherm model parameters are represented by the following equation (Ahamad et al., 2018):

$$\frac{q_e}{q_m} = K_e C_e \exp\left(-\frac{q_e}{q_m}\right)$$

where,

K_e: Elovich equilibrium constant (L/mg)

q_m: Elovich maximum adsorption capacity (mg/g)

C_e: equilibrium arsenic concentration (mg/L)

$q_{e:}$ adsorption capacity at equilibrium (mg/g)

The linearized form of the Elovich isotherm model equation is represented as:

$$ln\frac{q_e}{q_m} = lnK_e q_m - \frac{q_e}{q_m},$$

here graph is plotted between ln(q_e/C_e) versus q_e and value of q_m and K_e are then calculated based on the values of slope and intercept of the graph.

2.9 Adsorption Kinetics

Adsorption process in practical field is generally a part of continuous process which is mostly carried out in steady state condition. In such condition it is important to find out the kinetic parameter so that we can understand the performance of the adsorption process in the whole continuous process system. In adsorption process, equilibrium time and rate of adsorption plays significant roles in controlling the process efficiency. It is important to find such parameters. One of the easiest ways to understand the data from the batch experiment is to find the equilibrium time and concentration in that time and verify using models that describes adsorption kinetics.

2.9.1 Pseudo first order equation

The pseudo first order equation, also known as the Lagergren equation is probably the oldest empirical model to describe the rate of adsorption of the solid-liquid interface

(Eris & Azizian, 2017). This model assumes that the rate of occupying sorption sites is proportional to the number of unoccupied sites (Iqbal, Saeed, & Zafar, 2009). Pseudo first order equation is derived using the Langmuir kinetic model at the initial or the equilibrium phase of adsorption, where negligible changes occurs in solute concentration. The non-linear form of the equation is represented as (Qiu et al., 2009):

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

where, k_1: Pseudo first order rate coefficient (min^{-1})

q_e and q_t: Amount of arsenic adsorbed per gram of adsorbent at the equilibrium and at any time (mg/g)

At boundary condition, q= 0 at t=0 and q=q_t at t=t, the integrated form of pseudo first order is given as follow:

$$log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303},$$

This equation is used to plot the graph between log (q_e-q_t) and t and value of k_1 and q_e are obtained from the slope and intercept of the graph.

2.9.2 Pseudo second order equation

This model was proposed for divalent metal ions. This model is based on two assumptions. The first assumption is that two reactions will occur simultaneously in the adsorption process and the second assumption is that one of the reactions occurs at faster rate and reaches equilibrium quickly while the other reaction occurs at slow rate and continues until the adsorption process is complete. The equation that represents this model is given as (Qiu et al., 2009):

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

where, k_2 is the pseudo second order rate constant.

Integrating above equation at boundary condition, q_t= 0 at t=0, q=q_t at t=t, we get:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} * t$$

In this equation plot is between t/q_t and t.

Other linear forms of equation are (El-Khaiary, Malash, & Ho, 2010):

i. $\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 {q_e}^2} * \frac{1}{t}$, here plot is between t/q_t and 1/t.

ii. $q_t = q_e - \frac{1}{k_2 q_e} * \frac{q_t}{t}$, here plot is between q_t and q_t/t.

iii. $\frac{q_t}{t} = k_2 {q_e}^2 - k_2 q_e q_t$, here plot is between q_t/t and q_t.

The value of k_2 depends upon the concentration of adsorbate. The value of q_e depends upon certain experimental parameters. It should be clear that the pseudo second order equation can be applied only in the case that the adsorbate concentration changes noticeably (Eris & Azizian, 2017).

2.9.3 Elovich Equation

Elovich equation can be used to describe second order kinetic with an assumption that the solid surface of adsorbents are energetically heterogenous. If the adsorption process satisfy Elovich equation, then it can be concluded that the adsorption process is a chemisorption process (Ahamad et al., 2018). The Elovich equation describes that the adsorption rate decreases exponentially with an increase in quantity of adsorbed ions (Qiu et al., 2009). The equation is generally represented by the following equation:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$$

where,

q_t: adsorption capacity at time t (mg/g)

α: initial sorption rate (mg/g.min)

β: desorption constant (g/mg) and is also referred as activation energy required for chemisorption.

Chien and Clayton (1980) simplified the above equation with an assumption that the parameter $\alpha\beta >> 1$. So, integrating the equation at boundary conditions, q_t (t = 0) = 0 and q_t (t = t) = q_t yields a simplified and linearized form of Elovich equation as follows (Ahamad et al., 2018):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$$

The plot is between qt and ln(t) in this equation and the value of α and β is calculated based on the slope and intercept of the graph. Higher the value of α, greater is the adsorption rate compared with the desorption rate.

2.10 Types of Adsorbents

2.10.1 Natural adsorbents

Natural adsorbents refer to the locally available material depending upon different region. Natural material such as charcoal, clay, zeolites, different types of minerals can be used as adsorbents because of its metal binding capacity (Abdel Salam, Reiad, & ElShafei, 2011). Many studies regarding the arsenic removal using natural products have been done. Naturally available material was used to treat groundwater and drinking water which contain both forms of arsenic which is As(V) and As(III) (Elizalde-González, Mattusch, Einicke, & Wennrich, 2001). In the study the adsorption capacity of natural zeolites, volcanic stone, and the cactaceous powder with respect to As(V) and As(III) were examined. They showed significant removal in pH range of 4-11. Another study was done by Baskan and his team using natural and iron modified clinoptilolite for the removal of arsenic(Baskan & Pala, 2011). The study was carried out using laboratory scale batch experiments and influence of various parameter for the adsorption was studied. They mentioned that pretreatment of adsorbent could highly increase the adsorption capacity of adsorbents. Adsorbent treaed with NaCl has arsenic removal capacity of 92%, that treated with $FeCl_3$ has the removal capacity of 84% but the adsorbent without any treatment can remove only 15%. This showed that some of the adsorbents could be effectively be used if modified with some reagent. The result of the study also concluded the adsorption capacity does not only depend upon the iron content of the adsorbrnt but also depend on the initial concentration of arsenic which needs to be treated. Some of the other natural materials used for arsenic removal are mentioned in Table 2.4.

Table 2.4: Arsenic removal efficiency of different natural adsorbents.

Heavy Metals	**Adsorbents**	**Surface Area (m^2/g)**	**Initial Concentration (mg/L)**	**Adsorbent Dose (g/L)**	**pH**	**Contact Time (hr)**	**Adsorption Capacity(mg/g)**	**Reference**
Arsenic (As(III))	Siderite	-	1	20	-	3	1.04	(Guo et al., 2007)
	Hematite nanoparticles	50	0.2	10	7-8	8	2.89	(Dickson et al., 2017)
	Hematite aggregate	50	0.2	10	7-8	8	1.68	
Arsenic (As(V))	Siderite	-	1	20	-	3	0.52	(Guo et al., 2007)
	Zeolites (H-MFI-24)	450	10	2	6.35	1.6	35.80	(Chutia et al., 2009)
	Zeolites (H-MFI-90)	400	10	2	3.15	1.6	34.80	
	Hematite aggregate	50	0.2	10	7-8	8	2.61	(Dickson et al., 2017)
	Hematite nanoparticles	50	0.2	10	7-8	8	4.12	

2.10.2 Adsorbents from waste products

Modified adsorbents are those adsorbents prepared from agricultural by-products and wastes, industrial wastes, household waste, sewage sludge, etc. Materials from which the adsorbents are prepared include any plants, fruit wastes, vegetable waste, coconut shell, palm waste, tea waste, rice husk, solid waste from any industries, etc. These adsorbents can be classified as follows:

2.10.2.1 Industrial by-product as adsorbent

Industrial by-product could also be the potential material to use as an adsorbent. It may not be as efficient as the commercially used adsorbents but its availability and low cost make it a possible adsorbent. Some of the by-product from industries shows a promising capacity to treat arsenic contaminated water. Sugarcane bagasse, the by-product of sugar industry from Vietnam was used to study the adsorption mechanism for arsenate (As(V)) (Pehlivan et al., 2013). The sugarcane bagasse was powdered and then modified with ferric nitrate to carry out the batch experiments. The result showed that the carboxyl and hydroxyl are the major functional group present in the adsorbent responsible for adsorption. At optimum experiment condition of 3hr contact time at pH 4, the maximum adsorption value is 22.1 mg arsenic per gram of the modified adsorbents. This shows a great example that removal of arsenic is possible at low cost. It is even better if we can find some materials which can remove arsenic without any modification. Table 2.5 shows the removal efficiency of various industrial by product which have been used for the removal of arsenic.

Table 2.5: Arsenic removal efficiency of industrial by-product as adsorbents.

Heavy Metals	**Adsorbents**	**Surface Area (m^2/g)**	**Initial Concentration (mg/L)**	**Adsorbent Dose (g/L)**	**pH**	**Contact Time (hr)**	**Removal Capacity (%)/ Adsorption Capacity(mg/g)**	**Reference**
Arsenic (Total)	Palm oil waste clinker sand	-	250	0.5	9	1	18.08 mg/g	(Rehman et al., 2015)
	Palm oil waste clinker sand	-	25	0.75	6.5	1	7.54 mg/g	
Arsenic (As(III))	Red Mud	-	2.5-30	20	7.25	-	0.663 mg/g	(Mohan & Pittman, 2007)

	Basic Oxygen furnace slag (steel industry)	5	1	10	7	3	>80%	(Kanel & Choi, 2016)
Arsenic (As(V))	Brick power	-	1000	-	-	1	>90%	(De Gisi et al., 2016)
	Chemically treated Fly ash	140	50	2	6.5	8	19.46 mg/g	
	Solid waste from leather industry	3	50-60	-	1	24	26.4 mg/g	
	Red Mud	-	2.5-30	20	3.50	-	0.514 mg/g	(Mohan & Pittman, 2007)

2.10.2.2 Agricultural waste as adsorbent

After industrial by product and natural materials, agricultural waste is another rich sources of low-cost adsorbents (Abdel Salam et al., 2011). If the agricultural waste could be utilized in the removal of heavy metal from water bodies then the in one hand the waste is also managed while in other hand heavy metal removal could be done in low cost. Manju, Raji, and Anirudhan (1998) studied the efficiency of coconut husk carbon for the removal of arsenic(III). They modified coconut husk carbon and used for the adsorption of arsenic from water under kinetic and equilibrium conditions. Batch experiments were carried out by varying different parameters and the results obtained were used to check the efficiency in synthetic and industrial wastewater. They concluded that coconut husk carbon could be a promising adsorbent if used at higher pH value that is around 12. Similarly, other material related to agricultural waste has been used in different studies which are summarized in Table 2.6.

Table 2.6: Arsenic removal efficiency of different agricultural waste as adsorbents.

Heavy Metals	**Adsorbents**	**Surface Area (m^2/g)**	**Initial Concentration (mg/L)**	**Adsorbent Dose (g/L)**	**pH**	**Contact Time (hr)**	**Removal Capacity (%)/ Adsorption Capacity(mg/g)**	**Reference**
Arsenic (As(III))	Rice straw	-	0.1	6	6.5	-	65%	(Amin et al., 2006)
	Coconut husk (H_2SO_4 /Copper modified)	206	50	2	12	4	88.6%	(Manju et al., 1998)
Arsenic (As(V))	Oat Hulls	522 ± 21.4	0.25	0.015	5	24	58%	(Chuang et al., 2005)
	Rice straw	-	0.1	6	8	-	75%	(Amin et al., 2006)
	Wheat Straw loaded Fe_3O_4 (0.1mol/L Fe)	4.73 (Wheat Straw)	10	0.5	-	12	30.24 mg/g	(Tian, Wu, Lin, Huang, & Huang, 2011)
	Wheat Straw loaded Fe_3O_4 (0.2mol/L Fe)		10	0.5	-	12	27.24 mg/g	
	Wheat Straw loaded Fe_3O_4 (0.5mol/L Fe)		10	0.5	-	12	24.14 mg/g	

2.10.2.3 Household waste as adsorbents

The household wastes, mainly the waste from the kitchen, also show great capacity to adsorb arsenic from the water sources. In one study, lemon peel treated with ferric chloride was used to study the removal capacity of arsenic(V). Marín-Rangel et al. (2012) The study resulted that 474.8 µg of arsenic was adsorbed by 1g of the treated lemon peel. Oke, Olarinoye, and Adewusi (2008) studied the efficiency of powdered egg shell in the removal of arsenic(V). They carried out batch experiments varying the parameters such as pH, adsorbent dose, initial concentration, contact time and the size of adsorbent particle. This study revealed that the size of particle also influences the rate of adsorption. Powdered eggshell with particle size of 63 µm showed the efficiency of 99.6% of arsenic removal in synthetic water with initial concentration of 1.5 mg/L. But the efficiency decreased to 98.4% and 97.4% when the size of powdered eggshell increased to75 and 150 µm respectively. The result was seen within the first 6 hours. Thus, if we find a suitable adsorbent which is available in every household and investigate the effective suitable value of different parameters then we can treat water at household independently at lower cost. Some of the waste from our household as mentioned in Table 2.7 has been used in removal of arsenic.

Table 2.7: Arsenic removal efficiency of different household waste as adsorbents.

Heavy Metals	**Adsorbents**	**Initial Concentration (mg/L)**	**Adsorbent Dose (g/L)**	**pH**	**Contact Time (hr)**	**Removal Capacity (%)/ Adsorption Capacity(mg/g)**	**Reference**
Arsenic (As(III))	Pomegranate Peel ($FeCl_3$ treated)	20	1	9	2	70.7%	(Thapa & Pokhrel, 2013)
	Tea Waste (Autoclaved)	1.3	20	7.2	0.75	100%	(Murugesan et al., 2006)
	Tea Waste ($FeCl_3$ treated)	1.3	20	7.2	1	100%	
	Tea Leaves	0.1	6	6.5	-	57%	(Amin et al., 2006)
	Newspaper	0.1	6	6.5	-	18%	
	Orange peel (Activated by HCL)	1000	50		6	87.77%	(Sidhu, Sama, Parmar, & Bhatt)
	Turnip peel (Activated by HCL)	1000	50		5.5	81.73%	
	Peanut Shell (Activated by HCL)	1000	50		6	86.38%	
	Fish Scale	0.5	10	6.8	130	83%	(Rahaman et al., 2008)
	Chicken Fat	0.5	10	6.8	130	25%	

	Coconut Fiber	0.5	10	6.8	130	50%	
	Charcoal	0.32	10	6.8	130	50%	
	Human Hair	0.36	10	-	8	56.67%	(Wasiuddin, Tango, & Islam, 2002)
Arsenic (As(V))	Lemon Peel ($FeCl_3$ treated)	0.2	10	-	24	58.28%	(Marín-Rangel et al., 2012)
	Tea Waste (Autoclaved)	0.9	20	7.2	1.25	76%	(Murugesan et al., 2006)
	Tea Waste ($FeCl_3$ treated)	0.9	20	7.2	1.5	77%	
	Tea Leaves	0.1	6	8	-	58%	(Amin et al., 2006)
	Newspaper	0.1	6	8	-	55%	
	Fish Scale	0.33	10	6.8	130	94%	(Rahaman et al., 2008)
	Chicken Fat	0.33	10	6.8	130	34%	

2.11 Chemical Modifications of adsorbent

Adsorption Capacity also depends upon the modifying agent. One of the studies clearly showed the variation in adsorption capacity by same adsorbent but the adsorbent was chemically modified in different way (Elizalde-González, Mattusch, & Wennrich, 2008). Maize cobs was used as adsorbent for the removal of arsenic. For arsenic(III), initial metal concentration was 550µg/l, adsorbent dose was 10gm/l and pH was 7.5. Similarly, for arsenic(V) initial metal concentration was 300µg/l, adsorbent dose was 50gm/l and pH was 5.4. Contact time and temperature were fixed to 15 days and 24℃ respectively for both the cases. Table 2.8 shows the variation in removal percentage while using different modification method for the same adsorbent. Modifying agents brought changes in the acidic/basic groups present in the adsorbent and maximum adsorption took place when there was the highest number of basic groups and a smallest number of acidic groups.

Table 2.8: Arsenic removal efficiency of maize cob modified with different chemical reagents.

Heavy Metal	**Modifying Agent used to modify maize cob**	**Removal Percentage (%)**
Arsenic (As(III))	None	3
	1 M H3PO4 + 1 M urea (6 h, 90°C)	15
	1 M H3PO4 + NH4OH (25%) (6 h, 90°C)	98
	1 mM triethanolamine (6 h, 90°C)	20
	Diethylaminoethyl cellulose, anion exchanger	45
Arsenic (As(V))	None	3
	1 M H3PO4 + NH4OH (25%) (6 h, 90°C)	6
	1 M H3PO4 + 2 M urea (2 h, 60°C)	9
	1 mM diethylenetriamine (4 h, 60°C)	3
	Cellulose propionate	9
	Diethylaminoethyl cellulose, anion exchanger	99

2.12 Background of adsorbent used in the study

2.12.1 Egg Shell

Egg shells are the significant solid waste produced from bakeries, restaurants, poultries, homes, and food manufacturing units. Eggshell weighs about 10% of the total mass of an hen egg shell (Wei, Xu, & Li, 2009). Egg shell and egg shell membrane show good efficiency in removal of heavy metals, phenolic compounds, pesticides and dyes because of their better surface properties (Pettinato, Chakraborty, Arafat, & Calabro, 2015). Some of the heavy metal which are removed by adsorption using egg shell are listed in Table 2.9. One gram of powdered egg shell contains about 22.4 mg of iron (Fe), 12.45 mg of aluminium (Al^{3+}) and 401 mg of calcium (Ca^{2+}) (Otun, Oke, Olarinoye, Adie, & Okuofu, 2006). Basically, iron and aluminium based-coagulants are used for the removal of arsenic in coagulation and flocculation processes. In one study done by Hering et al. (1997) for the removal of arsenic, alum and ferric chloride showed significant removal of arsenic. So, based on the composition of egg shell, it is believed that it would show significant results in arsenic adsorption.

Table 2.9: Comparison of Adsorption Capacity of Egg Shell for different metals.

Heavy Metal	Removal Capacity (%)/ Adsorption Capacity(mg/g)	Conditions	Reference
Cr^{6+}	93%	Adsorbent: Egg Shell pH:5 Contact time: 1.5 hr	(Daraei, Mittal, Noorisepehr, & Mittal, 2015)
Cr^{6+}	529.6 mg/g	Adsorbent: Egg Shell Dose: 12.5 g/L Initial Metal Concentration: 24507.8 mg/L pH:2 Contact time: 30 min	(Rajendran & Mansiya, 2011)
Cr^{3+}	100%	Adsorbent: Egg Shell Dose: 2 g/L Initial Metal Concentration: 97.61 mg/L pH: 7 Contact time: 3 hr	(Ghazy, El-Asmy, & El-Nokrashy, 2008)
Ni^{2+}	73.1%	Adsorbent: Egg Shell Dose: 10 g/L Initial Metal Concentration: 100 mg/L pH: 5.76	(Ho et al., 2014)
Ag^{+}	59.8%	Adsorbent: Egg Shell Dose: 10 g/L Initial Metal Concentration: 100 mg/L pH: 4	
Ni^{2+}	79.1%	Adsorbent: Egg Shell with membrane Dose: 10 g/L Initial Metal Concentration: 100 mg/L pH: 5.76	
Ag^{+}	58%	Adsorbent: Egg Shell with membrane Dose: 10 g/L Initial Metal Concentration: 100 mg/L pH: 5.2	
Al^{3+} + Zn^{2+} + Fe^{2+}	Al^{3+}:~93% Zn^{2+}:~50% Fe^{2+}:~69%	Adsorbent: powdered Egg Shell + Egg shell membrane Dose: 10 g/L Initial Metal Concentration (mg/L): Al^{3+}:6; Zn^{2+}:12; Fe^{2+}:6.5 Contact time: 2 hr	(Pettinato et al., 2015)

Cu^{2+}	~100%	Adsorbent: Egg Shell with membrane Dose: 2.5 g/L Initial Metal Concentration: 50 mg/L pH: 7-8 Contact time: 3 hr	(Rohaizar, Hadi, & Sien, 2013)
F^-	95 %	Adsorbent: Egg shell Dose: 24 g/L Initial Metal Concentration: mg/L pH: 6 Contact time: 100 min	(Bhaumik et al., 2012)

2.12.2 Banana Peel

Bananas are one of the mostly consumed fruit in the world. Once the pulp is consumed, the peel is removed and discarded as a waste. Banana peel are rich in polymers such as pectin, lignin and hemicellulose. Banana peels are used in many application including medicinal use, ethanol fermentation, generate fungal biomass, used as an adsorbent to treat heavy metals contaminated water (Bankar, Joshi, Kumar, & Zinjarde, 2010). Table 2.10 show he list of heavy metals removed by using banana peel at different experimental conditions. Latundan banana (*Musa acuminate×Musa balbisiana)* is one of the species of banana that is most common in south-east asia.

Table 2.10: Comparison of Adsorption Capacity of Banana Peel for different metals.

Heavy Metal	**Removal Capacity (%)/ Adsorption Capacity(mg/g)**	**Conditions**	**Reference**
Pb^{2+}	7.97 mg/g	Dose: 10 g/L Initial Metal Concentration: 15 mg/L pH:5.89 Contact time: 24 hr	(Annadurai, Juang, & Lee, 2003)
Ni^{2+}	6.88 mg/g	Dose: 10 g/L Initial Metal Concentration: 15 mg/L pH:6.89 Contact time: 24 hr	
Zn^{2+}	5.80 mg/g	Dose: 10 g/L Initial Metal Concentration: 15 mg/L pH:6.54 Contact time: 24 hr	
Cu^{2+}	4.75 mg/g	Dose: 10 g/L Initial Metal Concentration: 15 mg/L pH:5.92 Contact time: 24 hr	

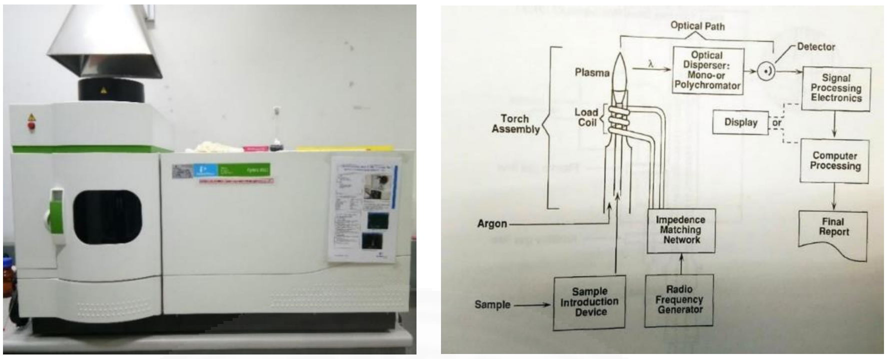
Co^{2+}	2.55 mg/g	Dose: 10 g/L Initial Metal Concentration: 15 mg/L pH:6.66 Contact time: 24 hr	
Cd^{2+}	89.2 %	Dose: 30 g/L Initial Metal Concentration: 50 mg/L pH:3 Contact time: 0.33 hr	(Anwar, Shafique, Salman, Dar, & Anwar, 2010)
Pb^{2+}	85.3 %	Dose: 40 g/L Initial Metal Concentration: 50 mg/L pH:5 Contact time: 0.33 hr	

2.13 Measurement and characterization instruments

2.13.1 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)

Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) is an analytical instrument used to measure chemical elements in liquid and gases. Dissolved metals present in the water sample are analysed using ICP-OES after the sample is properly filtered. Solid samples could also be measure but they need acid digestion or extraction in order to dissolve the analyte in the liquid (Hou & Jones, 2000). The lowest limit of detection of ICP-OES for arsenic without any error is 50 µg/L (Petrusevski, Sharma, Schippers, & Shordt, 2007).

Instrumentation and working principle: The general principal in which ICP-OES works is through the measurement of the photons emitted spontaneously when the atoms at excited state return to the ground state. At first argon gas is used to create the plasma. As shown in Figure 2.8, plasma is generated at the end of the torch with the help of the argon gas. The ICP-torch contains silica tubes coiled on the torch. The tubes generate alternate current of high frequency and hence alternate magnetic field is induced. When the liquid sample is injected, it is converted to an aerosol which is directed to the plasma. As they reach the plasma, they get vaporized because of the high temperature of about 10,000 K in plasma. Hence the analyte elements in the sample are released as free electrons. These electrons get additional energy due to the alternate magnetic field generated in plasma and go to the excited state. As they return back to the ground state, they emit energy as photons (light) at a particular wavelength. This light intensity is detected by the detector and the wavelength is displayed as result. The concentration of the element is hence calculated from the wavelength using the calibration curve.



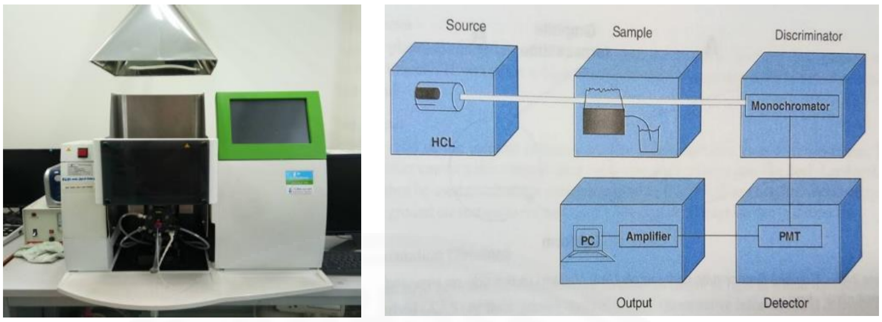
(a) (b)

Figure 2.8: (a) ICP-OES (b) Schematic diagram of an ICP-OES.

2.13.2 Atomic Absorption Spectrometer (AAS)

Atomic Absorption Spectrometer (AAS) is an instrument for quantitative measurement of elements in liquid samples. Hollow cathode lamps are used as a source in order to measure the element. So, for each element, specific cathode lamps should be used to emit atomic spectrum of that particular element. AAS is very and reliable technique to measure the concentration of element.

Instrumentation and working principle: The basic principal of AAS is that when a beam of light is passed through any sample, some of the beams are absorbed while some of the beams are emitted depending upon the wavelength of radiation. First the liquid sample is converted into aerosol which is mixed with combustible gases and then passed to the flame for ignition. Air-acetylene and nitrous-oxide acetylene mixture are the most commonly used flames. The radiation emitted from the hollow cathode lamp for a specific element is passed through the molecules in the flames. Due to the radiation, electrons get excited and jumps to the higher energy levels as they absorb some radiation while some spectra of radiation that are not absorbed are emitted. The spectra emitted from the molecules are detected by a monochromator and it selects particular wavelength of the emitted spectra. Then the spectra are converted as an electric signal by the detector and finally the value of absorbance is shown as a result. The concentration of the element in the sample is revealed based on the amount of radiation absorbed. Therefore, the elemental concentration can be found out based on the absorbance value from the calibration curve. Figure 2.9 shows the AAS used in this study with the schematic diagram of the working principle of AAS.



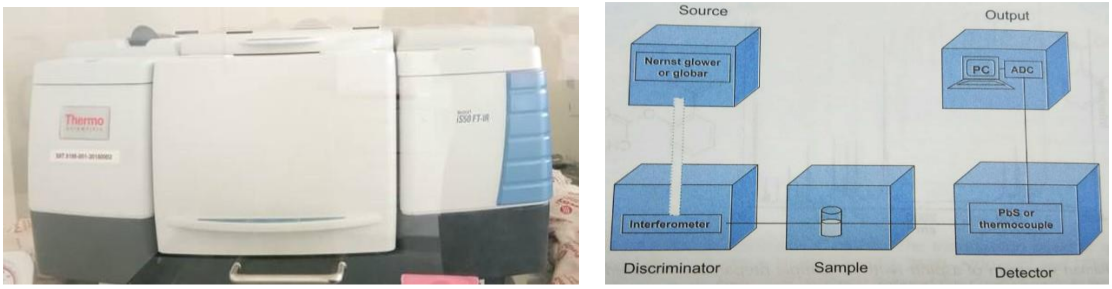
(a) (b)

Figure 2.9: (a) AAS (b) Schematic diagram of AAS.

2.13.3 Fourier Transform Infrared Spectrometer (FTIR)

Fourier Transform Infrared Spectrometer (FTIR) is an analytical instrument used for understanding the structure of chemical compound specially the molecular groups in terms of the functional group, orientation of the groups and information on isomers (McMahon, 2008).

Instrumentation and working principle: The actual mechanism that involves in this analysis is that infrared rays are passed through the sample among which some rays are absorbed by the sample while some of them are transmitted by the sample. The wavelength of transmitted light is measure with a detector and it displays result on the screen. The absorbed and transmitted spectrum helps us to quantify the components present in the sample. There are certain bonds between the different atoms. The bonds present in the chemical compound may have either single bond, double bond or triple bond. When the sample comes in contact with the IR light, the molecules get excited with different frequencies as per the type of bond. The wavelength of absorbed light depends on the type of chemical bond. Figure 2.10 shows the FTIR used in this study with the schematic diagram of the working principle of FTIR.



(a) (b)

Figure 2.10: (a) FTIR (b) Schematic diagram of an FTIR.

Chapter 3

Methodology

The methodological framework which was adopted in the study is illustrated in Figure 3.1. The experiments of adsorption were carried out in laboratory of Bio-Chemical Engineering and Technology department of Sirindhorn International Institute of Technology, Thammasat University, Thailand. The batch experiments mainly focused on the study of the factors influencing adsorption process. A detail description of each of the process is discussed further.

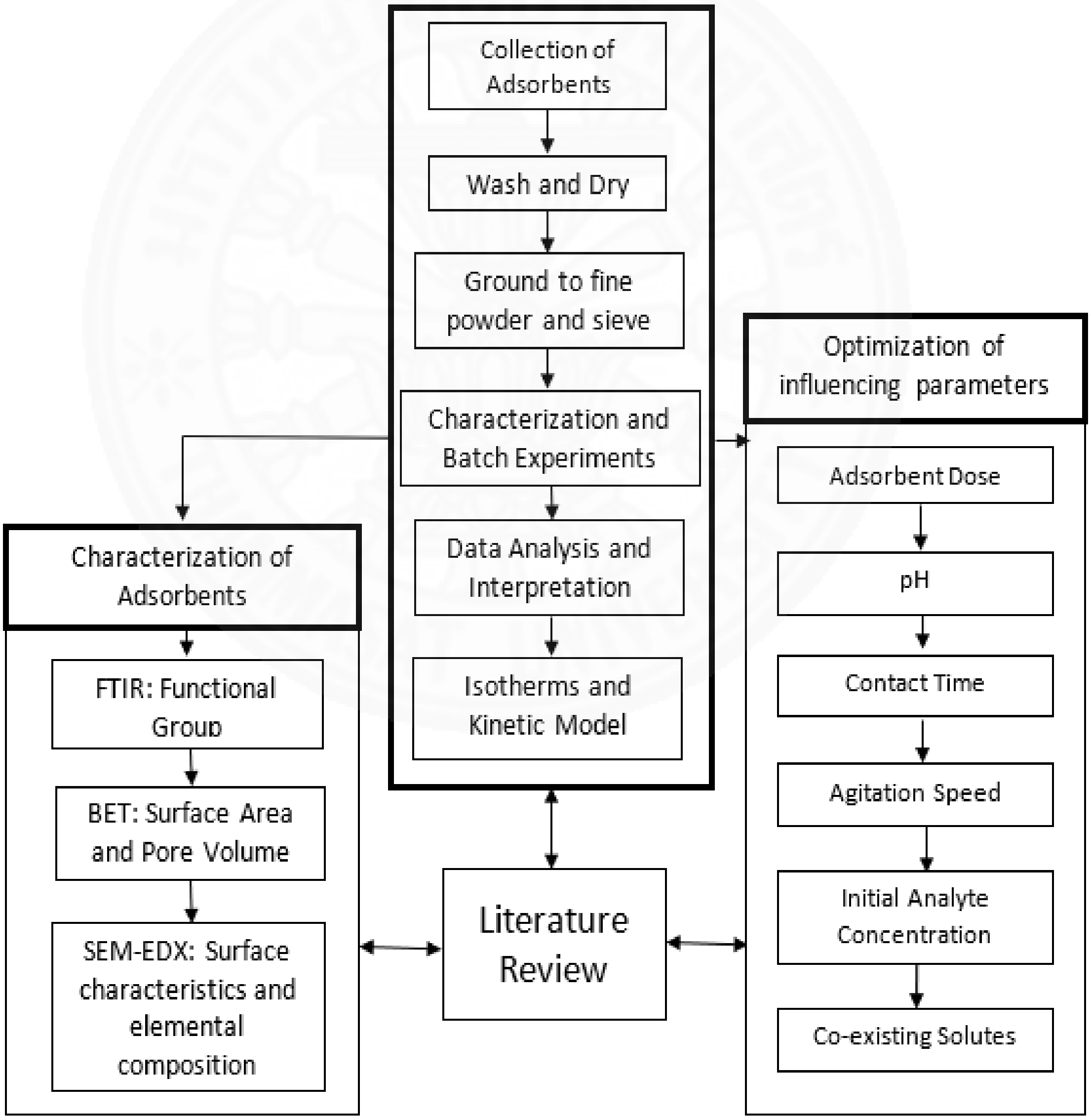


Figure 3.1: Methodological Framework of the Study.

3.1 Preparation of stock solution

3.1.1 Arsenite(III) Solution

Stock solution of arsenite, As(III) was prepared from arsenic trioxide (As_2O_3) (Thermo Fisher Scientific). 1.320 g of As_2O_3 was dissolved in 1000 ml distilled water containing 4 g of NaOH to prepare a stock solution of 1000mg/L (Ndrew, 2005). 10 ml of the resultant solution was diluted to 1000ml with DI water containing 5 ml of conc. HCl to get a standard solution of 10 mg/L. Specific volumes of this standard solution was taken to obtain the desired concentrations for the subsequent analysis. Stock solution was stored in dark and cool place to prevent oxidation and was serially diluted to prepare concentrations as required.

3.1.2 Arsenate(V) Solution

Stock solution of arsenate, As(V) was prepared from Sodium heptahydrate ($Na_2HAsO_4.7H_2O$) salt (≥98.0%, Sigma Aldrich). 4.164 g was dissolved in 1 L to make a stock solution of 1000 mg/L. Specific volumes of this solution will be taken to obtain the desired concentrations for the subsequent analysis. Low concentration solutions were made from serial dilution (Ndrew, 2005).

3.1.3 pH adjustment solution

For pH adjustment, 0.1 N HCl (Lobal Chemie) and 0.1 N NaOH (Merck) solutions were used. 0.1 N HCl solution was prepared by diluting 0.87 ml of 35.4% concentrated HCl solution to 100 ml. Similarly, 0.1 N NaOH solution was prepared by dissolving 0.4 g of NaOH in 100 ml of DI water. pH was measured using portable pH meter (ST300, Ohaus Corporation, USA).

3.2 Primary screening test of biomass for arsenic removal

A number of adsorbents were employed initially to identify the adsorbents which show the maximum arsenic removal efficiency. Each material chosen for study were firstly washed with distilled water, dried in hot air oven at 100°C for 24 hours, grinded to fine powder and finally sieved to particle size less than 250 mic. Initial experiments for arsenic removal were conducted using adsorbents prepared from peels of pineapple, pomelo and watermelon. For the experiment, a 5 mg/L arsenite solution was prepared from stock solution and was adjusted at neutral pH around 6-8. The adsorbents are aimed to be used to treat contaminated groundwater, therefore adsorption studies were carried out at neutral pH. 50 mL aliquots of these solutions were subjected to adsorbent doses ranging from 1 g/L to 20 g/L. The solutions were allowed to shake in rotary shaker for 2 hours at 170 rpm, filtered, and subsequent measurements were taken. Measurement of arsenic in the sample was done by using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Optima 8000, PerkinElmer, USA). After analysing the results, there was a need to select other adsorbents for the arsenic removal.

In the second set, the chosen adsorbents include sugarcane bagasse, rice husk, coconut, coconut husk and onion peels. A working solution of 5 mg/L of neutral pH was prepared and taken in different conical flask. 5 g/L of each adsorbent was added in the conical flask and were allowed to shake in rotary shaker for 3 hours. Some portion of the samples were filtered and used for arsenic measurement while the remaining samples were again kept for 24 hours to see the arsenic removal in longer contact time.

In the third set of experiment, the adsorbents were chosen very precisely. Some of the detoxifying materials (ginger, turmeric, onion, garlic and culantro), high iron content food (broccoli: iron is favourable for arsenic adsorption) and adsorbents used for removal of other metal (egg shell and banana peel) were chosen. During this experiment, the initial analyte concentration of the working solution was decreased to 2 mg/L. 5g/L of each adsorbent were added in the conical flask containing 2 mg/L arsenic solution. From the result of the preliminary test the adsorbents which showed the greater removal efficiency were selected for further experiments and characterization.

3.3 Preparation of selected adsorbents

From the primary test of adsorbents, egg shell and banana peel (latundan banana, *Musa acuminate×Musa balbisiana)* were chosen to do further experiments. Egg shell and banana peel were collected from the food shop in SIIT, Thailand. The peels were first thoroughly washed with water to remove the exerting dirt and any other foreign particles. Then, they were cut down into small pieces, washed with distilled water and subjected to hot air oven in 100±5℃ until the constant weight of the adsorbents was not achieved. The dried peels were then grounded and sieved to a particle size less than 250 µm. The powdered egg shell (ES) and banana peel (BP) were stored in an air tight container for further application. In this way ES and BP adsorbents were prepared without any modifications.

Then after, the powdered ES and BP adsorbents were subjected to physicochemical modification to see the effects in arsenic removal efficiency of adsorbents. A certain amount of the powdered sample was taken to activate thermally at high temperature while some amount of the powdered sample was taken to activate chemically by using certain acid. Thermal activation was done by heating the powdered sample in the muffle furnace at 700±5°C for 5 hours in contact with air. The resultant adsorbents were carbonized egg shell (CES) and carbonized banana peel (CBP). Chemical activation was done by acid modification to obtain acid modified egg shell and acid modified banana peel. In this process, the powdered ES and BP were mixed with 1 M HCl and 1 M H_3PO_4 in the ratio of 1:4 (mass: volume ratio) separately. The dried samples were allowed to soak in acid solution for 24 hours. After 24 hours, the samples were washed with DI water until the filtrate pH was neutral. Finally, they were dried in hot air oven at 100°C for 24 hours and stored in an air tight container for further use. Therefore, four acid modified adsorbents were obtained i.e. HCl modified banana peel (HCl-BP), H_3PO_4 modified banana peel (H_3PO_4-BP), HCl modified egg shell (HCl-ES) and H_3PO_4modified egg shell (H_3PO_4-ES).

3.4 Characterization of Adsorbents

The selected adsorbents were characterized using different techniques to find out their physical and chemical properties. There are various ways in which adsorbate and adsorbent interact with each other. The physical and chemical properties of adsorbent are required to know and interpret the adsorption mechanism of the metal ion on the adsorbent surface. The characteristics of adsorbents help us to understand the factors that have the contribution for adsorption. Basically, adsorption process occurs due to three main characteristics of adsorbent. They are the functional groups present in the adsorbent, surface area and pore volume. The technique which were used to characterize the adsorbents to find out their functional group, surface area and pore volume are as follows:

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a chemical characterization technique to know the functional group present in the adsorbents. The functional groups were determined by infrared spectroscopy before and after adsorption. FT-IR measurements were carried out using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, USA) by employing KBr pellet method. In this technique the sample was mixed with potassium bromide (KBr) (>99%, Thermo Fisher Scientific, USA) in the ratio of 1:50 and the mixture was grounded into fine powder. Consequently, the well mixed fine powder was transferred to pellet forming die and a force of approximately 1 ton was applied to the die with the aid of manual bench press. This resulted to the formation of pellets of each sample. The infrared radiation is passed through the sample inside the spectrophotometer. The FT-IR spectra were collected from 32 scans at a resolution of 4 cm-1 in the range of 4,000–400 cm-1. The evaluation was done automatically by OMNIC version 9 software attached to the system. The actual mechanism that involves in this analysis is that some of the infrared rays were absorbed by the sample while some of them were transmitted by the sample. Through the spectrum of the peaks of absorbed and transmitted rays, the functional group present in the adsorbent were identified. While taking the measurements of the sample, the background measurement was taken using the pellets of pure KBr that helped to correct the scattering of infrared light and also the moisture adsorbed while forming the pellets. Therefore, the background absorbance from the scan of pure KBr was automatically subtracted from the sample spectra.

3.4.2 Brunauer Emmett Teller (BET) Technique

Surface area of adsorbent is a major parameter that influences the efficiency of adsorption. The most widely used technique for determining the surface area, pore volume and pore diameter of the adsorbent is BET surface area analysis. The Brunauer-Emmett-Teller (BET) is a physical characterization method that is done using nitrogen gas at the boiling point of the gas at 77K. The basic principal behind the BET Surface area analysis is the adsorption of gas molecule on the solid surface at a temperature around the boiling point of gas. It follows the Langmuir model of adsorption process. In this context, the surface area, pore volume and pore diameter of prepared adsorbents were determined. Surface areas were obtained using a 3 Flex Version 3.02 (Micromeritic, USA) according to the Brunauer- Emmett-Teller (BET) protocol. Before allowing the gas to be adsorbed on the solid surface degassing of the sample should be done prior to removal of moisture content and purifying the sample. Hence degassing of each sample was done under vacuum at different temperature and degassing time as mentioned in Table 3.1.

Table 3.1: Degassing temperature and time for different adsorbents.

Adsorbent	Degas Temperature (℃)	Degas Time(hr)
Banana Peel	100	10
Carbonized Banana Peel	100	10
Acid Modified Banana Peel	100	10
Egg Shell	196	6
Carbonized Egg Shell	196	6
Acid Modified Egg Shell	196	6

3.4.3 Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-Ray Spectroscopy (EDX)

The surface feature, shape of particles and pore arrangement help to understand the characteristics of adsorbent and the mechanism of adsorption. Likewise, the elemental composition of the adsorbents before and after adsorption would give an idea about the elements being involved in adsorption. The surface morphology of the adsorbents before and after adsorption were studied using a Field Emission Scanning Electron Microscope (JEOL, JSM-7800F, Japan) equipped with an Energy Dispersive X-ray Fluorescence Spectrometer (Oxford Instruments, X-Max^{N}, USA) that measures the elemental composition. SEM produces image of a specimen by scanning beam of electrons of the specimen surface operating inside a vacuum chamber. EDX gives a spectrum of the elemental composition of a specimen i.e. the bulk concentration of the specimen. The basic principal behind SEM is the scanning of the electrons in surface of a specimen and EDX is the measurement of energy when atoms move from higher energy level to lower energy level. Few amounts of sample were kept on an aluminium stub containing carbon adhesive tape and then were coated with gold to make the sample conductive. Then the stub was kept in the SEM sample compartment and system was allowed to reach to the vacuum mode. Finally, SEM images were captured and elemental compositions were recorded. EDX analysis was done on three points and the average of them is reported.

3.5 Optimization of influencing parameter

Adsorption experiments were carried out based on different parameters: adsorbent dosage, pH, agitation speed, contact time and initial concentration for both the arsenite and arsenate forms of arsenic. Optimization of the experimental parameter was done by using BP and ES and later the adsorption efficiency of modified adsorbents was observed in the optimum conditions. According to Smedley and Kinniburgh (2002), the maximum concentration of arsenic in groundwater is 2.5 mg/L in Bangladesh, 3.2 mg/L in West Bengal, 1.8 mg/L in Taiwan, 5.3 mg/L in Vietnam, 5.3 mg/L in Argentina and 1.0 mg/L in Northern Chile. Based on the range of these concentrations and concentrations shown in Table 2.1, the initial concentration of arsenic was taken as 2 mg/l to carry out the experiments. All experiments were done in triplicates and samples were filtered using Nylon syringe filters of 0.22-micron pore size and 25 mm diameter. The filtrate concentration was measured using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Optima 8000, PerkinElmer, USA).

3.5.1 Adsorbent Dose

Optimum adsorbent dose is necessary in the process of adsorption as higher the adsorbent dose greater would be the surface area for adsorption resulting in the increased capacity and vice versa. For the experiment, a 2 mg/L arsenite solution was prepared from stock solution by serial dilution and was adjusted to neutral pH. These solutions were subjected to adsorbent doses ranging from2 to 10 g/L. The solutions were allowed to shake in rotary shaker at 100 rpm for 2 hours, and filtered, and subsequent measurements were taken. This enabled the determination of the optimum dose required for the removal of arsenic ions from solution. The minimum dose which has the maximum capacity to remove arsenic ions was considered as the optimum dose. The process was repeated taking different adsorbents. Similar procedure was carried out for arsenate solution.

3.5.2 pH

The arsenic uptake capacity of adsorbents depends upon a key parameter i.e., pH of the solution, as pH determines the adsorbent's surface charge and degree of ionization of adsorbate (Abdel Salam et al., 2011). Change in pH changes the functional group and surface charge of the adsorbent which will automatically change the process of adsorption and adsorption capacity. So, experiment should be done to find the optimum value of pH that is necessary for the process of adsorption. For the experiment, again 2 mg/L arsenite solution was prepared from stock solution by serial dilution. 50ml of the solution was taken in 8 conical flasks separately and optimum dose of adsorbent was added in the solution. The sample in each beaker was maintained at different pH levels starting from 4 to 11. For each solution, pH was adjusted using the solution of 0.1 N HCl and 0.1 N NaOH. Next the samples were subjected to rotary shaker at 100 rpm for 2 hours, filtered and then measurement was taken. Finally, one optimum pH value was chosen for the adsorbent at which the maximum removal occurs. Similar process was repeated for each adsorbent and for arsenate solution. The pH was measured using a portable pH meter (ST300, Ohaus Corporation, USA).

To study the surface charge of the adsorbents in different value of pH, point of zero charge (pHpzc) analysis of adsorbents was determined. To determine pHpzc, 0.01 M NaCl (Thermo Fisher Scientific, USA) solution was prepared and 50 mL of that solution were taken in different conical flask of 125 mL. The solution in different conical flasks were then maintained at pH values ranging from 2-11 (pH_i) with addition of 0.01M of HCL or NaOH. 500 mg of the adsorbents were added to the conical flask. The conical flasks were allowed to shake at 120 rpm for 24 hr to reach equilibrium. The final pH (pH_f) of the supernatant was measured and pHpzc was determined. pHpzc is the point of pH where the difference of the initial and final pH is zero ($\Delta pH = pH_i - pH_f = 0$).

3.5.3 Contact Time

To find the optimum contact time, the optimum values of adsorbent dose and pH were used. For this, 2 mg/L arsenite solution was prepared from stock solution by serial dilution and 50 mL aliquots was withdrawn and placed in 6 different 250-mL conical flasks. An optimum adsorbent dose of each adsorbent was taken for each adsorbent and added to the solutions. The solutions were maintained at optimum pH and were placed in rotary shaker at 100 rpm. Then the arsenic concentration at different time intervals of 40 min, 80 min, 120 min, 160 min, 200 min and 240 min were measured. A removal profile at different retention time was developed and maximum retention time for adsorption was known. The processes were repeated for each adsorbent and for arsenate solution as well.

3.5.4 Agitation Speed

The effect of agitation speed was investigated at different agitation speeds specifically at 50 rpm, 100 rpm, 150 rpm, 200 rpm and 250 rpm. For the process, 2 mg/L arsenite solution was prepared from stock solution by serial dilution and 50ml was taken in 5 different conical flasks. The optimum dose of each adsorbent was added in the solution and optimum pH was maintained in the solution. Next, the conical flasks were agitated at 50-250 rpm for optimum contact time and finally optimum speed was selected after the measurement of arsenic concentration.

3.5.5 Initial Analyte Concentration

The solutions of concentrations 0.1-10 mg/L were prepared and the optimum dose of adsorbents was added based on the previous analysis. The concentration was taken in this range due to the fact that the maximum arsenic concentration in different countries lies in this range as mentioned earlier. The prepared solutions were maintained at optimum pH and was allowed to stand for the optimum equilibration time at optimum speed. After that it was filtered and the corresponding concentration values was noted. Finally, the optimum analyte concentration was also known. This entire process was carried out two times for arsenite and arsenate, respectively.

The amount of adsorption at the equilibrium phase is determined using the given formula:

$$q_e = \frac{V * (C_i - C_f)}{M}$$

where,

q_e: Adsorption amount (mg/g)

V: Volume of solution (L)

M: Mass of adsorbent (g)

C_i: Initial adsorbate concentration

C_f: Equilibrium adsorbate concentration

The percent adsorption (%) is calculated using the given equation (Erdem et al., 2004):

$$Percent\ Adsorption = \frac{C_i - C_f}{C_i} * 100$$

where,

C_i: Initial adsorbate concentrations

C_f: Equilibrium adsorbate concentrations.

3.5.6 Co-existing Ions

Groundwater contains many anions like silicate, sulfate, carbonate, chloride, phosphate, nitrate, etc. Presence of these anions may have adverse effect on efficiency of As(III) and As(V) removal. In this study, the effect of presence of phosphate (PO_4^{3-}) and nitrate (NO_3^-) on arsenic removal efficiency were investigated. Standard solution of phosphate and nitrate were prepared from potassium dihydrogen orthophosphate (Thermo Fisher Scientific, USA), and potassium nitrate (Thermo Fisher Scientific, USA) respectively. At first, solutions containing arsenic ion (concentration of 2 mg/L) and co-existing ion (varying concentration from 0 to 200 mg/L) was prepared and maintained at neutral pH. Solutions were prepared such that the ratio of concentration of arsenic to concentration of co-existing ion is 1:0, 1:0.1, 1:1, 1:10 and 1:100 taking a constant concentration of 2 mg/L for arsenic. Then the resultant solutions were subjected to adsorbents and arsenic removal efficiency was evaluated under optimum conditions.

3.6 Adsorption Isotherm

The adsorption isotherm study was done to understand the distribution of adsorbed molecules of the liquid phase to the surface of the solid phase at equilibrium state. The adsorption capacity resulted from the batch experiments of various initial analyte concentration with other optimized parameters and neutral pH, were used to check the suitable model of adsorption. The adsorbents are aimed to be used to treat contaminated groundwater, therefore adsorption studies were carries out at neutral pH. The analysis of adsorption model is important as it develops an equation that accurately describes the result and hence can be used for design purposes. Adsorption model is different for different adsorbents. Three isotherm models, namely Langmuir, Freundlich and Elovich models that are based on the assumption of either formation of homogenous layer or heterogenous layer, were studied.

3.6.1 Langmuir Adsorption Isotherm

For the study of Langmuir model, the methodology which was followed is mentioned below.

1. A linear form of equation, $\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$, was used. The graph was plotted between $\frac{C_e}{q_e}$ and C_e
2. The value of correlation coefficient (R^2) represents the suitability of the equations to describe experimental data. The higher the value of R^2 the greater would be the suitability of the model.
3. From the graph the value of Q_o and b were calculated.
4. Higher value of b signifies the existence of stronger bonds between adsorbate and adsorbent.
5. The nature of adsorption process was determined using the equation:

   $$R_L = \frac{1}{1 + \mathrm{b}C_i}$$

   where:

   C_i = Initial concentration of metal ions (mg/L);

   b = Langmuir constant indicating adsorption rate (L/mg)
6. Adsorption nature was studied with the help of value of $R_{L.}$ The lower value of R_L reflects that adsorption is more favourable. Actually, value of R_L indicates the adsorption nature.

   $R_L > 1$ means unfavourable,

   $R_L = 1$ means linear,

   $0 < R_L < 1$ means favourable

   $R_L = 0$ means irreversible

3.6.2 Freundlich Adsorption Isotherm

For the study of Freundlich model, the methodology which was followed is mentioned below.

1. Logarithmic equation $log\, q_e = log\, k_f + \frac{1}{n} logC_e,$ was used. The graph was plotted between log q_e and log C_e.
2. The value of correlation coefficient (R^2) represents the suitability of the equations to describe experimental data. The higher the value of R^2 the greater would be the suitability of the model.
3. From the graph the value of k_f and 1/n were calculated.
4. The value of n describes the adsorption process. The higher value of n (smaller value of 1/n) signifies strong interaction between adsorbents and metal ion. Values of n between 2 and 10 represent good adsorption.

3.6.3 Elovich Adsorption Model

To study whether the adsorption process followed the Elovich adsorption model, the procedure listed below was carried out.

1. The equation used was $ln\frac{q_e}{q_m} = lnK_e q_m - \frac{q_e}{q_m}$. The graph of ln ($q_e$/$C_e$) versus q_e was plotted. These values were obtained from the experimental data at various initial concentration at pH 7.
2. Form the graph the value of correlation coefficient (R^2) and an equation was obtained.
3. The value of q_m and K_e was obtained from the slope and the intercept of the graph.
4. The value of q_m and K_e were substituted to the original equation and then the value of adsorption capacity at different equilibrium concentration was calculated.

3.7 Adsorption Kinetics

Kinetic parameter that helps us to understand the performance of the adsorption process were studied. The methodology to evaluate the kinetic parameters was similar to that of batch equilibrium experiments. The adsorption capacity resulted from the batch experiments, mainly while carrying out the investigations varying the contact time was used. The equilibrium time and concentration in that time was noted and verified using models used for describing adsorption kinetics. Three kinetic models, namely pseudo first order, pseudo second order and Elovich equation were used in this study.

3.7.1 Pseudo first order kinetic model

For the study of pseudo first order kinetic model, the methodology which was followed is mentioned below.

1. The equation, $log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303}$, was used to analyse the pseudo first order model. Here k_1 is the pseudo-first-order rate constant.
2. Graph was plotted between log (q_e-q_t) and t.
3. Value of k_1 and q_e were obtained.

3.7.2 Pseudo second order kinetic model

For the study of pseudo second order kinetic model, the methodology which was followed is mentioned below.

1. The equation, $\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} * t$, was used to analyse the pseudo second order model. Here k_2 is the pseudo-second-order rate constant.
2. Graph was plotted between t/q_t and t.
3. Value of k_2, h and q_e were obtained

3.7.3 Elovich Equation

To analyse the suitability of Elovich equation for adsorption kinetics following procedure were applied.

1. The equation $q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t)$ was used to analyse the suitability of elovich equation. Here α is the initial sorption rate (mg/g.min) and β is the desorption constant (g/mg)
2. Graph was plotted between ln(t) and q_t.
3. Value of α and β were obtained.

3.8 Analysis of best-fitting Isotherm Model and Kinetics

One of the common procedures to select and compare between the models is done through the comparison of the R^2 values. However, it is not always appropriate to evaluate the goodness of fit of a model based on the R^2 value, especially when the data points undergo linear transformations (El-Khaiary & Malash, 2011). A study done by Subramanyam and Das (2014) revealed that the value of isotherm constant changes as a non-linear equation is linearized to different form of linear equation. The adsorption capacity from Langmuir isotherm model was in a range of 41.67 mg/g to 52.65 mg/g using different linearized equation for same original equation. So, it is not reliable to consider only the R^2 value to choose a model. In order to investigate the suitable model that represents arsenic adsorption on the adsorbents, some error analysis tools were applied. These tools help to find the deviation of the theoretical data obtained from the model compared with the experimental data. Actually, R^2 value represents how close the data are fitted to regression line but error analysis tools give the difference between the exact value and the model value. So, it would be more reliable to evaluate the goodness of fit of a model using some statistical tools. Once we get the isotherm constant values from the model, the values were substituted in the original non-linearized equation for isotherm model and in the linearized equation for kinetic model. Finally, adsorption capacity values were calculated from the equation. The error between the calculated and the experimental values were obtained using three error analysis tools that are given below.

3.8.1 Chi-Square Test (χ^2)

The chi-square test is basically the summation of square of the difference between the experimental value and the theoretical value obtained from the model with each squared difference divided by the corresponding value obtained from the model. The lower the value of chi-square test, the better is the model. The equation used for the chi-square test is as follows (Ahamad et al., 2018):

$$\chi 2 = \sum_{i=1}^{N} \frac{\left(q_{e,exp,i} - q_{e,cal,i}\right)^2}{q_{e,exp,i}}$$

where,

$q_{e,exp}$: adsorption capacity obtained from the experiment (mg/g)
$q_{e,cal}$: adsorption capacity obtained from theoretical calculation from the model (mg/g)
N: Number of observations

3.8.2 Root Mean Square Error (RMSE)

Root mean square error is the square root of the summation of square of the difference between the experimental value and the theoretical value obtained from the model divided by the number of experimental observations. The equation used for the RMSE is as follows (Ahamad et al., 2018):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(q_{e,cal,i} - q_{e,exp,i}\right)^2}{N}}$$

where,
$q_{e,exp}$: adsorption capacity obtained from the experiment (mg/g)
$q_{e,cal}$: adsorption capacity obtained from theoretical calculation from the model (mg/g)
N: Number of observations

3.8.3 Average Percentage Error (APE)

Average Percentage Error is the summation of the absolute value of the difference between the experimental value and the theoretical value obtained from the model with each difference divided by the corresponding experimental data and finally the summation is divided by the number of experimental observations. Average Percentage error is expressed in terms of percentage and the equation is given as (Ahamad et al., 2018):

$$APE(\%) = \frac{\sum_{i=1}^{N}\left|\frac{q_{e,exp,i} - q_{e,cal,i}}{q_{e,exp,i}}\right|}{N} * 100$$

where,
$q_{e,exp}$: adsorption capacity obtained from the experiment (mg/g)
$q_{e,cal}$: adsorption capacity obtained from theoretical calculation from the model (mg/g)
N: Number of observations

3.9 Comparison of adsorption capacity with Lead and baseline adsorbent

Finally, arsenic adsorption by egg shell and banana peel were compared with adsorption of another heavy metal and arsenic adsorption by activated carbon, a baseline adsorbent. First set of experiments were done using same adsorbent i.e. ES and BP for the removal of lead, a different heavy metal than arsenic. Then the second set of experiments were done using a baseline adsorbent i.e. commercial activated carbon for arsenic removal. Initial Analyte concentration for these experiments were taken as 2 mg/L, as arsenic removal study was also done taking 2 mg/L as initial concentration. After that, the initial concentration of the solution was increased to see the removal efficiency at higher concentration. This time the adsorbent dose was chosen based upon the optimum dose of ES and BP for arsenic removal. Basically, the optimum dose to treat 2 mg/L solution and initial concentration which could be removed by 6 g/L of adsorbent dose were studied. The results were then compared with arsenic removal capacity of BP and ES. Concentration of lead in solution was measured using Atomic Absorption Spectrometer (AAnalyst 200, PerkinElmer, USA).

Chapter 4

Results and Discussion

This chapter discusses the result obtained from the adsorption of arsenic using different adsorbents. The physical and chemical properties of the adsorbents are briefly described. The influencing parameters for the removal of arsenic are optimized. The distribution of arsenic ions in the surface of the adsorbent are studied using three isotherms and adsorption mechanism are studied using three kinetic model. The best isotherm and kinetic model are selected and the ways to select is described in detail in this chapter. Arsenic adsorption capacity of the adsorbents is also compared with lead adsorption capacity.

4.1 Primary screening test of biomass for arsenic removal

In order to select suitable adsorbents for the removal of arsenic, various locally available materials were chosen and investigated for the removal efficiency. Arsenic removal efficiencies of the selected materials in the first set of experiments are shown in Figure 4.1. As observed in Figure 4.1, none of the adsorbent show significant arsenic removal efficiency and watermelon peel even has negative removal efficiency. The negative removal efficiency is because of the adsorbents absorbing water instead of the metal ions. Watermelon peels were in dried and powdered state which absorbed water leading to less amount of water in bulk phase. This increased the analyte concentration that consequently showed negative removal efficiency. While comparing the removal efficiency of these three materials, pomelo peel removed 29.63 % of arsenic from 5 mg/L arsenic contaminated water at an adsorbent dose of 10 g/L. But 29.63 % arsenic removal is very low using such a high amount of adsorbent dose even if it is a waste material. Therefore, there was a need to test for other adsorbents.

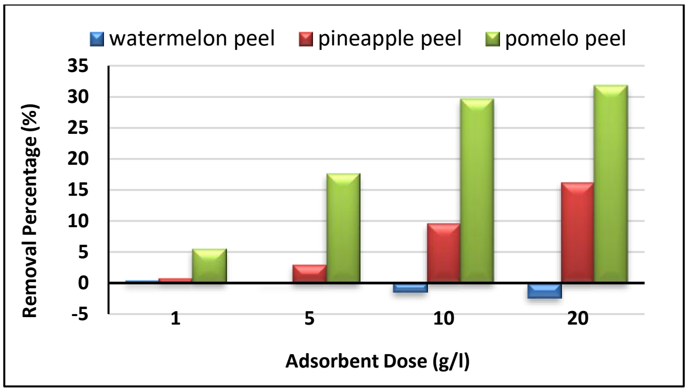


Figure 4.1: As(III) removal efficiency of adsorbents at different adsorbent dose.

(Initial arsenic concentration: 5 mg/L; pH~7; time:2 hrs; Speed: 170 rpm)

In the second set of experiment, the chosen adsorbents include sugarcane bagasse, rice husk, coconut, coconut husk and onion peels. As no significant adsorption was observed in the first set of experiment, the contact time in the second set was increased to 3 hours and 24 hours to see the removal efficiency for longer period of contact time. Arsenic removal efficiencies of these adsorbents are plotted and are shown in Figure 4.2. The second set of adsorbents also did not depict high adsorption for arsenic. The removal efficiencies of these adsorbents were even poor than the first set of adsorbents. Among the adsorbents, coconut husk shows maximum efficiency of 7.93 % at contact time of 3 hour and onion peel shows 10.99 % at 24 hours. As shown in Figure 4.2, increasing the contact time also did not support for the greater adsorption of arsenic. Preliminary results indicated that all these adsorbents are not suitable for the adsorption of arsenic.

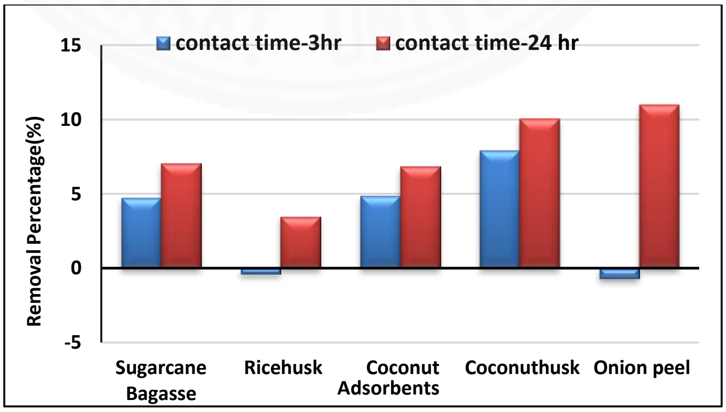


Figure 4.2: As(III) removal efficiency of different adsorbents.

(Initial arsenic concentration: 2 mg/L; dose: 5 g/L pH~7; Speed: 170 rpm)

Finally, third set of adsorbents were used to investigate the arsenic removal capacity. Figure 4.3 shows the arsenic removal efficiencies of various adsorbents which were selected for the third set. The removal efficiency of these adsorbents was better compared with the adsorbents chosen before. As shown in Figure 4.3, egg shell had the maximum removal efficiency of 50.16% among the selected adsorbents. Following the egg shell, banana peel, broccoli and culantro has the removal efficiencies of 45.91%, 29.78% and 22.2%, respectively. Other adsorbents did not show significant removal efficiency. As studied in many literatures, removal efficiency increases with different optimum experimental conditions and through some modification of the adsorbents. Hence egg shell and banana peel were selected for further investigation for arsenic removal in this study. From 100 g of raw banana peel we get 15.78 g of BP and 1.62 g of CBP. Likewise, from 100 g of raw egg shell we get 84.27 g of ES and 69.03 g of CES.

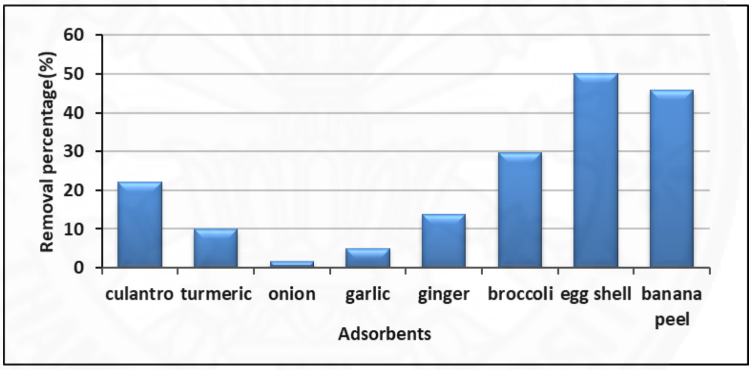


Figure 4.3: As(III) removal efficiency of different adsorbents.

(Initial arsenic concentration: 2 mg/L; dose: 5 g/L; pH~7; time: 2hr; Speed: 170 rpm)

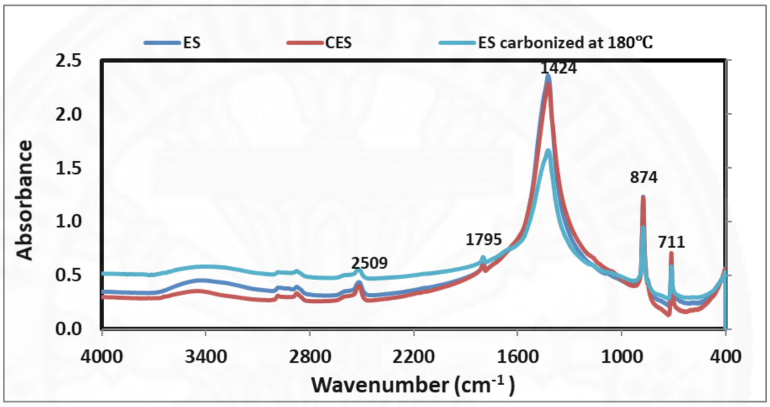
4.2 Characterization of selected adsorbents

4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

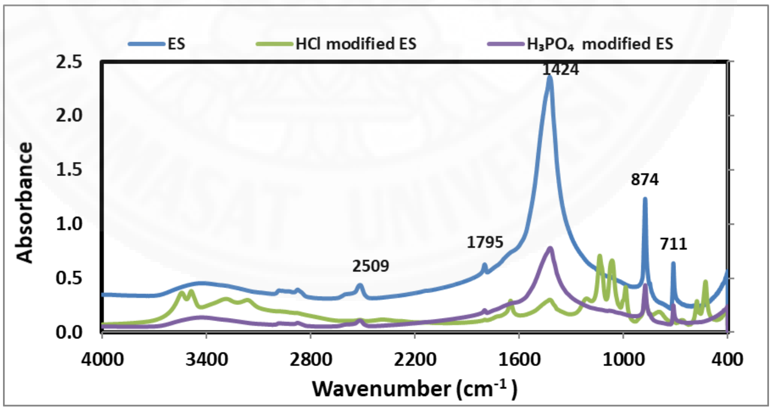
Functional groups of adsorbents are one of the major factors that affect the process of adsorption. Functional groups of the adsorbents were determined and the results are discussed in the section below.

4.2.1.1 FTIR spectra of egg shell

FTIR spectra of ES is shown in Figure 4.4. It can be seen that the most significant peak occurs at the wavenumber of about 1424 cm^{-1} which is the characteristic peak of the carbonate (CO_3^-) group. This indicates that egg shell has the carbonate (CO_3^-) group. Peaks at a wavenumber of about 875 cm^{-1} and 712 cm^{-1} could be seen in the spectra. Those peaks are related with the out-plane deformation mode and in-plane deformation mode respectively, indicating the presence of calcium carbonate. Similar analysis of functional group of egg shell was done previously by Tsai et al. (2006). ES carbonized at different temperature has the peak in the same wavenumber as unmodified ES. But ES modified with acid showed a vast change in the functional group. The peak of calcium carbonate group completely disappears in ES modified with HCl and it decreased drastically in ES modified with H_3PO_4.



(a)

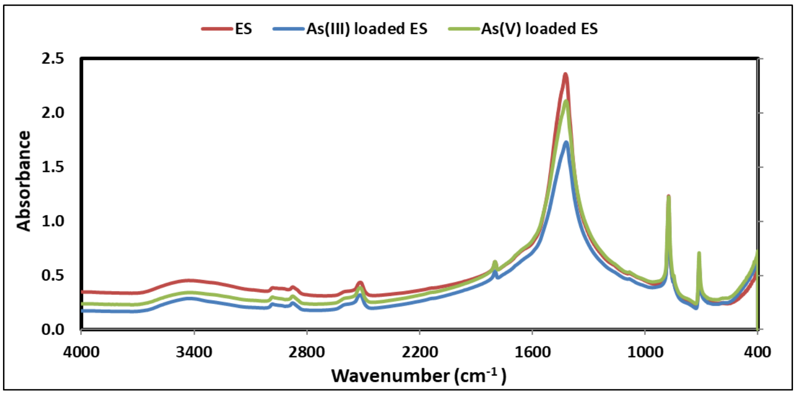


(b)

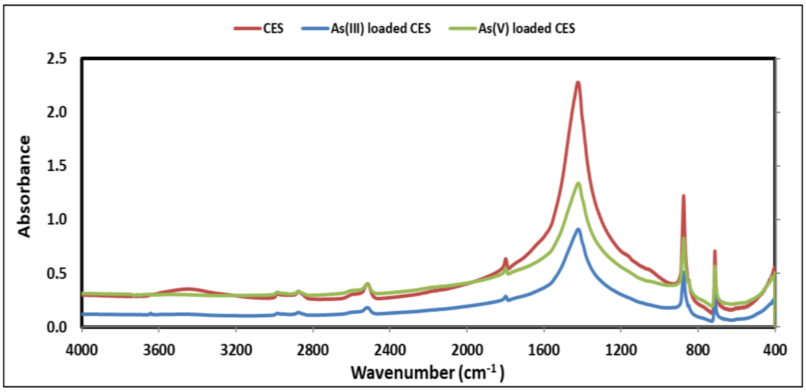
Figure 4.4: FTIR spectra of (a) ES, ES carbonized at 700°C and ES carbonized at 180°C (b) ES, HCl modified ES, H_3PO_4 modified ES.

4.2.1.2 Comparison of FTIR spectra of egg shell before and after adsorption

The batch experiments were done by using the unmodified and the carbonized egg shell while the acid modified egg shell was discarded because no improvement was observed in removal efficiency. While carrying out batch experiment in optimum conditions, the sample were filtered and the residue were dried in oven at 100°C. FTIR spectra of those arsenic ion loaded adsorbents were obtained to see the changes in the original sample. Figure 4.5 shows the FTIR spectra of the adsorbents before and after adsorption. We can observe from the spectra that the peak at wavenumber 1424 cm^{-1} is gradually decreased on the spectra of arsenic loaded adsorbents. The decrement in the absorbance value in different samples is illustrated clearly in Table 4.1. There is a decrement in the absorbance value in the three peaks at wavenumber 1424, 874, 711 cm^{-1}. All these peaks are associated with the presence of calcium carbonate. This decrement in the band intensity suggested that the calcium carbonate group was either destructed or used significantly by arsenic ion. Zhang, Yang, Dou, He, and Wang (2005) showed the involvement of hydroxyl group for As(V) adsorption and the peak of the hydroxyl group of metal oxides decreased and gradually disappeared with As(V) adsorption. In this study, it is concluded that the calcium carbonate group is responsible for arsenic adsorption. In addition to that, the absorbance value for As(III) loaded CES is lower than As(III) loaded ES but the adsorption capacity of CES is greater than ES for As(III) adsorption. This proves that the decrement in the absorbance or band intensity is due to the increment in adsorption capacity (Zhang et al., 2005). Similar case is observed for the As(V) loaded adsorbents. The absorbance value for As(V) loaded CES is lower than As(V) loaded ES and the adsorption capacity of CES is greater than ES for As(V) adsorption. The absorbance value of the peak at 1424 cm^{-1} of carbonate group for ES, CES > As(V) loaded ES > As(III) loaded ES > As(V) loaded CES > As(III) loaded CES.



(a)



(b)

Figure 4.5: FTIR spectra of (a) ES, As(III) loaded ES and As(V) loaded ES (b) CES, As(III) loaded CES and As(V) loaded CES.

Table 4.1: Comparison of FTIR peaks before and after adsorption.

Wavenumber (cm^{-1})	Sample	Absorbance	
		ES	CES
1424	Original sample	2.36	2.28
	As(V) loaded sample	2.11	1.34
	As(III) loaded sample	1.73	0.91
874	Original sample	1.23	1.22
	As(V) loaded sample	1.22	0.83
	As(III) loaded sample	1.04	0.51
711	Original sample	0.64	0.71
	As(V) loaded sample	0.63	0.57
	As(III) loaded sample	0.62	0.32

In order to verify that the decrease in the carbonate group is due arsenic adsorption, FTIR spectra of ES subjected to pure DI water was compared with the FTIR spectra of ES subjected to As(III) solution. Figure 4.6 shows the graph of the spectra obtained. The peak at 1424 cm^{-1} decreased in the spectra of ES subjected to pure water but the decrement is not as much as in the case of As(III) loaded ES. This means that the carbonate group in eggshell is destructed even by DI water. However, more decrement in carbonate group in arsenic loaded sample reveals that calcium carbonate group is used by arsenic ions for adsorption.

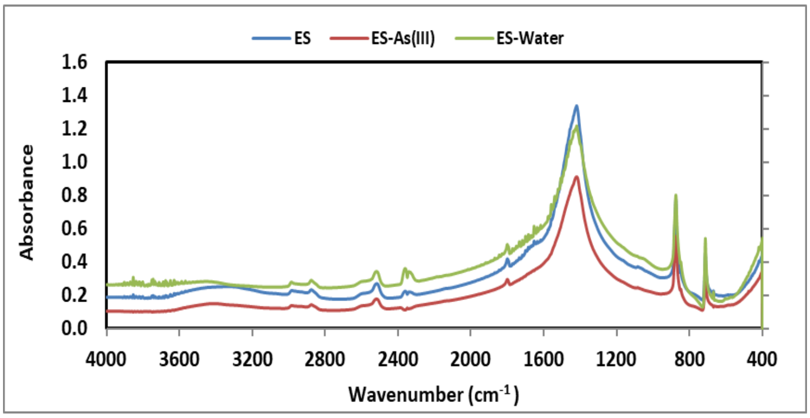
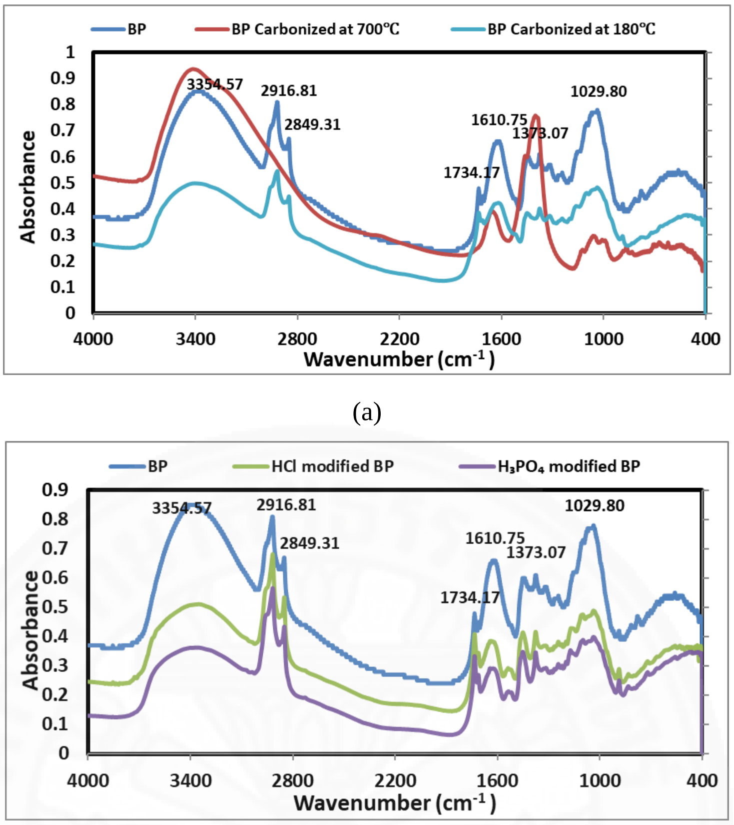


Figure 4.6: FTIR spectra of ES, As(III) loaded ES and ES subjected to DI water.

4.2.1.3 FTIR spectra of banana peel

Figure 4.7 shows the FTIR spectra of BP and modified BP. In the spectra of unmodified BP, the dominant peak at 3354.57 cm^{-1} is associated with the O-H stretching of the hydroxyl group. The C-H stretching of alkane and alkene is identified by a peak at 2916.81 cm^{-1} and it represents the aliphatic nature of adsorbent. The small absorption peak at 1734.17 cm^{1} represents the C-H and C=O bond of carboxylic acids and ester (Memon et al., 2008). Furthermore, the peak at 1610.75 cm^{-1} represents the COO− anion stretching, 1373.07 cm^{-1} represents the C-O carboxyl band resulting from complexation of the carboxyl oxygen and 1029.80 cm^{-1} is due to Si-O stretching and Si-O bending indicating the presence of silica. The absorption bands at from 1734.17 to 1373.07 cm^{-1} are characteristics of C=C in aromatics rings. Presence of the hydroxyl group in the spectra suggests that banana peel could be a suitable adsorbent for the removal of arsenic. Previously, many studies showed that adsorbents containing the hydroxyl group show significant removal efficiency of arsenic and hydroxyl group is the major functional group attributed for arsenic adsorption (Akhtar & Shoaib, 2012; Goldberg & Johnston, 2001; Jia, Xu, Wang, & Demopoulos, 2007; Pehlivan et al., 2013). In the FTIR spectra of BP carbonized at 700°C, the peak at 2916.81 cm^{-1} representing the C-H stretching disappears and also some changes in the functional group occurs at the region of 1700 cm^{-1} to 1000 cm^{-1}. Carbonization at low temperature i.e. at 180°C did not show any changes in the functional group. When we observe the spectra of BP sample modified with HCl and H_3PO_4, no changes appear in the peaks but there was a decrease in the value of absorbance.



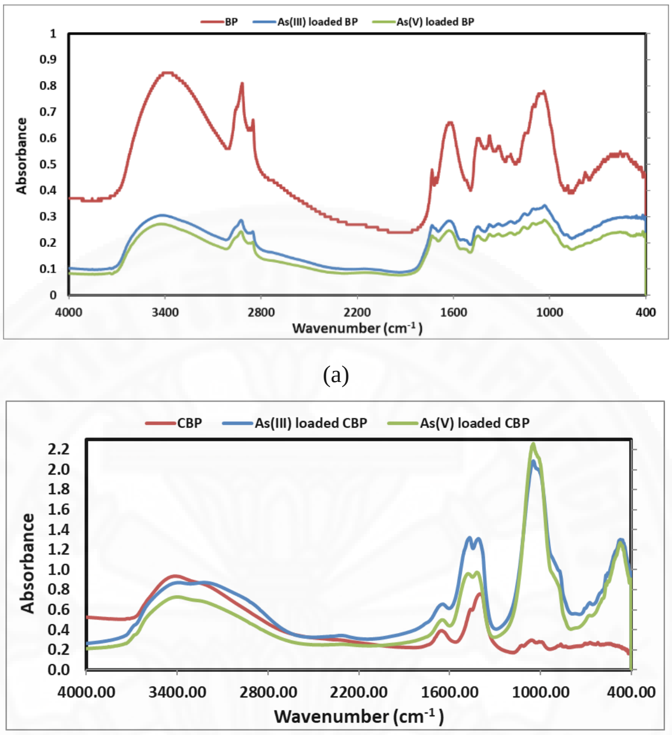
(a)

(b)

Figure 4.7: FTIR spectra of (a) BP, BP carbonized at 700°C and BP carbonized at 180°C (b)BP, HCl modified BP, H_3PO_4 modified BP.

4.2.1.4 Comparison of FTIR spectra of banana peel before and after adsorption

Unmodified banana peel and carbonized banana peel were selected to do the batch experiments. So, the FTIR spectra of only two of the modified samples after adsorption was carried out. The solution containing the adsorbents after the batch experiment was filtered and the residue was dried in oven at 100°C. FTIR spectra of those dried adsorbents were taken and the spectra is represented in Figure 4.8. It is seen that the broad spectra of the hydroxyl group in the region 3354 cm^{-1} has decreased drastically in As(III) loaded BP and As(V) loaded BP. This suggests the involvement of hydroxyl group in adsorption process. The characteristics changes in the position of the peak and the absorbance value is due to the adsorption of arsenic ion in the adsorbents. New peaks were observed in the case of arsenic loaded CBP spectra. The characteristic peak formed at a region of 1020 cm^{-1} in As loaded CBP corresponds to the C-O stretching of epoxide ring. The peak at 1460 cm^{-1} represent the occurrence of $-CH_2-NHR_2$ type nitrogen and stretching vibration of aliphatic C-N (Anirudhan, Divya, & Parvathy, 2013). The peak at 1620 cm^{-1} is due to the stretching vibration of -C-CH$_2$ (Jin, Liu, Tong, & Hou, 2012). These changes in the peak values and occurrence of new peak reveals that some modification took place on the adsorbent due to arsenic adsorption.



(a)

(b)

Figure 4.8: FTIR spectra of (a) BP, As(III) loaded BP and As(V) loaded BP (b) CBP, As(III) loaded CBP and As(V) loaded CBP.

4.2.2 BET Surface area analysis

One of the main physical parameters that is related with the efficiency of the adsorbent to adsorb the metal ion is its surface area. Greater the surface area, higher would be the efficiency of adsorption. Surface area helps us to understand about the binding sites of the metal ion and adsorbent. The basic principal behind the BET Surface Area analysis is the adsorption of gas molecules on the pores present in the solid surface. The pores present in the sample are classified by International Union of Pure and Applied Chemistry (IUPAC) according to their size (Thommes et al., 2015):

i. Pores of size not greater than 2 nm are known as micro pores.
ii. Pores of size from 2 nm to 50 nm are called mesopores.
iii. Pores of size greater than 50 nm are called macropores.

The adsorbed molecule first gets settled in the macropores followed by mesopores and micropores. Generally, micropores are present in huge numbers and it covers the largest portion of the adsorbent and of total pore volume. As seen in FTIR results that BP and ES carbonized at 180°C doesn't have any effect on functional group so they were discarded and BET surface area analysis was done for the remaining 8 samples. The surface area of the 8 samples along with their pore size and pore volume is given in Table 4.2.

Table 4.2: Different adsorbents with their surface area and pore volume.

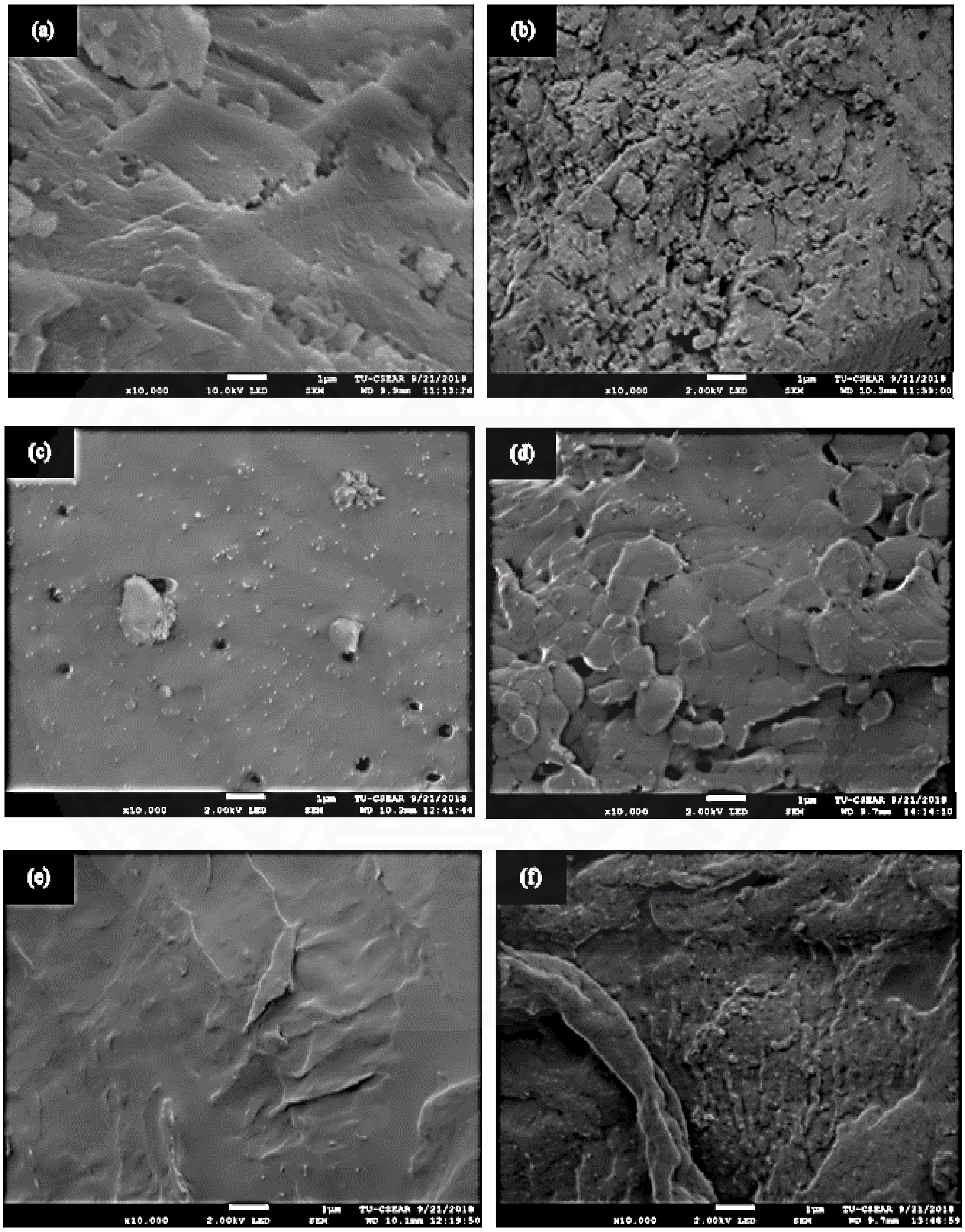
Adsorbents	Sample Weight (g)	BET Surface Area (m^2/g)	R^2 value of BET surface area plot	BJH total pore volume (cm^3/g)	BET Pore Diameter (nm)
ES	0.6764	0.7757±0.0041	0.999	0.00263	7.763
Carbonized ES	0.6194	0.4386±0.0114	0.995	0.0013	6.319
HCl Modified ES	0.5527	8.8772 ± 0.0187	0.999	0.03863	10.659
H_3PO_4 Modified ES	0.633	0.8368 ± 0.0045	0.999	0.00304	8.786
BP	0.3998	0.4031 ± 0.0664	0.958	0.00132	8.718
Carbonized BP	0.3402	1.4590 ± 0.0161	0.999	0.00633	6.545
HCl Modified BP	0.3958	0.6009 ± 0.0849	0.964	0.00153	6.766
H_3PO_4 Modified BP	0.3743	0.4404 ± 0.0869	0.939	0.00147	8.698

From Table 4.2, it is seen that the BET surface area of BP is 0.40 m^2/g and that of egg shell almost two times greater than BP which is 0.77 m^2/g. The pore diameter of all the adsorbents lies between 2-50 nm, hence the pores are classified as mesopores. When we compare the BET surface area of BP with modified BP, it can be observed that carbonization of BP at temperature 700°C helped to increase the surface area by almost three times compared with the non-carbonized BP. In case of acid modification, some enhancement on surface area took place but not as strongly as in the case of carbonization. In contrast, carbonization of ES lowered the surface area and modification of ES with HCl increased the surface area by ten times than the original sample. Therefore, the increase in surface area of adsorbents after modification depends upon the original sample.

When we compare the surface area of these adsorbents with other adsorbents used for arsenic removal, it is very low. Some minerals used for arsenic removal such as zeolite and hematite had the surface area of 450 m^2/g and 50 m^2/g, respectively (Chutia et al., 2009; Dickson et al., 2017). But some of the biomass like tea waste and pomegranate peel having lower surface area of 0.79 m^2/g and 1.28 m^2/g, respectively, were also used for arsenic adsorption (De Gisi et al., 2016; Pathak, Mandavgane, & Kulkarni, 2016). For adsorption, both surface area and functional groups play role. BET surface area is highly dependent upon the degassing process temperature. The process involved in degassing the sample is very complex and may result in low surface area (Pathak et al., 2016). The common reason of the resultant low surface area could be due to the difficulties that occur while degassing the lignocellulosic sample (Pathak & Mandavgane, 2015). As reported in literature, surface area of banana peel is also in a wide range. One study found the surface area of banana peel as 1.87 m^2/g (Poudyal & Babel, 2017) while other studies reported as 13 m^2/g (Memon et al., 2009) and 22.59 m^2/g (Hossain, Ngo, Guo, & Nguyen, 2012). In case of egg shell also, the present study shows the surface area of 0.77 m^2/g and in some literature it is reported as 2.209 m^2/g (Tsai et al., 2006) and 1.023 m^2/g (Arami, Limaee, & Mahmoodi, 2008). This wide range of difference could be attributed to the different degassing temperature and procedure.

4.2.3 Scanning Electron Microscopy (SEM)

The surface morphology of adsorbents before and after adsorption was seen using SEM analysis. SEM images before and after adsorption revealed that significant changes occurred on the surface of adsorbents due to adsorption. It can be seen from Figure 4.9 that adsorbents before adsorption exhibit flat and uniform surface while arsenic loaded adsorbents exhibited particles cluttered on the adsorbent surface. These changes seen in adsorbent surface from homogeneous layer to heterogenous layer could possibly be due to the adsorption of arsenic. Before adsorption the adsorbents surface were smooth which drastically changed into irregular, uneven and rough surfaces. The flat shaped surface in adsorbents, is also one of the reasons for the lower surface area of the adsorbents, as it was shown by BET surface area analysis. Some pores were seen in the surface of the carbonized adsorbents. These pores may be the result of release of volatile gases or decomposition of the organic compounds during the process of carbonization (Pathak & Mandavgane, 2015).



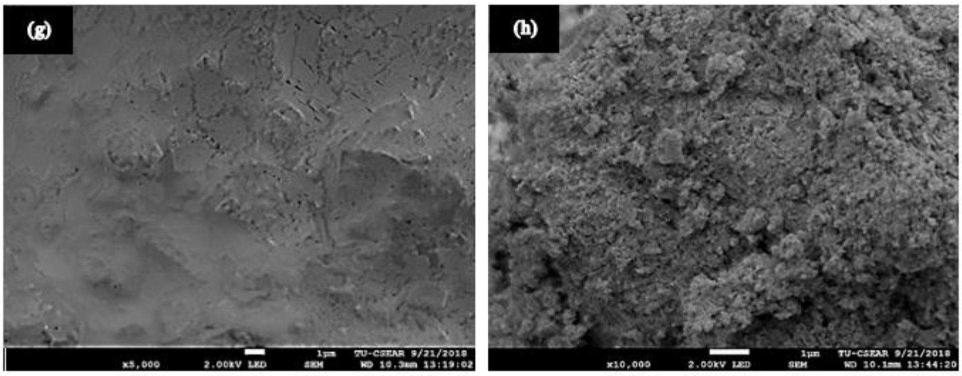


Figure 4.9: SEM images of (a) ES, (b) ES after adsorption, (c) CES, (d) CES after adsorption, (e) BP, (f) BP after adsorption, (g) CBP, (h) CBP after adsorption (10000 X).

4.2.4 Energy-Dispersive X-Ray Spectroscopy (EDX)

EDX analysis was done in order to get information about the chemical composition of the adsorbents before and after adsorption. ES and CES revealed the presence of C, O, Mg, and Ca as shown in Table 4.3. ES also had an additional element i.e. Na. In comparison of the elemental weight before and after adsorption, the weight percentage of C and O was decreased while that of Ca was increased. This can be attributed to the ion exchange mechanism during adsorption (Iqbal et al., 2009). ES and CES consist of $CaCO_3$ as a chemical compound. During the process of adsorption, Ca would be used to adsorb arsenic ion and CO_3 would be substituted. The decrease in carbonate group was represented by FTIR analysis in Figure 4.5 as well. However, the elemental weight of arsenic was not observed in the adsorbents after adsorption due the lower adsorption capacity of the adsorbents. Iqbal et al. (2009) showed the disappearance of Ca and K ion after lead adsorption due to the involvement of these ion in ion exchange mechanism.

Table 4.3: Elemental composition of ES and CES before and after adsorption.

Element weight (%)	ES before adsorption	ES after adsorption	CES before adsorption	CES after adsorption
C	16.38	8.97	14.42	10.51
O	55.01	34.83	58.00	53.52
Mg	0.44	-	0.54	0.34
Ca	28.04	56.20	27.05	30.63
Na	0.13	-	-	-

Elemental analysis of BP and CBP before and after arsenic adsorption is shown in Table 4.4. The results revealed that BP is composed of different element like C, O, Mg, Cl, K and Ca with higher weight percentage of C, O and K. The elements such as C, O, K and Ca are the main components of cellulose and lignin present in the biomass (Mitic-Stojanovic et al., 2011). The mechanism of adsorption of metal anion on adsorbents containing carbon atom can be explained by electrochemical theory. This theory states that “Carbon in contact with water reduces oxygen to a hydroxyl group” and is shown by (Amin et al., 2006):

$O^2 + 2H_2O + 2e^- = H_2O_2 + 2OH^-$

This way the carbon becomes positively charged which remains in combined form with the negatively charged hydroxyl ion. Once they come in contact with solution containing metal anion, hydroxyl ion is replaced by metal anion and adsorption takes place (Amin et al., 2006).

$$\mathrm{carbon} - (\mathrm{OH})_2 + \mathrm{HAsO_4}^{2-} = \mathrm{carbon} - \mathrm{HAsO_4} + 2\mathrm{OH}^-$$

Other changes in the elemental composition of adsorbent includes decrement in the elemental weight of K with increment in the elemental weight of Mg and Ca. This demonstrates the dissolution of KCl from BP, resulting in enhancement of Mg and Ca, when the biomass is used for arsenic adsorption (Memon et al., 2009). Cl ion present in BP disappeared after adsorption and new element i.e. Ca was seen in the arsenic adsorbed sample. Elemental composition of Si and P was increased in CBP after adsorption. Such, changes in the elemental composition of biomass before and after adsorption proved some effect of arsenic adsorption in the biomass. However, the arsenic ion composition was not seen in this case as well due to lower adsorption capacity.

Table 4.4: Elemental composition of BP and CBP before and after adsorption.

Element weight (%)	BP before adsorption	BP after adsorption	CBP before adsorption	CBP after adsorption
C	55.44	64.00	4.63	3.06
O	19.19	13.85	14.11	22.44
K	25.22	10.83	74.86	24.68

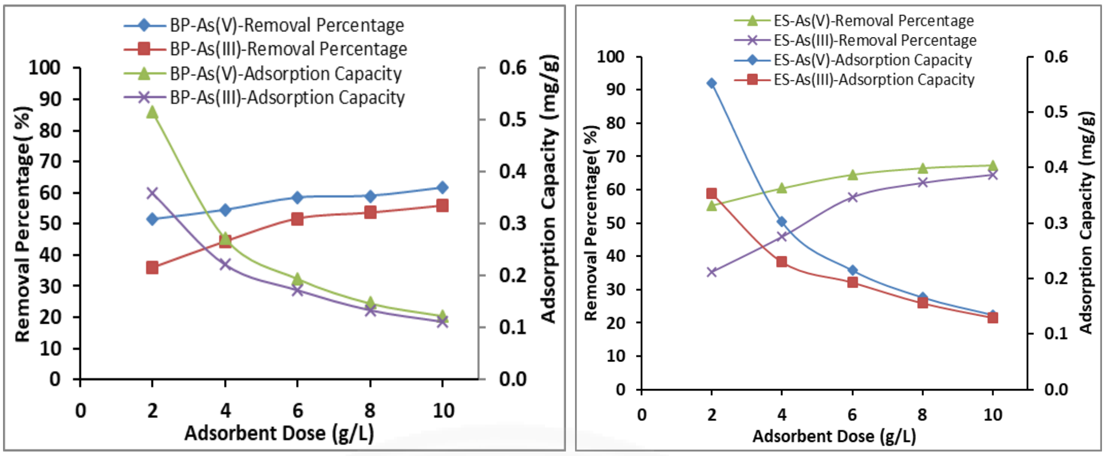
Mg	-	3.41	1.43	3.76
Cl	0.14	-	-	-
Ca	-	7.92	-	32.82
Si	-	-	-	4.37
P	-	-	4.97	8.88

4.3 Optimization of influencing parameter

4.3.1 Adsorbent dose

The adsorption of arsenic by ES and BP from 2 mg/L arsenic solution as a function of adsorbent dose is plotted in graph as shown in Figure 4.10. The experimental observation, within the range of study indicated that increased adsorbent dose increased the removal percentage. As(III) removal efficiency increased from 35 to 55%, 34 to 62% with 2-10 g/L BP and 2-10 g/L ES, respectively. Similarly, As(V) removal efficiency increased from 51 to 61% and 54 to 65% by increasing dose from 2 to10 g/L BP and 2-10 g/L ES, respectively. As the quantity of adsorbent increases, the total surface area and the number of active sites for adsorption also increases, with enhanced adsorption. However, a significant change in removal was not observed beyond the adsorbent dose of 6 g/L due to the overlapping of binding sites. Hence 6 g/L was used as the optimum dose for further experiments. When comparing between the adsorbents, egg shell has higher BET surface area (0.77 m^2/g) than banana peel (0.403 m^2/g). This may be the reason of egg shell of having higher potential to remove arsenic in comparison with banana peel. The actual mechanism for the removal of arsenic from egg shell is due to the presence of promising amount of $CaCO_3$, which is described as follows (Kanel, Choi, Kim, Vigneswaran, & Shim, 2006).

$HAsO_3^{2-} + Ca^{2+} + nH_2O \rightarrow CaHAsO_3.nH_2O$



(a) (b)

Figure 4.10: Effect of adsorbent dose on the removal of As(III) and As(V) by using (a) BP and (b) ES. (pH:7; time:2 hrs; speed: 100 rpm).

4.3.2 pH

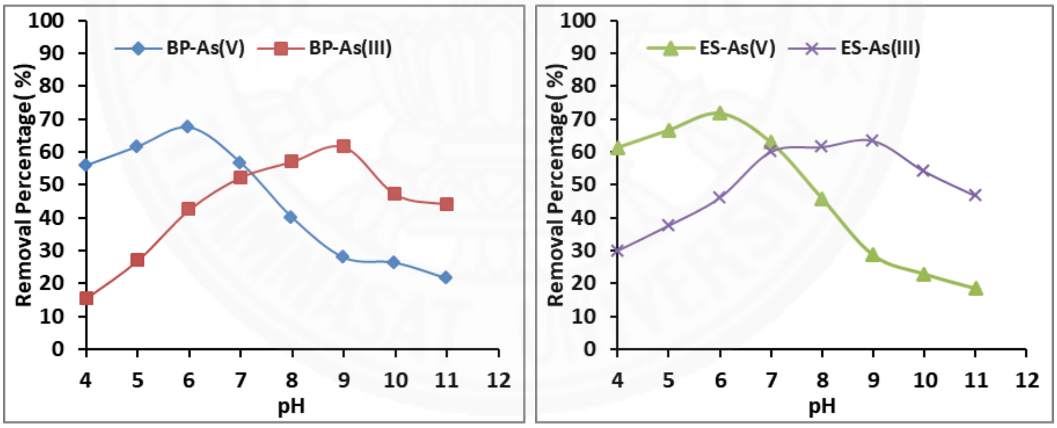
Figure 4.11 shows the effect of pH variation on adsorption with optimum dose of 6 g/L. As pH increased, As (III) removal efficiency increased and reached a maximum value of 61.50% and 63.37% with BP and ES, respectively, at pH 9. At lower pH, the concentration of H^+ ion is high and adsorbents favour to adsorb H^+ ions over the metal ions (Annadurai et al., 2003). When we observe the arsenic speciation graph in Figure 2.2, $H_2AsO_3^-$ state of arsenite start to appear and increase from pH 7. This led to the adsorption of arsenic ion and became maximum at pH 9. When the pH is greater than 9, As (III) exists in anion form as $H_2AsO_3^-$ and $HAsO_3^{2-}$ (Kanel et al., 2006). As the pH reach maximum value, the form of arsenic becomes more negatively charged as AsO_3^{3-}. Moreover, at high pH values the surface of adsorbents also becomes negatively charged (Liu et al., 2012). Hence, the negatively charged species has higher electrostatic repulsion with the adsorbents that weakens the adsorption capacity. This resulted in decrement of adsorption capacity at higher pH value. Similar results were obtained for iron modified bamboo charcoal for arsenite adsorption (Liu et al., 2012). In case of eggshell containing calcium carbonate, following reaction occurs between arsenite and calcium ion from pH 9 to 11 (Mohan & Pittman, 2007).

$2H_2AsO_3^- + Ca^{2+} + nH_2O \rightarrow Ca(H_2AsO_3)_2.nH_2O$

For As(V), there was higher adsorption at pH of 6 and adsorption capacity decreased continuously as the pH raised. At pH 6, As(V) removal efficiency is 67.53% and 71.77% with BP and ES, respectively. As(V) exists in the form of oxyanions ($H_2AsO_4^-$ and $HAsO_4^{2-}$) at neutral pH and $H_2AsO_4^-$ is present at lower value of pH (Kanel et al., 2006). As(V) species remain in the form of anion regardless of the pH of the solution. But, as pH increases, adsorbent surface gains more negativity that enhances electrostatic repulsion among the adsorbent surface and the negatively charged As(V) species (Liu et al., 2012). Arsenate ions and calcium ions present on egg shell undergoes a chemical reaction at pH 2-7 (Mohan & Pittman, 2007). The chemical reaction is as follows:

$2H_2AsO_4^- + Ca^{2+} + nH_2O \rightarrow Ca(H_2AsO_4)_2.nH_2O$

Hence As(V) adsorption favours a lower pH. Additionally, the removal efficiency at neutral pH shows favourable conditions for both states of arsenic that suggests the practical application of these adsorbent to treat groundwater. For further experiments, As(III) solution was adjusted at pH 9 and As(V) solution was adjusted at pH 6.



(a) (b)

Figure 4.11: Effect of pH on the removal of As(III) and As(V) by using (a) BP and (b) ES. (time:2 hrs; speed: 100 rpm)

In order to understand the influence of pH on adsorption more clearly, it is necessary to determine point of zero charge of adsorbents. For that, difference of the initial and final pH (ΔpH) vs initial pH was plotted in a graph as shown in Figure 4.12. The point of zero charge is the point where ΔpH=0 and was found to be at pH 7.06 for BP and pH 8.03 for ES. Actually, the surface of the adsorbent is positive at pH below pHpzc and is negative at pH above pHpzc (Brady & Walther, 1992). So, pH below pHpzc is favourable for anions while pH above pHpzc is favourable for cations. Arsenate ions remain in the form of oxyanions throughout the pH range and hence adsorption is favoured at pH below pHpzc. There would be an electrostatic attraction between the arsenate ions and positively charged adsorbent's surface during the adsorption process. But in case of arsenite ions, it stays in protonated form until pH 7 so pH below pHpzc was not favourable for greater adsorption.

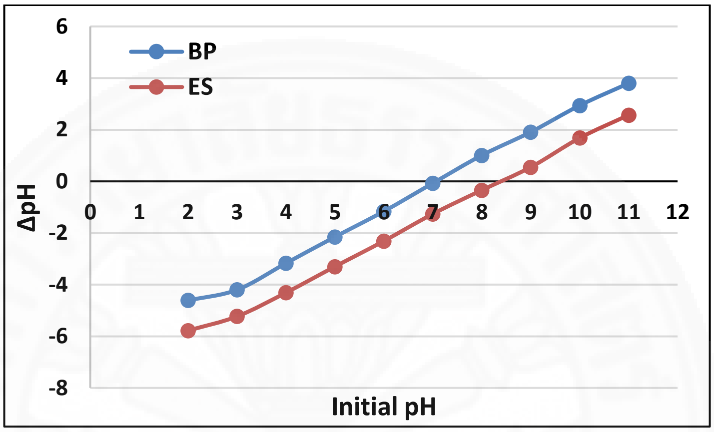
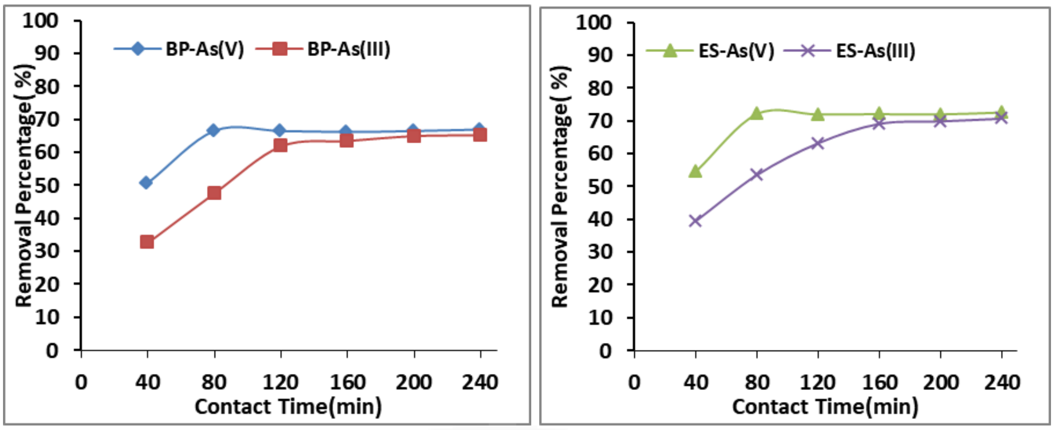


Figure 4.12: Point of zero charge (pHpzc) curve of BP and ES.

4.3.3 Contact time

Adsorption capacity was also optimized with respect to retention time. Figure 4.13 shows the variation in As(III) and As(V) adsorption capacity with a change in retention time. The results revealed that as the retention time increased, the adsorption capacity of the adsorbents enhanced and gradually reached constant after a certain period of time. This is because, at the initial phase more vacant sites are present for adsorption but as time passes by, the vacant sites are occupied and no further adsorption takes place. The constant removal percentages after 160 min for As(III) and 80 min for As(V) suggest the equilibrium time. Consequently, further experiments were done until the equilibrium time.

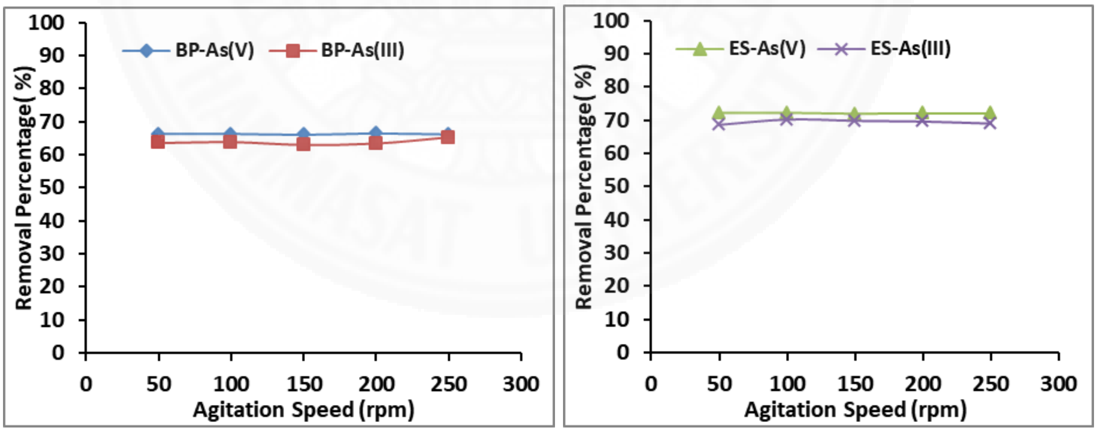


(a) (b)

Figure 4.13: Effect of retention time on the removal of As(III) and As(V) by using (a) BP and (b) ES. (Speed: 100 rpm)

4.3.4 Agitation speed

Optimum agitation speed should be determined to prevent either agglomeration of the adsorbents at the bottom due to low speed or to prevent dissolving adsorbents due to rapid speed. The effect of agitation speed is insignificant in removal efficiency of arsenic species as shown in Figure 4.14.



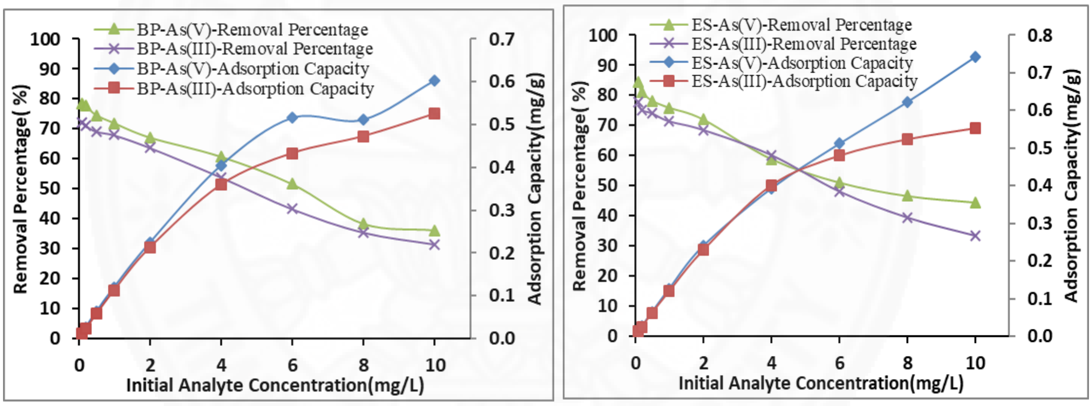
(a) (b)

Figure 4.14: Effect of agitation speed on the removal of As(III) and As(V) by using (a) BP and (b) ES.

4.3.5 Initial analyte concentration:

There was a slight improvement in the removal efficiency when the initial analyte concentration decreased. As the initial analyte concentration decreased from 2 mg/L to

0.1 mg/L, an increase in the removal capacity was seen by almost 10%. Conversely, removal percentage decreased with increased analyte concentration. As shown in Figure 4.15, increasing arsenic concentration by five folds brought a decrease in removal efficiency by almost 30%. For the same adsorbent dose, the active sites present on the adsorbent surface are effective in removing the metal ions from low concentration solutions. But as the concentration increases, the sites are filled completely and saturation is attained. This leads to an increased concentration in the solution itself, which results in a lowered removal efficiency. However, there was a continuous increase in arsenic adsorption capacity with the same adsorbent dose as shown in Figure 4.15. The increment in adsorption capacity is due to the presence of huge number of arsenic ion in the solution of higher concentration that causes greater interaction between adsorbent and ions (Liu et al., 2012).



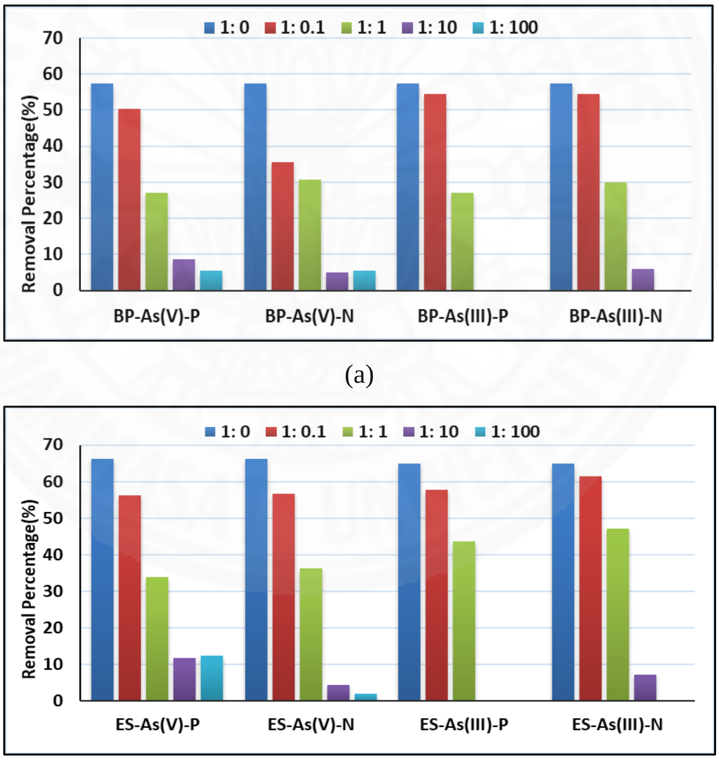
(a) (b)

Figure 4.15: Effect of initial analyte concentration on removal of As(III) and As(V) by using (a) BP and (b) ES.

The optimum conditions obtained until now is for the water contaminated with either As(III) or As(V). But as we know, groundwater contains both forms of arsenic in combined form, optimum condition to treat real groundwater should be addressed. Optimum dose obtained for both forms of arsenic is 6 g/L, hence while treating groundwater, the optimum dose can be taken as 6 g/L. Groundwater has neutral level of pH i.e. pH value around 7. But, optimum pH for As(III) removal is 9 while that for As(V) is 6. However, at pH 7, both forms of arsenic are removed significantly. Thus, while treating groundwater it is better not to change pH of the solution and do adsorption in neutral pH. This is also a positive aspect as it is not required to maintain pH which will automatically makes the process easier and more economic. For the optimum contact time to treat groundwater, the longer period of time is chosen. It is known optimum time to remove As(III) is 160 min and to remove As(V) is 80 min. If optimum contact time of 160 min to treat real groundwater is chosen, then it will cover the optimum time for both forms of arsenic. Therefore, to treat real groundwater samples, adsorbents should be added at a dose of 6 g/L and allowed to adsorb ions for 160 min.

4.3.6 Co-existing Ions

Figure 4.16 show the efficiency of ES and BP to remove As(III) and As(V) in presence of competing solutes including phosphate and nitrate.



(a)

(b)

Figure 4.16 : Amount of arsenic removed in presence of Phosphate(P) and Nitrate(N) ions at different ratio by using (a) BP and (b) ES. (pH:7; initial arsenic concentration: 2 mg/L)

It can be seen from Figure 4.16 that phosphate and nitrate ions have a great influence on arsenic removal efficiency at pH 7. Results indicated that arsenic ions and these ions compete to be adsorbed on the adsorbents surface decreasing arsenic removal efficiency. Adsorbents surface shows higher affinity towards competing ion rather than the arsenic ions. As the concentration of co-existing ion increases, arsenic removal efficiency decreases and even becomes zero in case of As(III) adsorption. When the ratio of arsenic ion and competing ion is 1:0.1, the results are slightly affected but as soon as the concentration increases the removal efficiency is significantly decreased. Phosphate ions show higher affinity towards adsorbents surface even at low concentration and compete with arsenic ions for binding sites as arsenic ions and phosphate ion resemble in structure (Jeong, Maohong, Van Leeuwen, & Belczyk, 2007). Jeong et al. (2007) and Kanel, Manning, Charlet, and Choi (2005) also showed sharp decrement in As(V) and As(III) removal efficiency with addition of phosphate ion but no such effect was reported in removal efficiency with addition of nitrate. The effect of co-existing ion depends upon the pH of the solution and functional group present in the adsorbent. In this study nitrate ion equally affected the removal efficiency as affected by the phosphate ion. Concentration of phosphate in groundwater is usually low while nitrate concentration is relatively higher than phosphate. Concentration of phosphate found in some groundwater is 0.1 mg/L (Shipley, Yean, Kan, & Tomson, 2009), 0.216 mg/L (Shipley et al., 2009), 0.35 mg/L (Kanel et al., 2005) and 0.2 mg/L (Kanel et al., 2005). Likewise concentration of nitrate in groundwater is 18.5 mg/L (Logan & LaPoint, 2002), 21 mg/L (Logan & LaPoint, 2002) and 40.3 mg/L (Babiker, Mohamed, Terao, Kato, & Ohta, 2004). Hence lower concentration will not affect arsenic removal to higher extent but if the concentration is high then arsenic adsorption will not be favourable in such conditions.

4.3.7 Arsenic removal efficiency of modified adsorbents at optimum conditions

The optimum conditions obtained were used for the further experiment to find out the arsenic removal capacity of the modified adsorbents. Figure 4.17 shows the arsenic removal capacity of BP and ES along with the modified adsorbents under optimum conditions obtained for BP and ES. Optimum condition for As(III) removal is 6 g/L of adsorbent dose, pH 9 and contact time of 160 min. Likewise, optimum condition for As(V) removal is 6 g/L of adsorbent dose, pH 6 and contact time of 80 min.

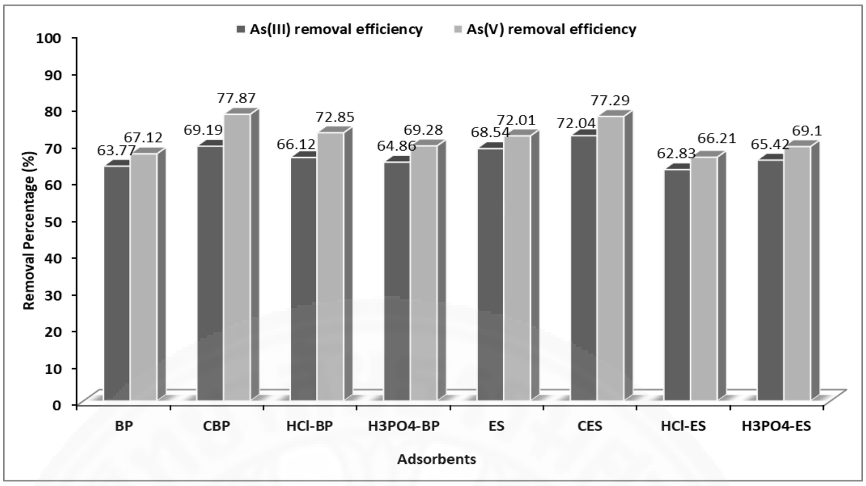


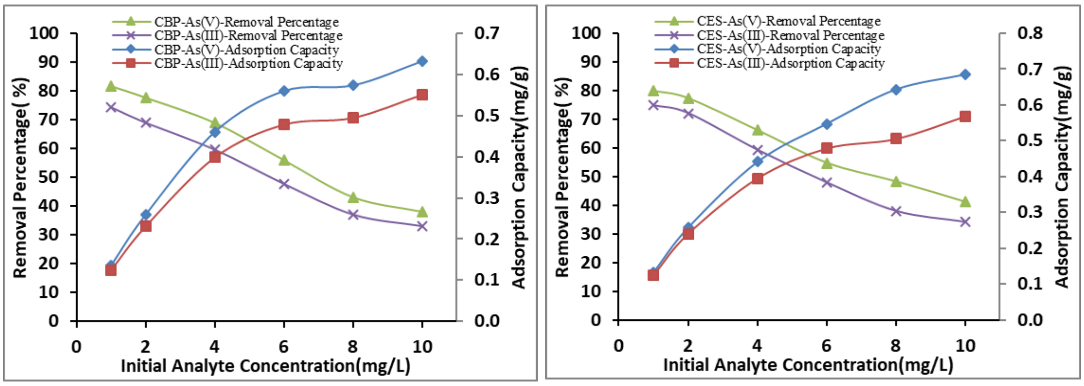
Figure 4.17: Arsenic removal capacity of modified and unmodified adsorbents at optimum conditions.

Removal percentage of BP increased from 63.77 % to 69.19 % for As(III) adsorption and it increased from 67.12 % to 77.87 % for As(V) adsorption due to carbonization at 700°C. As BET surface area play a major role in the adsorption process, this increment in the removal efficiency is due to the increment in BET surface area. As shown in Table 4.2, the BET surface area of carbonized BP is 3 times greater than the original BP. Also, the pore volume increased nearly by 4 times. This increment in BET surface area and pore volume increased the arsenic removal efficiency by 5.42 % in case of As(III) adsorption and by 10.75 % in case of As(V) adsorption. When BP was modified with HCl, As(III) removal efficiency increased from 63.77 % to 66.12 % and As(V) removal efficiency increased from 67.12 % to 72.85 %. In this case, BET surface area increased by 1.5 times compared with the original BP. When we see the FTIR spectra of HCl modified BP in Figure 4.7, there was a reduction in the absorbance peak of the hydroxyl group which is responsible for arsenic adsorption. The absorbance value of the peak decreased from 0.85 to 0.51. Hence, increment in the adsorption capacity is due to the combined effect of the increment in BET surface area and decrement in the absorbance value of the hydroxyl group. In the case of H_3PO_4 modified BP, there is no significant improvement in the removal efficiency.

Increment or decrement in arsenic removal capacity due to modification depends on the original adsorbent. It is seen that the removal percentage of BP increased because of the carbonization of the sample. This increase in removal efficiency suggests that carbonization of BP favoured adsorption. However, in case of ES, carbonization did not help to increase the removal efficiency as observed in BP. In fact, carbonization of ES even reduced the BET surface area and pore volume by half compared to that of the original ES. But surface area is not only the factor responsible for adsorption. Functional group is another factor that influence the adsorption process. The decrement in the surface area also resulted few improvements in the adsorption capacity. The improvement was because of more utilization of the calcium carbonate group as shown in Figure 4.5(b). When ES is modified with HCl, there is an increment in BET surface area by almost 11 times than compared with original ES. When we see the FTIR spectra of HCl modified ES in Figure 4.4, the peak of carbonate group disappeared completely. Hence there is reduction in the removal efficiency by HCl modified ES compared with the original ES. Hence, only carbonized samples were chosen for further experiments.

4.3.8 Adsorption by CBP and CES

From the experiments to optimize the influencing parameters, the optimum conditions were found out to be 6 g/L of adsorbent dose; pH 6 for As(III) and pH 9 for As(V) removal; contact time of 160 min for As(III) and 80 min for As(V) removal. These conditions were applied for As(III) and As(V) removal using CBP and CES and the graph obtained is shown in Figure 4.18. Carbonization enhanced the capacity of BP to remove arsenic ions. At optimum conditions, As(III) removal percentage is 69.19 % for As(III) adsorption and 77.87 % for As(V) adsorption from 2 mg/L of arsenic solution. Likewise, the removal efficiency of CES for As(III) removal is 72.04 % and As(V) removal is 77.29 %. There is decrement in removal percentage and increment in adsorption capacity as the initial analyte concentration increases from 2-10 mg/L. This trend was similar as observed in the case of non-modified adsorbents.



(a) (b)

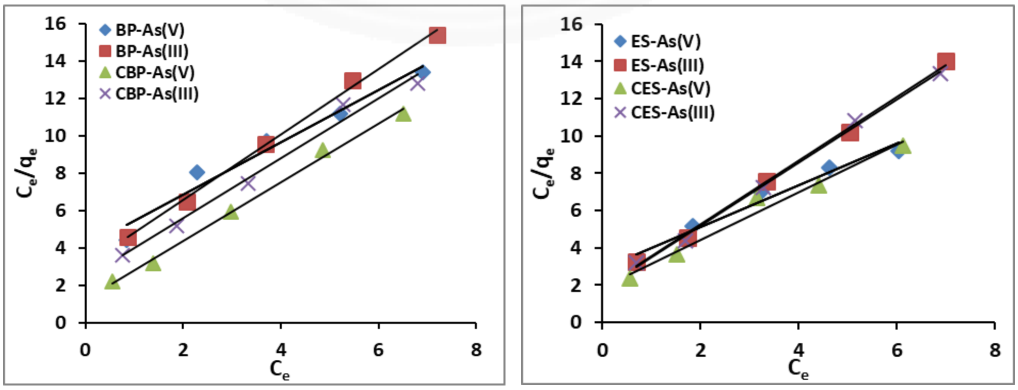
Figure 4.18: As(III) and As(V) removal by using (a) CBP and (b) CES at different analyte concentration.

4.4 Adsorption Isotherm

Adsorption isotherms were carried out to see the distribution of arsenic ions in the surface of the adsorbent. The isotherms were developed based on the adsorption capacity of 6 g/L of adsorbents at pH 7, contact time of 160 min for As(III) and 80 min for As(V), and various initial concentration of arsenic. The adsorbents are aimed to be used to treat contaminated groundwater, therefore adsorption studies were carried out at neutral pH. The isotherms which were analysed are briefly described below.

4.4.1 Langmuir Isotherm Model

Langmuir adsorption parameters were determined using the linear form of equation. Figure 4.19 represents the curve obtained for Langmuir isotherm model.



(a) (b)

Figure 4.19: Langmuir adsorption isotherm for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

Values of Langmuir constants such as adsorption rate (b) and monolayer adsorption capacity (Q_0), were calculated based on the slope and intercept of the curves. The line equation along with the R^2 values and Langmuir constants are listed in Table 4.5.

Table 4.5: Langmuir Isotherm parameters for different adsorbents.

Form of Arsenic	Adsorbent	Equations	R^2	b	Q_0
Arsenite As(III)	BP	y = 1.75x + 3.05	0.997	0.573	0.571
	CBP	y = 1.6x + 2.38	0.984	0.672	0.625
	ES	y = 1.72x + 1.8	0.997	0.955	0.581
	CES	y = 1.69x + 1.81	0.996	0.933	0.591
Arsenate As(V)	BP	y = 1.40x + 4.04	0.963	0.346	0.714
	CBP	y = 1.56x + 1.26	0.994	1.238	0.641
	ES	y = 1.12x + 2.87	0.964	0.390	0.892
	CES	y = 1.26x + 1.94	0.988	0.649	0.793

The higher correlation coefficient (R^2) value, as listed in Table 4.5, suggests the linear relationship between the equilibrium concentration and ratio of equilibrium concentration to adsorption capacity. The value of R^2 approaching to 1 reveals that monolayer adsorption is taking place between arsenic ions and adsorbents. In case of As(III) adsorption, ES and BP shows the greatest fit to the Langmuir model with a R^2 value of 0.997. The value of adsorption rate is higher with ES compared with other adsorbents and CBP has the maximum monolayer adsorption capacity for As(III). Similarly, CBP shows the greatest fit to the model for As(V) adsorption. In addition, the higher value of b of CBP for As(V) adsorption signifies stronger bonds between arsenate ions and carbonized banana peel as compared with other adsorbents. Lastly, ES has the greater monolayer adsorption capacity to adsorb As(V). A dimensionless factor called the separation factor (R_L) is used to determine the nature of adsorption process. R_L value of different adsorbents at different concentration is listed in Table 4.6.

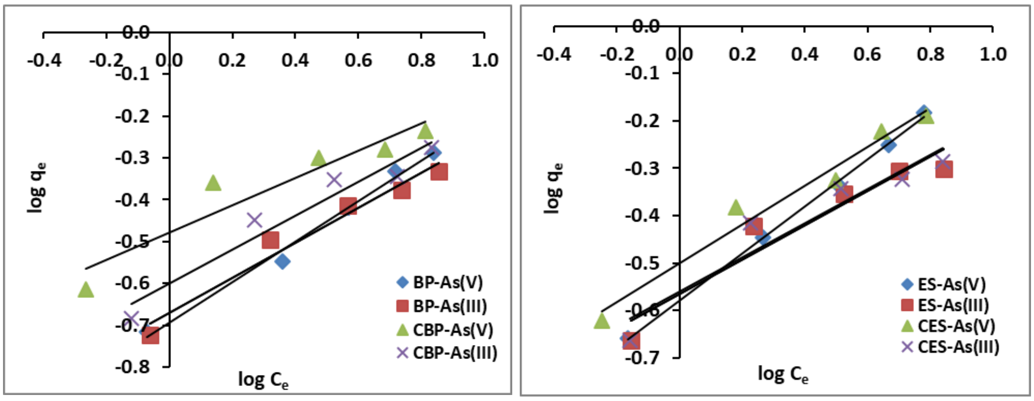
Table 4.6: Separation Factor of different adsorbents at different analyte concentration.

Form of Arsenic	Initial Arsenic Concentration	R_L Values			
		BP	CBP	ES	CES
Arsenite As(III)	2	0.466	0.427	0.344	0.349
	4	0.304	0.271	0.207	0.211
	6	0.225	0.199	0.149	0.152
	8	0.179	0.157	0.116	0.118
	10	0.149	0.130	0.095	0.097
Arsenate As(V)	2	0.591	0.288	0.562	0.435
	4	0.419	0.168	0.391	0.278
	6	0.325	0.119	0.299	0.204
	8	0.265	0.092	0.243	0.161
	10	0.224	0.075	0.204	0.134

The value of R_L reflects whether adsorption is favourable or unfavourable for an adsorbent. The lower the value of R_L, more favourable is the adsorption process. Based on the R_L value, ES is more favourable for As(III) adsorption while CBP is more favourable for As(V) adsorption in comparison with other adsorbents. All the values of R_L listed in Table 4.6 lie in the range of 0 to 1 for arsenic concentration of 2-10 mg/L. This represents the adsorption process is favourable for the selected adsorbents under the specified optimum conditions.

4.4.2 Freundlich Adsorption Isotherm

Freundlich adsorption parameters were determined using a logarithmic form of equation. Figure 4.20 represents the curve obtained for Freundlich isotherm model.



(a) (b)

Figure 4.20: Freundlich adsorption isotherm for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

Values of Freundlich constants i.e. adsorption capacity (K_f) and adsorption intensity (n), were calculated based on the slope and intercept of the curves. The line equation along with the R^2 values and Freundlich constants are listed in Table 4.7.

Table 4.7: Freundlich Isotherm parameters for different adsorbents.

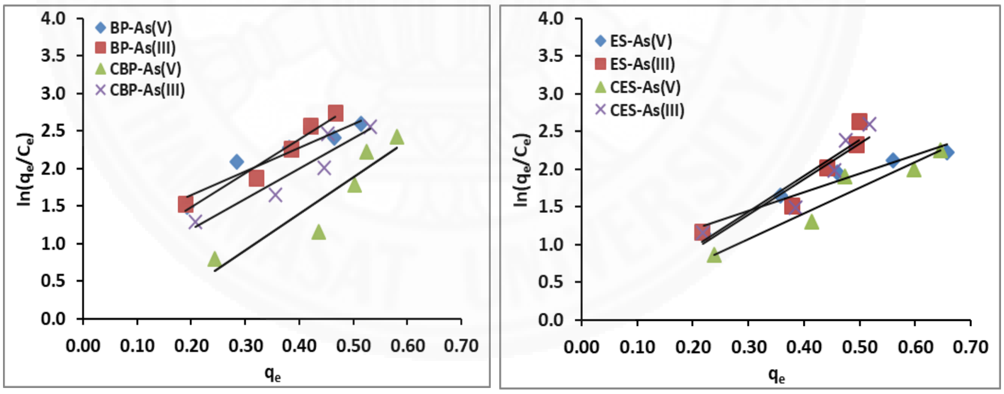
Form of Arsenic	Adsorbent	Equations	(R^2)	K_f	1/n	n
Arsenite As(III)	BP	y = 0.42x - 0.67	0.964	0.213	0.42	2.38
	CBP	y = 0.40x - 0.60	0.942	0.251	0.40	2.5
	ES	y = 0.36x - 0.57	0.919	0.269	0.36	2.78
	CES	y = 0.36x - 0.56	0.910	0.275	0.36	2.78
Arsenate As(V)	BP	y = 0.48x - 0.69	0.990	0.204	0.48	2.08
	CBP	y = 0.32x - 0.48	0.895	0.331	0.32	3.12
	ES	y = 0.50x - 0.58	0.998	0.263	0.50	2.00
	CES	y = 0.41x - 0.50	0.969	0.316	0.41	2.44

It can be observed from Table 4.7 that the value of R^2 for the curve of ES used for As(V) removal is maximum and close to 1. Among the four cases of As(III) adsorption, BP is most suited for Freundlich isotherm under identical experimental conditions.

Maximum value of adsorption capacity (K_f) is shown by CES in case of As(III) adsorption and CBP in case of As(V) adsorption. The value of n between 2 to 10 represents good adsorption and it can be seen that the value of n is between 2 to 10 in all the cases. The value of n actually represents the adsorption intensity and 1/n represents surface heterogeneity. For As(III) adsorption, maximum value of 1/n i.e. 0.42 is seen when using BP as adsorbent. Higher value of 1/n for BP represents that removal of As(III) when using BP is more favourable compared with the other adsorbents (Anwar et al., 2010). Likewise, for As(V) adsorption, the value of 1/n is maximum for ES i.e. 0.50, indicating more favourable adsorption with ES compared with other adsorbents. Moreover, 1/n value for As(V) adsorption is greater than As(III) adsorption that implies As(V) adsorption is more favourable than As(III) adsorption.

4.4.3 Elovich Adsorption Isotherm

Elovich adsorption parameters were determined using a linearized form of the Elovich isotherm model equation. Figure 4.21 represents the curve obtained for Elovich isotherm model.



(a) (b)

Figure 4.21: Elovich adsorption isotherm for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

Elovich equilibrium constant (K_e) and Elovich maximum adsorption capacity (q_m) were calculated based on the slope and intercept of the curves. The line equation along with the R^2 values and Elovich constants are listed in Table 4.8.

Table 4.8: Elovich Isotherm parameters for different adsorbents.

Form of Arsenic	Adsorbent	Equations	R^2	q_m	K_e
Arsenite As(III)	BP	y = 4.50x + 0.59	0.956	4.50	0.59
	CBP	y = 4.06x + 0.37	0.889	4.06	0.37
	ES	y = 4.76x + 0.002	0.877	4.76	0.002
	CES	y = 4.73x - 0.02	0.862	4.73	-0.02
Arsenate As(V)	BP	y = 3.11x + 1.03	0.918	3.114	1.026
	CBP	y = 4.87x - 0.55	0.848	4.87	-0.55
	ES	y = 2.47x + 0.70	0.949	2.47	0.70
	CES	y = 3.33x + 0.09	0.978	3.33	0.09

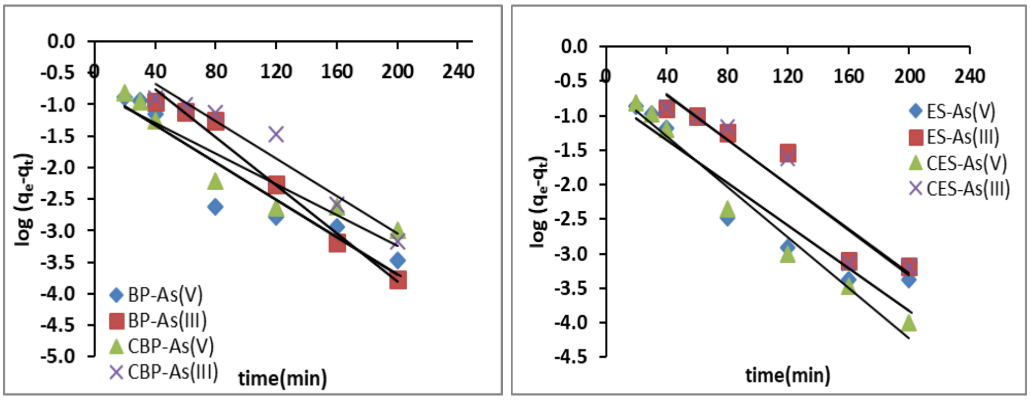
As seen from Table 4.8, the Elovich equation curve exhibited poor coefficients of correlation as compared with the Langmuir and Freundlich values. However, As(III) adsorption by using BP and As(V) adsorption by CES has the maximum R^2 value of 0.956 and 0.978, respectively, indicating exponential covering of adsorption sites. Elovich maximum adsorption capacity of 4.76 mg/g was observed in ES for As(III) uptake and 4.87 mg/g in CBP for As(V) uptake. Some adsorbents showed negative value for Elovich equilibrium constant which nullifies the assumption of the exponential covering of adsorption sites in that case. Most suitable adsorption model for each adsorbent is explained afterwards.

4.5 Adsorption kinetics

In order to understand the adsorption process and the factors affecting adsorption process three kinetic models, pseudo first order and pseudo second order and Elovich kinetic models were studied. The kinetic models were developed based on the adsorption capacity of 6 g/L of adsorbents at pH 7, initial concentration of 2 mg/L and various contact time.

4.5.1 Pseudo first order equation

The pseudo first order equation describes the rate of adsorption of the solid-liquid interface. The curves obtained within the range of study are presented in Figure 4.22.



(a) (b)

Figure 4.22: Pseudo first-order kinetic model for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

The value of k_1 (pseudo first order rate coefficient, min^{-1}) and q_e (adsorption capacity at the equilibrium, mg/g) obtained from the curve equation along with the experimental value of q_e is listed in Table 4.9. The pseudo first order kinetic equation and the R^2 value for different adsorbents and different arsenic solution is also given in Table 4.9.

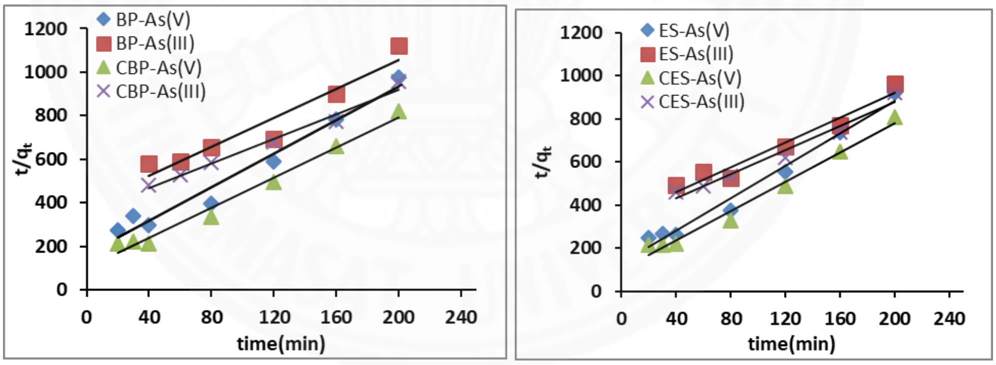
Table 4.9: Pseudo first-order kinetic model parameters for different adsorbents.

Form of Arsenic	Adsorbent	Equations	R^2	k_1	q_e	q_e (experiment)
Arsenite As(III)	BP	y = -0.02x + 7E-05	0.98	0.044	1	0.178
	CBP	y = -0.015x - 0.08	0.944	0.034	0.831	0.21
	ES	y = -0.016x - 0.06	0.911	0.037	0.874	0.208
	CES	y = -0.016x - 0.038	0.917	0.037	0.916	0.217
Arsenate As(V)	BP	y = -0.015x - 0.74	0.892	0.034	0.182	0.205
	CBP	y = -0.012x - 0.79	0.895	0.028	0.161	0.245
	ES	y = -0.015x - 0.73	0.909	0.036	0.187	0.218
	CES	y = -0.018x - 0.55	0.975	0.042	0.28	0.247

If we observe the R^2 values listed in Table 4.9, we get the clue that pseudo first order equation does not fit for adsorbents for As(V) removal except for CES. The R^2 values close to 1, for the adsorbents used for As(III) removal suggest the fitting of the curve for pseudo first order equation. Based on the value of q_e, this model suggests that BP is best adsorbent for As(III) removal and CES is best adsorbent for As(V) removal. But when we compare the calculated and experimental equilibrium adsorption capacity, then there is a huge difference. The difference in the values indicates that this kinetic model does not fit well in the range of the time studied. Comparing the value of k_1 between the adsorbents, BP used for As(III) solution has the highest value. Higher the value of k_1, faster would be the rate of adsorption. Similarly, CES used for As(V) uptake has the highest k_1 value indicating faster rate of adsorption compared with other adsorbents.

4.5.2 Pseudo second order equation

The curves obtained within the range of the study for pseudo second order equation are presented in Figure 4.23.



(a) (b)

Figure 4.23: Pseudo second-order kinetic model for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

The value of k_2 (pseudo second order rate constant, min^{-1}), h (initial sorption rate) and q_e (adsorption capacity at the equilibrium, mg/g) along with the experimental value of q_e is listed in Table 4.10. The pseudo second order kinetic equation and the R^2 value for different adsorbents and different arsenic solution is also given in Table 4.10.

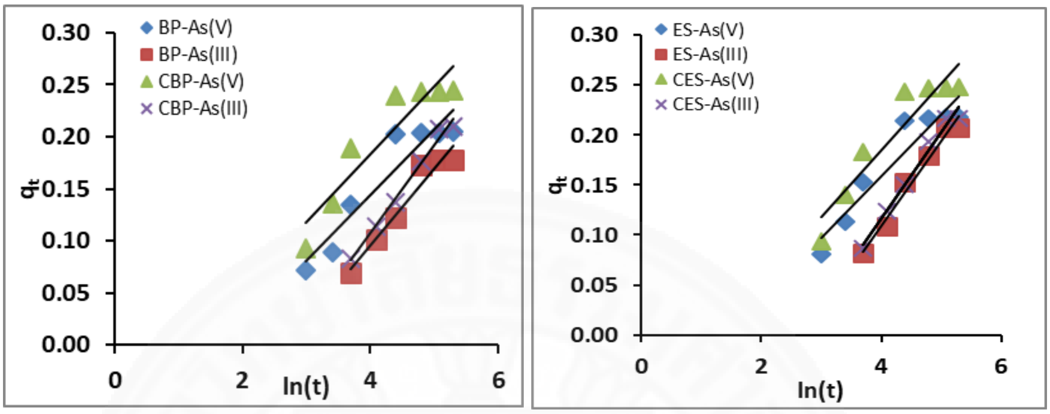
Table 4.10: Pseudo second-order kinetic model parameters for different adsorbents.

Form of Arsenic	Adso-rbent	Equations	R^2	q_e	q_e (experiment)	k_2	$h=k_2q_e^2$
Arsenite As(III)	BP	y = 3.34x + 390.34	0.925	0.299	0.178	0.0286	0.0025
	CBP	y = 2.83x + 355.8	0.981	0.354	0.21	0.0224	0.0028
	ES	y = 2.86x + 347.42	0.95	0.349	0.208	0.0236	0.0029
	CES	y = 2.82x + 317.06	0.968	0.355	0.217	0.0251	0.0032
Arsenate As(V)	BP	y = 3.84x + 165.48	0.967	0.26	0.205	0.0894	0.006
	CBP	y = 3.47x + 99.808	0.983	0.288	0.245	0.1203	0.01
	ES	y = 3.79x + 127.94	0.98	0.264	0.218	0.164	0.0078
	CES	y = 3.4x + 101.18	0.983	0.294	0.247	0.1141	0.01

The R^2 values of the curve for pseudo second order kinetic model show a better fit to the model as most of the values are close to unity. Comparing the R^2 values of two kinetic model, the adsorbent shows the greater fit to the pseudo second order kinetic model. This indicates that two reactions occur simultaneously in the adsorption process as assumed by the pseudo second order kinetic model. One of the reactions occurs at faster rate and reaches equilibrium quickly while the other reaction occurs at slow rate and continues until the adsorption process. Based on the value of q_e, this model suggests CES is the better adsorbent for both As(III) and As(V) removal. The calculated and experimental equilibrium adsorption capacity for As(V) solution are close to each other comparing with the As(III) solution showing better fit to the model. As(III) uptake by using BP and As(V) uptake by using ES has the highest k_2 value indicating faster rate of adsorption compared to other adsorbents. In addition, value of k_2 is much higher in case of As(V) adsorption than in As(III) adsorption revealing that As(V) can be removed in short period of time. When we compare the value of h for the different cases of adsorption, As(III) and As(V) uptake by using CES is the maximum. This indicates that initial sorption rate of CES is greater than other adsorbents.

4.5.3 Elovich Equation

Elovich equation assumes that the adsorption rate decreases exponentially with an increase in quantity of adsorbed ions. The graph obtained from the Elovich equation is shown in Figure 4.24.



(a) (b)

Figure 4.24: Elovich model for As(III) and As(V) adsorption by using (a) BP and CBP (b) ES and CES.

From the intercept and slope of the curve, the value of α (initial sorption rate, mg/g.min) and β (desorption constant, g/mg) were obtained. The equation of the curves, their R^2 values and the value of α and β are listed in Table 4.11.

Table 4.11: Elovich equation parameters for different adsorbents.

Form of Arsenic	Adsorbents	Equations	R^2	α	β
Arsenite As(III)	BP	y = 0.0736x - 0.1983	0.947	0.0786	13.698
	CBP	y = 0.084x - 0.2283	0.987	0.0913	11.905
	ES	y = 0.0841x - 0.2271	0.971	0.0915	11.890
	CES	y = 0.0864x - 0.2289	0.98	0.0942	11.574
Arsenate As(V)	BP	y = 0.0633x - 0.1089	0.891	0.0674	15.798
	CBP	y = 0.0649x - 0.0764	0.866	0.06925	15.408
	ES	y = 0.0619x - 0.0886	0.892	0.0658	16.155
	CES	y = 0.0669x - 0.0828	0.882	0.0715	14.947

As(III) removal show better fit to Elovich equation than As(V) removal as observed from the R^2 value listed in Table 4.11. The value of $R^2 > 0.9$ for As(III) adsorption represents goodness of fit for Elovich equation. This indicates that As(III) adsorption rate decreases exponentially with an increase in quantity of adsorbed ions. The initial rate of adsorption (α) is found to be high while using CES suggesting better adsorbent for arsenic ions. This result is similar as obtained in pseudo second order kinetic model. Arsenic removal with CES also has the lowest value of desorption constant (β). Hence from Elovich equation it is concluded that the rate of adsorption is faster by using CES compared with other adsorbents in the initial phase.

4.6 Analysis of best-fitting Isotherm Model and Kinetics

In order to select the suitable model and kinetics that represents arsenic adsorption on the adsorbents, some error analysis tools were applied. These tools help to find the deviation of the theoretical data obtained from the model compared with the experimental data. Three error analysis tools were applied in this study. The error values of adsorption capacity for different adsorbents along with the R^2 values for three isotherm model is given in Table 4.12 and for three kinetic model is given in Table 4.13.

Table 4.12: Error analysis of adsorption capacity of each adsorbent for different isotherm model.

Error function/ Adsorbents	**R^2**			**Chi-square test**			**Root Mean Square Error**			**Average Percentage Error**		
	Langmuir	**Freundlich**	**Elovich**	**Langmuir**	**Freundlich**	**Elovich**	**Langmuir**	**Freundlich**	**Elovich**	**Langmuir**	**Freundlich**	**Elovich**
BP-As(III)	**0.997**	0.964	0.956	**0.0007**	0.0059	15.5468	**0.0075**	0.0198	3.6744	**1.6131**	5.5518	928.7152
CBP-As(III)	**0.984**	0.9418	0.889	**0.0039**	0.0117	10.3181	**0.0193**	0.0298	2.6407	**3.6961**	7.2968	568.8709
ES-As(III)	**0.997**	0.919	0.877	**0.0023**	0.0148	26.8855	**0.0120**	0.0334	0.3822	**3.1391**	7.8865	92.5158
CES-As(III)	**0.996**	0.91	0.862	**0.0030**	0.0160	N/A	**0.0144**	0.0345	N/A	**3.7360**	8.5117	N/A
BP-AsV	0.963	**0.99**	0.918	0.0103	**0.0019**	13.7043	0.0224	**0.0113**	3.2248	7.1872	**2.5648**	830.8538
CBP-As(V)	**0.994**	0.895	0.848	**0.0047**	0.0204	N/A	**0.0199**	0.0395	N/A	**4.0462**	8.5552	N/A
ES-AsV	0.964	**0.998**	0.949	0.0104	**0.0006**	6.4547	0.0275	**0.0080**	1.7608	6.7838	**1.2058**	355.4470
CES-As(V)	**0.988**	0.969	0.978	0.0114	**0.0088**	0.2877	0.0316	**0.0274**	0.1640	6.4305	**5.0880**	32.4725

The highest R^2 value and the lowest χ^2, RMSE, APE(%) values among three isotherm models are in bold. N/A: Not Analyzed

Table 4.13: Error analysis of adsorption capacity of each adsorbent for different kinetic model.

Error function/ Adsorbents	**R^2**			**Chi-square test**			**Root Mean Square Error**			**Average Percentage Error**		
	Pseudo first order equation	Pseudo second order equation	Elovich Equation	Pseudo first order equation	Pseudo second order equation	Elovich Equation	Pseudo first order equation	Pseudo second order equation	Elovich Equation	Pseudo first order equation	Pseudo second order equation	Elovich Equation
BP-As(III)	**0.98**	0.925	0.947	4.8762	**0.0070**	0.0071	0.9670	**0.0153**	0.0160	893.0653	8.9525	**8.8017**
CBP-As(III)	0.944	0.981	**0.987**	0.3287	**0.0136**	0.0214	0.0964	**0.0213**	0.0290	55.5715	**14.1504**	18.1065
ES-As(III)	0.911	0.95	**0.971**	3.7151	0.0056	**0.0053**	0.7819	**0.0144**	0.0145	626.4364	9.0411	**8.1097**
CES-As(III)	0.917	0.968	**0.98**	3.8936	**0.0043**	0.0045	0.8200	**0.0135**	0.0143	619.8731	6.8324	**6.1870**
BP-AsV	0.892	**0.967**	0.891	0.0284	**0.0140**	0.0190	0.0295	**0.0207**	0.0260	23.5638	**15.3490**	18.2306
CBP-As(V)	0.8954	**0.9829**	0.866	0.3287	**0.0136**	0.0214	0.0964	**0.0213**	0.0290	55.5715	**14.1504**	18.1065
ES-AsV	0.908	**0.980**	0.892	0.0333	0.1531	**0.0172**	0.0341	0.0556	**0.0254**	21.9244	38.2229	**16.8918**
CES-As(V)	0.975	**0.983**	0.882	0.0716	**0.0123**	0.0200	0.0544	**0.0205**	0.0287	40.1758	**13.1715**	17.0594

The highest R^2 value and the lowest χ^2, RMSE, APE(%) values among three isotherm models are in bold.

At first, a thorough comparison was made between three isotherm models based on the R^2 values listed in Table 4.12. The higher correlation coefficient (R^2) value for As(III) adsorption on each adsorbent was observed in the Langmuir isotherm then the Freundlich and Elovich isotherm. Similarly, based on the R^2 value, As(V) adsorption on BP and ES show a fit to the Freundlich isotherm model and then the Langmuir and Elovich model. As(V) adsorption on CBP and CES show a fit to the Langmuir isotherm model followed by the Freundlich and Elovich model. After that, the determination of suitable model was done through the error analysis values. The results from error analysis yielded that, the error values is in accordance to the R^2 values for As(III) adsorption. As(III) adsorption showed greatest fit to the Langmuir model with the least calculated error values and high R^2 values. This reveals that monolayer adsorption is taking place between As(III) ions and adsorbents. In addition, there is a linear relationship between the equilibrium concentration and ratio of equilibrium concentration to adsorption capacity for As(III) adsorption.

R^2 values and error analysis values also gave a consistent result for As(V) adsorption using BP, ES and CBP. As(V) adsorption on CBP exhibit the best fit to the Langmuir isotherm model suggesting monolayer adsorption on CBP. Likewise, As(V) adsorption on BP and ES exhibit the best fit to the Freundlich isotherm model followed by the Langmuir and Elovich isotherm model. This indicates that adsorption of As(V) on the surface of BP and ES occurs in multilayer. But in the case of As(V) adsorption by using CES, error analysis result is just opposite to the R^2 value result. Langmuir model was suggested by the R^2 value but all of the three error analysis values showed the adsorption is best fit for the Freundlich model. This proves that R^2 value is not always appropriate to evaluate and select a suitable model. However, it is clear from the error values that As(V) adsorption on CES exhibit the best fit to the Freundlich isotherm model suggesting multilayer adsorption in CES. Elovich isotherm model resulted lower R^2 value with much higher error analysis values. This nullifies the assumption of Elovich isotherm that the adsorption sites increase exponentially with adsorption.

The approach of determination of kinetics parameter by linear regression resulted that As(V) adsorption fits to the pseudo second order kinetic equation with respect to the R^2 values. Likewise As(III) adsorption using CBP, ES and CES fits to the Elovich kinetic equation and by using BP fits to the pseudo first order kinetic equation. But as mentioned before, linearization may result some bias, error analyses tools were applied to select a suitable kinetic model. Each error values so obtained showed a clear result for As(V) uptake. Least error values were observed in pseudo-second order kinetic equation for As(V) adsorption on BP, CBP and CES. And least error values were observed in Elovich equation for As(V) adsorption on ES. This result also contradicts with the result of R^2 value. In spite of the high R^2 value obtained for pseudo second order kinetic equation, this equation does not perfectly describe the equilibrium data and hence As(V) adsorption on ES is best described by Elovich equation.

Error analysis tools did not gave a steady result for As(III) adsorption and an overall optimum kinetic model was difficult to identify. In such case, normalization and combination of error value for each set was done for better comparison of the different error. The error value obtained from each error function for each model was divided by the largest error value for that set of error function. After that the normalized error value of each kinetic model was combined and are listed as summation of the normalized error (SNE) value in Table 4.14. Based on the SNE value, it is resulted that adsorption of As(III) on ES follows Elovich kinetic equation while adsorption of As(III) on BP, CBP and CES follows pseudo-second order kinetic equation. The distinct result obtained from R^2 values and error analysis values shows the importance of error analysis while selecting a model.

In conclusion, adsorption of As(III) and As(V) on BP, CBP and CES follows pseudo-second order kinetic equation indicating that two reactions occur simultaneously in the adsorption process as assumed by the pseudo second order kinetic model. One of the reactions occurs at faster rate and reaches equilibrium quickly while the other reaction occurs at slow rate and continues until the adsorption process. Moreover, the adsorption process is controlled by chemisorption process (Satish, Sameer, & Naseema, 2013). Adsorption of As(III) and As(V) on ES follows Elovich kinetic equation, which also suggests adsorption process is a chemisorption process (Ahamad et al., 2018). But adsorption rate on ES decreases exponentially with an increase in quantity of adsorbed ions as described by the model. Table 4.15 show the summary of the best fitting isotherm and kinetic model of As(III) and As(V) adsorption on each adsorbent.

Table 4.14: Summation of the normalized error (SNE) value of kinetic model

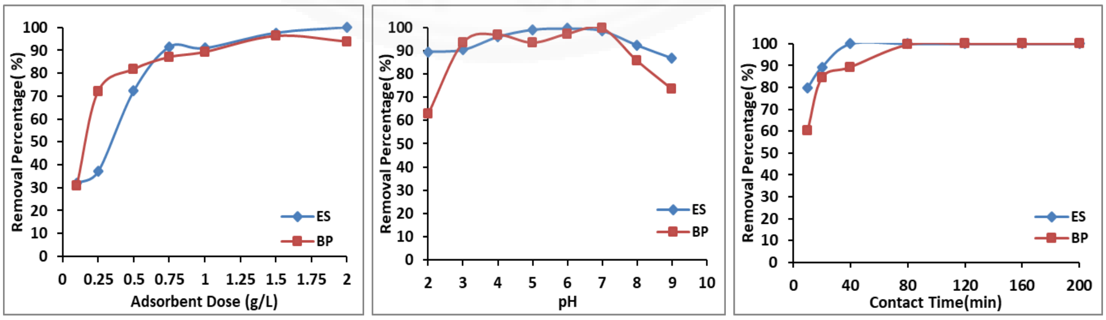
	Pseudo first order equation	Pseudo second order equation	Elovich Equation
BP-As(III)	3	**0.0273**	0.0279
CBP-As(III)	3	**0.0251**	0.0258
ES-As(III)	3	0.0344	**0.0329**
CES-As(III)	3	**0.02858**	0.02862
BP-AsV	3	**1.8453**	2.3234
CBP-As(V)	3	**0.5167**	0.6915
ES-AsV	1.405	3	**1.0119**
CES-As(V)	3	**0.8773**	1.2320

Table 4.15: Summary of the best fitting Isotherm Model and Kinetics

Form of Arsenic	Adsorbent	Isotherm	Kinetic Equation	Remark
Arsenite As(III)	BP	Langmuir	Pseudo second order	Monolayer and chemical adsorption
	CBP			Monolayer and chemical adsorption
	ES		Elovich	Monolayer and chemical adsorption with exponential decrease in adsorption rate
	CES		Pseudo second order	Monolayer and chemical adsorption
Arsenate As(V)	BP	Freundlich		Multilayer and chemical adsorption
	CBP	Langmuir		Monolayer and chemical adsorption
	ES	Freundlich	Elovich	Multilayer and chemical adsorption with exponential decrease in adsorption rate
	CES		Pseudo second order	Multilayer and chemical adsorption

4.7 Comparison of adsorption capacity of adsorbents for Lead removal

ES and BP were used for lead adsorption to compare the adsorption capacity of ES and BP for arsenic and lead removal. At first, the optimum condition for lead removal were investigated based on various adsorbent dose, pH and contact time. Figure 4.25 shows the effect of variation of adsorbent dose, pH and contact time on the lead removal efficiency of ES and BP. The adsorption of lead by ES and BP from 2 mg/L lead solution as a function of adsorbent dose is plotted in graph as shown in Figure 4.25(a). Removal efficiency of 91.45 % and 87.05 % was observed with ES and BP, respectively at a dose of 0.75 g/L. The removal efficiency was further increased with the increment of adsorbent dose but 0.75 g/L was taken as optimum dose for further experiments. In case of removal efficiency at various pH, there was no significant difference in removal efficiency from pH 4-7 as shown in Figure 4.25(b). However, natural water exists at neutral pH and the removal efficiency of ES and BP is 98.55 % and 99.55 % respectively at pH 7. Hence, pH 7 was taken as optimum pH and further experiments were done at pH 7. To find the optimum contact time, time was varied from 10 min to 200 min. The removal efficiency at different period of time is shown in Figure 4.25(c). Lead was adsorbed in shorter period of time with ES compared with BP. Removal efficiency of 100 % and 99.55 % was observed after 40 min and 80 min in case of ES and BP, respectively. This reveals that water contaminated by lead at concentration of 2 mg/L could be treated with ES and BP at a dose of 0.75 g/L, pH 7 and contact time of 40 min and 80 min for ES and BP, respectively.



(a) (contact time: 2 hr) (b) (Dose: 0.75 g/L; time: 2 hr) (c) (Dose: 0.75 g/L; pH: 7)

Figure 4.25: Effect on removal capacity of lead due to various (a) adsorbent dose, (b) pH, (c) contact time. (Initial analyte concentration: 2mg/l, agitation speed: 100 rpm)

The optimum conditions were further used to see the removal efficiency of ES and BP at higher concentration. Figure 4.26 shows the adsorption capacity of 0.75 g/L at higher initial concentration. The results show that ES and BP shows good removal capacity at higher concentration as well. Although initial concentration was increased from 2 mg/L to 25 mg/L, ES could adsorb 70 % of lead and BP could adsorb 79.49 % of lead at 25 mg/L concentration. There was continuous increase in the adsorption capacity as well.

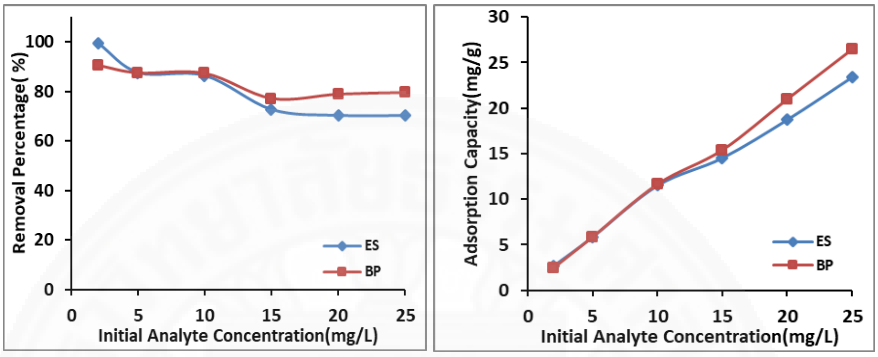


Figure 4.26: Lead removal efficiency of adsorbents at different initial analyte concentration. (Dose: 0.75 g/L; pH:7; contact time: 40 min for ES, 80 min for BP; Speed: 100 rpm)

When experiments for arsenic were done, the optimum dose of adsorbent was taken as 6 g/L. In order to see lead removal capacity of 6 g/L of adsorbents, a set of experiments was done with varying initial analyte concentration. Figure 4.27 represents the resultant graph of removal efficiency and adsorption capacity of 6 g/L of adsorbent at different initial analyte concentration. 6 g/L ES and BP could remove 96.73 % and 98.32 % of lead at an initial concentration of 10 mg/L. But if we see Figure 4.15, arsenic removal capacity is very poor in comparison with the lead removal capacity. ES could remove 44.54 % of As(V) and 33.23 % of As(III) at optimum conditions from 10 mg/L of arsenic concentrated solution. Similary, BP has the potential to remove 36.23 % of As(V) and 31.48 % of As(III). In addition to the comparison of the removal of two metals, optimum dose required to remove certain concenration is also compared. From Figure 4.25(c), it can be seen that 0.75 g/L of ES and BP could remove almost 100 % and 99.55 % of 2 mg/L lead solution. But if we observe arsenic removal efficiency of same adsorbent, even 6 g/L of ES and BP could not remove arsenic more than 72 %. This suggests that it is difficult to remove arsenic in comparison with lead using ES and BP. One of the probable reason is that lead species occurs in the form of cation while arsenic species occur in the form of anion in water (Kanel et al., 2006; Machida, Yamazaki, Aikawa, & Tatsumoto, 2005).

When lead is adsorbed by egg shell, one of the possible mechanisms incudes the ion exchange mechanism. Lead ions gets attached to the surface of the adsorbent substituting the calcium ion of egg shell (Liao et al., 2010). The ion exchange mechanism is illustrated below:

$$Pb^{2+}_{(solution)} + Ca^{2+}_{(adsorbent)} \longrightarrow Pb^{2+}_{(adsorbent)} + Ca^{2+}_{(solution)}$$

The mechanism of adsorption for lead and arsenic is entirely different. In case of arsenic, ions combine with calcium ion and hence is removed from water but lead ions substitute calcium ion. This difference may have caused the variation in the removal efficiency of adsorbent for arsenic and lead removal. Adsorption of lead by using banana peel is due to the presence of functional groups such as OH^-, COO^-. As lead is positively charges ion, these ion gets attached to the surface of banana peel through elctrostatic attraction or Van der Waals force of atraction. But in case of arsenic adsorption, arsenic ions replaces OH^- groups and combines with carbon molecule present in the adsorbent. This mechanism is well explained earlier in edx analysis of banana peel. Therefore, the differences in adsorption mechanism may have resulted in different adsorption capacity for lead and arsenic.

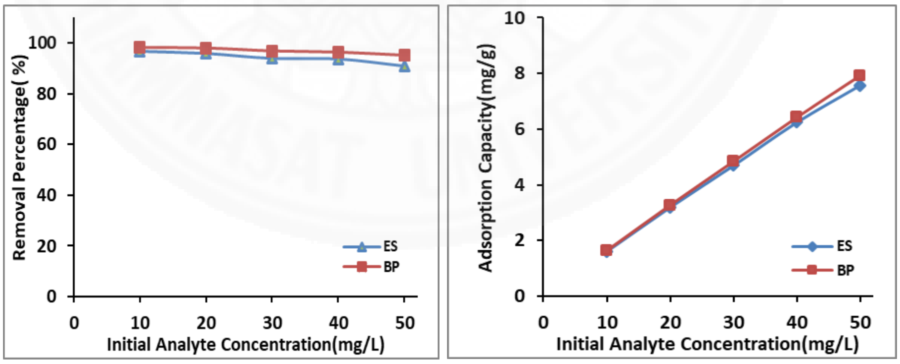
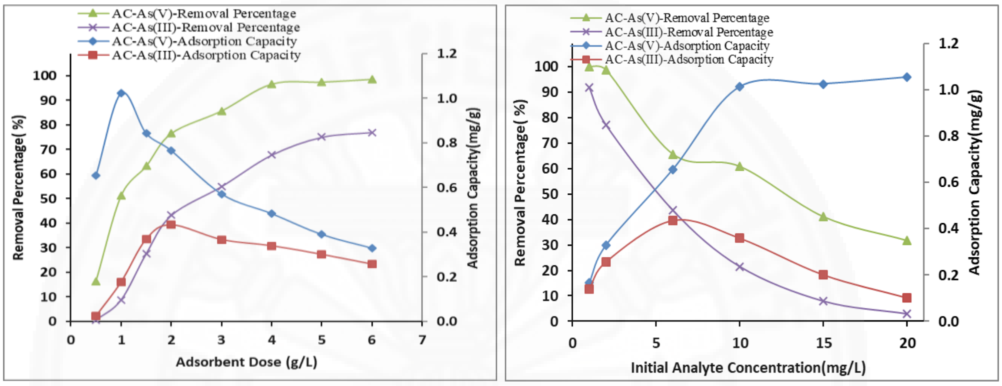


Figure 4.27: Lead removal efficiency of adsorbents at different initial analyte concentration. (Dose: 6 g/L; pH:7; contact time: 40 min for ES, 80 min for BP; Speed: 100 rpm)

4.8 Comparison of adsorption capacity of adsorbents with commercial activated carbon

Arsenic removal capacity of ES and BP was compared with the removal capacity of commercial activated carbon (AC), a baseline adsorbent. Experiments were done to observe the removal capacity of different dosage of AC for 2 mg/L arsenic solution. And other set of experiments were done to investigate the adsorption capacity of 6 g/L of AC for different initial analyte concentration. Figure 4.28 shows the removal efficiency of AC at different adsorbent dose and at various analyte concentration.



(a) (b)

Figure 4.28: Arsenic removal capacity of activated carbon at (a) different adsorbent dose and (b) different initial analyte concentration.

The overall capacity of AC to remove arsenic from solution is higher for As(V) solution compared with As(III) solution. If we observe Figure 4.28(a), arsenic removal percentage increases with the increase in adsorbent dose but adsorption capacity increase at lower dosage and then start to decrease after reaching certain point. The maximum adsorption capacity was 1.02 mg/g to adsorb As(V) at an adsorbent dose of 1 g/L and 0.43 mg/g to adsorb As(III) at an adsorbent dose of 2 g/L. When we use 6 g/L of AC to treat As(III) and As(V) solution at various concentration from 1-20 mg/L, the removal efficiency decreased from 91.67 % to 3.03 % for As(III) uptake and 99.92 % to 31.63 % for As(V) uptake. When As(V) solution is at concentration of 1 mg/L, the treated solution also meets the arsenic standard of 10 µg/L as set by WHO. And As(V) solution at concentration of 2 mg/L also nearly meets the standard after the treatment. But As(III) ions are not effectively removed as As(V) ions. AC removed

96.69 % of As(V) ions from 2 mg/L solution by using a dose of 4 g/L while it removed 77.02 % of As(III) ions by using a dose 6 g/L AC.

When we compare the arsenic adsorption capacity of AC with BP and ES, AC has much higher adsorption capacity then BP and ES. At pH 7, As(III) uptake is 56.66 % , 62.22 %, 64.98 %, and 65.28 % by using BP, CBP, ES and CES, respectively, with a dose 6 g/L. When the study for As(III) adsorption was done with AC, the removal efficiency was found to be 77.02 %. Arsenic removal capacity of AC is much better than the low-cost adsorbents. More improvement is seen in As(V) removal capacity using AC. BP, CBP, ES and CES could remove 57.67 %, 72.94 %, 65.69 %, and 71.62 % of As(V) ion, respectively with 6 g/L adsorbent dose. But when we use AC to adsorb As(V) ion, even 2 g/L of AC could remove 76.58 % of As(V) ion and 6 g/L could remove 98.65 % of As(V) ion. When arsenic concentration increased from 1 to 20 mg/L, As(III) removal efficiency decreased from 91.67 % to 3.03 % and As(V) removal efficiency decreased from 99.92 % to 31.63 % as shown in Figure 4.28 (b). Hence, it is concluded that commercial activated carbon is more efficient to remove arsenic from water. But as we know activated carbon are expensive, the adsorbents used in this study are more suitable to use for arsenic removal in low cost.

4.9 Comparison of adsorption capacity of adsorbents with previous studies

Table 4.16 and Table 4.17 show the summary of the removal efficiency of the adsorbents used in this study for As(III) and As(V) removal, respectively. It is seen that As(III) ions is best removed by CES with 65.28 % removal efficiency. Likewise, As(V) is best removed by CBP with 72.94 % removal efficiency. From this we knew that As(III) removal is lower than As(V) removal and also takes longer period of time to reach equilibrium. Table 4.16 and Table 4.17 also show the comparison of the optimum condition obtained for the removal of arsenic along with the comparison of the isotherm constants with previous studies. Comparing the removal efficiency of the adsorbents used in this study with previously studied adsorbents, it is found that these adsorbents are less efficient than other adsorbents. But when we observe the conditions of the removal then it is noticed that the adsorbents are either toxic and chemically treated that are unfavourable for drinking water treatment or they are not removed in neutral pH or they have very high contact time. In addition, when we compare the isotherm constants, the value of n of the adsorbents used in this study are greater than 2 that represents good adsorption. But most of the adsorbents used previously has the value of n less than 2 that represents moderately difficult adsorption. Taking the optimum conditions into consideration the adsorbents used in this study are considered as better adsorbents than other to treat groundwater. Hence it is encouraging to use a locally available, non-toxic waste material for the treatment of arsenic contaminated water.

Table 4.16: Comparison of optimum condition and isotherm constants of As(III) adsorption with other studies.

Adsorbents	**Optimum Conditions**	**Removal Percentage/ Adsorption Capacity**	**Langmuir**		**Freundlich**		**Reference**
			b (L/mg)	**Q_o (mg/g)**	**K_f**	**n**	
Banana Peel	Initial Concentration (mg/L): 2 Adsorbent Dose (g/L): 6 pH:7 Contact Time (hr): 2.67	56.66 %	0.573	0.571	0.213	2.38	This Study
Banana Peel carbonized at 700 ℃		62.22 %	0.672	0.625	0.251	2.5	
Egg Shell		64.98 %	0.955	0.581	0.269	2.78	
Egg Shell carbonized at 700 ℃		65.28 %	0.933	0.591	0.275	2.78	
Basic Oxygen furnace slag (steel industry)	Initial Concentration (mg/L): 1 Adsorbent Dose (g/L): 10 pH: 7; Contact Time: 12	99.9 %	1.10	1.40	0.502	1.71	(Kanel & Choi, 2016)
Pomegranate Peel ($FeCl_3$ treated)	Initial Concentration (mg/L): 20 Adsorbent Dose (g/L): 1 pH: 9; Contact Time (hr): 2	70.7 %	0.873	50	2.51	1.79	(Thapa & Pokhrel, 2013)
Fish Scale	Initial Concentration (mg/L): 0.5 Adsorbent Dose (g/L): 10 pH: 6.8; Contact Time (hr): 130	83 %	5.2	0.025	0.685	1.64	(Rahaman et al., 2008)
Siderite	Initial Concentration (mg/L): 1 Adsorbent Dose (g/L): 20 Contact Time (hr): 3	1.04 mg/g	1.9	1.040	0.013	0.59	(Guo et al., 2007)

Table 4.17: Comparison of optimum condition and isotherm constants of As(V) adsorption with other studies.

Adsorbents	**Optimum Conditions**	**Removal Percentage/ Adsorption Capacity**	**Langmuir**		**Freundlich**		**Reference**
			b (L/mg)	**Q_o (mg/g)**	**K_f**	**n**	
Banana Peel	Initial Concentration (mg/L): 2 Adsorbent Dose (g/L): 6 pH:7 Contact Time (hr): 1.33	57.67 %	0.346	0.714	0.204	2.08	This Study
Banana Peel carbonized at 700 ℃		72.94 %	1.238	0.641	0.331	3.12	
Egg Shell		65.69 %	0.390	0.892	0.263	2.00	
Egg Shell carbonized at 700 ℃		71.62 %	0.649	0.793	0.316	2.44	
synthetic zeolites (H-MFI-90)	Initial Concentration (mg/L): 10 Adsorbent Dose (g/L): 2 pH: 3.15; Contact Time (hr): 1.6	34.80 mg/g	0.011	34.8	4.21	1.12	(Chutia et al., 2009)
Siderite	Initial Concentration (mg/L): 1 Adsorbent Dose (g/L): 20 Contact Time (hr): 3	0.52 mg/g	6.6	0.516	0.064	0.28	(Guo et al., 2007)
Orange Peel	Initial Concentration (mg/L): 10 Adsorbent Dose (g/L): 10 pH: 7; Contact Time(hr): 2	4.7 mg/g	-	-	0.42	0.72	(Khaskheli et al., 2011)
Oat hulls	Initial Concentration (mg/L): 0.25 Adsorbent Dose (g/L): 0.015 pH:5; Contact Time (hr): 24	58 %	-	2.04	0.42	2.48	(Chuang et al., 2005)
Fish Scale	Initial Concentration (mg/L): 0.33 Adsorbent Dose (g/L): 10 pH: 6.8; Contact Time (hr): 130	94 %	8.8	0.027	0.396	1.54	(Rahaman et al., 2008)

Chapter 5

Conclusions and Recommendations

This chapter presents the conclusions drawn from this study where the adsorption of As(III) and As(V) was investigated using different adsorbents. Some recommendations for future study are also made.

5.1 Conclusions

Several adsorbents investigated including pineapple peel, watermelon peel, pomelo peel, rice husk, coconut husk, sugarcane bagasse, onion, garlic, cilantro, etc, were not found suitable for arsenic adsorption. However, banana peel and egg shell gave better efficiency compared to others. These adsorbents can be found easily by local people and can be used in a simple and economic way. Following conclusions are made for the results obtained using ES and BP.

- FTIR spectra showed that the distinct functional group present in ES is the carbonate group due to the presence of calcium carbonate. Likewise, a broad spectra of hydroxyl group was observed in BP. Involvement of these functional group were noticed while comparing the spectra of the adsorbents before and after adsorption of arsenic.
- BET surface area of BP and ES was 0.4 m^2/g and 0.77 m^2/g and they contain mesopores. From BET surface area analysis of modified samples, it was clear that same modification technique will not favour every adsorbent to increase the surface area, rather it depends upon the original sample itself.
- SEM images revealed that the adsorbents are composed of particles with smooth surfaces.
- EDX analysis showed some changes in chemical composition of adsorbents before and after adsorption. In case of ES, ion exchange mechanism was seen during adsorption.
- Arsenic removal capacity of ES is greater than the arsenic removal capacity of BP under same experimental conditions.

- Arsenic ions are present in different forms which is strongly dependent on pH. Only specific form of arsenic is adsorbed on adsorbents so adsorption processes is highly influenced by pH of the solution. Maximum As(III) ions were adsorbed on pH 9 and maximum As(V) ions were adsorbed on pH 6. In addition, pHzpc of BP is at pH 7.06 and of ES is at 8.03.
- Optimization of contact time revealed that As(III) takes longer time to reach equilibrium than As(V).
- At optimum condition As(III) and As(V) removal efficiency of BP is 63.77 % and 67.12 % respectively. Likewise As(III) and As(V) removal efficiency of ES is 68.54 % and 72.01 % respectively.
- Carbonization of BP helped to improve the removal efficiency from 63.77 % to 69.19 % for As(III) removal and from 67.12 % to 77.8 % for As(V) removal. Such a greater improvement was not seen in case of ES.
- Presence of phosphate and nitrate ions have a great influence on arsenic removal efficiency at pH 7. As the concentration of these ions increases, arsenic removal efficiency of the adsorbents decreases.
- As(III) ions are adsorbed by forming a monolayer on the adsorbents surface and it followed Langmuir adsorption. As(V) adsorption on CBP also showed the best fit to the Langmuir isotherm model suggesting monolayer adsorption. But, As(V) adsorption on BP, ES and CES followed the Freundlich isotherm model indicating multilayer adsorption.
- Adsorption of As(III) and As(V) on BP, CBP and CES followed pseudo-second order kinetic equation indicating that the adsorption process is controlled by chemisorption process. Adsorption of As(III) and As(V) on ES followed Elovich kinetic equation. This also suggests adsorption process is a chemisorption process but adsorption rate on ES decreases exponentially with an increase in quantity of adsorbed ions.
- In some cases, different results were obtained from R^2 value and error analysis tools while selecting the best model and isotherm. This proved that it is not reliable to evaluate the goodness of fit of a model only with the R^2 value, especially when the data points undergo linear transformations.

Thus, it can be concluded that, waste materials like banana peel and egg shell can be used as an adsorbent to treat arsenic contaminated water. Once the adsorbents are put in the water, they are heavy enough to be settled down and can be separated easily. The energy required for the adsorption process is minimum and it is economic as well. This suggests the practical application of the adsorbents to remove arsenic from contaminated water.

5.2 Recommendations for future research

In the present study, batch experiments were done using synthetic water to find out the adsorption capacity under certain conditions. To check the applicability of the adsorbents, future research could be focused on the following points.

- A more detailed characterization of the adsorbents is required in order to understand the adsorption process.
- Investigation of the application of the adsorbents in real groundwater sample should be done.
- Groundwater quality and arsenic contamination level could be studied for a specific area and experiment can be carried out accordingly.
- Household level arsenic filter or filter candle could be designed using adsorbents so that it is easier to filter water rather than doing batch treatment.

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Appendix

Appendix A

Photographs of Experimental Work


Banana Peel and Egg Shell collected from food shop

Grinding the adsorbents in powdered form


Carbonization in muffale furnace


pH meter used during the experiment


Sample preparation for FTIR in the manual bench press


FTIR used during the study

Smart vacuum (sample preparing instrument for surface area analysis).

Flex (N_2 adsorption instrument used for surface area analysis)


Instrument used to do gold coating

Samples coated with gold for SEM-EDX


Standard solution for calibration curve


Sample measurement using WinLab software for ICP-OES


Syringe filters used to filter sample

FESEM equipped with an EDX


Arsenic measurement using ICP-OES


Samples in rotary shaker