REMOVAL OF ARSENIC FROM DRINKING WATER USING ADSORPTION

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
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in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

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CANDIDATE'S DECLARATION

I here by declare that the work, which is being presented in the dissertation work, entitled **"Removal of Arsenic from Drinking water using Adsorption"**, submitted in partial fulfillment of the requirements for the award of **Master of Technology** in **Chemical Engineering** with the specialization in **Industrial Pollution Abatement, Indian Institute of Technology Roorkee, Roorkee** is an authentic record of my own work carried out during the period from July 2005 to June 2006 under the guidance of **Dr.Shri Chand**, Professor & head, Chemical Engineering Department ,Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this project work has not been submitted for the award of any other degree.

Date: 28/06/06

Place: Roorkee

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Increasingly stringent legislation on the permissible concentrations of arsenic in drinking water has led to increased investigations of the occurrence, chemical speciation and mobility of arsenic in natural waters and of methods for removing arsenic during water treatment. Epidemiological studies suggest that there are significant health risks, including cancer, associated with prolonged exposure to elevated arsenic concentrations in drinking water even at quite low concentrations. Although background arsenic concentrations in natural environments are usually low, arsenic concentrations are high in many parts of the world due to mobilization from natural geological sources or at a smaller scale from industrial pollution. While arsenic associated with industrial pollution can be managed by improving process engineering and environmental management practices, making water that has a naturally high arsenic content safe to drink requires some form of water treatment to reduce arsenic concentrations.

In the present study laboratory scale experiments have been carried out using the charcoal (CC) and activated carbon (AC) as adsorbent for the removal of Arsenic. Batch experiments were carried out to determine the effect of various factors such as contact time, pH, adsorbent dose and temperature on adsorption process. Results obtained from these results have been analyzed by various kinetics. From the results it is clear that the removal efficiency will be more for AC than CC at its natural pH in water. Moreover the reaction was completed almost 4 h for AC. Temperature study shows that the uptake of metals by adsorbents was more at the normal temperature (30 °C). The parameters of Pseudo-First order and Pseudo-Second order kinetics have been found. Equilibrium isotherms have been analyzed using Langmuir isotherm and Freundlich isotherm, and parameters have been calculated for both isotherms from the plots.

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INTRODUCTION

1.1 General

Arsenic is a naturally occurring chemical found in the earth's crust, but can be dangerous to humans when released into drinking water supplies when rocks, minerals, and soil erode. Studies have linked long-term exposure to arsenic contamination with cancer and cardiovascular, pulmonary, immunological, neurological and endocrine effects. Arsenic (As) contamination of drinking water is a major health concern, because drinking arsenic contaminated water is linked to several types of cancers. Arsenic is a cancer causing substance which is predominantly present as inorganic species in natural water system. Long-term uptake of arsenic contaminated water causes liver, lung, kidney, bladder, skin and nerve tissue injuries.

The contribution of arsenic to the groundwater from man-made sources is low. Most of the problems arise from natural deposits. Water often passes through many layers of rock on its way to the water table. In some cases, conditions are right for water to pick up arsenic along the way. For example, the combination of sulfur bearing ores, oxygen, and water can produce sulfuric acid that lowers the pH of the water and causes metals including arsenic to leach into the water. In extreme cases, concentrations of arsenic have been found in wells at more than 4,000 ppm.

Unfortunately, there is no known cure for arsenic poisoning and therefore providing arsenic free drinking water is the only way to diminish the adverse health affects of arsenic. Consequently, several methods are proposed to provide arsenic-free water. These methods suggest either the treatment of arsenic contaminated groundwater, or looking for the alternative options (e.g. surface water treatment, rain-water harvesting, etc). The use of alternative water sources, however, can only be possible after a major and costly technological shift and thus, the treatment of arsenic contaminated water to the guideline values is the preferred option. High concentrations of arsenic in water and soil have been documented in Taiwan, Argentina, the USA, Chile and many other countries (Table-1), but of these, the most severe outbreaks of arsenic poisoning have been associated with ground waters in the Bengal Delta including Bangladesh and West Bengal (Eastern India) where an estimated total of 120 million people (80 million in Bangladesh, 40 million in India) are at risk. Arsenic contamination in the affected districts of the Bengal Delta is potentially the greatest environmental calamity ever reported.

Arsenic is an environmental health concern, because long-term epidemiological studies demonstrate that it is toxic to humans and other living organisms. Arsenic is also a social concern in Bangladesh because women affected by arsenic are reportedly discriminated against in their working environments and many have to leave their jobs when skin changes caused by arsenic contaminated water become apparent, leading to economic hardship and social disruption

1.2 SOURCE:

Arsenic is widely distributed throughout the earth's crust. Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks. Industrial effluents also contribute arsenic to water in some areas. Arsenic is also used commercially e.g. in alloying agents and wood preservatives. Combustion of fossil fuels is a source of arsenic in the environment through disperses atmospheric deposition.

Background arsenic concentrations in natural water are low, but elevated arsenic concentrations are common in groundwater as a result of natural conditions or anthropogenic impacts. Natural oxidation and/or reduction reactions involving arsenic-bearing rocks under favorable temperature and pH conditions may mobilize the arsenic and increase arsenic concentrations in groundwater. Human activities that could increase arsenic concentrations in ground waters and surface waters include; oil and coal burning power plants, waste incineration, cement works, disinfectants, household waste disposal,

Table 1.1-World-wide arsenic contaminated areas

Country	Area
Argentina	-----
Bengal Delta	Bangladesh and India
Brazil	Iron Quadrangle
Canada	Nova Scotia and Eastern part
China	Inner Mongolia and Xiangjiang River
Chile	Antofagasta and Chiu Chiu
Denmark	Storstrøms, Århus, Fyns, and Vejle
France	North Mortagne
Finland	Northern part
Germany	Eastern part
Ghana	Ashanti region
Greece	Thessaloniki
Hungary	-----
India	Calcutta
Japan	South Chikugo Fukuoka, Fukul, Takatsuki and Kumamoto
Mexico	Northern part
Norway	-----
Sweden	-----
Russia	western half of the Russian Kola Peninsula
Taiwan	Southwest part
Thailand	Southern part
Turkey	Kütahya and Gediz
UK	----
USA	Central Arizona, New Jersey, Lane County (WA), Nevada, Idaho and Utah
Vietnam	Hanoi Area

glassware production, electronics industries, ore production and processing, metal treatment, galvanizing, ammunition factories, dyes and colours, wood preservatives, pesticides, pyrotechnics, drying agents for cotton, oil and solvent recycling and pharmaceutical works. For more information on the natural and anthropogenic sources of arsenic see the excellent reviews of Matschullat (2000), and Bissen and Frimmel (2003).

Inorganic arsenic can occur in the environment in several forms but in natural waters, and thus in drinking-water, it is mostly found as trivalent arsenite (As (III)) or pentavalent arsenate (As (V)). Organic arsenic species, abundant in seafood, are very much less harmful to health, and are readily eliminated by the body. Drinking-water poses the greatest threat to public health from arsenic. Exposure at work and mining and industrial emissions may also be significant locally.

However, recent studies seem to favor the reduction of Fe/As oxhydroxides as the source for arsenic contamination in groundwater (Nickson et al., 1998). Arsenic forms co-precipitates with ferric oxyhydroxide. Burial of the sediment, rich in ferric oxyhydroxide and organic matter, has led to the strongly reducing groundwater conditions. The process has been aided by the high water table and fine-grained surface layers which impede the penetration of air to the aquifer. Microbial oxidation of organic carbon has depleted the dissolved oxygen in the groundwater. The highly reducing nature of the groundwater explains the presence of arsenite (< 50%) in the water. The "pyrite oxidation" hypothesis is therefore unlikely to be a major process, and the "oxyhydroxide reduction" hypothesis (Nickson et al., 1998) is probably the main cause of arsenic contamination in groundwater. Although the oxyhydroxide reduction hypothesis requires further validation, there is no doubt that the source of arsenic in West Bengal and Bangladesh is geological, as none of the explanations for anthropogenic contamination can account for the regional extent of groundwater contamination. During the past 30 years the use of phosphate fertilizers has increased threefold in this region. The widespread withdrawal of groundwater may have mobilized phosphate derived from fertilizers and from the decay of natural organic materials in shallow aquifers. The increase in phosphate concentration could have promoted the growth of sediment biota and the desorption of arsenic from sediments, and the combined microbiological and chemical process might have increased the mobility of arsenic (Acharyya et al., 1999).

Table 1.2 ARSENIC IN PERIODIC TABLE

Atomic Number	33
Symbol	As
Atomic Weight	74.9216
Discovery	Albertus Magnus 1250? Schroeder published two methods of preparing elemental arsenic in 1649.
Electron Configuration	$[Ar]4s^2 3d^{10} 4p^3$
Word Origin	Latin *arsenicum* and Greek *arsenikon*: yellow orpiment, identified with *arenikos*, male, from the belief that metals were different sexes; Arabic *Az-zernikh*: the orpiment from Persian zerni-zar, gold
Properties	Arsenic has a valence of -3, 0, +3, or +5. The elemental solid primarily occurs in two modifications, though other allotropes are reported. Yellow arsenic has a specific gravity of 1.97, while gray or metallic arsenic has a specific gravity of 5.73. Gray arsenic is the usual stable form, with a melting point of 817°C (28 atm) and sublimation point at 613°C. Gray arsenic is a very brittle semi-metallic solid. It is steel-gray in color, crystalline, tarnishes readily in air, and is rapidly oxidized to arsenous oxide (As_2O_3) upon heating (arsenous oxide exudes the odor of garlic). Arsenic and its compounds are poisonous.
Uses	Arsenic is used as a doping agent in solid-state devices. Gallium arsenide is used in lasers which convert electricity into coherent light. Arsenic is used pyrotechny, hardening and improving the sphericity of shot, and in bronzing. Arsenic compounds are used as insecticides and in other poisons.
Sources	Arsenic is found in its native state, in realgar and orpiment as its sulfides, as arsenides and sulfaresenides of heavy metals, as arsenates, and as its oxide. The most common mineral is *Mispickel* or arsenopyrite (FeSAs), which can be heated to sublime arsenic, leaving ferrous sulfide.

1.3 ARSENIC IN BANGLADESH

In Bangladesh, West Bengal (India) and some other areas, most drinking-water used to be collected from open dug wells and ponds with little or no arsenic, but with contaminated water transmitting diseases such as diarrhea, dysentery, typhoid, cholera and hepatitis. Programmes to provide "safe" drinking-water over the past 30 years have helped to control these diseases, but in some areas they have had the unexpected side-effect of exposing the population to another health problem - arsenic.

Arsenic in drinking-water in Bangladesh is attracting much attention for a number of reasons. It is a new, unfamiliar problem to the population, including concerned professionals. There are millions of people who may be affected by drinking arsenic-rich water. Last, but not least, fear for future adverse health effects as a result of water already consumed.

1.3.1 Background

- In recent years, extensive well drilling programme has contributed to a significant decrease in the incidence of diarrhoeal diseases.
- It has been suggested that there are between 8-12 million shallow tube-wells in Bangladesh. Up to 90% of the Bangladesh population of 130 million prefers to drink well water. Piped water supplies are available only to a little more than 10% of the total population living in the large agglomerations and some district towns.
- Until the discovery of arsenic in groundwater in 1993, well water was regarded as safe for drinking.
- It is now generally agreed that the arsenic contamination of groundwater in Bangladesh is of geological origin. The arsenic derives from the geological strata underlying Bangladesh.

1.3.2 Situation

- The most commonly manifested disease so far is skin lesions. Over the next decade, skin and internal cancers are likely to become the principal human health concern arising from arsenic.
- According to one estimate, at least 100,000 cases of skin lesions caused by arsenic have occurred and there may be many more (Smith, et al, 2000).
- The number of people drinking arsenic-rich water in Bangladesh has increased dramatically since the 1970s due to well-drilling and population growth.
- The impact of arsenic extends from immediate health effect to extensive social and economic hardship that effect especially the poor. Costs of health care, inability of affected persons to engage in productive activities and potential social exclusion are important factors.
- The national standard for drinking-water in Bangladesh is 0.05 mg/L, same as in India.
- District and sub-district health officials and workers lack sufficient knowledge as to the identification and prevention of arsenic poisoning.
- The poor availability of reliable information hinders action at all levels and may lead to panic, exacerbated if misleading reports are made. Effective information channels have yet to be established to those affected and concerned.

1.3.3 Remedial actions

- Within Bangladesh, a number of governmental technical and advisory committees have been formed and a coordinating mechanism established among the interested external support agencies. These committees include the Governmental Arsenic coordinating Committee headed by the Minister of Health & Family Welfare (MHFW) and several technical committees. One of the positive outcomes of this collaboration (including work with local institutes) has been the testing of new types of treatment technologies.
- So far, many initiatives have focused on water quality testing and control with a view to supplying arsenic-free drinking-water, thereby reducing the risk of further

arsenic-related disease. The amount of testing required and the need to provide effective feedback to those using well water, suggest use of field testing kits.

- Only a few proven sustainable options are available to provide safe drinking-water in Bangladesh. These include: obtaining low-arsenic groundwater through accessing safe shallow groundwater or deeper aquifers (greater than 200 m); rain water harvesting; pond-sand-filtration; household chemical treatment; and piped water supply from safe or treated sources

1.4 ENVIRONMENTAL LEVELS AND STANDARDS

Concentrations in water are usually < 10 µg/l, although higher concentrations can occur near natural mineral deposits or anthropogenic sources. Arsenic levels in groundwater average about 1–2 µg/l, except in areas with volcanic rock and sulfide mineral deposits where arsenic levels can range up to 3400 µg/l. In some mining areas arsenic concentrations of up to 48 mg/l have been reported.

WHO's activities on arsenic

WHO's norms for drinking-water quality go back to 1958. The International Standards for Drinking-Water established 0.20 mg/L as an allowable concentration for arsenic in that year. In 1963 the standard was re-evaluated and reduced to 0.05 mg/L. In 1984, this was maintained as WHO's "Guideline Value"; and many countries have kept this as the national standard or as an interim target. According to the last edition of the WHO Guidelines for Drinking-Water Quality:

- Inorganic arsenic is a documented human carcinogen.
- 0.01 mg/L was established as a provisional guideline value for arsenic.
- Based on health criteria, the guideline value for arsenic in drinking-water would be less than 0.01mg/L.
- Because the guideline value is restricted by measurement limitations, and 0.01 mg/L is the realistic limit to measurement, this is termed a provisional guideline value.

The WHO Guidelines for Drinking-water Quality is intended for use as a basis for the development of national standards in the context of local or national environmental, social, economic, and cultural conditions.

1.5 EFFECTS ON HUMANS

Arsenic has long been known because of its acute and long-term toxicity. The first indications for the latter came mainly from its medicinal uses for different purposes. Arsenic has effects on widely different organ systems in the body. It has produced serious effects in humans after both oral and inhalation exposure, it has many end-points, and exposure is widespread all over the world. A peculiarity of arsenic carcinogenicity is that the information mainly comes from experience with exposed humans: it has been unusually difficult to find any animal models. The health effects of arsenic have been reviewed by many national and international organizations (IARC, 1973, 1980, 1987; ATSDR, 1993, 2000; NRC, 1999).

1.5.1 Short-term effects

Ingestion of large doses of arsenic may lead to acute symptoms within 30–60 min, but the effects may be delayed when the arsenic is taken with food. Acute gastrointestinal syndrome is the most common presentation of acute arsenic poisoning. This syndrome starts with a metallic or garlic-like taste associated with dry mouth, burning lips and dysphagia. Violent vomiting may ensue and may eventually lead to haematemesis. Gastrointestinal symptoms, which are caused by paralysis of the capillary control in the intestinal tract, may lead to a decrease in blood volume, lowered blood pressure and electrolyte imbalance. Thus, after the initial gastrointestinal problems, multi-organ failure may occur, including renal failure, respiratory failure, failure of vital cardiovascular and brain functions, and death. Survivors of the acute toxicity often develop bone marrow suppression (anaemia and leukopenia), haemolysis, hepatomegaly, melanosis and polyneuropathy resulting from damage to the peripheral nervous system. Polyneuropathy is usually more severe in the sensory nerves, but may also affect the motor neurones (IPCS, 1981; ATSDR, 2000).

Fatal arsenic poisonings have been described after oral exposure to estimated doses of 2 g, 8 g and 21 g , and cases with non-fatal outcome (usually after treatment and often with permanent neurological sequelae) have been reported after oral doses of 1–4 g up to 8–16 g arsenic. Serious, non-fatal intoxications in infants have been observed after doses of 0.7 mg of arsenic trioxide (As_2O_3) (0.05 mg/kg), 9–14 mg and 2400 mg (4 mg/kg). Incidents of continuous or repeated oral exposure to arsenic over a short period of time have been described. When they drank water containing 108 mg As/litre for 1 week 2 out of 9 exposed persons died, 4 developed encephalopathy and 8 gastrointestinal symptoms. No deaths, but symptoms mainly from the gastrointestinal tract and skin, were observed among 220 patients studied among 447 who had been exposed to arsenic in soy sauce at a level of 100 mg/litre for 2–3 weeks; the estimated daily dose of arsenic was 3 mg. In a mass poisoning in Japan, where 12 000 infants were fed with milk powder inadvertently contaminated with arsenic at a level of 15–24 mg/kg, leading to an estimated daily dose of 1.3–3.6 mg for a period of varying duration, 130 of the infants died.

Fig 1: Causes of Arsenic

1.5.2 Long-term effects: historical introduction

A case of lung cancer associated with exposure to arsenical dust was brought to the notice of the British Factory Department, and some further cases were detected in the early 1940s. These reports were followed by an investigation of the matter, and a remarkably elevated relative cancer mortality rate from lung and skin cancer was observed in a sheep-dip factory manufacturing sodium arsenite. Several further case series also reported unexpectedly high lung cancer mortality in different occupational exposure situations.

Chronic skin effects of arsenic, including pigmentation changes, hyperkeratosis and skin cancer, from medicinal use but also from drinking-water, were reported as early as the 19th century. A large number of case series on arsenical skin cancer after exposure via drinking-water were published from Argentina, Chile, Mexico and Taiwan in the early 1900s.

An endemic peripheral vascular disease (PVD), known as black foot disease (BFD), leading to progressive gangrene of the legs, has been known in Taiwan since the 1920s. It has increased in prevalence since the 1950s, and has been the subject of intense investigation since the late 1950s.

1.6. Arsenic Measurement Methods:

To measure the total inorganic arsenic present in the Water Sample there are so many analytical and instrumental methods are available. Here some of the methods have been described. For our process Atomic Absorption Spectroscopy and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) have been used.

- Spectrophotometric Methods

  Marsh test (not a Spectrophotometric method, only to determine the presence of arsenic). Molybdenum blue method (only arsenate can be measured, method interferes with the presence of phosphate and silicate) Silver diethyldithiocarbamate method (commonly used for determination of arsenic in water).

- Electrochemical Techniques

  Not commonly used due to severe interferences, Can be used to measure As(III) in the presence of As(V).

- Atomic Absorption Spectrometry

  i) FAAS1 (serious interferences and high detection limit (1 mg/L))
  ii) GFAAS2 (widely used but matrix modifiers are needed)

- Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES)

  High detection limit (30 µg/L), Suffers from interferences, Frequently coupled with hydride generation system to overcome interference and high detection limit.

- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Superior to other methods due to very low detection limit and multi-element capability.

- Hydride Generation Techniques (HG)

Widely used and can be connected to various detection systems, Arsenic speciation is possible with a pH control of hydride generation reaction.

CHAPTER-2

ARSENIC REMEDIATION TECHNOLOGIES

2.1 General Processes for Arsenic Removal

There are nine general categories of remediation processes for arsenic removal:

1. Oxidation

Of the two predominant forms of arsenic in water, arsenate and arsenite, most treatment processes are effective at removing arsenate, but not arsenite, since arsenite is typically non-charged below pH 9.2. Therefore, treatment for the removal of arsenic often includes an oxidation step to convert arsenite to arsenate.

Oxidation can be simply the addition of oxygen to a compound, or more generally, any reaction involving the loss of electrons from an atom. Aeration, the supplying of air, oxidizes arsenic, converting arsenite to arsenate, and the iron that co-occurs. This is precipitated as $FeAsO_4$. Arsenic can also be oxidized by a number of other chemicals including chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide and Fenton's reagent (H_2O_2/Fe^{2+}). Photochemical oxidization proceeds from the reaction of radiant energy and a chemical system. Oxidation alone does not remove arsenic from solution but must be combined with an arsenic removal process.

2. Coagulation/Co-Precipitation

Coagulation encompasses all reactions, mechanisms and results in the overall process of particle growth (floc formation) and particle aggregation within water being treated, including in situ coagulant formation, chemical particle destabilization and physical inter-particle contacts. Coagulation involves the removal of colloidal (0.001 - 100 microns) and settleable (> 100 microns) particles. However the term also commonly refers to the removal of dissolved ions (< 0.001 microns), which is actually precipitation. Chemical precipitation is the process by which dissolved ions in solution form an insoluble solid via a chemical reaction. For example, naturally occurring dissolved iron in groundwater, when exposed to oxygen, forms a precipitate. Co-precipitation occurs when an inorganic contaminant forms an insoluble complex with the coagulant. Both the valence of the inorganic contaminant and the pH of the solution are important removal by co-precipitation.

There are 4 types of co-precipitation:

- *Inclusion*: Mechanical entrapment of a portion of the solution surrounding the growing particle. Typically, this only is significant for large crystals.

- *Adsorption*: The attachment of an impurity onto the surface of a particle or precipitate. This type of co-precipitation is generally not important if the particle size is large, because large particles have very small surface areas in preparation to the amount of precipitate they contain. Adsorption may be a major means of contaminant removal if the particles are small.

- *Occlusion*: A contaminant is trapped in the interior of a particle of precipitate. This type of co-precipitation occurs by adsorption of the contaminant onto the surface of a growing particle, followed by further growth of the particle to enclose the adsorbed contaminant.

- *Solid-solution formation:* Another type of occlusion where a particle of precipitate becomes contaminated with a different type of particle that precipitates under similar conditions and is formed from ions whose sizes are nearly equal to those of the original precipitate.

Coagulation converts soluble arsenic into insoluble reaction products, allowing separation by sedimentation and/or filtration. Factors affecting arsenic removal by coagulation/precipitation include coagulant type and dose, mixing time and speed, pH, arsenic oxidation state and concentration, presence of inorganic solutes.

Three mechanisms are potentially involved in arsenic removal:

- Precipitation: The formation of insoluble compounds Al (AsO_4) or Fe (AsO_4).
- Co-precipitation: Incorporation of soluble arsenic species into the metal hydroxide floc.
- Adsorption: The electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxides.

Direct precipitation plays the least important role in arsenic removal however; co-precipitation and adsorption are both active arsenic removal mechanisms.

3. Sedimentation

Sedimentation is the gravity separation of solids from liquid by settling. It is generally used in conjunction with coagulation/precipitation.

4. Filtration

Conventional filtration is the separation of solid particles from water by passing the solution through a medium. Particles are removed during filtration as a result of any one or combination of mechanisms: mechanical straining, sedimentation, flocculation, adsorption and/or biological metabolism (AWWA, 1999). The filter medium may be of various materials, for example, sand, anthracite coal, activated carbon, cloth, paper, that retains the solid on its surface and allows the water to pass through. Common particulates removed by filtration include silt, clay, colloidal and precipitated natural organic matter, naturally-occurring iron and manganese precipitates, precipitates from metal salt or polymer coagulation, microorganisms. Filters may be classified in various ways, according to the type of granular medium used, by the hydraulic system (e.g. gravity, up-flow, etc.), rate of filtration, and/or by the location of particle accumulation (e.g. cake filtration, depth filtration).

5. Adsorption

Adsorption is the accumulation of materials at an interface, the liquid/solid boundary layer. It is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces.

Adsorption can take place on suspended particles, as part of the process of coagulation/co-precipitation, or on fixed media. Since adsorption is a surface phenomenon, the greater the surface area of the medium, the greater it's capacity to accumulate material. Each adsorbent medium has different associated properties, performances and costs. Arsenic is adsorbed onto the surface of various granular, activated, clay and celluosic adsorbents, including:

- Oxides (e.g. hydrated ferric oxide, titanium oxide, silicium oxide)
- Iron oxide-coated or MnO_2-coated sand
- Bauxite, hematite, feldspar
- Clay minerals (e.g. kaolinite, bentonite, Bijoypur clay)
- Synthetic anion exchange resins;
- Chitin and chitosan
- Bone char
- Cellulose materials (sawdust, newspaper pulp).

6. Ion Exchange

Ion exchange is the reversible interchange of ions between the solid and the liquid phase where there is no permanent change in the structure of the solid. Developed for large-scale applications, ion exchange is probably not appropriate for small hand-pumped wells, but could potentially be used on a village scale in Bangladesh.

Synthetic ion exchange resins are based on a cross-linked polymer matrix, typically composed of polystyrene cross-linked with vinyl benzene. Charged functional groups are attached to the matrix through covalent bonding and fall into four groups

- Strongly acidic
- Weakly acidic
- Strongly basic
- Weakly basic

Various strong base anion exchange resins are commercially available that can effectively remove arsenic from water, producing effluents with less than 1 μg/L arsenic.

Arsenic, being uncharged, is not removed, unless an oxidation step to convert arsenite to arsenate is included in the process.

Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Ion exchangers are typically down-flow, packed bed columns with ion exchange resin beads pre-saturated with an exchangeable ion. Source water is passed through the packed bed until the appearance of the unwanted contaminant in the effluent. At this stage, the ion exchange media is reactivated with a regenerant solution and rinsed with water in preparation for another treatment cycle. Both the redox potential and pH are important factors with regard to arsenic removal by ion exchange.

7. Membrane/Reverse Osmosis

Membrane separation uses semi-permeable membranes that are selectively permeable to water and certain solutes to separate impurities from water. Membranes are able to remove many different kinds of dissolved solids, including arsenic, from water. However, they are usually expensive and therefore are typically considered in applications such as desalination, brackish water conversion and for removal of specific ions, such as arsenic, that are difficult to remove by other means. There are many different membrane alternatives including microfiltration, reverse osmosis, electrodialysis, ultra filtration and nanofiltration. Membrane process treatment performance is dependent on the quality of the feed water and the desired quality of the product water. Generally the more contaminated the feed water and the higher the desired product water quality, the greater the likelihood of membrane fouling caused by particulate matter, scaling and biofouling.

8. Biological

Biological treatment transforms, stabilizes and/or removes arsenic by means of microorganisms. Microorganisms, primarily certain specific bacteria, accomplish this by oxidation/reduction, mineralization, detoxification or methylation. Critical factors include energy and carbon source; aerobic, anoxic or anaerobic conditions; temperature; pH.

9. Other

- *Dug Wells*
- *Deeper Tube Wells*
- *Ponds*
- *Solar Distillation*

  Solar distillation uses the sun's energy to evaporate water, which then recondences. The process of evaporation and recondensation separates all chemicals, including arsenic, from the water. In Bangladesh, where solar energy is plentiful, this approach may be especially suited for application in crisis areas, and, if cost-effective approaches can be developed, in rural areas generally.

2.2 Comparing Arsenic Removal Technologies

This section provides a comparison for the most commonly used arsenic removal methods, the main advantages and disadvantages of each method. Various treatment technologies have been proposed in the literature for the removal of arsenic from water.. Although many of these technologies are well developed (with some already implemented at the community level), they are often considered expensive and consequently, new cost effective technologies applicable at small scales remain in demand.

When choosing a removal method, it is necessary to consider the final desired concentration as well as the associated costs and the feasibility of monitoring this goal. The natural distribution of inorganic arsenic species i.e. arsenite and arsenate in water influences both the treatment strategy and the removal efficiency. The anionic characteristics of arsenate promote its removal, whereas the neutral characteristics of arsenite limit its removal efficiency in conventionally applied physicochemical treatment methods at near neutral pH values.

Here, it is proposed that for an appropriate arsenic removal technique the following requirements should be fulfilled:

2.2.1 Water quality

- The selected method must be effective enough to meet the required water quality standards for arsenic.
- The necessity of meeting other water quality standards besides arsenic is highlighted. If the applied method is not capable of meeting the standards for other water contaminants or if the technology itself is a source of unwanted contaminants to the water, a secondary treatment may be needed, hence increasing the overall cost.
- The selected method must perform well in the combined presence of potentially competing ions such as phosphate, silicate, sulfate and bicarbonate, and the method should be tested using natural water samples.

2.2.2 Economy

The expected cost of the method in terms of set-up, operation and maintenance should be affordable.

2.2.3 Operation & Maintenance

- Simple operational and maintenance requirements should be preferred in addition to minimal energy requirements.
- Optimum pH range for the removal needs to be taken into account, as changing the pH during, before or after the treatment may not be practical. Moreover, if the method is effective within a small range of pH it may be difficult to maintain this pH throughout the removal.

2.2.4 Safety & Reliability

- Operation of the process should be safe, reliable and robust.
- Storage and handling of any required chemicals should be addressed, including the associated costs.
- The method should preferably be effective in removing both arsenite and arsenate species.

2.2.5 Social acceptance

The likely acceptance of the method by local residents should be evaluated.

2.2.6 Environmental effects

- If other pollutants are produced as a result of the treatment such as wastewater and toxic sludge, their treatment should be addressed.
- Occupational health (hazard potential of the utilised chemicals) should be considered.

2.2.7 The process must also be evaluated by answering the following questions:

- Can the process meet new stringent standards?
- If a sorption process is applied, is the regeneration of the sorbent possible and favorable, and is it possible to address the safe handling and disposal of the spent regenerate?

In the following sections the main arsenic removal methods and their process characteristics are reported, and those most widely used are accompanied by a brief description of their main advantages and disadvantages.

2.3 Oxidation

Most of the arsenic removal technologies perform better when removing anionic arsenate than uncharged arsenite at circum-neutral pH values. Therefore, a pre-oxidation step before applying the main removal process is commonly included as the first treatment step towards arsenic-free drinking water. Although arsenite should be readily oxidised to arsenate by dissolved oxygen, it persists in aerated waters due to slow oxidation reaction kinetics .Chlorine, ozone, potassium permanganate, manganese oxides and hydrogen peroxide can be used to accelerate oxidation and promising results have been reported using UV light for the oxidation at the presence of dissolved iron compounds. All oxidants have their advantages and disadvantages that should be taken into account when choosing the one to be used. For instance, although high oxidation efficiency is obtained using chlorine, the possibility of producing elevated concentrations of unwanted disinfection by-products with organic matter, and the release of taste and odor compounds from algal cells should be considered. Potassium permanganate, on the other hand, produces no harmful by-products, but may produce colour in the water and cause filtration problems later in the treatment plant. It should be noted that oxidation alone cannot serve as a sufficient technology for arsenic removal, though it may well be employed as a pre-treatment step to increase the efficiency of the main removal method. Biological oxidation of iron and manganese may be inexpensive, but is not yet fully established.

2.4 Chemical Precipitation through Coagulation-Filtration

Chemical precipitation through coagulation filtration includes alum coagulation, iron coagulation and lime softening. Coagulants are those substances that are capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about. Entrapment during coagulation removes the particulate arsenic but mechanisms other than entrapment are required to remove soluble arsenic. Co-precipitation occurs when an inorganic contaminant (e.g. arsenic) forms an insoluble complex (e.g. metal hydroxide flocs) with the coagulant. This may occur via adsorption, inclusion or occlusion (Edwards, 1994). Aluminum or ferric chlorides/sulfates can be added as coagulants, and following their addition the relevant amorphous aluminum hydroxide (Al $(OH)_3$) or ferric hydroxide ($Fe(OH)_3$) is precipitated. Moreover, the addition of aluminum or iron coagulants facilitates the conversion of soluble inorganic arsenic species into insoluble products by precipitation, co precipitation or adsorption. The formation of these insoluble products facilitates their subsequent removal from the water by means of sedimentation and filtration processes. The following reactions illustrate the arsenate, and arsenite, adsorption involved in the process (after Edwards, 1994):

$$Fe - OH + H_2AsO_4^- + H^+ \rightarrow Fe - H_2AsO_4 + H_2O$$
$$Fe - OH + H_3AsO_3^- \rightarrow Fe - H_2AsO_3 + H_2O$$

These reactions can be used to represent the arsenate and arsenite adsorption in the processes, respectively. Here, Fe-OH is a hydroxide surface site. At high coagulant dosages the adsorption of inorganic arsenic to precipitated metal hydroxide solids takes place, but entrapment of adsorbed contaminants in the interior of the growing particle and solid-solution formation may also take place, especially at low coagulant dosages. Lime treatment is similar to coagulation with trivalent metal salts but instead of metal hydroxides, hydrated lime ($Ca(OH)_2$) or $Mg(OH)_2$ solids form. Here the main arsenic removal mechanisms involve calcite precipitation (less effective) and sorption to $Mg(OH)_2$ solids (more effective).

The process, however, can not serve as a major arsenic removal mechanism due to the low removal efficiencies, and unfavorable operating conditions (very high pH and chemical dose rates are required). Previous studies have concluded that arsenate is more effectively removed than arsenite when using coagulation, thus a pre-oxidation step to oxidise arsenite to arsenate is beneficial. In addition, coagulation also has other limitations. In particular, coagulation has the disadvantage of high daily toxic sludge production. Consequently, the method cannot be readily applied to small and intermittent flows. Furthermore, if the water contains large amounts of phosphate and fluoride along with the arsenic, optimum conditions for arsenic removal may not be compatible with conditions favoring the removal of these other anions. The costs associated with this method include coagulation chemicals, pH adjustment before and after treatment, and sludge residue management.

The advantages of this method can be summarised as:

- The method is already in use in many water treatment facilities.
- No monitoring of a breakthrough point is required (though it may still be used to confirm the arsenic removal).
- The chemicals required are simple and low cost.
- The process has been tested in full scale applications.
- Arsenic removal efficiency may be independent of the initial arsenic concentration.

Whereas the associated disadvantages are:

- The procedure is effective only over a narrow pH range and coagulant dosage.
- Disposal of arsenic contaminated coagulant sludge (toxic) poses problems.
- The presence of competing ions needs to be considered.
- Safe storage of chemicals needs to be addressed.
- Arsenite needs to be oxidised to arsenate for effective removal.
- Disinfection is needed (but chlorination may have some adverse effects).
- Secondary treatment is necessary to meet the arsenic standard in lime treatment systems.

2.5 Adsorption, Surface Precipitation and Ion Exchange

Adsorption systems are becoming more popular, especially in small scale treatment systems such as at the household level (Thirunavukkarasu et al., 2003). This is important in countries like Bangladesh, where the water system is not centralised and individual households or small groups are served by their own well. Adsorption is a mass transfer process, which refers to the accumulation of sorbates at the liquid/solid interface. Arsenic can be sorbed to several sorbents. Some of the widely used arsenic sorbents are later compared in terms of their adsorption capacity. Adsorption data in the literature cannot, however, be easily compared with one another due to large reported (or not reported) differences in experimental procedures and conditions.

Thus, the comparison is made by simply providing the reported experimental conditions along with the adsorption capacity data. One of the most common methods for arsenic removal from water is the precipitation of arsenic as calcium arsenates or ferric arsenates at an optimum pH range, which varies for each and exhibits solubility minima. In these precipitation processes, dissolved ions in a solution form an insoluble solid via a chemical reaction e.g. naturally occurring dissolved iron forms a precipitate when it is exposed to air.

Although ion exchange resins can be used to remove arsenic from water over a wide pH range, different resins have different exchange capacities; e.g. conventional sulfate resins are particularly suited for arsenate removal, but uncharged arsenite cannot be removed. In addition, another concern is that competing anions, especially sulfate, obstruct arsenic removal because most of the resins are more selective towards sulfate. The associated costs of these methods include pH adjustment, operation and maintenance costs, the cost of the sorbent itself, and safe handling of the spent sorbent (disposal or regeneration).

The advantages of this method can be summarized as:

- User friendly at the household level (e.g. chemical addition may not be required).
- These methods may be cheap depending on the adsorbent used.
- Several low cost new adsorbents are available, or there are endless possibilities to develop new ones.
- There is no daily sludge production problem.
- The efficiency of the ion exchange process is less sensitive to the pH of the water.

Whereas the main disadvantages are:

- Periodic regeneration of the sorbent may be required depending on the sorbent.
- Requires monitoring of breakthrough or filter use.
- These methods may be expensive depending on the sorbent.
- pH adjustment before and after the process may be necessary.

- Chemical handling may be difficult for some small systems.
- Pre-oxidation is generally required, but the oxidants may harm the ion exchange resin.
- Ion exchange efficiency will be limited by competition with other anions (e.g. sulfate, phosphate, nitrate etc.) and pre-treatment may be necessary.
- Bicarbonate removal during the ion exchange process reduces the pH and increases the corrosiveness of the treated water.
- If ion exchange is used beyond the point of sulfate exhaustion, the removed arsenic may be released back into the treated water.

2.6 Membrane Technologies

Membrane units include coagulation/microfiltration, reverse osmosis (e.g. nanofiltration and hyper filtration) and electrodialysis and uses special filter media that physically retain the impurities present in water. When arsenic contaminated water passes through the media, all kinds of impurities, including arsenic, are removed from the water. The process is expected to have high arsenic removal efficiency as a result of the small molecular weight of dissolved arsenic species (<150 Daltons). Furthermore, when the membrane is slightly negatively charged, it is advantageous for the removal of arsenic from water. Source water quality and the effluent concentration to be reached are important design parameters. If the water is free of suspended solids before the membrane treatment, then the process can be very effective, but high capital and operational costs are major concerns. The costs associated of these methods include the cost of membrane unit construction (e.g. pumps, etc.) as well as additional treatment costs (especially at high initial arsenic concentrations).

The advantages of membrane can be summarized as:

- Membrane technologies can be very effective at the household level.
- Pre-oxidation may not be necessary.
- The process efficiency is independent of pH within the pH 4-8 range.
- The process requires little space.
- Well defined high removal efficiency is superior to other methods.
- The process functions without any chemical addition.
- No solid waste produced as a result of the treatment.
- The process is capable of removal of other dissolved contaminants, if any.
- Disposal of used membranes is simple.

Whereas the associated disadvantages are:

- High running and investment cost is a limitation.
- The method usually requires a power source that may not always be available (e.g. in the Bangladesh delta area) or may be unreliable.
- Pressure, flow rate, and pH needs to be controlled.
- Guideline values are not met for high initial arsenic concentrations.
- Pre-treatment of the water may be necessary e.g. for removing salts.
- Re-adjustment of water quality after the treatment may be required.
- More highly contaminated wastewater is produced as a result of the process.
- Membrane technologies work better for arsenate, but the membrane may not withstand the oxidant used to oxidise any arsenite.
- For long term use of these methods fouling must be considered.

2.7 Other Processes

In addition to the widely used methods discussed above, some other methods are also reported in the literature including microbial processes, *in-situ* immobilization, point of use units and taking advantage of naturally occurring iron.

2.7.1 Microbial processes

Several bacteria are capable of oxidizing arsenite to arsenate thereby eliminating the need for the use of oxidants in other treatments. Furthermore, during biological treatment, the microorganisms can not only change arsenic speciation, but can also remove arsenic at various conditions of temperature, pH, etc. The action of sulfate reducing bacteria is reported by Jong and Parry (2003) to decrease the soluble arsenic concentration, but the exact removal mechanism involved is not yet clear.

2.7.2 *In-situ* immobilization

The cost of *in-situ* immobilization includes both the cost of the chemical used (e.g. potassium permanganate or zero valent iron) and the cost of applying the chemical where it can interact with the arsenic contaminated water. The advantage of the method is that since it is *in-situ* no concentrations of waste are produced. Unfortunately, only a few studies have examined in-situ immobilization, and the effect on the environment is not well established.

2.7.3 Point-of-use units

With point-of-use units that make use of one or more of the techniques discussed above, the costs include those of the sorbent as well as costs associated with monitoring and maintenance. The method can be reliable and easy to handle and may be cost-effective, particularly where electricity is not required. However, regeneration of the sorbent and monitoring and maintenance are required and may not be easily undertaken in remote or under developed areas where arsenic contamination in drinking water is a problem. This method can only be a temporary solution.

2.8 Using naturally occurring iron

In Bangladesh and India the groundwater often contains excess iron in addition to the arsenic and this situation may be taken advantage of to remove arsenic. The naturally occurring iron is present in the groundwater as the dissolved ferrous iron and under appropriate redox and pH conditions this ferrous iron readily oxidises to form a fresh ferric hydroxide ($Fe(OH)_3$) precipitate that will remove arsenic. High arsenic removal efficiencies may be achieved where iron concentrations are sufficiently high (Mamtaz and Bache, 2001). Although the method looks promising and may be useful in some areas, it has a major limitation because there is no clear correlation between the iron and the arsenic concentrations in the groundwater. However, the method could be applied effectively by aerating extracted groundwater and removing any arsenic contaminated ferruginous precipitate by simple filtration using a sand filter. Even where there is insufficient iron in the water, this method could be used to remove some of the arsenic before final water treatment using one of the other methods, thereby reducing the costs involved in the final treatment

CHAPTER-3

ADSORPTION FUNDAMENTALS

3.1. General

Adsorption is a surface phenomenon. The material adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent. In the water purification, adsorbents are used to remove organic impurities, particularly those that are non-biodegradable or associated with taste, color, and odor. Although adsorption is applied in low concentration, recent physical-chemical processes use adsorption as a primary technique to remove soluble organics from the wastewater. The adsorption is called physical when relatively weak intermolecular forces cause the attachment and, chemical when chemical bonding like forces causes this attachment.

During adsorption, the solid adsorbent becomes saturated or nearly saturated with the adsorbate. To recover the adsorbate and allow the adsorbent to be reused, it is regenerated by desorbing the adsorbed substances (i.e. the adsorbates).

3.2. Physical Adsorption Vs. Chemisorption

Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent. In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved. In chemisorption, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals, which are bound separately.

Physical adsorption from a gas occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat, similar in magnitude to the heat of condensation.

Physical adsorption occurs quickly and may be monomolecular (unimolecular) layer or monolayer, or two, three or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

In contrast, chemisorption is monolayer, involves the formation of chemical bonds between the adsorbate and adsorbent, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater than 200 ^{0}C, and may be slow and irreversible.Most commercial adsorbents rely on physical adsorption; while catalysis relies on chemisorption. A comparison between physical adsorption and chemical adsorption is given in Table 4.1.

3.3 Intraparticle Diffusion Process

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites with the particles. This can be broken conceptually into a series of consecutive steps.

- Diffusion of adsorbate across a stationary solvent film surrounding each adsorbent
- Diffusion through the macro pore
- Diffusion through micro pore
- Adsorption at an appropriate site

It is assumed that the fourth step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So, it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "intra-particle transport" which comprises of surface diffusion and molecular diffusion. Several researchers have shown that surface diffusion is the dominant mechanism and is the ratedetermining step. A functional relationship common to most of the treatments of intra-particle transport is that the uptake varies almost proportionally with square root of time.

3.4. Stages In Adsorption Process

Adsorption is thought to occur in three stages, as the adsorbate concentration increases.

Stage I: First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it.

Stage II: As the fluid concentration is further increased, second, third etc., layers form by physical adsorption; the numbers of layers which can form are limited by the size of the pores.

Stage III: Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

3.5. Adsorption Isotherms

When a solution is contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amounts of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The equilibrium data at a given temperature are represented by adsorption isotherm and the study of adsorption is important in a number of chemical processes ranging from the design of heterogeneous chemical reactors to purification of compounds by adsorption.

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. Langmuir, Freundlich, Brunauer-Emmet-Teller (BET), Redlich-Peterson (R-P) etc. are most commonly used adsorption isotherm models for describing the dynamic equilibrium. The isotherm equations used for the study are described follows:

3.5.1. Langmuir Isotherm

This equation based on the assumptions that:

1. Only monolayer adsorption is possible.
2. Adsorbent surface is uniform in terms of energy of adsorption.
3. Adsorbed molecules do not interact with each other.
4. Adsorbed molecules do not migrate on the adsorbent surface

The adsorption isotherm derived by Langmuir for the adsorption of a solute from a liquid solution is:

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e}$$

where,

Q_e = Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium

Q_m = Amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer adsorption (limiting adsorbing capacity).

K_A = Constant related to enthalpy of adsorption

C_e = Concentration of adsorbate solution at equilibrium

The Langmuir isotherm can be rearranged to the following linear forms:

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m}$$

Or

$$\frac{1}{Q_e} = \left(\frac{1}{K_A Q_m}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{Q_m}\right)$$

3.5.2. Freundlich Isotherm

The heat of adsorption in many instances decreases in magnitude with increasing extent of adsorption. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer .The equation that describes such isotherm is the Freundlich Isotherm, given as:

$$Q_e = K_F C_e^{\frac{1}{n}}$$

where ,

K_F and n are the constants

C_e = the concentration of adsorbate solution at equilibrium

By taking logarithm of both sides, this equation is converted into a linear form:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Thus a plot between ln Q_e and ln C_e is a straight line. The Freundlich equation is most useful for dilute solutions over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on to the activated carbon. A high K_F and high 'n' value is an indication of high adsorption through out the concentration range. A low K_F and high 'n' indicates a low adsorption through out the concentration range. A low 'n' value indicates high adsorption at strong solute concentration

3.5.3. Redlich-Peterson isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R–P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$$

Where K_R is R–P isotherm constant (L/g), a_R is R–P isotherm constant (L/mg) and β is the exponent which lies between 1 and 0, where β=1

$$Q_e = \frac{K_R C_e}{1 + a_R C_e}$$

It becomes a Langmuir equation. Where β=0

$$Q_e = \frac{K_R C_e}{1 + a_R}$$

i.e. the Henry's Law equation

Eq. (4.6) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{Q_e} - 1\right) = \ln a_R + \beta \ln C_e$$

Plotting the left-hand side of equation (4.9) against ln C_e to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R andβ. Therefore, a minimization procedure was adopted to solve equation (4.9) by maximizing the correlation coefficient between the theoretical data for Q_e predicted from equation (4.9) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with any suitable computer programme.

3.5.4. The Temkin isotherm

It is given as

$$q_e = \frac{RT}{b}\ln(K_T C_e)$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where $B_1 = \frac{RT}{b}$

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin and Pyzhev, 1940; Kim et al. 2004). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively. K_T is the equilibrium binding constant (l mol^{-1}) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption.

3.5.5. Dubinin-Radushkevich (D-R) isotherm

It is given as:

$$q_e = q_s \exp(-B\varepsilon^2)$$

Where, q_s is the D-R constant and ε can be correlated as:

$$\varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{\mathrm{C_e}}\right)$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [Hasany and Chaudhary, 1996]:

$$E = 1/\sqrt{2B}$$

3.6. ADSORPTION PRACTICES

Adsorption systems are run either on batch or on continuous basis. Following text gives a brief account of both types of systems as in practice.

3.6.1. Batch Adsorption Systems

In a batch adsorption process the adsorbent is mixed with the solution to be treated in a suitable reaction vessel for the stipulated period of time, until the concentration of adsorbate in solution reaches an equilibrium value. Agitation is generally provided to ensure proper contact of the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or settling. The adsorbent can be regenerated and reused depending upon the case.

3.6.2. Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of waste wasters and are widely used for treating domestic and industrial wastewaters. They may be operated either in the up flow columns or down flow column. Continuous counter current columns are generally not used for wastewater treatment due to operational problems. Fluidized beds have higher operating costs. So these are not common in use. Wastewater usually contains several compounds which have different properties and which are adsorbed at different rates. Biological reactions occurring in the column may also function as filter bed retaining solids entering with feed. As a result of these and other complicating factors, laboratory or pilot plant studies on specific wastewater to be treated should be carried out. The variables to be examined include type of adsorbent, liquid feed rate, solute concentration in feed and height of adsorbent bed.

3.7. Factors Controlling Adsorption

The amount adsorbed by an adsorbent from the adsorbate solution is influenced by a number of factors are given as:

1. Initial concentration
2. Temperature
3. pH
4. Contact time
5. Degree of agitation
6. Nature of adsorbent

3.7.1. Initial Concentration

The initial concentration of pollutant has remarkable effect on its removal by adsorption. The amount of adsorbed material increases with the increasing adsorbate concentration as the resistance to the uptake to the solution from solution of the adsorbate decreases with increasing solute concentration. Percent removal increases with decreasing concentrations.

3.7.2. Temperature

Temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents.

3.7.3. pH

Adsorption from solution is strongly influenced by pH of the solution. The adsorption of cations increases while that of the anions decreases with increase in pH. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by pH of solution. Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. It is an evident observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions.

3.7.4. Contact time

The studies on the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption, most of the adsorbate species are adsorbed on the adsorbent surface with in short contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. Strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of heavy metals is fast at the initial stages of the contact period, and there after it becomes slow near equilibrium.

3.7.5. Degree of agitation

Agitation in batch adsorbers is most important to ensure proper contact between the adsorbent and the solution. At lower agitation speed, the stationary fluid film around the particle is thicker and the process is mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film reduces and after a certain point, the process becomes intra particle diffusion controlled. Whatever is the extent of agitation the solution inside the process remain unaffected and hence for intraparticle mass transfer controlled process agitation has no effect on the rate on the adsorption.

3.7.6. Nature of adsorbent

Many solids are used as adsorbents to remove the impurities from fluids. Commercial adsorbents generally have large surface area per unit mass. Most of the surface area is provided by a network of small pores inside the particles. Common industrial adsorbents for fluids include activated carbon(ACC), silica gel, activated alumina, molecular sieves etc. Adsorption capacity is directly proportional to the exposed surface. For the non-porous adsorbents, the adsorption capacity is directly proportional to the particle size diameter whereas for porous materials it is practically independent of particle size.

ACC is the most widely used adsorbent for water purification. In the manufacture of activated carbon, organic materials such as coal nutshells, bagasse is first pyrolysed to a carbonaceous residue. Larger channels or pores with diameter 1000 degree Å are called macro pores. Most of the surface area for adsorption is provided by micropores, which are arbitrarily defined as pores with diameter from 10-1000 Å.

Table.3.1: Comparison of Physical and Chemical Adsorption

Sl. No.	Physical Adsorption	Chemical Adsorption
1.	Vander walls adsorption	Activated adsorption
2.	Heat of absorption = 5 kcal/mol	Heat of adsorption = 20-100 kcal/mol
3.	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature
4.	No activated energy involved in the adsorption process	Activation energy may be involved
5.	Mono and multi layer adsorption	Almost mono layer adsorption
6.	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is low i.e. only active surface sites are important
7.	Extent of adsorption depends upon the properties of adsorbent	Extent of adsorption depends on both adsorbate and adsorbent
8.	Rate of adsorption controlled by resistance mass transfer	Rate of adsorption controlled by resistance reaction

Table.3.2: Various commercial adsorbents.

Adsorbent	**Properties& method of preparation**	**Application**
Silica gel	Hard, granular and very porous product made from gel precipitated by sodium silicate.	Drying of gases, refrigerants, organic solvents. Desiccant in packing and double glazing. Due point control of natural gas.
Activated alumina	Hard, hydrated aluminum hydroxide which is activated by heating to drive moisture.	Dry of gases,organic solvents, transformer oils. Desiccant in packing and double glazing. Removal of HCl from hydrogen.
Carbon	Activated carbon is the residue obtained from various carbonaceous material like coal,wood,paper mills sludge, agro waste.	Nitrogen from air. Recovery of certain vapors. Purification of helium. Water purification.
Polymeric and Resin	These are hydrophobic adsorbents which are obtained from pyrolysis and activation of polymeric compounds.	Separation of fatty acids from water and toluene. Separation of aromatics from aliphatics. Removal of colour from syrups.
Fuller's Earth	These are natural clays The clay is heated and dried during which it develops a porous structure.	Treatment of edible oils. Removal of organic pigments. Refining of mineral oils.
Zeolites	It is insoluble and chemically stable aluminum silicate mineral that was formed from the glass component of volcanic ash.	Removing water from azeotropes. Sweetening sour gases and liquids. Purification of hydrogen. Separation of ammonia and hydrogen. Recovery of carbon dioxide. Separation of xylene and ethyl benzene.

Table.3.3: Typical non conventional adsorbents.

Adsorbent	**Application**
Coal fly ash	Heavy metals, organic compounds, COD of waste water, phosphate, phenolic compounds.
Bagasse fly ash	Sugar and distillery effluents, heavy metals, chlorinated phenols.
Peat	Heavy metals, cyanide, phosphate, oil in water, color and dyes.
Lignite	Ammonia dyes.
Activated carbon from lignin sludge, bark, rice husk.	Color, heavy metals, dyes, distillery waste.
Coconut husk, peanut skin, bagasse pitch.	Heavy metals, dyes.
Hardwood, softwood, saw dust.	Heavy metals, dyes, COD.
Waste rubber.	Heavy metals.
Hematite, slag.	Heavy metals.
Tannery hair	TOC, soluble organic dyes, virus.
China clay, wollastonite.	Dyes, oxalic acid and Fluorides.

Chapter-4

LITERATURE REVIEW

General

Several investigations have been worked on the removal of arsenic by using different adsorbents. These are reported below.

Review

MANJU *et al.* (1998) studied that the adsorption isotherm of As (III) on copper impregnated activated carbon was obtained in a batch reactor. Various parameters such as reaction time, adsorbent dose, and initial concentration of adsorbate, pH, and temperature were studied to establish optimum conditions. Maximum adsorption capacity was observed at pH 12.0. The adsorption isotherm was also affected by temperature since the adsorption capacity was increased by raising the temperature from 30 to 608°C. The experimental adsorption data plotted reasonably well to the Langmuir isotherm. The mass transfer coefficients as a function of initial sorbate concentration have been determined. Arsenic (III) can be successfully removed from synthetic and industrial wastewaters. Desorption studies revealed that spent adsorbent can be regenerated and reused by 30% H_2O_2 in 0.5 M HNO_3.

United States maximum contaminant level for arsenic in drinking water is set at 50 µg/l. Because of the cancer risks involved, Canada has already lowered the maximum contaminant level to 25 µg/l; the United States Environmental Protection Agency is reviewing the current allowable level for arsenic with a view of lowering it significantly. Various treatment methods have been adopted to remove arsenic from drinking water. These methods include 1) adsorption-coprecipitation using iron and aluminum salts, 2) adsorption on activated alumina, activated carbon, and activated bauxite, 3) reverse osmosis, 4) ion exchange and 5) oxidation followed by filtration. Because of the promise of oxidation-filtration systems, column studies were conducted by **Viraraghavan *et al.* (1999)** to examine oxidation with $KMnO_4$ followed by filtration using manganese greensand and iron-oxide coated sand to examine the removal of arsenic from drinking water; these results were compared with the data from ion exchange studies. These studies demonstrated that As (III) could be reduced from 200 µg/l to below 25 µg/l by the manganese greensand system. In the case of manganese greensand filtration, addition of iron in the ratio of 20:1 was found necessary to achieve this removal.

Pattanayak *et al.*(2000) investigated As(V) and As(III) removal efficiency of a char-carbon (CC), derived from fly ash. The results were compared with those of a commercially available Darco activated carbon (DC) and a carbon produced by arcing of graphite rods (AC). The results indicate that CC and AC adsorbents remove almost equal amounts of As (V) at optimum conditions; however, on a percent basis CC removes more As (III) than does AC. In comparison, sample DC was found ineffective for the removal of As (III) and As (V). The adsorption of As (V) onto CC is influenced by pH, initial metal concentration and temperature. Zeta potential measurements were obtained to explain the metal removal behavior of the adsorbents used in this investigation. Since CC shows significant removal efficiency for both As (V) and As (III), there are good prospects for arsenic fixation on CC in practical applications.

Gregor (2001) studied the effect of forms and concentrations of arsenic on its removal through **aluminium-based** coagulation treatment processes were tracked for three drinking-water treatment plants. This has **provided** direct evidence of where and how arsenic is removed. In general, soluble As (V) is converted to particulate As (V) by adsorption during rapid mixing, and is removed along with naturally occurring particulate arsenic predominantly by clarification. Soluble As (III) tracks through the treatment processes and is converted to soluble As (V) during final chlorination. The ability of a water treatment process to achieve the maximum acceptable concentration for arsenic in drinking water is dependent on the concentration of As (III) in the source water.

Einicke *et al.*(2001) were conducted experiments on arsenic sorption from aqueous solutions by natural solids to test the feasibility of these materials to act as concentrator for arsenic removal from groundwater and drinking water. The solids considered were natural zeolites, volcanic stone, and the cactaceous powder CACMM. The arsenic species studied were As (III), As(V), dimethylarsinic acid (DMA) and phenylarsonic acid (PHA). The arsenic removed was determined from the data obtained by measuring the concentration diminution of the arsenic species in the liquid phase at equilibrium before and after the adsorption experiment by means of ICP-AES for the total concentration of arsenic and IC-ICP-MS to determine the arsenic species. The latter method allowed the detection of As (V) additionally formed as a result of the oxidation of As(III) on some of the zeolites. The sorption of the arsenic species onto zeolites was studied on both non-activated and activated zeolites, as well as on zeolites hydrogenated or modified with iron, and with respect to varying pH. The kinetics and the ability to desorb and readsorb the arsenic species were investigated for selected zeolites.

Leist *et al* .(2001) reported that arsenic has widespread use in agriculture and industry to control a variety of insect and fungicidal pests. Most of these uses have been discontinued, but residues from such activities, together with the ongoing generation of arsenic wastes from the smelting of various ores, have left a legacy of a large number of arsenic-contaminated sites. The treatment and/or removal of arsenic is hindered by the fact that arsenic has a variety of valence states. Arsenic is most effectively removed or stabilized when it is present in the pentavalent arsenate form. For the removal of arsenic from wastewater, coagulation, normally using iron, is the preferred option. The solidification or stabilization of arsenic is not such a clear-cut process. Factors such as the waste's interaction with the additives e.g. iron or lime. as well as any effect on the cement matrix, all impact on the efficacy of the fixation. Currently, differentiation between available solidification or stabilization processes is speculative, partly due to the large number of differing leaching tests that have been utilized. Differences in the leaching fluid, liquid-to-solid ratio, and agitation time and method all impact significantly on the arsenic leachate concentrations.

This paper reviews options available for dealing with arsenic wastes, both solid and aqueous through an investigation of the methods available for the removal of arsenic from wastewater as well as possible solidification or stabilization options for a variety of waste streams.

Nakajima ***et al.*****(2002)** prepared novel adsorbent, aluminum-loaded Shirasu-zeolite P1 (Al-SZP1), and employed for the adsorption and removal of arsenic(V) (As(V)) ion from aqueous system. The process of adsorption follows first-order kinetics and the adsorption behavior is fitted with a Freundlich isotherm. The adsorption of As(V) is slightly dependent on the initial pH over a wide range (3–10). Al-SZP1 was found with a high As(V) adsorption ability, equivalent to that of activated alumina, and seems to be especially suitable for removal of As(V) in low concentration. The addition of arsenite, chloride, nitrate, sulfate, chromate, and acetate ions hardly affected the As(V) adsorption, whereas the coexisting phosphate greatly interfered with the adsorption. The adsorption mechanism is supposed as a ligand-exchange process between As(V) ions and the hydroxide groups present on the surface of Al-SZP1. The adsorbed As(V) ions were desorbed effectively by a 40mM NaOH solution. Continuous operation was demonstrated in a column packed with Al-SZP1. The feasibility of this technique to practical utilization was also assessed by adsorption/desorption multiple cycles with *in situ* desorption/regeneration operation

Altundogan ***et al.*****(2002)** tested heat treatment and acid treatment methods on red mud to increase its arsenic adsorption capability. The results indicate that the adsorptive capacity of red mud can be increased by acid treatment. This treatment causes sodalite compounds to leach out. As(III) and As(V) adsorption characteristics of activated red mud have similar tendencies with raw red mud. Batch adsorption studies have shown that activated red mud in dosages ranging from 20 to 100 g /l can be used effectively to remove arsenic from aqueous solutions. The process is pH dependent, the optimum range being 5.8–7.5 for As(III) and 1.8–3.5 for As(V). The maximum removals are 96.52% for As(V) and 87.54% for As(III) for solutions with a final pH of 7.25 and 3.50, respectively, for the initial arsenic concentration of 133.5 mmol /l (10 mg /l), activated red mud dosage of 20 g /l, contact time of 60 min and temperature of 25 °C. The adsorption data obtained follow a first-order rate expression and fit the Langmuir isotherm well. The isotherms were used to obtain the thermodynamic parameters. It was found that the adsorption of As(III) was exothermic, whereas As(V) adsorption was endothermic.

Chakravarty (2002) used low cost ferruginous manganese ore (FMO) for the removal of arsenic from groundwater. The major mineral phases present in the FMO are pyrolusite and goethite. FMO can adsorb both As(III) and As(V) without any pre-treatment, adsorption of As(III) being stronger than that of As(V). Both As(III) and As(V) are adsorbed by the FMO in the pH range of 2–8. Once adsorbed, arsenic does not get desorbed even on varying the pH in the range of 2–8. Presence of bivalent cations, namely, Ni^{2+}, Co^{2+}, Mg^{2+} enhances the adsorption capability of the FMO. The FMO has been successfully used for the removal of arsenic from six real groundwater samples containing arsenic in the range of 0.04–0.18 ppm. Arsenic removals are almost 100% in all the cases. The cost of the FMO is about 50–56 US$ per metric tonne.

Korfiates *et al.*(2002) conducted aboratory and field tests to evaluate the effectiveness of a household filtration process and investigate the effects of phosphate and silicate on the removal of arsenic from Bangladesh groundwater by ferric hydroxides. Fe/As ratios of greater than 40 (mg/mg) were required to reduce arsenic to less than 50 mg/l in Bangladesh well water due to the presence of elevated phosphate and silicate concentrations. The household filtration process included co-precipitation of arsenic by adding a packet (approximately 2 g) of ferric and hypochlorite salts to 20 l of well water and subsequent filtration of the water through a bucket sand filter. A field demonstration study was performed to test the treatment system in seven households in Bangladesh in March and April 2000. Experimental results obtained from the participating families proved that the household treatment process removed arsenic from approximately 300 mg/l in the well water to less than 50 mg/l. The participating families liked this simple and affordable process and used it to prepare clean water for drinking and cooking. A larger scale field test is currently underway

Thirunavukkarasu *et al*(2003) perfoemed column studies using manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and ion exchange resin in Fe3þ form, to examine the removal of organic arsenic (dimethylarsinate) spiked to required concentrations in tap water. Batch studies were conducted with IOCS-2, and the results showed that the organic arsenic adsorption capacity was 81 g/g IOCS-2. Higher bed volumes and high arsenic removal capacity (5.71 g/cm3) were achieved by the ion exchange resin among all the media studied. Poor performance was observed with MGS and IOCS-1.

Zaw & Emett(2003) revealed that consumption of groundwater containing natural arsenic at several hundred g/l (ppb) in countries such as Bangladesh has lead to the increased occurrence of many cancers particularly those of the skin and bladder, while concerns in the USA and Australia regarding the unknown health impact of drinking water containing tens of ppb of arsenic is leading to increasingly stringent maximum contaminant levels. The anaerobic conditions of these ground waters result in the arsenic being present in its reduced form, hence the use of an oxidant is necessary if the arsenic is to be successfully removed by precipitation or ion exchange methods. Advance oxidation methods which utilise ultraviolet light and a photo absorber have been developed and patented, in which both iron salts and sulphite can be used as the photo absorber. The former absorber has been developed for arsenic removal in rural areas of Bangladesh and the latter for groundwater in countries such as the USA.

Ning (2003) has shown that arsenic is widely distributed in nature in air, water and soil. Acute and chronic arsenic exposure via drinking water has been reported in many countries, especially Argentina, Bangladesh, India, Mexico, Mongolia, Thailand and Taiwan, where a large proportion of ground water is contaminated with arsenic at levels from 100 to over 2,000 micrograms per liter (ppb). Public health standards of maximum of 50 ppb have been adopted by the US and World Health Organization in the 1970s and the 80s. Carcinogenicity and genotoxicity led to the WHO recommendation of 10 ppb maximum level in 1993, followed by the US adoption of the same in 2001, with the US estimate hat 5% of all US community water systems will have to take corrective actions to lower the current levels of arsenic in their drinking water. In high arsenic areas of the world, the need for better water treatment and resulting economic impact would be even greater. In this article, they briefly reviewed the geochemistry, natural distribution, regulation, anthropogenic sources and removal mechanisms of arsenic, pointing especially to the promise of reverse osmosis (RO) as a practical means of purification. They concluded that arsenic in the commonly high oxidation states of (V) is very effectively removed by RO. With further attention to the removal of the weakly acidic arsenic (III) species in waters by the operation of RO at sufficiently high pHs made possible by the newer antiscalants, practical processes can be developed with RO to remove all major species of arsenic from water. Further studies were needed in the characterization of the arsenic species being treated and in the design of the RO process to match the demands.

Zhang *et al* (2004) tested natural iron ores were tested as adsorbents for the removal of arsenic from contaminated water. Investigated parameters included pH, adsorbent dose, contact time, arsenic concentration and presence of interfering species. Iron ore containing mostly hematite was found to be very effective for arsenic adsorption. As(V) was lowered from 1mg/l to below 0.01mg/l (US standard limit for drinking water) in the optimum pH range 4.5–6.5 by using a 5 g/l adsorbent dose. The experimental data fitted the first order rate expression and Langmuir isotherm model. The adsorption capacity was estimated to be 0.4 mg As(V)/g adsorbent. The presence of silicate and phosphate had significant negative effects on arsenic adsorption, while sulphate and chloride slightly enhanced. The negative effect of silicate could be minimized by operating at a pH around 5. The interference of phosphate would necessitate the use of a relatively high dose of the adsorbent to achieve arsenic levels conforming to drinking water standards. The mechanisms of interference of silicate and phosphate on As(V) adsorption are also discussed.

Guptha ***et al*** **(2005)** investigated that leaching of arsenic from industrial wastewater into groundwater may cause significant contamination, which requires proper treatment before its use as drinking water. The present study describes removal of arsenic(III) on iron oxide-coated sand in batch studies conducted as a function of pH, time, initial arsenic concentration, and adsorbent dosage. The results were compared with those for uncoated sand. The adsorption data fitted well in the Langmuir model at different initial concentration of As(III) at 20 g/l fixed adsorbent dose. Maximum adsorption of As(III) for coated sand is found to be much higher (28.57 μg/g) than that for uncoated sand (5.63 μg/g) at pH 7.5 in 2 h. The maximum As(III) removal efficiency achieved was 99% for coated sand at an adsorbent dose of 20 g/l with initial As(III) concentration of 100 μg/l in batch studies. Column studies have also been carried out with 400 μg/l arsenic (pH 7.5) by varying the contact time, filtration rate, and bed depth. Results of column studies demonstrated that at a filtration rate of 4 ml/min the maximum removal of As(III) observed was 94% for coated sand in a contact time of 2 h. The results observed in batch and column studies indicate that iron oxide-coated sand is a suitable dsorbent for reducing As(III) concentration to the limit (50 μg/l) recommended by Indian Standards for Drinking Water.

Lenoble ***et al.*****(2005)** had concluded that under natural conditions, arsenic is often associated with iron oxides and iron (III) oxidative capacity towards As(III) is well known. In this study, As(III) and As(V) removal was performed using synthesized iron(III) phosphate, either amorphous or crystalline. This solid can combine (i) As (III) oxidation by iron(III) and (ii) phosphate substitution by As(V) due to their similar properties. Results showed that adsorption capacities were higher towards As(III), leading to Fe^{2+} and HAsO4 $^{2-}$ leaching. Solid dissolution and phosphate/arsenate exchange led to the presence of Fe^{3+} and $PO4^{3-}$ in solution, therefore various precipitates involving As(V) can be produced: with Fe^{2+} as $Fe^3(AsO4)^2{\cdot}8H_2O(s)$ and with Fe^{3+} as $FeAsO_4{\cdot}2H_2O(s)$. Such formations have been assessed by thermodynamic calculations. This sorbent can be a potential candidate for industrial waste treatment, although the high release of phosphate and iron will exclude its application in drinking water plants

Wilkin *et al.* **(2005)** conducted batch and column studies to (i) assess the effectiveness of zero-valent iron for arsenic remediation in groundwater, (ii) determine removal mechanisms of arsenic, and (iii) evaluate implications of these processes with regard to the stability of arsenic and long-term remedial performance of the permeable reactive barrier (PRB) technology. A high concentration arsenic solution (50mg/l was prepared by using sodium arsenite (arsenic (III)) to simulate groundwater at a heavily contaminated Superfund site in the USA. Batch studies indicate that the removal of arsenic is a two-step reaction with fast initial disappearance of arsenite followed by a slow subsequent removal process. Flow-through columns were conducted at a flow rate of 17ml/h under reducing conditions for 6.6 mo. Kinetic analysis suggested that arsenic removal behaves as a zero-order reaction at high arsenic concentrations. Arsenic removal rate constants decreased with time and arsenic breakthrough was observed in the column study. Arsenic removal capacity of zero-valent iron was determined to be approximately 7.5mgAs/g Fe. Carbonate green rust was identified from the analysis of surface precipitates; arsenite uptake by green rust may be a major mechanism responsible for arsenic remediation by zero-valent iron. Analysis of HCl-extractable arsenic from iron samples indicated that approximately 28% of arsenic was in the form of arsenate suggesting that a surface oxidation process was involved in the arsenic removal with zero-valent iron.

Kovanda *et al* **(2005)** studied effective removal of arsenic compounds from strongly contaminated mining water with a high content of As (about 50 mg/l) and other metals, especially iron (about 5000 mg/l). The process ran in two steps. At first, the raw acid mining water containing predominantly Fe^{2+} ions was partially precipitated with a small amount of an alkaline agent. On a small portion of the precipitated iron (about 30–40%), more than 90% of the arsenic was adsorbed forming a toxic precipitate, which was then stirred under an inert agent (Ar) and further in air for 1 h. Secondly, the precipitation of the first step liquid residue (using the same or a different alkaline agent) enabled the final treatment of the mining water at pH ~8.5. While arsenic was substantially removed by the first precipitation, the other components including residual iron, manganese, zinc and sulfates were precipitated quantitatively during the second step. The mass of the second precipitate depended strongly on the alkaline agent used in the second step. The mechanism and kinetics of arsenic sorption onto iron species, and phase changes of the sorbent during the sorption process were investigated. The composition of the precipitates was verified by XRD and XRF analyses, as well as by infrared and Raman spectroscopy. The precipitation of a raw mining water resulted in formation of a complex inorganic system where amorphous phases dominated. Various crystalline phases, predominantly concerning Fe(II)–Fe(III), As, Zn and sulfates also appeared, depending on the actual oxidizing state of the whole system and on redistribution of its components. The two-step precipitation of arsenic contaminated mining water results in a significant cological and economical improvement due to the decrease in the amount of waste toxic mass.

CHAPTER-5

EXPERIMENTAL PROCEDURES AND PROCESSES

5.1 General

In the present study charcoal and activated carbon have been utilized for the treatment of arsenic aqueous solution. Experimental details of the process have been discussed in this chapter. These details include properties of adsorbents, measurement of arsenic, batch process and experimental procedures.

5.1Adsorbents

5.1.1 Activated carbon

The activated carbon granular LR grade was supplied by s.d. Fine-Chem (Boisar, India) in the size range 2–5 mm. It was manufactured from coconut shells, and was treated with acid wash before delivery. These were subsequently pulverized and sieved through 18 to 44 BS mesh to get the activated carbon particles of the desired size range. The uniform sized particles as retained on different sieves were mixed and the average diameter was estimated to be 0.536 mm. In order to remove any fines attached to these particles and any leachable matter, this was further washed several times with distilled water. The activated carbon was considered fit for use when the distilled water obtained after washing was visibly clear. After washing the activated carbon, it was dried in an oven at 105 °C for 72 h. This time was sufficient to drive off the moisture. After drying, this was stored in a glass bottle until use.

5.1.2 Charcoal

The charcoal LR grade was supplied by s.d. Fine Chemicals Limited which is sieved through 300-350 BS mesh. The impurities present in the coal and properties have been tabulated below.

Table 5.1 Properties of charcoal

S.No	Properties	Quantity
1	Ash	2 %
2	Acid Solubles	1%
3	Water Solubles	0.2 %
4	Alcohol Solubles	0.2 %
5	Phosphate(PO_4)	Negligible
6	Chloride (Cl)	0.01 %
7	Iron (Fe)	0.01 %
8	Sulphate (So_4)	0.01 %
9	Zinc	0.001 %

5.2 Adsorbate

Sodium Arsenate ($Na_2HAsO_4.7\ H_2O$) has been taken as a source of As(V) element. This was been purchased from s.d. Chemicals Limited. Molecular weight for the Sodium arsenate is 312.01gmole/mole, Sp.Gravity-1.871, MeltingPoint 125 °C, solubility in cold water 60 parts in 100 parts of water.

5.3 Measurements

The treated samples were analyzed by using the Atomic Absorption Spectroscopy (AAS). The sample was ionized by using the nitrous oxide-air mixed flame at the wavelength of 193.7 nm. The ionized particle was analyzed and the results were given by direct concentration of arsenic in ppm. The results reported were the average of three replicated runs.

5.4 Batch Experiments

Stock solution was prepared having various concentrations ranging from 10-1000 ppm. To study the effect of parameters like the pH, adsorbent dosage, contact time, temperature, etc. on the adsorptive removal of As, batch experiments were conducted at 30 ± 1 °C. For each experimental run, 50 ml of As solution of known concentration, pH and a known amount of the adsorbent were taken in a 100 ml stoppered conical flask. This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 145 rpm at 30 ± 1°C. Upon completion of the experiments, each solution was taken out and filtered through a Whatman filter paper No. 5. The filtrate obtained was stored at 275 K until it was analyzed.

5.4.1 Effect of Adsorbent Dosage

To find the optimum adsorbent dosage the analysis was done at the different amount of adsorbents like 1, 2, 5, 10, 30, 50, 100 g/l. with the initial concentration of 100 mg/l of arsenic. The pH had not been adjusted for these runs. The measured pH was 6.6 for charcoal in water and 6 for the activated carbon in water. Temperature was maintained at 30 ± 1 ° C. The run was conducted for six hours. The samples were collected at different time interval of 15, 30, 60,120,240,360 min. The samples were collected and refrigerated upto the time of analysis.

5.4.2 Effect of pH

After analyzing the effect of adsorbent dosage the optimum amount of adsorbent dose was found for both adsorbents. To find the effect of pH on these adsorption of arsenic the test was conducted at different pH like 2,4,6,8,10. The amount adsorbent was the optimum as found before. The temperature was maintained at 30 ± 1 ° C. The run was conducted for six hours duration. The samples were collected at the same time intervals as before. The samples were preserved in cool environment upto the time of analysis.

5.4.3 Effect of Time

From the above runs optimum dose and optimum pH were obtained. To find the effect of time on removal of arsenic for the optimum dose and the pH the runs were repeated for the time interval 15, 30, 60, 120, 240, 360 min. The samples were collected on these time interval.

5.4.4 Effect of Temperature

To find the effect of temperature for the removal of arsenic on the adsorbents, the different temperature run were conducted at the optimum dose, time and pH. The temperature was maintained at 30, 40, 50, 60 °C.

CHAPTER-6

RESULTS AND DISCUSSIONS

6.1 General

This chapter deals with the various results obtained from the experimental data. These results include the batch adsorption studies and the kinetics models.

6.2 Batch Adsorption Studies

In order to study the effect of different parameters, the batch operations were found most suitable. Batch adsorption experiments were carried out in 100 ml stoppered conical flask for removal of arsenic from synthetic solutions of known concentrations by using Activated Carbon (AC) and Charcoal(CC). The effect of various operating parameters, viz. concentration, adsorbent dose, contact time and pH is studied and presented here.

6.2.1 Effect of adsorbent dose

The effect of AC and CC dose on the removal of arsenic from drinking water was investigated by varying the concentration from 1 g/l to 50g/l under the selected initial solute concentration. For this experiment the maintained speed was 160 rpm, temperature 30 ± 1 ° C. The run was maintained upto 6 hrs and samples were collected at the regular intervals. The results were plotted as time vs. % arsenic removal (fig 6.1). It was observed that as the dose increases, the amount of solute adsorbed increases and reaches a maximum value corresponding to a certain dose. The minimum amount of adsorbent corresponding to the maximum adsorption was declared as the optimum dose. The optimum dose observed in the present study was 20 g per litre of the solution with a concentration of 100 g/l for the AC, 10 g per litre of the solution with a concentration of 100 g/l for the CC.

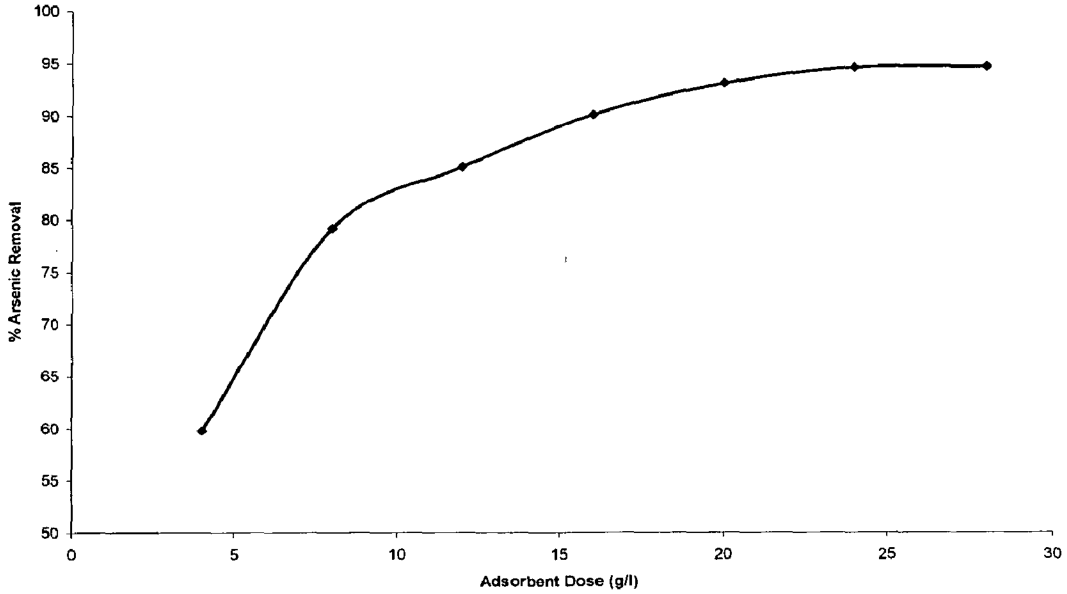

Fig 6.1 Effect Of Adsorbent Dose on % Arsenic Removal Using AC (Time 6 hr;pH 6.3)

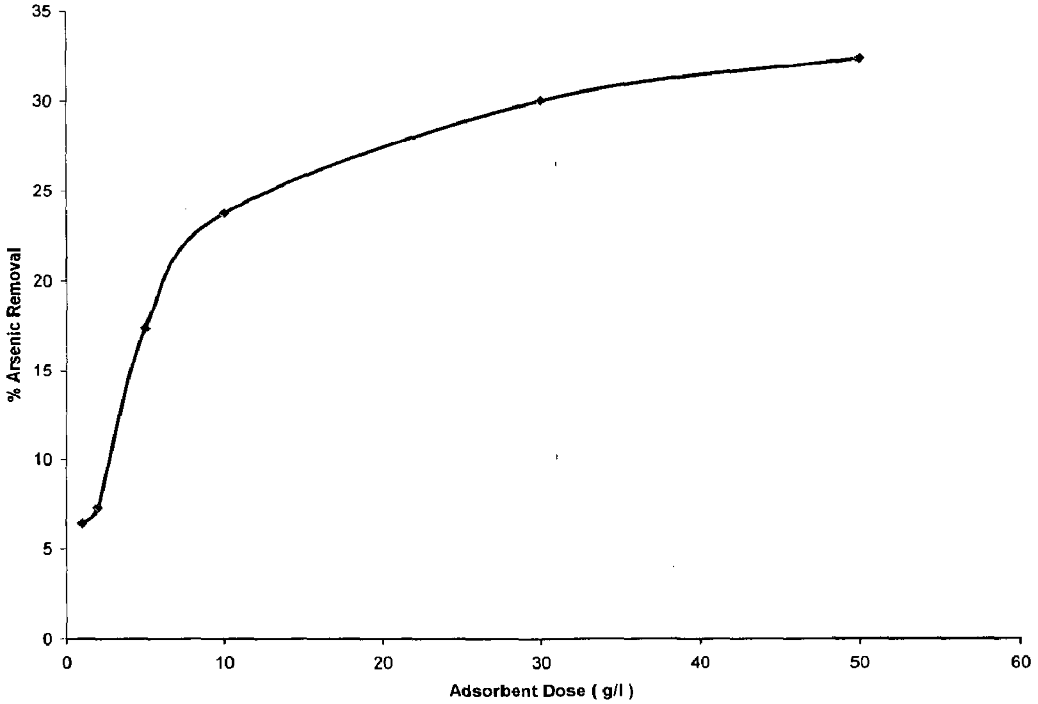

Fig 6.2 Effect of Adsorbent Dose on % Arsenic Removal Using CC (Time 6h; pH 6.6)

6.2.2 Effect of Contact time

The effect of contact time for the removal of arsenic using AC and CC was investigated by analyzing the samples collected at the different time intervals. The maintained parameters were initial concentration 100 g/l, adsorbent dose 20 g/l for AC, 10 g/l for CC, agitation speed 160 rpm .temperature 30 ± 1 ° C. The results were plotted in graph time Vs % arsenic removal. It is clear from the figure 6.2 that the uptake of As increases slowly with the lapse of time and reaches to saturation in 4h in presence of AC and 2 h in presence of CC. Once this time reached the percentage removal of arsenic from the drinking water was not varying in high difference. Thus after the 4h, 2h of contact with AC and CC respectively, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. Increase upto the time 24 hr showed that the removal of arsenic from drinking water is increasing only 2- 3 % over these obtained from 4h , 2h for AC and CC respectively. The metal uptake versus time curves is single, smooth and continuous leading to saturation, suggesting the possible monolayer coverageof metal ions on the surface of the adsorbent.

The contact time between the pollutant and the adsorbent is of significant importance in the treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

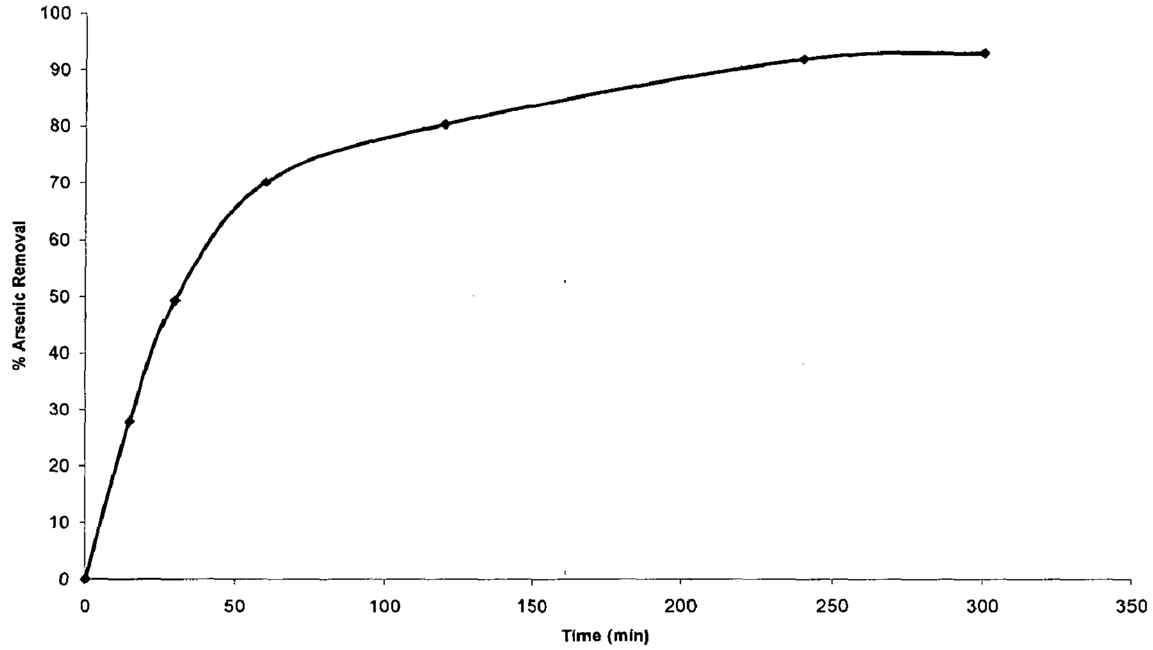

Fig 6.3 Effect of Treatment Time on % Arsenic Removal using AC (Dose 20 g/l;pH 6.3)

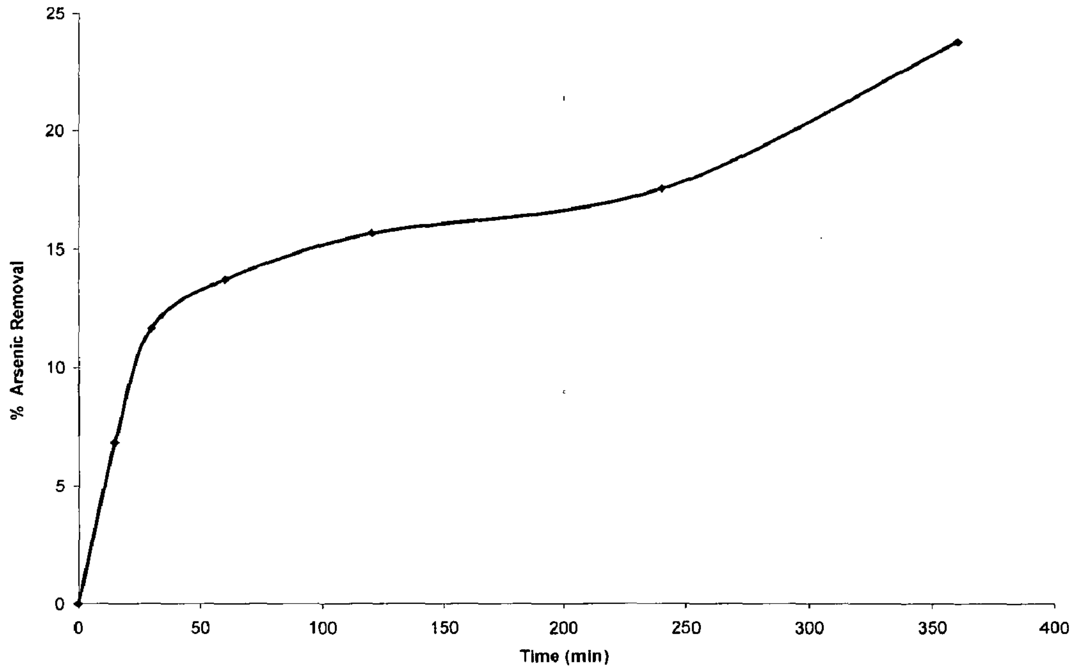

Fig 6.4 Effect of Treatment Time on % Arsenic Removal Using CC (Dose 10g/l;pH-6.6)

6.2.3 Effect of pH

The adsorption of solute from water is influenced by the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization as well as the speciation of the solute. The effect of adsorption of arsenic from drinking water on AC and CC were studied by varying the pH from 2-10. The run was conducted at 100 g/l of initial concentration, for adsorbent dose of 20 g/l for AC and 10 g/l for CC, temperature 30 ± 1 ° C. The pH for the solution of AC and CC in water were found that 6.3 and 6.6.The pH was adjusted by using hydrochloric acid and sodium hydroxide solutions. The pH measurement was done by digital pH meter. The results were plotted in a graph pH vs. % arsenic removed(fig 6.3). It was observed that the amount of arsenic metals intake is increases with increasing the pH while AC as adsorbent and % reduction was not more after the neutral pH. The increase of pH upto 10 shows only 0.5 % more reduction than the neutral condition. For CC the amount of arsenic metal ions intake was increases slowly and reached the maximum and started to decrease. The optimum % adsorption for both the adsorbents were found at their neutral pH i.e. 6.3 for AC and 6.6 for CC.

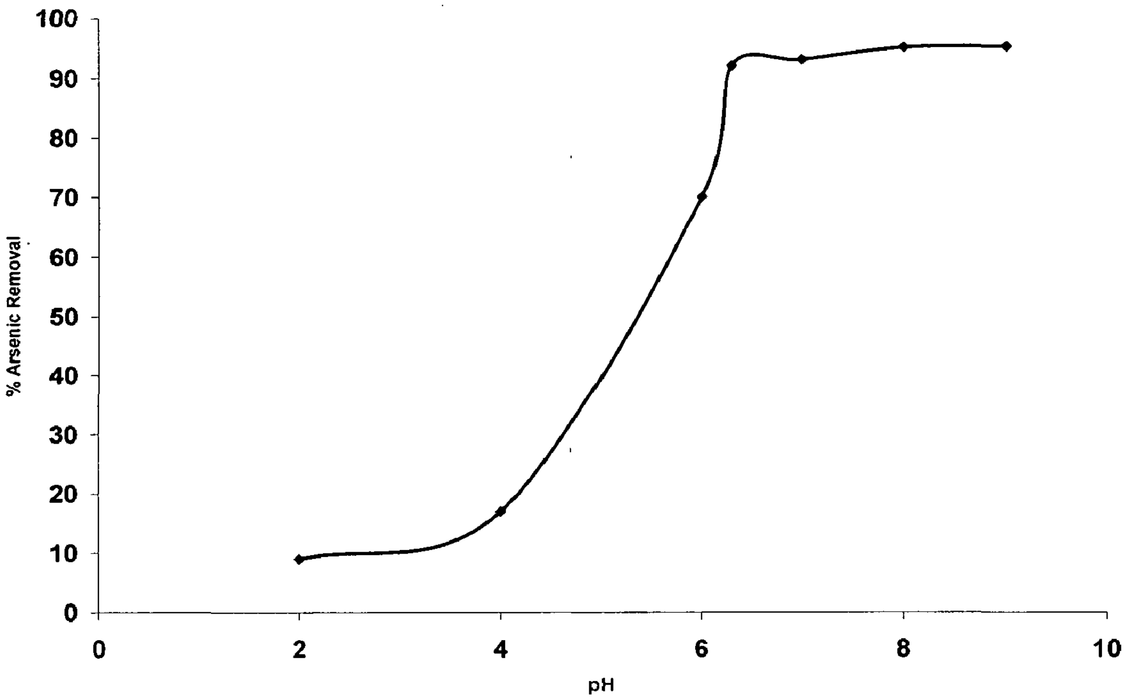

Fig 6.5 Effect of pH on % Arsenic Removal Using AC(Dose 20g/l, Time 240 min)

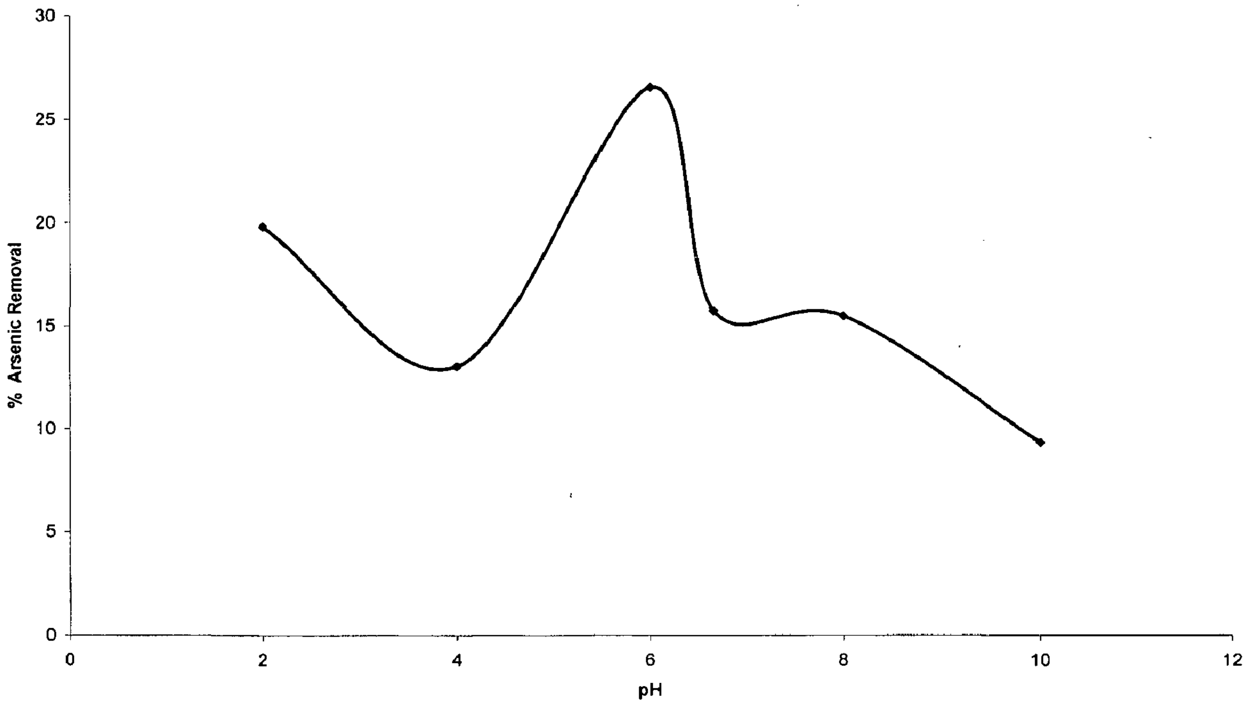

Fig 6.6 Effect of pH on % Arsenic Removal Using CC(Dose =10 g/l : Time=120 min)

6.2.4 Effect of Temperature

The effect of temperature on the removal of arsenic on AC and CC from drinking water was studied by varying the temperature from 25 to 45°C. The maintained conditions for these experiments were initial concentration on 100 g/l, contact time of 4 h, with adsorbent dose of 20 g/l for AC and 10 g/l for CC. It was observed that the amount of uptake of arsenic metals by the AC particle is decreasing steeply with increase in temperature. For CC it was just increasing with increasing the temperature from 25 to 45 ° C. Due to its production in an inert atmosphere, AC is hypothesized to contain little or no surface oxygen. However, an increase in temperature (up to 338 K and at pH of 7.5) could result in the oxidation of carbon AC which would introduce negative charges on its surface. The repulsion between the surfaces (due to their newly created negative charges) and the oxyanions of As, especially at higher temperatures, could lead to lower metal uptakes.

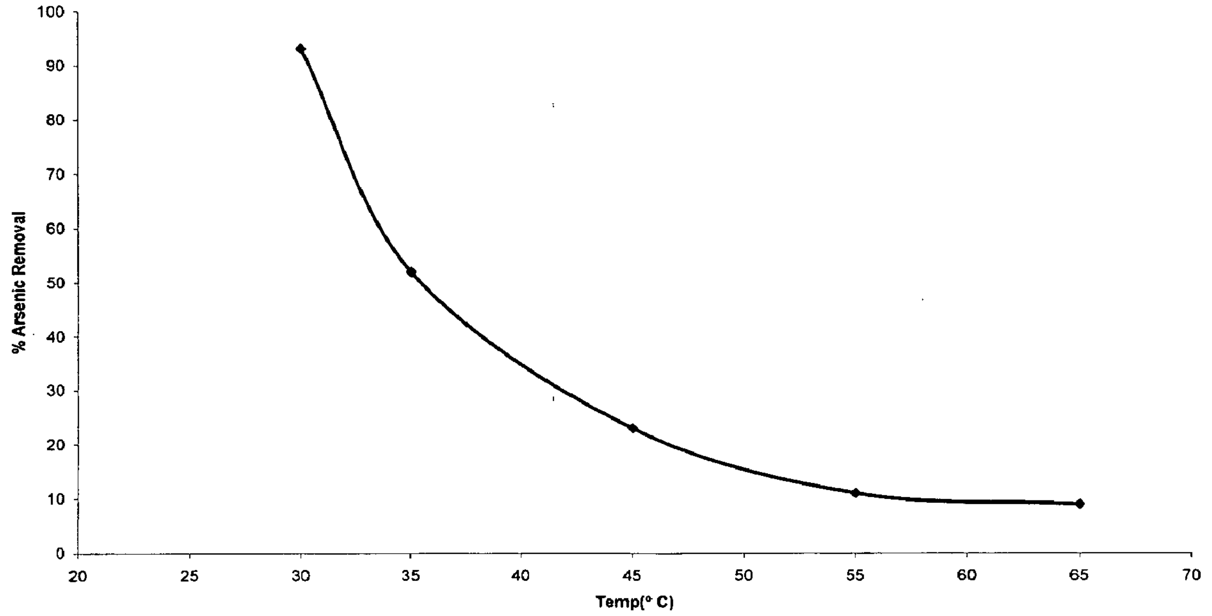

Fig 6.7 Effect of Temperature on % Arasenic Removal Using AC (Dose 20 g/l,Time 240 min,pH 6.3)

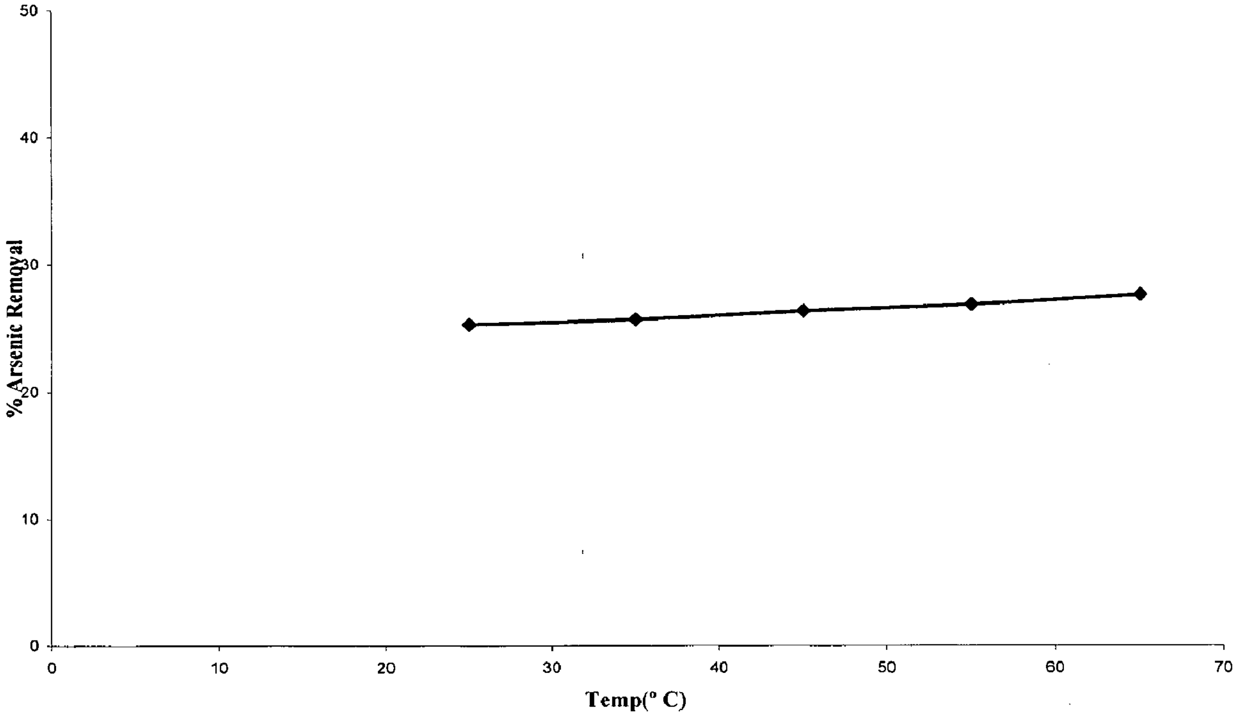

Fig 6.8 Effect of Temperature on % Arasenic Removal Using AC (Dose 0 g/l,Time 120 min,pH 6.6)

6.2.5. Effect of Initial Concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The effect of initial concentration of arsenic in water on the removal of arsenic was studied by varying the initial concentration of arsenic from 50-400 ppm. The optimum parameters were considered for these experiments. The results were plotted in a graph, time vs. % arsenic removal. It was observed that the % removal was decreasing with increasing the initial concentration of solution. But it shows the effective % removal with the initial concentration of 100 g/l. It can be concluded that high removal at low concentration is important in terms of industrial application. The metal uptake versus time curves are ingle, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. These observed readings were used for the adsorption kinetic study.

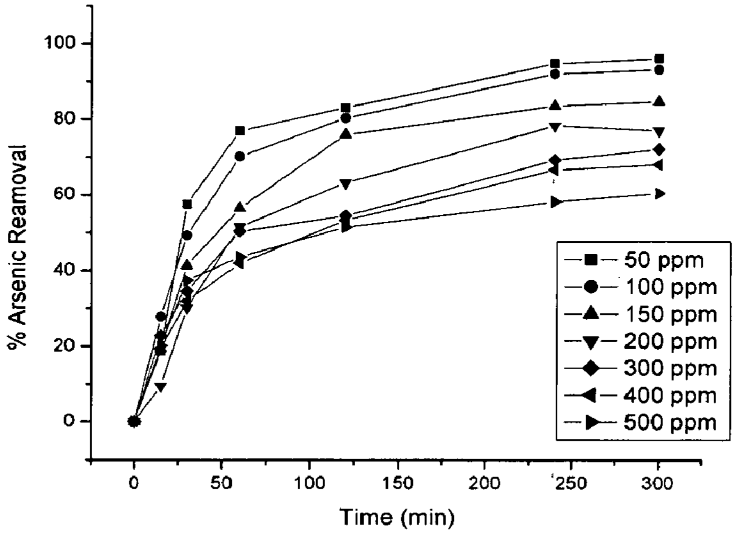

Fig 6.9 Effect of Initial Concentration on the % Arsenic Removal Using AC

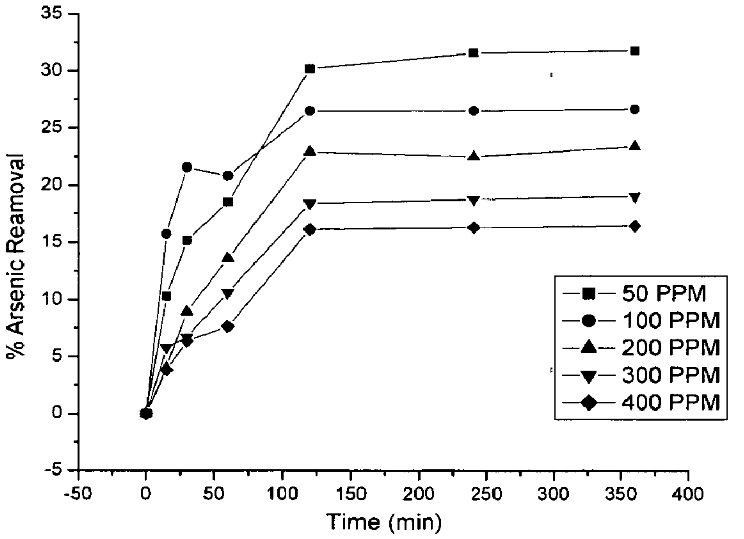

Fig 6.10 Effect of Initial concentration on % Arsenic Removal using CC

6.3 Adsorption Kinetic Study

In order to investigate the adsorption processes of arsenic on AC and CC two kinetic models were used including pseudo-first-order, pseudo-second-order.

6.3.1 Pseudo-first-order model

The pseudo-first-order equation is

$$\frac{dq_t}{dt} = k_f(q_e - q_t)$$

Where, q_t is the amount of adsorbate adsorbed at time t (mg/g),

q_e is the adsorption capacity in equilibrium (mg/g),

k_f is the rate constant of pseudo-first-order model (min_1), and

t is the time (min).

The amount of adsorbate adsorbed can found using following equation

$$q_t = \frac{v(C_o - C_t)}{m}$$

Where, v is the volume of solution taken

m is amount of adsorbent

C_o initial concentration of the solution

C_t concentration of solution at time **t**

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes,

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t$$

Values of adsorption rate constant (k_f) for arsenic adsorption of arsenic on AC and CC were determined from the plot log (q_e-q_t) vs. time. From the slope and Intercept the values of k_f and q_e(cal) were found and tabulated. These values indicate that the adsorption rate was very fast at the beginning of adsorption and that rate of removal of arsenic on the AC. The values of adsorption rate constants are tabulated for the different initial concentration solutions.

Table 6.1 Kinetic parameters for the removal of Arsenic on AC and CC

Pseudo-first-order model					
	Initial Concentration (mg/l)	k_f	q_e Values		R^2
			q_e (Cal)	q_e (Exp)	
For Activated Carbon	50	0.017042	1.949845	2.39168	0.9714
	100	0.017733	4.057887	4.857321	0.9891
	150	0.017963	6.025596	7.437434	0.9984
	200	0.017042	8.074209	9.847237	0.9904
	300	0.012667	9.065672	14.9368	0.9712
	400	0.01543	15.92209	19.93187	0.9823
For Charcoal	50	0.021648	1.572896	1.543942	0.9822
	100	0.022569	1.625549	2.5376	0.8155
	200	0.019345	4.167734	4.607063	0.8411
	300	0.018885	5.282019	5.676911	0.9055
	400	0.021648	6.535819	6.522278	0.8784

6.3.2 Pseudo-second-order model

The pseudo-second-order model can be represented in the following form

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2$$

where k_S is the rate constant of pseudo-second-order model (in g/mg min).
After integrating the above equation for boundary conditions

$q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$

the following form of equation can be obtained

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

the initial sorption rate, h (mg/g min), as $t = 0$ can be defined as

$$h = k_s q_e^2$$

The initial sorption rate (h), the equilibrium adsorption capacity (qe), and the pseudosecond-order constant k_s can be determined experimentally from the slope and intercept of plot of t/qt versus t. Calculated correlation coefficients, both linear and non-linear, for pseudo-first-order model and pseudo-second-order model by using regression procedure for AC and CC adsorption are shown in table.

Since calculated correlation coefficients are closer to unity for pseudosecond-order kinetics model than the pseudo first-order kinetic model, therefore the adsorption kinetics could well be approximated more favourably by pseudosecond- order kinetic model for both adsorbents.

Table 6.2 Kinetic parameters for the removal of Arsenic on AC and CC

Pseudo-Second-order model

	Initial Concentration (mg/l)	k_f	q_e Values		R^2
			q_e (Cal)	q_e (Exp)	
For Activated Carbon	50	0.016441	2.516356	1.719973	0.9983
	100	0.005237	5.194805	3.832584	0.9978
	150	0.003303	7.347539	5.536708	0.9982
	200	0.001857	9.302326	7.013143	0.9962
	300	0.001998	11.93317	14.92745	0.9894
	400	0.00121	15.89825	19.87845	0.9949
For Charcoal	50	0.011736	1.850139	1.543942	0.9833
	100	0.00361	2.665956	2.5376	0.9966
	200	0.00187	6.40615	4.607063	0.948
	300	0.002079	7.473842	5.676911	0.9615
	400	0.001422	8.841733	6.522278	0.9299

6.4 Adsorption equilibrium study

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, RedlichePeterson, Dubinin and Radushkevich, Tempkin, RadkoePraunitz and Toth equations. Here we have discussed about both Freundlich and Langmuir isotherms.

Freundlich and Langmuir isotherms

Freundlich studied the sorption of a material onto animal charcoal and demonstrated that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes and it has been used to explain the sorption of dyes onto various adsorbents. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The linearised Freundlich and Langmuir isotherms are represented by the following equations:

Freundlich isotherm

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

where

K_F is Freundlich constant (l/mg),

1/n is the heterogeneity factor,

K_L is the Langmuir adsorption constant (l/mg) related to energy of adsorption

q_m signifies adsorption capacity (mg/g).

The fig shows the Freundlich and Langmuir plot for AC and CC respectively for the removal of arsenic from drinking water. The data have been analyzed and the coefficients are tabulated.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L which describes the type of isotherm and is defined by

$$R_L = \frac{1}{1 + K_L C_o}$$

If $R_L > 1$, unfavorable;

$R_L = 1$, linear;

$0 < R_L < 1$, favorable;

$R_L = 0$, irreversible.

The values of R_L are tabulated for both AC and CC for the removal of arsenic.From the table it is found that the Langmuir isotherm is favourable for the adsorption of arsenic on Activated Carbon and CharCoal.

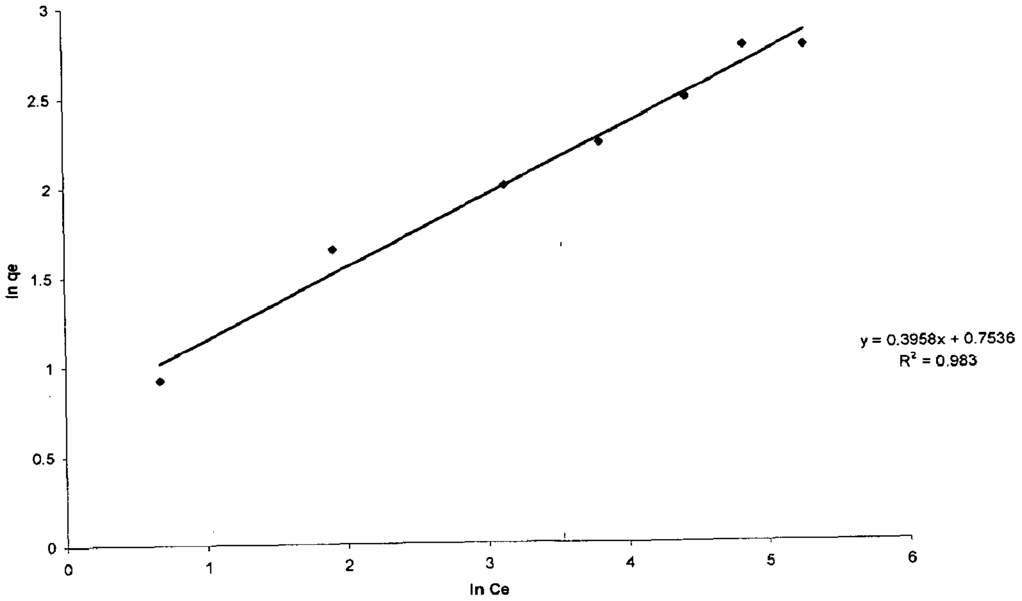

Fig 6.11 Freundlich isothern plots for the removal of Arsenic On AC (Contact Time 240 min, Dose 20 g/l)

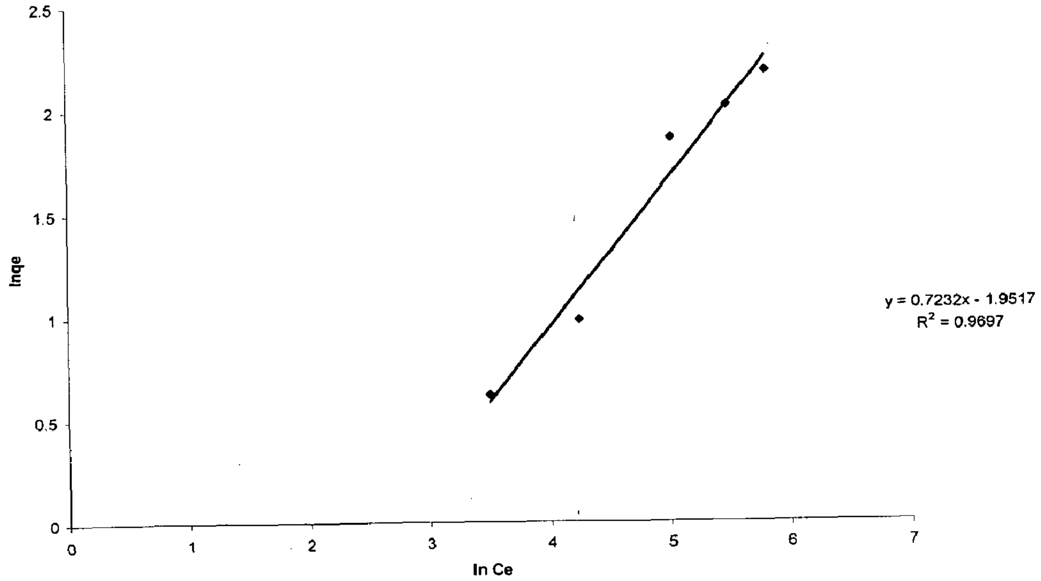

Fig 6.12 Freundlich isothern plots for the removal of Arsenic on CC (Contact Time 120 min, Dose 10 g/l)

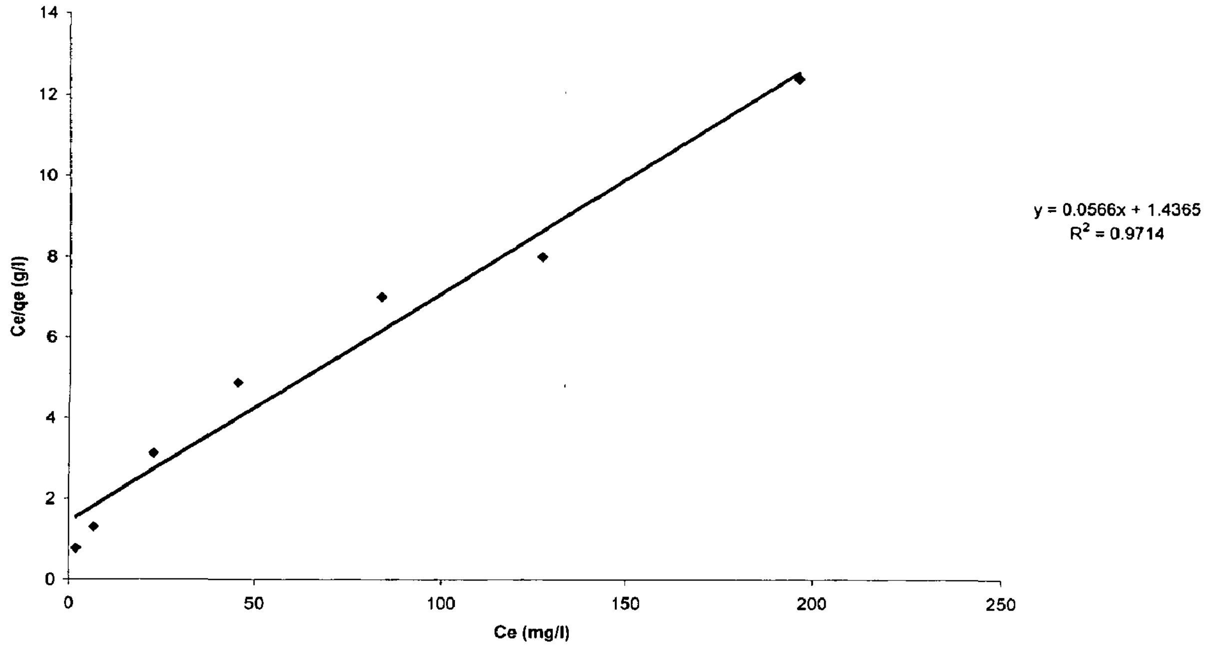

Fig 6.13 Langmuir Isothern plot for the removal of Arsenic On AC (Contact Time 240 min, Dose 20 g/l)

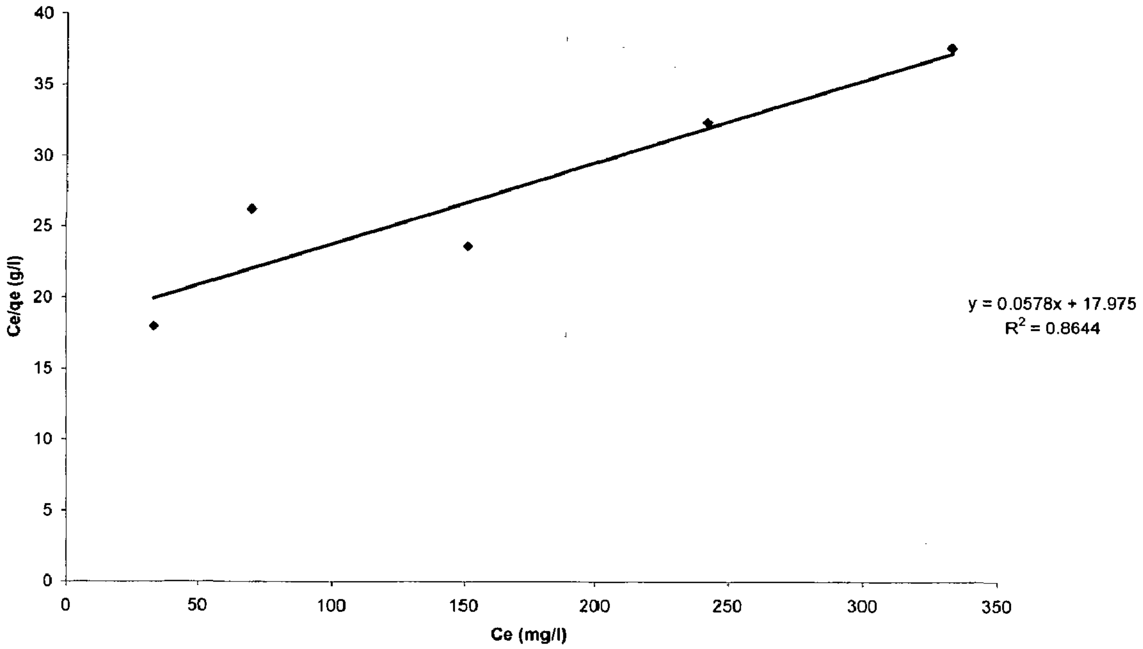

Fig 6.14 Langmuir isothern plots for the removal of Arsenic on CC (Contact Time 120 min, Dose 10 g/l)

Table 6.3 Freundlich isotherm parameters for removal of Arsenic Using AC and CC

	Adsorbents	**K_F(mg/g)(mg/l)$^{1/n}$**	**1/n**	**R^2**
Freundlich isotherm	Activated Carbon	2.124635	0.3958	0.983
	Charcoal	0.142032	0.0578	0.9697

Table 6.4 Langmuir isotherm parameters for removal of Arsenic Using AC and CC

	Adsorbents	**K_L (1/mg)**	**q_m (mg/ l)**	**R_L**	**R^2**
Langmuir isotherm	Activated Carbon	0.039401	17.66784	0.202425	0.9714
	Charcoal	0.003216	17.30104	0.756659	0.8644

CHAPTER-7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

Based on the complete work the following major conclusions can be presented in a nutshell:

- Activated Carbon is viable alternative for the removal of arsenic from drinking water. This comparative study shows that the uptake of arsenic metal ions is more for Activated Carbon when compared with the charcoal.
- Time consumption for the removal process is 4 h for Activated Carbon and 2h for Charcoal. Even though the time taken by Activated carbon is more, the removal efficiency at 2 h is more than charcoal.
- The various optimum conditions for the Activated Carbon and Charcoal are given

  Activated Carbon: Time - 4h, pH – 6.3, Temperature- 30° C, Dose-20g/l.
  Charcoal: Time-2h, pH-6.6, Temperature-30°C, Dose-10g/l.
- The removal efficiency for Activated carbon up to 95 % while 30% for Charcoal.
- The parameters of Pseudo-First order and Pseudo-Second order kinetics have been found. From the results it was found that adsorption follows the second order kinetics.
- Adsorption Equilibrium studies were done using Freundlich and Langmuir isotherms from the results it is clear that adsorption shows a favorable condition for the removal of arsenic from drinking water.

7.2 RECOMMONDATIONS

- Further pilot scale studies are required to evaluate the suitability of Charcoal and Activated carbon for the adsorptive removal on plant scale.
- Column studies can be carried out to examine the effect of bed height, diameter, flow rate and concentration of adsorbate.
- Charcoal prepared by different things can be characterized for physio-chemical parameters and surface characteristics, so the result can be correlated and may be utilized in effluent treatment.
- Many more combination of different adsorbents could be tried to get much better result

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