ARSENIC (III) REMOVAL FROM WATER USING NATURAL SEDIMENTARY ROCKS

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In the name of Allah, the Most Gracious, the Most Merciful,

This page is especially dedicated to my beloved sister, Noorhayatie Yusof, mum, Che Zaharah binti Yamin, dad, Yusof bin Mohammad, sisters and brother for their inspiration, support and happiness.

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ABSTRACT

Arsenic (As) in groundwater is recognized as a threat to public health worldwide. Toxicity of As(III) is greater than As(V) on human health. Most of the arsenic removal techniques are effective only in removing As(V) and not As(III). In this study, ten locally available low cost adsorbents were screened for their capability to remove As(III). The shale sedimentary rock (SSR) and caustic sedimentary rock (CSR) were selected based on high As(III) removal. Based on the characterization of adsorbents using XRD, FESEM-EDX, BET and TGA analyses, it was found that raw SSR contains a mixture of goethite and hematite as its major composition whereas the major composition for CSR adsorbent was goethite. Upon calcination at 500^{o}C, the composition of both adsorbents was completely changed to hematite. The activation of adsorbent was carried out by thermal treatment (250–600°C), acid treatment (0.1–1 M H_2SO_4) and metal impregnation (0.2-1 M of $MnC1_2$ and $MgCl_2$) in order to choose the best treatment method for As(III) removal. Results showed that only by heating the adsorbents at 500°C for 1h, 0.2 g of each adsorbent was capable of reducing the residual As(III) concentration below 10 µg/L, for initial concentration from 100 to 700 µg/L and optimum pH ranges between 3 to 9 after 24 h of contact time. The experimental data were fitted to kinetic and diffusion models, such as pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models. The pseudo-second order model presented the best correlation (R^2=0.999) for all adsorbents studied. The good fit of equilibrium data with the Langmuir isotherm indicated favourable As(III) sorption reaction with SSR-P (0.29 mg/g), SSR-G (0.36 mg/g) and CSR-G (0.65 mg/g), while the CSR-P (0.24 mg/g) was better fit with the Freundlich isotherm. The As(III) sorption occurred with catalytic oxidation of As(III) to As(V) of the surface oxide of adsorbents as evidenced from XPS investigation. Assessment of the breakthrough curve of granular SSR through a column study was examined for the effect of contact time based on operation parameters of bed depth and flow rate. The breakthrough times (10 µg/L) for contact time of 3.167, 4.75 and 6.33 min (10, 20, and 30 cm bed depth, flow rate of 3mL/min) were found to be 28, 90, and 150 h, with treated water of 5.04, 16.20 and 27 L respectively, while for the contact time of 2.85, 3.57 and 4.75 min (flow rates of 3, 4 and 5 mL/min, bed depth of 15 cm), 27, 21.6 and 15 L water can be treated at a breakthrough time of 150, 90 and 50 h respectively. Modeling of breakthrough point was carried out using bed depth/service time (BDST) model, Thomas model and Yoon-Nelson model. The BDST model gave results that were in very good agreement (R^2=0.999) with the experimental results. The data obtained from the batch adsorption study was used to train back propagation learning algorithm having a 5-11-1 architecture. The model uses a tangent sigmoid transfer function and a linear transfer function. The network was found to be working satisfactorily since it gave a good degree of correlation (R^2=0.919) indicating that the model is able to predict the percentage As (III) removal with reasonable accuracy. This adsorbent proved to be a promising method to meet the needs of rural populations of arsenic contaminated regions since it can effectively reduce arsenic concentration from water to environmentally acceptable levels using a simple method at affordable cost.

ABSTRAK

Kehadiran arsenik (As) dalam air bumi diperakui sebagai satu ancaman terhadap kesihatan awam di seluruh dunia. Ketoksikan As(III) adalah lebih tinggi daripada As(V) terhadap kesihatan manusia. Kebanyakan daripada teknik-teknik penyingkiran arsenik hanya berkesan dalam penyingkiran As(V) dan tidak untuk As(III). Dalam kajian ini, sepuluh bahan penjerap berkos rendah yang mudah diperolehi telah disaring keupayaannya untuk penyingkiran As(III). Batuan endap syal (SSR) dan batuan endap kaustik (CSR) dipilih berdasarkan penyingkiran As (III) yang tinggi. Berdasarkan pencirian bahan penjerap menggunakan analisis XRD, FESEM-EDX, BET dan TGA, SSR telah disahkan mengandungi goetit dan hematit manakala komposisi utama CSR telah disahkan mengandungi goetit. Setelah dipanaskan pada suhu 500ºC, komposisi kedua-dua bahan penjerap bertukar sepenuhnya kepada hematit. Pengaktifan bahan penjerap telah dijalankan melalui olahan haba (250-600ºC), rawatan asid (0.1-1 M H_2SO_4) dan penempelan logam (0.2-1 M of $MnC1_2$ dan $MgCl_2$) untuk memilih kaedah rawatan terbaik bagi penyingkiran As(III). Keputusan kajian menunjukkan bahawa hanya dengan pemanasan bahan penjerap pada suhu 500°C selama 1 jam, 0.2 g bahan penjerap berkebolehan mengurangkan kandungan As(III) di bawah 10 µg/L, bagi kepekatan awal As(III) dari 100 kepada 700 µg/L dan julat pH optimum antara 3 hingga 9 selepas 24 jam masa sentuhan. Data ujikaji dimuatkan untuk memperagakan model kinetik dan resapan, seperti pseudo tertib pertama, pseudo tertib kedua, Elovich dan resapan intra zarah. Model pseudo tertib kedua menunjukkan korelasi terbaik (R^2=0.999) terhadap data ujikaji bagi semua bahan penjerap yang digunakan. Padanan keseimbangan data yang sesuai diperagakan oleh isoterma Langmuir dengan muatan ekalapis yang tinggi menunjukkan tindak balas penyerapan yang baik bagi SSR-P (0.29 mg/g), SSR-G (0.36 mg/g) dan CSR-G (0.65 mg/g) manakala CSR-P (0.24 mg/g) menunjukkan padanan yang lebih sesuai dengan keseimbangan Freundlich. Penjerapan As(III) berlaku melalui pengoksidaan bermangkin As(III) kepada As(V) pada permukaan bahan penjerap melalui bukti dari siasatan menggunakan XPS. Penilaian lengkung bulus granul SSR melalui kajian turus telah diperiksa bagi kesan masa sentuhan terhadap parameter operasi seperti kedalaman turus dan kadar alir. Masa bagi titik perkembangan (10 µg/L) untuk masa sentuhan 3.167, 4.75 dan 6.33 min (kedalaman turus 10, 20 , dan 30 cm, kadar alir 3 mL/min) telah didapati pada 28, 90 , dan 150 jam, dengan isipadu air yang dirawat adalah sebanyak 5.04, 16.20 dan 27 L, setiap satunya, manakala untuk masa sentuhan 4.75, 3.57 dan 2.85 min (kadar alir 3, 4 dan 5 mL/min, panjang turus 15 cm), 27, 21.6 dan 15 L air boleh dirawat pada titik masa perkembangan 150, 90 dan 50 jam. Pemodelan titik perkembangan dijalankan menggunakan model kedalaman turus/masa perkhidmatan, model Thomas dan model Yoon Nelson. Model BDST menunjukkan korelasi (R^2=0.999) yang sangat baik terhadap hasil kajian. Data yang diperolehi dari kajian penjerapan kelompok telah digunakan untuk melatih propagasi terbalik pembelajaran algoritma yang mengandungi senibina 5-11-1. Model ini menggunakan fungsi pemindahan sigmoid tangen dan fungsi pemindahan linear. Rangkaian ini didapati berfungsi secara memuaskan kerana ia memberi korelasi yang baik (R^2=0.919) menandakan model ini boleh meramal peratus penyingkiran As(III) dengan ketepatan yang munasabah. Bahan penjerap ini menunjukkan kaedah penyingkiran arsenik yang berkesan untuk memenuhi keperluan populasi luar bandar di kawasan yang tercemar dengan arsenik kerana ia boleh mengurangkan arsenik dengan berkesan ke tahap yang boleh diterima persekitaran menggunakan cara yang ringkas pada kos yang berpatutan.

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LIST OF ABBREVIATIONS

Ac - Activated Carbon
As(III) - Arsenic (III)
As(V) - Arsenic (V)
ATSDR - Agency for Toxic Substances and Disease Registry
BATS - Best Available Technologies
BDST - Bed Depth Service Time
BET - Brunauer-Elmer-Teller
BP-ANN - Back Propagation Neural Network
BSF - Biosand Filter
BUET - Bangladesh University of Engineering and Technology
C - Clay
SSR - Shale Sedimentary Rock
SSR-G - Shale Sedimentary Rock - Granular
SSR-P - Shale Sedimentary Rock - Powder
CSR - Caustic Sedimentary Rock
CSR-G - Caustic Sedimentary Rock - Granular
CSR-P - Caustic Sedimentary Rock -Powder
CIM - Composite Iron Matrix
DMPS - 3-Dimercapapto-1-Propanesulfonate
DMSA - Dimercapto Succinic Acid
DNA - Diribonucleic Acid
D-R - Dubinin-Radushkevitch
EAWAG - Swiss Federal Institue of Environmental Science and Technology
EDX - Energy Dispersive X-Ray
EPA - Environment Protection Agency

FBPB - Full Body Porcelain Black
FBPW - Full Body Porcelain White
FESEM - Field Emission Scanning Electron Microscopic
FTIR - Fourier Transform Infra-Red
HCl - Hydrochloric acid
HTA - Heat Treated Adsorbent
ICP-MS - Inductively Coupled Plasma-Mass Spectrometry
ICSD - Inorganic Crystal Structure Database
IOCC - Iron Oxide Coated Cement
KAF - Kanchan Arsenic Filter
LA - Latin America
LD_{50} - Lethal dose
M - Molarity
MCL - Minimum Concentration Limit
MIME - Ministry of Industry, Mines and Energy
MRD - Ministry of Rural Development
PG - Porcelain Glaze
PZC - Point of Zero Charge
RA - Raw Absorbent
RS - River Sand
SDC - Swiss Agency for Development and Cooperation
SE Asia - South East
SEM - Scanning Electron Microscopy
SORAS - Solar Oxidation And Removal of Arsenic
TGA - Thermogravimetric Analysis
USEPA - United State Environment Protection Act
WB - West Bengal
WHO - World Health Organization
XPS - X-Ray Photoelectron Spectroscope
XRD - X-Ray Diffraction Analysis

LIST OF SYMBOLS

µg/L - Microgram per liter

µm - Micrometer

b - Variation of adsorption energy

B_1 - Heat of adsorption

C_b - Desired solute concentration at breakthrough (mg/L)

C_e - Equilibrium As concentration

Co - Initial solute concentration (mg/L)

E_h - Redox potential

$FeAsS_2$ - Arsenopyrite or ferrous As sulphide

$FeOOH$ - Amorphous Hydrous Ferric Oxide

g/d - Gram per day

K - Adsorption rate constant (L/mg h)

k_1 - Rate constant of the pseudo-first order model

k_2 - Rate constant of the pseudo-second order model

k_{DR} - Constant related to the adsorption energy

k_F - Freundlich constant and is related to the adsorption efficiency

k_L - Langmuir constants related to the saturated monolayer adsorption capacity

K_T - Equilibrium binding constant (Lmg^{-1}) corresponding to the maximum binding energy

k_{Th} - Thomas rate constant (ml/ h mg)

k_{YN} - Yoon-Nelson rate constant (h^{-1})

LD_{50} - Lethal dose

m - Amount of adsorbent (g)

m^3 - Meter cubic

mg/g - Miligram per gram

mL min^{-1} - Mililiter per minute

mmol g^{-1} - Milimol per gram

mol L^{-1} - Mol per liter

mV - Milivolt

n - Dimensionless variable indicative of favourability of sorption

$NaAsO_2$ - Sodium arsenite

N_o - Adsorption capacity (mg solute/L adsorbent)

q_2 - Equilibrium adsorption capacity of theoretical value in the pseudo-second order model

q_e - Amount of As(III) adsorbed at equilibrium

q_t - Amount of As(III) adsorbed at contact time,t

R - Universal gas constant

R^2 - Correlation Coefficients

$t_{1/2}$ - Time required for 50% adsorbate breakthrough (h).

t_b - Time at which the metal concentration in the effluent reached 0.01 or 0.05 mg/L

V - Linear flow velocity of feed to bed (cm/h)

Z - Bed height (cm)

Zc - Critical bed depth

α - Initial sorption rate

α-FeOOH - Goethite

β - Parameter related to the extent of surface coverage and activation energy

ΔG^o - Gibbs free energy

ΔH^o - Enthalpy

ΔS^o - Entropy change

ε - Polanyi potential

μg/d - Microgram per day

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water plays important roles in human activities, the natural environment, and social development. One of the most important problems in water use is arsenic pollution due to its high toxicity. Arsenic pollution concerns the entire world, particularly in countries where water naturally has high arsenic concentrations especially for small communities in rural areas around the world, where groundwater comprises the main drinking water sources such as India, China, Hungary, Finland, Greece, Bangladesh and Cambodia (Urbano *et al*., 2012; Katsoyiannis, and Zouboulis, 2002).

Arsenic is classified as a Group A and Category 1 human carcinogen by the US Environmental Protection Agency and International Association for Research and Cancer, respectively and has been identified as a public health issue. Arsenic is a semi-metallic element that gradually accumulates, often without visible symptoms, in the human body until it reaches a concentration at which it causes chronic toxicity (Li *et al*., 2012). The majority of arsenic species in natural water is a mixture of arsenate (As (V)) and arsenite (As(III)), where arsenite is the predominant form normally found in groundwater. It has been established that the toxicity of arsenic depends on its specific chemical form. Arsenite, the trivalent form is more toxic in biological systems than arsenate whereas the toxicity of organo-arsenicals is generally lower than that of inorganic arsenic species (Katsoyiannis, and Zouboulis, 2002).

Gradual intake of arsenic contaminated water has been linked to arsenical dermatitis, skin cancer, neurological effects, enlargement of liver, heart disease and internal cancer. Studies have reported that arsenic effects are primarily due to consumption of arsenic contaminated water at concentrations around 100 µg/L. This is because, As(V) can replace phosphate in several biochemical reactions, whereas As(III) may react with critical thiols in protein and inhibit their activity (Mohapatra *et al.*, 2008).

Recent studies showed that arsenic in drinking water is more harmful to human health than expected. Arsenic concentrations greater than 10 mg/L have been reported in water supplies throughout the world in places like Bangladesh, West Bengal, Vietnam, Argentina, Argentina, Taiwan, Mexico and the Unites States. Many countries have considered arsenic in drinking water as an environmental priority pollutant and made strict guidelines for arsenic concentration in waste disposals and drinking water. Therefore, the World Health Organization (WHO) and the US Environment Protection Agency (EPA) have strictly reduced the maximum contaminant level recommended in drinking water supply from 50 µg/L to 10 µg/L in order to minimize the human risk (Urbano *et al.*, 2012). These legislative proposals are based on a revolution of chronic arsenic toxicity to humans as detected in relatively large populations receiving potable water with elevated arsenic levels over several decades. For some water in Bangladesh, a greater than 99% removal of arsenic is required to meet the WHO guidelines. However, many countries, including India and Bangladesh, still operate by the previous 50 µg/L standard (Mohapatra *et al.*, 2008).

The presence of arsenic in groundwater is largely as a result of minerals dissolving from weathered rocks and soils. Anthropogenic arsenic stems from industrial wastes including those from the production of pesticides and fertilizers, and from mining, smelting and the agricultural industry. In drinking water, the main source of arsenic is arsenic-rich rocks through which water has percolated. Arsenic also may be derived from mining or industrial activity in some area. In natural water, arsenic is primarily present in inorganic forms and exists in two predominant species, arsenate and arsenite. Arsenate is the major species in well-oxygenated water, whereas arsenite is the dominant arsenic species in groundwater. Arsenite is much more toxic, more soluble, and more labile than arsenate. Arsenate exists as the deprotonated oxyanions of arsenic acid (H_2AsO_{4-} and $HAsO_4^{2-}$) at neutral pH. On the other hand, arsenite exists as the neutral species (H_3AsO_3) (pKa1 = 9.2) at neutral pH condition (Mohan and Pittman, 2007).

To remove excessive arsenic from water, various methods have been employed, but most of them suffer from one or more drawbacks, limitations and scope of application. Several treatment technologies have been applied in the removal of arsenic from waters, such as coagulation/ filtration, ion exchange, lime softening, adsorption on iron oxides or activated alumina and reverse osmosis (Jekel, 1994; Kartinen and Martin, 1995; Zouboulis and Katsoyiannis, 2002). Most of these technologies are not efficient enough for the removal of As(III). Therefore, a preoxidation step is usually required to transform the trivalent form to pentavalent. The oxidation procedure is mainly performed by the addition of chemical reagents, such as potassium permanganate, chlorine, ozone, hydrogen peroxide or manganese oxides (Jekel, 1994; Driehaus *et al.*, 1995; Kim and Nriangu, 2000). Although these reagents are effective in oxidizing trivalent arsenic, they may cause several secondary problems arisen mainly by the presence of residuals or from by-products formation, inducing also a significant increase to operational costs of the methods. Therefore, it is essential that methods that allow those installations to supply drinkable water at low cost as well as superior efficiency towards As(III) and simple, should be developed.

1.2 Statement of Problem

The presence of dissolved arsenic in groundwater has provoked an international concern due to its known toxicity (AWWA, 2001). The decrease of the maximum arsenic level in drinking water down to10 μgL^{-1} imposed the need for modification of more than 4000 water supply systems utilised by 20 millions of people (EPA, 2002). The presence of arsenic, even at high concentrations is not accompanied by any change in tastes, odors and or visible appearance of water. The presence of arsenic in drinking water is therefore difficult to detect without complex analytical technique being employed, hence may present a significant hazard to community health. Exposure to high levels of acute arsenic poisoning is relatively less common, however, long term exposure to even low concentrations of arsenic in drinking water also presents a considerable health hazard (Malik *et al*., 2009). It is obvious that boiling of water for purification does not remove arsenic but on the contrary, this process increases arsenic concentration by evaporation. This is a fact commonly ignored by the potentially affected people (Litter *et al*., 2010).

Most treatment technologies, such as adsorption and precipitation, are effective in removing As(V) from waters because of the positive charge on the surface of the adsorbents. On the other hand, under mildly reducing conditions such as in groundwaters, As(III) is the thermodynamically stable form, which is presented as the non-ionic form of arsenious acid (H_3AsO_3) at neutral pH (Cullen and Reimer, 1989). Thus, As(III) is more difficult to be removed from water by means of adsorption and co-precipitation due to the lack of electrostatic attraction (Streat *et al*., 2007; Dinesh *et al*., 2007). Whereas, As-enriched groundwater is generally dominated by As(III), up to 96% (Smedley, and Kinniburgh, 2002).

Therefore, there is a great need for applying efficient methods for arsenic removal from drinking water since a large fraction of the regions exposed to high arsenic concentrations are developing countries with an important percentage of rural population (Robins, 2001). Arsenic removal from waters is not an easy task. Economical aspects are perhaps the most important factors for the selection of the technology, taking into account the size of the population, incidence of chronic illnesses, lack of safe water, poverty conditions, and other socioeconomic variables. In most cases, sophisticated, expensive techniques cannot be applied in populations with low economical resources. In addition, arsenic treatment units require very sensitive monitoring and maintenance arrangements, which falls far beyond the economic scope of poor isolated communities (Kemper and Minnatullah, 2005).

From a technical point of view, the physicochemical and microbiological characteristics of the waters and the available materials in the region will determine the most convenient technology for removal of arsenic in each site. The selection of the method depends greatly on arsenic speciation, chemical composition of the water, reduction potential, hardness, presence of silica, sulfate, phosphate, iron and other chemical species, volumes to be treated and degree of sophistication that may be applied. Basically, many of the existing processes are acceptable under the correct circumstances, but ‘‘the challenge is to determine which process goes with which set of circumstances’’ (Kartinen and Martin, 1995). Sometimes, the removal technology is suitable, but its application is not possible due to the reluctance of people to accept the changes on the organoleptic properties of waters they have been drinking for years. Additionally, the volume, handling and final disposal of the generated wastes should be considered (Hering *et al*., 1997; McNeill and Edwards, 1995; Meng *et al*., 2000; Sancha, 2003).

So far, a variety of methods have been developed for this purpose and several techniques effectively lower arsenic concentrations in aqueous solution such as coagulation/filtration, ion-exchange, membrane technologies, chemical precipitation and adsorption. Adsorption is considered to be the one of the most promising technologies because the system can be simple to operate and cost effective. Unfortunately, most of the mentioned methods present disadvantages that make them unsuitable for small-scale applications as required by disperse populations situated in rural areas. For example, reverse osmosis membranes have a relatively high cost, and the need for electric power and technically-skilled operators represents a disadvantage for isolated users. In the case of coagulation/filtration, its domestic application has the inconvenience of having to deal with sludge disposal, as well as the difficulty of achieving a complete separation of flocs. Ion-exchange and arsenic-specific adsorption media generally have relatively high costs for rural areas, and present availability and logistics constraints that make them mostly unsuitable for this type of application (Robins, 2001). This process has the disadvantage of releasing harmful chemicals into the environment when the resin is regenerated (Lenoble *et al*., 2005). Finally, membrane processes are commonly employed, but this technology is expensive, mainly because of the high energy requirements (EPA, 2003).

Although various studies have been undertaken by numerous local researchers, proven treatment methods for the specific water conditions have not yet been commercialized due to a lack of interest of authorities, local industries and international agencies for financial and technical cooperation. This is because, current remediation technologies are expensive, and thus any lowering of the standard will put increased economic pressure on rural communities with high levels of arsenic in their drinking water (Litter *et al*., 2010).

Among the methods used for arsenic removal from water, adsorption has proven to be a very efficient method to control the mobility and bioavailability of arsenic. The technology of adsorption is based on materials having a high affinity for dissolved arsenic. The adsorption of arsenic on solid materials such as goethite, basic Yttrium carbonate, red earth, activated carbon, zeolite and others have been conducted. The removal of arsenic from water by means of adsorption onto solid materials is a well-known process. However, the selection of the most appropriate forms of these materials for present application depends mainly on their adsorption capacity and commercial availability (Zhao *et al*., 2011). Activated carbons and a number of low-cost adsorbents such as agricultural residue, naturally occurring ores and minerals, and peat have been utilized for removal of arsenic (Clifford *et al*., 1986). However, major disadvantages of these adsorbents are their low loading capacities and their relatively weak interactions with arsenic as evidenced by a low arsenic binding constant. The ideal features are strong affinity to target sorbate and high surface area with more accessible binding sites (Swapan *et al*., 2012).

In order to improve the adsorption of arsenic using activated carbon, a study by Huang and Vane (1989), has found that impregnation with different iron salts increase ten times the original arsenic adsorption capacity of carbon. Other than that, arsenic removal by activated carbon can also be improved by doping with metals having a high affinity for arsenate and arsenite such as copper (Cu) and zirconium (Zr). However, Cu and Zr can be released in the solution, thus presenting other toxic effects. Adsorption of arsenic by iron compounds has been established by several authors (Manning and Goldberg, 1997; Manning and Ferdorf, 1998; Wilkie and Hering, 1996). Elementary iron (Lackovic and Kikoluidis, 2000; Su and Puls, 2001a; Su and Puls, 2001b), granular iron hydroxides, and ferrihydrites (Driehars *et al*., 1998; Thirunavukkarasu *et al*., 2001; Raven *et al*., 1998; Badruzzamana *et al*., 2004) have been proposed for the removal of arsenic from water.

Most of these technologies are not efficient enough for the removal of As(III). Therefore, a pre-oxidation step is usually required to transform the trivalent form to pentavalent followed by coprecipitation/adsorption of the As(V) formed onto the metal oxyhydroxides. The oxidation procedure is mainly performed by the addition of chemical reagents, such as potassium permanganate, chlorine, ozone, hydrogen peroxide or manganese oxides (Jekel, 1994; Driehaus *et al*. 1995; Kim and Nriangu, 2000). Although these reagents are effective in oxidizing trivalent arsenic, they may cause several secondary problems arising mainly by the presence of residuals or from by-products formation, inducing also a significant increase to operational costs of the methods (Zouboulis and Katsoyiannis, 2005). However, manganese dioxide was emphasized as an effective oxidizing agent of As(III) and its oxidation potential is relatively low and fit for specific oxidation of As(III). Manganese dioxide can also be used as adsorbent for removal of arsenic, but its adsorption is low (Lenoble *et al*., 2004) and this limits its application.

To improve the removal efficiency, many composite adsorbents containing MnO_2 have been synthesized. Two natural Fe–Mn-mineral materials (Chakravarty *et al*., 2002; Deschamps *et al*., 2005) whose main components are Fe_2O_3 and MnO_2, have been investigated for As(III) and As(V) removal from water and both of them are more effective for As(III) removal than that of As(V). However, their adsorption capacities for both As(III) and As(V) are very low. Besides, synthetic Fe oxide-coated MnO_2 (Oscarson *et al*.,1983) has also been studied for the oxidation and sorption of As(III), but it's As(III) adsorption capacity was lower than that of pure Fe oxide since MnO_2 was coated by Fe oxide and could hardly oxidize As(III). A study by Wu *et al*., (2011) demonstrated the use of Fe–Mn binary composite that combines the oxidation property of manganese dioxide and the adsorption features to As(V) of iron oxides, able to oxidize As(III) and have good adsorption capacity for As(V) simultaneously. However, this method needs to combine with a coagulation process (poly-aluminium chloride) to facilitate the arsenic removal in order to meet the guideline limit of 10µg/L.

These absorbents show a certain capacity to adsorb arsenic, but they still contain many inherent limitations such as the adsorbents have a limited adsorption capacity and leaking of metal impregnated for adsorbing arsenic species. Other than that, these methods have to adjust pH and some operation problems as well as complexity of adsorbent preparation. The problems in term of either efficiency or in cost and so on make it less attractive as a chosen method for removing of arsenic from aqueous medium. In order to meet the needs of people of arsenic contaminated regions, alternative techniques are required that can effectively reduce arsenic concentrations from water to environmentally acceptable levels at affordable cost (Zhao *et al*., 2009).

1.3 Objectives of Study

The objectives of this study are as follows:

1. To screen the potential low cost materials for As (III) adsorption and to study the effect of adsorbent treatment method on As (III) removal.
2. To characterize the selected adsorbents using instrumental analysis such as field emission scanning electron microscopy combined with electron dispersive X-ray spectroscopy (FESEM-EDX), Brunauer-Elmer-Teller (BET) analysis, X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).
3. To study the effect of particle size on adsorption parameter, adsorption isotherm and kinetic studies for As (III) removal as well as to investigate the mechanisms responsible for As (III) removal using the adsorbents.
4. To evaluate the removal of As (III) from water using a column study for the effect of contact time based on flow rate and bed depth as well as modeling study.
5. To predict the As (III) removal using a multilayer feed forward back propagation neural network (BP-ANN) model in order to reduce the cost for experimental runs.

1.4 Scope of Study

The potential low cost materials used in this study were naturally occurring rocks (shale sedimentary rock (SSR), caustic sedimentary rock (CSR), sedimentary rock from cambodia (CR) and river sand (RS)) ceramic factory by-products (porcelain glaze (PG), full body porcelain black (FBPB), ceramic glaze (CG), full body porcelain white (FBPW) and clay (C)) and the common commercially available water purifier, activated carbon (AC), have been used for As(III) adsorption. For the study on the effect of adsorbent activation method on As(III) removal, three methods of activation were used namely heat treatment, acid treatment and impregnation of adsorbent using metal ions such as Mn and Mg. Then, the adsorbents that were prepared using the best activation method was characterized using instrumental analysis (electron dispersive X-ray spectroscopy (FESEM-EDX), Brunauer-Elmer-Teller (BET) analysis, X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA)) in order to define their morphology, surface structure and properties of modified adsorbents. The study on the effect of particle size on adsorption parameter, adsorption isotherm and kinetic studies for As(III) removal were carried out using adsorbents with particle sizes of 75-106 µm and 0.5-1.18 mm. The mechanisms responsible for As (III) removal using modified natural adsorbents were investigated using instrumental analysis and adsorption parameters. Evaluation of adsorbent for the removal of As (III) from water using a column study was carried for the effect of contact time based on some parameters such as flow rate and bed depth. Lastly, the prediction of As (III) removal using a multilayer feed forward back propagation neural network (BP-ANN) model was carried out in order to reduce the cost for experimental run.

1.5 Significance of Study

Many technologies exist for removing arsenic from aqueous medium, but most of them suffer from one or more drawbacks, limitations and scope of application (USEPA, 2000). Adsorption and coagulation are two of the cheapest arsenic removal techniques, employed to date. Although coagulation with iron and aluminium salts is more effective, the requirement of a skilled operator limits its application in small community and household levels. Moreover, in some coagulation treatments, a large amount of salt must be added which introduces contaminants such as sulfate ions into the water that requires subsequent treatment. In addition, the cost of the chemical reagents used in such treatments can limit their commercial applicability. In comparison, solid adsorbents are easy to handle and are appropriate for use in the countryside of India and Bangladesh where the largest number of people affected by arsenic contamination live. Recently, the use of solid adsorbents particularly natural minerals has shown some promising results in the removal of arsenic from contaminated groundwater (Mohapatra *et al*., 2008).

Different adsorbents have been tried for arsenic removal, and there is a wide variation in their effectiveness, as well as cost. The latter becomes an important factor in determining the treatment technique in several developing countries like Bangladesh and India. The use of natural materials offers an advantage of abundance and cost. In addition, such materials are ideal for one time use requiring no regeneration. This is an important convenience, especially in areas which are remote, have no regeneration facility, or for communities where drinking water is usually handled by women and children who are not trained enough to handle regeneration. The use of natural materials such as mineral, ores and agricultural residue containing oxide and hydroxide shows an excellent method for arsenic mitigation (Mohapatra *et al*., 2007).

Goethite, α-FeOOH, one of the iron oxide minerals that are widely distributed, occurs in rocks, soils and throughout the global ecosystem, and has the diaspore structure which is based on hexagonal close packing. Generally, goethite is an oxidation, decomposition, weathering and hydrolyzation product of pyrite, siderite, magnetite and Fe-containing silicates (Cornell and Schwertmann, 2003). Although goethite displays a range of shapes and sizes, the most basic morphology is acicular with the length varying from tens of nanometer to several microns. Goethite is one of the most abundant and thermodynamically-stable Fe-containing crystalline compounds; therefore, goethite is the first oxide to form or is the end member of many transformations (Cornell and Schwertmann, 2003; Liu *et al*., 2012;

Schwertmann, 1971) in which the transformation of goethite to hematite generally occurs after heating between 180 and 300^{o}C (Ruan *et al*., 2001; Prasad *et al*., 2006).

Without any modification, natural iron oxide minerals have a limited adsorption capacity due to their small surface area. So, it is important to modify the minerals to increase the specific surface areas and thus improve adsorption capacities. There are various methods for the preparation of microporous minerals such as mechanical, thermal and chemical treatments as well as multiple adjustments. The most effective method is thermal treatment, including thermal modification and thermal chemical synthesis (Jia *et al*., 2012).

Thermal modification for preparing microporous minerals has attracted great attention since the 1970s. In thermal treatment of minerals, some reaction occurs such as dehydration, dehydroxylation and decomposition of minerals resulting in the modification of structures and characteristics (Gan *et al*., 2009). The improvements of microporous minerals after thermal treatment occur on specific surface area, pore volume, and adsorption capacity (Ozacar, 2003). Thermal treatment has been found to be good for preparing homogeneous microporous minerals (Meng and Park, 2010). Thus, the porous hematite prepared from thermal modification of goethite used in this study will provide high As(III) adsorption capacity, low cost and ease in operation. This adsorbent will be beneficial for people in rural areas since the preparation of the adsorbent is very simple and can be done by inexperienced persons. The adsorbents prepared do not involve any chemical and no pH adjustment is required for treated water.

Villagers can prepare their own adsorbent for groundwater filtration by collecting natural ore mineral-goethite-rich (natural goethite-yellow colour) which is abundant and easily available throughout the globe. To reduce the size, natural iron ore can be crushed using a hammer or any hard material. The crushed natural iron ores are then washed to remove unwanted particles before it was put in a metal container such as a pot for heating process. This can be done for one to two hours with mild heating using firewood. The temperature for the heating process not necessarily be measured or controlled since thermal decomposition of hydrous and hydroxyl group can occur at temperatures as low as 180^{o}C. Almost no cost is involved in the preparation of this adsorbent and the preparation is very simple. With that, poor peoples in rural areas will have a chance to consume As-free water at affordable cost.

1.6 Thesis Outline

This thesis is divided into seven chapters. The first chapter is the introduction of the study which comprise of the background of study, statement of problem, objectives, scope and significance of study as well as the framework of the thesis. In this chapter, the problem which led to the research being conducted, the aim of the study and the importance of this research was clearly stated.

Chapter 2 deals with the Literature Review. In this chapter the overview of arsenic contamination in groundwater, sources and arsenic chemistry as well as the toxicity of arsenic to human health were thoroughly reviewed in order to provide an insight about the crucial problem of arsenic around the world. Other than that, the technology used for arsenic removal from water were discussed but the focus is more on the adsorption technique using low cost adsorbent materials such agricultural wastes, industrial by-products and natural materials. The use of small scale and low cost method for As(III) removal in rural area was evaluated and the use of artificial neural network (ANN) for modeling of arsenic removal study in order to reduce the cost for experimental run was discussed.

Chapter 3 covers the screening of low cost adsorbents, treatment and characterization of adsorbents for As (III) removal. Screening of adsorbents is necessary in order to select the most potential and low cost material to be applied in the study. The activation (heat, acid and impregnation/metal treatment) of selected adsorbents were discussed in order to overcome the problem regarding low porosity as well as low specific surface area of natural adsorbent. To facilitate the understanding of the adsorption process for the selected adsorbents, characterization of adsorbents using instrumental analysis was explored thoroughly in this section.

Chapter 4 deals with the experimental performance, mathematical models and mechanism of As (III) adsorption on calcined SSR and CSR. In this chapter, the principles of adsorption, both the physics and chemistry perspectives are presented in a broad brush approach to the mathematical solutions of complex adsorption isotherm. Mathematical modeling of adsorption is useful mostly for providing a conceptual appreciation of the mechanism and a good knowledge of the adsorption theory is required in order to optimize the process.

Chapter 5 discussed about the As (III) removal from water in a fixed bed using SSR adsorbents: covering both experimental and modeling studies. In this chapter, the effect of contact time based on operation parameters such as bed depth and flow rate was explained based on the breakthrough time. Several model fitting such as the bed depth service time, Thomas and Yoon-Nelson models were explained.

In Chapter 6, the use of artificial neural network modeling of As (III) removal from water by SSR and CSR were discussed. This modeling is an alternative tool to evaluate the adsorption removal without doing a lot of experiments. In other words, the missing data can be incorporated into the model for the model to predict the desired output. The last chapter i.e Chapter 7, covers the conclusions and recommendations for future work. The research framework for this present study is shown in Figure 1.1.

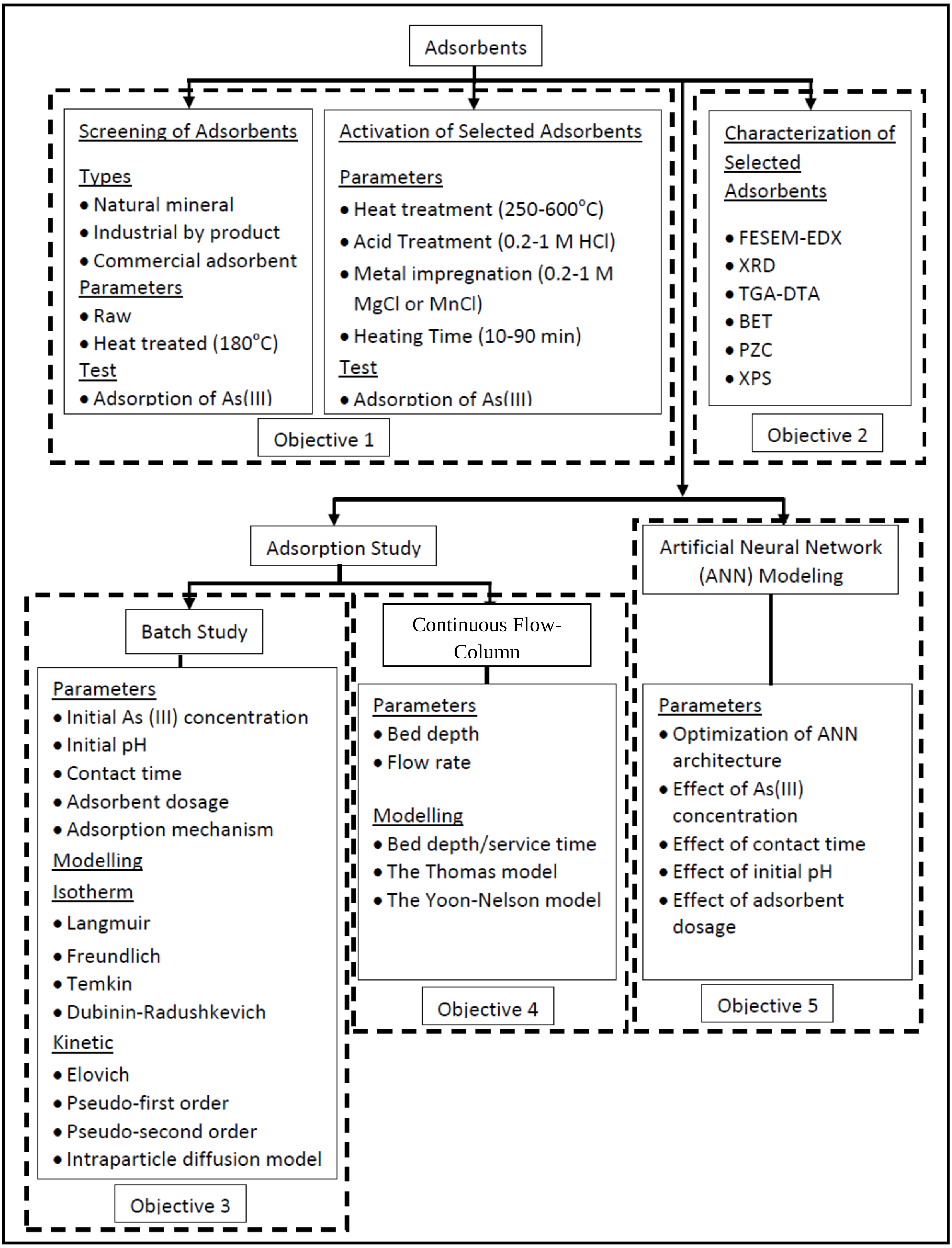

Figure 1.1: Research framework.

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