Study on the Effects of *Cupressus sempervirens* and *Pinus pinaster*-derived Adsorbents on Arsenic (III) Removal from Polluted Water

Advisor : Prof. Lim Jun Heok

By
Kavugho Sophie Mission

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By

Kavugho Sophie Mission

Approved By :

Prof. Yong Sun Won

Prof. Do Jin Im

Prof. Jun Heok Lim

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Kavugho Sophie Mission

Department of Applied Chemical Engineering, Major of Chemical
Engineering, The Graduate School,
Pukyong National University

Abstract

The present study investigated the effects of *Cupressus sempervirens* (cypress) leaves, cones, bark and *Pinus pinaster* (pine) cone chips and bark on the removal of arsenic (III) from polluted water. The study aimed to observe the effects in the conditions close to the natural water systems, that is pH 6~7, room temperature, and using tap water for its high resemblance with water in the field in comparison to the deionized or distilled water with its pH adjusted with citric acid from lemon juice to avoid the addition of industrial chemicals (in fact, more likely unavailable to populations of concern).

The effects of various adsorbents for the arsenic (III) removal were observed with regard to the following two parameters: adsorbent dose and arsenic initial concentration. The analysis showed that the removal efficiency increases in proportion to the adsorbent dose for cypress leaves, cones, bark and pine cone chips but decreases with the increase of the adsorbent dose for the pine bark. On the other hand, the removal efficiency hardly showed any relation with the arsenic initial concentration except for pine bark. Among the studied materials, cypress leaves exhibited a great potential in the removal of arsenic (III), followed by cypress cones and pine cones. Cypress bark and pine bark, on the contrary, showed precarious results.

Equilibrium and kinetic experiments were conducted with cypress leaves as an adsorbent at the arsenic (III) initial concentrations of 0.1, 0.2 and 10 ppm, which was found to be the most efficient among the five types of studied adsorbents. Isotherm calculations showed that the adsorption of As (III) onto cypress leaves fitted both Langmuir and Freundlich models. And, kinetics studies indicated that the adsorption was better represented by a pseudo-2nd order system followed by intra-particle diffusion.

Keywords: Drinking water treatment, Arsenic removal, natural adsorbents, cypress derived adsorbent, pine derived adsorbent.

Cupressus sempervivens 및 *Pinus pinaster* 흡착제의 폐수 중 비소 (III) 제거에 관한 연구

요약

본 연구는 오염 된 물에서 비소 (III)의 제거에 cupressus sempervirens (노송나무) 잎, 열매, 나무껍질과 Pinus Pinaster (소나무)의 열매 칩과 껍질의 효과를 조사 하였다. 본 연구의 목적은 자연 수계에 가까운 조건에서 이들의 효과를 관찰하는 것으로써, pH 6 ~ 7, 실온의 조건과 탈 이온 수 또는 증류수보다 자연 수계에 매우 유사한 수돗물을 사용하고 사람들이 쉽게 얻을 수 없는 산업 화학 물질들의 첨가를 방지하기 위해 레몬주스의 구연산으로부터 pH를 조정하였다.

제거의 효과는 흡착제 용량 및 초기 비소 농도 두 개의 매개 변수에 따라 관찰되었다. 노송나무 잎, 열매, 껍질 솔방울 칩의 흡착제

량에 따라 제거 효율이 증가하였지만, 소나무 껍질에 대한 흡착제 용량의 증가하였을 때는 제거 효율이 감소하였다. 반면에, 소나무 껍질에서 제외 제거 효율은 초기 비소 농도와 아무 관계를 보이지 않았다. 연구 자료 중, 노송나무 잎은 노송나무 열매 및 소나무 열매 칩 다음으로 비소의 제거에 큰 잠재력을 보였다. 반면에 노송나무 껍질과 소나무 껍질은 위태로운 결과를 보여 주었다.

노송나무 잎 흡착제는 연구 된 다섯 가지 유형 중에서 가장 효율적인 것으로 밝혀졌기 때문에 평형 속도 실험은 노송나무 잎 흡착제를 이용했고 비소 초기 농도는 0.1, 0.2, 10 ppm로 연구를 하였다. 등온선 계산을 통해 노송나무 잎 상으로 (III)의 흡착은 Langmuir 모델이 우위에 있지만 Langmuir와 Freundlich 모델 모두에 적합함을 확인하였다. 또한, 역학 연구에서는 이번 흡착이 입자 내 확산 다음으로 가상의 2차계를 잘 나타냄을 확인하였다.

CHAPTER 1

INTRODUCTION

While clean drinking water may not be a problem in developed countries, it is still a struggle in so many developing countries [1] [2-4]. In fact, water pollution problems are said to be directly proportional to poverty and obviously, no economic development is possible without water [5]. Drinkable water scarcity is directly related to high morbi-mortality levels and to low economic development; therefore, several vicious and virtuous circles are established from and to water situation [1]. Fig. 1.1 shows the relationship between water, poverty and human development [1].

According to another study, 40% of the earth population lack proper sanitation infrastructures and problems with water quality are reported to be the fifth cause of death (above AIDS, tuberculosis, or malaria). More than one in six do not have access to safe freshwater [6]. Considering that 2.5 billion people live without basic sanitation [7] which has a tight correlation with water shortage, this makes even higher the number of people who lack access to safe freshwater.

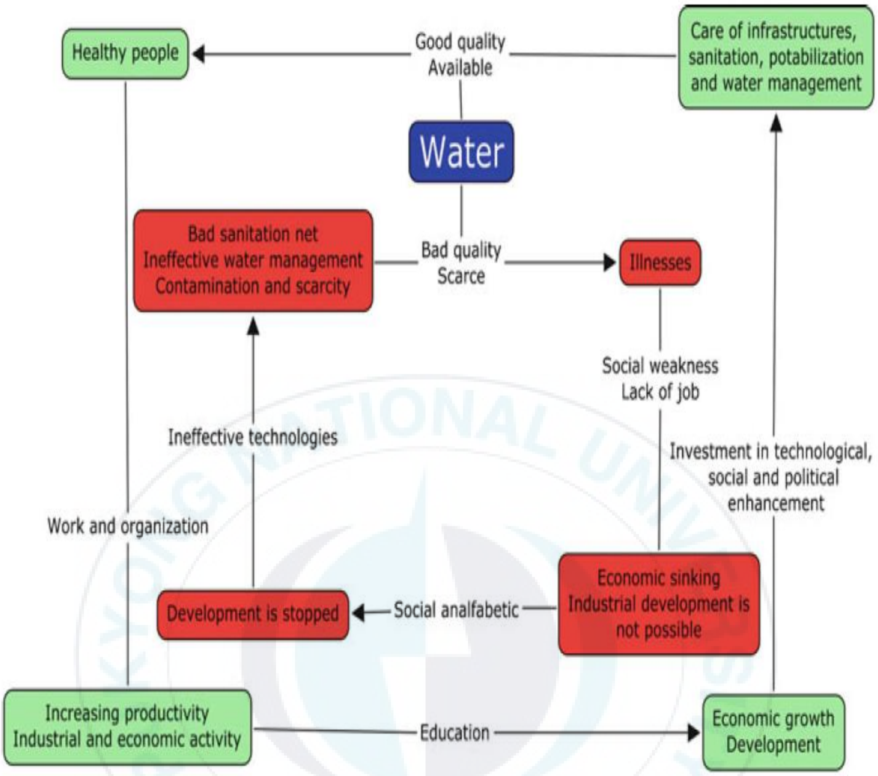


Figure 1.1. Relationship between water, poverty and human development [1].

In addition some developing countries are currently struggling with particular pollutants which are not easy to be removed from water sources. The most covered cases up to date are metal pollution in several Asian countries such as India, Nepal, Bangladesh, China, etc. [1] [3] [8] [9] [10].

Recently a lot of researchers have studied particularly arsenic removal from water in these countries but none have studied the case in African countries although they are also severely touched by this problem. A study done in Bukavu, a city located in the East of the Democratic Republic of Congo revealed that the drinking water scarcity, physical, chemical, bacteriologic quality of water etc. were a serious problem [2]. Among the chemicals found in drinking water in and around Bukavu city, several toxic substances in concentrations way too high than the World Health Organization (WHO) recommendations were found, namely arsenic (2 ppm), total chlorine (2 ppm), bromine (4.5 ppm), chloride dioxide (5 ppm), volatile acids (2800 ppm), iron (3 ppm), etc. [2]. Arsenic known for its high toxicity is present in a concentration of up to 2 ppm, 200 times higher than the WHO recommendation of 10 ppb [3-4] [11], while phosphate is found to be 30 mg/l making it 6 times higher than the WHO recommendation of 5 ppm.

Due to the high toxicity of arsenic, and its alarming concentration in water found in Bukavu, this study aimed to find a solution adapted to this region of the world, according to the idea of appropriate technologies. Not that there exist no methods efficient to remove arsenic from water, but these methods as it will be discussed throughout the chapter 2 of this thesis, are unfortunately not adapted to the economic condition of the populations in need. And, to a relatively considerable level, they are inadequate to their technologic skills as well. It is important to remember the context in which populations of developing countries live. In most of the time, they are abandoned to themselves without any support from their governments. Therefore, it would not be appropriate to propose to them solutions that will require expensive equipment, difficult and complex technologies that require engineer level skills or materials unavailable in their environment resulting in a need of materials importation from abroad.

Having this context in mind, it is clear that new methods that include available material, easy manipulation and low expenses criteria should be actively researched upon according to each region concerned. Natural biomass used as adsorbent have been proved in so many studies now to be efficient in removing heavy metals from aqueous solutions [1][12-21]. These methods have the advantages of being simple, direct and natural [16].

Whether in removal of heavy metals such as Nickel, Lead, Aluminum, Cadmium, Cupper [1][14-15][20] or dyes such as methylene blue and rhodamine B [1][18][21], surfactants [1], metalloids particularly arsenic [3-4][11][22], adsorbents derived from trees were successfully studied and cypress as well as pine trees have the advantage of being present in all the continents. Especially cypress is a common tree that can be found almost everywhere [23]. Based on the success that these trees have in other researches, and on their availability, this study applied their derivative adsorbents on arsenic removal. Except from pine leaves investigated in a previous study [4], cypress leaves, cones, bark, pine cones and pine bark have never been used in arsenic removal from aqueous solution. Actually, cypress leaves, cypress cones, and pine leaves have been studied in heavy metal and dyes removal [14-15][20-21] but only pine leaves and pine cones chips char have been used in the arsenic removal studies so far [4][24].

From this point, this study focused on cypress leaves, cones, bark, pine cones and bark for arsenic (III) removal from water, as an approach to bring a new solution to arsenic water pollution in regions where cypress and/or pine is a common tree.

CHAPTER 2

THEORY AND LITERATURE SURVEY

2.1. Water Pollution

There are many ways to define water pollution. Usually, it refers to a buildup of one or more substances in water to such an extent that they cause problems for animals or people. Oceans, lakes, rivers, and other inland waters are capable of naturally cleaning up a certain amount of pollution by dispersing it harmlessly. Thus, water pollution is all about quantities or in other words, pollutants' concentration: how much of a polluting substance is released and how big is the volume of water it is released in. A small quantity of a toxic chemical may have little effect if it is poured into the ocean from a ship. However, the same amount of the same chemical can have a much important impact released into a lake or river, where there is less clean water to disperse it [25].

Water pollution does not always occur naturally but often caused by human beings and animals. Pollution is a human problem as it is a relatively recent development in the planet's history. In fact, before the 19th century Industrial Revolution, people lived more in harmony with their immediate environment. As industrialization has spread around the globe, the problem of pollution has spread with it too. In periods where Earth's population was much smaller, it could not be believed that pollution would ever present a serious problem. It was even once popularly believed that the oceans were way too big to pollute. But today, with around 7 billion people on the planet, it has become obvious that there are limits. Pollution is among the indications that humans have gone past those limits [25].

Surface waters and groundwater are the two types of water resources that are affected by pollution. Also pollution can occur in two different ways. The pollution that comes from a single location, such as a discharge pipe attached to a factory, is known as point-source pollution. Other examples of point source pollution include a discharge from a smoke stack (factory chimney), an oil spill from a tanker, or somebody pouring oil from their car down a drain. A large part of water pollution does not happen from one single source but from many different scattered sources. This is known as nonpoint-source pollution [25].

When point-source pollution enters the environment, the area immediately around the source is usually the place most affected. For example, when a tanker accident occurs, the oil slick is concentrated around the tanker itself and, in the right ocean conditions; the further away from the tanker you go the pollution disperses. This is less likely to happen with nonpoint source pollution which, by definition, enters the environment from many different places at once [25].

Sometimes pollution that enters the environment in one place has a consequence hundreds or even thousands of kilometers away. This phenomenon is known as trans-boundary pollution. One example is the way radioactive waste travels through the oceans from nuclear reprocessing plants in England and France to nearby countries such as Ireland and Norway [25].

Several causes of water pollution can be listed below [25] [26]:

1) Sewage
2) Nutrients
3) Waste water
4) Chemical Waste
5) Radioactive waste
6) Oil pollution
7) Plastics

8) Alien species: alien species are a major issue. Alien species; sometimes known as invasive species, are animals or plants that have been introduced from one region to a different ecosystem where they do not belong. Outside their normal environment, they rapidly grow wild, crowding out the usual animals or plants that thrive there because they have no natural predators. Zebra mussels in the Great Lakes of the USA, which were carried there from Europe by ballast water (waste water flushed from ships), are common examples of alien species.
9) Other forms of pollution can include sediments (fine-grained powders that flow from the rivers into the sea), thermal pollution from power plants and factories, etc.

Water pollution touches the entire biosphere (organisms and plants) living in water (e.g. lakes, rivers, oceans, aquifers and groundwater). In almost all cases the effect is not only damaging to individual species and population, but also to the natural biological communities [27].

The great majority of evident water-related health problems result from microbial contamination (bacterial, viral, protozoan or other biological).

Nevertheless, an appreciable number of serious health concerns may come from chemical contamination of drinking-water [2] [28].

According to the Environmental Campaign Organization WWF, pollution from toxic chemicals threatens life on this planet. Every ocean and every continent, from the tropics to the once-pristine Polar Regions, is contaminated [25]. This massive water contamination results into safe water scarcity at the global level. The water scarcity is a global situation that reaches unacceptable levels. It has been reported that 40% of the total earth population lack proper sanitation infrastructures and that problems with water quality are the fifth cause of death (above AIDS, tuberculosis, or malaria). Nowadays, more than one in six does not have access to safe freshwater [6]. This is even more serious if the fact that the shortage of safe water has a concomitant effect with living without basic sanitation, which is the case of 2.5 billion people, is taken into account [7]. In addition, emerging economies like India or China are currently suffering from a pollution problem with special pollutants that are not easy to remove from water effluents. These are called refractory pollutants and the most important groups are the dyes, surfactants, and heavy metals and metalloids [1].

Among the metalloids category, the presence of elevated levels of arsenic in groundwater has become a major concern around the world, especially in South Asia [27], Argentina, Mexico, Hungary, Taiwan, Bangladesh, China, India [3], Democratic Republic of Congo [2].etc. In Bangladesh alone, more than 60% of ground water is reported to contain arsenic concentrations higher than the WHO recommendation value [29] and this is estimated to affect the health of millions of people [3].

2.1.1. Arsenic Poisoning Exposure

Arsenic is only one of many chemicals labeled under the category of toxic chemicals, however, in many regions of developing countries such as India, Nepal, Bangladesh, China, and African countries, as it has been mentioned in the previous sections, arsenic has become a very important threat to populations health as it is highly found in many sources of waters, most of the time leaving these populations with no other choices for safe freshwater.

Not always being a health threat, Arsenic is an element that occurs naturally in rocks and soil and is used for a variety of purposes within industry and agriculture. It can also be a byproduct of copper smelting, mining, and coal burning. Arsenic can combine with other elements to make chemicals used to preserve wood and to kill insects on cotton and other agricultural crops [26].

However, Arsenic can enter the water supply from natural deposits in the earth or from industrial and agricultural pollution. It is widely believed that naturally occurring arsenic dissolves out of certain rock formations when ground water levels drop significantly [26][30]. According to the same articles, it has been reported that once released, arsenic remains in the environment for a long time. Arsenic is also removed from the air by rain, snow, and gradual settling. Once on the ground or in surface water, arsenic can slowly enter ground water. High arsenic levels in private wells also may come from certain arsenic containing fertilizers used in the past or industrial waste. It may also result from improper well construction or overuse of chemical fertilizers or herbicides in the past [26].

Arsenic concentrations depend on geographic location. When arsenic levels are found to be particularly high at a certain location, it may be necessary to remove it by treating drinking water [30].

Arsenic usually exists in two different forms or valences, in a natural setting according to the amount of oxygen available in groundwater. While in shallower aquifers with higher levels of oxygen, arsenic will usually exist as arsenate As (V), in deeper, anaerobic ground waters, arsenic usually occurs as arsenite As (III) [30-32]. In the pH range of 4 to 10, the predominant As (III) compound is neutrally charged, while As (V) species are negatively charged. Following this reality, removal efficiencies for As (III) are usually less than those of As (V) due to As (V)’s negative charge. In many cases, pretreatment of As (III) to oxidize it to As (V) may be necessary to efficiently remove arsenic from drinking water [27][30][32]. This is much more important as it has been observed that trivalent arsenic As (III) which occurs in reducing condition is sixty times more toxic than pentavalent As (V) found in oxidizing environment [27][31].

Many studies have been conducted to understand the way arsenic, especially inorganic arsenic toxicity affect health. Health effects of arsenic differ by route of exposure [33] as it can be seen bellow:

-Inhalation exposure can cause immunological and lymphoreticular effects

-Oral exposure causes death (exposure to arsenic high concentration in drinking water causes death due to respiratory disease, cardiovascular disease, and cancer.), systemic effects [34-36], cardiovascular effects [34][37], gastrointestinal effects [38-39], muscular effects [40], hepatic effects [41], renal effects, endocrine effects [42-57], dermal effects [58-68], and ocular Effects.

From these studies, it is clear that exposure to arsenic is a severe threat to the human being and animals. Also they show that contamination mostly happens through drinking water. Therefore, the most efficient way to fight arsenic exposure is by appropriate water treatment.

2.1.1.1. The case of Democratic Republic of Congo

Although many studies have been conducted in several regions of the world in order to solve the problem of water contamination by arsenic, a few study if none at all has been conducted in the Democratic Republic of Congo where nonetheless arsenic has been found in drinking water, particularly in Bukavu, one city located in the East of the country. A study conducted in 2012 on drinking water quality in Bukavu revealed a high concentration of several metals and other dangerous elements found in water with a very high concentration far away from the WHO recommendation. Among these elements, arsenic was found to be exaggeratedly higher than the WHO recommendation with up to 2 ppm [2] which is 200 times higher than the WHO norm.

This is what inspired this study, in order to propose a solution adapted to this particular region of the world where until today, no research considering water treatment with particular regard to arsenic has never been done. The aim of this study is that population living in regions like Bukavu in terms of climate, technological and economic aspects can also have access to safe freshwater.

Table 2.1. Chemical analysis of several sources of drinking water consumed in Bukavu, Democratic Republic of Congo [2]

Chemical Analysis from Bukavu water	
Chemical Substance	Concentration (ppm)
Arsenic	0~2
Tot. Chlorine	0~2
Free Chlorine	0~2
Bromine	0~4.5
Chlorine Dioxide	0~5
Oxygen	0~15
Aluminum	0~0.80
Sulfate	0~70
Cyanide	0~0.240
Volatile Acid	0~2800
Nitrate	0~0.5
Nitrite	0~0.5
Ferrous Irion	0~3
Tot. Iron	0~3
Manganese	0~30
Phosphate	0~30

2.1.2. Consumable Water Composition Requirements

The WHO produces international norms on water quality and human health in the form of guidelines that are used as the basis for regulation and standard setting, in developing and developed countries worldwide.

There are three main types of microorganisms that can be found in drinking water: bacteria, viruses and protozoa. They can exist naturally or be the result of contamination by fecal material of human or animal origin. The sources of surface water, lakes, rivers and reservoirs are more likely to contain microorganisms than groundwater sources, unless the latter are influenced by surface water. The quality of drinking water must comply with chemical, bacteriological, organoleptic, and biological standards [2].

Regulatory Parameters are:

- Organoleptic quality: color, turbidity, order, taste
- Physicochemical: temperature, pH, ions etc.
- Unwanted substances: nitrates, nitrites, pesticides, etc.
- Toxic substances (arsenic, cadmium, lead, hydrocarbons, etc.)
- Microbiological parameters (water should not contain pathogenic organisms) [2] [30].

These parameters may be summarized into three which are: physical, microbiological and chemical parameters. Physical parameters include taste and odor of water (water appearance). Although these constituents may have no direct health effects, water that is highly turbid or highly colored or has an objectionable taste or odor may be regarded by consumers as unsafe and rejected. In extreme cases, aesthetically unacceptable but otherwise safe drinking-water may be avoided by consumers in favor of more pleasant but potentially unsafe sources. Changes in the normal appearance, odor or taste of a drinking-water supply may indicate changes in the quality of the raw water source or deficiencies in the treatment process and should be investigated.

Microbiological problems may be effectively addressed by disinfection, which is an effective barrier to many pathogens (especially bacteria) during drinking-water treatment and should be used for surface waters and for groundwater subject to faecal contamination. Although the use of chemical disinfectants in water treatment usually results in the formation of chemical by-products, the risks to health from these by-products are extremely small in comparison with the risks associated with inadequate disinfection; therefore it is important that disinfection efficacy not be compromised by the attempt to control such by-products [28].

Chemical parameter on the other hand, which is the focus of this study, deserves a particular attention due to its high potential of harm because the removal of chemical constituents from water is not as easy as can be the elimination of microorganisms which could be killed by boiling or disinfecting with chlorine... This fact is confirmed by the WHO water quality guideline 4th edition, according to which the health concerns associated with chemical constituents of drinking-water differ from those associated with microbial contamination and arise primarily from the ability of chemical constituents to cause adverse health effects after prolonged periods of exposure [28]. According to the same guideline, there are few chemical constituents of water that can lead to health problems resulting from a single exposure, except through massive accidental contamination of a drinking-water supply. Moreover, experience shows that in many, but not all, such incidents, the water becomes undrinkable due to unacceptable taste, odor and appearance [28].

In situations where short-term exposure is not likely to lead to health impairment, it is often most effective to concentrate the available resources for remedial action on finding and eliminating the source of contamination, rather than on installing expensive drinking-water treatment for the removal of the chemical constituent, recommends the WHO guideline [28].

Table 2.2. Parameters on water chemical [2]

a) Physicochemical parameters

Parameters	**Norms in ppm**
Aluminium($Al^{3+)}$	max 0.2
Chlorine (Cl^-)	max 200
Magnesium ($Mg^{2+)}$	max 50
pH	6.5 ~ 9
Potassium (K)	max 12
Sodium (Na^+)	max 150
Sulfates (SO^-)	max 250

However, in the other situation where long-term exposure is observed, diseases related to contamination of drinking-water constitute a major burden on human health. Interventions to improve the quality of drinking-water provide significant benefits to health.

Table 2.2. Parameters on water chemical [2]

b) Toxic substances

Parameters	Norms in ppb
Arsenic (As)	max 10
Cadmium (Cd^{2+})	max 5
Soluble Chromium (Cr)	max 50
Cyanides (Cn^{-})	max 0.05
Mercury (Hg)	max 1
Nickel (Ni)	max 50
Phosphorus (P)	max 5
Lead (Pb)	max 50

Table 2.2. Parameters on water chemical [2]

c) Undesirable substances

Parameters	Norms
Ammonium (NH_4^+) in ppm	max 0.5
Silver (Ag^+) in ppb	max 10
Soluble Cupper (Cu) in ppm	max 1
Soluble Iron (Fe) in ppm	max 0.2
Fluorides (F^-) in ppm	max 1.5
Manganese (Mn) in ppm	max 0.05
Nitrates (NO_3^-) in ppm	max 50
Nitrites (NO_2^-) in ppm	max 0.1
Oxidability (O_2 to $KMnO_4$) in ppm	max 5

Table 2.2. Parameters on water chemical [2]

d) Pathologies generated by some mineral constituents

Substance	Effect on Health at higher concentration
Arsenic	Risk of cancer
Cadmium	Neurotoxic and cardiovascular effect
Lead	Accumulation in blood and tissues
Mercury	Neurological impairment
Nitrite	Methemoglobinemia

Table 2.3. Status of arsenic contamination in natural water in various countries

No	**Pays**	**Region**	**Total As (ppb)**	**Type of water**	**Refferences**
1	Argentina	Cordoba	>50	Groundwater	[69]
2	Afganistan	Ghazni	10-500	Groundwater	[70]
3	Australia	Victoria (around the gold-mining regions)	1-12,1-73,1-220	Groundwater, Drinkingwater, Surface water)	
4	Bangladesh	Noakhali	<1-4730	Groundwater	[10], [70]
5	Brazil	Minas Gerais (Southeastern Brazil)	0.4-350	Surface water	[70]
6	Cambodia	Prey Veng, Kandal-Mekong delta	0-900, 1-1610	Surface water	
7	Canada	Nova Scotia (Halifax Country)	1.5-738.8	Groundwater	
8	China		50-4440	Groundwater	
9	D. R. Congo	Bukavu (Northeastern D.R Congo)	0-2000 µg/l	Drinking Water	[2]

Table 2.3. Status of arsenic contamination in natural water in various countries (continue)

10	Finland	Southwest Finland	17-980	Groundwater	[70]
11	Greece	Fairbanks (mine tailings)	0-10000	Groundwater	
12	India	West Bengal, Uttar Pradesh	10-3200	Groundwater	
13	Japon	Fukuoka Prefecture (Southern region)	1-293	Groundwater	
14	Mexico	Lagunera	8-620	Groundwater	
15	Nepal	Rupandehi	0-2620	Groundwater	
16	Pakistan	Muzaffargarh	0-906	Groundwater	
17	Taiwan		10-1820	Groundwater	
18	Thailand	Ron Phibun	1->5000	Groundwater	
19	USA	Tulare Lake	0-2600	Groundwater	
20	Vietnam	Red River Delta (Northern Vietnam), Mekong Delta (Southern Vietnam)	<1-3050	Groundwater	

2.2. Water Purification and Purification Methods

Water is essential to sustain life, and a satisfactory supply (adequate, safe and accessible) must be available to all. Improving access to safe drinking-water can result in tangible benefits to health. Therefore, every effort should be made to achieve drinking-water that is as safe as well as practicable. Safe drinking-water, as defined by the WHO Guidelines, does not represent any significant risk to health over a lifetime of consumption, including different sensitivities that may occur between life stages [30].

Water purification is defined as the transition of dirty harmful (contaminated) water into clean safe water. In general, this means removing any kind of impurity contained in water such as contaminants or micro-organisms [12].

There exists a range of common water treatments methods that include:

- Chemical methods: Coagulation, Flocculation, combined with Flotation and Filtration, Precipitation, Ion exchange.
- Biological methods: Biodegradation methods such as Fungal decolorization, Microbial degradation, Adsorption by microbial biomass

- Physical Methods: Membrane-filtration process (Nano-filtration, Reverse Osmosis, Electro-dialysis, etc.) and Adsorption techniques.

However, all do not respond to the same particular problems. Some impurities such as heavy metal, dyes, and surfactants will be more sensitive to one method and not to the other, requiring an appropriate technology designed especially to target them from the water.

Contaminants such as surfactants, dyes, or heavy metals get into the alimentary chain and appear almost everywhere, and usually there is not a specific procedure for their removal, mostly in places where water treatment is almost a luxuriant process. Because of this, it is necessary for the development of new materials and methods to fit into the large variety of economic situations, both in the First and the so-called Third World. Natural products are perhaps one of the most interesting options of making water treatment a universal chance. Accessing clean water becomes then a cheaper and affordable possibility [1].

2.2.1. Adsorption Method

Adsorption is a process that uses solids for removing substances from either gaseous or liquid solutions. Adsorption phenomena are operative in most natural chemical, biological, and physical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are used widely in industrial applications for purification of waters and wastewaters [32].

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Physical adsorption is mainly caused by electrostatic forces and Van der Waals forces between the atoms which compose the adsorbent surface and the adsorbate molecules. Adsorption capacity depends on adsorbate chemical properties, adsorbent properties, pH, temperature, etc.

Although there are many available activated carbons, only a few are selective. These are also expensive. Therefore the research thirst over the years is to find improved and tailor-made materials, which meet several requirements such as regeneration capability, easy availability, cost effectiveness etc. Consequently, low-cost adsorbents have captured many researchers attention and characteristics as well as application of many such adsorbents have been reported [31-32].

Using biomaterial derived from non-living dried plants materials may be a more convenient and effective method for the removal of toxic metal (loid)s [1][3-4].

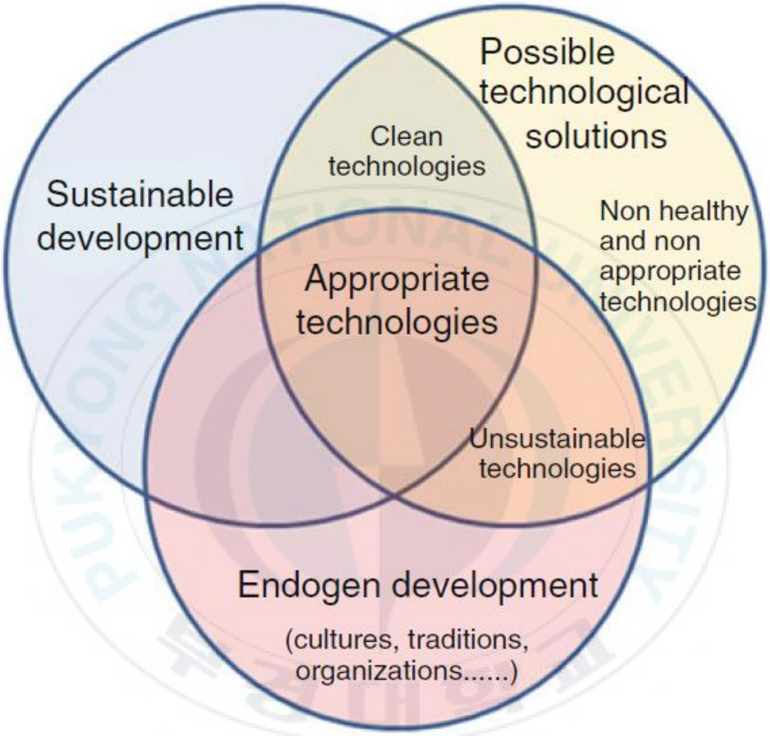
2.2.2. Adsorption Using Natural Adsorbents

One of the mechanisms human beings can apply to fight against poverty is technology [71], but since it is a cultural construct, it is not free from social implications [72].The concept of appropriate technology (Fig. 2.1) which started in the mid-1970s included some aspects that may be especially cared for in order to guarantee social and environmental feasibility of a technical proposal. The objective is to develop a new technological paradigm suitable mostly in developing countries (but not only) that can be executed on the following principles [73]:

- Environmental-friendly (sustainability): It does not endanger resources of subsequent generations.
- Cultural suitability: The solutions to given problems does not interfere with social manners or modals
- Technological transfer, no external dependency of mechanisms, apparatuses, or equipment.

These statements can be summarized into one: Technology must match both the user and the need in complexity and scale [72].

Figure 2.1. Appropriate technologies inside the general scenario of possible technologies (Source: Own elaboration from [74])



Having all the above in mind, this chapter will deal with two main natural sources: *Pinus pinaster* (Pine) and *Cupressus sempervirens* (Cypress) derivatives. Both seem to present rather interesting properties in order to become important agents of water treatment by removing contaminants according to appropriate technology principles.

Several methods have been suggested for the removal of toxic metals (including lead) from polluted water. These include precipitation [75], adsorption on activated carbon [76], ion exchange [77], complexation [78], ozonation [79] and the removal by hair [80-81], by fly-ash [82] and by water hyacinth [83-84].

Decaying leaves and leaf extracts have been found also capable of removing several toxic metals such as aluminum [85-87], nickel [88-89] and cadmium [90] from polluted water. These methods have the advantages of being simple, natural and direct [15].

In order to apply the same principles to arsenic removal which is the subject of this study, investigations on powder derivatives of *Pinus pinaster* (Pine) and *Cupressus sempervirens* (Cypress) were conducted. Because up to date, there is no effective treatment for curing health impacts due to the intake of high levels of arsenic [27], arsenic contamination prevention by removal technologies is of great importance. A wide range of technologies has been developed for the removal of high concentrations of arsenic from drinking water. The most common arsenic removal technologies use coagulation, precipitation, oxidation, ion exchange, membrane techniques (such as reverse osmosis), and adsorption [27] [30].

Each of these methods have their advantages and disadvantages, the late being mostly a high installation and operation cost, complexity of the equipment, maintenance, water taste alternation (Reverse Osmosis), competing ions can reduce the effectiveness , addition of chemicals which may result in by-products formation that will need to be treated, thus increasing the cost, etc.

One of the possible ways of minimizing the multiple concerns that have recently arisen on water and refractory pollutants is the implementation of new treatments based on natural products [1]. Both adsorption and coagulation are well-known processes for eliminating these kinds of contaminants; yet, new agents must be developed.

Today there is a global challenge regarding water management: Water resources may be optimized in order to guarantee an adequate availability for the large majority of the people. This is the first and main motivation to continue research on these kinds of resources.

This study focused on cypress leaves, cypress cones, cypress bark, pine cone chips and pine bark to respond to this challenge regarding water treatment by natural adsorbents in regions where these conifers are common trees; thus responding to the principles of appropriate technology (Environmental-friendly, Cultural suitability, Technological transfer, no external dependency of mechanisms, apparatuses, or equipment).

Although several studies have been reported on the use of dried plant material as a potential industrial instrument for metal removal [91-92] these studies have not focused on the removal of arsenic from aqueous solutions using cypress leaves, cones, bark or pine cones chips and pine bark powder.

An appropriate technology for arsenic removal, particularly in the context of less developed countries, should respond to the following criteria:

(1) The technology must be of simple design and easily produced;

(2) It must be low cost;

(3) It must use local, easily accessible materials;

(4) It must have a rural focus [3] [93].

The goals of our studies were:

1) To work without the addition of chemicals but citric acid in the form of lemon juice to adjust pH to neutral value, which is the most likely to be found in water on the filed

2) To investigate the efficiency of the As (III) removal at a neutral pH (pH = 6-7) with locally available materials and

3) To conduct the treatment experiment in tap water, a condition closer to the field by water composition in opposition to the deionized or distilled water.

CHAPTER 3

EXPERIMENTAL METHOD AND EQUIPMENT

3.1. Materials

3.1.1. Adsorbents Description

Cypress leaves, Cypress cones, Cypress bark, Pine cones and Pine bark were collected fresh from the trees in Santa Maria del Paradiso Contrada S.Maria della Scala property in Noto, Sicilia, Italy.

Each type of material was thoroughly rinsed with tap water then air-dried for couple of hours to prevent boiling to happen once put to dry completely in the oven at 65^{o}C, then 105^{o}C until the lowest humidity measured by a Moisture Analyzer (KERN DBS 60-3) was stable. The dried material was first crushed in an Albrigi grinding mill for cypress leaves, cones, bark, pine bark and in a home appliance crusher (Tokebi s6) for pine cones and both were screen-sieved with a Chung Gye Sang Gong Sa Standard testing sieve 710 micrometer to obtain a fine powder. The powder so obtained is the adsorbent used during this study.

(1) (2) (3) (4) (5)

Figure 3.1. (1) Cypress Leaves (2) Cypress Cones (3) Cypress Bark (4) Pine Cone (5) Pine Bark before processed into powder.

(1) (2) (3) (4) (5)

Figure 3.2. Adsorbents Powder (1) Cypress leaves C-L (2) Cypress Cones C-C (3) Cypress Bark C-B (4) Pine Cones Chips P-C (5) Pine Bark P-B

3.1.2. Pollutant Description

Arsenic is a naturally occurring element found in soils and groundwater. Arsenic concentrations vary in accordance with geographic location. When arsenic levels are found to be too high at a specific location, it may be necessary to treat drinking water to remove it [30].

Arsenic usually exists in two different forms, or valences, in a natural setting depending on the amount of oxygen available in groundwater [30]. In more shallow aquifers with higher levels of oxygen, arsenic will usually exist as arsenate, As (V). In deeper, anaerobic ground waters, arsenic usually occurs as arsenite, As (III). In the pH range of 4 to 10, the predominant As (III) compound is neutral in charge, while As (V) species are negatively charged. Removal efficiencies for As (III) are usually less than those of As (V) because of As (V)'s negative charge. In many cases, pretreatment of As (III) to oxidize it to As (V) may be necessary to efficiently remove arsenic from drinking water [30].

In this study, however, in order to perform the experiments in conditions the closest possible to conditions in the field, a fisher Sodium Arsenite (NaAsO2) was mixed to tap water to provide the most abundant species of arsenic found in the ground water; Arsenic (III) and the pH was adjusted to a neutral zone (6~7), the most similar to water on the field.

3.1.3. Experimental Equipment

A 250 ml glass beaker was used in each process of batch removal efficiency experiments while a 500 ml glass beaker was used for equilibrium experiments and a magnetic stirrer was used in both experiments.

3.2. Experimental Procedure

3.2.1. Arsenic Stock Solution Preparation

A proper amount of $NaAsO_2$ was added to tap water in order to obtain a 100mg/l solution of As (III). Tap water was preferred over deionized water because the aim of this study was to perform the experiments in conditions the most close to the field conditions like neutral pH, presence of other ions such as F^-, Cl^- , SO_4, NO_3, etc. The mixture was then stirred for about 3 minutes then citric acid in the form of lemon juice was progressively added drop by drop to the mixture to adjust the pH to the desired level of 6.8. The mixture was then kept in a refrigerator for later use.

For each adsorption experiment, the appropriate quantity of the stock solution was added to the corresponding quantity of tap water in order to obtain a 10 ppm solution for investigation of the adsorbents effect on a very high arsenic concentration (1000 times higher than the WHO recommendation). A similar procedure was followed for the arsenic solution 0.1 ppm and 0.2 ppm to observe the effect of adsorbents on much lower concentrations and try to understand the relationship between arsenic initial concentration and removal efficiency of the adsorbents. The solutions obtained like this were analyzed with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to confirm the accuracy of the initial concentrations for the upcoming experiments.

All the initial concentrations were purposely selected higher than the WHO recommended value so that the adsorbent capacity to reduce the As concentration from any value to 10 micrograms/liter or less could be investigated.

3.2.2. Removal Efficiency Experiments

An amount of 2 g, 3 g, 4 g, 5 g, and 6 g of adsorbents namely cypress leaves (C-L), Cypress cones (C-C), Cypress Bark (C-B), Pine Cone chips (P-C), and Pine Bark (P-B) was added to 100 ml of 10 ppm arsenic solution (pH 6.8), stirred for 1 hour with a magnetic stirrer at a speed of 500 rpm. At the end of adsorption experiment, 10 ml of supernatant solution was collected and separated completely from the adsorbent waste by filtration using a 0.45 micrometer filter. The experiment was run 3 times for each adsorbent mass variable for accuracy. Then an amount of 2 g, 3 g, and 4 g of C-L, C-C,C-B, P-C, and P-B were added to 100 ml of arsenic solution 0.1 ppm (pH 6.95) and 0.2 ppm at a (pH 6.92), stirred for 1 hour. Similarly to the previous experiment, 10 ml of supernatant solution was collected at the end of each experiment for sample analysis. The experiments of the two last arsenic initial concentrations of 0.1 ppm and 0.2 ppm were duplicated for accuracy.

3.2.3. Equilibrium Experiment

One variable of the most efficient adsorbent, namely cypress leaves were selected for the equilibrium experiments and samples were collected every 5 minutes for the 30 first minutes then every 10minutes for the last half of the hour to determine the equilibrium time. The sampling procedure was the same as in the previous step. Three runs were performed as well for accuracy.

3.3. Analysis Methods and Equipment

Total Arsenic was measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) from Perkin-Elmer (USA), Optima 7300DV. Samples were filtered with a GelmanSciences PTFE Acrodisc 13 syringe filter 0.45 micrometer to separate adsorbents waste from the water before analysis.

3.4. Precautionary Measures

Because arsenic is a compound with a highly toxic profile, it was mandatory to manipulate it appropriately in order to avoid any accident. Solutions were pipetted by rubber suckers. Disposable gloves and masks were used when dealing with spent sorbent or arsenic solutions. The residuals (contaminated powder of materials and solutions) were placed in a container marked as ‘‘hazardous waste’’ and sent to external treatment.

CHAPTER 4

RESULTS AND ANALYSIS

4.1. Removal Efficiency with respect to Arsenic (III) Initial Concentration

ICP-EAS analytical results showed that the removal efficiency of arsenic (III), in general, was independent from the initial concentration of As (III) as there was no generalized tendency in accordance with the arsenic initial concentration except from Pine Bark. The removal efficiency tendency follows a different path in each adsorbent experiment and most of the time different from what would be expected. For instance, the higher removal efficiencies within C-L and P-C were found in 10 ppm > 0.1 ppm > 0.2 ppm; in C-C it was 0.1 ppm > 10 ppm > 0.2 ppm; in C-B it was 0.2 ppm > 0.1 ppm > 10 ppm and only in P-B the removal efficiency increased with the decrease of As initial concentration like follows 0.1 ppm > 0.2 ppm > 10 ppm.

Cypress Leaves adsorbent comes first with 49.8% when arsenic initial concentration is 10 ppm, the five highest removal efficiencies are observed within cypress leaves and As initial concentration of 10 ppm (41.5 ~ 49.8%). Cypress leaves occupy the leading positions also within arsenic initial concentration is 0.1 ppm with 27.9% and comes second with 21.9% when the initial concentration is 0.2 ppm leaving here the first place to cypress bark with 23.6%.

The following highest efficiency by adsorbent type is observed with pine cones chips with a highest removal of 31.6% when arsenic initial concentration was 10 ppm after cypress leaves, followed by cypress cones chips with 27.9% when arsenic initial concentration was 0.1 pm. At the fourth place comes cypress cones with 26.2% as initial concentration of arsenic was 10 ppm, then cypress bark with 23.6% within 0.2 ppm, cypress leaves with 21.9% for initial concentration 0.2 ppm. The seventh position is occupied by pine cones chips with 21.3% for initial concentration 0.1ppm, followed by cypress bark with 20.6% in 10 ppm of initial concentration, then cypress bark 19.4% for initial concentration 0.1 ppm etc.

While the highest removal efficiency is observed with the cypress leaves within the initial concentration of 10 ppm, the lowest efficiency paradoxically is also observed within the same initial concentration, however with pine bark 8.9%. On the other hand, pine bark is always closing the list with 14.7% within 0.1 ppm of initial concentration, 12.4% within 0.2 ppm initial concentration and finally as already mentioned 8.9% within 10 ppm.

4.2. Removal Efficiency with respect to Adsorbents Concentration

In opposition with arsenic initial concentration, the removal efficiency had a clear correlation with the adsorbent dose in most of the adsorbent types. Within arsenic initial concentration 10 ppm, the removal efficiency increased with the adsorbent dose in the case of cypress leaves, cypress cones, cypress bark and pine cones but decreased with the adsorbent dose increasing in the case of pine bark. This phenomenon is also observed with 0.1 ppm initial concentration as well as in initial concentration 0.2 ppm. The removal efficiency was calculated using the equation below:

$$\% = 100(Co - Ct)/Co \qquad (1)$$

Where Co represents the initial concentration of arsenic (III) in the solution, Ct is the final concentration at which the sample is collected.

The removed amount of arsenic was calculated by using the relation:

$$Q = V\,(Co - Ct)/m \qquad (2)$$

Where Co and Ct are the same as in equation *(1)* expressed in mg/l, V is the volume in liter of arsenic solution, m the mass of the adsorbent in gram, and Q the quantity of arsenic removed expressed in mg/g.

4.2.1. Effect of Cypress Leaves Concentration

Like announced previously, cypress leaves occupied the top of the list with 49.8% observed in arsenic solution 10 ppm. The removal efficiency increased from 2g with 41.5% and reached the maximum at 6g with 49.8%. In the arsenic solution 0.1 ppm, the removal increased from 2g with 23.1%, reached the maximum at 4 g with 27.9%. Finally, within the initial concentration of 0.2 ppm, the removal efficiency increased with the adsorbent dose from 2g with 19.9% until it reached the maximum at 4g with 21.9%. The general tendency reveals a removal efficiency increasing with the increasing dose of the adsorbent.

4.2.2. Effect of Cypress Cones Concentration

From the experiments done with arsenic solution 10 ppm to the rest of experiments, cypress cones removal efficiencies increased with the adsorbent dose. The maximum points were reached at 6 g in 10 ppm with 26.2%, 4 g in 0.1 ppm with 27.9% and finally 4 g in 0.2 ppm with 17.5%. With these results cypress cones occupies the third place in the hierarchical order of the most efficient adsorbent.

4.2.3. Effect of Cypress Bark Concentration

While the other two cypress based adsorbent occupied the first and third places of honor on the list of the most efficient adsorbent, cypress bark is the second less efficient of the list. The highest removal efficiencies obtained from cypress bark were: 6 g with 20.6%, 4 g with 19.4%, and 4 g with 23.6% in 10 ppm, 0.1 ppm and 0.2 ppm respectively. The removal efficiencies increased with adsorbent dose.

4.2.4. Effect of Pine Cone Chips Concentration

Pine cone chips occupied the second position on the list of the most efficient adsorbent with its removal efficiency increasing with the adsorbent dose. The highest removal efficiencies were observed in 6g with 31.6%, 4 g with 21.3% and 4 g 16.1% in 10 ppm, 0.1 pm and 0.2 ppm respectively.

4.2.5. Effect of Pine Bark Concentration

Pine bark is the least efficient adsorbent of all the 5 types studied during this research with its removal efficiency decreasing with the adsorbent dose in 10 ppm, 0.2 ppm and 0.1 ppm. It has all the lowest efficiencies recorded during this study in all three initial concentrations of arsenic solution (6 g with 8.9%, 4 g with 12.4% and 4 g with 14.7% in 10 ppm, 0.2 ppm and 0.1 ppm respectively). The highest removal efficiencies recorded for this adsorbent are as follow: 2 g with 12.3%, 2 g with 15.8% and 2 g with 16.5% in 10 ppm, 0.2 ppm and 0.1 ppm respectively.

The graphs below show the removal efficiency of arsenic (III) by cypress leaves, cones, bark, pine cones chips and pine bark with respect to adsorbent dose within As (III) initial concentrations 0.1 ppm, 0.2 ppm and 10 ppm.

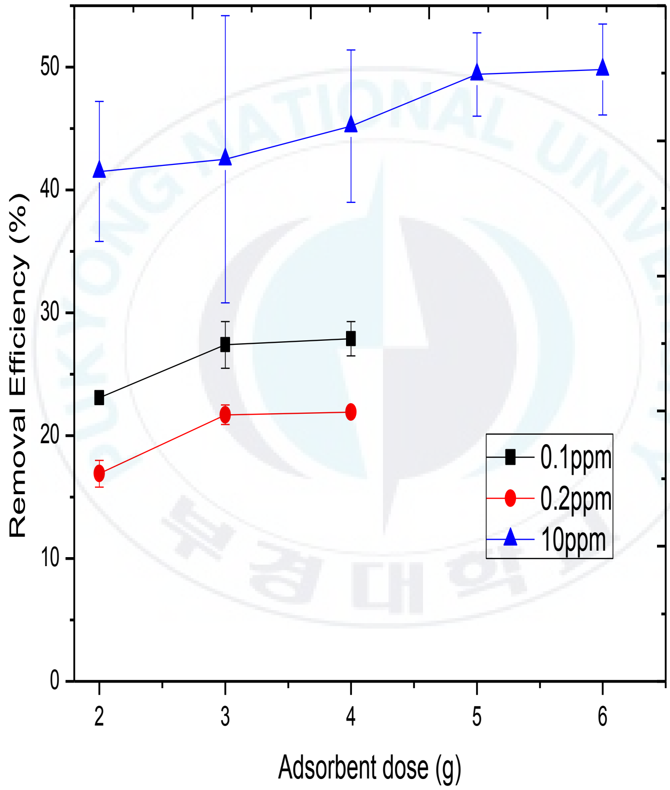


Figure 4.1. Removal efficiency by cypress leaves from arsenic (III) 0.1 ppm, 0.2 ppm and 10 ppm solution

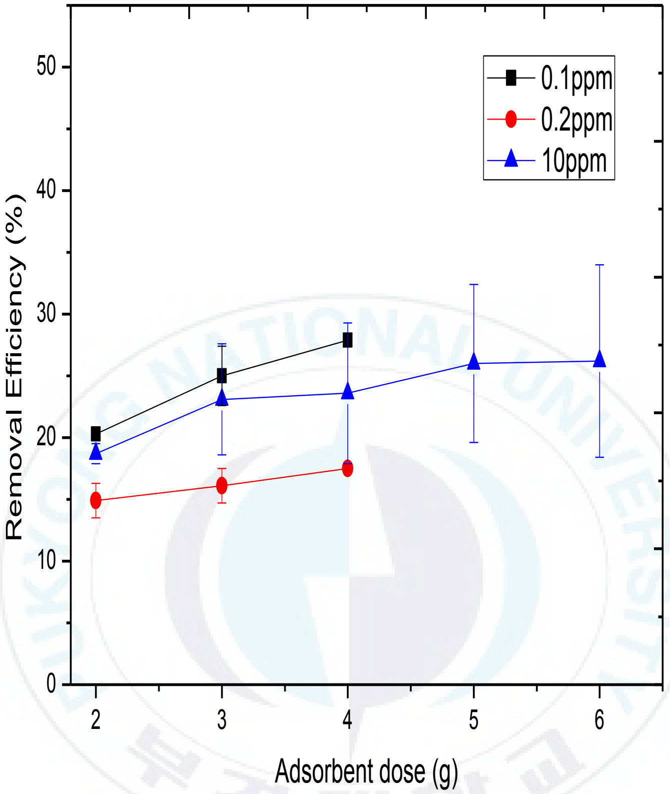


Figure 4.2. Removal efficiency by cypress cones from arsenic (III) 0.1 ppm, 0.2 ppm and 10 ppm solution.

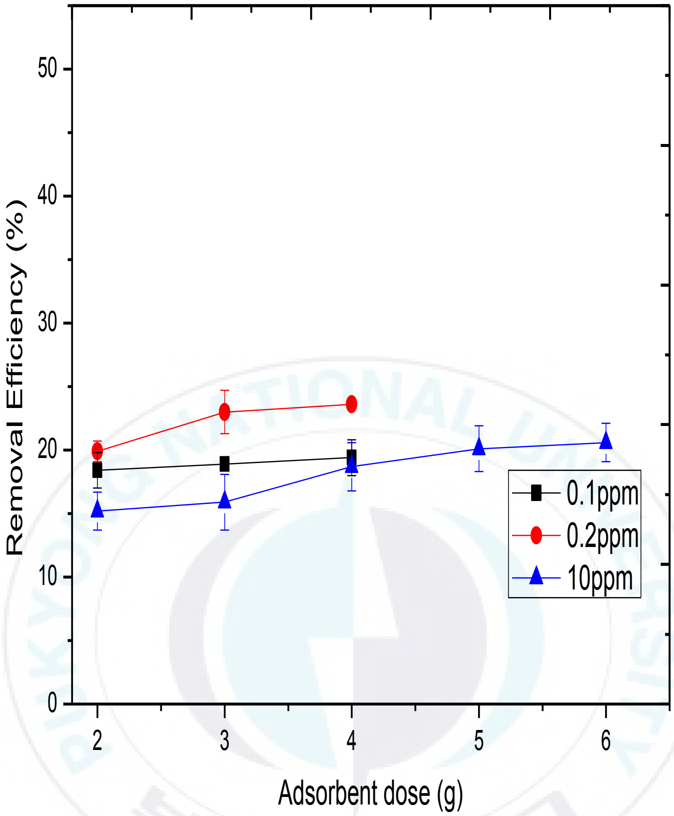


Figure 4.3. Removal efficiency by cypress bark from arsenic (III) 0.1 ppm, 0.2 ppm and 10 ppm solution

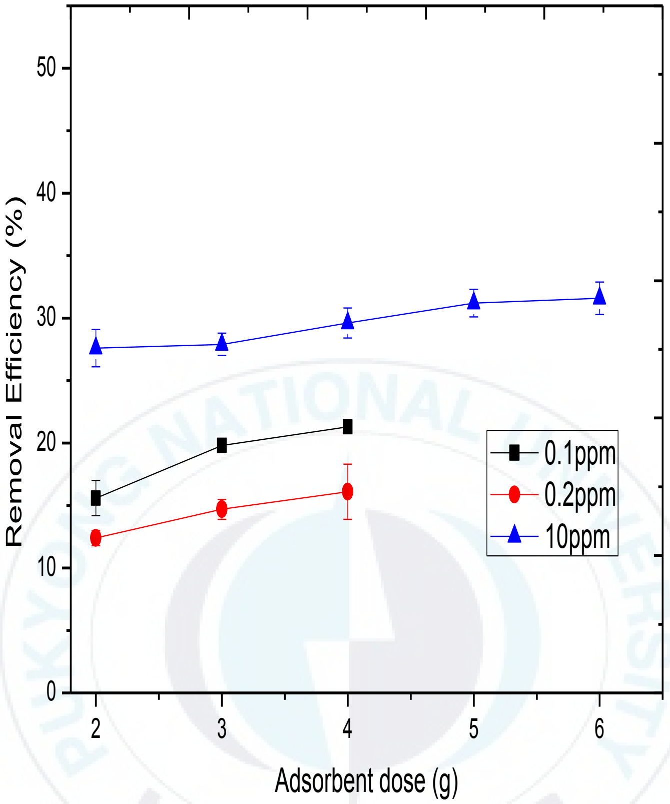


Figure 4.4. Removal efficiency by pine cone chips from arsenic (III) 0.1 ppm, 0.2 ppm and 10 ppm solution

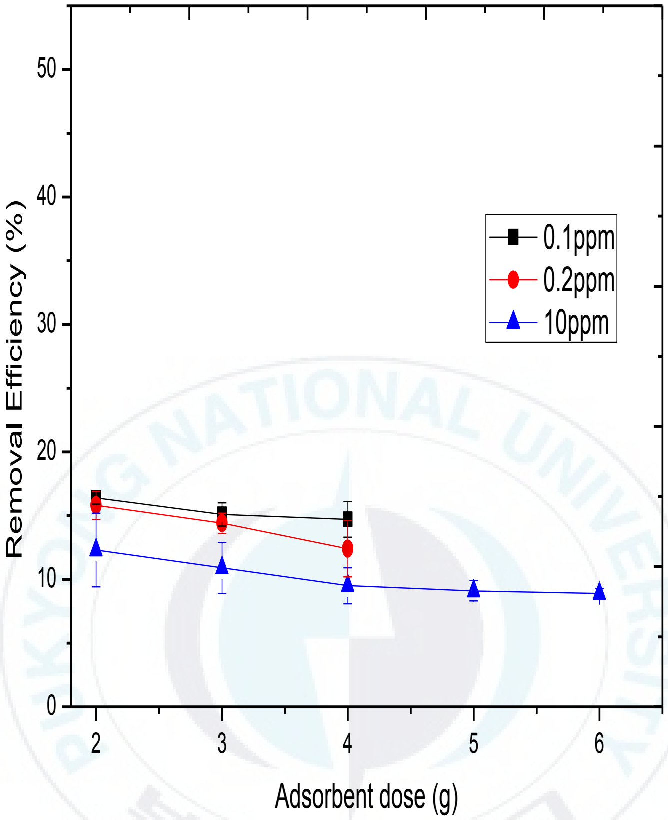


Figure 4.5. Removal efficiency by pine bark from arsenic (III) 0.1 ppm, 0.2 ppm and 10 ppm solution.

4.2.6. Overall Comparison of the five Types of Adsorbents

Compiling all the results of the removal efficiency experiments, the order of the most efficient adsorbent among the five types investigated during this study was found to go like this within the given As initial concentration (considering only the highest removal efficiency by each adsorbent):

0.1 ppm: Cypress Leaves and cypress cones are first with 27.9%, followed by pine cones chips with 21.3%, then cypress bark with 19.4% and finally pine bark with 16.5%

C-L & C-C > P-C > C-B > P-B

0.2 ppm: Cypress bark is first with 23.6% followed by cypress leaves with 21.9%, then cypress cones with 17.5%, pine cones chips with 16.1% and finally pine bark with 15.8%.

C-B > C-L > C-C > P-C > P-B

10 ppm: Cypress leaves comes first with 49.8%, followed by pine cone chips with 31.6%, cypress cones with 26.2%, cypress bark with 20.6% and finally pine bark with 12.3%.

C-L > P-C > C-C > C-B > P-B

In general terms of highest removal efficiency by adsorbent type, it could be established this order: Cypress leaves came first with 49.8% of removal efficiency within the initial concentration of 10 ppm, followed by pine cone chips with 31.6% in As initial concentration of 10 ppm, cypress cones 27.9% in 0.1 ppm initial concentration, then cypress bark with 23.6% in 0.2 ppm initial concentration and finally pine bark with 16.5% in 0.1 ppm initial concentration.

C-L> P-C> C-C> C-B> P-B

Table 4.1. Order of efficiencies of the 5 adsorbents investigated in this study.

THE HIGHEST REMOVAL EFFICIENCY PER INITIAL CONCENTRATION					
BY DECREASING ORDER	0.1 ppm	BY DECREASING ORDER	0.2 ppm	BY DECREASING ORDER	10 ppm
ADSORBENT	%	ADSORBENT	%	ADSORBENT	%
C-L	27.863	C-B	23.645	C-L	49.796
C-C	27.863	C-L	21.931	P-C	31.561
P-C	21.259	C-C	17.462	C-C	26.225
C-B	19.372	P-C	16.065	C-B	20.568
P-B	16.542	P-B	15.786	P-B	12.263

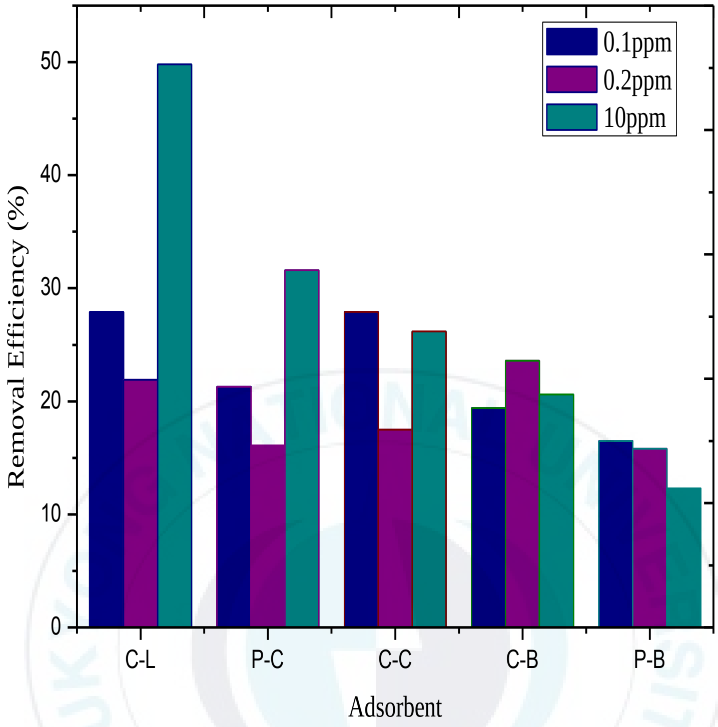


Figure 4.6. Adsorbents removal capacities comparison

Compared to conventional methods and other natural materials that have been used for As removal, results obtained in this study were relatively low and farther studies to determine the optimum conditions are required.

Table 4.2. Conventional methods used in As removal [94], [95-99]

Technologies	Adsorbents	Advantage	Disadvantage	POU and POE Initial Cost/Maintenance (US Dollars)
Oxidation/Precipitation	**Air Oxidation**	Relatively simle,low-cost but slow process, Relatively simple and rapid process, Oxidizes other impurities and kills microbes	The processes remove only a part of arsenic	Low [99]
	Chemical oxidation			
Coagulation/ Co-precipitation	**Alum Coagulation**	Relatively low capital cost, Relatively simple operation, Common Chemicals available	Produces toxic sludges, Low removal of As(III), Pre-oxidation may be required	POU 16.7/9.7 [98]
	Iron Coagulation			

Table 4.2. Conventional methods used in As removal [94], [95-99] (continue)

Sorption Techniques	**Activated Alumina**	Relatively well known and commercially available, Well defined technique, Plenty possibilities and scope of development	Produces toxic solid waste, Replacement/regeneration required, High tech operation and maintenance, Relatively high cost	POE 2000/ 200-400 per year [96]
	Iron Coated sand			POE 5.68-22.48~ [97]
	Iron Exchange			x
	Others Sorbents			POU 300-700/300-500 every 6 months-1year; POE 2400-4500/700-900 per year [95]
Membrane Techniques	**Nanofiltration**	Well defined and high removal efficiency, No toxic solid wastes produced, Capable of removal of other contaminants	Very high capital and running cost, High tech operation and maintenance, Toxic wastewater produced	x
	Reverse Osmosis			POU 300-1200/100-200 each 1-2years; POE 5000-12000/250-500 per every 1-2 years [95]
	Electrodialysis			x

POU: Point-Of-Use, POE: Point-Of-Entry

Table 4.3. Comparison of some natural adsorbents used for As (III)

Some Natural Adsorbents used in As(III) removal					
Adsorbents	**(As) adsorbed amount (mg/g)**	**Initial Concentration (mg/l)**	**Initial pH**	**Type of Water**	**Reference**
Biomass	0.047	100	6	NS	[32]
Coak byproducts	~0.160	25	5.2	Aqueous solution	[100]
Cypress Leaves	0.018-0.19	0.1-10	6.8	Tap water	Present study
Cypress Cones	0.018-0.07	0.1-10	6.8	Tap water	
Cypress Bark	0.019-0.05	0.1-10	6.8	Tap water	
Fish scale	0.247	0.2-1	4	NS	[32]
Orange juice residue	97	NS	10	NS	
Pine Cones Chips	0.018-0.12	0.1~10	6.8	Tap water	Present study
Pine Bark	0.018-0.037	0.1~11	6.8	Tap water	
Pine Wood char	0.0012	0.01-0.1	3.5	Drinking water	[22]
Raw Pine Cone Biochar	0.0057	0.1	4	Aqueous solution	
Zinc-loaded Pine Cone Biochar	0.007	0.1	4	Aqueous solution	
Tea fungal biomass	0.45	0.9-1.3	7.2	NS	[32]
Water Hyacinth roots	0.1905	0.2	6	Tap water	[3]

NS: No Specified

4.3. Equilibrium Studies with Respect to Time

From the previous experiments on arsenic (III) removal efficiency, the most efficient of the five types, namely cypress leaves adsorbent was selected to continue with the equilibrium experiment.

4.3.1. Cypress Leaves Equilibrium Studies

In order to perfom this experiment, 10 g of cypress leaves was added to 200 ml of arsenic (III) polluted water 0.1, 0.2 and 10 ppm and stirred for 1hour at 500 rpm. The pH was 6.8 and temperature was in the range of 23~25^{0}C. Supernatant solution was collected every 5 minutes during the first 30 minutes then every 10 minutes during the last 30 minutes. The samples so collected were then filtered with a 0.45 micromiter filter before analysis. Three replicates were done for accuracy.

The results showed that the major removal took place during the first 15 minutes achieving 45.9% then increased slowly until it reached the maximum point at 50 minutes with 46% and dropped back slightly to 45.5% at 60 minutes for intitial concentration of 10 ppm. This may be due to the fact that the critical micellar conceration was reached (so properties may change dramatically) and to the denaturation of proteigns in the presence of adsorbate [54]. Similar observations were noted for the other initial concentrations although their removal efficiencies stayed lower than the one of cypress leaves at equilibrium (27.9% for 0.1 ppm and 21.9% for 0.2 ppm).

Removal efficiencies observed from adsorbents used in this study were lower than expected. These less satisfactory efficiencies could be caused by a high speed of agitation (500 rpm) that was used during this study. In fact, it has been reported in a previous study about arsenic (V) removal by pine leaves that an agitation speed of 100 rpm was the optimum speed of agitation for that study. In other words, when speed was slow, powder of leaves instead of spreading in the solution conglomerated and buried many active sites under the top layers of adsorbent. As a result, the adsorption occurred only by the top layers and the under buried layers did not take part in the process, since they had no contact with As (V). On the other hand, high agitation speed caused random collisons between particles (adsorbent-adsorbent, adsorbent-adsorbate and adsorbate-adsorbate) and did not provide enough time to the As (V) ions to make a bond with surface of the pine leaves [7].

Despite the fact that As (V) does not react exactly like As (III), the above adsorption principles and the fact that arsenic (III) is hardly removed compared to As (V) could be another cause of low efficiencies obtained.

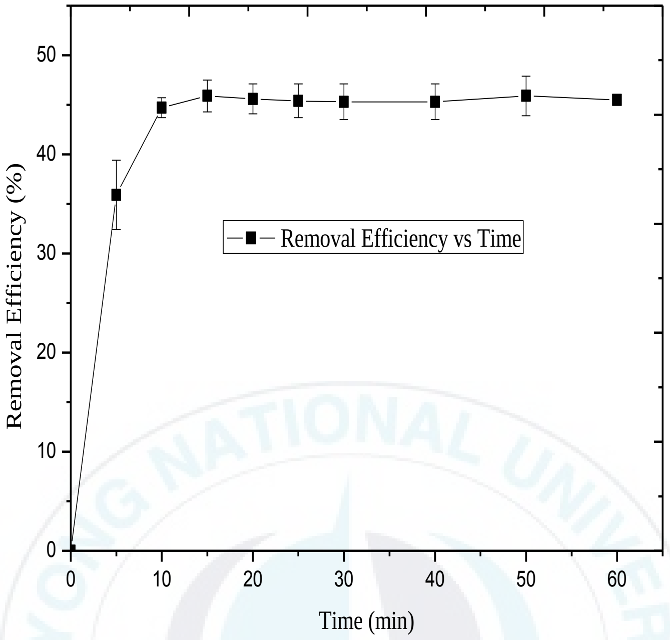


Figure 4.7.1. Equilibrium rate of arsenic (III) removal from a 10 ppm solution by cypress leaves

Another parameter to consider in order to understand the differences between removal efficiencies of the adsorbents compared to each other is the difference in their physicochemical properties themselves. For example, the pH of each adsorbent material differs from the other’s. For instance, cypress leaves pH was found to be 6.34 while pine leaves had a pH of 6.00 as it has been reported in [20]. This parameter could interfer in the solution pH and affect the outcome of the process.

It is also known that the process of adsorption consits of a separation of a substance from one phase followed by its accumulation or concentration at the surface of another. Particulalry, physical adsorption is mainly caused (but not only) by van der Waals forces and electrostatic forces between the atoms which compose the adsorbent surface and the adsorbate molecules. Therefore, adsorption capacity depends, on adsorbent properties, adsorbate chemical properties, temperature, pH etc.[32]. And because the net surface charge of an adsorbent is negative when the pH of the solution is over the pH of point zero charge (pHpzc), and positive when it is below pHpzc, adsorption of positively charged molecules, such as cationic ions may be favored when the solution pH is over pHpzc and negatively charged molecules such as anionic ions like As (V) may be favored when solution pH is below pHpzc [21] and non charged compounds like As (III) will benefit of only less electrostatic attraction forces to the adsorbent.

The pHpzc (point of zero charge) means the pH value in which the number of positive surface charges equals the number of negative surface charges in the material. This is an important information because the pH influences not only the charges present at the sorbent surface but also the chemical speciation of the sorbate in solution. Thus, it is possible to infer the likelihood of attraction and repulsion between adsorbent and adsorbate [100]. From previous explanations, it appears that adding adsorbents to a solution will automatically alter the solution pH and this change will affect differently the adsorption of the neutral charged As (III) to each adorbent depending on the resulting solution pH.

Knowing that As (III) is predominantly uncharged below pH 9.2 while As (V) is negatively charged under the same conditions [28][31], adsorption of As (V) will more likely to be favored by the electrostactic forces while the adsorption of As (III) will depend on different mechanisms such as Van der Waals forces or micro-precipitation. Micro-precipitation of sorbate on the sorbent surface has been reported in the litterature as a favored mechanism resulted from an appropriate environment created by the change of initial pH [101].

Due to the fact that chemical structures and surface functional groups are not well identified, it is difficult to know the sorption mechanisms responsible for the sorption when using natural or waste materials from different origin in sorption studies[102]. In addition, dispite the fact that both were processed following similar procedures, the size of adosrbent particles may not be the same due to differences in material texture, elastiticity, porosity, ect. Thus, each adorsbent would have a different surface area resulting in differences in contact area between the adsorbent and the adsorbate. Unfortunately, due to financial limitations, characterization of adsorbents could not be performed.

4.3.2. Distribution Coefficient and Equilibrium Constant

The distribution coefficient K_d is an important parameter to estimate the affinity between the adsorbent and the adsorbate in aqueous solution [103]. The distribution coefficients for cypress leaves in initial concentration of 0.1, 0.2 and 10 ppm was calculated for temperature 25° C using equation [103] [104]:

$$K_d = (qe/Ce) \times 10^3 \tag{3}$$

Where qe is the amount of As (III) adsorbed onto cypress leaves at equilibrium (mg/g), Ce is the concentration of As (III) at equilibrium (mg/l) and K_d is the distribution coefficient.

The equilibrium constant Kc was calculated using the equation

$$K_c = qe/Ce \tag{4}$$

The data in Table 4.4. indicates the value of K_d which corresponds to the degree of affinity of cypress leaves adsorbent to As (III) in the aqueous solutions and the corresponding equilibrium constant. It may be noticed that the values of distribution coefficient K_d increase with the decrease in initial concentrations, indicating that the affinity of cypress leaves adsorbent for As (III) decreased with the increase of initial concentration. However, as it has been mentioned previously, experimental data showed the highest removal efficiencies within initial concentration of 10 ppm followed by 0.1 ppm and the finally 0.2 ppm. These results once again confirm that removal of As (III) in this study did not depend on the initial concentration for some reason that is yet to be determined. Until then, the highest removal efficiency for each initial concentration is to be determined experimentally and on a case-by-case basis.

Table 4.4. Distribution coefficient and equilibrium constant for cypress leaves adsorbent for As (III) removal from aqueous solution

Co (mg/l)	K_c (l/g)	K_d (l/g)
0.1	0.2105	210.4737
0.2	0.1167	116.6645
10	0.0169	16.9993

4.4. Cypress Leaves Equilibrium Isotherms Study

Experimental sorption equilibrium parameters can be analyzed using several isotherm equations. Among them, the most commonly used are Langmuir and Freundlich models [105]. The Langmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorption between molecules [106].

A well-known linear form of the Langmuir equation can be expressed as follow:

$$\boldsymbol{Ce/qe=(Ce/Qmax) + (1/K_{L}Qmax)} \qquad (5)$$

Where qe is the amount of As (III) adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (ppm) and Qmax and K_L are Langmuir constant related to the maximum adsorption capacity (ppm) and energy of adsorption.

Equation *(3)* suggests that when the adsorption obeys the Langmuir equation, a plot of Ce/qe versus Ce should be a straight line with a slope of 1/Qmax and intercept 1/QmaxK_L [107]. This important characteristic of the Langmuir isotherm can be expressed in terms of a separation factor (dimensionless factor) R_L [108], which is written below:

$$\boldsymbol{R_L=1/\,(1+K_LCo)} \qquad (6)$$

The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$) , favorable ($0 < R_L <1$), or irreversible ($R_L = 0$).

Table 4.5. Equilibrium model equations, *x* and *y* values, slope and intercept for the isotherm equations

Langmuir Isotherm		
Non Linear	Linear	Slope and Intercept
$qe = (QmaxK_LCe)/1 + (K_LCe)$	$Ce/qe = (Ce/Qmax) + (1/K_LQmax)$	Slope = $1/Qmax$; Intercept = $1/QmaxK_L$
Freundlich Isotherm		
Non Linear	Linear	Slope and Intercept
$qe = K_F\ Ce^{1/n}$	$Logqe = logK_F + (1/n)logCe$	Slope = $1/n$; Intercept = $logK_F$

On the other hand, the Freundlich isoterhm model not restricted to the formation of a monolayer applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules. It therefore assumes that the concentration of adsorbate on the adsorbent surface increases as the adsorbate concentration increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centres of the adsorbent. The well known expression of the Freundlich model is given by the following equation [103][108].

$$Logqe = logK_F + (1/n)logCe \qquad (7)$$

Where qe is he amount of adsorbed at equilibrium (mg/g) , K_F the Freundlich constant [(mg /g)(mg/l)/(1/n)], 1/n the hetergeneity factor which are related to capacity and intensity of adsorption respectively, Ce is the equilibrium concentration(mg/l). The values of K_F and 1/n can be obtained from the slope and intercept of the plot of logqe against log Ce [105]. If a value of n = 1, the adsorption is linear, for n < 1 the adsorption is chemisorption, and for n > 1 the adsoption is a favorable physical process [103][107].

The Langmuir and Freundlich isotherms for As (III) removal by cypress leaves are shown in Figures 4.7.2 and 4.7.3. The correlation coefficiencts calculated by fitting the experiment equilibrium data for As (III) using both Langmuir and Freundlich isotherms are presented in Table 4.6.

These results show a Langmuir factor R_L between 0 and 1 which suggest a favorable adsorption. The correlation coefficients R^2 for both models are closer to the unity which indicates that the adsorption of As (III) onto Cypress Leaves fits well both models due to the low concentration ranges. However, the Langmuir R^2 is slightly less than the Freundlich's. This means that the Langmuir model is the best fit for this adsorption process.

Table 4.6. Langmuir and Freundlich parameters

C-L	**Parameters**	**Langmuir**	**Parameters**	**Freundlich**
	R^2	0.9973	R^2	0.9831
	Qmax (mg/g)	0.1014	K_F[(mg/g)(mg/l)/(1/n)]	0.2594
	K_L (l/g)	1.8049	1/n	0.4158
	R_L	0.5448	n	2.4048

The Freundlich parameter n = 2.4 suggests a favorable physical adsorption process. Langmuir model predicted a maximum amount adsorbed of 0.101 mg/g closer to the experimental amount of 0.092 mg/g. This consolidates the conclusion that when it comes to As (III) adsorption onto Cypress Leaves, the Langmuir's model predominantly fits.

Langmuir and Frendlich isotherms are shown in Figures 4.7.2 and 4.7.3

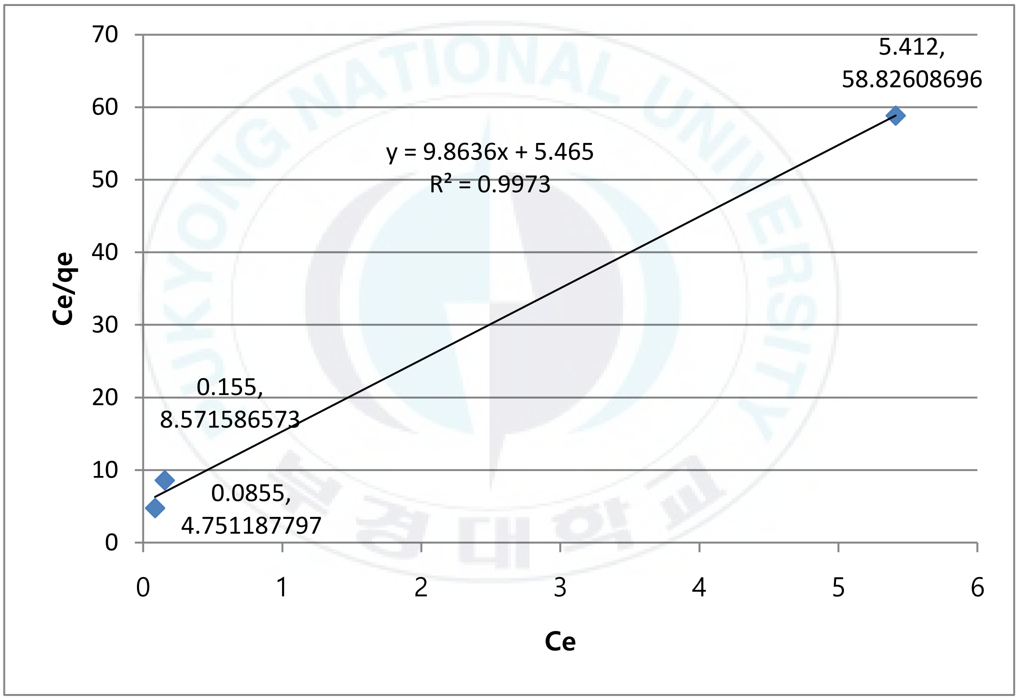


Figure 4.7.2. Langmuir isotherm for adosption of As (III) onto cypress leaves.

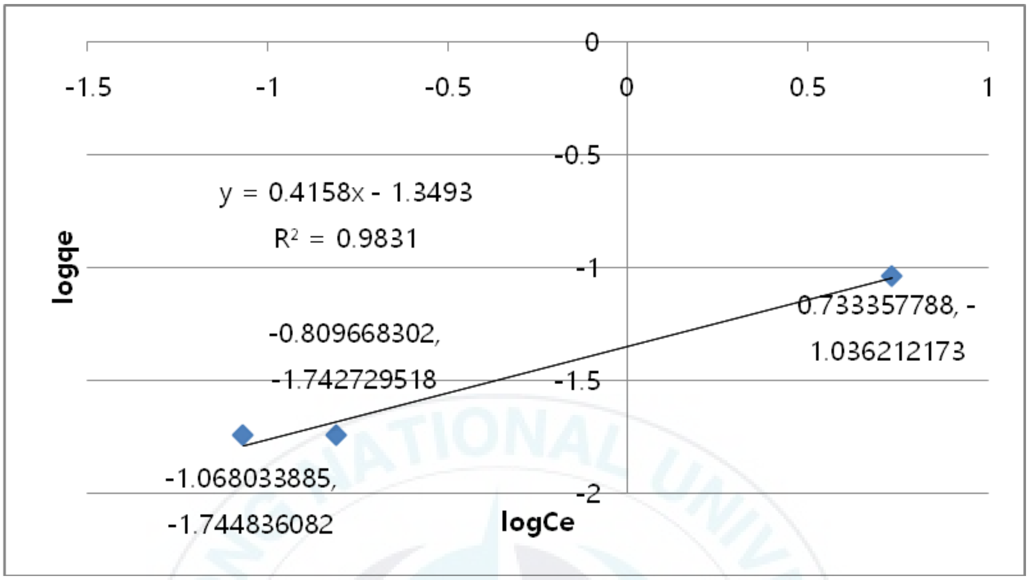


Figure 4.7.3. Freundlich isotherm for adosption of As (III) onto cypress leaves.

4.5. Cypress Leaves Kinetic Study

In this study, several kinetic models were applied to the experimental data to investigate the controlling mechanism of As (III) adsorption from aqueous solution onto cypress leaves among which the pseudo-first order, pseudo-second order and intra-particle diffusion. Lagergren's pseudo-first order rate equation is the earliest known to give a description of the adsorption rate based on adsorption capacity [105].

The linear form of Lagergren's pseudo-first order rate equation is written as follow[109]:

$$Ln(qe-qt) = lnqe - K_1t \qquad (8)$$

Where qe is the amount of As (III) adsorbed at the equilibrium(mg/g), qt is the amount of As (III) adsored at any time t (mg/g) and K_1 (min^{-1}) is the rate constant of the pseudo first order adsorption which can be calculated from the slope of the linear plot of ln(qe –qt) vs t. (Slope = K_1 , qe = exp (intercept)) [105].

A second order model for sorption of divalent metal ions onto peat particles based on the expression capacity of the adsorbents with the goal of differientiating the kinetics of a second-order rate expression based on the adsorbent concentration from models which are based on the solute concentration and represent a pseudo-second order rate expression has been proposed by Ho [105].

The linearized form of the pseudo-second order model given by Ho [110] is

$$1/qt = (1/K_2qe^2) + (t/qe) \qquad (9)$$

Where K_2 (g/mg.min) is the rate constant of the pseudo-second order adsorption, qe is the amount of As (III) adsorbed on the adsorbent at equilibrium (mg/g), and qt is the amount of As (III) adsorbed at any time t (mg/g). K_2 can be calculated from the slope and intercept of the plot of t/qt against t.

The intra-particle diffusion equation [111] can be expressed as follow:

$$Qt=Kipdt^{1/2}+C \qquad (10)$$

Where qt is the amount of the As (III) adsorbed at time t (mg/g), C is the intercept and Kipd is the intra-particle diffusion rate constant (mg/g.min).

The pseudo first and second order log(qe-qt) and t/qt plots vs t and the intra-particle diffusion $t^{1/2}$ vs t pot are represnted in figures 4.7.4, 4.7.5, and 4.7.6. Their calculated values K_1, K_2, Kipd, qe and R^2 are presented in Table 4.7.

From these results, the correlation coefficients of the speudo second order and the Intra-particle diffusion are closer to the unity suggesting that the adsorption system can be better represented by these kinetic systems than by the pseudo-first oder equation which shows a very low value of R^2. The correlation coefficient for the intra-particle diffusion is slightly lower than the one for the pseudo-second order kinetics. This indicates that the pseudo-second order system may be followed by the intra-particle diffusion. In addition, the intra-particle diffusion plot is curved in the small time limit, which might be due to a mass transfer effect [105].

Table 4.7. Pseudo 1st order, pseudo 2nd order and intra-particle diffusion parameters

	Parameters	Experimental	Pseudo 1st order	Pseudo 2nd order	Intra-particle Diffusion
C-L	R^2		0.3844	1	0.9091
	qe (mg/g)	0.092	0.0128	0.9419	5.1622
	K		-0.0912	0.9992	0.1135

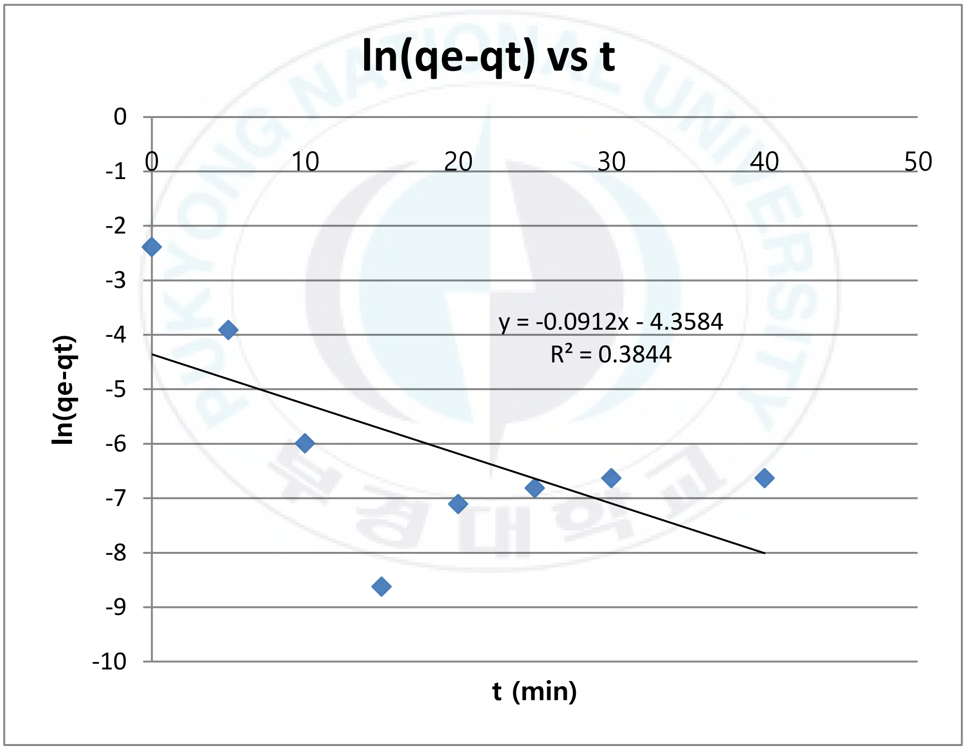


Figure 4.7.4. Pseudo 1st order kinetic plot for the adsorption of As (III) onto cypress leaves

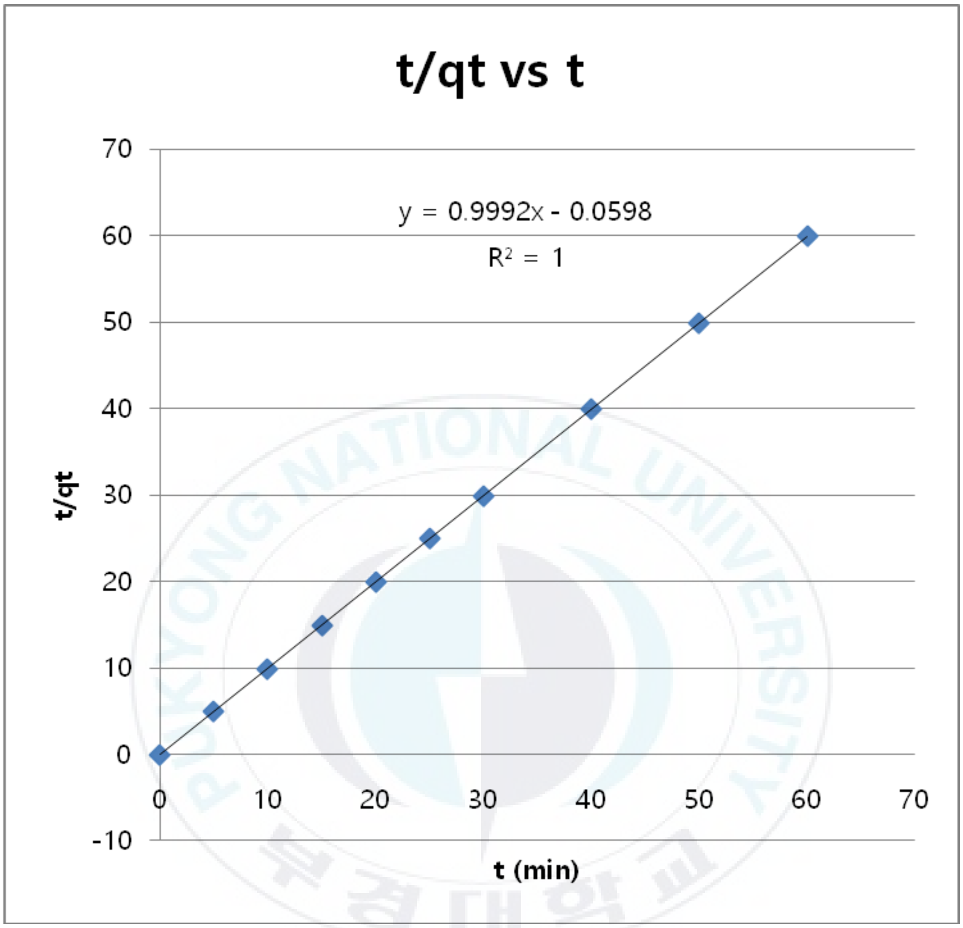


Figure 4.7.5. Pseudo 2nd order kinetic plot for the adsorption of As (III) onto cypress leaves

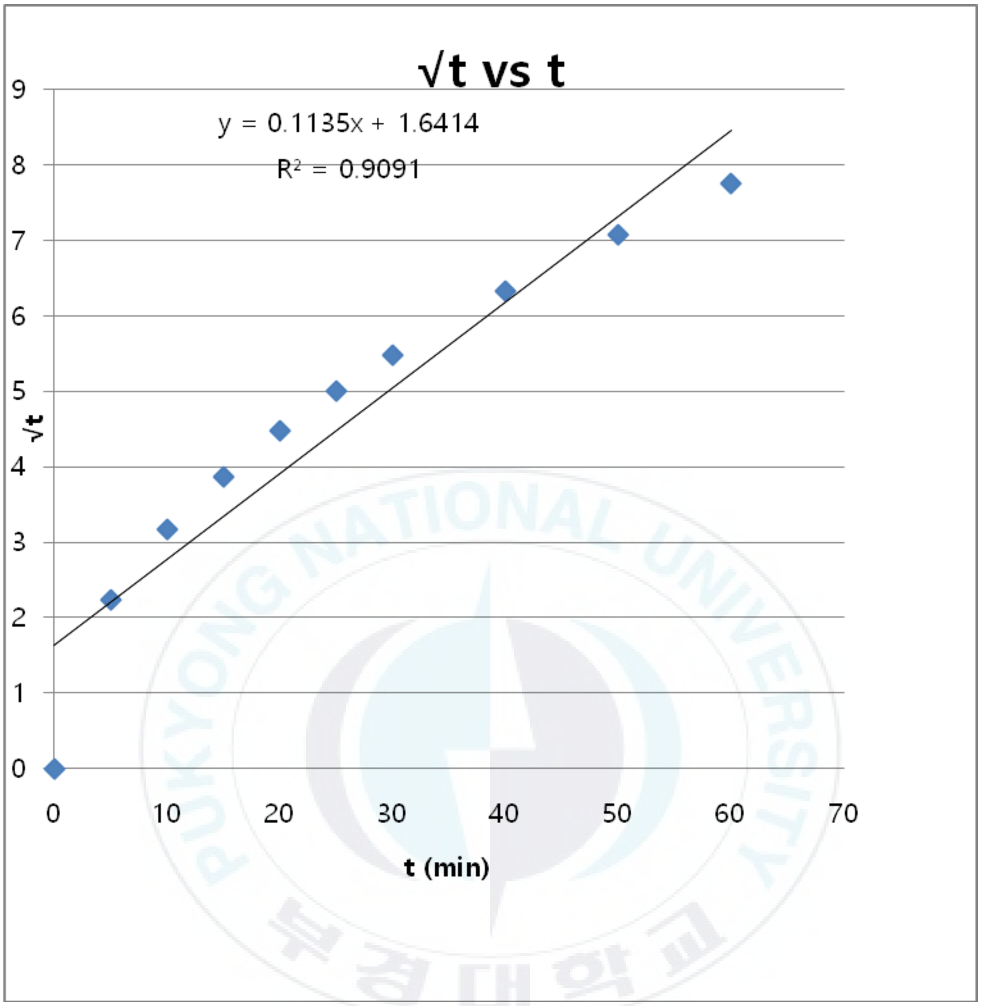


Figure 4.7.6. Intra-particle diffusion plot for the adsorption of As (III) onto cypress leaves

CHAPTER 5

CONCLUSION

General Summary

Adorpton of arsenic (III) onto cypress leaves, cypress cones, cypress bark, pine cone chips and pine bark powder has been studied at some extend. It was concluded that among the studied adsobents:

- Removal efficiencies increased with the adsorbent dose but were independant from the As (III) initial concentration except from pine bark powder for which the removal efficiency decreased with the increase of adsorbent dose as well as the increase of the initial concentrations of As (III).
- Cypress leaves present great potentiality of an excellent adsorbent for removing toxic As (III) from water followed by cypress cones and pine cones.
- Cypress bark and pine bark were found to be the least efficient of all five materials used for this study.
- Equilibrium studies showed that the major removal took place within the first 15 minutes achieving a maximum of 45.9 % thus, a maximum adsorbent amount of 0.092 mg of As (III) per gram of cypress leaves .

Kinetics and Isotherms

- The correlation cofficient values R^2 showed that the adsorption of As (III) onto cypress leaves fits both Langmuir and Freundlich models with a predominance of the Langmuir model.

- The Langmuir's model predicted a maximum amount adsorbed of 0.101mg/g closer to the experimental one (0.092 mg/g) . The Langmuir parameter $R_L = 0.5448$ ($0 < R_L < 1$) suggested a favorable adsorption and the Freundlich parameter $n = 2.4$ indicated that the adsoption is a favorable physical process.

- The kinetic results showed that the adsorption of As (III) onto Cypress Leaves can be better represented by the pseudo-second order model followed by the intra-particle diffusion.

Further Studies

- The results in the present study were obtained from investigations of arsenic intial concentraion, adsorbent dose and contact time effects in a batch system. Further investigations should include pH effect and speed of agitation effect to dertemine the optimum conditions. If great results are then obtained, removal in dynamic system should be studied for future scale-up.

- Also, because removal of As (V) is much more easier than As (III) while on the other hand As (III) is the most abundant in ground water and also the most dangerous (sixty times more toxic than As (V)),combining a quick oxidation process of As (III) to As (V) prior to adsorption could increase the chance of adsorbents used in this study as well as of many other bio-adsorbents available in touched populations environments to remove arsenic from drinking water and save lots of lives.

REFERENCES

1. J. Sanchez-Martın and J. Beltran-Heredia in *Advances in Water Treatment and Polution Chap 12.* S.K. Sharma and R. Sanghi Eds., Springer Science+Business Media Dordrecht, Badajoz, Spain (2012).

2. F.S. Salumu , *Approvisionnement en eau dans la ville de Bukavu et son impact sur les maladies de mains sales, Mémoire de Licence de Santé Publique*,Université Officielle de Bukavu, Bukavu, République Démocratique du Congo (2010).

3. S.W. Al Rmalli, C.F. Harrington, M. Ayub and P.I. Haris, *The Royal Society of Chemistry* **7**, 279-282 (2005).

4. U. Shafique, A. Ijaz, M. Salman, W.U. Zaman, N. Jamil, R. Rehman and A. Javaid, *Journal of the Taiwan Institute of Chemical Engineering* **43**, 256-263 (2012).

5. PEP, Poverty-Environment Partnership and World Health Organization, Ginebra (2006).

6. WHO and UNICEF, *Joint program on water supply and sanitation*. WHO Library Cataloguing-in-Publication Data, Geneva (2009).

7. WHO, *United Nation-global annual assessment of sanitation and drinking water,* WHO Library Cataloguing-in-Publication Data, Geneva (2008).

8. Wikipedia: *Water pollution*, https://en.wikipedia.org/wiki/Water_pollution, Last update September 2^{and}, 2016.

9. R. Shrestha, *Environment and Public Health Organization*, ENPHO, Dorothee Spuhler (Seecon international gmbh).

10. M. Wegelin, D. Gechter, S. Hug, A. Mahmud and A. Motaleb, *SORAS-A simple arsenic removal process*, Accessed from: http://users.physics.harvard.edu/~wilson/arsenic/remediation/sodis/SORAS_Paper.html (2000).

11. S. Akhtar and A. Shoaib, *The Journal of Animal &Plant Sciences*, 22(3) 659-664 (2012).

12. Dr. S. A. Azeem in *Development of new sorbents for removal of contaminants from water,* Fayoum University, February 20, (2013).

13. A.B. Anderson, *Econ Bot.*, **9**, 108 (1955).

14. R. Salim, *Journal of Environmental Science and Health*, **A23 (4)**, 321-334 (1988).

15. R.Salim, M.M. Al-Subu and S. Qashoa, *Journal of Enviroment Science and Health*, **A29 (10)**, 2087-2114 (1994).

16. J. Sanchez-Martin, J. Beltran-Heredia and V. Encinas-Sanchez, in *Heavy Metals Uptake from Aqueous Effluents by Novel Adsorbent Derived from Tannin Extracts Chap 8*, University of Extremadura, Badajoz, Spain (2014).

17. J. Beltran-Heredia, P. Palo, J. Sanchez-Martin, J.R. Dominguez and T. Gonzalez, *Industrial & Engineering Chemistry Research*, **51**, 50-57 (2012).

18. M. E. Fernandez, G. V. Nunell, P. R. Bonelli and A. L. Cukierman, *Bioresource Technology*, **101**, 9500-9507 (2010).

19. J. Sanchez-Martin, J. Beltran-Heredia and P. Gibello-Perez, *Chemical Engineering Journal*, **168**, 1241-1247 (2011).

20. M. M. Al-Subu, *Advances in Environment Research*, **6**, 569-576 (2002).

21. M. E. Fernandez, G. V. Nunell, P. R. Bonelli and A. L. Cukierman, *Bioresource Technology*, **106**, 55-62 (2012).

22. N. V. Vinh, M. Zafar, S. K. Behera, H. S. Park, *Int.J.Environ.Sci.Technol*, **12**, 1283-1294 (2015).

23. D. Poiret, *Plantes medicinales*, Last accessed from: http://www.mr-plantes.com/2014/12/cypres/ , Last update: December 6th, 2014.

24. N. V. Vinh, M. Zafar, S. K. Behera and H. S. Park, *Int.J.Environ. Sci. Technol*, **12**, 1283-1294 (2015).

25. C. Woodford, *Water pollution: an introduction*, http://www.explainthatstuff.com/waterpollution.html, Last update June 5th, 2016.

26. Centers for Disease Control and Prevention, *Arsenic and Drinking Water from private Wells*, National Center for Emerging and Zoonotic Infectious Diseases (NCEZID), Division of Foodborne, Waterborne and Environmental Diseases http://www.cdc.gov/healthywater/drinking/private/wells/disease/arsenic.html, Last update July 1st , 2015.

27. Wikipedia: *Water pollution*, https://en.wikipedia.org/wiki/Water_pollution, Last update September 2and, 2016.

28. WHO, *Guidelines for Drinking-water quality- fourth edition*, Library Cataloguing-in-Publication Data 2011.

29. K. Tanabe, H. Yokota, H. Hironaka, S. Tsushima and Y. Kubota, *Appl. Organomet. Chem.*, **15**, 241-251 (2001).

30. Oregon Health Authority, Drinking Water Program Fact sheet, *Recommendations for Arsenic Removal from Private Drinking Water Wells in Oregon.*

31. R. Roy, M. Sah, A. Mazumdar and S. S. Ray, *International Journal of research in Environment Science and Technology,* **4(1)**, 10-15 (2014).

32. M. Chiban, M. Zerbet, G. Carja and F. Sinan, *Journal of Environment Chemistry and Ecotoxicology*, **4(5)**, 91-102 (2012).

33. Agency for Toxic Substances and Disease Registry, *Addendum to the toxicological profile for arsenic*, Division of Toxicology and Human Health Sciences, Atlanta, GA 30329-4027 (2016).

34. F. Parvez, Y. Chen and P. W. Brandt-Rauf , *Thorax*, **65(6)**, 528-533 (2010).

35. F. Parvez , Y. Chen and M. Yunus, *Am J Respir Crit Care Med.*, **188 (7),** 813-819 (2013).

36. A. H. Smith, M. Yunus and A. F. Khan, *Int J Epidemiol*, **42(4)**, 1077-1086 (2013).

37. Y. Chen, J. H. Graziano and F. Parvez, *BMJ*, **342**, d2431. (2011b.).

38. M. Rahman, N. Sohel and M. Yunus M, *BMC Public Health*, **14**, 174 (2014).

39. K. K. Majumdar, D. N. G. Mazumder and N. Ghose, *Indian J Med Res*, **129**, 75-82 (2009).

40. E. H. Syed, S. Melkonian and K. C. Poudel, *J Occup Environ Med.*, **55(1)**, 59-66 (2013).

41. C. Odstrcil Adel, S. N. Carino and J. C. Ricci, *Exp Toxicol Pathol.*, **62(3)**, 243-249 (2010).

42. C. L. Chen, H. Y. Chiou and L. I. Hsu, *Environ Res*, **110(5)**, 455462 (2010c).

43. J. W. Chen, H. Y. Chen and W. F. Li, *Chemosphere*, **84(1)**, 17-24 (2011a).

44. J. W. Chen, S. L. Wang and Y. H. Wang, *Chemosphere*, **88(4)**, 432-438 (2012a).

45. J. A. Coronado-González, L. M. Del Razo and G. García-Vargas, *Environ Res.*, **104(3)**, 383-389 (2007).

46. L. M. Del Razo, G. G. Garcia-Vargas and O. L. Valenzuela, *Environ Health*, **10**, 73 (2011).

47. M. O. Gribble, B. V. Howard and J. G. Umans, *Am J Epidemiol*, **176(10)**, 865-874 (2012).

48. R. Islam, I. Khan and S. N. Hassan, *Environ. Health*, **11**, 38 (2012b.).

49. K. A. James, J. A. Marshall and J. E. Hokanson, *Environ. Res.*, **123**, 33-38 (2013).

50. Y. Kim and B. K. Lee, *Sci Total Environ.*, **409(19)**, 4054-4062 (2011).

51. N. H. Kim, C. C. Mason and R. G. Nelson, *Am J Epidemiol.*, **177(9),** 962-969 (2013).

52. X. Li, B. Li and S. Xi, *Environ Sci Pollut Res Int.*, **20(11)**, 8151-8161 (2013a).

53. A. Navas-Acien, E. K. Silbergeld and R. Pastor-Barriuso, *JAMA*, **300(7),** 814-822 (2008).

54. A. Navas-Acien, E. K. Silbergeld and R. Pastor-Barriuso, *Epidemiology*, **20(6)**, e816-e820 (2009).

55. W. C. Pan, W. J. Seow and M. L. Kile, *Am J Epidemiol*, **178(10)**, 1563-1570 (2013).

56. S. Y. Rhee, Y. C. Hwang and J. T. Woo, *J Korean Med Sci*., **28(6)**, 861-868 (2013).

57. C. Steinmaus, Y. Yuan and J. Liaw, *Epidemiology*, **20(6)**, 807-815 (2009).

58. A. S. Ettinger, A. R. Zota and C. J. Amarasiriwardena, *Environ Health Perspect*, **117(7)**, 1059-1064 (2009).

59. M. Argos, T. Kalra and B. L. Pierce, *Am J Epidemiol*., **1742(2)**, 185-194 (2011).

60. A. H. Barati, A. Maleki and M. Alasvand, *Sci Total Environ*, **408(7)**, 15231529 (2010).

61. Z. Fatmi, I. Azam and F. Ahmed, *Environ Res*., **109**, 575-581 (2009).

62. Z. Fatmi, I. N. Abbasi and M. Ahmed, *Environ Geochem Health*, **35(3)**, 341-346 (2013).

63. J. H. Hashim, R. S. M. Radzi and S. M. Aljunid, *Sci Total Environ*. **463-464**, 1210-1216 (2013).

64. A. L. Lindberg, M. Rahman and L. A. Persson, *Toxicol Appl Pharmacol*., **230(1)**, 9-16 (2008).

65. S. Melkonian, M. Argos and B. L. Pierce, *Am J Epidemiol*., **173(2)**, 183-191 (2011).

66. G. R. Pesola, F. Parvez and Y. Chen, *Eur Respir J*., **39(5),**1076-1083 (2012).

67. B. L. Pierce, M. Argos and Y. Chen, *Am J Epidemiol*., **173(3)**, 345-354 (2011).

68. Y. Xia, T. J. Wade and K. Wu, (2009). *Int J Environ Res Public Health*, **6**, 1010-1025.

69. A. Perez-Carrera and A. Fernandez-Cirelli, *J Dairy Res*., **72 (1)**, 122-4 (2005).

70. S. Shankar, U. Shanker, Shikha, *The Scientific Wolrd Journal*, **2014**, 304524 (2014).

71. WHO, *Appropriate technology for the treatment of wastewaters for small rural communities,* WHO Library Cataloguing-in-Publication Data, Geneva (1985).

72. R. C. Dorf, *Sustainable and appropriate technologies, technology, humans, and society,* Academic, San Diego (2001).

73. B. Bowonder, *Technol Forecast Soc Change,* **15**, 55–67 (1979).

74. A. Boni and G. Ferrero, *Introduction to development cooperation,* Politechnical University of Valencia, Valencia, Spain (1997).

75. SPAIN, *Plan Director de Cooperaci´on para el Desarrollo 2009–2010/Development Cooperation Director Plan 2009–2010,* Madrid (2009).

76. K.H.Lanouette, *Chem. Eng*., **Oct.** 73-80 (1977).

77. R.M. Harrison and D.P.H.Laxen, *Lead pollution : Causes and control*, Univ. Press, Cambridge, 1981.

78. J. W. Lee, S. P. Choi, R. Thiruvenkatachari, W. G. Shim and H. Moon, *Dye Pigment*, **69**, 196–203 (2006).

79. G. M. Shaul, T. J. Holdsworth, C. R. Dempsey and K. A. Dostal, Chemosphere, **22**, 107–119 (1991).

80. E. Guibal and J. Roussy, *React Funct Polym*,**67**, 33–42 (2007).

81. B. Shi, G. Li, D. Wang, C. Feng and H. Tang, *J Hazard Mater*, **143**, 567–574 (2007).

82. C. O'Neill, F. R. Hawkes, D. L. Hawkes, N. D. Lourenco, H. M. Pinheiro and W. Dele´e, *J Chem Technol Biotechnol*, **74**, 1009–1018 (1999).

83. H. Zollinger, *Colour chemistry-synthesis: Properties and application of organic dyes and pigments*, VCH Publishers, New York (1987).

84. L. E. Gaini, M. Lakraimi, E. Sebbar, A. Meghea and M. Bakasse, *J Hazard Mater*, **161**, 627–632 (2009).

85. K. T. Chung, S. C. Chen and L. D. Claxton, *Mutat Res/Rev Mutat Res*, **612**, 58–76 (2006).

86. D. Myers, *Surfactant science and technology*, Wiley, New Jersey (2006).

87. C. Edser, *Focus Surfactant*, **11**, 1–2 (2008).

88. T. Cserh´ati, E. Forg´acs and G. Oros, *Environ Int*., **28**, 337–348 (2002).

89. C. A. Basar, A. Karagunduz, A. Cakici and B. Keskinler, *Water Res*., **38**, 2117–2124 (2004).

90. M. Clara, S. Scharf, C. Scheffknecht and O. Gans, *Water Res*., **41**, 4339–4348 (2007).

91. Y. Hao, A. L. Roach and G. L. Ramelow, *J. Environ. Sci. Health*, **28**, 2333–2343 (1993).

92. G. X. Wang, M. C. Fuerstenau and R. W. Smith, *Miner. Metall. Process.*, **16**, 1–47 (1999).

93. D. E. Salt, I. J. Pickering, R. C. Prince, D. Gleba, S. Dushenkov,

R. D. Smith and I. Raskin, *Environ. Sci. Technol.*, **31**, 1636–1644 (1997).

94. M. F. Ahmed, *Civ.Eng.*, **2001**, 251-269 (2001).

95. Ohio Department of Health, *Arsenic Treatment and Removal for Private Water System Wells*, Bureau of Environmental Health, Private Water Systems , USA (2012).

96. J. J. Hurd, *Thesis of Master of Engineering in Civil and Environmental Engineering*, Massachusetts Institute of Technology, USA (2001).

97. B. R. Poole, *Thesis of Master's in Civil and Environment Engineering*, Massachusetts Institute of Technology, USA (2002).

98. K. H. Soon, *Thesis of Master's of Civil and Environmental Engineering*, Massachusetts Institute of Technology, USA (2002).

99. L. Feenstra, J. Van Erkel and L. Vasak, International Groundwater Resources Assessment center, Report nr. SP 2007-2 (2007).

100. N. Fiol and I. Villaescusa, *Environment Chemistry Letters*, **7**, 79-84 (2009).

101. V. C. Taty-Costodes, H. Fauduet, C. Porte and A. Delacroix, *J Hazard Mater*, **B105**, 121-142 (2003).

102. N. Fiol and I. Villaescusa, *Environ Chem. Lett* ., **7**, 79-84 (2009).

103. M. Vasudevan, P. L. Sakaria, A. S. Bhatt, H. M. Mody and H. C. Bajaj, *Ind.Eng. Chem. Res.*, **50**, 11432 (2011).

104. S. B. Adarsh, L. S. Praful, M. Vasudevan, R. P. Radheshyam, N. Sudheesh, C. B. Hari and M. M. Haresh, *RSC Advances*, **2**, 8663-8671 (2012).

105. G. Vijayakumar, R. Tamilarasan and M. Dharmendirakumar, J. Mater. Environ. Sci , **3(1)**, 157-170 (2012).

106. I. Langmuir, *J American Chem. Soc*., **40**, 1361 (1918).

107. M. Roulia and A. A. Vassiliadis, *Microporous Mesoporous Materials*, **116**, 732 (2008).

108. S. D. Faust and O. M. Aly, Burterworth publishers, Stoneham M.A., USA (1987).

109. S. Lagergren and K. S. V. Kapsakademiens, *Handlingar*, **24**, 1 (1898).

110. Y. S. Ho, *Ph.D. Thesis*, Univ.Birmingham , Birmingham, UK. (1995).

111. T. Furusawa and J. M. Smith, *AIChE J*., **20 (1)**, 88 (1974).

Personal Reflection

Nobody gets through an expirience and comes out of it the same. That’s a fact and my experience of master’s program taught me a lot in terms of scientific skills as well as social and personal lessons.

Through this experience I came to improve my sens of organization which is a very important factor in succeeding any research plan. You have got to plan things in advance, to anticipate in order to mitigate the unforseen. Because in fact, there is a little difference between theorical schedule and real execution of the schedule. This brings me to another lesson I gained during this program: there is no need to be tough on yourself because your aspirtaions do not always match with the reality. Facts are facts. And we can only deal with it. However, anticipating has the advantage of gaining in time. And that is important, especially when you have to work within a short period of time.

Where you might expect it less, a research program could give you also a lesson about collaboration with people. I learned to ask for help at the right time in the right place. All this has a link with the sence of anticipation of course but in addition, when dealing with a third person, what is more needed is patience. In a context where time is precious, you have got to be patient although this does not mean to be passive. In other words, being diplomatic in order to obtain from your collaborators what you need in a reasonnable period of time without pushing on them.

There’s a lot of things I learned about myself and the others, my strength and my limitations. And one thing is for sure, I am not the same as before I start all this. And that is a gain. Like said Nelson Mandela :” I never lose. Either I win or I learn”.

K. S. Mission

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K. S. Mission