UNIVERSITI PUTRA MALAYSIA

REMOVAL OF ARSENIC FROM WATER USING NATURAL COAGULANT (MORINGA OLIEFERA)

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By

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Thesis Submitted to the school of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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This work is dedicated

To

My Parents, My wife and My Brothers and Sisters

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chairman: Assoc. Prof. Dr. Azni bin Idris

Faculty: Engineering

Tin industry was once a major contributor to the Malaysian economy as Malaysia was the world's largest tin-producing country, from the 1950s to 1980s. As the mining practice used was mainly surface mining, large mine pools were left behind. The pools are contaminated with the heavy metals, especially arsenic from naturally occurring minerals in excess from the mining. When the cities expand and the need for more building ground arises, ex-tin mining pools will be filled with construction site waste or other available discards and built upon. Arsenic contamination of drinking water is a world-wide problem. Long term exposure to arsenic via drinking water leads to wide range of health problems including: skin cancer, gangrene of the limbs, vascular diseases, conjunctivitis, central nervous system damage and hyperkeratosis. Coagulation flocculation and sedimentation is widely used for water treatment. Alum, as the common coagulant used in this process can lead to rise in the pH which requires further treatment for pH adjustment prior to discharge, besides its low ability for As (III) removal. Therefore, alternative coagulants have been investigated. *Moringa oleifera* is considered as one of the environmentally friendly coagulant used in turbidity removal. In this study, coagulation and flocculation process using *M. Oleifera* seeds and alum followed by sedimentation was used to compare their abilities for As (III) removal. In this experimental setup, the concentration of coagulant, initial As (III) levels and pH were varied to study their effect on As (III) removal. The mixing speeds (rapid and slow) were fixed at 100 and 40 rpm for 2 and 20 minutes, respectively, and the sedimentation time used was 30 minutes. While As (III) removal using alum, as coagulant was less than 10%, *M. Oleifera* achieved very high As (III) removal. At initial concentration of 0.5 ppm arsenic, 1000 and 2000 mg/l of *M. Oleifera* were able to remove 91.9 and 95.8 % of arsenic respectively. The As (III) residual level achieved in this study complied with the Malaysian Standard Drinking Water, which permits level for 0.05 ppm of arsenic. At higher initial As (III) concentrations of 2.0 and 3.0 ppm, 4000 and 5000 mg/l of *M.Oleifera* were able to remove 97 and 96.8 % of arsenic, respectively. The residual level of As (III) complied with the Malaysian Standard Discharge Water which permits level for 0.1 ppm of arsenic. When the concentration of initial arsenic was increased to 5.0 and 10.0 ppm, 1000 and 1500 mg/l of *M.Oleifera* removed 70.4 and 65.6 % of arsenic, respectively. Although, the residual level of As (III) was higher than the permitted discharge level, perhaps due to the high concentrations of As (III), the removal achieved is noticeably higher than that achieved by alum. The results showed that *M. Oleifera* is a promising natural polymer for removing heavy metals from the ground water.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PEMINDAHAN ARSENIK DARIPADA AIR DENGAN KEGUNAAN KOAGULANT SEMULAJADI *MORINGA OLEIFERA* (KACANG KELOR)

Oleh

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April 2003

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Industri timah pernah sekali jadi penyumbang utama kepada ekonomi Malaysia sedangkan Malaysia merupakan negara pengeluar bijih timah terbesar di dunia, daripada tahun 1950-1980-an. Kebanyakan cara pelombongan yang dijalankan merupakan perlombongan permukaan, akibatnya, kolam-kolam perlombongan besar ttertinggal. Kolam-kolam tersebut sering dipercemarkan oleh logam berat, terutamanya arcenik daripada bahan galian semulajadi yang berlebihan dari lombong. Apabila pengeluasan kawasan-kawasan bandar berlaku dan keperluan tapak bangunan meningkat, kolam perlombongan lama akan diisikan dengan sisa tapak pembinaan atau bahan buangan lain dan kemudian membina bangunan di atas. Pencemaran arsenik pada air minum merupakan suatu masalah serantau dunia. Pendedahannya secara tempoh masa yang panjang kepada arsenik melalui air minuman akan menyebabkan pelbagai masalah kesihatan termasuk: kanser kulit, peluputan siku, penyakit urat, konjunktiviti, kerosakan sistem saraf pusat dan hiperkeratosis. Koagulasi-pememejalan dan pemendakan adalah digunakan secara

meluas untuk rawatan air. Alum, sebagai kogulant yang biasa diguna dalam proses ini boleh menyebabkan peningkatan pH dimana pengawalan pH yang berlebihan diperlukan sebelum air rawatan itu dilepaskan, tambahan lagi ia memiliki keupayaan memindahkan As (III) yang agak rendah. Oleh demikian, koagulant yang lain telah ditinjaukan. *M. Oleifera* telah ditimbangkan sebagai salah satu koagulant yang tak-ancam alam sekitar yang digunakan dalam pemindah Lumpur. Dalam kajian ini, proses koagulasi-pememejalan biji bernih *M. Oleifera* dan alum diikuti dengan pemendakan digunakan untuk perbandingan dalam keupayaan pemindahan As (III). Dalam penyediaan ujikaji, kandunagn dan kepekatan koagulant, kepekatan awal dan pH As (III) dipelbagaikan untuk kajian kesan As (III). Kelajuan pencampuran (laju atau perlahan) akan ditetapkan pada 100 rpm selama 2 minit dan 40 rpm selama 20 minit masing-masing, dan masa pemendakan diguna adalah 30 minit. Sedangkan pemindahan As (III) guna alum sebagai koagulant adalah kurang daripada 10%, *M. Oleifera* telah mencapaikan pemindahan As (III) yang sangat tinggi. Pada kepakatan awal As (III) 0.5ppm, kadar pemindahan yang tercapai adalah 91.9% and 95.8% pada kuantiti *M. Oleifera*sebanyak 1000 dan 2000 mg/l masing-masing. Tahap As tertinggal yang tercapai dalam proses ini adalah mematuhi tahap kebenaran arsenik dalam air minuman di Malaysia (0.05 ppm). Pada kepekatan As (III) yang lebih tinggi, 2 ppm dan 3ppm, kadar pemindahan dengan *M. Oleifera* (4000 dan 5000 mg/l) adalah 97% dan 96.8 % masing-masing. Tahap As tertinggal yang tercapai dalam proses ini adalah mematuhi tahap kebenaran arsenik dalam air terlepas di Malaysia (0.1 ppm). Tambahan lagi, ia juga mencapaii 70.4% dan 65.6% pada kuantiti *M. Oleifera* 1000 mg/l dan 1500 mg/l masing-masing, dengan kepekatan As (III) 5ppm dan 10ppm. Sungguhpun tahap tertinggal As (III) adalah lebih tinggi daripada tahap pelepasan yang dibenarkan, mungkin disebabkan oleh kepekatan As

(III) yang terlampau tinggi, pemindahan tercapai, pemindahan yang tercapai jelas dinampak adalah lebih tinggi daripada yang dicapaikan oleh alum. Hasil kajian ini menunjukkan *M. Oleifera* merupakan satu polimer semulajadi yang terjamin untuk pemindahan logam berat daripada air atas tanah.

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INTRODUCTION

One of the major factors affecting the development of the human settlement has been the preoccupation with securing and maintaining an adequate supply of water. Water quality concerns dominated the earliest developmental phases. Population increases, however, exert more pressure on limited high-quality surface sources and contaminated water sources with human wastes, which led to deteriorating water quality. Thus, water quality of sources could no longer be overlooked in water supply development. Water treatment can be defined as the manipulation of water source to achieve a water quality that meets goals or standards set by the community through its regulatory agencies. An adequate supply of good quality safe water is essential to the promotion of public health.

1.1 Background on Arsenic Problem in Malaysia

Malaysia was the world's largest tin-producing country from 1950s to I980s. The industry was once a major contributor to the Malaysian economy. Indeed, Kuala Lumpur, the capital city has its origin in tin mining industry. Tin has been used for tinning, foil, tubes, amalgam, and in other alloys, e.g. solder, type metal and Rose's metal. However, the growth of the industry in Malaysia has been in negative trends since the global demand and price of tin have significantly decreased in the I980s. In

1979, Malaysia was producing almost 63,000 tones, accounting for 31 percent of world output, and employed more than 45,000 people. By 1994, in contrast, the country's production had fallen to 6,000 tones with only 3,000 people employed in the industry.

Tin mining has been carried out in large areas of mainly the western part of the Malaysian peninsula. The practiced mining technique was mostly surface mining, whether gravel or dredge mining, leaving large mine pools behind of sometimes more than 50 hectares in area. The pools are contaminated with the heavy metals, especially arsenic from naturally occurring minerals in excess from the mining. When the cities expand and the need for more building ground arises, ex-tin mining pools will be filled with construction site waste or other available discards and built upon. However, some pools remain and the others are developed for secondary usage in the form of garden lakes for recreational purposes, including recreational fishing.

1.2 Issues on Heavy Metals in Water

Heavy metals are electronegative metals with a density of more than 5g / cm^3. Generally these metals are good thermal and electric conductors. An important chemical property of heavy metals is their inertness. Some examples of heavy metals are zinc, arsenic, aluminium, copper, lead, cadmium, nickel and mercury.

The common perception is that all heavy metals are highly toxic, that is a very small quantity can kill living-beings. While this is true for most metals, some metals like copper and zinc are needed by living-beings in small quantities. Highly toxic metals include mercury, arsenic, lead and cadmium.

This study is mainly concerned with the extent of heavy metal pollution in natural and drinking sources. The heavy metal to be used in this study is arsenic.

1.3 Arsenic (As)

Arsenic (As), is a metallic main group element, found in group Vb of the periodic table. Atomic Number: 33, Relative Atomic Mass: 74.92. Arsenic and its compounds are highly toxic. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5), but in natural waters is mostly found in inorganic forms as oxyanions of trivalent arsenite (As (III) or pentavalent arsenate (As (V)). Arsenic toxicity depends on its chemical form, with inorganic forms of arsenic being more toxic than the organic forms. Inorganic arsenic can be present as the anionic and neutral forms arsenate, As (V), and arsenite. Although is acutely more toxic, human metabolic processes can convert As (V) to As (III). Thus, current and proposed environmental organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution.

Arsenic may also be found in water, which has flowed through arsenic rich rocks. Severe health effects have been observed in population drinking arsenic-rich water over long periods in countries worldwide. According to (NRC, 1999; Smith, et al, 2000) there are 20 countries where groundwater arsenic contamination episodes in the world are known. However, the world's four biggest cases of groundwater contamination and the worst sufferings of the people have been in Asia. In order of magnitude these are; Bangladesh, West Bengal-India, Inner Mongolia-P.R. China and Taiwan In all these countries, more and more groundwater withdrawal are taking place because of agricultural irrigation. In South East Asia, Bangladesh and West Bengal India are the most arsenic affected countries. More than 100 million people in these countries are at risk. Nine districts in West Bengal India and 47 districts in Bangladesh have arsenic level in groundwater above World Health Organization (WHO) maximum permissible limit of 50 μg/l. The guideline value of arsenic in drinking water of WHO is 10 μg/l. The area and population of the 47 districts in Bangladesh and 9 districts of West Bengal are 104578 km^2 and 90.2 million and 38.865 km^2 and 42.7 million respectively.

Figure 1.1: Arsenic ore (from Viessman and Hammer 1993)

1.4 Sources of Arsenic

- Arsenic is widely distributed throughout the earth's crust.
- Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks.
- Industrial effluents also contribute arsenic to water in some areas.
- Arsenic is also used commercially e.g. in alloying agents and wood preservatives.
- Combustion of fossil fuels is sources of arsenic in the environment through disperse atmospheric deposition.
- Inorganic arsenic can occur in the environment in several forms but in natural waters, and thus in drinking water, it is mostly found as trivalent arsenite (As (III)) or pentavalent arsenate (As (V)). Organic arsenic species, abundant in seafood, are very much less harmful to health, and are readily eliminated by the body.
- Drinking water poses the greatest threat to public health from arsenic. Exposure at work and mining and industrial emissions may also be significant locally.

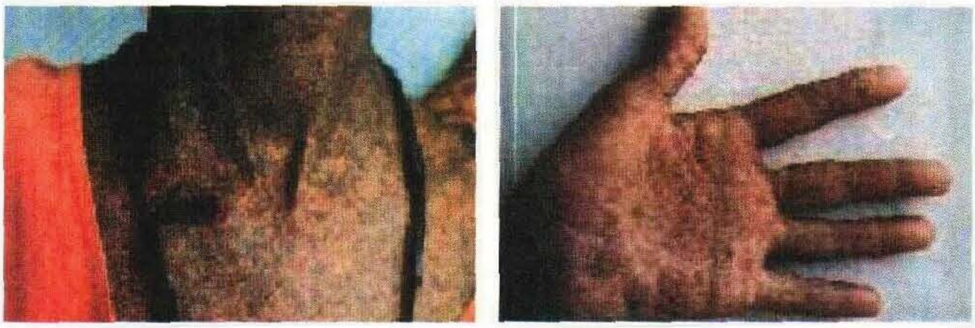
1.5 Effects of Arsenic on Human Health

- Chronic arsenic poisoning, as occurs after long-term exposure through drinking-water is very different to acute poisoning. Immediate symptoms on an acute poisoning typically include vomiting, oesophageal and abdominal pain, and bloody "rice water" diarrhoea. Chelation therapy may be effective in acute poisoning but should not be used against long-term poisoning.

- The symptoms and signs of arsenic causes appear to differ between individuals, population groups and geographic areas. Thus, there is no universal definition of the disease caused by arsenic. This complicates the assessment of the burden on health of arsenic. Similarly, there is no method to identify those cases of internal cancer that were caused by arsenic from cancers induced by other factors.
- Long-term exposure to arsenic via drinking water causes cancer of the skin, lungs, urinary bladder, and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis).
- Increased risks of lung and bladder cancer and of arsenic-associated skin lesions have been observed at drinking-water arsenic concentrations of less than 0.05mg/l.
- Absorption of arsenic through the skin is minimal and thus hand washing, bathing, laundry, etc. with water containing arsenic do not pose human health risk.
- Following long-term exposure, the first changes are usually observed in the skin: pigmentation changes, and then hyperkeratosis. Cancer is a late phenomenon, and usually takes more than 10 years to develop.
- The relationship between arsenic exposure and other health effects is not clear-cut. For example, some studies have reported hypertensive and cardiovascular disease, diabetes and reproductive effects.
- Exposure to arsenic via drinking water has been shown to cause a severe disease of blood vessels leading to gangrene in China (Province of Taiwan), known as 'black foot disease'. This disease has not been observed in other parts of the world, and it is possible that malnutrition contributes to its development.

However, studies in several countries have demonstrated that arsenic causes other, less severe forms of peripheral vascular disease.

- According to some estimates, arsenic in drinking water will cause 200,000 - 270,000 deaths from cancer in Bangladesh alone (National Research Council, 1999; Smith, et al, 2000).



Arsenic lesions on skin cancer   Arsenic lesions on hand cancer

Figure 1.2: Effects of arsenic on human health (from Richard Wilson 1995)

1.6 Objectives of the Study

The objectives of this study are:

1. To investigate the effectiveness of *Moringa oleifera* seeds in the removal of arsenic from ground water.
2. To determine the efficiency of the removal arsenic processes using coagulation, flocculation and sedimentation.