Novel Adsorbents and Electrocoagulation in Arsenate Removal from Water

by Thi Thuc Quyen Nguyen

Thesis submitted in fulfilment of the requirements for
the degree of Doctor of Philosophy

under the supervision of

Principal supervisor	: **Dr. Tien Vinh Nguyen**
Co-supervisor	: **Prof. Saravanamuthu Vigneswaran**
Co-supervisor	: **Prof. Huu Hao Ngo**

University of Technology Sydney
Faculty of Engineering and Information Technology

January 2021

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Thi Thuc Quyen Nguyen declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

Production Note:
Signature removed prior to publication.

Thi Thuc Quyen Nguyen
January 2021

ACKNOWLEDGEMENT

By this thesis, I wish to thank all the people whose assistance was an important milestone in the completion of my study.

I wish to express my sincere appreciation to my principal supervisor, **Dr. Tien Vinh Nguyen**, and co-supervisor, **Professor Saravanamuthu Vigneswaran** who have guided, encouraged, and supported me on the tough road of scientific research. Without their support, sometimes, I think I could not overcome obstacles on this pathway. I also wish to show my gratitude to my co-supervisor, **Professor Huu Hao Ngo** for the invaluable assistance that he provided during my study.

I wish to show my gratitude to **Assoc. Prof. Paripurnanda Loganathan** for his great support and guidance throughout my study, who spent a lot of time on each of my works.

I am indebted to **the manager and staff at Environmental Lab and Tech Lab** for their useful help in carrying out my experiments.

My special thanks approve to **Dr. Leonard Tijing** and **Dr. Gayathri Danasamy**. Their valuable comments and caring were help me improving my study in time.

I would like to thank the Australian Government Department of Foreign Affairs and Trade's (DFAT) innovationXchange (iXc) and Aus4Innovation programs for the financial support for my research.

I wish to acknowledge my family for their substantial financial support during my study, especially **my parents Nguyen Dinh Khanh - Nguyen Thi Be, my husband Cao Anh Tuan, my older sister and brother-in-law Thuc Doan – Tien Dung.** Particularly, I would like to thank my loved husband and my beloved daughter **Khanh An**. Together, we

spent the most difficult and arduous days in this strange land. Without them, I think I could not overcome every challenge from study to daily life.

Finally, I would like to give special thanks to my friends at UTS, especially the Vietnamese friends and Ms. Van Le - School Academic Officer in FEIT. They gave me many unforgettable memories in school time.

With love, I wish that all of you would always be happy and successful in your life.

DEDICATION

This thesis is deeply dedicated to the following people:

To My Lovely Parents ***Nguyen Dinh Khanh - Nguyen Thi Be***

To My Lovely Husband ***Cao Anh Tuan*** *and My Lovely Daughter* ***Cao Khanh An***

To My Brothers, Sister, Brother-In-Law

Hoai Vuong – Tien Dung – Thuc Doan – Hoai Van – Hoai Vu

My Nieces and Nephews

Khanh Vy – Khanh Dang – Khanh Diep

To My Family - In – Law

Parents: ***Tran Anh Dung – Cao Thi Nguyen***

Family of My Sister – In – Law: ***Trong Le – Anh Tu – Nhat Anh***

ACHIEVEMENTS

A. PUBLICATIONS

Nguyen, T.T.Q., Loganathan, P., Nguyen, T.V., Vigneswaran, S. 2020, Removing arsenic from water with an original and modified natural manganese oxide ore: batch kinetic and equilibrium adsorption studies, *Environmental Science and Pollution Research*, vol. 27, no. 5, pp. 5490-502.

Nguyen, T.T.Q., Loganathan, P., Nguyen, T.V., Vigneswaran, S., Ngo, H.H. 2020, Iron and zirconium modified *luffa* fibre as an effective bioadsorbent to remove arsenic from drinking water, *Chemosphere*, p. 127370.

Nguyen, T.T.Q., Loganathan, P., Nguyen, T.V. & Vigneswaran, S. 2020, 'Removing arsenate from water using modified manganese oxide ore: column adsorption and waste management', *Journal of Environmental Chemical Engineering*, p. 104491.

Nguyen, T.T.Q., Loganathan, P., Dinh, B.K., Nguyen, T.V. Vigneswaran, S., Ngo, H.H., 2020, Removing arsenate from water using batch and continuous-flow electrocoagulation with diverse power sources (submitted to *Journal of Environmental Chemical Engineeringl*).

B. CONFERENCES, SHOWCASES, AND SCHOLARSHIPS

N**guyen, T.T.Q.**, Loganathan, P., Nguyen, T.V., Vigneswaran, S., Ngo, H.H., Arsenate removal from water using *luffa* fibre, *'Technology and Innovation Research Showcase'* organised by the Consulate General of the Socialist and Repulic of Vietnam in Sydney - Australia, Science and Technology Representative Office, September 2018.

N**guyen, T.T.Q.**, Loganathan, P., Nguyen, T.V., Vigneswaran, S., Arsenate removal from water using novel adsorbents and electrocoagulation process, The 2020 FEIT 3MT Faculty Heat, video presentation, July 2020.

N**guyen, T.T.Q.**, Loganathan, P., Nguyen, T.V., Vigneswaran, S., Novel green method for arsenate removal for drinking water, UTS Visualise Your Thesis Competition 2020, 60s video presentation, August 2020.

N**guyen, T.T.Q.**, Loganathan, P., Nguyen, T.V., Vigneswaran, S., Ngo, H.H., Arsenate removal from groundwater using dried *luffa* plant coating iron, 9th International Summit on Global Warming and Environmental Science, Stockholm, Sweeden, oral presentation (webinar), 10th - 11th August 2020.

Faculty of Engineering and Information Technology Scholarship (Google DFAT Project)

TABLE OF CONTENTS

LIST OF FIGURE

LIST OF TABLE

NOMENCLATURE/ABBREVIATION

As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
A_T	Temkin isotherm equilibrium binding constant (L/g)
B	Constant related to heat of sorption (J/mol)
BET	Brunauer-Emmett-Teller nitrogen adsorption
BJH	Barrett-Joyner-Halenda method
b_T	Temkin isotherm constant
BV	Bed volume
C_e	Equilibrium concentration of arsenate (V) (mg/L)
$C_{electrode}$	Electrode consumption concentration (mg/L)
C_o	Initial concentration of arsenate (mg/L)
CO_3^{2-}	Bicarbonate
C_t	As(V) concentration in effluent at time t (mg/L)
C_{WHO}	WHO guideline concentration
DC	Direct current
E	Arsenic removal efficiency (%)
EC	electrocoagulation
EDS	Energy-dispersive X-ray spectroscopy
EIL	Ecological investigation level
Fe	Iron
Fe^a-VMO	Iron coating Vietnamese manganese oxide ore

FLF-3	Iron grafting *luffa* fibre
FTIR	Fourier transform infrared
h	hour
H	Bed-height (cm)
HNO_3	Nitric acid
HRT	Hydraulic retention time (min)
I	Current intensity (A)
k_1	Rate constant of pseudo-first order adsorption (L/h)
k_2	Rate constant of pseudo-second order (g/mg.h)
k_f	Freundlich constant related to adsorption capacity (L/g)
k_L	Langmuir isotherm constant (L/mg)
KOH	Potassium hydroxide
k_p	Intra-particle diffusion rate constant (mg/g. $h^{1/2}$)
K_{Th}	Thomas rate constant (L/h/mg)
LEAF	Leaching Environmental Assessment Framework
LF	*Luffa* fibre
m	Mass of adsorbent (g)
m_{Fe}	Mass of Fe generated (mg)
min	minute
Mn	Manganese
n	Heterogeneity factor, dimensionless
$NaNO_3$	Sodium nitrate
NaOH	Sodium hydroxide
PFO	Pseudo-first order

PO_4^{3-}	Phosphate
PSO	pseudo-second order
Q	Flow velocity (L/h)
q_e	Amount of As adsorbed per unit mass of adsorbent (mg/g)
q_{exp}	Experimental As
q_m	maximum amount of the As adsorbed per unit mass of the adsorbent (mg/g)
q_t	Amount of As adsorbed at time t (mg/g)
q_T	Thomas model adsorption capacity (mg/g).
R	Universal gas constant (8.314 J/mol/K)
RCPT	Rapid chloride penetrability test
R_L	Equilibrium parameter
rpm	Revolutions per minute
S/S	Solidification/stabilisation
SEM	Scanning electron microscopy
SiO_3^{2-}	Silicate
SO_4^{2-}	Sulphate
T	Temperature (^{o})
t	Time (h) or (min)
TCLP	Toxicity characteristic leaching procedure
U	Voltage (V)
USEPA	The United States Environmental Protection Agency
V	Volume of solution (L)
VMO	Vietnamese manganese oxide ore
VPV	Volume of permeable voids

WHO	World Health Organisation
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZLF-3	Zirconium grafting *luffa* fibre
ZPC	Zero point of charges
Zr	Zirconium
Zr^a-VMO	Zirconium coating Vietnamese manganese oxide ore
α	Initial adsorption rate (mg/g.min)

ABSTRACT

Arsenic (As) is one of the most dangerous substances and especially when it exists in its inorganic form in water, wastewater, air, and food. Elevated concentrations of inorganic As have been discovered in groundwater sources in many places worldwide, particularly Bangladesh, India, Nepal, Cambodia, Vietnam, and some areas of Australia. In many developing countries, As-contaminated groundwater is used as the primary drinking water source. Its concentration can reach as high as 1,000 μg/L, which is much larger than the WHO recommended standard of 10 μg/L. Inorganic As can lead to a number of diseases such as gastrointestinal symptoms, severe disturbances of the cardiovascular system, central nervous systems, and cancer. In natural aqueous systems, the most toxic species of As are trivalent arsenite (As(III)) and pentavalent arsenate (As(V)). As(III) is more toxic than As(V) and can be oxidized to As(V).

Research on As removal, particularly As(V), began several decades ago, and many treatment technologies have been devised and implemented. However, the high treatment cost and complicated nature of As treatment systems present the main challenges in applying these technologies, especially at a decentralised scale and in rural or isolated areas. Consequently, the main objective of this research is to develop novel and cost-effective methods that can be applied widely to remove As (V), particularly for vulnerable groups of people. Cost-effective adsorption based on novel adsorbents and electrocoagulation with solar energy was the focus of this study. Simplicity and cost-efficiency during design and operation were the main topics analysed here.

In the first part of this research, **two novel adsorbents** were developed and used to adsorb As(V) from water. A low-cost **manganese oxide ore** from Vietnam (VMO) (containing 25.6% Mn and 16.1% Fe mainly in the forms of cryptomelane and goethite

minerals) was firstly evaluated for its performance in As(V) removal from water. VMO was then modified by grafting with iron oxide and zirconium oxide to improve its adsorption capacity. Results show that the Langmuir maximum adsorption capacity of new modified VMO, namely Fe^a-VMO and Zr^a-VMO were 2.19 mg/g and 1.94 mg/g, respectively, nearly 20 times higher than that of the original VMO (0.11 mg/L). These adsorbents were used in a column study to remove As(V) from synthetic contaminated water under various conditions. Column adsorption data fitted well to the Thomas model and the predicted adsorption capacities followed the same order as that observed in the batch experiment for these three adsorbents: Fe^a-VMO > Zr^a-VMO > VMO. At an influent concentration of 0.25 mg As(V)/L, and flow velocity of 0.15 L/h, the Thomas model adsorption capacities of VMO, Fe^a-VMO, and Zr^a-VMO were 0.151, 1.145, and 0.925 mg/g, respectively.

Other novel adsorbents, namely FLF-3 and ZLF-3 have also been produced from a popular agricultural by-product, ***luffa* plant fibre** (LF), by grafting LF with iron oxide and zirconium oxide. This is the first time a *luffa* plant, an agricultural by-product, was used to treat As(V) from water. The Langmuir adsorption capacity of LF, at the influent As(V) concentration of 0.5 mg/L and pH 7, was found to be only 0.035 mg/g. Although the adsorption capacity of LF was poor, it improved remarkably after modification, in fact up to 2.55 mg/g for FLF-3 and 2.89 mg/g for ZLF-3. The adsorption capacities of FLF-3 and ZLF-3 are comparable or higher than those of many other chemically modified bio-adsorbents. In the column study, the experimental data also fitted well to the Thomas model and the As(V) adsorption capacity of ZLF-3 proved to be the highest (2.7 mg/g at initial As(V) concentration of 0.1 mg/L), followed by FLF-3 (1.26 mg/g) and LF (0.06 mg/g).

In the second part of this research, **a novel electrocoagulation** method using different power sources (including new renewable energy - solar panel or rechargeable battery) was applied to remove As(V) in water. This method can be applied to remove As(V) in rural and isolated areas because of its capability of operating without electricity. For an initial As(V) concentration of 0.1 mg/L, an operational time of 5 min, an electrical potential difference of 7.5 V, and electrodes distance of 1 cm were identified as optimal conditions for removing As(V). In the batch study using a 9 V rechargeable battery and 12 V solar panel, the electrocoagulation reactor could remove 93 and 98% of As(V), respectively, from 0.1 mg As(V)/L solution. As(V) concentration in treated water was smaller than that of the WHO drinking water guidelines. In the continuous study, a small, cost-effective system (cost $15AUD) using DC electrical power or a small solar panel of 12V could successfully treat 12L contaminated water per hour (similar flow rate as many commercial household filters). During 4 hours of continuous testing, the As(V) removal efficiency maintained at more than 91% for DC electrical system and 96% for the solar energy system, respectively

Finally, **the third part of this research** focused on **managing the toxic waste** resulting from the adsorption process. Solidification/stabilisation method (for VMO and modified VMOs) and phytoremediation method (by *Pityrogramma calomelanos* (fern plant) for LF and modified LFs) were investigated. The quality tests of concrete used for solidification (compressive strength, rapid chloride penetrability test, and volume of permeable voids) and leaching tests confirm that the concrete produced from the solidification/stabilisation can be safely disposed of or used as a structural construction material for driveways or pavements. To manage the exhausted LF and modified LFs, phytoremediation results show that As(V) could be well transferred from waste

adsorbents to plants and diffused to all parts of the plants. As(V) concentration from the mixing of soil and exhausted LFs reduced significantly from 38.56 mg/kg to 9.92 – 10.20 mg/kg, much lower than the permissible level of the United States Environmental Protection Agency (USEPA) (24 mg/kg) and the ecological investigation level (EIL) limit of As in soil in Australia (20 mg/kg).

In summary, this study successfully developed two novel adsorbents and a novel electrocoagulation process for removing As(V) in water. The new adsorbents and treatment process includes features that favour As(V) removal such as cost-effectiveness, high removal efficiency, environmental friendliness and simple application. The exhausted adsorbents can be safely disposed into the environment once the treatment process is completed. The novel electrocoagulation process using renewable energy is also a promising approach. The most important feature of this approach is its independence from power, which allows its application in the rural and isolated areas with poor infrastructure.