UTS UNIVERSITY OF TECHNOLOGY SYDNEY

ARSENIC REMOVAL FROM WATER BY NOVEL IRON-BASED ADSORBENTS

by Thi Hai Nguyen

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, Thi Hai Nguyen declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering/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.

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AWARDS

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NOMENCLATURE

Al	: Aluminum
As	: Arsenic
As(III)	: Arsenite
As(V)	: Arsenate
C	: Cement
$C°$	: The selected standard state of As (C° = 1 mol/L)
C_d	: The total concentration of As (mg/L) in solution after desorption
C_e	: The total arsenic concentrations (mg/L) at equilibrium
C_o	: The total arsenic concentrations (mg/L) at beginning
C_t	: The total arsenic concentrations (mg/L) at time *t*
DI	: Deionized water
EBCT	: Empty bed contact time
EDS	: Energy-Dispersive X-ray Spectroscopy
Fe	: Iron
FTIR	: Fourier Transform Infrared Spectroscopy
g	: The exponent whose value must lie between 0 and 1 (dimensionless)
K	: The Khan equilibrium constant (L/mg)

k_1	: The rate constant of the pseudo-first-order equation (1/min)
k_2	: The pseudo-second-order rate constant [g/(mg×min)]
k_{AV}	: The Avrami kinetic constant (1/min)
$K_{Equilibrium}$	: The thermodynamic equilibrium constant (dimensionless)
K_F	: The Freundlich constant, which characterizes the strength of adsorption ((mg/g)(L/mg)n)
K_L	: The Langmuir constant related to the affinity between adsorbent and As (L/mg)
K_{LF}	: The Langmuir–Freundlich constant (L/mg)
K_{model}	: The Langmuir constant (KL)(L/mol)
K_{RP}	: The Redlich–Peterson constants (L/g)
k_{TH}	: The Thomas adsorption rate constant (L/h.mg)
L	: Lime
m_1	: The mas of adsorbent used (g)
m_2	: The mass of arsenic loaded adsorbent (g)
MCL	: The maximum contaminant limit
Mg	: Magnesium
Mn	: Manganese
Mn/Mg/Fe-LDH	: Mn/Mg/Fe-Layer Double Hydroxide
n_{AV}	: The fractional adsorption order corresponding to adsorption mechanism.

n_F	: The Freundlich intensity parameter, which indicates the magnitude of the adsorption driving force or surface heterogeneity(dimensionless; 0<n<1)
n_K	: The exponent of the Khan model (dimensionless)
n_{LF}	: An exponent of the Langmuir-Freundlich model(dimensionless; surface heterogeneity constant)
NLTT	: Natural laterite
nZVI	: Nanoscale zero-valent iron
PFO	: Pseudo-second-order
pH_{IEP}	: pH value at the isoelectric points
pH_{PZC}	: pH value at the point of zero charge
PPCI	: Pomelo peel biochar coated with iron
PSO	: Pseudo-first-order
Q	: The volumetric flow rate (L/h)
QCVN01:2009/BYT	: Vietnam Technical Regulation on Drinking Water Quality
q_d	: The mass of arsenic desorbed if the adsorption process is reversible (mg/g)
q_e	: The amount of arsenic adsorbed onto adsorbent at equilibrium (mg/g)
Q_K	: The Khan maximum adsorption capacity of adsorbent (mg/g)
Q_{LF}	: The Langmuir–Freundlich adsorption capacity of adsorbent (mg/g)

Q_{max}	: The Langmuir maximum adsorption capacity of adsorbent (mg/g)
q_r	: The mass of arsenic that remained adsorbed after desorption (mg/g)
q_t	: The amount of arsenic adsorbed onto adsorbent at time t (mg/g)
q_{TH}	: The maximum column As(V) adsorption capacity (mg/g)
R	: The gas constant [0.00831 kJ/(mol×K)]
R^2	: The determination coefficient values
S/S	: Solidification/stabilization
S_{BET}	: Brunauer-Emmett-Teller surface area
SEM	: Scanning Electron Microscope
T	: The absolute temperature (^{0}K)
TCLP	: Toxicity characteristic leaching procedure
TCVN 6355:2-2009	: Vietnam Technical Standard on Bricks Test Methods
TCVN 6477:2016	: Vietnam Technical Standard on Concrete Bricks
USEPA	: United States Environmental Protection Agency
V_1	: The volume of the arsenic solution (L)
V_2	: The volume of the desorbing agents (L)
V_{Total}	: Total Pore Volume
WHO	: World Health Organization

XPS	: X-ray photoelectron spectroscopy
XRD	: X-ray Diffraction
XRF	: X-ray Fluorescence
$\Delta G°$	: The standard Gibbs free energy change
$\Delta H°$	: The standard enthalpy change
$\Delta S°$	: The standard entropy change
$\chi 2$	: The Chi-Square values
a_{RP}	: The Redlich–Peterson constants (L/mg)g
α	: The initial rate constant of the Elovich equation [mg/(g×min)]
β	: The desorption constant during any one experiment (g/mg)
γ	: The activity coefficient of As in solution.

ABSTRACT

This thesis aims to develop novel iron-based adsorbents and investigate their performance in removing arsenic (As) from the water environment. Due to iron having a high affinity toward As ions, iron-containing adsorbents are deemed to be promising materials for removing As effectively from aquatic environments. In this study, 3 new iron-based adsorbents were successfully developed and investigated in detail in their ability to remove both arsenate (As(V)) and arsenite (As(III)) from synthetic and real contaminated groundwater. These were: (i) NLTT, a natural laterite obtained from natural iron–rich subsoil rock from Thach That district, Hanoi, Vietnam through the simple production process; (ii) PPCI, an iron-impregnated biochar derived from combination of iron coating and slow pyrolysis carbonization processes of an agricultural waste product - pomelo peel; and (iii) Mn/Mg/Fe-LDH, a Mn/Mg/Fe-layered double hydroxides adsorbent obtained through the simple co-precipitation method. Results of this study show that these three studied iron-based adsorbents can remove both As(III) and As(V) effectively from water environments. Mn/Mg/Fe-LDH exhibited the highest adsorption capacity toward both As ions and could be used for very high polluted water sources. The Langmuir maximum adsorption capacities of Mn/Mg/Fe-LDH toward As(III) and As(V) were 56.1 mg/g and 32.2 mg/g, respectively. The maximum adsorption capacities of PPCI were 11.77 mg/g for As(III) and 15.28 mg/g for As(V), respectively. PPCI could be a new solution of reusing pomelo peel, a widespread agricultural waste, for remediating As from contaminated water. Referring to immediate practical applications, NLTT is the most suitable candidate for As removal in Vietnam's rural areas due to its local availability, low cost (calculated commercial price of US$ 0.10/kg) and good As adsorption capacity (0.512 mg/g for As(III) and 0.580 mg/g for As(V)). NLTT has been successfully

implemented as a filter media in both household and community filters in the Red River Delta, Vietnam. The long-term monitoring results show that both household and community filtration systems packed with NLTT could produce safe drinking water with As levels below the WHO and Vietnam's drinking water limits after operating for 6–7 months. The exhausted NLTT adsorbent could be successfully managed by using solidification/stabilization method. The concrete bricks met the requirements of building materials as used in the construction industry. Although NLTT exhibited poorer adsorption capacities than PPCI and Mn/Mg/Fe-LDH, NLTT can quickly become a commercially viable As filter media. For PPCI and Mn/Mg/Fe-LDH, they have emerged as two practical promising adsorbents for removing As from water environments in the future.

Keywords: Arsenic removal; Adsorption; Laterite; Iron-impregnated biochar; Layer double hydroxides; Water treatment