UNIVERSITY OF TECHNOLOGY SYDNEY

SELECTIVE RESOURCE RECOVERY FROM ACID MINE DRAINAGE BY MEMBRANE DISTILLATION AND ADSORPTION PROCESS

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Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Saravanamuthu Vigneswaran

University of Technology Sydney
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June 2021

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, SeongChul Ryu, declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy (Engineering) in the Faculty of Engineering and IT 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.

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Date: 22/02/2021

ACKNOWLEDGEMENTS

My Doctoral study would be impossible without help from several people, to whom I would like to express my gratitude and appreciation through these acknowledgements.

First of all, I sincerely appreciate to my supervisor, Prof. Saravanamuthu Vigneswaran, who gave me generous opportunities and guidance during my doctoral studies at University of Technology Sydney. I also would like to thank Dr. Gayathri Naidu for her helpful and clear advices and assistances. Also, thanks to Prof. Hee Moon from Korea, I really appreciate to your endless love and all help during my entire journey in Sydney. Without a doubt, it would have been difficult to successfully complete my doctoral degree without my supervisors.

In addition, I am grateful to my seniors, colleagues and friends for their support, good conversations, motivation, and friendship; ADSEP members, Youngkwon Choi, Yunju Jo, Yunchul Woo, Myoungjun Park, Jungeun Kim, Sungil Lim, Michael Seo, David Kim, Paula Choi, Yonghyun Shin, Weonjung Sohn, Ralph Rolly Gonzales, Federico Volpin, Charith Fonseka.

Last but not the least, I would like to express my heartfelt appreciation to my family, my father Jeongun Ryu, my mother Hyejeong Jeong, and my younger brother Hyungbin Ryu, for their overwhelming support. They are the most important reasons why I was able to continue my study steadily and constantly, despite numerous issues and setbacks. Their constant support, both emotional and economic, allowed me to focus entirely on my study. I did not give up because of their unstinted care and love. I cannot go home to see you because of the Covid-19 pandemic, but I really miss you and love you so much, my family.

LIST OF PUBLICATIONS DURING CANDIDATURE

1. ***S. Ryu**, G. Naidu, MAH Johir, Y. Choi, S. Vigneswaran, Acid mine drainage treatment by integrated submerged membrane distillation-sorption system, Chemosphere, 218 (2019) 955-965.
2. ***S. Ryu**, G. Naidu, H. Moon, S. Vigneswaran, Selective copper extraction by multi-modified mesoporous silica material, SBA-15, Science of The Total Environment, 697 (2019) 134070.
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6. ***S. Ryu**, G. Naidu, H. Moon, S. Vigneswaran, Continuous and selective Cu recovery by multi-modified and granulated SBA-15, Chemosphere, 271 (2021) 129820.
7. ***S. Ryu**, C. Fonseka, G. Naidu, P. Loganathan, H. Moon, J. Kandasamy, S. Vigneswaran, Recovery of rare earth elements (Lu, Y) by adsorption using functionalized SBA-15 and MIL-101 (Cr), Chemosphere, 281 (2021) 130869.

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CONFERENCE PRESENTATIONS DURING CANDIDATURE

1. S. Ryu, G. Naidu, H. Moon, S. Vigneswaran, Hybrid membrane distillation and adsorption system for selective recovery of Cu^{2+} from acid mine drainage, 7th Membrane Society of Australia Early Career Researcher Membrane Symposium (MSA-ECR), Sydney, Australia, 1-2 Feb 2020.
2. S. Ryu, G. Naidu, H. Moon, T. Setiadi, S. Vigneswaran, Selective resource recovery from acid mine drainage by membrane distillation and adsorption hybrid system, 10th International Membrane Science and Technology Conference (IMSTEC), Sydney, Australia, 2-6 Feb 2020.
3. S. Ryu, C. Fonseka, G. Naidu, H. Moon, S. Vigneswaran, Recovery of valuable rare earth elements (REEs) by adsorption with modified SBA-15, 13th International Conference on the Challenges in Environmental Science and Engineering (CESE), online conference, 7-8 Nov 2020.

All activities in conferences during my doctoral candidature were oral presentations.

LIST OF ABBREVIATIONS

ACMPC	(4-chloro-2-mecraptophenyl)carbamodithioate
AMD	Acid mine drainage
APTES	(3-aminopropyl)triethoxysilane
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CL	Condenser lens
COF	Covalent-organic Frameworks
DCC	Dicyclohexylcarbodiimide
DCMD	Direct contact membrane distillation
DDAB	Dilauryl dimethyl ammonium bromide
DHDM	N,N’-(octane-1,8-diylidene)di(2-hydroxy-3,5-dimethylaniline)
DMF	N,N-dimethylformamide
EC	European Commission
EDX	Energy dispersive X-ray spectroscopy
FE-TEM	Field emission transmission electron microscope
FT-IR	Fourier transform infrared spectroscopy
ICP-MS	Inductively coupled plasma-mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LAS	Linear Alkylbenzene Sulfonate
LDFA	Linear driving for approximation
LARWG	Land Access for Resources Working Group
MD	Membrane distillation

MEC	Microbial electrolysis cell
MOF	Metal-organic Frameworks
MP-AES	Microwave plasma-atomic emission spectrometer
NETL	National Energy Technology Laboratory
NF	Nanofiltration
NRC	National Academy of Science
ODE	Ordinary differential equation
OL	Objective lens
PA	Phthaloyl diamide
PDEPE	Parabolic and elliptic partial differential equations
PDM	Pore diffusion model
PEST	Parameter estimation by sequential testing
PMIDA	N-(phosphonomethyl) iminodiacetic acid
PSD	Pore size distribution
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
REE	Rare earth element
RO	Reverse osmosis
SDA	Structure direct agent
SDM	Surface diffusion model
SEM	Scanning electron microscopy
SSQ	Sequential precipitation
TDS	Total dissolved solids

TEOS	Tetraethyl orthosilicate
TSNT	(tetrakis(3-carboxysalicylidene))naphthalene-1,2,5,5-tetramine
XRD	X-ray diffraction
XPS	X-ray photoelectron
VCF	Volume concentration factor

LIST OF SYMBOLS

$\emptyset$	Association factor of solvent	
b	Langmuir isotherm constant	L/mg
C_b	Bulk concentration	mg/L
C_e	Equilibrium concentration	mg/L
C_i	Initial concentration	mg/L
C_p	Concentration at inside of particle	mg/L
D_L	Axial dispersion coefficient	m^2/s
D_m	Molecular diffusivity	m^2/s
D_p	Pore diffusion coefficient	m^2/s
D_s	Effective surface diffusion coefficient	m^2/s
ε_p	Porosity of particle	
ε	Bed porosity	
k_1	Pseudo first order parameter	h^{-1}
k_2	Pseudo second order parameter	h^{-1}
k_f	Film mass transfer coefficient	m/s
k_s	Mass transfer coefficient	1/s
K_F	Freundlich constant	$g^{1-n}\ L^n g^{-1}$
m	Mass of adsorbent	g
M	Molecular weight	
μ	Viscosity of fluid	Pa·s
n	Adsorption isotherm constant for Freundlich and Sips	
$\bar{Q}$	Average value of adsorbed particle amounts	ng/g

Q_e	Equilibrium adsorption capacity	mg/g
Q_m	Maximum adsorption capacity	mg/g
Q_t	Adsorption capacity in terms of time	mg/g
r	Radial distance	mg/g
Re	Reynolds number	
R_p	Particle radius	m
Sc	Schmidt number	
ρ_f	Density of fluid	kg/m^3
ρ_p	Particle density	kg/m^3
t	Time	h
T	Temperature	K
v	Superficial velocity of the fluid	m/s
V	Volume of solution	L

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ABSTRACT

The formation of acid mine drainage (AMD) is a natural process attributed to the oxidation of sulphide minerals such as pyrites. AMD is characterized by low pH and high concentration of sulphate, as well as high concentrations of heavy metals. Nearby water streams are susceptible to AMD infiltration, resulting in discoloration of streams, decrease in pH and accumulation of heavy metals. The long-term impact of AMD contaminant on aquatic organisms, plant growth and human health is a significant concern, which necessitates AMD treatment. On the other hand, heavy metals such as Cu are used in many industrial applications such as semi-conductor, electric circuit boards, etc. If Cu ions can be recovered selectively and reused in industrial applications, it will be beneficial both to environment and industry.

Conventionally, AMD has been treated by the addition of chemical neutralizing agents, often limestone, to raise the pH and precipitate metals in the form of carbonate and hydroxides. Although efficient, precipitation results in large volumes of sludge containing heavy metals that require safe disposal. In this regard, the uptake of heavy metals by reusable adsorbents are especially promising as a cost-effective treatment method for AMD.

In this thesis, following are researched in detail:

(i) Treatment of synthetic AMD by integrated submerged membrane distillation – adsorption system using zeolite. Synthetic AMD which has similar composition was used to control the composition of heavy metals and other constituents of AMD.

(ii) Selective Cu adsorption using functionalised mesoporous absorbents (such as multi-modified SBA-15) in batch and continuous systems,

(iii) Selective Cu recovery by membrane distillation and adsorption system from pH modified synthetic acid mine drainage, and

(iv) Recovery of valuable rare earth elements (REE) which are also found in AMD by surface modified SBA-15 and metal organic frameworks (MOF).

Firstly, the performance of an integrated submerged direct contact membrane distillation (DCMD) – zeolite hybrid adsorption system for synthetic AMD treatment was evaluated. The results showed that modified (heat treated) zeolite achieved 26 – 30% higher removal of heavy metals compared to natural untreated zeolite. Heavy metal sorption by heat treated zeolite followed the order of Fe>Al>Zn>Cu>Ni. Slight pH adjustment from 2 to 4 removed Fe and Al (close to 100%) through a combination of adsorption and partial precipitation mechanisms. Fe and Al are also found in AMD. An integrated system of submerged DCMD with zeolite for synthetic AMD treatment enabled to achieve 50% water recovery in 30 h. The integrated system provided a favourable condition for zeolite to be used in powder form with full contact time in a storage tank. Likewise, heavy metal removal from AMD by zeolite, specifically Fe and Al, mitigated membrane fouling on the surface of the hollow fibre submerged membrane. The integrated system produced high quality fresh water while concentrating sulfuric acid and valuable heavy metals (Cu, Zn and Ni).

However, although the above system could remove toxic heavy metals and produce pure water, it was not able to recover valuable heavy metals. For this reason, as a next step, hexagonal structured mesoporous silica material, SBA-15, with amine-grafting (SBA-15-NH_2) and manganese loading along with amine-grafting (Mn-SBA-15-NH_2) were fabricated using $KMnO_4$ and 3-aminopropyltriethoxysilane. The results established the 2.08 mmol/g of Cu adsorption capacity on Mn-SBA-15-NH_2. Furthermore, in a mixed heavy metal solution, high selective Cu adsorption capacity on Mn-SBA-15-NH_2 (2.01 mmol/g) was achieved while maintaining 96% adsorption amount as that of a single Cu solution. Comparatively, Cu adsorption on SBA-15-NH_2 decreased by half due to high competition with other heavy metals.

Optimal Cu adsorption occurred at pH 5. This pH condition enabled grafted amine group in Mn-SBA-15-NH_2 to form strong chelating bonds with Cu, avoiding protonation of amine group (below pH 5) as well as precipitation (above pH 5). High regeneration and reuse capacity of Mn-SBA-15-NH_2 was achieved by maintaining 90% adsorption capacity in a multiple adsorption-desorption cycle experiment. Cu was selectively extracted from Mn-SBA-15-NH_2 with an acid solution.

Selective recovery of Cu from heavy metal wastewater not only mitigates the pollution of environment but also metal recycle in industrial applications. To achieve this, Mn loaded, and amine grafted SBA-15 (MN-SBA) was granulated using alginic-acid (GMN-SBA) to be used dynamic column adsorption process. Adsorption capacities of MN-SBA for heavy metals such as Cu, Zn, Ni and Mn were 2.11, 1.24, 1.74 and 1.25 mmol/g and they decreased to 1.23, 0.68, 0.86 and 0.65 when it was granulated (GMN-SBA). Even though the adsorption capacities of GMN-SBA for heavy metals decreased by 40 – 50%, it enabled easy regeneration and separation process when applied in continuous fixed-bed column adsorption mode. Specifically, the results demonstrated that GMN-SBA was able to be reused for 5 times while maintaining over 80% adsorption capacities of the virgin GMN-SBA. Fixed-bed adsorption results were well explained by dynamic adsorption model incorporated with linear driving force approximation (LDFA) model. The simulation of fixed-bed adsorption tests was conducted successfully with varying bed length, feeding concentration and flow rate. In multi-component adsorption, the breakthrough curves showed a high overshoot phenomenon for Zn, Ni and Mn compared to Cu. This reflected the high affinity of Cu towards GMN-SBA compared to other heavy metals.

From synthetic AMD solution, valuable resource of Cu was selectively recovered by membrane distillation and adsorption system. Direct contact membrane distillation (DCMD) system enabled to concentrate the Cu concentration in AMD by more than 2.5 times while recovering 80% of high-quality water for reuse. SBA-15 multi-modified with Mn and amine grafting was used for selective Cu adsorption. Under acidic conditions, heavy metals were not able to be adsorbed on amine grafted SBA-15. Therefore, the pH of synthetic AMD (pH=2.2) needed to be adjusted to the range of 5.0 – 5.2 to enable adsorption of Cu on modified SBA-15 (this is to prevent protonation of amine groups grafted on prepared SBA-15). Moreover, increase of pH helped to precipitate more than 99% of Fe and Al (predominant metal contents in AMD). Cu adsorption on modified SBA-15 was 24.53 mg/g for KOH treated AMD. However, Cu adsorption on modified SBA-15 decreased by 26% (18.11 mg/g) for NaOH treated AMD. Cu adsorption with modified SBA-15 was significantly improved to 55.75 mg/g when Cu concentration was concentrated by DCMD. Cu adsorption was efficiently carried out by coupling membrane distillation and adsorption. Prior concentration by DCMD increased the Cu adsorption capacity of 55.85 mg/g which is 85% of the maximum Cu adsorption capacity. As a result, higher Cu was successfully adsorbed with high selectivity in addition to 80% of high quality of water recovery.

Further, AMD not only contains heavy metals, but also rare earth elements (REEs). Due to increasing demand and application in many fields such as plasma tubes, hybrid batteries and super magnet, the recovery of rare earth elements has become an emerging issue. Especially, Yttrium (Y) and Lutetium (Lu) are widely used as catalysts in many industries. In order to extract those two rare earth metals, the SBA-15 modified with 1,4-phthaloyl diamido-propyltriethoxysilane (1,4-PA-APTES) ligands; and Chromium based metal organic frameworks (MOF) modified with PMIDA (MIL-101-PMIDA) were prepared in this study. The adsorption capacities for Lu and Y on the modified SBA-15 significantly increased to 17.02 and 17.86 mg/L from that of SBA-15. The virgin SBA-15 without any modification had near zero adsorption. In addition, the adsorption capacities of Lu and Y on MIL-101-PMIDA were 63.36 and 25.27 mg/g, respectively. Both adsorbents maintained more than 90% of adsorption capacities even after 5 times of regeneration of adsorbents.

Increasing cost of mining activities and stringent environment regulations have made treatment of AMD an additional cost to the industry. Identifying sustainable and economically viable treatment methods is essential to encourage AMD treatment within the mining industry to prevent environment pollution. Resource recovery from AMD has long being considered as a viable approach to offset cost of treatment and meet the demand for scarce metals in the international market. Treatment of AMD combining membrane distillation and subsequent adsorption presented in this study is an innovative approach for resource recovery. Membrane distillation is used for recovery of fresh water and functionalized adsorbents are synthesized for selective recovery of dissolved metals from concentrated feed. This will enable wide use of the technology in the mining industry and help create a circular economy for valuable metals in the international market.