UNIVERSITI TEKNOLOGI MARA

REMOVAL OF HEAVY METALS BY IRON REDUCTANTS AND COBALAMIN IN ANAEROBIC ENVIRONMENT

JALINA BINTI KASSIM

Thesis submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy** (Civil Engineering)

School of Civil Engineering

February 2022

ABSTRACT

This study highlights the removal of Cr and Zn by iron reductant with the present of Cobalamin under various experimental condition that is significant in the engineered or natural anaerobic environment. New findings on the role of enzymatic compound that significantly contribute to the removal of heavy metals in anaerobic environment was also reported. SEM analyses verify that particles size of synthesized nZVI and nFe₃O₄ were in the range of 25-70 nm (< 100 nm). Iron (Fe) is reported as dominant composition in both nZVI (73.87%) and nFe₃O₄ (58.88%). Batch experiments were carried out to elucidate the removal kinetics of Cr and Zn by nZVI and Co for the effects of metal concentration, pH, nZVI amount and Co concentration. From the effects of metals concentration, both Cr and Zn attained highest removal under nZVI-Co suspension at 0.5ppm having removal kinetic, $k=1.0560 \text{ min}^{-1}$, $R^{2}=0.9981$ for Cr and $k=1.4409 \text{ min}^{-1}$, R²=0.9996 for Zn. Effects of pH reveal highest removal of Cr was obtained under nZVI-Co suspension at pH 7 and pH 9 for Zn under nZVI-Co suspension. From the effects of different nZVI amount, both Cr and Zn removal increases with the increase of nZVI amount in the system having removal kinetic, k=1.1462 min⁻¹, R^2 =0.9975 for Cr and removal kinetic, k= 1.5035 min⁻¹, R^2 =0.9997 for Zn. From the effects of Co concentration, highest removal of Cr and Zinc was best achieved in nZVI-Co suspension having Co concentration of 1.5 mM where removal kinetic, k = 1.0324 min-1 min⁻¹, R²=0.9965 was attained for Cr and removal kinetic, k =1.1950 min⁻¹, R²=0.9963 for Zn. Second sets of batch experiment were carried out to elucidate the removal kinetics of Cr and Zn by nFe₃O₄ and Co under different effects of metal concentration, pH, nFe₃O₄ amount and Co concentration. Effects of metal concentration reveal, highest Cr and Zn removal was obtained under nFe₃O₄-Co suspension having metal concentration of 0.5ppm with removal kinetic, $k = 1.4215 \text{ min}^{-1}$ ¹, R²=0.9978 for Cr and removal kinetic, $k = 0.3162 \text{ min}^{-1}$, R²= 0.9996 for Zn. Effects of pH reveal both Cr and Zn shows highest removal at pH 9 under nFe₃O₄-Co having removal kinetic, $k = 0.8741 \text{ min}^{-1}$, $R^{2} = 0.9963$ for Cr and removal kinetic, $k = 1.3553 \text{ min}^{-1}$ ¹, $R^2=0.9976$ for Zn. The effects of different nFe₃O₄ amount towards the removal of Cr and Zn shows highest removal was obtained under nFe₃O₄-Co suspension having nZVI amount of 0.15g of nFe₃O₄ with removal kinetic, k=1.2916 min⁻¹, $R^{2}=0.9944$ for Cr and removal kinetic, $k=1.4437 \text{ min}^{-1}$, $R^2=0.9954$ for Zn. Effects of Co concentration reveal, highest Cr and Zn removal was obtained under nFe₃O₄-Co suspension having Co=1.5mM with removal kinetic, $k=0.7869 \text{ min}^{-1}$, R²=0.9965 for Cr and removal kinetic. $k = 1.0942 \text{ min}^{-1} \text{ R}^2 = 0.9930$ for Zn. All of the removal kinetics, k of Cr and Zn removal fit the pseudo-first-order rate law having $R^{2}>0.95$. Results strongly imply that the presents of Co is significant in enhancing removal of Cr and Zn by iron reductant.

ACKNOWLEDGEMENT

All praise to Almighty Allah for the blessing, the strength, and the opportunity to complete my challenging PhD journey.

My sincere gratitude to my supervisor Dato' Prof. Ts. Ir. Dr. Hj. Mohd Fozi Ali for your guidance, concern and never give up on me and to my co-supervisor Ir. Dr. Amnorzahira Amir for the knowledge and meaningful lesson in life.

Special acknowledgement to the Ministry of Higher Education, Malaysia for granting me the scholarship and Universiti Teknologi MARA for the RIF Grant (600-RMI/DANA 5/3/RIF (740/2012). My appreciation is extended to the Bioremediation Research Centre (BioREC), Post Graduate Office, School of Civil Engineering, UiTM Shah Alam for the laboratory facilities and assistance. Special thanks to my lab mates Nurul Aqilah binti Abdul, Nur Dalila binti Mohamad, Roasadibah binti Mohd Towel and Nurul Atiqah Iliyani for helping me throughout my research. Not forgetting beloved HB and JL, relatives, colleagues and friends for your endless support and motivation.

This thesis is a heartfelt dedication to my loving family especially Pa and Ma, My Man, My Amili and My Nuh for their unconditional love and support.

TABLE OF CONTENTS

Page

CONFORMATION BY PANEL OF EXAMINERS		ii iii iv v vi		
AUT				
ABSTRACT ACKNOWLEDGEMENT TABLE OF CONTENTS LIST OF TABLES LIST OF FIGURES				
			xi	
			xiv	
		LIST	COFABBREVIATION	xvii
		СНА	APTER ONE INTRODUCTION	
1.1	Background of Study	1		
1.2	Problem Statement	3		
1.3	Hypothesis	4		
1.4	Research Objectives	5		
1.5	Scope of Work	6		
1.6	Significance of Study	8		
СНА	APTER TWO REVIEW OF LITERATURE			
2.1	Heavy Metals Contamination	9		
	2.1.1 Chromium Contamination	11		
	2.1.2 Zinc Contamination	12		
2.2	Treatment of Heavy Metals	13		
2.3	Iron Remediation Technologies	20		
	2.3.1 Nano Vero Valent Iron	21		
	2.3.2 Magnetite Nano Particles	24		
	2.4.3 Adsorbtion Process	30		

2.4	Heavy Metals in Biotic and Abiotic Environment	36
2.6	Electron Transfer Mediator	41
	2.6.1 Cobalamin	43

CHAPTER ONE

INTRODUCTION

1.1 Background of study

To date, heavy metals contamination due to anthropogenic factor has become national and international concern. Laboratory studies proven heavy metals such as lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), mercury (Hg) cadmium (Cd) and nickel (Ni) are the most common contaminants found in soil and groundwater (Jose et al., 2011; Zhang, Pu, 2011; Peng et al., 2009). A groundwater quality monitoring in Malaysia reported arsenic (As), iron (Fe), manganese (Mn), lead (Pb) and chromium (Cr) exceeds the benchmark of National Guideline for Raw Drinking Water Quality (NGRDWQ), 2000 (Department of Environment (DoE), 2012). In small amount, these metals are common and naturally found in our environment. However in large amount, acute or chronic toxicity is very much significant. Exposure of heavy metals toxicity may contribute to damage of nervous function, blood composition, lungs, kidneys and other vital organs. Concentration of most heavy metals when introduce in soil may persists for long duration but however changes of their speciation and bioavailability are possible (Wuana and Okieimen, 2011; Bradl, 2004; U.S.EPA, 2000). Chromium for example is very mobile and toxic in the form of Cr^{6+} but however through reduction process Cr^{6+} will be converted to Cr^{3+} that is less toxic and less mobile thus making it presents safer in the environment.

Soil and groundwater contaminations have been a great environmental challenge over the past decades. The root of contaminations often relates with anthropogenic factor such as industrial activity, agricultural or improper disposal of waste (Borch et al, 2010; Amarasinghe and Williams, 2007; Bahadir et al., 2007). Such activities produce pharmaceutical wastes, persistent organic pollutants, hydrocarbons, pesticides and heavy metals which were discharged directly to soil or being washed off by runoffs will enter our surface water or infiltrate to the ground and thus further contaminate the groundwater.