UNIVERSITI PUTRA MALAYSIA

MAGNETITE NANOPARTICLES FROM WASTE MILL SCALE AS A NANOADSORBENT FOR COPPER METAL REMOVAL IN AQUEOUS SOLUTIONS

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By

SYAZANA BINTI SULAIMAN

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

July 2021

DEDICATION

Special dedication to:

My pillar of strength,
Sulaiman Awang Mat & Rusmawati Ahmad

My beloved siblings,
Syuhaidah, Syazwani & Muhammad Naufal

Thank you for all the support, love, prayers and encouragement. May Allah bless all of you.

"And if whatever trees upon the earth were pens and the sea [was ink], replenished thereafter by seven [more] seas, the words of Allah would not be exhausted. Indeed, Allah is Exalted in Might and Wise."
(Surah Luqman, verse 27)

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

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July 2021

Chairman : Associate Professor Raba'ah Syahidah Azis, PhD
Faculty : Science

Heavy metal pollution has become one of the main concerns in the environment owing to continuous growth in the global population, industrial activities, and development. The ability and the potential of magnetite nanoparticles (MNP) from waste mill scales as low-cost metal adsorbents were examined for the adsorptive removal of copper (Cu) ions from an aqueous solution. The adsorption technique and inexpensive adsorbent were used as a fascinating alternative for the removal of Copper from wastewater. The purpose of this work was to develop an adsorbent by using waste mill scale product for the adsorption of copper ions, owing to its abundance of waste product worldwide, and could serve as an alternative for a low-cost absorbent. The waste mill scales were synthesized via high energy ball milling (HEBM) to obtain magnetite nanoparticles (MNP). The resultant MNP were analysed utilising X-ray Diffraction (XRD), Vibrating Sample Magnetometer (VSM), Transmission Electron Microscopy (TEM), Brunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR), Zeta Potential and Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (*FESEM-EDX*). The sorption characteristics were studied together with kinetic and isotherm equilibrium studies. Also, the adsorption studies were performed to investigate the influence of significant parameters including contact time, starting concentrations, pH, temperature, and adsorbent dosage. It was noticed that the MNP adsorption kinetics study was best fitted by the Pseudo-second-order kinetic model with superior correlation coefficients (R^2) of 0.999. Batch studies indicated that about 63.6% of copper ions were removed in the first 30 mins of the adsorption test at optimum pH 5.4 at a temperature of 26 °C. The isotherm experimental data were examined using Langmuir, Freundlich and Temkin model. The adsorption behaviour of copper ions was fitted with Temkin isotherm model and the highest adsorption capacities, q_{max} was 4.408 mg/g. The highest

adsorption capacity, q_e of 4.408 mg/g with removal efficacy (%*RE*) of 63.6% was attained at the best treatment condition of pH 5.4, adsorbent dosage of 0.05 g and 240 minutes of contact time. The MNP reusability and regeneration efficiency of 70.23% was achieved after three cycles, thereby indicating its suitability as a promising low-cost adsorbent for copper for industrial application and good remediation performance. This study suggests the use of MNP obtained from the waste mill scales are affordable adsorbent for the adsorptive removal of other heavy metals from water.

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

ZARAH NANO MAGNETIT DARI PROSES SISA BUANGAN SEBAGAI NANOADSORBEN UNTUK PENGHAPUSAN LOGAM DALAM AIR

Oleh

SYAZANA BINTI SULAIMAN

Julai 2021

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Pencemaran logam berat telah menjadi salah satu kebimbangan global utama dalam persekitaran akibat pertumbuhan global yang berterusan dalam aktiviti perindustrian dan pembangunan. Keupayaan dan potensi zarah nano magnetit (ZNM) daripada sisa skala kilang sebagai penyerap logam berkos rendah telah disiasat untuk penyingkiran ion tembaga (Ku) daripada larutan berair. Teknik penyerapan dan penyerap murah sebagai pilihan yang menarik untuk penyingkiran Ku dari sisa air. Tujuan kajian ini membangunkan satu penyerap dengan menggunakan produk sisa skala kilang untuk penyingkiran ion Ku, disebabkan produk sisa yang banyak di seluruh dunia, dan digunakan sebagai alternatif untuk penyerap kos rendah dalam kajian ini. Skala sisa kilang telah disintesis menggunakan pengisar bebola berkuasa tinggi (HEBM) untuk menyediakan ZNM. ZNM dicirikan oleh Pembelauan Sinar-X (XRD), Magnetometer Sampel Bergetar (VSM), Mikroskopi Elektron Transmisi (TEM), Brunauer-Emmett-Teller (BET), Spektroskopi Inframerah Transformasi Fourier (FTIR), Potensi Zeta dan Pengimbasan Pelepasan Medan Mikroskopi Elektron dengan Spektroskopi X-Ray Dispersive, Tenaga (FESEM-EDX). Ciri-ciri penyingkiran penyerap ZNM dikaji kinetik dan keseimbangan isotermanya. Juga, kajian penjerapan dengan kesan beberapa parameter seperti masa sentuh, kepekatan awal, pH, suhu, saiz penjerap dan dos penjerap. Didapati bahawa kajian kinetik penjerapan ZNM dapat dipadan dengan baik oleh model kinetik Pseudo-peringkat-kedua dengan pekali korelasi tinggi (R^2) 0.999. Kajian kumpulan menunjukkan bahawa kira-kira 63.6% Ku disingkirkan dalam 30 minit pertama kacau. pH dan suhu optimum diperhatikan pada pH 5.4 dan 26°C. Data eksperimen isoterm dianalisis menggunakan model Langmuir, Freundlich dan Temkin. Tingkah laku penjerapan Ku sesuai dengan model suaian Isoterm Temkin dan kapasiti penjerapan maksimum, q_{max} Ku adalah 4.408 mg/g. Kapasiti penjerapan, q_e tertinggi adalah 4.408 mg/g dengan kecekapan penyingkiran sebanyak 63.6% dicapai pada keadaan rawatan terbaik pH 5.6, dos penyerap

0.05 g dan 240 minit masa sentuh. Kebolehgunaan semula dan regenerasi 70.23% telah diperoleh setelah tiga kitaran. Oleh itu, regenerasi dan penggunaan semula ZNM yang baik dapat menjanjikan sebagai penjerap penyingkiran Ku dalam aplikasi industri dengan kos yang lebih rendah dan prestasi pemulihan yang baik. Hasilnya menunjukkan ZNM yang diekstrak daripada sisa skala kilang adalah berpatutan untuk penyerapan logam berat dari air.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

BET	Branauer-Emmett-Teller
BPR	Ball-to-powder ratio
CTST	Curie Temperature Separation Technique
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
H_c	Coercivity
HEBM	High Energy Ball Milling
HRTEM	High Resolution Scanning Electron Microscope
k_1	Rate constant of first order adsorption
k_2	Pseudo-second-order rate constant adsorption
K_F	Constant related to the overall adsorption capacity
K_L	Langmuir isotherm constant
MNP	Magnetite nanoparticles
M_s	Saturation magnetization
MST	Magnetic Temperature Separation Technique
nm	Nanometer
q_m	Langmuir monolayer saturation capacity
t	Time
VSM	Vibrating Sample Magnetometer
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffraction
UPM	Universiti Putra Malaysia

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Water undoubtedly plays a prominent role in human well-beings, all living things, livelihoods and socio-economic development as the continuous expansion in world population and expeditious urbanisation resulting in the demand for clean and fresh water. The prevalence of water pollution keeps increasing at an alarming rate in all age groups. According to the World Health Organization, the global population is expected to expand from 6.9 billion in 2010 to 9.1 billion by 2050. Over the past years, billion tons of fertilisers, chemical wastes, industrial waste were discarded into rivers, lakes, and oceans hence pose a vast amount of hazardous waste. In every growing nation, the industrial progression leads to the presence of heavy metals such as chromium (Cr), lead (Pb), copper (Cu), cadmium (Cd), cobalt (Co), nickel (Ni), mercury (Hg) and etcetera in the environment (Mirsha et al., 2019). These metals have a tendency to build up in living organisms, triggering plentiful illnesses and diseases. Exposure to non-biodegradable heavy metals is very poisonous and have a tendency to build up in human being organs and other dwelling organisms, undermine the water quality supply, trigger various difficulties on human health, aquatic ecosystem and cause numerous illnesses and disorders. As such, the removal of heavy metals has a pivotal role in the world, society and community (Adeel et al., 2019).

To date, several reports on heavy metals pollution published by the mass media have captured the attention of the local community. In Malaysia, for instance, people living in Johor, Port Klang, and Pulau Pinang, where heavy metal industries operate, have been advised to eat less shell-seafood due to heavy metal contaminations and severe water pollutions. The contamination of the river is increasingly recognised as a serious, worldwide public health concern. Several issues have been elevated about the safety of the river in Malaysia that contributing to thousands of fishes were found dead. This issue is further amplified by the rise cases on the west coast of Peninsular Malaysia because of a high risk of heavy metals poisoning. Over the last decade, extensive studies have emerged using various methods to obviate copper ions from an aqueous solution; these include membrane, adsorption, phytoremediation, coagulation, flocculation, photo-catalysis, and advance oxidation and osmosis (Benzaoui et al., 20018; Parmar et al., 2009; Ostroski et al., 2009; Bakar et al., 2009; Greenlee et al., 2009; Zeng et al., 2009). However, adsorption is recognised as a promising fundamental and alternative for wastewater treatment owing to its simplicity, versatility, and low-cost in removing various concentrations of heavy metals (Wang et al., 2011). Besides, the adsorption technique aids in decreasing the cost of waste disposal and one of the most efficient and ecofriendly water treatment technologies worldwide.

In recent years, numerous attempts have been made to synthesis economical sorbents from agricultural and urban waste resources reported in the current literature review to remove several heavy metals. The utilisation of waste materials as affordable adsorbents is captivating owing to their enormous input to the depletion of waste disposal expenses, thus contributing to healthy environment (Afroza et al., 2018). The researchers have sought to determine the adsorbent that possesses sorption propensity and high removal efficiency with a low-cost and simple production and preparation (Pakade et al., 2019). Numerous literature reviews that the inexpensive adsorbents have presented the remarkable potential for the removal of many heavy metals contaminants. Various adsorbents such as activated carbon (AC), rice husk, mesoporous silica, graphene, reduced graphene oxide (RGO), carbon nanotubes (CNT) have been utilised to eliminate heavy metals from generated effluent before discharge (Singh et al., 2018; Crini et al., 2019; Ivanets et al., 2014). In particular, enormous studies reported that magnetite offers a fast rate of adsorption, percentage removal efficiency and high removal capacity (Panda et al., 2021).

In Malaysia, steel industries are the largest industry, and Mansor (1998) had reported that the steel factories produce about 80 000 metric tons of mill scale annually. Mill scale is made up of hot steel rolling, metallic iron and iron oxide; since then, the abundant of mill scale has excellent potential for magnetic material sources. The main component of iron oxide is wuestite, magnetite and hematite. In recent years, studies have revealed that non-purified waste mill scale could eliminate a certain amount of metal through the separation of the ions (Eissa et al., 2015) and co-precipitation (Khosroshahi et al., 2010) methods. Waste mill scale also generates valuable iron oxide at a low-cost and has significant advantages for magnetic material sources. As the waste mill scale is abundantly available and cost-effective, it has been selected as the starting materials to produce magnetite nanoparticles (MNP). MNP has shown a strong adsorption affinity to the copper ions and the nano-sized particles have unique properties for high-tech applications in the industries.

In addition, more study is required to explore the practical and sustainable use of economical adsorbents on an industrial scale. Nowadays, magnetite is certainly considered a universal adsorbent for removing diverse types of contaminants from wastewater. Researchers come up with plentiful adsorbents to fulfil the operating cost, high efficiency, sustainability, regeneration, and broader potential of magnetite for industrial-scale wastewater (Pap et al., 2020). However, the widespread use of commercial AC reveals some notable drawbacks, such as higher maintenance expenses and operation downtime. Thus far, previous studies have reported the nanoparticles are broadly examined for their practicality as a filter and an excellent result in wastewater treatment (Nematchoua et al., 2020). Interestingly, in Malaysia, there are several attempts in synthesised and recycling waste mill scale in the practical product, especially in Universiti Putra Malaysia (Azis et al., 2013). Thus, it provides an alternative in transforming waste mill scale into beneficial material water sustainability. Previously, Azis (2013) studied and purified wuestite from the waste mill scale and converted it into pure hematite in many applications. In spite of their advantages in eliminating numerous metals, this work intended to investigate the efficacy of MNP for diverse particles size at different milling times. Synthesis, surface characterisation of adsorbent, and information on the feasibility of the MNP in the removal of copper ion were discussed critically. The highlight of this study is to focus on MNP in the elimination of copper metal from aqueous solution. Accordingly, the adverse impacts of copper metal on the environment will be introduced. Finally, the main conclusion and future perspective will be discussed and presented.

1.2 Problem Statement

Nowadays, water pollution has become a severe problem. According to the United Population Prospects 2019, the world populace in 2100 is predicted to be about 10.87 billion people compared to 7.71 billion people in 2019 (World Population Prospects, 2019). It implies the demand for clean and fresh water that urged scientists and researchers to find solutions and alternatives to improve the water quality. Herein, a study on applying low-cost materials to substitute high-cost adsorbent is desirable and practical for wastewater treatment and removal of heavy metal ions.

In the steel industries, copper is one of the heavy metals usually found in wastewater. Prolonged exposure and high concentration of copper may result in many serious diseases, such as cancer, nervous system damage, kidney failures, and even death (Zhao et al., 2017). So, Cu are usually associated with toxicity and environmental problems. However, since it is in lower level, the suitable treatment method used is magnetic separation technique due to cost-effectiveness, ease of operation, flexibility and simplicity. In the light of this, it can be inferred that the studies using MNP from locally obtainable industrial milled chips using high-energy ball milling technique to remove Cu ions from water are rather limited, and it has been scarcely applied in spite of its impressive potential. Besides, the sustainability of an adsorbent is another significant factor. So, the regeneration experiment has been done for industrial purposes.

1.3 Significant of Study

In this study, the waste mill scale is used to extract the magnetite, as mill scale is a natural, low-cost and reusable adsorbent. Besides, the abundant and cheap mill scale justify the usage of mill scale in water purification. This approach reduces the cost of waste disposal and contributes to by-products recycling for heavy metal treatment. The result shows an excellent removal of adsorption capacity towards the heavy metal contaminants. Thus, the present study was purposed to elucidate the information on feasibility of magnetite nano-adsorbent in copper ion metal.

1.4 Research Objective

The core objective of this work is to synthesize MNP from low-cost waste mill scale for the removal of copper metal from an aqueous solution. The specific objectives of this study include:

i. To synthesize and characterize MNP from waste mill scale and its application for the removal of copper ion from an aqueous solution.
ii. To study the influence of contact time, adsorbent dose, pH, starting concentration, and the temperature on adsorption performance.
iii. To investigate the adsorption isotherm, thermodynamics and kinetic modelling and regeneration of MNP via batch adsorption studies.

1.5 Scope of Study

The overall structure of the thesis is composed of six chapters. Chapter 1 starts by revealing the significant research study of the adsorption capacity and removal efficacy of heavy metals by the MNP. Chapter 2 begins by laying out the theoretical dimensions of the research and literature review that mainly focused on and related to the work. Chapter 3 presents all the basic theories and the fundamental of magnetization of ferrites. Chapter 4 is explicating the methodology employed for this work. Chapter 5 examines the data gathered and addresses the research findings, and focuses on waste mill scale and magnetite characterizations. The final chapter, Chapter 6 aims to reflect the summary and conclusion of the project as well as some recommendation for future works. The list of publications, biography of the author, appendices and references are available at the end of the thesis.

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