

UNIVERSITI PUTRA MALAYSIA

MODIFICATION OF MAGNETITE EXTRACTED FROM MILL SCALES WASTE WITH CTAB AND CHITOSAN FOR CADMIUM IONS REMOVAL FROM AQUEOUS SOLUTION

NUR ASYIKIN BINTI AHMAD NAZRI

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By

NUR ASYIKIN BINTI AHMAD NAZRI

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

December 2021

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair : Raba'ah Syahidah Azis, PhD Institute : Nanoscience and Nanotechnology

The goal of this research is to improve the stability of magnetite recovered from millscales waste (MSW) by modifying it with Cetyltrimethyleammonium Bromide (CTAB) and Chitosan (Chi) for use in Cd(II) removal from aqueous solution. Magnetite was subjected to High Energy Ball Milling (HEBM) for 5 distinct milling hours, namely 4, 8, 12, 16, and 20 hours, before being modified with the CTAB and Chi. From the characterization results there were found that the characteristics on magnetite milled for 8 h obviously more stable $(\pm 10.9 \text{ mV})$ and had highest ability in removing the cadmium ions. Therefore, M8 was chosen to be modified with CTAB and Chi. As the results, the stability of the modified MNS (M8-CTAB and M8-Chi) had enhanced from -10.9 to -39.5 and -48.5 mV respectively. This was supported with the high-resolution transmission electron microscopy (HRTEM) images that shows higher dispersion after the modification. The higher dispersion occurred was successfully enhanced the surface area from 2.58 to 19.19 and 22.49 $m^2 g^{-1}$ for M8-CTAB and M8- Chi respectively. The magnetic saturation had reduced due to the modification which became 32.16 and 31.91 emu g^{-1} after the modification with CTAB and chitosan respectively. Meanwhile, the magnetic saturation before the HEBM is 20.58 emu g^{-1} and increased to 50.36 emu g^{-1} . Fourier transform infrared (FTIR) spectrum shows the appearance of functional groups such -CH, -NH, -COO, and -OH contributed from CTAB and Chi which proved the success modification through the heterocoagulation (self-assembly) method. The adsorption properties obeyed the Langmuir isotherm model and the maximum uptake of the Cd(II) from the solution onto the M8, M8-CTAB, and M8-Chi is 10.31, 26.70 and 30.86 mg g^{-1} respectively. Regeneration results for MNS showed small reduced on the performance as the cycles used in Cadmium removal for 5 time (1st cycle, 98%, 5th cycle 92%). The regeneration performance suggests the sustainability of the magnetic nanosorbent (MNS) to be used in industries. The best MNS (M8-Chi2) in this works manage to remove for about 98.6% (2.96 mg L^{-1}) of the initial 3 mg L^{-1} Cd(II) which indicated that it able to remove the Cd(II) more than the permissible Cd(II) level in

drinking water (0.5 μ g L⁻¹). The M8-Chi2 MNS also characterized with XPS in order to confirm the adsorption of Cd(II) perfectly occurs onto it. Interestingly, it was found that the XPS spectrum showed the peak for the Cd(II) on the MNS after the adsorption. From this works, it can be concluded that the prepared MNS (M8-Chi2) can be a promising advanced adsorbent in environmental pollution clean-up.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

MODIFIKASI KE ATAS MAGNETIT YANG DIEKSTRAK DARIPADA SISIK BESI BUANGAN DENGAN MENGGUNAKAN CTAB DAN CHITOSAN UNTUK PENYAHAN ION-ION KADMIUM DARIPADA LARUTAN AKUES

Oleh

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Matlamat penyelidikan ini adalah untuk meningkatkan kestabilan magnetit yang diperoleh daripada sisa skala kilang (MSW) dengan mengubah suainya dengan Cetyltrimethileammonium Bromide (CTAB) dan Chitosan (Chi) untuk digunakan dalam penyingkiran Cd(II) daripada larutan akueus. Magnetit telah tertakluk kepada Pengilangan Bebola Bertenaga Tinggi (HEBM) untuk 5 tempoh kisaran yang berbeza, iaitu 4, 8, 12, 16, dan 20 jam, sebelum diubah suai dengan CTAB dan Chi. Daripada keputusan pencirian yang dibuat selepas modifikasi, didapati kestabilan MNS (M8-CTAB dan M8-Chi) telah meningkat dari -1.9 kepada -39.5 dan -48.5 mV. Keupayaan zeta yang menigkat itu didapati sejajar dengan imej yang ditunjukkan oleh mikroskop electron beresolusi tinggi (HRTEM) di mana setiap zarah berada dalam keadaan diperisiti yang tinggi selepas diubahsuai. Disperisiti yang tinggi itu telah menyebakan luas permukaan zarah bertambah baik daripada 2.58 kepada 19.19 dan 22.49 m² g⁻¹ untuk sampel M8-CTAB dan M8-Chi masing-masing. Namun begitu, didapati terdapat penuruan pada keamatan kemagnetan menjadi 32.16 dan 31.91 emu g⁻¹ selepas diubah suai dengan CTAB dan chitosan. Spektrum Fourier transformasi infrared (FTIR) menunjukkan kemunculan kumpulan fungsi seperti -CH, -NH, -COO, dan -OH daripada CTAB dan Chi yang mana telah membuktikan kejayaan dalam pengubahsuaian melalui 'self-assemble'. Sifat penyerapan oleh M8, M8-CTAB, dan dapat dijelaskan dengan Langmuir isotherm dam maksimum pengeluaran yagn Berjaya adalah 10.31, 26.70 dan 30.86 mg g⁻¹ masing-masing. Keputusan kitar semula bahan penyerap menunjukkan penurunan kecekapan selepas 5 kali penggunaannya. (kitaran 1, 98%, kitaran 5 98%). Kecekapan dalam penggunaan semula menunjukkan kebolehan penyerap magnetic bersaiz nano (MNS) untuk menyerap. The regeneration performance suggests the sustainability of the MNS to be used in industries. MNS yang terbaik melalui kajian ini adalah (M8-Chi2) yang mana telah dapat menyerap 98.6% (2.96 mg L⁻¹) daripada 3 mg L⁻¹ Cd(II) menunjukkan ianya boleh digunakan untuk menyerap Cd(II) sehingga takat air yang selamat diminum. (0.5µg L⁻¹). M8-Chi2 MNS juga telah melalui pencirian menggunakan XPS untuk mengenalpasti dan memastikan penyerapan Cd(II) ke atas MNS berlaku dengan sempurna. Menariknya, didapati puncak pada spektrum XPS jelas menunjukkan kehadiran Cd(II) selepas proeses penyerapan. Melalui kajian ini, kesimpulan yang boleh dibuat adalah MNS (M8-Chi2) boleh menjanjikan penyerapan logam berat dengan baik untuk digunakan di dalam pembersihan air tercemar.



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

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic Adsorption Spectroscopy
As	Arsenic
b	Langmuir isotherm constant (dm ³ mg ⁻¹)
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
b _T	Tempkin isotherm constant
С	Carbon
C _{BET}	BET adsorption isotherm relating to the energy of surface interaction $(L mg^{-1})$
Cd(II) @ Cd ²⁺	Cadmium ions
Ce	equilibrium concentration (mg L ⁻¹)
Chi	chitosan (C6H11NO4)n
Co	adsorbate initial concentration (mg L ⁻¹)
Cs	adsorbate monolayer saturation concentration (mg L ⁻¹)
CTAB	Cetyltrimethylammonium bromide
CTST	Curie temperature separation technique
d	spacing (nm)
DI	deionized water
Е	mean free energy (kJ mol ⁻¹)
EDX	energy dispersive x-ray composition analysis
Fe ₂ O ₃	hematite
Fe ₃ O ₄	magnetite
FeO	wustite
FESEM	Field Emission Scanning Electron Micrograph
FTIR	Fourier Transform InfraRed Spectroscopy

	FWHM	full wave half maximum
	h	hour
	H ₂ O	water
	H _c	coercivity
	Hg	mercury
	HRTEM	High resolution Transmission electron microscopy
	ICDD	International Centre for Diffraction Data
	IEP	isoelectric point
	IMS	impurities magnetic separation
	Ю	iron oxide (mixed of FeO, Fe ₂ O ₃ , Fe ₃ O ₄)
	JCPDS	Joint Committee on Powder Diffraction Standards data JCPDS
	K _{ad}	Dubinin–Radushkevich isotherm constant (mol ² kJ ⁻²)
$K_{\rm F}$		Freundlich isotherm constant (mg g ⁻¹) (dm ³ g ⁻¹)
	K _L	Langmuir isotherm constant (L mg ⁻¹)
	М	magnetite extracted from millscales waste
	MNPs	Magnetic nanoparticles
	M _R	magnetic remanence
	Ms	Saturation magnetization
	MSW	milscale wastes
	n	related to adsorption capacity
	N @ N ₂	Nitrogen gas
	NPs	Nanoparticles
	0	Oxygen
	p/p°	relative pressure
	Pb	Plumbum
	рН	degree of acidity and alkali
	hubsc	point of zero charge (pri)

ppb	part per billion (mg mL ⁻¹)
ppm	part per million (mg L ⁻¹)
Qe	amount of adsorbate in the adsorbent at equilibrium (mg g ⁻¹)
Qe,calc	calculated adsorbate concentration at equilibrium (mg g ⁻¹)
Qo	maximum monolayer coverage capacities (mg g ⁻¹)
Qs	theoretical isotherm saturation capacity (mg g ⁻¹)
Q_t	adsorption capacity at certain time
r 📃	inverse power of distance from the surface
R	universal gas constant (8.314 J mol ⁻¹ K ⁻¹)
R ²	correlation coefficient @ regression
R _L	separation factor
RP	removal percentage (%)
MSW	Millscales waste
S _{BET}	specific surface area (m ² g ⁻¹)
Т	temperature (K)
VSM	vibrating sample magnetometer
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffactometer
β	Dubinin–Radushkevich isotherm constant
ΔG°	Gibbs energy change (kJ mol ⁻¹)
ΔH°	enthalpy
ΔS°	entropy
3	Dubinin-Radushkevich isotherm constant
θ	degree of surface coverage

GLOSSARY

Terminology	Definition/meaning
Amphoteric	a metal oxide or hydroxide able to react both as a base and as an acid.
Cationic polymer @ cationic surfactant	Cationic polymers are a class of polymers bearing a positive charge or incorporating cationic entities in their structure
deprotonation	Deprotonation (or dehydronation) is the removal (transfer) of a proton (or hydron, or hydrogen cation)
heterocoagulation	Hetero-coagulation is a process where dissimilar colloidal particles coagulate irreversibly in a suspension that leads to a solid or a gel-like structure
Inorganic materials	are defined as chemical compounds that contain no carbon (C)
Isoelectric point (IEP)	sufficient charge to confer stability
Lewis acid	a compound or ionic species which can accept an electron pair from a donor compound
Moderate stability	assuming that electrostatic charge is the only mechanism that stabilizes the colloidal system.
Nonionic polymer	uncharged (nonionic) polymers, such as poly(vinyl alcohol), polyacrylamide, polyethylene glycol (polyethylene oxide) and polyvinyl pyrrolidone.
Organic	to the large source of carbon-based compounds found within natural and engineered
polymer	a substance which has a molecular structure built up chiefly or completely from a large number of similar units bonded together
Precipitation	is the process of transforming a dissolved substance into an insoluble solid from a super-saturated solution

protonation	protonation (or hydronation) is the addition of a proton (or hydron, or hydrogen cation)
Self assemble	Molecules, polymers, colloids or nanoparticles, organized into ordered and/ or functional structures or patterns as a consequence of specific, local interactions among the components themselves.
Stabilizer	Use to increase the stability of nanoparticles. The stability usually indicated by the zeta potential values.
Steric hindrance	the slowing of chemical reactions due to steric bulk. Steric hindrance is often exploited to control selectivity, such as slowing unwanted side-reactions
Surfactant	a substance which tends to reduce the surface tension of a liquid in which it is dissolved
Zeta potential	At that pH particles having the same positive and negative charge (neutral/no charge)
π-π bond	pi bonds (π bonds) are covalent chemical bonds where two lobes of an orbital on one atom overlap two lobes of an orbital on another atom and this overlap occurs laterally.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The pollution of water and groundwater is one of the most serious environmental problems facing humanity. Heavy metals contamination in water is a serious environmental problem because these substances are not biodegradable and are very toxic to living organisms (Huang et al., 2009; Sall et al., 2020). The appearance of the toxic metals in the wastewater would change the pH depending on the type of the pollutants (Burakov et al., 2018; Masindi et al., 2018).

Heavy metal ions are toxic and carcinogenic at even comparatively low concentrations (Jaishankar et al., 2014; Sall et al., 2020). They are not biodegradable and can accumulate in living organisms. Therefore, the removal of these metal ions from wastewaters is of considerable importance from an environmental viewpoint. Among the heavy metals, cadmium is one of the extremely toxic and has been classified as a human carcinogen and teratogen impacting lungs, liver and kidney (Pyrzynska, 2019).

1.2 Background of study

Magnetic separation method is one of the most studied method compared to other conventional methods such as ion osmosis (Cui et al., 2014; Bhatia et al., 2017), coagulation-flocculation (Sun et al., 2020), chemical reduction (Mohammed et al., 2011), and precipitation (Adeleye et al., 2016) due to the ability of removing lower concentrations of heavy metals (Mudila et al., 2019). Therefore, more emphasis has been placed on producing better magnetic sorbents that will be more efficient in adsorbing toxic metals from wastewater with a facile technique (Ambashta et al., 2010).

Researchers believed that, when reducing the size to nanometer scales, the toxic metals are able to adsorb to the magnetic nano sorbents (MNS) through the magnetic separation method. The commercial activated carbon used in the industries are non-regenerated and the production produces secondary pollution. Therefore, researchers intensively investigate a new type of MNS which can be used in a magnetic separation system that has the ability to remove ionic toxic particles. However, the low stability of Fe₃O₄ NPs is attributed to react with surrounding particles that are possible to oxidise to another form and thus eliminating its magnetic properties (Petrova et al., 2011). In addition, the aggregation of NPs would automatically decrease the surface area of the MNPs. This reduces the removal capacity and reactivity, thereby, limiting the treatment performance (Kydralieva et al., 2016).

From the economic aspect, researchers have managed to determine Fe₃O₄ from Mill scales waste (MSW) is one of the potential magnetic sorbents. In fact, a non-chemical process of high-energy ball milling used to maintain the low toxicity of the magnetic NPs has been reported by Ismail et al. (2019) to remove dye and organic contaminants. This study can be expanded to remove heavy metals. Therefore, MSW has the potential to be used in heavy metal treatment with some surface modifications. Nevertheless, novel MNS must go through equilibrium studies. The information from the quantitative investigations using adsorption and kinetics isotherm models is important to confirm the ability to conduct further studies for industrial application. In addition, the regeneration study used to prove the sustainability of the MNS is also important to reduce cost.

In recent years, numerous publications on turning the MSW into valuable materials in many applications, especially in wastewater treatment, have been reported. Due to the higher percentages of iron in MSW, researchers have engineered a method to extract the valuable Fe_3O_4 from the MSW (Abdul et al., 2017; Doliente et al., 2017; Ismail et al., 2019; Nur et al., 2019; Shahid et al., 2018, 2019).

Magnetite nanoparticles are one of the most potential MNS reported in heavy metals removal in wastewater treatment systems. This is due to the ability to react with other particles in both acidic and base solutions. Unfortunately, the highly reactive behavior causes the drawbacks which it easily tends to aggregate into micron-sized or larger particles because of direct inter-particle interactions such as van der Waals forces and magnetic interactions. Aggregation reduces the specific surface area and the interfacial free energy, thereby decreasing particle reactivity and losing the unique property of nanoparticles (Palanisamy et al. 2013). To prevent agglomeration of nanoparticles, various stabilizers have been found effective for stabilizing nanoparticles, including carboxylic acids (Prozorov et al. 1999), and polymers (Ditsch et al. 2005; Fu et al. 2011). The application of magnetite in wastewater treatment is also believed to enhance when modified with suitable polymers and stabilizers (Lui et al., 2021).

Although there is an outstanding interest in finding good adsorbent, the research is still ongoing with many types of magnetic nano sorbent (MNS). To declare the MNS as a good adsorbent that can be commercialized, it needs to have several criteria such as shorter contact time, low adsorbent dosage, wide range of optimum pH, lower involvement of chemicals usage and regeneration. As long as the MNS does not meet those criteria, the research will be still active with much more innovative types of MNS.

1.3 Problem statement

Magnetite nanoparticles tend to aggregate into micron-sized or larger particles because of direct inter-particle interactions such as van der Waals forces and magnetic interactions. Aggregation reduces the specific surface area and the interfacial free energy, thereby decreasing particle reactivity and losing the unique property of nanoparticles (Palanisamy et al., 2013). To prevent agglomeration of nanoparticles, various stabilizers have been found effective for stabilizing nanoparticles, including carboxylic acids (Kataby et al., 1999), and polymers (Ditsch et al., 2005; Fu et al., 2011). The application of magnetite in wastewater treatment also believed to enhance when modified with suitable polymers and stabilizers (Ahmad et al., 2015).

Recent technologies had introduced various method for the modification Fe_3O_4 . However, there are limited publications on modifications of the Fe_3O_4 through the physical linkages. Physical linkages involved the modification by self-assembly. In other word, the modification is not in situ process, which it can be done on as prepared iron oxides.

Magnetite is an amphoteric solid which can develop charges in the protonation (Fe-OH +H⁺ \leftrightarrow Fe-OH₂ and deprotonation (Fe-OH \leftrightarrow Fe-O⁻ + H⁺) reactions of OH sites on surface. These surface reactions can be interpreted as the specific adsorption of H⁺ and OH- ions at the hydrated solid/water interface. Therefore, the unstable Fe₃O₄ possess the ability to easily heterocoagulate with suitable surfactant and polymer (Tombacz et al., 2006). The most suitable surfactants are cationic surfactants, while cationic polymers are the most suitable polymers.

Covering particles with adsorption layer usually results in enhanced resistance against the particle aggregation. In aqueous medium, electrostatic, steric and combined stabilization layers can develop. The thicker coating provides better stability, especially in the case of magnetic fluids, since the spacing (typically 2-3 nm) between magnetic domains is important, if magnetic field is applied (Tombacz et al., 2006).

Cetyltrimethylammonium bromide (CTAB) is the most studied cationic surfactant used in wastewater treatment (Fisli et al., 2018) due to the polarity of this surfactant in a solution. The used of CTAB as a stabilizer is due to the ability to self-assemble. Besides, it is also used to be cross linkages in many applications.

Natural cationic polymer is chitosan that produced from chitin, that develops in the hard outer shells of crustaceans such as crabs, lobsters and shrimps. Several publications describe the efficacy of chitosan sorbents in the removal of several pollutants such as metals, dyes, and phenols (Jin et al., 2017; Nguyen et al., 2016; Yang et al., 2016). Laus et al., (2010) studied the adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan crosslinked with epichlorohy-drin-triphosphate. However, there was no reported removal of Cd(II) by using magnetite extracted from MSW modified with chitosan.

Coating the magnetite with surfactants and the polymer will develop more active sites on the magnetite surface so that it achieve higher removal of Cd(II). CTAB will

and Hov MS provide hyroxil groups surround the magnetite which believe use to gain higher affinity to Cd(II) adsorption. Meanwhile, chitosan provides amine groups which believe one of the active sites that functioning in enhancing the affinity of the composite. The question is how to prepare this kind of composite material.

According to the problem statement, the hypothesis of this research project is the modification of magnetite extracted from mill scale waste without using any cross linkages ligands can be successful by adjusting the pH of both materials. Besides, smaller size of magnetic adsorbent result in the enhancement of the adsorption capacities through low involvement of chemicals. The used of MSW was believed to reduce the production cost of the MNS. In addition, regeneration of the MNS also might contribute to lower the production and the processing cost. Thus, this research has aimed to assess the potential of Fe_3O_4 NPs extracted from MSW to modify with a CTAB and chitosan due the limited study.

1.4 Hypothesis of the research

According to the problem statement, the hypothesis of this research project is the modification of magnetite extracted from MSW without using any cross linkages or ligands. Besides, a smaller size of magnetic adsorbent would result in the enhancement of the adsorption capacities through low involvement of chemicals. The use of MSW was believed to reduce the production cost of the MNS. In addition, regeneration of the MNS also to ensure the sustainability of the MNS.

Thus, this research has aimed to assess the potential of Fe_3O_4 NPs extracted from MSW to modify with a CTAB and Chitosan through physical linkages method. This study has investigated the removal of Cd(II) using prepared Fe_3O_4 NPs based on MSW at the laboratory scale. The research has aimed to investigate the adsorption process involved in Cd(II) removal from an aqueous solution. Adsorption behaviour of Cd(II) removal will be explained based on the experimental results and information available in the literature.

In this study, MSW has been used as the core magnetic material, with modification by a surfactant (CTAB) (Abdul et al., 2017) and a natural polymer (chitosan) (Peralta et al., 2019), used to treat different concentrations of Cd(II) in aqueous solution at different possible temperatures. The modification was a self-assembly (anchored base on electrostatic attraction) process performed by adjusting the pH of the medium for both materials to an optimum pH. This study has also suggested the possibility of the Fe₃O₄ NPs to anchor as the active site attachment so that the Cd(II) removal would increase. In addition, with the modification, higher stability and dispersity can be achieved. Consequently, adsorption capacity can be increased as well.

1.5 Objectives of the study

The aim of this research was to develop a new magnetic nanosorbent (MNS) that can be used in a wide range of pH, low adsorbent dosage used, low chemicals involvement, with higher ability to remove toxic metals in a short time and can be regenerated with a novel method on modifying as prepared Fe_3O_4 NPs extracted from MSW.

To achieve this, several objectives must be met. The objectives were to:

- i. Extract magnetite from MSW, to fabricate magnetic nanoparticles (MNPs) and modify with CTAB and chitosan to be used as magnetic nano-adsorbent (MNS).
- ii. Characterise the structural, morphological, magnetic and surface charge (zeta potential) properties and evaluate the adsorption abilities of the MNPs, MNPs/ CTAB and MNPs/ chitosan from MSW.
- iii. To assess the Cd adsorption using MNPs, MNPs/CTAB, MNPs/chitosan MNS based on the adsorption isotherm, adsorption kinetics, adsorption capacity, adsorption modelling parameters, thermodynamic study and regeneration.

1.6 Scope of study

Our new approach in this research study is to find the best method to modify the magnetite that extracted from MSW with minimal chemicals involvement. To begin the research findings, we need to have some knowledge on finding the best way on preparation and characterization of the samples. Since the research findings will contribute on application, it is an advantage to find a low-cost route for powder preparation such as solid-state reaction along with huge amount of production. The other interest in the present study is to test absorption ability of the modified MNS has also been investigated. It is found that the adsorption performance of nanocomposite containing the Chi and CTAB were enhanced compared to bare Fe₃O₄ extracted from MSW. The main intention for this research project is to prove the ability of the extracted Fe₃O₄ self-assembly anchored to Chi and CTAB for Cd(II) absorption from aqueous solution. We intend to observe the clear effect on the present of the stabilizers (CTAB and Chi) addition in improvising the Cd(II) removal. We therefore commence on an ambitious project in which we worked with the selected materials in order to develop a new best material with the best composition that could be successfully have a good potential in waste water treatment application.

1.7 Outline of the thesis

Chapter 2 mainly focused on the literature review of this work. Chapter 3 is used as the references for all the theories involved along these works. While, Chapter 4 described the details explanation on the methodology of the preparation of magnetic nanoparticles from mill scale waste, modify it with a surfactant (CTAB) and a polymer

(chitosan) and the performance in adsorption of Cd(II) from aqueous solution. Chapter 5 presents the result on the characterization and adsorption performance of magnetic nanoparticles from MSW, modifying it with a surfactant (CTAB) and a polymer (chitosan). Chapter 6 is to conclude this project and suggestion for future works that can be explored.



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