SYNTHESIS AND APPLICATIONS OF NEW MODIFIED MAGNETIC SPOROPOLLENIN AND GRAPHENE OXIDE-BASED MATERIALS FOR REMOVAL OF SELECTED HEAVY METALS FROM INDUSTRIAL WASTEWATER

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ABSTRACT

The presence of heavy metal ions in aqueous environment even at low concentrations is a serious concern and the polluting industries must conform to strict environmental limits and regulations. Conventional techniques such as evaporation, nanofiltration, precipitation and electrocoagulation have been used to remove heavy metals from wastewaters. However, these techniques are tedious, expensive or ineffective. Thus, adsorption is considered as a promising technique for heavy metals removal from wastewater and the search for cost effective, environmentally friendly and sustainable materials for this application has been intensified. In this study two new magnetic sporopollenin-based materials and one new magnetic graphene oxide-based material were synthesized for the removal of three selected heavy metals namely Pb(II), Ni(II) and Cd(II) from industrial wastewater samples. The first magnetic sporopollenin-based materials were synthesised from magnetite (M), sporopollenin (Sp), and 3-aminopropyltrimethoxysilane (APTMS) to give a ternary composite, MSp@SiO_2-NH_2, which was then modified with silica-coated graphene oxide (GO@SiO_2) to finally form a quinary composite, GO@SiO_2-MSp@SiO_2-NH_2. The other magnetic sporopollenin-based material was synthesised from magnetite (M), Sp, 3-Chloropropyltrimethoxysilane (CPTMS), and tetrakis(4-hydroxyphenyl) porphyrin (THPP) to give a quaternary composite, MSp@SiO_2-THPP. The magnetic graphene oxide-calix-4-arene based material was synthesized from magnetite (M), GO, silica, calix-4-arene (Calix) and APTMS to give a quinary composite, MGO@SiO_2-Calix@SiO_2-NH_2. These newly synthesized materials were applied for the first time as adsorbents for removal of three heavy metals namely Pb(II), Ni(II) and Cd(II) from aqueous solution of industrial wastewater samples. The newly synthesized materials were characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis, field emission-scanning electron microscopy, energy dispersive X-Ray analysis and vibrating sample magnetometry. The effect of important adsorption parameters such as solution pH, temperature, contact time, adsorbent dose, initial concentration and co-existing ions were studied and optimized. Evaluation of the adsorption performance of the materials at optimum conditions using batch adsorption technique reveals that the heavy metal ions removal efficiencies of the adsorbents were in the order Pb^{2+}> Ni^{2+}> Cd^{2+} and maximum adsorption capacity (q_{max}) of GO@SiO_2-MSp@SiO_2-NH_2 for Pb(II), Ni(II) and Cd(II) were 323, 278 and 256 mg/g, respectively. The q_{max} values of MSp@SiO_2 -THPP for Pb(II), Ni(II) and Cd(II) were 454, 435 and 416 mg/g, respectively and the q_{max} values of MGO@SiO-Calix@SiO_2NH_2 for Pb(II), Ni(II) and Cd(II) were 256, 243 and 222 mg/g, respectively. MSp@SiO_2-THPP was found to offer the highest q_{max} values probably due to the strong affinity of porphyrins for the metal ions. The initial and final concentrations of the metal ions in the wastewater samples were analyzed using flame atomic absorption spectroscopy. The adsorption behaviors of the respective metal ions on the adsorbents were studied using Langmuir, Freundlich, Dubinin-Radushkevich (DRK) and Temkin isotherms models. The experimental data and values of coefficient of determination (R^2) showed that the adsorption fitted the Langmuir and DRK models better for all the materials and the divalent cations, suggesting chemisorption through monolayer coverage. According to thermodynamic studies, the adsorption processes are endothermic and spontaneous. Furthermore, kinetics studies reveal that the adsorption processes followed a pseudo second order rate model. The findings show that the synthesized materials are excellent adsorbents for the removal of the heavy metals from wastewater samples and could be reused for up to 10 cycles without significant deterioration of the signal response. Analytical ecoscale analysis confirmed the greenness of these developed methods.

ABSTRAK

Kehadiran ion logam berat dalam persekitaran akueus walaupun pada kepekatan rendah adalah membimbangkan dan industri pencemaran harus mematuhi had persekitaran dan peraturan yang ketat. Teknik konvensional seperti penyejatan, penapisan nano, pemendakan dan elektro-penggumpalan telah digunakan untuk mengeluarkan logam berat dari air sisa. Walau bagaimanapun, teknik ini memakan masa, mahal atau tidak berkesan. Oleh itu, penjerapan dianggap sebagai teknik yang berpotensi untuk penyingkiran logam berat daripada air sisa dan pencarian untuk bahan kos efektif, mesra alam dan mampan bagi aplikasi ini telah dipergiatkan. Dalam kajian ini, dua bahan baharu berasaskan sporopollenin bermagnet dan satu bahan baharu berasaskan grafin oksida bermagnet telah disintesis untuk menyingkirkan tiga logam berat terpilih iaitu Pb(II), Ni(II) dan Cd(II) dari sampel air sisa industri. Bahan pertama berasaskan sporopollenin bermagnet telah disintesis daripada magnetit (M), sporopollenin (Sp), dan 3-aminopropiltrimetoksisilana (APTMS) untuk menghasikan komposit ternari, MSp@SiO_2-NH_2 yang kemudiannya disalut dengan silika terubah suai grafin oksida (GO@SiO_2) untuk membentuk komposit kuiner, GO@SiO_2-MSp@SiO_2-NH_2. Satu lagi bahan berasaskan sporopollenin bermagnet disintesis daripada magnetit (M), Sp, 3-kloropropiltri-metoksisilana (CPTMS), dan tetrakis(4-hidroksifenil)porfirin (THPP) untuk memberikan komposit kuaterner, MSp@SiO_2-THPP. Bahan berasaskan grafin oksida-kaliks-4-arena bermagnet disintesis daripada magnetit (M), GO, silika, kaliks-4-arena (kaliks) dan APTMS untuk menghasilkan komposit kuiner, MGO@SiO_2-kaliks@SiO_2-NH_2. Bahan baharu yang disintesis ini telah digunakan untuk kali pertama sebagai penjerap untuk penyingkiran tiga logam berat iaitu Pb(II), Ni(II) dan Cd(II) dari larutan akueus sampel air sisa industri Bahan baharu yang disintesis telah dicirikan menggunakan spektroskopi inframerah transformasi Fourier, analisis termogravimetri, mikroskopi imbasan elektron pancaran medan, analisis sinar-X tenaga terserak dan magnetometri sampel bergetar. Kesan parameter penjerapan penting seperti pH larutan, suhu, masa sentuhan, dos penjerap, kepekatan awal dan kewujudan ko-ion telah dikaji dan dioptimumkan. Penilaian terhadap prestasi penjerapan bahan pada keadaan optimum menggunakan teknik penjerapan berkelompok mendedahkan bahawa susunan kecekapan penyingkiran ion logam berat oleh penjerap adalah $Pb^{2+} > Ni^{2+} > Cd^{2+}$ dan kapasiti penjerapan maksimum (q_{max}) bagi GO@SiO_2-MSp@SiO_2-NH_2 untuk Pb(II), Ni(II) dan Cd(II) masing-masing ialah 323, 278 dan 256 mg/g. Nilai q_{max} bagi MSp@SiO_2-THPP untuk Pb(II), Ni(II) dan Cd(II) masing-masing ialah 454, 435 dan 416 mg/g dan nilai q_{max} bagi MGO@SiO_2-kaliks@SiO_2NH_2 untuk Pb(II), Ni(II) dan Cd(II) masing-masing ialah 256, 243 dan 222 mg/g. MSp@SiO_2-THPP didapati menawarkan nilai q_{max} tertinggi mungkin disebabkan oleh daya tarik porfirin yang kuat terhadap ion logam. Kepekatan awal dan akhir ion logam dalam sampel air sisa telah dianalisis menggunakan spektroskopi serapan atom nyala. Kelakuan penjerapan setiap ion logam pada penjerap telah dikaji menggunakan model isoterma Langmuir, Freundlich, Dubinin-Radushkevich (DRK) dan Temkin. Data eksperimen dan nilai pekali penentuan (R^2) menunjukkan bahawa penjerapan sesuai dengan model Langmuir dan DRK untuk semua bahan dan kation dwi-valens, mencadangkan bahawa penjerapan kimia adalah melalui liputan monolapisan. Menurut kajian termodinamik, proses penjerapan adalah endotermik dan spontan. Tambahan lagi, kajian kinetik mendedahkan bahawa proses penjerapan mengikuti model kadar pseudo tertib kedua. Kajian menunjukkan bahawa bahan yang disintesis adalah penjerap yang sangat baik untuk penyingkiran logam berat daripada sampel air sisa dan boleh diguna semula sehingga 10 kitaran tanpa perubahan ketara gerak balas isyarat. Analisis skalaeko mengesahkan kehijauan kaedah yang dikembangkan ini.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC	-	Activated carbon
ACF	-	Activated carbon felt
APTMS	-	Aminopropyltrimethoxysialne
APPS-CA	-	p-tert-[(dimethylamino)methyl]-1,3-bisglyciyl calix[4]arene/aminopropypoly siloxane
ASA-Calix	-	3-Aminopropilsilica gel aldehyde pointed calix[4]arene
Calix	-	Calix-4-arene
CS/G	-	Chitosan/graphene
CS/GO	-	Chitosan/graphene oxide
CC-GO	-	Magnetic cyclodextrin–chitosan modified graphene oxide
CS/GO-SH	-	Chitosan/sulfydryl-functionalized graphene oxide
C[6]APS	-	Amino propyl silica gel-immobilized calix[6]arene
CH-CR	-	C-4-hydroxyphenylcalix[4]resorcinarene
CPPCR	-	C-4-phenacyloxy phenyl calix[4]resorcinarene
CNM	-	Carbon nanomaterials
CEP-Sp	-	carboxylated epi-chlorohydrine-sporopollenin
CAC	-	p-tert-butylcalix[4]-aza-crown
CPTS	-	3-chloropropyltrimethoxysilane
DTC-Sp	-	Dithiocarbamated-Sp
DAE	-	Ethylenediamine
DAEC-Sp	-	Carboxylated-diaminoethyl modified sporopollenin
bDAEG-Sp	-	bis-diaminoethyl-glyoxime sporopollenin
3D-MGOH	-	3Dimentional graphene oxide hydrogel
3D-SRGO	-	3Dimentional sulfonated reduced graphene oxide
DA-host	-	5,11,17,23-tetra(diethylaminomethyl)–2,8,14,20-tetraundecylcalix [4] resorcinarene-4,6,10,12,16, 18, 22,24-octol
DEA-Calix@Si-MNPs	-	Diethanolamine functionalized p-tert-butylcalix [4]arene silica-coatedmagnetic nanoparticles

EDA	-	Ethylene diamine
EPA	-	Environmental protection agency
EDX	-	Energy dispersive X-ray analysis
FTIR	-	Fourier transform infrared
FESEM	-	Field emission scanning electron microscopy
FBSC-GO	-	Fixed-bed sand column based graphene oxide
F-$TPPH_2$	-	Fructose / tetraphenylporphyrin
Fe_3O_4-Sp	-	magnetic nanoparticles modified sporopollenin
GO	-	Graphene oxide
GDP	-	Gross Domestic Product
GOF	-	Graphene oxide foam
GF-AAS	-	Graphite furnance atomic absorption spectrometry
GO/CMC-	-	Carboxymethyl cellulose/ chitosan–gelatin/graphene oxide
GONH	-	Amino functionalized graphene oxide
GOSH	-	Thiol functionalized graphene oxide
GOSN	-	Amino, thiol dual-functionalized graphene oxide
GO–SBA-15	-	SBA-15 grafted graphene oxide
GO-PEI	-	Polyethylenemine cross-linked graphene oxide
GSC	-	Graphene/Sucrose/Sand
G–MgAl-LDHv	-	Graphene/MgAl-layered double hydroxides
GO/CdS(en)	-	Graphene oxide-Cadmium-Sulphur/ ethylenediamine
GCFF	-	Graphene oxide / copper ferrite form
GCZ8A	-	Chitosan– graphene oxide/ZIF
GA-Sp	-	Glutaraldehyde immobilized sporopollenin
GO@SiO_2-MSp@SiO_2-NH_2	-	3-aminopropyltrimethoxysilane/Fe_3O_4/silica coated graphene oxide
HMCRO	-	2, 18, 14, 20-tetra (3-hydroxy-4-methoxybenzyl) calix[4]resorcinarene 4,6,10,12,16,18,22,24-octol
L	-	Litre
LDHG	-	Layered double hydroxide /graphene
LLE	-	Liquid - liquid extraction
M	-	Magnetic

MN	-	Magnetic nanaparticles
Mg	-	Milligram
MS	-	Melamine sponge
MSp	-	Magnetic Sporopollenin
MOH	-	Ministry of health Malaysia
MS@GG	-	Melamine sponge glutathione based graphene oxide
MGO	-	Magnetic graphene oxide
M-RGO	-	Magnetite reduced graphene oxide
MGNCs	-	Magnetic graphene nano platelet composites
MMSP-GO	-	Polyethylenimine magnetic mesoporous silica grafted graphene oxide
MGO/SiO_2-CN	-	Silica-cyanopropyl functionalized magnetic graphene oxide
MWCNTs	-	multiwall carbon nanotubes
MGO/SiO_2-CN	-	Silica-cyanopropyl magnetic graphene oxide Spropollenin - Sp
MNPs-Sp-HEP	-	1-(2-hydroxyethyl) piperazine magnetic nano-particles-Sp
M-Fe3O4-GO	-	3-mercaptopropyltrimethoxysilane functionalized magnetic graphene oxide
MGO/β-CD	-	Magnetic graphene oxide-supported-cyclodextrin
ME-MGO	-	2-mercaptoethylamine magnetic graphene oxide
MBTA-GO	-	5-methylbenzotriazole modified graphene oxide
NA	-	Not available
NF	-	Nanofiltration
NH_2-SBA-15	-	Amino-SBA-15
NPs	-	Nanoparticles.
N-host	-	2,8,14,20-tetraundecylcalix[4]resorcinarene 4,6,10,12, 16,18,22,24–octol
PAH	-	Poly(allylamine hydrochloride)
PDA	-	Polydopamine
PoPD/RGO	-	Poly(o-phenylenediamine) /reduced graphen oxide
Ppy–Fe_3O_4/rGO	-	Polypyrrole (Ppy) was grafted on magnetite reduced-graphene oxide
PEI	-	Polyethylenimine

PD	-	polydopamine
PANI	-	Polyaniline
PANI/RGO	-	Polyaniline reduced graphene oxide
PEDOT:PSS	-	Poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate)
p-C-XAD-4	-	p-tertbutylcalix[8]areneoctamide impregnated amberlite
PV-Calix	-	Polyvinylcalix[4]arene
PSp	-	Pretreated sporopollenin
p-t-bCalix-Sp	-	p-tert-butylcalix[4]arene-Sporopollenin
PNaSS	-	Poly(sodium 4-styrenesulfonate)
PSF	-	Polysulfone
R	-	Universal Gas Constant
RO	-	Reverse osmosis
Sp	-	Sporopollenin
Sp-HPBA	-	Sporopollenin / E-4-((2-hydroxyphenylimino) methyl) benzoic acid
SiNTPP	-	2-formyl-5,10,15,20-tetraphenyl porphyrin/silica
SDDP-GO	-	Sulfuric acid doped diaminopyridine polymers grafted graphene oxide
SMG	-	Smart magnetic graphene
SGO/Fe-Mn	-	Thiol-functionalized graphene oxide/Fe-Mn
S-doped-GS	-	Sulphur doped modified graphene sponge
T	-	Temperature
TGA	-	Thermogravimetric analysis
TOA-EGO	-	Trioctylamine (TOA) modified exfoliated graphene oxide
THPP	-	Tetrakis(4-hydroxyphenyl)porphyrin
TCPP	-	Tetrakis(4-carboxyphenyl)porphyrin
TF5PP	-	5,10,15,20-tetrakis(pentafluorophenyl)porphyrin
TMPyP	-	5,10,15,20-tetrakis(4-N-methylpyridyl) porphyrin p-toluene-sulfonate.
VSM	-	Vibrating sample magnetometery
WHO	-	World Health Organization

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Clean and portable water is a basic human need that cannot be over-emphasized. However, population growth, modern industrialization, rapid industrialization, urbanization, domestic and industrial waste generation and other anthropogenic sources of toxic pollutants have made many water resources detrimental to man and the environment in many nations, due to the discharge of domestic waste and industrial effluents into the aquatic environment, posing a great threat to the ecosystem and public health. Industries that produces large volumes of effluents include textile, breweries, mineral processing, poultry processors, paper and fibre plants, meat packers, fruit and vegetable packing operations, fertilizer plants, refining and petrochemical operations, and many more.

These wastewaters generally contain different pollutants such as heavy metals, dyes and pesticides among other pollutants (Sayrabh *et al.,* 2005). Heavy metals are metallic elements or metalloids that have a relatively high atomic density greater than 4~4.5 g/cm^3 and are toxic and poisonous even at low concentration (Duffus, 2002; Hustton and Symon, 1986). Rapid increase in contamination of industrial and urban wastewaters by heavy metal ions are seriously worrying environmental problems (Ulmanu *et al.*, 2003).

Due to their relatively high solubility, mobility, non-biodegradable and persistence in the environment, heavy metals are adsorbed by organisms, then enter the food chain and subsequently ingested by human beings (biomagnefication). These heavy metal ions, such as Pb(II), Cd(II), Cr(III), Cr(VI), Hg(II), As(III), As(VI), Ag(II), Zn(II), Cu(II) and Ni(II), tends to accumulate in the human body (bioaccumulation) if ingested above the permissible limit is detrimental to human wellbeing, causing severe health problems and diseases (Ayenimo *et al*., 2009; Babel and Kurniawan, 2004).

Due to the toxicity of heavy metals, environmental regulatory authorities have set strict regulations to maintain the level of heavy metals in industrial waste discharge at permissible limits. These metals are allowed to be discharged only in very low concentrations levels in industrial effluents, inoder to protect public streams and water resources from being contaminated. Therefore, the polluting industries must use effective technology and materials to treat their respective effluents to conform to rigid environmental guidelines and standards prior to discharge.

Wastewater can be treated using three methods, namely: the primary, secondary and tertiary/advanced processes. The primary method removes suspended materials from the wastewater; the secondary treatment removes biodegrabable materials through biodegradation, whilst tertiary/advanced treatment methods mainly remove non-biodegradable wastes. Removal of non-biodegradable wastes is not possible using secondary methods. Therefore, advanced wastewater treatment methods such as ion exchange (Hamoda and Fawzi, 2004), precipitation (Espinoza et al., 2012), membrane separation (Caetano et al., 1995), ultra-filtration (Trivunac and Stevanovic, 2006) and electrolysis (Rajkumar and Palanivelu, 2004) may be used to remove the persistent wastes. Most of these methods are either costly, tedious and require high level of expertise; hence, not applicable to many end-users.

Conventional tertiary wastewater treatment methods such as ion exchange, membrane separation and electrolysis are costly and may not effectively treat heavy metals contaminated waters (Barakat, 2011; Liu et al., 2013). Other advanced techniques such as chemical precipitation, coagulation and flocculation are associated with slow metal precipitation and settling (Huang et al., 2016), these techniques also involves the production of toxic sludge. Disposal of the sludge produced from these techniques is detrimental to the environment due to its hazardous nature.

Thus, adsorption technology has gained a wider application. It is simple, cost effective, versatile and robust (Yang et al., 2009; Imamoglu and Tekir, 2008). Adsorption can be described as a mass transfer process through which metal ions are transferred from a solution onto the surface of a solid material (adsorbent) and becomes attached by either chemical or physical interactions.

The success of an adsorption process starts with the choice of the adsorbent material. Thus, the search for effective sustainable materials as adsorbents which are cost effective and with good adsorption capacities for metal ions have been intensified. Materials such as zeolites (Yazan et al., 2017), activated alumina (Rajurkar et al., 2011), carbon nanomaterials (CNM) (Ruparelia et al., 2008), multiwall carbon nanotubes (MWCNTs) (Tawabini et al., 2010) and activated carbon (AC) (Pyrzynska and Bystrzejewski, 2010) were used as adsorbents to remove heavy metal ions from water. Unfortunately, most of these materials are either costly or inefficient in treating effluents containing high concentration of metal ions due to low adsorption capacities and efficiencies. Thus, to address these drawbacks of conventional adsorbents, the use of easily modifiable low cost adsorbents such as sporopollenin (Sp) (Sener, et al., 2016) and graphene oxide (GO) (Tan et al., 2015a) for wastewater treatment has attracted attention in recent years.

Sp is a natural macromolecule of plant origin from *Lycopodium clavatum*, which has a molecular structure resistant to acids and alkalis. The nature of Sp has not been fully understood, it consist of an aliphatic chain with aromatic groups and sufficient hydroxyl groups attached to its network (Gezici, et al., 2006; Kamboh and Yilmaz, 2013). The prospect of Sp-based materials as adsorbent in water treatment is promising because of its inherent natural properties. Sp is chemically and physically very stable. It was found intact in 500 million years old sedimentary rocks (Grahame et al., 2015), suggesting that Sp and Sp-modified materials can withstand rough conditions, thus making Sp a good solid support for grafting materials with surface functionalities that have excellent adsorption affinity for target pollutants. It forms composites with other material by physically incorporating materials into the Sp's micro structure (Amro et al., 2016) and chemical grafting through the functional groups (OH, COOH, CO) on the Sp (Ahmad et al., 2017). Additionally, Sp is environmental friendly and biocompatible (Grahame et al., 2015). Therefore, Sp-based materials can serve as sustainable adsorbents in wastewater treatment when modified with other suitable functional materials such as GO and porphyrins, which have excellent affinity for heavy metal ions.

Porphyrins are large ring biomolecules consisting of four pyrroles to which a variety of side chains are attached (Biesaga et al., 2000). The nitrogen atoms in the tetrapyrrole ring of porphyrins act as ligational sites that attract metal ions due to their strong electron-donor properties, thus providing high affinity for metal ions via the formation of metal–nitrogen coordination bonds (Biesaga et al., 2000; Lee et al., 2004; Kumar and Shim, 2011).

On the other hand, GO is water-soluble material derived from the oxidation of graphite (Park et al., 2009) and has high specific surface areas (theoretical value of 2620 m^2/g) (Zhao et al., 2011). The oxidation of graphite to GO provides sufficient oxygenated functional groups on GO, such as OH, COOH, and CO, which can be used as anchoring sites for metal ion complexation and grafting of desired surface functionality with high affinity for metal ions (Seenivasan et al., 2015; Zhang et al., 2011). Furthermore, GO could serve as a support for macrocyclic molecules such as calixarenes, offering promising improvements to the sorption technology of calixarenes based materials (Zhang et al., 2016). Calixarenes are macrocyclic compounds that are composed of phenolic units connected by methylene bridges. They are capable of recognizing and selectively binding anions and cations (Perin et al., 1993; Mcmoham et al., 2003) and can be modified by introducing functional groups such as ester, ketone, amide, amine, azo, tioether, and cyanide onto its phenolic units, thus improving its affinity for target pollutant (Ludwig and Dzung, 2000; Ungaro 2000). One of the intresting features of calixarenes is their abiity to form cavity and clusters around target pollutants (Steed and Atwood 2000).

However, magnetic nanoparticles (Fe_3O_4) incorporated with GO based materials have been reported as adsorbents for magnetic solid phase removal of heavy metals from aqueous solution. Such as Fe_3O_4 modified-GO (Fe_3O_4/GO) (Nodeh et al., 2016), magnetic GO grafted polymaleicamide dendrimer (GO/Fe_3O_4-

g-PMAAM) (Ma et al., 2017) and carbon gel-supported Fe(III)-graphene disks (Fe-G/RF-C) (Mishra et al., 2017). Magnetic separation provides a promising technique for the separation of adsorbent materials from sample solution using an external magnetic field, it is less tedious, highly efficient and required less time compared to filtration and centrifugation (Huang and Yuan, 2016).

In this work, the quest to harness the full potentials of sporopollenin, porphyrin, calixarene and graphene oxide based materials as adsorbents for environmental applications, specifically the removal of toxic heavy metal ions from aqueous environment, led us to the synthesis for the first time of three new materials; two new magnetic sporopollenin-based and one new magnetic graphene oxide-calix-4-arene based. These materials were used as robust hybrid adsorbents to remove heavy metal ions from industrial wastewater samples using batch adsorption technique.

1.2 Problem Statement

Heavy metals contamination of rivers, lakes and other water resources due to the discharge of domestic wastes and industrial effluents into the aquatic environment has become a global environmental problem nowadays, due to their toxicity and persistence in the environment (Volesky, 1999). These heavy metals are discharged in quantities that are hazardous to the environment and living organisms. In human being, heavy metals are potent carcinogens and can cause other adverse health effects such as irritation of respiratory system and lung damage, cardiovascular diseases, liver and kidney damage, loss of appetite, nausea etc (Jeon and Cha, 2015). Thus, regulating authorities have become increasingly concerned with the problems associated with the discharge of untreated effluents.

Recently, research efforts and works have been intensified with the aim of finding effective alternatives and environmental friendly adsorbents for water treatment, particularly for the removal of heavy metal ions from aqueous environment. Natural biopolymer such as sporopollenin (Sp), has remarkable potentials as adsorbent for this purpose. Nevertheless, its potentails are yet to be fully harnessed. Thus, the material requires proper and effective modification to fully harness its heavy metals adsorption potentials and other environmental applications.

Most of the Sp-based materials reported in literature have low adsorption capacities for heavy metal ions and overall weak performance in treating effluents with high concentrations of these toxic metals. Therefore, modification of Sp with functional materials that have high affinity for heavy metal ions is paramount for this application. Functional materials used to modify Sp in this work, such as 3-aminopropyltrimethoxysilane, graphene oxide and porphyrin, significantly improved the heavy metals adsorption performance of Sp, compared to the available Sp-based materials in literatures.

However, the utilization of porphyrins in different chemical processes has several setbacks such as decomposition during reaction, oxidative self-destruction in oxidizing media and recovery problems at the end of reaction for re-usage (Jeong et al., 2011). To address these problems, it is important to enhance the stability of porphyrin and utilize its remarkable properties by supporting the desired derivative of porphyrin onto a polymeric backbone or a solid support. For this reason, porphyrin (THPP) supported on silica coated MSp reported in this work for the first time recorded significant stability, as well as improvements in heavy metal adsorption performance of porphyrin based materials.

Similary, a macrocyclic compound like calixarene, will require appropriate solid support for effective performance in environmental applications. Ion extraction studies using calixarenes usually involve liquid –liquid extraction (LLE). However, LLE using macrocyclic compounds such as calixarenes is time consuming, labor intensive and difficulty in separating phases caused by the formation of emulsions (Camel, 2003). Thus, the reason for using magnetic solid phase extraction (MSPE) in this work is to overcome the limitation posed by LLE.

Calixarenes can recognize and selectively bind heavy metal ions (Perin *et al*., 1993). This property opens up numerous potential applications of calixarenes in heavy metals recovery and removal from aqeous environment (Perin *et al*., 1993; Mcmoham *et al*., 2003), but the full potentials of these materials for this application has not been fully realize. Overall, most of the reported calixarene based materials in literature have low adsorption capacities, stability and recovery problems at the end of a reaction for re-usage. Thus, could not effectively treat effluents and wastewaters containing high concentrations of heavy metal ions.

To address these drawbacks and utilize the properties of calixarenes in harnessing its full potentials in removing heavy metals from aqeous environment, for the first time, 3-aminopropyltrimethoxysilane functionalized calix-4-arene grafted onto silica coated magnetic graphene oxide is reported in this work. This material recorded significant improvements in the sorption technology of calixarene-based materials, with improved heavy metals adsorption performance.

1.3 Aim and Objectives of the Work

The overall aim of this research is to remove hazardous heavy metals ions from industrial effluents using three new materials, i.e. two new sporopollenin-based and one new magnetic graphene oxide-calix-4-arene based as potential adsorbents. The specific objectives of this study are to:

1. Synthesize two new magnetic sporopollenin-based materials and one new magnetic graphene oxide-calix-4-arene based material as hybrid adsorbents for the removal of selected heavy metals namely Pb(II), Ni(II) and Cd(II) from industrial wastewater samples and characterize the synthesized adsorbents using Fourier transform infrared spectroscopy (FTIR), Field-emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM).
2. Optimize the effective parameters for the adsorbents performance, which includes the pH, temperature, contact time, adsorbent dosage, and initial concentration and to evaluate each of the adsorbents adsorption

capacities, perform kinetics, thermodynamics and equilibrium sorption studies of the processes and perform regeneration studies of the spent adsorbents.

3. Assess the greenness of developed methods based on the use of these three new sorbents for selected metal ions.

1.4 Significance of Study

It is forecasted that by the year 2030, there would be a global 40% shortfall of water demand and available supply (World Bank, 2017). As the global population increases, the demand for portable water also increases. Water resource is scarce globally and the scarcity is perceived as one of the major threats to global prosperity and stability. According to World Bank, 40% of the global population live in water scarce areas and about ¼ of world's gross domestic product (GDP) is vulnerable to this adversity. By the year 2025, about 1.8 billion people will be living in regions or countries with total water scarcity (World Bank, 2017) and more than half of the world population will be faced with water-based vulnerability due to pollution (Rijsberman, 2006).

To strengthen our water resources against this backdrop of increasing demand, scarcity and pollution, we must protect our water resources and invest significantly in innovative technologies and materials for water treatment and management. Contaminated water resources negatively affect the wellbeing of human, aquatic life and biodiversity. Contaminated water resources have been identified as a leading cause of diseases and deaths, globally (WWDR4, 2012). In many developing countries, poorly treated effluents and domestic wastes are often discharged into water streams (Gupta, 2008), which is probably due to economic problems, lack of awareness and access to adequate technology and materials for water treatment. Thus, common people in most of the developing nations go through the health and toxicological effects of drinking heavy metals contaminated water.

Findings from this research work will present new hybrid, effective materials as absorbents for the removal of hazardous heavy metal ions from water, particularly industrial wastewater prior to discharge into the environment. Furthermore, the synthesized adsorbents have improved performance and adsorption capacity for this purpose. In addition, this study involves the use of sporopollenin, which is a sustainable biomaterial as the main component in two of the synthesized sorbents (GO@SiO_2-MSp@SiO_2-NH_2 and MSp@SiO_2-THPP). Sporopollenin is an abundant natural material, biodegradable and non toxic. Thus, it is environmental friendy. Nevertheless, the removal method using the synthesized adsorbents in this study is green and eco-friendy.

1.5 Scope of Work

This study is divided into three major parts; synthesis of materials, characterization of materials and the application of the synthesized materials for heavy metals removal from industrial wastewater. In the first part, magnetic sporopollenin (MSp) and magnetic graphene oxide (MGO) were each synthesized through co-precipitation of magnetite (Fe_3O_4) with Sp and GO, respectively. Thereafter, MSp was coated and functionalized with 3-aminopropyltrimethoxysilane (APTMS), then grafted onto GO-coated silica (GO@SiO_2) to produce the first material (GO@SiO_2-MSp@$SiO_2$$NH_2$). The second material was synthesized via coating of MSp with 3-chloropropyltrimethoxysilane and then grafted onto 4-hydroxylphenylporphyrin (THPP) to produce MSp@SiO_2-THPP. The third material was synthesized through grafting of APTMS functionalized calix-4-arene onto silica coated MGO to produce MGO-Calix@$SiO_2$$NH_2$.

The second part of this study involves the characterization of the synthesized materials using FTIR, FESEM, EDX, TGA and VSM. The third part of this study involves the optimization of adsorption parameters and application of the synthesized materials as adsorbents to remove heavy metals from real samples, i.e. industrial effluents. The parameters optimized are pH, temperature, adsorbent dosage, contact time and concentration. Adsorption equilibrium, kinetics and thermodynamics of the removal processes are studied in this section, in addition to regeneration studies of the spent adsorbents and finally, the greenness of these methods was evaluated using analytical ecoscale analysis (AES).

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APPENDIX A

LIST OF PUBLICATIONS

Journal with Impact Factor

1. **Hassan, A.M**., Wan Ibrahim, W.A., Bakar M.B., Sanagi, M.M., Saturman, Z.A., Nodeh, H.R. and Mokhter, M. A. (2020) New effective 3-aminopropyl trimethoxysilane functionnalized magnetic sporopollenin-based silica-coated graphene-oxide adsorbent for removal of Pb(II) from aqueous environment. *Journal of environmental management* 253, 109658. **ISI** (**Q1, IF: 4.865)**
2. **Hassan, A.M**., Wan Ibrahim, W.A., Bakar, M.B. and Saturman, Z.A. (2020) Silica-coated magnetic sporopollenin supported tetrakis-4-hydroxylphenyl porphyrin as hydrid biosorbent for sustainable removal of cadmium from industrial wastewater. *Journal of Environmental Chemical Engineering* **submitted article**. (**Q1, IF: 4.300)**

Indexed Journal

1. Wan Ibrahim, W.A., **Hassan, A.M**., Saturman, Z.A. and Bakar, M.B. (2020) A mini review on sporopollenin-based materials for removal of heavy metal ions from aqueous solution. *Malaysian Jounal of Analytical Sciences* 24(3)**,** 300-312. **Indexed by Scopus (Q4, SRJ: 0.18)**

Conference Proceedings

1. **Hassan, A.M.,** Wan Ibrahim, W.A., Bakar M.B., Sanagi, M.M., Saturman, Z.A.,and Nodeh, H.R. (2017) Highly effective new 3-amino propyltrimethoxysilane functionalized magnetic sporopollenin-based silica coated graphene oxide adsorbent for removal of Pb(II) from industrial

wastewater, Malaysia Separation Science Conference, (MySSC 2017), Johor Bahru Malaysia.

2. **Hassan, A.M.,** Wan Ibrahim, W.A., Bakar M.B., Sanagi, M.M. and Saturman, Z.A. (2018) Silica Coated Magnetic Sporopollenin Supported Tetrakis (4-hydroylphenyl) porphyrin (THPP) for Sustainable Removal of Cadmium from Aqueous Environment, 1st UTM Emerging Scientists Conference 2019 (UTM-ESCon 2OI8), Johor Malaysia.