POLYVINYL ALCOHOL-ALGINATE FERRO PHOTO GELS FOR MERCURY(II) REMOVAL

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Bioprocess)

Faculty of Chemical & Energy Engineering
Universiti Teknologi Malaysia

DECEMBER 2015

This entire research is dedicated with deepest love to my dearest parents, brother and sisters.

Thank you for the never ending love, trust, understanding, support, and motivation.

May Allah give you the best reward and may the blessings of Allah be upon you.

ACKNOWLEDGEMENT

In the name of Allah, the Most Compassionate, the Most Merciful. All praise is due to Allah S.W.T. for granted my prayer to complete this research. Knowledge and experiences gained are worth to all the sacrifices and hard work that had been made. It is not an easy task indeed but the satisfaction is beyond the words. Thus, I would like to thank people who had supported me throughout this research.

First and foremost, I would like to express my sincere gratitude to my supervisor, Prof Dr Ani Idris for her valuable guidance and constant supervision. The inspiration and examples shown by her had motivates me to be successful. Also, thank you to Universiti Teknologi Malaysia (UTM) for giving me the opportunity to continue my study here. I am indebted to Ministry of Higher Education (MoHE) for the financial support.

Finally, special thanks and honorable mention goes to my parents, A.Rahman bin Bakar and Maimunah binti Abdul Rahim, my siblings, Zarina Samiha, Amir Alif and Amira Yuha and my friends for their continuous support and motivation. Their endless love and encouragement are the reasons why I chose not to give up.

ABSTRACT

Mercury (Hg(II)) is considered as one of the most noxious heavy metals due to its high toxicity and probability of bioaccumulation in human body. Adsorption is one of the most commonly used technique to treat Hg(II) in wastewater but it requires a two stage process where the toxic Hg(II) is not being converted into non-toxic medium but need to be recovered. Thus photocatalytic process was introduced where the photocatalyst reacts by converting the toxins into toxic-free wastes; henceforth there is no necessity for additional disposal. In this study nano-sized maghemite (γ-Fe_2O_3) embedded in polyvinyl alcohol (PVA) and alginate matrix was used as photocatalyst to remove Hg(II). Besides being a photocatalyst, the γ-Fe_2O_3 nanoparticles possess supermagnetism properties which enabled the beads to be easily recovered with the application of an external magnetic field. The influences of pH, initial concentration and photocatalyst dosage on Hg(II) removal were also investigated. The photocatalyst beads were then used for the reduction of Hg(II) in aqueous solution both under sunlight and away from sunlight. The synthesized maghemite nanoparticles were characterized using transmission electron microscopy, x-ray diffraction and vibrating sample magnetometer; and the size distribution of the beads were determined. The current results revealed that 96% of Hg(II) was reduced in four hours under sunlight. However, when the experiment was done in the dark, the percentage of Hg(II) reduction achieved was only 5%. The low reduction rate was due to the minimal absorption activity of Hg(II) onto the beads surface. In addition, the maximum Hg(II) reduction was found at pH 11 whilst the photocatalyst dosage was kept at 16% (v/v). An 8% (v/v) dosage of maghemite nanoparticles loading was found to be capable only to reduce until 67% of Hg(II), while Hg(II) reduction performance was not significantly improved when 24% (v/v) of photocatalyst dosage was used. Excessive addition of catalyst dosage increased the active sites on the beads surface but it also blocked some sunlight illumination as the voluminous load of photocatalyst clogged the reaction region thus reducing the photon availability to be absorbed. At a fixed optimum parameters, it was revealed that increasing the initial concentration of Hg(II) degraded the reduction capability because the photons path length into the solution reduced as concentration of Hg(II) increased. Field emission scanning electron microscopy images and energy dispersive x-ray showed that the beads possessed significant porosity structure that greatly supported mass movement of Hg(II) inside the beads. The maghemite embedded PVA-alginate beads towards reduction of Hg(II) strongly fitted Langmuir-Hinshelwood kinetics model with correlation coefficient, R^2 value of 0.9771. In conclusion, this study proved that the γ-Fe_2O_3-PVA-alginate beads are applicable in reducing and treating Hg(II) in water.

ABSTRAK

Raksa (Hg(II)) dianggap salah satu daripada logam berat paling berbahaya disebabkan sangat bertoksik dan kebarangkalian bioakumulasi di dalam badan manusia. Penjerapan adalah salah satu teknik yang selalu digunakan untuk merawat Hg(II) dalam sisa air tetapi ia memerlukan proses dua peringkat di mana Hg(II) bertoksik tidak ditukar kepada bahan tidak bertoksik tetapi perlu untuk diperoleh semula. Oleh itu proses fotopemangkin telah diperkenalkan di mana fotomangkin bertindak balas dengan menukarkan toksin kepada sisa bebas daripada toksik; sekaligus tiada keperluan untuk pelupusan tambahan. Di dalam kajian ini, maghemit bersaiz nano (γ-Fe_2O_3) yang telah dimasukkan ke dalam polivinil alkohol (PVA) dan matriks alginat telah digunakan sebagai fotomangkin untuk menyingkirkan Hg(II). Selain bertindak sebagai fotomangkin, partikel bersaiz nano γ-Fe_2O_3 ini memilik sifat superkemagnetan yang membolehkan manik itu mudah diperoleh semula dengan menggunakan medan magnet luaran. Pengaruh daripada pH, kepekatan awal dan dos fotomangkin terhadap penyingkiran Hg(II) juga telah disiasat. Manik fotomangkin ini kemudiannya digunakan untuk merawat Hg(II) di dalam larutan air di bawah sinaran matahari dan tanpa cahaya matahari. Partikel bersaiz nano maghemit yang ditelah disediakan telah dicirikan dengan menggunakan mikroskopi pancaran elektron, pembelauan sinar-x dan magnetometer sampel getaran; dan taburan saiz manik telah ditentukan. Keputusan menunjukkan bahawa 96% Hg(II) telah dirawat dalam empat jam di bawah sinaran matahari. Walau bagaimanapun, apabila eksperimen dilakukan di dalam gelap, peratusan penurunan Hg(II) hanya mencecah 5%. Kadar penurunan yang rendah adalah disebabkan oleh aktiviti penyerapan Hg(II) yang minima ke atas permukaan manik-manik. Selain itu, didapati bahawa pengurangan maksima Hg(II) adalah pada pH 11 di mana dos fotomangkin digunakan pada 16% (v/v). Dos maghemit zarah nano pada 8% (v/v) hanya mampu mengurangkan sehingga 67% Hg(II) sementara prestasi penurunan Hg(II) tidak banyak berubah apabila 24% (v/v) dos fotomangkin digunakan. Penggunaan berlebihan dos pemangkin akan menambah ruang aktif di permukaan manik, tetapi ia juga akan menghalang kemasukan cahaya matahari kerana fotomangkin yang berlebihan menyumbat kawasan tindakbalas sekaligus mengurangkan penyerapan foton. Pada parameter optimum yang telah ditetapkan, didapati dengan meningkatkan kepekatan awal Hg(II), keupayaan penurunan merosot kerana jarak laluan foton di dalam larutan berkurangan setelah kepekatan Hg(II) ditingkatkan. Imej mikroskopi pengimbas pancaran medan elektron dan tenaga serakan sinar-x menunjukkan bahawa manik memiliki struktur berliang ketara yang membantu pergerakan jisim Hg(II) di dalam manik. Manik-manik PVA-alginat berisi maghemit menuju kepada penurunan Hg(II) melengkapi model kinetik Langmuir-Hinshelwood dengan pekali korelasi, R^2 bernilai 0.9771. Kesimpulannya, kajian ini membuktikan bahawa manik γ-Fe_2O_3-PVA-alginat boleh digunakan dalam mengurangkan dan merawat Hg(II) di dalam air.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Aliquat 336	-	Tri-Octyl Methylammonium Chloride
Au-Fe_3O_4	-	Gold-Ferrous-Ferric Oxide
Ag	-	Argentum / Silver
$BDETH_2$	-	Benzene-1, 3-Diamidoethanethiol
CdS	-	Cadmium Sulfide
CH_3Hg	-	Monomethylmercury
$(CH_3)_2Hg$	-	Dimethylmercury
Co-Mn	-	Cobalt-Manganese
Cr(III)	-	Trivalent Chromium
Cr(VI)	-	Hexavalent Chromium
CrO_4^-	-	Chromate ion
$CuCrO_2$	-	Copper-Chromium Oxide
CVAAS	-	Cold Vapor Atomic Absorption Spectrometer
DBT	-	Dibenzothiophene
DNA	-	Deoxyribonucleic Acid
DOE	-	Department of Environment
EDTA	-	Ethylenediamine Tetraacetate
EDX	-	Energy Dispersive X-Ray
FESEM	-	Field Emission Scanning Microscopy
Fe_2O_3	-	Maghemite
Fe_3O_4	-	Magnetite / Iron(II) Di-Iron(III) Oxide
$Fe(OH)_3$	-	Iron(III) Oxide-Hydroxide
$FeTiO_3$	-	Iron Titanium Oxide
H_2	-	Hydrogen
Hg^0	-	Elemental Mercury
Hg^{2+}	-	Mercuric ion
Hg(II)	-	Divalent Mercury

$HgCl_2$	-	Mercury(II) Chloride
$Hg(OH)_2$	-	Mercury(II) Hydroxide
$Hg(NO_3)_2$	-	Mercury(II) Nitrate
HVAC	-	Heating, Ventilation, and Air Conditioning
L-H	-	Langmuir-Hinshelwood
M-M	-	Mannuronate-Mannuronate Blocks
MgO	-	Magnesium Oxide
MN	-	Maghemite Nanoparticles
MRI	-	Magnetic Resonance Imaging
NiPc	-	Nickel Phthalocyanine
PAD	-	Photo-Assisted Deposition
PEI	-	Polyethyleneimine
POM	-	Polyoxometalates
$PW_{12}O_{40}^{3-}$	-	1-Equiv reduced tungstophosphate
ppb	-	Parts per billion
ppm	-	Parts per million
PPEI	-	Phosphonomethylated Polyethyleneimine
PVA	-	Polyvinyl Alcohol
$PyDETH_2$	-	Pyridine-2-6-Diamineethanethiol
ROS	-	Reactive Oxygen Species
SDTC	-	Sodium Dimethyldithiocarbamate
SH-Fe_3O_4-NMPs	-	Sulfur-containing ligands mercapto-functionalized Nano-Fe_3O_4 Magnetic Polymers
SIRIM	-	Standards and Industrial Research Institute of Malaysia
$SiW_{12}O_{40}^{4-}$	-	One-electron-reduced 12-tungstosilicate
STC	-	Sodium Thiocarbonate
TEM	-	Transmission Electron Microscopy
TiO_2	-	Titanium Dioxide
TMT	-	Trimercapto-1, 3, 5-Triazine
UV	-	Ultraviolet
UV-vis	-	Ultraviolet-visible
VOC	-	Volatile Organic Compounds
VSM	-	Vibrating Sample Magnetometer

V-TiO_2	-	Vanadium-doped Titanium Dioxide
WO_3	-	Tungsten Oxide
WS_2	-	Tungsten Sulfide
XRD	-	X-Ray Diffractometer
ZnO	-	Zinc Oxide
ZnS	-	Zinc Sulfide
4-BPDB	-	1,4-Bis(4-Pyridyl)-2,3-Diaza-1,3-Butadiene
γ-Fe_2O_3	-	Maghemite
α-Fe_2O_3	-	Hematite / Iron(III) Oxide

LIST OF SYMBOLS

C_0	-	Initial concentration of solution (mg/L)
C	-	Concentration of solution (mg/L)
C_W	-	Concentration of water molecules
d	-	Diameter
E_{CB}	-	Conduction band-edges
E_{VB}	-	Valence band-edges
eV	-	Electronvolt
e^-	-	Electron
h	-	Initial sorption rate (mg/L h)
hυ	-	Surplus energy, E
g	-	Gram
k	-	Rate constant of pseudo second-order equation (L/mg h)
k_r	-	Reaction rate constant (mg/L min)
k_{app}	-	Reaction rate (min^{-1})
K_{LH}	-	Adsorption constant of the reactant (L/mg)
K_W	-	Solvent adsorption constant
L	-	Litre
m^2	-	Square metre
mg	-	Miligram
min	-	Minute
ml	-	Mililitre
mm	-	Milimetre
ng	-	Nanogram
nm	-	Nanometre
r	-	Reduction rate (mg/L min)
R^2	-	Correlation coefficient
r_o	-	Initial rate of photocatalytic reduction

t	-	Illumination time (minute)
w/v	-	Weight/volume
q_e	-	Solute loading on the solid phase (mg/g)
λ	-	Wavelength
Å	-	Ångström or 0.1 nm
μg	-	Microgram

CHAPTER 1

INTRODUCTION

1.1 Overview

On 1956, an irresponsible release of methylmercury by a chemical company into the sea caused a deathly syndrome in Japan. This severe mercury poisoning which is called Minamata disease had haunted the Japanese people for 36 years as acute effects continued to rise. Some of them experienced hearing and speech damage, hands and feet numbness, insanity, paralysis, effect on the foetus in the womb and even death (Zhang *et al*., 2004).

In Malaysia, mercury wastes are mainly originate from agricultural pesticides and they also emerge from the chlorine-alkali industry. Moreover, mercury is used as a catalyst in the chemical and petrochemical industries, used in electrical apparatus, cosmetics, thermometers, gauges, batteries, painting and coating industries, mining, extractive metallurgy and many other industries (Parham *et al*., 2012). This environmental pollution stimulates concerns about the dangers posed to human being, thus numerous efforts have been taken to handle this problem, essentially aiming at cost effectiveness. Hence, Malaysian Department of Environment (DOE) sets tolerance limit release for Hg(II) at 0.005 mg/L for standard A and 0.05 mg/L for standard B.

Mercury is considered as one of the most noxious heavy metals acknowledged by mankind, due to high toxicity and probability of bioaccumulation in body. It forms different salts with anionic mechanisms in water and can change from one form to another in various diverse aquatic environments (Parham *et al*., 2012). Some severe and chronic signs caused by mercury poisoning are metallic taste, inflammation in mouth, kidney collapse and excessive salivation (Parham *et al*., 2012).

Many methods have been used to remove Hg(II) from wastewater such as ion exchange, precipitation as sulphide, membrane filtration, ion exchange, electrodeposition, coagulation, reverse osmosis, electro-deposition, ultrafiltration and adsorption (Li *et al*., 2008). One of the techniques that is most widely used to date is adsorption. Adsorption method is chosen because of its high efficiency, availability of different adsorbents, sorbent materials can be generated and recycled, easy handling and most importantly cost effectiveness (Xiong *et al*., 2009). Unfortunately, a secondary method need to be introduced to desorb the heavy metals before disposing the adsorbents.

In a recent study, maghemite nanoparticles (γ-Fe_2O_3) were proven as an excellent adsorbent for removing heavy metals due to the vast surface area which improves the adsorption, many methods to synthesize maghemite and at the same time, it is commercially available. Also, easy separation of metal and magnetic adsorbent from treated water, and ultimately, no secondary waste will be produced (Tuutijärvi *et al*., 2009).

By applying external magnetism to the magnetic particles, excellent disintegration will be accomplished (Hu *et al*., 2005). Accordingly, studies have been initiated by combining magnetic separation with biosorption technique. This method is well known of treating many heavy metals in wastewater in a short time, while no contaminants will be formed (Rocher *et al*., 2008). In addition, several studies have recorded positive results; encapsulation of maghemite nanoparticles (γ-Fe_2O_3) in sodium alginate were used to remove Pb(II) and to reduce Cr(VI) to less toxic Cr(III), γ-Fe_2O_3 was incorporated into PVA and alginate matrix photocatalyst to reduce Cr(VI) to Cr(III) and was used to removal of Cs^+ from radioactive waste water (Idris *et al*., 2010, 2012; Majidnia and Idris, 2015). Likewise, Cu(II) was also successfully removed by maghemite nanoparticles doped with cobalt entrapped in PVA-alginate beads (Wong *et al.,* 2014).

The maghemite nanoparticles (γ-Fe_2O_3) which are embedded in binding materials such as alginate which has been used to encapsulate magnetic particles to form into beads, can be recycled (Ngomsik *et al*., 2006, 2009). Being hydrophilic, biodegradable, inexpensive, non-toxic, naturally available and with existence of binding sites contribute from its carboxylate functions, have favour alginate over other materials. On the other hand, Liu *et al*. (2008) has found that drug delivery ferrogels with magnetic-stimuli performance is very much influenced on the concentration of PVA. PVA is nontoxic, inexpensive, robust and possesses an uncomplicated chemical structure which allows alteration to be made by executing a chemical reaction, and it is combined with alginate to reduce PVA’s agglomeration.

Besides that, there are various semiconductor materials that are chosen in photocatalytic practice, for example titanium dioxide (TiO_2), zinc oxide (ZnO), WO_3 (tungsten oxide) and polyoxometalate anions (POM). Based on Ullah and Dutta (2008) findings, these semiconductors have individual band gap in ultraviolet (UV) region, thus aiding photocatalysis with radiance from UV emission.

1.2 Problem Statement

Many techniques were developed to treat wastewater; among them were absorption and photocatalyst reduction. Parham *et al.* (2012) used altered magnetic iron oxide nanoparticles with 2-mercaptobenzothiazole as an adsorbent for Hg(II) removal and results revealed a complete removal of mercury ions within 4 minutes, and the modified magnetic iron oxide nanoparticles can be reutilized three times without decreasing adsorption efficiency. However, in adsorption, the impurities are being absorbed into the bioadsorbents but then again are not being converted into non-toxic medium. Thus photocatalytic process was introduced where the photocatalyst reacts by converting the toxins into toxic-free wastes; henceforth there is no necessity for additional disposal. Recently, magnetic nanoparticles iron oxide (γ-Fe_2O_3) was used as a photocatalyst and it has an excellent efficiency in converting hazardous metal ion such as chromium(VI) to chromium(III) (Idris *et al*., 2010, 2011). The photocatalyst reaction comes from electrons couples which photoproduction from the valence and conduction ranges, with absorption of UV radiation with energy equivalent or greater than the range. However the use of γ-Fe_2O_3 was never applied for the removal of Hg(II).

Thus in this study, maghemite nanoparticles (γ-Fe_2O_3) which is the photocatalyst is embedded in the alginate-PVA matrix is used to treat wastewater containing Hg(II). Photocatalytic experiments will be performed in the dark and under sunlight and several some parameters such as pH, photocatalytic dosage, initial feed concentration were investigated.

1.3 Objectives

The main objective of this study is to remove Hg(II) from aqueous solution using maghemite γ-Fe_2O_3 embedded in PVA-alginate. In order to focus on this objective, the following need to be addressed:

i) To prepare the γ-Fe_2O_3 PVA-alginate beads
ii) To study its physicochemical properties
iii) To test the performance of the catalyst on removal of Hg(II)
iv) To study the kinetics of the photocatalytic reaction

1.4 Scope of The Study

In order to achieve the objectives mentioned, the encompassed work includes the following:

i) The maghemite nanoparticles were synthesized using the coprecipitation method and then embedded in the PVA-alginate matrix.
ii) The synthesized maghemite nanoparticles were characterized using TEM (Transmission electron microscopy), XRD (X-ray diffraction) and VSM (Vibrating Sample Magnetometer); and the size distribution of the beads were determined.
iii) The photocatalytic experiments were then performed in darkness and sunlight, using maghemite nanoparticles and without using maghemite nanoparticles.
iv) The photocatalytic experiments were performed at various pH ranging from 2 until 13.

v) The influence of photocatalyst dosage on Hg(II) removal was determined; where maghemite γ-Fe_2O_3 dosages were varied at 8%, 16% and 24%.

vi) Hg(II) initial concentration was determined and varied at 25 ppm, 50 ppm, 75 ppm and 100 ppm. The effect of Hg(II) initial concentration on the Hg(II) removal was analysed.

vii) Hg(II) elements in the beads before and after the experiment was analysed with CVAAS (Cold-vapour atomic absorption spectrometry).

viii) Kinetic analysis of photoreduction was determined for the optimum photocatalytic.

1.5 Significance of The Study

Earlier studies (Idris *et al*., 2010, 2012) have used ferrophoto gel beads with embedded maghemite nanoparticles in the photocatalyst process to treat Cr(VI). López-Muñoz *et al*. (2011) used TiO_2 in his photocatalyst study, while other techniques on Hg(II) removal on the other hand did not apply photocatalytic process. Parham *et al.* (2012) removed mercury from wastewater with magnetic iron oxide nanoparticles modified with 2-mercaptobenzothiazole using adsorption process. Thus in this study, effectiveness of γ-Fe_2O_3 embedded PVA-alginate beads in removal of Hg(II) using photocatalytic process is investigated for the first time.

REFERENCES

Aguado, M.A., Cervera-March, S. and Giménez, J. (1995). Continous Photocatalytic Treatment of Mercury(II) on Titania Powders. Kinetics and Catalyst Activity. *Chemical Engineering Science*. 50, 1561-1569.

Akbal, F. and Camci, S. (2011). Copper, Chromium and Nickel Removal from Metal Plating Wastewater by Electrocoagulation. *Desalination*. 269, 214-222.

Amara, D., Felner, I., Nowik, I. and Margel, S. (2009). Synthesis and Characterization of Fe and Fe_3O_4 Nanoparticles by Thermal Decomposition of Triiron Dodecacarbonyl. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 339 (1-3), 106-110.

Atwood, D. A. and Zaman, M. K. (2006). Mercury Removal from Water. *Recent Developments in Mercury Science*. 120, 163-182.

Bee, A., Massart, R. and Neveu, S. (1995). Synthesis of Very Fine Maghemite Particles. *Journal of Magnetism and Magnetic Materials*. 149 (1-2), 6-9.

Bessbousse, H., Rhlalou, T., Verchère, J. F. and Lebrun, L. (2008). Removal of Heavy Metal Ions from Aqueous Solutions by Filtration with A Novel Complexing Membrane Containing Poly(ethyleneimine) In a Poly(vinyl alcohol) Matrix. *Journal of Membrane Science*. 307, 249-259.

Beydoun, D., Amal. R., Low. G. and McEvoy, S. (2002). Occurrence and Prevention of Photodissolution at the Phase Junction of Magnetite and Titanium Dioxide. *Journal of Molecular Catalysis A. Chemical*. 180, 193-200.

Bhattacharyya, A., Dutta, S., De, P., Ray, P. and Basu, S. (2010). Removal of Mercury(II) from Aqueous Solution Using Papain Immobilized on Alginate Bead: Optimization of Immobilization Condition and Modeling of Removal Study. *Bioresource Technology*. 101, 9421-9428.

Blais, J.F., Djedidi, Z., Cheikh, R., Tyagi, R., and Mercier, G. (2008). Metals Precipitation from Effluents: Review. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management.* 12, 135-149.

Briand, L.E., Bonetto, R.D., Sanchez, M.A. and Thomas, H.J. (1996). Structural Modelling of Coprecipitated VTiO Catalysts. *Catalysis Today*. 32, 205-213.

Cavaco, S.A., Fernandes, S., Quina, M.M. and. Ferreira, L.M. (2007). Removal of Chromium from Electroplating Industry Effluents by Ion Exchange Resins. *Journal of Hazardous Materials*. 144, 634-638.

Chakrabarty, K., Saha, P. and Ghoshal, A.K. (2010). Simultaneous Separation of Mercury and Lignosulfonate from Aqueous Solution using Supported Liquid Membrane. *Journal of Membrane Science*. 346, 37-44.

Chen, D. and Ray, A.K. (1999). Photocatalytic Kinetics of Phenol and Its Derivatives Over UV Irradiated TiO_2. *Applied Catalysis B: Environmental*. 23, 143-157.

Chen, D. and Ray, A.K. (2001). Removal of Toxic Metal Ions from Wastewater by Semiconductor Photocatalysis. *Chemical Engineering Science*. 56, 1561-1570.

Chen, Y.H and Li, F.A. (2010). Kinetic Study on Removal of Copper(II) using Goethite and Hematite Nano-photocatalysts. *Journal of Colloid and Interface Science*. 347, 277-281.

Chen, Y.H. (2011). Synthesis, Characterization and Dye Adsorption of Ilmenite Nanoparticles. *Journal of Non-Crystalline Solids*. 357, 136-139.

Chomoucka, J., Drbohlavova, J., Huska, D., Adam, V., Kizek, R. and Hubalek, J. (2010). Magnetic Nanoparticles and Targeted Drug Delivering. *Pharmacological Research*. 62, 144-149.

Collasiol, A., Pozebon, D. and Maia, S.M. (2004). Ultrasound Assisted Mercury Extraction from Soil and Sediment. *Analytica Chimica Acta.* 518, 157-164.

Dalrymple O. K., Stefanakos, E., Trotz, M.A. and Goswami, D.Y. A Review of The Mechanisms and Modeling of Photocatalytic Disinfection. Applied Catalysis B: Environmental. 98, 27-38.

Dong, J., Xu, Z. and Wang, F. (2008). Engineering and Characterization of Mesoporous Silicacoated Magnetic Particles for Mercury Removal from Industrial Effluents. *Applied Surface Science.* 254, 3522-3530.

Dou, B., Dupont, V., Pan, W. and Chen, B. (2011). Removal of Aqueous Toxic Hg(II) by Synthesized TiO_2 Nanoparticles and TiO_2/Montmorillonite. *Chemical Engineering Journal*. 166, 631-638.

Dujardin, M.C., Caze, C. and Vroman, I. (2000). Ion-Exchange Resins Bearing Thiol Groups to Remove Mercury. Part 1: Synthesis and Use of Polymers Prepared from Thioester Supported Resin. *Reactive and Functional Polymers*. 43, 123-132.

Fábrega, F.d.M. and Mansur, M.B. (2007). Liquid-Liquid Extraction of Mercury(II) from Hydrochloric Acid Solutions by Aliquat 336. *Hydrometallurgy*. 87, 83-90.

Feltin, N. and Pileni, M.P. (1997). New Technique for Synthesizing Iron Ferrite Magnetic Nanosized Particles. *Langmuir*. 13, 3927-3933.

Galán, B., Castañeda, D. and Ortiz, I. (2005). Removal and Recovery of Cr(VI) from Polluted Ground Waters: A Comparative Study of Ion-exchange Technologies. *Water Research*. 39, 4317-4324.

Gao, J., Jiang, R., Wang, J., Wang, B., Li, K., Kang, P., Li, Y. and Zhang, X. (2011). Sonocatalytic Performance of Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$ in Organic Dye Degradation. *Chemical Engineering Journal*. 168, 1041-1048.

Gkika, E., Troupis, A., Hiskia, A. and Papaconstantinou, E. (2006). Photocatalytic Reduction of Chromium and Oxidation of Organics by Polyoxometalates. *Applied Catalysis B: Environmental*. 62, 28-34.

Gok, C. and Aytas, S. (2009). Biosorption of Uranium(VI) from Aqueous Solution Using Calcium Alginate Beads. *Journal of Hazardous Materials*. 168, 369-375.

Guettaï, N. and Amar, H.A. (2005). Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part II: Kinetics Study. *Desalination*. 185, 439-448.

Hu, J., Chen, G.H. and Irene, M.C.L. (2005). Removal and Recovery of Cr(VI) from Wastewater by Maghemite Nanoparticles. *Water Research*. 39, 4528-4536.

Hyeon, T., Lee, S.S., Park, J., Chung, Y. and Na, H.B. (2001). Synthesis of Highly Crystalline and Monodisperse Maghemite Nanocrystallites without a Size-Selection Process. *Journal American Chemical Society*. 123, 12798-12801.

Idris, A., Misran, E., Hassan, N., Abdul Jalil, A. and Seng, C.E. (2012). Modified PVA-Alginate Encapsulated Photocatalyst Ferro Photo Gels for Cr(VI) Reduction. *Journal of Hazardous Materials*. 227-228, 309-316.

Idris, A., Mohd Zain, N.A. and Suhaimi, M.S. (2008). Immobilization of Baker's Yeast Invertase in PVA-Alginate Matrix Using Innovative Immobilization Technique. *Process Biochemistry*. 43, 331-338.

Idris, A., Hassan, N., Mohd Ismail, N.S., Misran, E., Mohd Yusof, N., Ngomsik, A.F. and Bee, A. (2010). Photocatalytic Magnetic Separable Beads for Chromium (VI) Reduction. *Water Research*. 44, 1683-1688.

Idris, A., Hassan, N., Rashid, R. and Ngomsik, A.F. (2011). Kinetic and Regeneration Studies of Photocatalytic Magnetic Separable Beads for Chromium (VI) Reduction under Sunlight. *Journal of Hazardous Materials*. 186, 629-635.

Iwasaki, T., Kosaka, K., Yabuuchi, T., Watano, S., Yanagida, T. and Kawai, T. (2009). Novel Mechanochemical Process for Synthesis of Magnetite Nanoparticles Using Coprecipitation Method. *Advanced Powder Technology*. 20, 521-528.

Jeffrey, C.S., Wu and Chen,C.H. (2004). A Visible-Light Response Vanadium-Doped Titania Nanocatalyst by Sol-Gel Method. *Journal of Photochemical and Photobiology*. *A*. 163, 509-515.

Jing, L., Xu, Z., Shang, J., Sun, X., Cai, W. and Guo, H. (2002). The Preparation and Characterization of ZnO Ultrafine Particles. *Materials Science and Engineering*. A332, 356-361.

Jose, A.J., Wong, L.S., Merrington, J. and Bradley, M. (2005). Automated Image Analysis of Polymer Beads and Size Distribution. *Industrial and Engineering Chemistry Research.* 44, 8659-8662.

Kang, Y.S., Risbud, S., Rabolt, J.F. and Stroeve, P. (1996). Synthesis and Characterization of Nanometer-size Fe_3O_4 and γ-Fe_2O_3 Particles. *Chemistry of Materials*. 8, 2209-2211.

Kawahara, T., Yamada, K. and Tada, H. (2005). Visible Light Photocatalytic Decomposition of 2-Naphthol by Anodic-Biased α-Fe_2O_3 Film. *Journal of Colloid and Interface Science.* 294, 504-507.

Ketir, W., Bouguelia, A. and Trari, M. (2008). Photocatalytic Removal of M^{2+} (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Ag^{+}) Over New Catalyst $CuCrO_2$. *Journal of Hazardous Materials.* 158, 257-263.

Kim, C.S. and Yi, Y.S. (1999). Growth of Ultrafine Co-Mn Ferrite and Magnetic Properties by a Sol-Gel Method. *Journal of Applied Physics*. 85, 5223-5225.

Lai, J.I., Shafi, K.V.P.M., Ulman, A., Loos, K., Lee, Y., Vogt, T., Lee, W.L. and Ong, N.P. (2005) Controlling the Size of Magnetic Nanoparticles Using Pluronic Block Copolymer Surfactants. *Journal of Physical Chemistry B*. 109, 15-18.

Lee, T., Lim, H., Lee, Y. and Park, J.W. (2003). Use of Waste Iron Metal for Removal of Cr(VI) from Water. *Chemosphere.* 53, 479-485.

Lee, S.J., Jeong, J.R ., Shin, S.C., Kim, J. C. and Kim, J.D. (2004). Synthesis and Characterization of Superparamagnetic Maghemite, *Journal of Magnetism and Magnetic Materials*. 282, 147-150.

Lenzi, G.G., Fávero, C.V.B., Colpini, L.M.S., Bernabe, H., Baesso, M.L., Specchia, S. and Santos, O.A.A. (2011). Photocatalytic Reduction of Hg(II) on TiO_2 and Ag/TiO_2 Prepared by The Sol-Gel and Impregnation Methods. *Desalination*. 270, 241-247.

Levankumar, L., Muthukumaran, V. and Gobinath, M.B. (2009). Batch Adsorption and Kinetics of Chromium (VI) Removal from Aqueous Solutions by *Ocimum Americanum* L. Seed Pods. *Journal of Hazardous Materials*. 161, 709-713.

Li, H., Li, Z., Liu, T., Xiao, X., Peng, Z. and Deng L. (2008). A Novel Technology for Biosorption and Recovery Hexavalent Chromium in Wastewater by Bio-Functional Magnetic Beads. *Bioresource Technology*. 99, 6271-6279.

Liu, T.Y., Hu, S.H., Liu, K.H., Liu, D.M and Chen, S.Y. (2008). Study on Controlled Drug Permeation of Magnetic-Sensitive Ferrogels: Effect of Fe_3O_4 and PVA. *Journal of Controlled Release*. 126, 228-236.

Lloyd-Jones, P.J., Rangel-Mendez, J.R. and Streat, M. (2004). Mercury Sorption from Aqueous Solution by Chelating Ion Exchange Resins, Activated Carbon and A Biosorbent. *Process Safety and Environmental Protection*. 82B4, 301-31.

López-Muñoz, M.J., Aguado, J., Arencibia, A. and Pascual, R. (2011). Mercury Removal from Aqueous Solutions of $HgCl_2$ by Heterogeneous Photocatalysis with TiO_2. *Applied Catalysis B: Environmental*. 104, 220-228.

Lu, W., Shen, Y., Xie, A. and Zhang, W. (2010). Green Synthesis and Characterization of Superparamagnetic Fe_3O_4 Nanoparticles. Journal of Magnetism and Magnetic Materials. 322, 1828-1833.

Maity, D., Choo, S.G., Yi, J., Ding, J. and Xue, J.M. (2009). Synthesis of Magnetite Nanoparticles via A Solvent-Free Thermal Decomposition Route. *Journal of Magnetism and Magnetic Materials*. 321, 1256-1259.

Majidnia, Z. and Idris, A. (2015). Evaluation of Cesium Removal from Radioactive Waste Water Using Maghemite PVA-Alginate Beads. *Chemical Engineering Journal.* 262, 372-382.

Makovec, D., Košak, A., Žnidaršič, A. and Drofenik, M. (2005). The Synthesis of Spinel-Ferrite Nanoparticles using Precipitation in Microemulsions for Ferrofluid Applications. *Journal of Magnetism and Magnetic Materials*. 289, 32-35.

Manohar, D.M., Anoop Krishnan, K. and Anirudhan, T.S. (2002). Removal of Mercury(II) from Aqueous Solutions and Chlor-Alkali Industry Wastewater using 2-Mercaptobenzimidazole-Clay.

Martin, S.T., Morrison, C.L. and Hoffmann, M.R. (1994). Photochemical Mechanism of Size-Quantized Vanadium-Doped TiO_2 Particles. *Journal of Physical Chemistry*. 98, 13695-13704.

Massart, R. 1981. Preparation of Aqueous Magnetic Liquids in Alkaline and Acidic Media. *IEEE Transactions on Magnetics*. 17, 1247-1248.

Matlock, M.M., Howerton, B.S. and Atwood, D.A. (2001). Irreversible Precipitation of Mercury and Lead. *Journal of Hazardous Materials.* B84, 73-82.

Matthews, R.W. (1988). Kinetics of Phototcatalytic Oxidation of Organic Solutes Over Titanium Dioxide. *Journal of Catalysis*. 111, 264-272.

Mekatel, H., Amokrane, S., Bellal, B., Trari, M. and Nibou, D. (2012). Photocatalytic Reduction of Cr(VI) on Nanosized Fe_2O_3 Supported on Natural Algerian Clay: Characteristics, Kinetic and Thermodynamic Study. *Chemical Engineering Journal*. 202-202, 611-618.

Mercader-Trejo, F. E., Rodríguez de San Miguel, E. and de Gyves, J. (2009). Mercury(II) Removal using Polymer Inclusion Membranes Containing Cyanex 471X. *Journal of Chemical Technology and Biotechnology*. 84 (9). 1323-1330.

Meng, Y., Huang, X., Wu, Y., Wang, X and Qian, Y. (2002). Kinetic Study and Modeling on Photocatalytic Degradation of Para-Chlorobenzoate at Different Light Intensities. *Environmental Pollution*. 117, 307-313.

Mills, G. and Hoffmann, M.R. (1993). Photocatalytic Degradation of Pentachlorophenol on TiO_2 Particles: Identification of Intermediates and Mechanism of Reaction. *Environment Science and Technology*. 27, 1681-689.

Mohamed, R.M. and Aazam, E.S. (2012). Enhancement of Photocatalytic Activity of ZnO–SiO2 by Nano-Sized Ag for Visible Photocatalytic Reduction of Hg(II). *Desalination and Water Treatment.* 50, 140-146.

Mohapatra, P., Samantaray, S. K. and Parida, K. (2005). Photocatalytic Reduction of Hexavalent Chromium in Aqueous Solution Over Sulphate Modified Titania. Journal *of Photochemistry and Photobiology A: Chemistry*. 170 (2), 189-194.

Mornet, S., Vasseur, S., Grasset, F. and Duguet, E. (2004). Magnetic Nanoparticle Design for Medical Diagnosis and Therapy. *Journal of Materials Chemistry.* 35, 113-119.

Muthukrishnan, M. and Guha, B.K. (2008). Effect of pH on Rejection of Hexavalent Chromium by Nanofiltration. *Desalination*, 219, 171-178.

Navaro, R. R., Wada, S., and Tatsumi, K. (2005). Heavy metal precipitation by Polycation-Polyanion Complex of PEI and Its Phosphonomethylated Derivative. *Journal of Hazardous Materials*. 123, 203-209.

Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B. and Murugesan V. (2002). Solar/UV-Induced Photocatalytic Degradation of Three Commercial Textile Dyes. *Journal of Hazardous Materials*. B89, 303-317.

Ngomsik, A.F., Bee, A., Siaugue, J.M., Cabuil, V. and Cote, G. (2006). Nickel Adsorption by Magnetic Alginate Microcapsules Containing an Extractant. *Water Research*. 40, 1848-1856.

Ngomsik, A.F., Bee, A., Siaugue, J.M., Talbot, D., Cabuil, V. and Cote, G. (2009). Co(II) Removal by Magnetic Alginate Beads Containing Cyanex 272®. *Journal of Hazardous Materials*. 166, 1043-1049.

Nishio, Y., Yamada, A., Ezaki, K., Miyashita, Y., Furukawa, H. and Horie, K. (2004). Preparation and Magnetometric Characterization of Iron Oxide Containing Alginate-poly(vinyl alcohol) Networks. *Polymer*. 45, 7129-7136.

Nriagu, J.O. (1988). A Silent Epidemic of Environmental Metal Poisoning? *Environmental Pollution*. 50, 139-161.

Oster, J., Parker, J. and Brassard, L. (2001). Polyvinyl-alcohol-based Magnetic Beads for Rapid and Efficient Separation of Specific or Unspecific Nucleic Acid Sequences. *Journal of Magnetism and Magnetic Materials.* 225, 145-150.

Pal, B. and Sharon, M. (2002). Enhanced Photocatalytic Activity of Highly Porous ZnO Thin Films Prepared by Sol-Gel Process. *Materials Chemistry and Physics*. 76, 82-87.

Pan, S., Shen, H., Xu, Q., Luo, J. and Hu, M. (2012). Surface Mercapto Engineered Magnetic Fe_3O_4 Nanoadsorbent for The Removal of Mercury from Aqueous Solutions. *Journal of Colloid and Interface Science.* 365, 204-212.

Parham, H., Zargar, B. and Shiralipour, R. (2012). Fast and Efficient Removal of Mercury from Water Samples Using Magnetic Iron Oxide Nanoparticles Modified with 2-Mercaptobenzothiazole. . *Journal of Hazardous Materials*. 205-206, 94-100.

Pazouki, M. and Moheb. A. (2011). An Innovative Membrane Method for the Separation of Chromium Ions from Solutions Containing Obstructive Copper Ions. *Desalination*. 274, 246-254.

Pradhan, A., Jones, R.C., Caruntu, D., O'Connor,C.J and Tarr, M.A. (2008). Gold-Magnetite Nanocomposite Materials Formed via Sonochemical Methods. *Ultrasonics Sonochemistry*. 15, 891-897.

Ramadevi, A. and Srinivasan, K. (2004). Agricultural Solid Waste for The Removal of Inorganics: Adsorption of Mercury (II) from Aqueous Solution by Tamarind Nut Carbon. *Indian Journal of Chemical Technology*. 12, 407-412.

Reeves, P., Ohlhausen, R., Sloan, D., Pamplin, K., Scoggins, T., Clark, C., Hutchinson, B., Green, D., (1992). Photocatalytic Destruction of Organic Dyes in Aqueous TiO_2 Suspensions Using Concentrated Simulated and Natural Solar Energy. *Solar Energy*. 18 (6), 413-420.

Ritter, J.A. and Bibler, J.P. (1992). Removal of Mercury from Waste Water: Large-Scale Performance of An Ion Exchange Process. *Water Science & Technology*. 25 (3), 165-172.

Rocher, V., Siaugue, J.M., Cabuil, V. and Bee, A. (2008). Removal of Organic Dyes by Magnetic Alginate Beads. *Water Research*. 42, 1290-1298.

Rocher, V., Bee, A., Siaugue, J.M. and Cabuil, V. (2010). Dye Removal from Aqueous Solution by Magnetic Alginate Beads Crosslinked with Epichlorohydrin. *Journal of Hazardous Materials*. 178, 434-439.

Shafi, K.V.P.M., Ulman, A., Yan, X., Yang, N.L., Estournes, C., White, H. and Rafailovich, M. (2001). Sonochemical Synthesis of Functionalized Amorphous Iron Oxide Nanoparticles. *Langmuir*. 17, 5093-5097.

Shan, G.B., Xing,J.M., Luo,M.F., Liu, H.Z. and Chen, J.Y. (2003). Immobilization of *Pseudomonas delafieldii* with Magnetic Polyvinyl Alcohol Beads and Its Application in Biodesulfurization. *Biotechnology Letters*. 25, 1977-1981.

Shen, C., Wang, Y.J., Xu, J.H. and Luo, G.S. (2012). Facile Synthesis and Photocatalytic Properties of TiO_2 Nanoparticles Supported on Porous Glass Beads. *Chemical Engineering Journal.* 209, 478-485.

Smith, Y.R., Raj, K.J., Subramanian, V. (R). and Viswanathan, B. (2010). Sulfated Fe_2O_3-TiO_2 Synthesized from Ilmenite Ore: A Visible Light Active Photocatalyst. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 367, 140-147.

Skubal, L.R. and Meshkov, N.K. (2002). Reduction and Removal of Mercury from Water Using Arginine-Modified TiO2. *Journal of Photochemistry and Photobiology A: Chemistry*. 148, 211-214.

Soleimani, M., Mahmodi, M.S., Morsali, A., Khani, A. and Afshar, M.G. (2011). Using A New Ligand for Solid Phase Extraction of Mercury. *Journal of Hazardous Materials.* 189, 371-376.

Tavares, D.S., Lopes, C.B., Daniel-da-Silva, A.L., Duartea, A.C., Trindade, T. and Pereira, E. (2014). The Role of Operational Parameters On the Uptake of Mercury by Dithiocarbamate Functionalized Particles. *Chemical Engineering Journal.* 254, 559-570.

Tian, B., Li, C., Gu, F., Jiang, H., Hu, Y. and Zhang, J. (2009). Flame Sprayed V-Doped TiO_2 Nanoparticles with Enhanced Photocatalytic Activity Under Visible Light Irradiation. *Chemical Engineering Journal*. 151, 220-227.

Turchi, C.S. and Ollis, D.F. (1990). Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack. *Journal of Catalysis.* 122, 178-192.

Tuutijärvi, T., Lu, J., Sillanpää, M. and Chen, G. (2009). As(V) adsorption on maghemite nanoparticles. *Journal of Hazardous Materials.* 166, 1415-1420.

Ullah, R. and Dutta, J. (2008). Photocatalytic Degradation of Organic Dyes with Manganese-Doped ZnO Nanoparticles. *Journal of Hazardous Materials*. 156, 194-200.

Urgun-Demirtas, M., Benda, P.L., Gillenwater, P.S., Negri, M.C., Xiong, H. and Snyder, S.W. (2012). Achieving Very Low Mercury Levels in Refinery Wastewater by Membrane Filtration. *Journal of Hazardous Materials*. 215-216, 98-107.

Vijayakumar, R., Koltypin, Yu., Felner, I. and Gedanken, A. (2000). Sonochemical Synthesis and Characterization of Pure Nanometer-sized Fe_3O_4 Particles. *Materials Science and Engineering A*. 286, 101-105.

Wang, Z.H. and Zhuang, Q.Z. (1993). Photocatalytic Reduction of Pollutant Hg(II) on Doped WO_3 Dispersion. *Journal of Photochemistry and Photobiology A: Chemistry*. 75, 105-111.

Wang, Y.H., Lin, S.H. and Juang, R.S. (2003). Removal of Heavy Metal Ions from Aqueous Solutions using Various Low-Cost Adsorbents. *Journal of Hazardous Materials*. 102, 291-302.

Wong, E. T., Chan, K. H., Irfan, M. and Idris, A. (2014). Investigation of Cu(II) Removal by Cobalt-Doped Iron Oxide Captured in PVA-Alginate Beads. *Desalination and Water Treatment*. 1-12.

Wang, L., Wang, N., Zhu, L., Yu, H. and Tang, H. (2008). Photocatalytic Reduction of Cr(VI) Over Different TiO_2 Photocatalysts and the Effects of Dissolved Organic Species. *Journal of Hazardous Materials*. 152, 93-99.

Wu, W., He, Q. and Jiang, C. (2008). Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. *Nanoscale Research Letter*. 3, 397-311.

Xiong, C. and Yao, C. (2009). Synthesis, Characterization and Application of Triethylenetetramine Modified Polystyrene Resin in Removal of Mercury, Cadmium and Lead from Aqueous Solutions. *Chemical Engineering Journal*. 155, 844-850.

Xu, J., Yang, H., Fu, W., Du, K., Sui, Y., Chen, J., Zeng, Y., Li, M. and Zou, G. (2007). Preparation and Magnetic Properties of Magnetite Nanoparticles by Sol-Gel Method. *Journal of Magnetism and Magnetic Materials*. 309, 307-311.

Yang, L., Xiao, Y., Liu, S., Li, Y., Cai, Q., Luo, S. and Zeng, G. (2010). Photocatalytic Reduction of Cr(VI) on WO_3 Doped Long TiO_2 Nanotube Arrays in the Presence of Citric Acid. *Applied Catalysis B: Environmental*. 94, 142-149.

Yang. S., Jang, Y.H., Kim, C.H., Hwang, C., Lee, J., Chae, S., Jung, S. and Choi, M. (2010). A Flame Metal Combustion Method for Production of Nanoparticles. *Powder Technology*. 197, 170-176.

Yang, X., Ma, F., Li, K., Guo, Y., Hu, J., Li, W., Huo, M. and Guo, Y. (2010). Mixed Phase Titania Nanocomposite Co-Doped with Metallic Silver and Vanadium Oxide: New Efficient Photocatalyst for Dye Degradation. *Journal of Hazardous Materials*. 175, 429-438.

Yang, X., Li, Y., Lu, A., Yan, Y., Wang, C. and Wong, P.K. (2011). Photocatalytic Reduction of Carbon Tetrachloride by Natural Sphalerite under Visible Light Irradiation. *Solar Energy Materials & Solar Cells*. 95, 1915-1921.

Ying, X. and Fang, Z. (2006). Experimental Research on Heavy Metal Wastewater Treatment with Dipropyl Dithiophosphate. Journal *of Hazardous Materials*. 137 (3), 1636-1642.

Zhang, F.S., Nriagu, J.O. and Itoh, H. (2004). Mercury Removal from Water Using Activated Carbons Derived from Organic Sewage Sludge. *Water Research*. 39, 389-395.

Zhang, Y., Li, Q., Sun, L., Tang, R. and Zhai J. (2010). High Efficient Removal of Mercury from Aqueous Solution by Polyaniline/Humic Acid Nanocomposite. *Journal of Hazardous Materials*. 175, 404-409.

Zhou, J., Deng, C., Si, S., Shi, Y. and Zhao, X. (2011). Study on The Effect of EDTA on The Photocatalytic Reduction of Mercury onto Nanocrystalline Titania Using Quartz Crystal Microbalance and Differential Pulse Voltammetry. *Electrochimica Acta*. 56, 2062-2067.