COMBINED MAGHEMITE - TITANIA NANOPARTICLES EMBEDDED IN POLYVINYL ALCOHOL-ALGINATE BEADS FOR HEAVY METALS AND RADIOACTIVE IONS REMOVAL

ZOHREH MAJIDNIA

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Bioprocess Engineering)

Faculty of Chemical Engineering
UniversitiTeknologi Malaysia

JUNE 2015

To my parents, my husband; SayyedAli Yahyazadeh and beloved daughter, SayyedehTabassomYahyazadeh for their support and sacrifices.

ACKNOWLEDGEMENT

A multitude thanks to Allah Almighty for bestowing upon me this opportunity to embark on a journey that I ever dreamed. Indeed lessons have widened my horizons of knowledge and opened me to the new perspectives. In the name of Allah, most benevolent, ever-merciful, all praise to be Allah, Lord of all worlds.

First and foremost, I extend my gratitude to my supervisor Prof. Dr Ani Bte Idris for her enthusiasm, support and endless guidance towards my development as a researcher. Her advice and constant encouragement have given me motivation and valuable input throughout this study. I am lucky to have Prof who puts a tremendous amount of effort in providing opportunities for me to learn and grow. Her caring personality and expertise make my working experience with her very useful for my future research activities and career.

My deepest gratitude and sentiment also goes to my beloved mother and father for their blessings, patience and absolute love. The very special person, Sayyed Ali Yahyazadeh, who has given me constant encouragement and infinitive support from beginning to the end of this study, always take a care of my heart and spirit. I humbly express my deep sense of gratitude to my beloved daughter; SayyedehTabassomYahyazadeh, my sisters and brother for their great patience and being my internal support. May this thesis being an inspiration for your future and achievements.

My study would not have been possibly completed without the invaluable guidance and help from my kind and experienced supervisor. Her enthusiasm, guidance, suggestions and encouragement enabled me to handle this study with confident. May Allah reward her in the hereafter.

ABSTRACT

The presence of heavy metal ions in the environment is of major concern due to their toxicity to many life forms. Their toxicity affects the ecosystem and presents human health risk. Thus, wastes that contain heavy metals ionsmust be well treated so on to protect the people and environment.In this study, potential method for removal of heavy metal ions (such as: lead(II), cadmium(II), cesium(I), barium(II) and iodine(I) ions) from aqueous solution using combined maghemite (γ-Fe_2O_3) and titania (TiO_2) nanoparticles embedded in PVA-alginate beads were investigated. In addition, control experiments that involved the study of TiO_2 nanoparticles in polyvinyl alcohol (PVA)-alginate beads and γ-Fe_2O_3 nanoparticles in PVA-alginate beads were also performed. For this purpose, TiO_2 and Fe_2O_3 nanoparticles were synthesized by hydrothermal and co-precipitation method, respectively. The average size of TiO_2 and Fe_2O_3 nanoparticles was 15 and 9 nm, respectively. The nanoparticles and the beads were characterized by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) and transmission electron microscopy (TEM). These beads were used in batch sorption experiments for removal of heavy metal ions and iodine ions from aqueous solution under sunlight. Several operating conditions such as initial ion concentration, pH and contact time were investigated to evaluate their effects on the process. The results showed γ-Fe_2O_3 and TiO_2 PVA-alginate beads could remove Pb(II), Cd(II), Cs(I), Ba(II) and I(I) ions, with efficiency of around 100, 100, 93, 99 and 99%, respectively. Also, the combined γ-Fe_2O_3 and TiO_2 PVA-alginate beads showed best efficiency among three types of beads. After sunlight exposure, the beads were characterized by x-ray photoelectron spectroscopy (XPS) and energy-dispersive x-ray (EDX) system.The results revealed the mechanism for ton removal of photocatalytic process. These beads can be easily recovered from the aqueous solution and they can be recycled for a maximum of seven times before losing their original properties.

ABSTRAK

Kehadiran ion-ion logam berat dalam persekitaran adalah menjadi perhatian disebabkan oleh ketoksikannya terhadap banyak bentuk kehidupan. Ketoksikannya memberi kesan negatif kepada ekosistem dan kesihatan manusia. Oleh itu, sisa yang mengandungi ion logam berat mesti dirawat dengan baik untuk melindungi manusia dan alam sekitar. Dalam kajian ini, kaedah yang berpotensi untuk penyingkiran ion logam berat seperti: ion plumbum (II), kadmium(II), cesium(I), barium (II) dan iodin(I) dari larutan akueus dengan menggunakan gabungan maghemite (γ-Fe_2O_3) dan titania (TiO_2) nanopartikel terbenam dalam manik PVA-alginat telah disiasat. Di samping itu, eksperimen kawalan yang melibatkan nanopartikel TiO_2 dalam manik PVA-alginat dan nanopartikel γ-Fe_2O_3 dalam manik PVA-alginat juga telah dijalankan. Untuk tujuan ini, nanopratikel TiO_2 dan γ-Fe_2O_3 telah disintesis oleh kaedah hidroterma dan kaedah pemendakan. Saiz purata nanopartikel TiO_2 dan γ-Fe_2O_3 adalah masing-masing pada15 dan 9 nm. Nanopartikel dan manik telah dicirikan oleh belauan sinar-x (XRD), mikroskop imbasan elektron pancaran medan (FESEM), spektrofotometer inframerah transformasi fourier (FTIR) dan mikroskop transmisi elektron (TEM). Manik ini telah digunakan dalam eksperimen erapan kelompok untuk penyingkiran ion logam berat dan ion iodine daripada larutan akueus di bawah cahaya matahari. Beberapa keadaan operasi seperti kepekatan ion awal, pH dan masa sentuh telah disiasat untuk menilai kesan-kesannya terhadap proses. Keputusan menunjukkan bahawa manik maghemit dan titania PVA-alginat boleh menyingkir ion Pb(II) dan Cd(II) sebanyak 100%. Kadar penyingkiran ion Cs(I), Ba(II) dan I(I) masing-masing kira-kira 93, 99 dan 99%. Juga, gabungan γ-Fe_2O_3 dan TiO_2 PVA-alginat telah menunjukkan kecekapan terbaik di antara tiga jenis manik. Selepas proses cahaya matahari, manik-manik dicirikan oleh sistem spektroskopi fotoelektron sinar-x (XPS) dan analisis penyerakan tenaga sinar-x (EDX). Keputusan telah mendedahkan mekanisme penyingkiran setiap ion adalah proses fotopemangkinan. Manik-manik ini dapat dipulihkan secara mudah daripada penyelesaian akueus dan boleh digunakan semula untuk tempoh maksimum selama tujuh kali sebelum kehilangan sifat-sifat asal.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

r - Rate of Photo-reduction treatment
C - Concentration of the reactant
t - Illumination time
K_{LH} - removal coefficient
k_r - reaction rate constant
q_e - the equilibrium adsorption capacity of ions
q_{max} - the maximum capacity of adsorbent
k_F - Freundlich constant
λ - X-ray wavelength
δ - Average crystallite size of the particles
θ - Maximum(saturation) surface coverage
k - Sorption rate constant
m - Weight of sorbent
-

LIST OF ABBREVIATIONS

AAS - Atomic Absorption Spectrophotometer

Pb(II) - Lead ion

Cd (II) - Cadmium ion

Cs(I) - Cesium ion

Ba(II) - Barium ion

I(I) - Iodine ion

TiO_2 - Titanium dioxide

$FeCl_2$ - Ferrous chloride iron(II) chloride

$FeCl_3$ - Ferrous chloride iron(III) chloride

γ- Fe_2O_3 - Maghemite

Fe_3O_4 - Magnetite

ZnO - Zinc Oxide

WO_3 - Tungsten Oxide

$Fe(NO_3)_3$ - Iron (III) nitrate

FTIR - Fourier Transform Infrared Spectroscopy

FESEM - Field Emission Scanning Electron Microscope

XRD - X-ray Diffraction

TEM - Transmission electron microscopy

XPS - X-ray photoelectron spectroscopy

AAS - Atomic absorption spectrophotometer

L-H - Langmuir-Hinshelwood

CHAPTER 1

INTRODUCTION

1.1 Introduction

The toxic organic and inorganic materials found in soil, water and air via the photocatalyst approach is flexible enough to be applied for treatment to a diverse range of noxious and non-biodegradable compounds. This technique is reported to have the ability to treat and recover the pollutants from inaccessible areas such as in wastewater that have occurred recently. The damage that these pollutants may incur upon the environment and the economy can be contained by speedy mediation. Moreover, alternate power sources, such as solar power, may prove more successful in remote areas as opposed to the primary power supply. As a non-binding example, nanostructured photoactive films can be mentioned to improve light harvesting and charge separation, and to extend the photoactivity into the visible light region by altering the band structure of the materials, as well as to develop improved photoreactor units using solar light. There is a whole field of research dedicated to improving the efficacy of photocatalytic techniques and materials. Reaction temperatures are critical and photocatalysis should take place at normal environment temperatures.

1.2 Research background

Environmental pollutant by heavy metal ions has become a major issue and has sequentially received global attention. Metal ions contaminations are often found in industrial and urban aqueous surroundings and they are harmful to health and environment. Many metal ions such as Cr(VI), Pb(II), Zn (II), Hg(II), Ba(II) and Cd(II) can be found in waste water. Some heavy metals for instance, lead and cadmium are classified as toxic materials and their presence in large concentrations can create diseases such as anemia, brain damage, kidney damage and anorexia that they are dangerous for both adults and children (Agency, 1999).

Radioactive by-products of nuclear power generation and other nuclear technology, for instance, cesium, barium and iodine ions, put all life forms at risk, which is why they must be monitored, supervised and regulated by the government. The main difference between other toxic waste and radioactive waste is that the latter decays over a period of time, depending on the material's half-life which is why they must be treated with more caution. The period of time radioactive waste must be stored depends on the type of waste and radioactive isotopes. The time period that radioactive waste must be confined is unique to the half-life of the radioactive isotope which may fall anywhere between a number of days to millions of years. For example, iodine and barium have a half-life, $t_{1/2}$ = 8 and 10 days respectively, whereas ^{137}Cs has a half-life, $t_{1/2}$ = 30.17 years (Sato *et al.,* 2011). These radioactive ions are extremely hazardous as they can easily incorporate themselves into the biochemical processes of living organisms.

There are many treatments methods for removal of heavy metal ions and radioactive ions from aqueous solution. However, the selection is very much dependent on factors such as economic, surrounding and the chemical synthesis of the wastewater to be removed. The common treatment method includes chemical precipitation process, ion exchange, osmosis, reverse osmosis, nanofiltration, electrolydialysis, adsorption and solvent derivation. These methods have been used for large scale processes (Saeed *et al.,* 2005). Adsorption is a renowned equilibrium separation approach and has attained much success in water treatment applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances (Fu and Wang, 2011).

In recent years, easy treatment techniques were introduced without secondary waste such as photocatalytic process. Some of these technologies include materials that can be quickly reused on a large scale for industries. The pursuit for new methods for heavy metal removal has resulted in the use of biosorbents and magnetic nanoprticles. The use of biosorbents such as calcium alginate and PVA as encapsulation materials for nanoparticles such as maghemite is fast becoming attractive. The availability of carboxylate functional groups provide sufficient binding sites responsible for removal of heavy metals for example Cd(Il), Cu(lI) and Pb(I1) (Grant *et al.*, 1973). A significant amount of research has been conducted on the natural polymer, alginate for the elimination of toxic, heavy metal ions due to its cost-effectiveness and high capacity for adsorption. The carboxylate function of this polysaccharide is found to be responsible in capturing the heavy metals cations such as Cd(II), Pb(II), Cu(II).

Heterogeneous photocatalysis appears to be a very promising technique for the destruction of organic pollutants (Evgenidou *et al.*, 2006). It is generally known that photocatalytic reduction can be used for the removal of heavy metal ions by reducting them to their insoluble forms. In previous studies, the photoreduction of Cr(VI) ion (Chenthamarakshan *et al.*, 2000; Idris *et al.*, 2010; Khalil *et al.*, 1998), Hg(II) (Huang and Datye, 1996), Cd(II) (Chenthamarakshan *et al.*, 2000) and Ag(I) (Khalil *et al.*, 2002) were investigated. The reduction of organic compounds, such as benzoquinone (Richard, 1994), 4-nitrophenol (Brezová *et al.*, 1997) and hydrazine (Chatterjee, 2000) were also investigated. Semiconductor photocatalysts can be used to reduce transition metal ions by photocatalysis. In recent years, efforts have been devoted to the study of photochemical processes using semiconductor oxides, such as TiO_2, CdS, or ZnO, in heterogeneous system (Liu and Chiou, 2005).

Titanium oxide is the most common heterogeneous photocatalyst used in the photocatalysis process and it showed higher efficiency for the reduction and oxidation of organic and inorganic matters. However, commercial exploitation of this new technology is limited by the fact that titania is only active with UV light or radiation with wavelength below about 387nm, which makes it impossible to wider applications. Thus, there is a need to explore other possible photocatalysts for water treatment purposes by developing photocatalyst sensitive to sunlight (Hou *et al.*, 2006). Light can be understood as a chemical reagent that can convey about a wide variety of selective transformation, some of which are practically impossible to achieve using conventional reactant. An additional advantage is that light is even obtained at no cost when it comes from the sun.

γ-Fe_2O_3 is an intriguing n-type semiconducting material, with a band-gap of 2.2 eV, a suitable condidate for its application as a photocatalyst in the visible light region (Akhavan and Azimirad, 2009). Its photocatalytic nature has been thoroughly monitored in the photodegradation of organic pollutants, water splitting and semiconductor electrode applications. Additionally, by its narrow band-gap, it has found application as a sensitizer of TiO_2, which is another common photocatalyst. The irradiation with visible light, for the γ-Fe_2O_3 –TiO_2 composite film results in the excitation of γ-Fe_2O_3 valence electrons to leave holes and move to the conduction band. Using formation of the built-in field in Fe_2O_3–TiO_2 heterojunction, electrons in the valence bands of TiO_2 are driven into Fe_2O_3 (while photogenerated holes move into the valence band of TiO_2 in an opposite direction) (Akhavan and Azimirad, 2009). Additionally, the charge transport in the γ-Fe_2O_3 –TiO_2 plays an important role in improving photocatalytic efficiency as it improves the rate of electron-hole recombination (Akhavan and Azimirad, 2009).

1.3 Problem Statement

As an important semiconductor, TiO_2 has been extensively investigated for degrading organic pollutions and removing heavy metal ions from water due to its high photocatalytic activity, chemical or photocorrosion stability, low cost and safety to environment (Xu *et al.,* 2011). Due to the large bandgap (3.2 eV), TiO_2 is activated only by UV light, which constitutes only about 3-5% of the solar spectrum. This factor limits the use of the solar spectrum as a light source. Research regarding the photocatalytic activity of TiO_2 in the visible range is an important topic especially regarding its applications in energy storage and environmental pollution control. Therefore, TiO_2 nanoparticles were used for the removal of heavy metal ions under UV light as photocatalyst but its efficiency was rather low. TiO_2 nanoparticles only capable of removing Pb(II) from aqueous solution, with an efficiency of only 45% (Recillas *et al.*, 2009). From this standpoint, development of new approaches to produce TiO_2 with greater visible light adsorption is of great value (Collazzo *et al.*, 2012).

On the other hand, Maghemite nanoparticles are purposely incorporated with alginate and PVA to enhance the ability of bead as a biosorbent, in some case as a photocatalyst. Some studies showed the success of magnetic biosorbents using γ-Fe_2O_3 as magnetic nanoparticles embedded in alginate or chitosan in removal of Ni(II), Co(ll) and Au(lll). These ferrogels were also used for Cd(II) removal but the removal rate was slower where 99 % of Cd were removed after four hours illumination under sunlight and the removal was due to adsorption. Such magnetic biosorbents still require secondary treatment and require a longer duration. Similar experiments were performed for Pb(II) (Idris *et al.,* 2012) where the maghemite beads behave as adsorbent for Pb(II) removal. Recently, magnetic nanoparticles are embedded in biosorbents such as alginate and PVA to form ferrogels or beads and are used for removal of Cr(VI) in a photocatalysis process. Almost 100% of the Cr(VI) was reduced to Cr(III) within 30 minutes under sunlight and the beads can be reused at least five times (Idris *et al.*, 2012).

Besides Cr(VI), Cd(II) and Pb(II), these ferrogels have not been tested for other heavy metals such as: Cs(I), Ba(II) and I(I). Thus the challenge lies in identifying the possibility of removing heavy metals such as: Pb(II), Cd(II), Cs(I), Ba(II) and I(I) using photocatalysis process. Based on literature review the removal of the mentioned ions from aqueous solution by using the photocatalyst have yet to be explored. Thus, the possibility of improving the maghemite PVA-alginate gels by combining the TiO_2 and γ-Fe_2O_3 to enhance the efficiency of ions removal was investigated. It is hoped that the combination reduces the band gap of $TiO_{2,}$ thus improving its photocatalytic performance when applied under sunlight. Thus, in this study, maghemite and titania nanoparticles were embedded in PVA- alginate matrix in a bead form in order to enhance the photocatalytic removal of Pb, Cd, Cs, Ba and I from the aqueous solution under sunlight and to improve its reusability.

1.4 Research objective

The aim of the thesis is to combine both the maghemite and titanium oxide nanoparticles in PVA- alginate beads and investigate its effectiveness in removing heavy metal ions such as: Pb(II) and Cd(II) and radioactive ions such as: Cs(I), Ba(II) and I(I) via photocatalysis process. To attain the aim of study the following objectives need to be put in place.

1) To remove heavy metals such as: Pb(II) and Cd(II), Cs(I), Ba(II) and I(I) from aqueous solution using the synthesized maghemite and titanium oxide nanoparticles embedded in PVA-alginate beads.

2) To investigate the influence of pH, initial concentration of ions, temperature and ratio of maghemite and titanium oxide nanoparticles on the photocatalytic removal of mentioned heavy metal and radioactive ions.

3) To evaluate the kinetic models for the prepared photocatalyst.

4) To determine the mechanism of process for every ion removal.

5) To investigate the recycling and regeneration of beads for future use.

1.5 Scope of research

In order to achieve the objectives mentioned, the following need to be performed:

1) The titanium oxide nanoparticles and maghemite nanoparticles were synthesized by hydrothermal and coprecipitation methods respectively.
2) The nanoparticles were characterized by FESEM, FTIR, XRD and VSM.
3) The Fe_2O_3 coated with trisodiun citrate and TiO_2 nanoparticles prepared were then embedded in PVA and alginate in the form of beads.
4) Maghemite and titania PVA-alginate beads were characterized by FESEM, EDX, FTIR, XRD.
5) Photocatalytic experiments to remove heavy metal ions (Pb(II), Cd(II)) Ba(II)) and radioactive ions (Cs(I), Ba(II) and I(I)) from aqueous solution were performed. The influence of pH ($2<pH<12$), initial concentration (50, 100 and 200mg/L), temperature (25, 35 and 45°C) and ratio of TiO_2/ γ-Fe_2O_3 (1:1, 1:10 and 1:60) of solution on removal rate of heavy metals and radioactive ions were investigated.
6) The solution of heavy metal ions (Pb(II), Cd(II), Cs(I), Ba(II)) and iodine ions were prepared by using deionized water.
7) Control of experiments were performed: i) process under sunlight, ii) without sunlight, iii) using only maghemite beads and iv) using only titania beads.
8) The concentrations of heavy metal ions were measured by using AAS analysis and the concentration of iodine ion were measured by using ICP-MS.
9) Finally the recycling tests were performed for the various beads.
10) The kinetics of photoreduction activity for the various heavy metals and radioactive ions were also determined using first and second order model. The isotherm kinetic model was also applied.
11) The mechanisms of various metals removal were determined using XPS analysis.

The overall experimental approach is summarized in Figure 1.1.

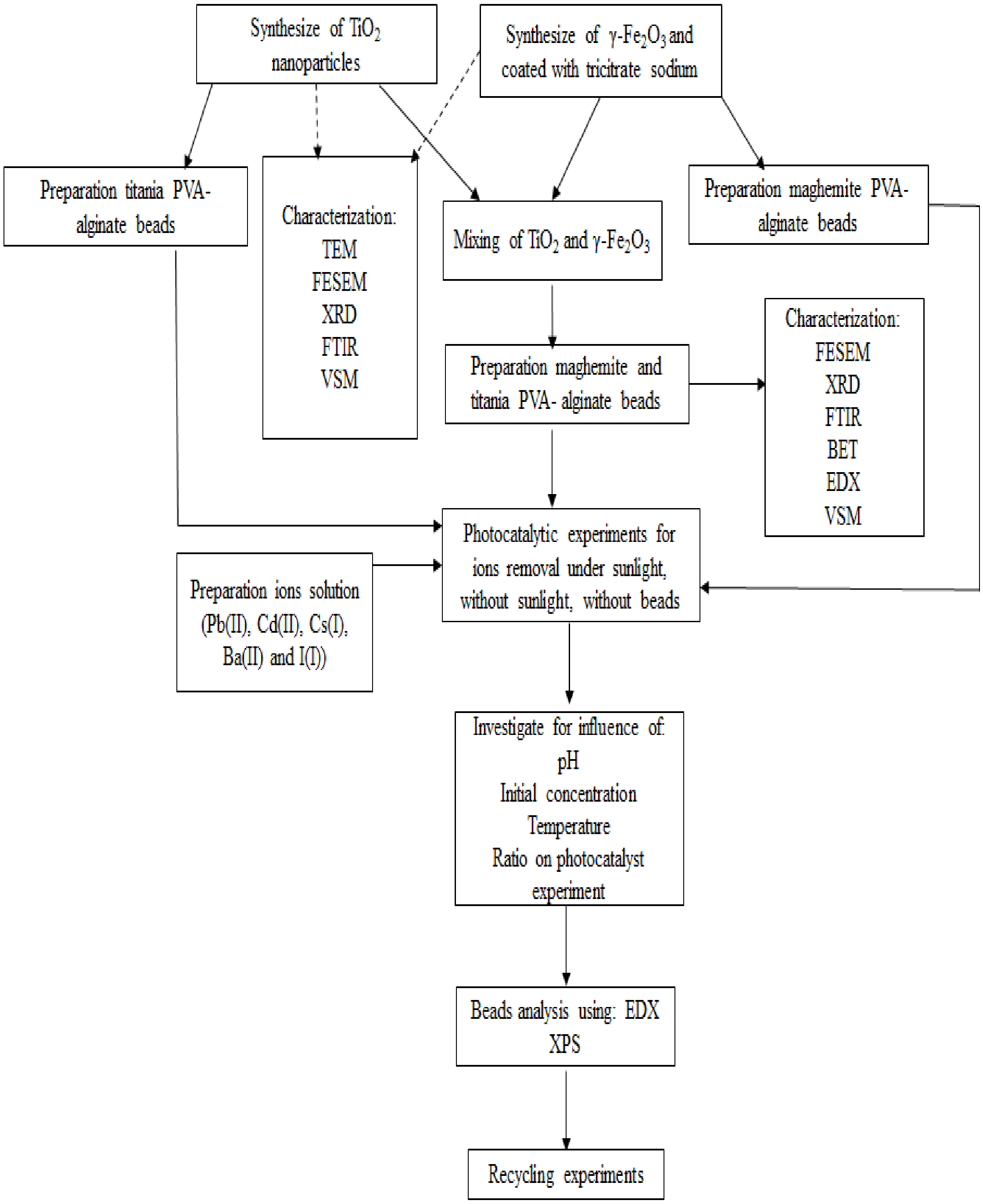

Figure 1.1 Schematic diagrams summarizing the overall experimental approach

1.6 Significance of study

The significance of the study is the combination of titanium oxide and maghemite nanoparticles in the PVA-alginate beads. The introduction of titanium oxide is believed to enhance the removal of heavy metals and radioactive ions from aqueous solution due to decrease the band gap of TiO_2 nanoparticles.

Previous studies (Idris *et al.*, 2010; Idris *et al.*, 2012) have shown that γ-Fe_2O_3 nanoparticles in PVA-alginate beads have been used successfully as adsorbents to remove Pb(II) and Cd(II). The γ-Fe_2O_3 nanoparticles in PVA- alginate beads were only used to reduce Cr(VI) to Cr(III) via photocatalyst. Thus, in this research an effort is made to improve the performance in removal of some heavy metal ions such as: Pb(II), Cd(II) and Ba(II) and radioactivity ions such as: Cs(I) and I(I) by using photo catalyst beads containing both TiO_2 and γ-Fe_2O_3 nanoparticles embedded in the PVA-alginate beads. In addition the optimum experimental conditions, kinetics of ions removal and reusability of maghemite and titania PVA - alginate beads were also determined.

1.7 Organization of thesis

This thesis is comprised of five chapters. In the first chapter, the background of research and problem statement are presented. The objectives of research, scope and significance of the study are also included in this chapter. Chapter two contains the literature review on the removal of heavy metal ions using different methods, ranging from the traditional to the state of the art technique. Also, semiconductor photocatalysts were introduced in this chapter. Chapter three is devoted to the detailed account of research methodology. Synthesis of maghemite and titanium oxide nanoparticles were explained in this chapter. The process for removal of heavy metal ions and iodine ion were explained in this chapter. Some operative parameters such as: pH, initial concentration, temperature and ratio of titania to maghemite nanoparticles used to determine maximum metal removal are detailed. Chapter four is dedicated to experimental results and discussions; which includes details for removal of every heavy metal ions and iodine ion, kinetic of removal and mechanism of process for every heavy metal ions and iodine ion. Finally, chapter five highlights the conclusions of this research and promising prospects are proposed.

REFRENCES

Agency, U.S.E.P. (1999). Integrated Risk Information System (IRIS)on Lead, National Center for Environmental Assessment. *Office of Research and Development*.

Akbarzadeh, A., Samiei, M. and Davaran, S. (2012). Magnetic Nanoparticles: Preparation, Physical Properties, and Applications in Biomedicine. *Nanoscale Research Letters.* 7, 144-157.

Akhavan, O. and Azimirad, R. (2009). Photocatalytic Caesium from Aqueous Solution on Binary Mixture of Iron Pillared Layered Montmorillonite and Goethite. *Chemical Engineering Journal*. 172, 230-236.

Allen, S.K.B. (2005). Decolourisation of Water/Wastewater using Adsorption. Journal of Chemical Technology and Metallurgy. 40, 175-192.

Alyüz, B. and Veli, S. (2009). Kinetics and Equilibrium Studies for the Removal of Nickel and Zinc from Aqueous Solutions by Ion Exchange Resins. *Journal of Hazardous Materials.* 167, 482-488.

Ambasta, R.K., Sharma, A. and Kumar, P. (2010). Nanoparticle Mediated Targeting of VEGFR and Cancer Stem Cells for Cancer Therapy. *Vascular Cell*. 3, 26-34.

Anpo, M. and Takeuchi, M. (2003). The Design and Development of Highly Reactive Titanium Oxide Photocatalysts Operating under Visible Light Irradiation. *Journal of Catalysis.* 216, 505-516.

Apiratikul, R., Marhaba, T.F., Wattanachira, S. and Pavasant, P. (2004). Biosorption of Binary Mixtures of Heavy Metals by Green Macro Alga, Caulerpa Lentillifera. *Journal of Science & Technology*. 26(1), 199-207.

Arteaga, K.A., Rodriguez, J.A. and Barrado, E. (2010). Magnetic Solids in Analytical Chemistry: A Review. *Analytica Chimica Acta*. 674, 157-165.

Augugliaro, V., Loddo, V., López-Muñoz, M.J., Márquez-Álvarez, C., Palmisano, G., Palmisano, L. and Yurdakal, S. (2009). Home Prepared Anatase, Rutile, and Brookite TiO_2 for Selective Photocatalytic Oxidation of 4-Methoxybenzyl Alcohol in Water: Reactivity and ATR-FTIR Study. *Photochemical and Photobiological Sciences*. 8, 663-669.

Bayat, A.E., Junin, R., Samsuri, A., Piroozian, A. and Hokmabadi, M. (2014). Impact of Metal Oxide Nanoparticles on Enhanced Oil Recovery from Limestone Media at Several Temperatures. *Energy Fuels.* 28, 6255-6266.

Bayülken, S., Başçetin, E., Güçlü, K. and Apak, R. (2011). Investigation and Modeling of Cesium(I) Adsorption by Turkish Clays: Bentonite, Zeolite, Sepiolite, and Kaolinite. *Environmental Progress & Sustainable Energy*. 30, 70-80.

Bee, A. and Chin, I.I.Y. (2007). Synthesis and Characterization of Magnetic Iron Oxide Nanoparticles via w/o Microemulsion and Massart's Procedure. *Journal of Materials Processing Technology*. 191, 235-237.

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

Bereket, G., Arog, A.Z., Özel, M.Z. (1997). Removal of Pb(II) , Cd(II) , Cu(II) , and Zn(II) from Aqueous Solutions by Adsorption on Bentonite. *Journal of Colloid and Interface Science*. 187, 338-343.

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 od Molecular Catalysis A.* 180, 193-200.

Bolto, B., Tran, T., Hoang, M. and Xie, Z. (2009). Crosslinked Poly(vinyl alcohol) Membranes. *Progress in Polymer Science*. 34, 969-981.

Brezová, V., Blažková, A., Šurina, I. and Havlínová, B. (1997). Solvent Effect on the Photocatalytic Reduction of 4-nitrophenol in Titanium Dioxide Suspensions. *Journal of Photochemistry and Photobiology A: Chemistry.* 107, 233-237.

Bruggen, B.V.D. and Vandecasteele, C.V. (2002). Membrane Filtration: Overview of Process Evolutions in Seawater Desalination. *Desalination*. 143, 207-218.

Byrappa, K. and Adschiri, T. (2007). Hydrothermal Technology for Nanotechnology. *Progress in Crystal Growth and Characterization of Materials*. 53, 117-166.

Castillo, S.J., Sotelo-Lerma, M., Zingaro, R.A., RamõÂrez-Bon, R., Espinoza-Beltran, F.J., Guillemette, R. and DomõÂnguez, M.A. (2001). ZnO/CdS

Bilayers Prepared by Concurrent Deposition from a Chemical Bath. *Journal of Physics and Chemistry of Solids*. 62, 1069-1073.

Caterina, G.C.M., Netto, H.E.T. and Andrade, L.H. (2013). Superparamagnetic Nanoparticles as Versatile Carriers and Supporting Materials for Enzymes. *Journal of Molecular Catalysis B: Enzymatic*. 85-86, 71-92.

Chang, Q. and Wang, G. (2007). Study on the Macromolecular Coagulant PEX Which Traps Heavy Metals. *Chemical Engineering Science.* 62, 4636-4643.

Chang, Q., Zhang, M. and Wang, J. (2009). Removal of Cu^{2+} and Turbidity from Wastewater by Mercaptoacetyl Chitosan. *Journal of Hazardous Materials.* 169, 621-625.

Chang, Y.C., Chang, S.W. and Chen D.H.(2006). Magnetic Chitosan Nanoparticles: Studies on Chitosan Binding and Adsorption of Co(II) Ions. *Reactive and Functional Polymer.* 66,335-341.

Chatterjee, D. (2000). Photocatalytic Reduction of Hydrazine to Ammonia Catalysed by $[RuIII(edta)(H_2O)]^-$ Complex in a Pt/TiO_2 Semiconductor Particulate System. *Journal of Molecular Catalysis A: Chemical*. 154, 1-3.

Chen, A., Zeng, G., Chen, G., Hu, X., Yan, M., Guan, S., Xie, G. (2012). Novel Thiourea-Modified Magnetic Ion-Imprinted Chitosan/TiO_2 Composite for Simultaneous Removal of Cadmium and 2,4-Dichlorophenol. *Chemical Engineering Journal*. 191, 85-94.

Chen, C., Hu, J., Shao, D., Li, J. and Wang, X. (2009). Adsorption Behavior of Multiwall Carbon Nanotube/Iron Oxide Magnetic Composites for Ni(II) and Sr(II). *Journal of Hazardous Materials*. 164, 923-928.

Chen, F., Shi, R., Xue, Y., Chen, L. and Wan, Q.H. (2010). Templated Synthesis of Monodisperse Mesoporous Maghemite/Silica Microspheres for Magnetic Separation of Genomic DNA. *Journal of Magnetism and Magnetic Materials*. 322, 2439-2445.

Chen, G. (2004). Electrochemicals Technologies in Wastewater Treatment. *Separation and Purification Technology*. 38, 11-41.

Chen, X. and Mao, S.S. (2007). Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chemical reviews.* 107, 2891-2959.

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.

Chenthamarakshan, C.R., Rajeshwar, K. and Wolfrum, E.J. (2000). Heterogeneous Photocatalytic Reduction of Cr(VI) in UV-Irradiated Titania Suspensions: Effect of Protons, Ammonium Ions, and Other Interfacial Aspects. *Langmuir*. 16, 2715-2721.

Chenthamarakshan, C.R., Yang, H., Ming, Y. and Rajeshwar, K. (2000). Photocatalytic reactivity of zinc and cadmium ions in UV-irradiated titania suspensions. *Journal of Electroanalytical Chemistry*. 494, 79-86.

Chin, A.B. and Yaacob, I.I. (2007). Synthesis and Characterization of Magnetic Iron Oxide Nanoparticles via w/o Microemulsion and Massart's Procedure. *Journal of Materials Processing Technology*. 191, 235-237.

Coey, J.M.D., Khalafalla, D. (1972). Superparamagnetic γ-Fe_2O_3. *physica status solidi*. 11, 229-241.

Collazzo, G.C., Foletto, E.L., Jahn, S. L. and Villetti, M.A. (2012). Degradation of Direct Black 38 Dye under Visible Light and Sunlight Irradiation by N-doped Anatase TIO_2 as Photocatalyst. *Journal of Environmental Management*. 98, 107-111.

Colombo, M., Romero, S.C., Casula, M.F., Gutiérrez, L., Morales, M.P., Böhm, I.B., Heverhagen, J.T., Prosperi, D., Parak, W.J. (2012). Biological Applications of Magnetic Nanoparticles,. *Chemical Society Reviews.* 41, 4306-4334.

Cong, Y., Li, Z., Zhang, Y., Wang, Q. and Xu, Q. (2012). Synthesis of Fe_2O_3/TiO_2 Nanotube Arrays for Photoelectro Fenton Degradation of Phenol. *Chemical Engineering Journal.* 191, 356-363.

Crini, G.(2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*. 97, 1061-1085.

Dabrowski, A. (2001). Adsorption from Theory to Practice. *Advances in Colloid and Interface Science*. 93, 135-224.

Dalrymple, O.K., Stefanakos, E., Trotz, M.A. and Goswami, D.Y. (2010). A Review of the Mechanisms and Modeling of Photocatalytic Disinfection. *Applied Catalysis B: Environmental.* 98, 27-38.

Delle, S.A. (2001). Factors Affecting Sorption of Organic Compound in Natural Sorbent/ Water System and Coefficient for Selected Pollutants. A Review. *Journal of Physical and Chemical Reference Data.* 30, 187-439.

Dhakal, R.P., Ghimire, K.N., Inoue, K., Yano, M. and Makino, K. (2005). Acidic Polysaccharide Gels for Selective Dsorption of Lead(II) Ion. *Separation and Purification* Technology. 42, 219-225.

Drbohlavova, J., Hrdy, R., Adam, V., Kizek, R., Schneeweiss, O. and Hubalek, J. (2009). Preparation and Properties of Various Magnetic Nanoparticles. *Sensors*. 9, 2352-2362.

Dultz, S., Riebe, B. and Bunnenberg, C. (2005). Temperature Effects on Iodine Adsorption on Organo-clay minerals: II. Structural Effects. *Applied Clay Science.* 28, 17-30.

Dumat, C., Quiquampoix, H. and Staunton, S. (2000). Adsorption of Cesium by Synthetic Clay−Organic Matter Complexes: Effect of the Nature of Organic Polymers. *Environmental Science Technology*. 34, 2985-2989.

Dwivedi, C., Kumar, A., Juby, K.A., Kumar, M., Wattal, P.K. and Bajaj, P.N. (2012). Preparation and Evaluation of Alginate-Assisted Spherical Resorcinol–Formaldehyde Resin Beads for Removal of Cesium from Alkaline Waste. *Chemical Engineering Journal*. 200-202, 491-498.

El-Naggar, I.M., Zakaria, E.S., Ali, I.M., Khalil, M. and El-Shahat, M.F. (2012). Kinetic Modeling Analysis for the Removal of Cesium Ions from Aqueous Solutions using Polyaniline Titanotungstate. *Arabian Journal of Chemistry*. 5, 109-119.

El Samrani, B.S.L. and Villiéras, F. (2008). Chemical Coagulation of Combined Sewer Overflow: Heavy Metal Removal and Treatment Optimization. *Water Research*. 42, 951-960.

Evgenidou, E., Konstantinou, I., Fytianos, K. and Albanis, T. (2006). Study of the Removal of Dichlorvos and Dimethoate in a Titanium Dioxide Mediated Photocatalytic Process Through the Examination of Intermediates and the Reaction Mechanism. *Journal of Hazardous Materials B.* 137, 1056-1064.

Faghihian, H., Moayed, M., Firooz, A. and Iravani, M. (2013). Evaluation of a New Magnetic Zeolite Composite for Removal of Cs^+ and Sr^{2+} from Aqueous Solutions: Kinetic, Equilibrium and Thermodynamic Studies. *Comptes Rendus Chimie*. 17(2), 108-117.

Foulkes, E.C. (1987). Interactions between Metals in Rat Jejunum: Implications on the Nature of Cadmium Uptake. *Toxicology*. 37, 117-125.

Fu, F. and Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters: A review. *Journal of Environmental Management*. 92, 407-418.

Fujishima, A., Rao, T.N. and Tryk, D.A. (2000). Titanium Dioxide Photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews.* 1, 1-21.

Ghaemi, A., Mostaedi, M.T. and Maragheh, M.G. (2011). Characterizations of Strontium(II) and Barium(II) Adsorption from Aqueous Solutions using Dolomite Powder. *Journal of Hazardous Materials.* 190, 916-921.

Grant, G.T., Morris, E.R., Rees, D.A., Smith, P.C.J. and Thom, D. (1973). Biological Interactions between Polysaccharides and Divalent Cations: The Egg-box Model. *FEBS Letter*. 32, 1021-1026.

Grebenyuk, V.D., Sorokin, G.V., Verbich, S.V., Zhiginas, L.H., Linkov, V.M., Linkov, N.A. and Smit, J.J. (1996). Combined Sorption Technology of Heavy Metal Regeneration from Electroplating Rinse Waters. *Water SA.* 22, 381-384.

Guettai, N., & Amar, H. A. (2005a). Photocatalytic Oxidation of Methyl Orange in Presence of Titanium Dioxide in Aqueous Suspension. Part I: Parametric Study. *Desalination*, 185, 427–437.

Gurboga, G. and Tel, H. (2005). Preparation of TiO_2-SiO_2 Mixed Gel Spheres for Strontium Adsorption. *Journal of Hazardeus Matererial*. 120, 135-142.

Gurboga, G., Tel, H. and Altas, Y. (2006). Sorption Studies of Cesium on TiO_2-SiO_2 Mixed Gel Spheres. *Separation and Purification Technology*. 47, 96-104.

Hamadanian, M. and Jabbari, V. (2014). Improved Conversion Efficiency in Dye-Sensitized Solar Cells Based on Electrospun TiCl4-Treated TiO_2 Nanorod Electrodes. *International Journal of Green Energy*. 11, 364-375,

Herrmann, J.M. (1999). Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants. *Catalysis Today*. 53, 115-129.

Ho, Y.S. and McKay, G. (1999). The Sorption of Lead(II) Ions on Peat. *Water Research*, 33, 585-587.

Hou, I.R., Yuan, C.Z. and Peng, Y. (2006). Preparation and Photocatalytic Property of Sunlight -driven Photocatalyst $Bi_{38}ZnO_{58}$. *Journal of Molecular Catalysis A: Chemical*. 252, 132-135.

Huang, E.T.M. and Datye, A.K. (1996). Removal of Silver in Photographic Processing Waste by TiO_2-based Photocatalysis. *Environmental Science Technology*. 30, 3084-3088.

Idris, A., Hassan, N., Ismail, N.S.M., Misran, E., Yusof, N.M., 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.

Idris, A., Ismail, N.S.M., Hassan, N., Misran, E. and Ngomsik, A.F. (2012). Synthesis of Magnetic Alginate Beads Based on Maghemite Nanoparticles for Pb(II) Removal in Aqueous Solution. *Journal of Industrial and Engineering Chemistry*. 18(5), 1582-1589.

Idris, A., Misran, E. and Yusof, N.M. (2012). Photocatalytic Reduction of Cr(VI) by PVA-Alginate Encapsulated γFe_2O_3 Magnetic Beads using Different Types of Illumination Lamp and Light. *Journal of Industrial and Engineering Chemistry*. 18(6), 2151-2156.

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

Iqbal, M., Saeed, A. and Zafar, S.I. (2009). FTIR Spectrophotometry, Kinetics and Desorption Isotherms Modeling, Ion Exchange, and EDX Analysis for Understanding the Mechanism of Cd^{+2} and Pb^{+2} Removal by Mango Peel Waste. *Journal of Hazardous Materials*. 164, 161-171.

Ishibashi, K.I., Watanabe, A.F.T. and Hashimoto, K. (2000). Detection of Active Oxidative Species in TiO_2 Photocatalysis using the Fluorescence Technique. *Electrochemistry Communications*. 2, 207-210.

Itoi, S., Nakamura, I. and Kawahara, T. (1980). Electrodialytic Recovery Process of Metal Finishing Wastewater. *Desalination.* 32, 383-389.

Ivanets, A.I., Kitikova, N.V., Shashkova, I.L., Oleksiienko, O.V., Levchuk, I. and Sillanpää, M. (2014). Removal of Zn^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} Ions from Aqueous Solutions using Modified Phosphate Dolomite. *Journal of Environmental Chemical Engineering*. 2, 981-987.

Jamalluddin, N.A. and Abdullah, A.Z. (2011). Reactive Dye Degradation by Combined Fe(III)/TiO_2 Catalyst and Ultrasonic Irradiation: Effect of Fe(III) Loading and Calcination Temperature. *Ultrasonics Sonochemistry*. 18, 669-678.

Janssen, L.J.J. and Koene, L. (2002). The Role of Electrochemistry and Electrochemical Tchnology in Environmental Protection. *Chemical Engineering Journal*. 87, 135-146.

Jeong, Y., Fan, M., Singh, S.,Chuang, C.L., Saha, B. and Leeuwen, J.H.V. (2007). Evaluation of Iron Oxide and Aluminum Oxide as Potential Arsenic(V) Adsorbents. *Chemical Engineering and Processing*. 46, 1030-1039.

Jia, H., Xu, H., Hu, Y., Tang, Y. and Zhang, L. (2007). TiO_2@CdS core–shell Nanorods Films: Fabrication and Dramatically Enhanced Photoelectrochemical Properties. *Electrochemistry Communications*. 9, 354-360.

Jia, L., Enzan, C., Haijia, S. and Tianwei, T. (2011). Biosorption of Pb^{2+} with Modified Soybean Hulls as Absorbent. *Chinese Journal of Chemical Engineering*. 19, 334-339.

Jin, Q., Fujishima, M. and Tada, H. (2011). Visible Light Active Iron Oxide Modified Anatase Titanium(IV) Dioxide. *Journal of Physical Chemistry C.* 115, 6478-6483.

Joseph, K., Kutty, K.V.G., Chandramohan, P. and Rao, P.R.V. (2009). Studies on the Synthesis and Characterization of Cesium Containing Iron Phosphate Glasses. *Journal of Nuclear Materials.* 384, 262-267.

Kabra, D., Song, M.H., Wenger, B., Friend, R.H. and Snaith, H.J. (2008). High Efficiency Composite Metal Oxide-Polymer Electroluminescent Devices: A Morphological and Material Based Investigation. *Advanced Materials.* 20, 3447-3452.

Kang, S.Y., Lee, J.U., Moon, S.H., Kim, K.W. (2004). Competitive Adsorption Characteristics of Co^{2+}, Ni^{2+}, and Cr^{3+} by IRN-77 Cation Exchange Resin in Synthesized Wastewater. *Chemosphere.* 56, 141-147.

Kaplan, D.I., Serne, R.J., Parker, K.E. and Kutnyakov, I.V. (2000). Iodide Sorption to Subsurface Sediments and Illitic Minerals. *Environmental Science Technology*. 34, 399-405.

Karamanis, D. and Assimakopoulos, P. A. (2007). Efficiency of Aluminum-pillared Montmorillonite on the Removal of Cesium and Copper from Aqueous Solutions. *Water Research*. 41, 1897-1906.

Karasyova, O.N., Ivanova, L.I., Lakshtanov, L.Z. and Lövgren, L. (1999). Strontium Sorption on Hematite at Elevated Temperatures. *Journal of Colloid and Interface Science*. 220, 419-428.

Kasuga, T., Hiramatsu, M., Hoson, A., Sekino, T. and Niihara, K. (1998). Formation of Titanium Oxide Nanotube. *Langmuir*. 14, 3160-3163.

Kentjono, L., Liu, J.C., Chang, W.C. and Irawan, C. (2010). Removal of Boron and Iodine from Optoelectronic Wastewater using Mg–Al (NO_3) Layered Double Hydroxide. *Desalination*. 262, 280-283.

Khalil, L.B., Mourad, W.E. and Rophael, M.W. (1998). Photocatalytic Reduction of Environmental Pollutant Cr(VI) over Some Semiconductors under UV/visible Light Illumination. *Applied Catalysis B: Environmental*. 17, 267-273.

Khalil, L.B., Rophael, M.W. and Mourad, W.E. (2002). The Removal of the Toxic Hg(II) Salts from Water by Photocatalysis. *Applied Catalysis B: Environmental*. 36, 125-130.

Khraisheh, M.A.M., Al-degs, Y.S. and Mcminn, W.A.M. (2004). Remediation of Wastewater Containing Heavy Metals using Raw and Modified Diatomite. *Chemical Engineering Journal*. 99, 177-184.

Kim, S.J., LEE, E.G., Park, S.D., Jeon, C.J., Cho, Y.H., Rhee, C.K. and Kim, W.W. (2001). Photocatalytic Effects of Rutile Phase TiO_2 Ultrafine Powder with High Specific Surface Area Obtained by a Homogeneous Precipitation Process at Low Temperatures. *Journal of Sol-Gel Science and Technology*. 22(1-2), 63-74.

Kim, T.K., Lee, M.N., Lee, S.H., Park, Y.C., Jung, C.K., Boo, J.H. (2005). Development of Surface Coating Technology of TiO_2 Powder and Improvement of Photocatalytic Activity by Surface Modification. *Thin Solid Films*. 475, 171-177.

Kontos, A.I., Likodimos, V., Stergiopoulos, T., Tsoukleris, D.S. and Falaras, P. (2009). Self-organized Anodic TiO_2 Nanotube Arrays Functionalized by Iron Oxide Nanoparticles. *Chemistry of Materials*. 21, 662-672.

Kuang, S., Yang, L., Luo, S., and Cai, Q. (2009). Fabrication, Characterization and Photoelectrochemical Properties of Fe_2O_3 Modified TiO_2 Nanotube Arays. *Applied Surface Science*. 255, 7385-7388.

Kumaresan, L., Mahalakshmi, M., Palanichamy, M. and Murugesan, V. (2010). Synthesis, Characterization, and Photocatalytic Activity of Sr^{2+} Doped TiO_2 Nanoplates. *Industrial and Engineering Chemistry Research.* 49, 1480-1485.

Kurniawan, T.A., Chan, G.Y.S., Lo, W. and Babel, S. (2006). Comparisons of Low Cost Adsorbents for Treating Wastewaters Laden with Heavy Metals,. *Science of the Total Environment*. 366, 409-426.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.H. and Babel, S. (2006). Physico–chemical Treatment Techniques for Wastewater Laden with Heavy Metals. *Chemical Engineering Journal.* 118(1-2), 83-98.

Lane, R.E. (1949). Care of the Lead Worker. *PubMed.* 6, 125-143.

Lansdown, A.B. and Sampson, B. (1996). Dermal Toxicity and Percutaneous Absorption of Cadmium in Rats and Mice. *PubMed.* 46, 549-555.

Lee, S. Y. and Park, S. J. (2013). TiO_2 Photocatalyst for Water Treatment Applications. *Journal of Industrial and Engineering Chemistry, 19,* 1761-1769.

Li, X.S., Zhu, G.T., Luo, Y.B., Yuan, B.F. and Feng, Y.K. (2013). Synthesis and Applications of Functionalized Magnetic Materials in Sample Preparation,. *TrAC Trends in Analytical Chemistry.* 45, 233-247.

Lin, Q., Wang, Q., Duan, Y., Wei, X., Wu, G., Luo, Y. and Xie, Q. (2013). Removal of Cu(II), Cr(III), and Cr(VI) from Aqueous Solution using a Novel Agricultural Waste Adsorbent. *Separation Science and Technology*. 48(18), 2843-2851.

Liu, H., Shon, H.K., Sun, X., Vigneswaran, S. and Nand, H. (2011). Preparation and Characterization of Visible Light Responsive Fe_2O_3–TiO_2 Composites. *Applied Surface Science.* 257, 5813-5819.

Liu, H.L. and Chiou, Y.R. (2005). Optimal Decolorization Efficiency of Reactive Red 239 by UV/TiO_2 Photocatalytic Process Coupled with Response Surface Methodology. *Chemical Engineering Journal*. 112, 173-179.

Long, H., Wu, P. and Zhu, N. (2013). Evaluation of Cs^+ rRemoval from Aqueous Solution by Adsorption on Ethylamine-modified Montmorillonite. *Chemical Engineering Journal*. 225, 237-244.

Madrakian, T., Afkhami, A., Zolfigol, M.A., Ahmadi, M. and Koukabi, N. (2012). Application of Modified Silica Coated Magnetite Nanoparticles for Removal of Odine from Water Samples. *Nano-Micro Letters.* 4, 57-63.

Majeda, A.M., Khraisheh, Y.S., Wendy, A.D. and Mcminn, A.M. (2004). Remediation of Wastewater Containing Heavy Metals using Raw and Modified Diatomite. *Chemical Engineering Journal.* 99, 177-184.

Manolopoulou, M., Vagena, E., Stoulos, S., Ioannidou, A. and Papastefanou, C. (2011). Radioiodine and Radiocesium in Thessaloniki, Northern Greece due to the Fukushima Nuclear Accident. *Journal of Environmental Radioactivity.* 102, 796-797.

Matos, J., Laine, J. and Herrmann, J.M. (2001). Effect of the Type of Activated Carbons on the Photocatalytic Degradation of Aqueous Organic Pollutants by UV-Irradiated Titania. *Journal of Catalysis.* 200, 10-20.

Mishra, S.P. and Singh, V.K. (1998). Ion part X. Aqueous Oxide Exchangers in Radioactive Waste Management Removal of Barium Ions from Solutions by Hydrous Bismuth using Radiotracer Technique. *Applied Radiation and Isotopes.* 49, 43-48.

Mishra, S.P. and Singh, V.K. (1995). Radiotracer Technique in Adsorption Study XIII. Adsorption of Barium and Strontium Ionsonchromium(IV) Oxide Powder. *Applied Radiation and Isotopes.* 46, 847-853.

Mishra, S.P. and Tiwary, D. (1999). Ion Exchangers in Radioactive Waste Management. Part XI. Removal of Barium and Strontium Ions from Aqueous Solutions by Hydrous Ferric Oxide. *Applied Radiation and Isotopes.* 51, 359-366.

Moawed, E.A., Abulkibash, A.B. and El-Shahat, M.F. (2015). Synthesis and Characterization of Iodo polyurethane Foam and Its Application in Removing of Aniline Blue and Crystal Violet Fromlaundry Wastewater. *Journal of Taibah University for Science*. 9, 80-85.

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

Mostaedi, M.T., Ghaemi, A., Ghassabzadeh, H. and Maragheh, M.G. (2011). Removal of Strontium and Barium from Aqueous Solutions by Adsorption onto Expanded Perlite. *Canadian Journal of Chemecial Engineering*. 89, 1247-1254.

Murruni, L., Conde, F., Leyva, G. and Litter, M.I. (2008). Photocatalytic Reduction of Pb(II) over TiO_2: New Insights on the Effect of Different Electron Donors. *Applied Catalysis B: Environmental.* 84(3), 563-569.

Murruni, L., Leyva, G. and Litter, M.I. (2007). Photocatalytic removal of Pb(II) over TiO_2 and Pt–TiO_2 powders. *Catalysis Today.* 129,125-137.

Mutzhas, M.F., Holzle, E., Hofmann, C. and Plewig, G. (1981). A New Apparatus with High Radiation Energy between 320-460 nm: Physical Description and Dermatological Applications. *Journal of Investigative Dermatology*. 76, 42-47.

Myung, N.V., Park, H., Ayala, P., Deshusses, M.A., Mulchandani, A. and Choi, H. (2008). Electrodeposition of mMaghemite(Fe_2O_3) Nanoparticles. *Chemical Engineering Journal.* 139, 208-212.

Naja, G.m. and Volesky, B. (2009). Toxicity and Soureces of Pb, Cd, Hg, Cr, As and Radionuclides in the Environment. *Heavy Metals in the Environment.*

Narasimhan, B.R.V., Prabhakara, S., Manoharb, P. and Gnanamb, F.D. (2002). Synthesis of Gamma Ferric Oxide by Direct Thermal Decomposition of Ferrous Carbonate. *Materials Letters*. 52, 295-300.

Nata, I.F., Salim, G.W. and Lee, C.K. (2010). Facile Preparation of Magnetic Carbonaceous Nanoparticles for Pb^{+2} Ions Removal. *Journal of Hazardous Materials*. 183, 853-858.

Ngomsik, A.F., Bee, A., Cabuil, V., Draye, M., Talbot, D. and Cote, G. (2004). Removal of Lanthanides from Aqueous Solutions using Ferrofluid Constituted of Citrate Coated Magnetic Nanoparticles. *XIX-th Ars. Separatoria*, Poland.

Ngomsik, A.F., Bee, A.S., Siaugue, J.M., Cabuil, V.R. and Cote, G.R. (2006). Nickel Adsorption by Magnetic Alginate Microcapsules Containing an Extractant. *water research.* 40(9), 1848-1856.

Ngomsik, A.F., Bee, A., Siaugue, J. M., Talbot, D., Cabuil, U. and Cote, G. (2009). Co(II) removal by magnetic alginate beads containing Cyanex 272. *Journal of Hazardous Materials.* 166, 1043-1049.

Nguyen, V.N.H., Amal, R. and Beydoun, D. (2003). Effect off Formate and Methanol on Photoreduction/removal of Toxic Cadmium Ions using TiO_2 Semiconductor as Photocatalyst. *Chemical Engineering Science.* 58, 4429-4439.

Nilchi, A., Saberi, R., RasouliGarmarodi, S. and Bagheri, A. (2012). Evaluation of PAN-Based Manganese Dioxide Composite for the Sorptive Removal of Cesium-137 from Aqueous Solutions. *Applied Radiationand Isotopes*. 70, 369-374.

Niu, X., Zheng, L., Zhou, J., Dang, Z. and Li, Z. (2014). Synthesis of an Adsorbent from Sugarcane Bagass by Graft Copolymerization and Its Utilization to Remove Cd (II) Ions from Aqueous Solution. *Journal of the Taiwan Institute of Chemical Engineers.* 45, 2557-2564.

Oh, J.K. and Park, J.M. (2011). Iron Oxide Based Superparamagnetic Polymeric Nanomaterials: Design, Preparation, and Biomedical Application. *Progress in Polymer Science*. 36, 168-189.

Okamura, Y., Fujiwara, K., Ishihara, R., Sugo, T., Kojima, T., Umeno, D. and Saito. K. (2014). Cesium Removal in Fresh Water using Potassium Cobalt Hexacyanoferrate Impregnated Fibers. *Radiation Physics and Chemistry*. 94, 119-122.

Pangeni, B., Paudyal, H., Inoue, K., Ohto, K., Kawakita, H. and Alam, S. (2014). Preparation of Natural Cation Exchanger from Persimmon Waste and its Application for the Removal of Cesium from Water. *Chemical Engineering Journal*. 242, 109-116.

Papageorgiou, S.K., Katsaros, F.K., Favvas, E.P., Romanos, G.E., Athanasekou, C.P., Beltsios, K.G. and Falaras, P. (2012). Alginate Fibers as Photocatalyst Immobilizing Agents Applied in Hybrid Photocatalytic/ultrafiltration Water Treatment Processes. *Water research.* 46, 1858-1872.

Pehlivan, E. and Arslan, G. (2007). Removal of Metal Ions using Lignite in Aqueous Solution, Low Cost Biosorbent. *Fuel Process Technology*. 88, 99-109.

Plattes, A.B.M., Schmitt, B., Sinner, J., Verstraeten, F. and Welfring, J. (2007). Removal of Tungsten Oxyanions from Industrial Wastewater by

Precipitation, Coagulation and Flocculation Processes. *Journal of Hazardous Materials*. 148, 613-615.

Polo, M.S., Utrilla, J.R., Salhi, E. and Gunten, U.V. (2006). Removal of Bromide and Iodide Anions from Drinking Water by Silver Activated Carbon Aerogels. *Journal of Colloid and Interface Science*. 300, 437-441.

Qin, C., Li, C., Hu, Y., Shen, J. and Ye, M. (2009). Facile Synthesis of Magnetic Iron Oxide Nanoparticles using 1-methyl-2-pyrrolidone as a Functional Solvent. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 336, 130-134.

Racuciu, M., Creanga, D.E. and Airinei, A. (2006). Citric Acid Coated Magnetite Nanoparticles for Biological Applications. *European Physical Journal*. 21, 117-121.

Rajeshwar, K., Chenthamarakshan, C.R., Ming, Y. and Sun, W. (2002). Cathodic Photoprocesses on Titania Films and in Aqueous Suspensions. *Journal of Electroanalytical Chemistry*. 538-539, 173-182.

Recillas, S., García, A., González, E., Casals, E., Puntes, V., Sánchez, A. and Font, X. (2009). Use of CeO_2, TiO_2 and Fe_3O_4 Nanoparticles for the Removal of Lead from Water Toxicity of Nanoparticles and Derived Compounds. *Desalination*. 277(1), 213-220.

Reddy, L.H., Arias, J.L., Nicolas, J. and Couvreur, P. (2012). Magnetic Nanoparticles: Design and Characterization, Toxicity and Biocompatibility, Pharmaceutical and Biomedical Applications. *Chemical Reveiws*. 112, 5818-5878.

Richard, C. (1994). Photocatalytic Reduction of Benzoquinone in Aqueous ZnO or TiO_2 Suspensions. *New Journal ofChemistry*. 18, 443-445.

Ritu, D. and Ambashta, M.S. (2010). Water Purification using Magnetic Assistance: A Review. *Journal of Hazardous Materials*. 180, 38-49.

Ryabchuk, V. (2004). Photophysical Processes Related to Photoadsorption and Photocatalysis on Wide Band Gap Solids: A Review. *International Journal of Photoenergy*. 6, 95-113.

Saeed, A., Waheed, A.M. and Iqbal, M. (2005). Removal and Recovery of Heavy Metals from Aqueous Solution using Papaya Wood as a New Biosorbents. *Seperation Purification Technology*. 45, 25-31.

Sala, F. and Trifirò, F. (1974). Oxidation Catalysts Based on Tin-antimony Oxides. *Journal of Catalysis*. 34(1), 68-78.

Santos, T.R. (2014). Sensors and Biosensors Based on Magnetic Nanoparticles. *Trends in Analytical Chemistry*. 62, 28-36.

Sato, I., Kudo, H. and Tsuda, S. (2011). Removal Efficiency of Water Purifier and Adsorbent for Iodine, Cesium, Strontium, Barium and Zirconium in Drinking Water. *The Journal of Toxicological Sciences*. 36, 829-834.

Sheha, R.R. (2012). Synthesis and Characterization of Magnetic Hexacyanoferrate (II) Polymeric Nanocomposite for Separation of Cesium from Radioactive Waste Solutions. *Journal of Colloid and Interface Science.* 388, 21-30.

Shin, K.Y., Hong, J.Y. and Jang, J. (2011). Heavy Metal Ion Adsorption Behavior in Nitrogen Doped Magnetic Carbon Nanoparticles: Isotherms and Kinetic Study. *Journal of Hazardous Materials*. 190, 36-44.

Siyal, A.N., Elçi, L., Memon, S.Q., Akdogan, A., Hol, A., Kartal, A.A. and Khuhawar, M.Y. (2014). Synthesis and Characterisation of Novel Chelating Resin for Selective Preconcentration and Trace Determination of Pb(II) Ions in Aqueous Samples by Innovative Microsample Injection System Coupled Flame Atomic Absorption Spectrometry. *International Journla of Environmental Analasys Chemistry.* 94, 743-755.

Skubal, L.R., Meshkov, N.K., Rajh, T. and Thurnauer, M. (2002). Cadmium Removal from Water using Thiolactic Acid Modified Titanium Dioxide Nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry.* 148, 393-397.

Smidsrod, O. (1970). Solution Properties of Alginate. *Carbohydrate research.* 13, 359-372.

Srivastava, N.K. and Majumder, C.B. (2008). Novel Biofiltration Methods for the Treatment of Heavy Metals from Industrial Wastewater. *Journal of Hazardous Materials.* 151, 1-8.

Stecher, H.A. and Kogut, M.B. (1999). Rapid Barium Removal in the Delaware Estuary. *Geochimica et Cosmochimica Acta*. 63, 1003-1012.

Stylidi, M., Kondarides, D.I. and Verykios, X.E. (2004). Visible Light Induced Photocatalytic Degradation of Acid Orange 7 in Aqueous TiO_2 Suspensions. *Applied Catalysis B: Environmental.* 47, 189-201.

Subbaiah, T., Mallick, S.C., Mishra, K.G., Sanjay, K. and Das, R.P. (2002). Electrochemical Precipitation of Nickel Hydroxide,. *Journal of Power Sources*. 112, 562-569.

Sun, J., Wang, X., Sun, J., Sun, R., Sun, S. and Qiao, L. (2006). Photocatalytic Degradation and Kinetics of Orange G using Nano Sized Sn(IV)/TiO_2/AC Photocatalyst. *Journal of Molecular Catalysis A: Chemical*. 200(1), 241-246.

Sun, Y.P., Li, X.Q., Zhang, W.X. and Wang, H.P. (2007). A Method for the Preparation of Stable Dispersion of Zero Valent Iron Nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 308, 60-66.

Susan, E., Bailey, T.J.O., Bricka, R.M. and Adrian, D.D. (1999). A Review of Potentially Low Cost Sorbents for Heavy Metals. *Water Research*. 33, 2469-2479.

Tada, H., Jin, Q., Nishijima, H., Yamamoto, H., Fujishima, M., Okuoka, S., Hattori, T., Sumida, Y., Kobayashi, H. (2011). Titanium(IV) Dioxide Surface-modified with Iron Oxide as a Visible Light Photocatalyst. *Angewandte Chemie*. 123, 3563-3567.

Tang, S.C.N. and Lo, I.M.C. (2013). Magnetic Nanoparticles: Essential Factors for Sustainable Environmental Applications,. *Water Research*. 47, 2613-2632.

Tang, W.Z. and An, H. (1995). UV/TiO_2 Photocatalytic Oxidation of Commercial Dyes in Aqueous Solutions. *Chemosphere*. 31, 4157-4170.

Tao, Y., Ye, L., Pan, J., Wang, Y. and Tang, B. (2009). Removal of Pb(II) from Aqueous Solution on Chitosan/TiO_2 Hybrid Film. *Journal of Hazardous Materials*. 161(2), 718-722.

Teng, X., Shi, X., Shan, Z., Jin, Y., Guan, H., Li, Y. and Teng, W. (2008). Safe Range of Iodine Intake Levels: A Comparative Study of Thyroid Diseases in Three Women Population Cohorts with Slightly Different Iodine Intake Levels. *Biological Trace Element Research*. 121, 23-30.

Thapa, R., Maiti, S., Rana, T.H. and Maiti, U.N. (2012). Anatase TiO_2 Nanoparticles Synthesis via Simple Hydrothermal Route: Degradation of Orange II, Methyl Orange and Rhodamine B. *Journal of Molecular Catalysis A: Chemical*. 363, 223-229.

Um, W., Serne, R.J. and Krupka, K.M. (2004). Linearity and Reversibility of Iodide Adsorption on Sediments from Hanford, Washington under Water Saturated Conditions. *Water Research*. 38, 2009-2016.

Vipin, A.K., Hu, B. and Fugetsu, B. (2013). Prussian Blue Caged in Alginate/Calcium Beads as Adsorbents for Removal of Cesium Ions from Contaminated Water. *Journal of Hazardous Materials.* 258-259, 93-101.

Visa, M., Carcel, R.A., Andronic, L. and Duta, A. (2009). Advanced Treatment of Wastewater with Methyl Orange and Heavy Metalson TiO_2, Fly Ash and Their Mixtures. *Catalysis Today.* 144, 137-142.

Wang, Q., Qian, H., Yang, Y., Zhang, Z., Naman, C. and Xu, X. (2010). Reduction of Hexavalent Chromium by Carboxymethyl Cellulose-stabilized Zero-valent Iron Nanoparticles. *Journal of Contaminant Hydrology*. 114, 35-42.

Wang, T.H., Li, M.H., Wei, Y.Y. and Teng, S.P. (2010). Desorption of Cesium from Granite under Various Aqueous Conditions. *Applied Radiation and Isotopes.* 68, 2140-2146.

Wang, Y., He, Y., Lai, Q. and Fan, M. (2014). Review of the Progress in Preparing Nano TiO_2: An Important Environmental Engineering Material. *Journal of Environmental Sciences.* 26, 2139-2177.

Wong, Y.C., Szeto, Y.S., Cheung, W.H. and Mckay, G. (2003). Equilibrium Studies for Acid Dye Adsorption onto Chitosan. *Langmuir.* 19, 7888-7894.

Wu, K.Y.A. and Wisecarver, K.D. (1992). Cell immobilization using PVA crosslinked with boric acid. *Biotechnology and Bioenergy.* 39, 447–449.

Xia, H., Zhuang, H., Zhang, T. and Xiao, D. (2008). Visible Light Activated Nanocomposite Photocatalyst of Fe_2O_3/SnO_2. *Materials Letters*. 62, 1126-1128.

Xu, S.C., Zhang, Y.X., Pan, S.S., Ding, H.L. and Li, G.H. (2011). Recyclable Magnetic Photocatalysts of Fe^{2+}/TiO_2 Hierarchical Architecture with Effective Removal of Cr(VI) under UV Light from Water. *Journal of Hazardous Materials.* 96, 29-35.

Yagub, M.T., Sen, T.K., Afroze, S. and Ang, H.M. (2014). Dye and Its Removal from Aqueous Solution by Adsorption: A Review. *Advances in Colloid and Interface Science.* 209, 172-174.

Yewale, A.K., Raghuwanshi, F.C., Belsare, N.G., Waghmare, R.V., joat, R.V., Wasnik, T.S., Raulkar, K.B., Wadatkar, A.S. and Lamdhade, T.G. (2011). Gas Sensitivity of TiO_2 Based Thick Film Sensor to Gas at Room Temperature. *International Journal of Advanced Engineering Technology*. 2(4), 226-230.

Yu, H., Irie, H., Shimodaira, Y., Hosogi, Y., Kuroda, Y., Miyauchi, M. and Hashimoto, K. (2010). An Efficient Visiblelight Sensitive Fe(III)-grafted TiO_2 Photocatalyst. *J. Physical Chemistry C*. 114, 16481-16487.

Zhang, X. and Lei, L. (2008). Preparation of Photocatalytic Fe_2O_3-TiO_2 Coatings in One Step by Metal Organic Chemical Vapor Deposition. *Applied Surface Science*. 254, 2406-2412.

Zhang, Y., Barber, A., Maxted, J., Lowe, C., Smitha, R. and Li, T. (2013). The Depth Profiling of TiO_2 Pigmented Coil Coatings using Step Scan Phase Modulation Photoacoustic FTIR. *Progress in Organic Coatings*. 76, 131-136.

Zhao, H., Fu, W., Yang, H., Xu, Y., Zhao, W., Zhang, Y. and Li, Y. (2011). Synthesis and Characterization of TiO_2/Fe_2O_3 Core–shell Nanocomposition Film and Their Photoelectrochemical Property. *Applied Surface Science*. 257, 8778-8783.

Zhao, J. and Yang, X. (2003). Photocatalytic Oxidation for Indoor Air Purification: A Literature Review. *Building and Environment*. 38, 645-654.