REMOVAL EFFICIENCY FOR HEAVY METALS IONS WITH GRANULAR RESIN AND FIBROUS ADSORBENT

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requirements for the award of the degree of
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Dedicated to my beloved husband
(Mohd Amri Yahaya)
my children
(Kayra Humaira, Aisy Naufal, Afiq Aryan, Kayla Huwaida)
my love
(Almarhum Hamdzah Md Daly, Hafizah Jaaffar, Hj. Jaaffar & Hjh. Hasnah)
Siblings
(Mohd Eezan & Mazeeha)
and
friends for their continuous support and encouragement throughout this study

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ABSTRACT

Pollution of wastewater in the battery industry with heavy metals such as Ni(II), Zn(II) and Pb(II) is an alarming environmental threat posing significant hazard to human, animal and aquatic life. Removal of these metal ions by ion exchange resins has been widely practiced. However, ion exchange technology has some limitations such as high cost of resins and slow kinetics of adsorption. In this study, a new sulfonated fibrous adsorbent (SFA) in a form of sulfonic acid containing poly(glycidyl methacrylate) (PGMA) grafted onto polyethylene (PE) nonwoven fabric was prepared by radiation induced graft copolymerization (RIGC) of glycidyl methacrylate (GMA) and subsequent sulfonation reaction. The obtained adsorbent was characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectrometer combined with attenuated total reflection (FTIR-ATR) to confirm the incorporation of PGMA and sulfonic acid groups. The performance of the SFA under various treatment conditions pertaining to equilibrium isotherms, kinetics, and breakthrough curves of selective adsorption of Ni(II), Zn(II) and Pb(II) from aqueous solutions were evaluated. The adsorption parameters were optimized using a response surface method (RSM) in both batch and fixed bed column modes through the central composite rotatable design (CCRD). Similar experiments were carried out with commercial granular sulfonated ion exchange resin (Dowex 50W) and used for comparison. The adsorption isotherms of the the tested metal ions on the new adsorbent was found to fit Freundlich model whilst the breakthrough curve followed Thomas model. The optimum parameters for adsorption on SFA in a batch mode were pH of 4.5-7.5 and contact time of 1.0-1.5 minutes for removal of > 90% of Zn(II) and Pb(II). Particularly, a time of less than 3.5 minutes was needed for 95% removal of Ni(II) from solution with 3 mg/L concentration. The column performance of the SFA with respect to combination of solute removal efficiency, resin utilization efficiency and breakthrough time, known as response function (RF), revealed that the highest value of RF was found at a flow rate of >15.2 mL/min and bed height of 5.2 cm. The results of this study suggest that the new fibrous adsorbent has higher adsorption capacity and faster kinetics than commercial granular resin (Dowex 50W). Thus, SFA is considered a potential substituent resin for removal of heavy metal ions from aqueous solutions.

ABSTRAK

Pencemaran logam berat daripada air sisa industri bateri seperti Ni(II), Zn(II) dan Pb(II) merupakan ancaman alam sekitar yang boleh membahayakan manusia, haiwan dan hidupan akuatik. Penyingkiran logam berat melalui teknologi penukaran ion telah diguna pakai secara meluas. Walau bagaimanapun, teknologi ini mempunyai kelemahan seperti memerlukan kos resin yang tinggi dan kinetik penjerapan yang rendah. Dalam kajian ini, penjerap fiber tersulfonat (SFA) baru dalam bentuk asid sulfonik yang mengandungi poliglisidil metakrilat (PGMA) dicangkukkan ke atas fiber polietalena (PE) telah dihasilkan dengan menggunakan kaedah pengkopolimerisasi cangkukan aruhan sinaran (RIGC) oleh glisidil metakrilate (GMA) dan seterusnya reaksi sulfonik. Penjerap fiber yang terhasil dicirikan dengan menggunakan mikroskop pengimbas elektron (SEM) dan spektrometer pengubah fourier inframerah digabungkan dengan pengurangan jumlah pantulan (FTIR-ATR) untuk mengesahkan pembentukan PGMA dan kumpulan asid sulfonik. Pencapaian SFA dinilai di bawah pelbagai keadaan berkaitan dengan keseimbangan isoterma, kinetik dan keluk bolos penjerapan terpilih ion logam Ni(II), Zn(II) dan Pb(II) daripada larutan akueus. Proses penjerapan dioptimumkan menggunakan kaedah gerak balas permukaan (RSM) pada kedua jenis eksperimen iaitu eksperimen kelompok dan lapisan turus tetap melalui kaedah rekabentuk komposit boleh gilir berpusat (CCRD). Eksperimen yang serupa dijalankan dengan menggunakan resin berbutir asid sulfonik komersial (Dowex 50W) sebagai perbandingan dengan SFA. Penjerapan isoterma ketiga-tiga ion logam yang diuji untuk penjerap fiber baru didapati sesuai dengan isoterma *Freundlich*, manakala keluk bolos bersesuaian dengan keluk model *Thomas*. Bagi ekperimen kelompok, parameter yang optimum bagi SFA ialah nilai pH 4.5-7.5, dan masa 1.0-1.5 minit untuk penjerapan lebih 90% Zn(II) dan Pb(II). Secara khususnya, masa penjerapan adalah kurang daripada 3.5 minit untuk penyingkiran 95% Ni(II) daripada larutan berkepekatan 3 mg/L. Bagi ekperimen lapisan turus tetap, pencapaian penjerapan SFA dinilai dengan kombinasi antara nilai kecekapan penyingkiran larutan ion logam, kecekapan penggunaan resin dan masa keluk bolos, dikenali sebagai fungsi tindak balas (RF), dengan nilai tertinggi RF pada kadar aliran 15.2 mL/min dan tinggi turus 5.2 cm. Hasil kajian ini mencadangkan bahawa SFA mempunyai kapasiti penjerapan dan kepantasan kinetik yang lebih tinggi berbanding dengan resin berbutir komersial (Dowex 50W). SFA terbukti berpotensi sebagai bahan ganti resin bagi menyingkir ion logam berat daripada larutan akueus.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
ATR	-	Attenuated total reflectance
ATRP	-	Atom transfer radical polymerization
CCRD	-	Central composite rotatable design
DG	-	Degree of grafting
DOE	-	Department of Environment
DVB	-	Divinylbenzene
EB	-	Electron beam accelerator
EU	-	European Union
EQA	-	Environmental Quality Act
FTIR	-	Fourier transform infrared spectrometer
GMA	-	Glycidyl methacrylate
IAEA	-	International Atomic Energy Agency
IEC	-	Ion exchange capacity
ICP-MS	-	Inductively coupled plasma optical mass spectrometry
IPA	-	Isopropyl alcohol
INWQS	-	Interim National Water Quality Standard
LOFT	-	Lack of fit test
LDPE	-	Low density polyethylene
MCL	-	Maximum contaminant level
NA	-	Not available
NMDG	-	N-methyl-D-glucamine
PAN	-	Polyacrylonitrile
PE	-	Polyethylene
PP	-	Polypropylene

PVA	-	Polyvinyl alcohol
QAPAN	-	Amino and Quaternary Ammonium Groups
RAFT	-	Reversible addition ragmentation chain transfer
RIGC	-	Radiation induced graft copolymerization
RD	-	Resin Dosage
RF	-	Response function
RSM	-	Response surface methodology
SEM	-	Scanning electron microscopy
SFA	-	Sulfonated poly(GMA) fibrous adsorbent
SV	-	Space velocity
WHO	-	World Health Organization

LIST OF SYMBOLS

a	-	Initial rate of sorption (mg min/g)
A_R	-	Redlich–Peterson isotherm constant (1/mg)
C	-	Thickness of the boundary layer (mg/g)
C_e	-	Concentration of metal ion in the solution at equilibrium (mg/L)
C_f	-	Final concentration of metal ion in the solution (mg/L)
C_0	-	Initial concentration of metal ion in the solution (mg/L)
ε_f	-	Efficiency of resin utilization
ε_r	-	Efficiency of metal removal
g	-	Redlich–Peterson isotherm exponent
h	-	Initial adsorption rate (mg/g min)
k_1	-	Rate constant of the pseudo-first order sorption (1/min)
k_2	-	Pseudo second order rate constant of sorption (g/mg min)
K_{BA}		Bohart Adam rate coefficient (mg.min/cm^3)
K_D	-	Equilibrium constant
K_F	-	Freundlich adsorption constant (mg/g) (L/mg)$^{1/n}$
k_{ip}	-	Rate constant for intra-particle diffusion (mg/g min$^{0.5}$)
K_L	-	Langmuir adsorption constants related to adsorption energy (L/g)
K_{TH}	-	Thomas rate coefficient (mL.mg/min)
M	-	Molecular weight (g/mol)
N_0	-	Exchange capacities (mg/cm^3)
Q	-	Flow rate (mL/min)
q_{cal}	-	Calculated adsorption capacity (mg/g)
q_e	-	Metal ion adsorption capacity at equilibrium (mg/g)

q_{max}	-	Maximum adsorption capacity (mg/g)
q_{exp}	-	Experimental adsorption capacity (mg/g)
Q_L	-	Langmuir adsorption constants related to adsorption capacity (mg/g)
q_{ref}	-	Solid phase concentration at time $t = t_{ref}$ (mg/g)
q_t	-	Amount of metal ion adsorbed at t time (mg/g)
r^2	-	Correlation coefficients
T	-	Time (min)
t_{br}	-	Breakthrough time (min)
t_{end}	-	Saturation time (min)
T	-	Temperature (K)
T_m	-	Melting temperature (^oC)
t_{ref}	-	Longest time in the adsorption process (min)
u	-	Linear velocity (cm/min)
V	-	Volume of the solution (mL)
W	-	Weight (g)
W_f	-	Final weight (g)
W_i	-	Initial weight (g)
Z	-	Total bed depth (cm)

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Heavy metal pollution is one of the most serious problems in our environment (Anirudhan & Sreekumari, 2011; Azimi *et al*., 2017; Tripathi and Ranjan, 2015). This is due to the rapid development of technology from various activities and industrial processes, which have been explored without limitation; hence endangering the environment and nature. Numerous heavy metals utilized in various process industries, resulted in large quantities of effluents containing high level of toxic heavy metals (Lakherwal, 2014). As an example, the concentrations of some toxic metals such as lead, nickel, zinc, arsenic, and mercury in battery-manufacturing and electroplating effluents are higher than its permitted discharge limits (Li *et al*., 2017; Gupta and Ali, 2013). Moreover, because of their high solubility in the environment, these heavy metals can be absorbed by living organism's metabolic system (Barakat, 2011).

About 78% of lead from global consumption was reported by UN Environment. Improper recycling of used lead acid batteries causes environmental pollution and health damage. The major use of lead is in energy storage batteries can cause damage to liver and kidney, reduction in hemoglobin formation, mental retardation, and infertility or abnormalities in pregnancy (Meena *et al.*, 2005).

Nickel is used extensively in the production of nickel-cadmium batteries on an industrial scale (Gautam *et al.*, 2014). Higher concentration of nickel in the ecosystem can cause cancer, dermatitis, headache, nausea, vomiting, chest pain, and extreme weakness (Meena *et al.*, 2005; Gautam *et al.*, 2014; Li *et al*., 2017). The permissible amount of zinc in Standard B, EQA (2009) is 1.0 mg/L. Exceeds concentrations of zinc can cause a threat to both human health and environment. Similarly to nickel, zinc toxicity causes nausea and vomiting in children, anemia, and cholesterol problems (El-Kafrawy *et al.,* 2017). Given that the ingested metal concentrations beyond limit could disrupts environmental natural processes and health of ecosystem because of their toxicity, carcinogenicity, and mutagenicity (Jaishankar *et al.*, 2014), all types of heavy metals should meet the environmental discharge limit before being discharged (Hahladakis *et al*., 2013; Azizi *et al*., 2016).

Increasing water consumption and tightening up of wastewater regulations have been the motivating factors to develop new processes for treating polluted water in industrial set-ups (Naidoo & Olaniran, 2014). In Malaysia, discharge limits have been enacted for metal content in effluents by the Environmental Quality (Industrial Effluents) Regulations 2009. Environmental engineers and scientists thus have been tasked to develop an appropriate low cost technology for effluent treatment and/or recycling. Hence, the degree of sophistication of separation methods have been increased tremendously to improve the conventional wastewater treatment system (Nasef *et al*., 2009; El-Kafrawy *et al*., 2017).

Various techniques have been developed for the removal of heavy metals from wastewater discharges. Some of the techniques include chemical precipitation, coagulation/flocculation, ion exchange, electrochemical treatment, and membrane processes. Above all, ion exchange is the most effective and efficient technology to remove heavy metals from wastewaters to low desired levels (Barakat, 2011; Fu and Wang, 2011; Tripathi and Ranjan, 2015; Gunatilake, 2015).

A number of commercial resins or adsorbents are available for treatment of variety of water streams in many industries. However, such resins or adsorbents are held-up by slow kinetics,-slow generation and channelling, and high pressure drop in fixed adsorption column (Nasef and Guven, 2012). Thus, huge efforts have been made to introduce new adsorbents to enhance adsorption performance. Generally, the new functional polymers or adsorbent materials must have combinations of high selectivity, fast regeneration, large number of regeneration cycles, fouling resistance, chemical stability, thermal resistance, mechanical integrity, and low-cost (Zwain *et al.*, 2014; Islam and Kabir, 2016). Thus, many studies have proposed variety of low-cost adsorbents from different waste materials including agricultural and industrial wastes (El-Kafrawy *et al.*, 2017). However, the obtained adsorbents have poor performance and small number of cycles in addition of being dedicated for specific metals, dyes or other pollutants (Babel and Kurniawan, 2003; Zwain *et al.*, 2014).

Among the newly searched adsorbents are functional fibrous adsorbents, which are attractive materials with unique physical and chemical characteristics enduring high efficiency in decontamination of chemical pollutants (Nasef *et al.*, 2014). Particularly, the use of functional fibrous adsorbents can overcome diffusion limitation and slow kinetics associated with conventional resins allowing operation at high flow rate while maintaining high selectivity (Kawai *et al.*, 2003; Hamabe *et al.,* 2009; Jyo *et al.*, 2010; Nasef and Guven, 2012; Azimi *et al.,* 2017; Abdel-Halim and Al-Hoqbani, 2015). These polymers can be prepared by grafting monomers carrying ionic groups capable of interacting with the target metal ions or grafting nonfunctional monomers that are functionalized in a post-grafting reaction. Grafting can be carried out using chemical initiation, photo-initiation, plasma initiation, and high energy initiation (with gamma rays or electron beam). The latter is known as radiation induced grafting and is highly convenient for introducing ionic groups to preformed substrates via side chain grafts (Nasef and Hegazy, 2004; Abdel-Ghaffar *et al*., 2016).

The use of radiation grafted adsorbents having fibrous structures for removal of heavy metal ions has been investigated in a number of occasions (El-Sawya *et al.*, 2007; Chowdhury *et al.*, 2012; El-Arnouty *et al*., 2017; Abdel-Ghaffar *et al.,* 2016), and recently reviewed in literature (Nasef and Guven, 2012). However, the radiation grafted adsorbents were dedicated to specific metals or dyes for which, the adsorbents showed high affinity. For instance, adsorptions of arsenic and metal ions (Cr(II), Mn(II), Fe(II), Ni(II), Cu(II), Co(II), Zn(II), Cd(II), and Pb(II)) were investigated using grafted adsorbent (Abdel-Ghaffar *et al.,* 2016; Abdel-Halim and Al-Hoqbani, 2015). Adsorption of Ni(II), Co(II), Cu(II), Pb(II) and Ag(I) from aqueous solutions was also tested by sulfonated grafted PE membrane (Nasef *et al.*, 2010). Initial concentration and pH of the medium became the most significant effects of metal ion adsorption on membrane. The maximum percentage of adsorption were obtained at 99, 97.2, 93, 89.8, and 79.7% at initial concentrations of 1.0 mg/L and pH 6.6 for Ni(II), Co(II), Cu(II), Pb(II), and Ag(I), respectively (Nasef *et al.*, 2010). Therefore, it is highly important to choose the appropriate functional groups, which allows imparting higher selectivity and more adsorption properties to the adsorbent materials.

1.2 Problem Statement

The accumulation of heavy metals in aquatic and terrestrial habitats has been increased dramatically, especially in industrial developing countries. The contamination of heavy metals might develop into severe health problems which can lead to chronic toxicity. The commonly encountered toxic heavy metals in industrial effluent are lead, arsenic, mercury, cadmium, nickel, zinc, copper and chromium (Abas *et al*., 2013; Lee *et al*., 2016). In Malaysia, effluent generated from battery industry particularly contains a high concentrations of lead, nickel and zinc. Due to the adverse health impact of these toxic heavy metals to the living things, their concentration level in wastewater needs to be removed and controlled to comply with the legislation requirement by Malaysian Department of Environment (DOE) with the limit of 0.5, 1, and 2 mg/l for effluent discharge standards B for lead, nickel and zinc, respectively (Environmental Quality Act, 2009).

The commercial resins used in heavy metal removal shows an exceptionally low running costs and low energy consumption. However, there are limitations such as low adsorption capacity and slow adsorption kinetics. Both limitations adversely affected the economy and also the performance of metal ions removal. In addition, the loss of capacity upon scaling up and after each regeneration cycle, the limited surface areas, uncontrollable pore structures and hydrophobicity characteristic of the resins have resulted in unsatisfactory performance of the commercial resins. Thus, various types of adsorbents have been developed recently to overcome the weaknesses of the commercial resins (Ariffin *et al.,* 2017; Azimi *et al.,* 2016). Although many techniques can be employed for the treatment of industrial effluent, the ideal technology should not only be suitable, appropriate and applicable to the local conditions, but also able to meet the established standards of maximum contaminant level (MCL) (Barakat, 2011). In order to find the ideal and feasible solutions for efficient technique and economic process of removing toxic heavy metal ions, considerations upon unconventional materials and processes are needed (Ariffin *et al.,* 2017) Therefore, synthesizing new monomers carrying the functional groups which are capable to interact with the target metal ions have been reported (Shoji *et al.,* 2001; Jyo *et al*., 2010; Nasef and Guven, 2012; El-Arnouty *et al*., 2016). One of the new innovative resins known as functional fibrous can overcome the diffusion limitations of conventional resins, enhance the kinetics of reaction and operate at high flow rate with high selectivity (Lee *et al*., 2008; Jyo *et al*., 2010; Nasef & Guven, 2012; El-Arnouty *et al*., 2016; Abdel-Ghaffar *et al*., 2016).

Heavy metal selective adsorbents having fibrous structure can be conveniently prepared by radiation induced graft copolymerization (RIGC) method and subsequent functionalization with desired ionic groups in large quantities (Nasef and Guven, 2012). The use of RIGC in preparation of such adsorbents offers a number of advantages compared to conventional grafting techniques (e.g. catalytic polymerization and plasma polymerization) such as ability to have a well-tuned composition, tailor properties suitable for specific application and modify substrates of various morphologies (films, fibres and fabrics) in addition to simplicity and absence of chemical initiators (El-Arnouty *et al*., 2016). However, studies on radiation grafted adsorbent having fibrous structure for heavy metals removal are very scarce. Thus, it is appealing to prepare an adsorbent for heavy metal removal by RIGC of monomers such as glycidyl methacrylate (GMA) onto polyethylene (PE) nonwoven fabric by radiation grafting and subsequent amination. The use PE which very cheap and has excellent chemical, thermal and mechanical properties beside having a good records for using in preparation in a number of functional materials by RIGC is rather promising. GMA is a versatile monomer that can impart grafts having pendant oxirane rings that can be opened by treatments with a variety of chemical reagents under mild reaction conditions. The use of sulfonating agent such as sodium sulfate/sulfuric acid covert the poly(GMA) grafted fabric to sulfonic acid containing adsorbent of fibrous nature.

1.3 Objectives of the Study

The aim of this study is to prepare, characterize and test a new fibrous adsorbent for removal of heavy metals (Ni(II), Zn(II) and Pb(II)) from synthetic solutions. This can be achieved by the following objectives:

i. To prepare the adsorbent comprising sulfonated poly(GMA) grafted onto PE non-woven fabric and evaluate it physico-chemical properties.

ii. To evaluate the performance of the sulfonated fibrous adsorbent for removal of selected metal ions in batch and dynamic modes (fixed bed column) under various conditions.

iii. To develop statistical models that correlate between the efficiencies of metal ions removal and the optimum operating parameter in terms of pH, bed height and flow rate.

iv. To establish equilibrium isotherms, kinetics and breakthrough curves for metal ions adsorption onto the sulfonated fibrous adsorbent in comparison with a commercial granular resin.

1.4 Scope of the Study

In order to achieve the above-mentioned objectives, several scopes of works have been drawn. Two types of resins were used in this study namely:

1. Preparation of a new adsorbent by radiation induced grafting of GMA and subsequent sulfonation. Details of the preparation steps of the sulfonated fibrous as follows:

i) PE non-woven fibrous was irradiated using electron beam (EB) (20kGy; 2 MeV; 5 mA) at ~ 28^{o}C.

ii) Grafting of PGMA onto PE non-woven fibrous (5 wt%; Tw-20 in aqueous solution).

iii) The grafted PE-g-PGMA were chemically modified using sodium sulfite (Na_2SO_3), solution of isopropyl alcohol (IPA) and water (ratio 10:15:75) within 5 hours at 80^{o}C. Then, the sheet were dried and immersed into sulfuric acid solution (1M) at 50^{o}C, and final samples were dried under vacuum at 60^{o}C overnight.

2. Evaluation of the performance of the newly prepared fibrous adsorbents in comparison with Commercial granular cation exchange resin, Dowex 50W. This

was carried out using synthetic solutions containing Pb(II), Zn(II) and Ni(II). These three types of heavy metals are resembling the wastewater from the battery industry effluent (Appendix G). Two types of experiments were conducted and the control operating parameters of each system are listed below:

i) Batch: Feed concentration (Cf) , pH, contact time (t).
ii) Dynamic in a Fixed bed column: Flowrate (Q), pH, bed height (BH).

In batch experiments, the level of feed concentration was varied between 10 to 50 mg/L. The contact time applied were from 30 to 120 minutes. The pH applied for both experiment were from 4.5 to 8.5. The flow rate applied in the column experiments were from 15 to 25 mL/min, with bed height varied in the range of 3.0 to 5.0 cm.

1.5 Significance of the Study

Ion-exchange technology has been widely utilized as a technology for compact and high performance system in various applications. For wastewater treatment applications, it is commonly used in industrial effluent treatment processes. The commercial ion exchange resins have shown their effective performances but generally poor selectivity towards different metal ions (Nilchi *et al*., 2009). Therefore, further development of innovative resin materials was aimed to specifically select different metal ions, higher exchange capacity and optimum operating conditions. A step forward in this direction could be made by having a deeper understanding of the interactions among active sites and ionic species in solution (Pagnanelli *et al*., 2004; Azimi *et al*., 2016). The following contributions are made in the present study:

i. A newly sulfonated fibrous adsorbent was prepared. It is capable to overcome the challenges facing the granular resin with respect of adsorption capacity and kinetics.

ii. A statistical model for optimization of the operating parameters and percentage of metal removal was developed.

iii. The adsorption capacity of newly prepared adsorbent (sulfonated fibrous adsorbent) three times higher compared to commercial resins in granular form.

iv. The obtained data can be used for scaling up the adsorption capacity for heavy metal removal.

1.6 Organization of the Thesis

The thesis consists of six chapters. Chapter 1 introduces the background of heavy metal pollution and problem statement to justify the conducted in this thesis. The objective of the thesis, the scope of work and contribution made are also covered in Chapter 1. This was followed by the objectives and the scopes of study. Chapter 2 covers the literature reviews on the theoretical background of studies conducted on ion exchange technology, particularly by previewing the engineering configurations, operating modes and systems for ion exchange processes. An intensive discussions on the development status of various ion exchange materials in wide range of applications related to the treatment of water and industrial wastewater are also described. This chapter also includes a review of previous pertaining metal ions adsorption equilibrium isotherms and kinetics study. Chapter 3 reveals the materials and methods used to prepare and test the new fibrous adsorbent, the methodology utilized in this study including the design of experiments, functionalization, characterization, adsorption capacity, and metal ions removal efficiency for batch and column process. Response surface methods (RSM) are described in this chapter. Chapter 4 are presented in three parts. The first part presents the research findings that have been obtained in the present study for granular resins (Dowex 50W). The second part discusses the research findings for new fibrous adsorbent film. Particularly, it discusses the results of the effects of various operating parameters on the removal efficiency of batch and column process. This part consists of four major parts and includes the study on characterization of the new fibrous adsorbent film, adsorption isotherm and kinetics study, response surface models and statistical analysis, and breakthrough curve analysis. Findings for the granular and fibrous resins were compared and discussed in the last part of this chapter. Finally, the conclusions derived from the study are presented in Chapter 5.

REFERENCES

Abas, S.N.A., M.H.S. Ismail, M.L. Kamal and S. Izhar, (2013). Adsorption process of heavy metals by low-cost adsorbent: a review. *World Applied Sciences Journal*. 28(11), 1518-1530.

Abdel Ghaffar A.M, El-Arnaouty M.B, Abdel Baky A.A and Shama S.A (2016). Radiation-induced grafting of acrylamide and methacrylic acid individually onto carboxymethyl cellulose for removal of hazardous water pollutants. *Designed Monomers and Polymers.* 19(8), 706-718.

Abdel-Halim E.S, Al-Hoqbani A.A. (2015). Utilization of Poly(Acrylic Acid)/Cellulose Graft Copolymer for Dye and Heavy Metal Removal. *Bioresource*, 10(2), 3112-3130

Abdelwahab O., Amin N.K., El-Ashtoukhy E-S.Z. (2013), Removal of Zinc Ions from Aqueous Solution using a Cation Exchange Resin. *Chemical Engineering Research and Design*. 91, 165-173.

Abdel Salam O.E., Reiad N.A., ElShafei M.M. (2011) A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*. 2(4), 297-303.

Afroze, S., Sen, T.K. and Ang, H.M. (2016) Adsorption performance of continuous fixed bed column for the removal of methylene blue (MB) dye using Eucalyptus sheathiana bark biomass, *Res. Chem. Intermed*. 42, 2343–2364.

Akar-Sen G. (2016). Application of Full Factorial Experimental Design and Response Surface Methodology by Chromite Beneficiation by Knelson Concentrator. *Mineral* 6(5),1-11.

Akpor O.B., Ohiobor G.O., Olaolu T.D. (2014). Heavy metal pollutants in wastewater effluents: Sources, effects and remediation. *Advances in Bioscience and Bioengineering*. 2(4), 37-43.

Ali S.A., Kazi I W., Ullah N. (2015) New Chelating Ion-Exchange Resin Synthesized via the Cyclopolymerization Protocol and Its Uptake Performance for Metal Ion Removal *Industrial & Engineering Chemistry Research*. 54(40), 9689-9698.

American Public Health Association, APHA. (2005). *Standard Methods for the Examination of Water and Wastewater*. (21th ed.). Washington, D.C: APHA

Andrejkovičová, S. Sudagar, A. Rocha, J. Patinha, C. Hajjaji, W da Silva, E. Ferreira Velosa, A. Rocha, F. (2016). The effect of natural zeolite on microstructure, mechanical and heavy metals adsorption properties of metakaolin based geopolymers. *Applied Clay Science*. 126, 141-152.

Anirudhan T.S. and Sreekumari S.S. (2011), Adsorptive Removal of Heavy Metal Ions from Industrial Effluents using Activated Carbon Derived from Waste Coconut Buttons. *Journal of Environmental Sciences*. 23(12), 1989-1998.

Ariffin N. , Abdullah M.M.A.B. , Mohd Arif Zainol M.R.R , Murshed M.F , Zan H , Faris M.A and Bayuaji R. (2017)· Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer. *MATEC Web of Conferences 97*, 01023.

Arshadi M., Amiri M.J, Mousavi S. (2014). Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash. *Water Resources and Industry*. 6, 1-17.

Asano, T. (ed.) (1998) *Wastewater Reclamation and Reuse*, In Water Quality Management Library, 10, Boca Raton, FL: CRC Press.

Aslan, N. (2008). Application of Response Surface Methodology and Central Composite Rotatable Design for Modeling and Optimization of a Multi-Gravity Separator for Chromite Concentration. *Powder Technology.* 185, 80-86.

Awual M.R., Jyo A, Ihara T, Seko N, Tamada M, Lim K.T (2011). Enhanced trace phosphate removal from water by zirconium (IV) loaded fibrous adsorbent. *Water Research*. 24(15), 4592-4600.

Awual M R., Shenashen M.A, Yaita. H., Shiwaku, H., Jyo A., (2012). Efficient arsenic(V) removal from water by ligand exchange fibrous adsorbent. *Water Research.* 46 (17), 5541-5550.

Awual M.R. Rahman I.M.M., Yaita T., Khalequ M.A (2014). pH dependent Cu (II) and Pd (II) ions detection and removal from aqueous media by an efficient mesoporous adsorbent. *Chemical Engineering Journal*. 236, 100-109.

Azimi, A., Azari, A., Rezakazemi, M. and Ansarpour, M. (2017), Removal of Heavy Metals from Industrial Wastewaters: A Review. *ChemBioEng Reviews*. 4, 37–59.

Azizi S, Kamika I, Tekere M (2016) Evaluation of Heavy Metal Removal from Wastewater in a Modified Packed Bed Biofilm Reactor. *PLoS ONE* 11(5): e0155462.

Babel S., and Kurniawan T.A., (2003) Low-cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review. *J. Hazard. Mater*. 97(1-3), 219-243.

Baker R.W. (2004) Membrane Technology and Application. Second Edition. John Wiley and Sons, Ltd. California

Barakat M. (2011). New Trends in Removing Heavy Metals from Industrial Wastewater. *Arabian Journal of Chemistry*. 4(4), 361-377.

Bernama. (2016, 25 May). 43 polluted rivers, mostly in urban areas. *New Strait Times.* p. 6.

Bhattacharya A, Misra B.N.(2004). Grafting: A Versatile Means to Modify Polymers: Techniques, Factors and Applications. *Progress in Polymer Science*. 29, 767–814.

Bhattcharya A., Rawlins J.W. and Ray P. (2009). Polymer Grafting and Crosslinking. Polymer Grafting and Crosslinking. *Journal of the American Chemical Society*. 131(20), 7204-7204.

Bhattacharya, A. and Ray, P. (2008) *Introduction, in Polymer Grafting and Crosslinking* (eds A. Bhattacharya, J. W. Rawlins and P. Ray), John Wiley & Sons, Inc., Hoboken, NJ, USA.

Biswas S. And Mishra U. (2015). Continuous Fixed-Bed Column Study And Adsorption Modeling: Removal Of Lead Ion From Aqueous Solution By Charcoal Originated From Chemical Carbonization Of Rubber Wood Sawdust. *Journal Of Chemistry*. 1-9.

Boparai H.K., Joseph M., O'Carroll D.M. (2011) Kinetics and Thermodynamics of Cadmium Ion Removal by Adsorption onto Nano Zerovalent Iron Particles. *Journal of Hazardous Material.* 186, 458-465.

Borba C.E., Antonio da Silva, E., Fagundes-Klen, M.R., Kroumov A.D., Guirardello, R. 2008. Prediction of the Copper (II) Ions Dynamic Removal from a Medium by using Mathematical Models with the Analytical Solution. *Journal of Hazardous Material*. 152, 366-372.

Chaudhary B.K. and Farrell, J. (2014). Preparation and Characterization of Homopolymer Polyacrylonitrile-Based Fibrous Sorbents for Arsenic Removal. *Environmental Engineering Science*. 31(11), 593-601.

Choi S-H, Lee K-P, Kang H-D, Park HG. (2004). Radiolytic Immobilization of Lipase on Poly(Glycidyl Methacrylate)-Grafted Polyethylene Microbead. *Macromolecular Research*. 12, 586–92.

Chowdhury Z.Z., Zain S.M., Rashid A.K., Rafique R.F., Khalid K. (2013). Breakthrough Curve Analysis For Column Dynamics Sorption Of Mn(II) Ions From Wastewater By Using Mangostana Garcinia Peel-Based Granular-Activated Carbon. *Journal of Chemistry*. 959761, 1-8.

Chowdhury, M.N.K., Khan, M.W., Mina, M.F., Beg, M.D.H., Maksudur R. Khan, Alam, A.K.M.M. (2012). Synthesis and Characterization of Radiation Grafted Films for Removal of Arsenic and Some Heavy Metals from Contaminated Water. *Radiation Physics and Chemistry*. 81, 1606-1611.

Chowrasia D and Sharma N (2015). *Analytical Chemistry-A Qualitative and Quantitative Approach*. KNOC education for better tomorrow. India

Chu K.H. 2010. Fixed bed sorption: Setting the Record Straight on the Bohart-Adams and Thomas Models. *Journal of Hazardous Material*. 177, 1006-1012.

Cren E.C, Filho L.C., Silva E.A., Meirelles A.J.A. 2009. Breakthrough Curves for Oleic Acid Removal from Ethanolic Solutions using a Strong Anion Exchange Resin. *Separation and Purification Technology*. 69, 1-6.

Cruz-Olivares J., Perez-Alonso C., Urena-Nunez F., Chaparro-Mercado M.C., Bilyeu B., (2013). Modeling of Lead (II) Biosorption by Residue of Allspice in a Fixed Bed Column. *Chemical Engineering Journal*. 228, 21-27.

Cruz, B J., Dehonor, M., Saldívar-Guerra, E. and González-Montiel, A. (2013) *Polymer Modification: Functionalization and Grafting*, in Handbook of

Polymer Synthesis, Characterization, and Processing (eds E. Saldívar-Guerra and E. Vivaldo-Lima), John Wiley & Sons, Inc., Hoboken, NJ, USA.

Dąbrowski A., Hubicki Z., Podkościelny P., Robens E. (2004). Selective Removal of the Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method. *Chemosphere*. 56(2), 91–106.

Delval F, Crini G, Vebrel J, Knorr M, Sauvin G, Conte E. (2003).Starch-modified Filters used for the Removal of Dyes from Waste Water. *Macromolecular Symposia*. 203, 165–72

Demarchi, CA, Campos, M, Rodrigues, CA (2013) Adsorption of textile dye Reactive Red 120 by the chitosan-Fe (III)-crosslinked: Batch and fixed-bed studies. *Journal of Environmental Chemical Engineering.* 1(4), 1350–1358.

Demirbas, A., Pehlivan, E., Gode, F., Altun, T., Arslan, G. (2005). Adsorption of Cu(II), Zn(II), Ni(II), Pb(II) and Cd(II) from Aqueous Solution on Amberlite IR-120 Synthetic Resin. *Journal of Colloid and Interface Science.* 282(1), 20-25.

Dolatyari L., Yaftian M.R, Rostamnia S. (2016). Fixed-bed column dynamic studies and breakthrough curve analysis of Eu(III) ion adsorption onto chemically modified SBA-15 silica material. *Separation Science and Technology*. 52(3), 393-403.

Desilva F (2011) Protecting Ion Exchange Resins from Suspended Solids. *WQP Magazine*. 24 March 2011:12-14

Dong, C., Zhang F., Pang, Z., Yang, G. (2013). Sulfonated modification of cotton linter and its application as adsorbent for high-efficiency removal of lead(II) in effluent. *Bioresource Technology*. 146, 512–518.

Dong, C., Zhang F., Pang, Z., Yang, G. (2016). Efficient and selective adsorption of multi-metal ions using sulfonated cellulose as adsorbent. *Carbohydrate Polymers.* 151, 230–236.

Dwivedi C.P, Sahu J.N, Mohanty C.R., Raj Mohan B, Meikap B.C. 2008. Column Performance of Granular Activated Carbon Packed Bed for Pb(II) Removal. *Journal of Hazardous Material.* 156, 596-603

El-Arnaouty, M.B., Abdel Ghaffar, A.M., Abdel Baky, A.A.K., Shama, S.A (2017). Radiation synthesis of hydrogels based on carboxymethyl cellulose and its application in removal of pollutants from wastewater. *Journal of Vinyl and Additive Technology.* doi:10.1002/vnl.21614

El-Kafrawy A.F, El-Saeed S.M, Farag R.K, Al-Aidy H, El-Saied, Abdel-Raouf M.E.S. (2017). Adsorbents based on natural polymers for removal of some heavy metals from aqueous solution. *Egyptian Journal of Petroleum*. 26(1), 23-32

El-Sawya, N M., Hegazy, E.S.A, El-Hag Ali, A., Motlab, M. S. A., Awadallah-F, A. (2007). Physicochemical Study of Radiation-Grafted LDPE Copolymer and Its Use in Metal Ions Adsorption. *Nucl. Instrum. Methods: Phys. Res. B*. 264, 227-234.

Environmental Quality Report (2015). Department of Environment, Ministry of Science, Technology and Environment, *Environmental Quality Report 2015*, Kuala Lumpur.

Fil A.A., Boncukcuoglu R., Yilmaz A.E., Bayar S. (2012). Adsorption of Ni(II) on ion exchange resin: Kinetivcs, equilibrium and thermodynamic studies. *Korean Journal of Chemical Engineering*. 29(9), 1232-1238.

Foo K.Y., and Hameed B.H. (2010) Insights into the Modeling of Adsorption Isotherm Systems. *Chemical Engineering Journal.* 156, 2–10.

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

Gaikwad R.W. Sapkal V.S. and Sapkal R.S. (2010). Ion exchange system design for removal of heavy metals from acid mine drainage wastewater *Acta Montanistica Slovaca Ročník.* 15(4), 298-304.

Gandhimathi R., Ramesh S.T., Nidheesh P.V., Nagendra B., Bharathi K.S. 2011. Breakthrough Data Analysis of Adsorption of Cd(II) on Coir Pith Column. *EJEAFChe*. 10(7), 2487-2505.

Garg, U.K, Kaur, M.P, Garg V.K and Sud, D. (2008). Removal of Nickel(II) from Aqueous Solution by Adsorption on Agricultural Waste Biomass using a Response Surface Methodological Approach. *Bioresource Technology.* 99, 1325-1331.

Gautam R.K, Sharma S.K., Mahiya S and Chattopadhyaya, M.C. (2014). CHAPTER 1 : Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation, in *Heavy Metals In Water: Presence, Removal and Safety*, RSC Publishing.1-24.

Ghribi, A. and Chlendi, M.(2011). Modeling of Fixed Bed Adsorption: Application to the Adsorption of an Organic Dye. *Asian Journal of Textile.* 1, 161-171.

Gode, F; Pehlivan, E (2006). Removal of Chromium(III) from Aqueous Solutions using Lewatit S 100: The Effect of pH, Time, Metal Concentration and Temperature. *Journal of Hazardous Materials.* 136, 330–337.

Gonzalo Montes-Atenas, Sven L. M. Schroeder. (2015). Sustainable natural adsorbents for heavy metal removal from wastewater: lead sorption on pine bark (*Pinus radiata* D.Don). *Surface and interface analysis*. 47(10), 996–1000.

Gunatilake S.K (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies*. 1(1), 12-18

Gupta, V.K. and Ali, I. (2013) Chapter 2 - Water Treatment for Inorganic Pollutants by Adsorption Technology. *Environmental Water*. Elsevier. 29-91.

Gürdağ G, and Sarmad S (2013) Cellulose Graft Copolymers: Synthesis, Properties, and Applications. In *Polysaccharide Based Graft Copolymers*. Kalia S., Sabaa M.W. (eds) Springer-Verlag Berlin Heidelberg. 15-57.

Hahladakis, J., Smaragdaki, E., Vasilaki, G. (2013). Use of Sediment Quality Guidelines and pollution indicators for the assessment of heavy metal and PAH contamination in Greek surficial sea and lake sediments. *Environmental Monitoring Assessment.*185, 2843-2853.

Hamabe Y, Matsuura R, Jyo A, Tamada M, Katakai A.(2009) Properties of Bifunctional Phosphonate Fibers Derived from Chloromethyl- Styrene Grafted Polyolefin Fibers. *Reactive and Functional Polymers*. 69, 1–8.

Hamdaoui O. (2009). Removal of Copper(II) from Aqueous Phase by Purolite C100-MB Cation Exchange Resin in Fixed Bed Columns: Modeling. *Journal of Hazardous Materials.* 161, 737-746.

Hamdzah M., Nasef M.M., Ujang Z., Abdullah N. and Dahalan F.A. (2016). Removal of Ni(II), Zn(II) and Pb(II) from aqueous solutions using cation-exchange resin in fixed-bed column. *Desalination and Water Treatment*. 57(40), 18770-18781.

Harland C.E. (1994). *Ion Exchange : Theory and Practice* : Edition 2 Royal Society of Chemistry.

Hassanvand A., Wei K., Talebi S., Chen G.Q., Kentish S.E. (2017). The Role of Ion Exchange Membranes in Membrane Capacitive Deionisation. *Membranes*. 7(3), 54-60.

Hashin M, Chu K.H., 2007. Prediction of Protein Breakthrough Behavior using Simplified Analytical Solution. *Sep. Pur. Technol*. 53, 189-197.

Hegazy E-SA, AbdEl-Rehim HA, Kamal H, Kandeel KA.(2001) Advances in Radiation Grafting. Nuclear Instruments and Methods. *Physics Research Section B*. 185, 235–240.

Ho Y.S., Porter J.F., McKay G. (2002) Equilibrium Isotherm Studies for the Sorption of Divalent Metal Ions onto Peat: Copper, Nickel and Lead Single Component Systems. *Water, Air, and Soil Pollution.* 141(1), 1–33.

Hubicki, Z, Kołodyńska, D, (2012). Selective Removal of Heavy Metal Ions from Waters and Waste Waters Using Ion Exchange Method. (Kilislioğlu A. eds). In *Ion Exchange Technologies*. InTech. Rijeka. 193-240.

Hufendiek A., Trouillet V., Meier M.A.R. (2014). Temperature Responsive Cellulose-graft-Copolymers via Cellulose Functionalization in an Ionic Liquid and RAFT Polymerization. *Biomacromolecules*. 15(7), 2563-2572.

Ikeda, K., Umeno, D., Saito, K., Koide, F., Miyata, E. and Sugo, T. (2011). Removal of Boron Using Nylon-Based Chelating Fibers. *Industrial and Engineering Chemistry Research*. 50, 5727-5732.

Inamuddin M.L. (2012). Ion Exchange Technology I-Theory and Materials, Springer Dordrecht Heidelberg New York, London.

International Atomic Energy Agency (IAEA) (2002) *Application of Ion Exchange Processes For The Treatment Of Radioactive Waste And Management of Spent Ion Exchangers Technical Reports Series No. 408*

Islam M.A and Kabir M.I (2016). Application of Coconut Shell's Activated Carbon for Heavy Metal Removal from Wastewater. *American-Eurasian Journal of Toxicological Sciences.* 8(2), 77-82.

Jaishankar M., Tseten T., Anbalagan N, Mathew B.B. and Beeregowda K.N. (2014). Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdiscip. Toxicol.* 7(2), 60-72.

Jarup L. (2003). Hazards of Heavy Metal Contamination. *Br Med Bull.* 68(1), 167-182

Jayakumar R, Prabaharan M, Reis RL, Mano JF (2005). Graft Copolymerized Chitosan—Present Status and Applications. *Carbohydrate Polymers*. 62, 142–158.

Jyo A, Hamabe Y, Matsuura H, Shibata Y, Fujii Y, Tamada M, Katakai A. (2010). Preparation of Bifunctional Chelating Fiber Containing Imin-Odi(Methylphosphonate) and Sulfonate and Its Performances in Column-Mode Uptake of Cu(II) and Zn(II). *Reactive and Functional Polymer*. 70, 508–615.

Kaczala F., Marques M., and Hogland W. (2014). Settling/Sedimentation Followed by Sorption with *Pinus sylvestris* Sawdust as “Green” Sorbent: On-Site Treatment of a Real Industrial Wastewater. *Journal of Environmental Protection*. 5, 368-375.

Kawai T, Saito K, Lee W.(2003). Protein Binding to Polymer Brush, Based On Ion-Exchange, Hydrophobic, and Affinity Interactions. *Journal of Chromatography B*. 790, 131–42.

Keller, M.C. (2005): Basic Ion Exchange for Residential Water Treatment Part 1. In: *Water Conditioning and Purification. 59-63.*

Kodama Y., Barsbay M., Guven O. (2014) Radiation-induced and RAFT-Mediated Grafting of Poly(Hydroxyethyl Methacrylate) (PHEMA) from Cellulose Surfaces. *Radiation Physics and Chemistry.* 94, 98-104.

Kragovic M., Dakovic A., Sekulic Z., Trgo M., Ugrina M., Peric J., Gatta G.D., (2012) Removal of Lead From Aqueous Solutions by Using the Natural and Fe(III)-Modified Zeolite, *Appl. Surf. Sci*. 258, 3667-3673.

Kumar P, Lau PW, Kale S, Johnson S, Pareek V, Utikar R, Lali A.(2006) Kafirin adsorption on ion-exchange resins: isotherm and kinetic studies. *J Chromatogr A*. 1356, 105-116

Kumar S. and Jain S. (2013). History, Introduction, and Kinetics of Ion Exchange Materials. *Journal of Chemistry*. 1-13.

Lakherwal D. (2014). Adsorption of Heavy Metals: A Review. *International Journal of Environmental Research and Developmen*t. 4(1), 41-48.

Lee CG, Song MK, Ryu JC, Park C, Choi JW, Lee SH. (2016). Application of carbon foam for heavy metal removal from industrial plating wastewater and toxicity evaluation of the adsorbent. *Chemosphere.* 153, 1-9.

Lee SW, Bondar Y, Han DH.(2008) Synthesis of a Cation-Exchange Fabric with Sulfonate Groups by Radiation-Induced Graft Copolymerization from Binary Monomer Mixtures. *Reactive and Functional Polymers.* 68, 474–82.

Li Y., Zhang C., Jiang Y., Wang T.J., Wang H. (2016) Effects of the Hydration Ratio on the Electrosorption Selectivity of Ions during Capacitive Deionization *Desalination*. 399, 171-177.

Li, Y. Yang, L. Xu, Z and Sun, Q (2017). Separation and recovery of heavy metals from waste water using synergistic solvent extraction. IOP Conference Series: *Materials Science and Engineering*. 167(1), 1-5.

Lim A. P. and Aris A. Z. (2014). "Continuous fixed-bed column study and adsorption modeling: removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons," *Biochemical Engineering Journal*. 87, 50–56.

Lim A.P., Aris A.Z. 2014. Continuous Fixed-Bed Column Study and Adsorption Modeling: Removal of Cadmium (II) and Lead (II) Ions in Aqueous Solution by Dead Calcareous Skeletons. *Biochemical Engineering Journal*. 87, 50-61.

Liu, R., Tang, H., Zhang, B. (1999). Removal of Cu(II), Cd(II) and Hg(II) from Wastewater by Poly(Acrylaminophosphonic)-type Chelating Fiber. *Chemosphere.* 38 (13), 3169-3179.

Lodeiro P, Cordero B, Herrero J.L, Sastre de Vieene M.E. (2006) The Use of Protonated *Sargassum muticum* as Biosorbent for Cadmium Removal in a Fixed-Bed Column, *J. Hazard Mater.*137, 244-253

Long Y, Lei D, Ni J, Ren Z, Chen C, and Xu H. (2014). "Packed bed column studies on lead(II) removal from industrial wastewater by modified Agaricus bisporus," *Bioresource Technology*. 152, 457–463.

López-Cervantes J., Sánchez-Machado D.I., Sánchez-Duarte R.G., Correa-Murrieta M.A. (2017). Study of a fixed-bed column in the adsorption of an azo dye from an aqueous medium using a chitosan–glutaraldehyde biosorbent . *Adsorption Science & Technology*. 36(1-2), 215-232.

Malek A., Farooq S. (1996) Comparison of Isotherm Models for Hydrocarbon Adsorption on Activated Carbon. *AIChE Journal*. 42(11), 3191-3201.

Mansoorian H.J., Bazrafshan E, Yari A., and Alizadeh M, (2014) Removal of azo dyes from aqueous solution using Fenton and modified Fenton processes. *Health Scope*. 3(11), 1-9

Mary A.L. (2014). Preparation and Characterization of Homopolymer Polyacrylonitrile-Based Fibrous Sorbents for Arsenic Removal. *Environmental Engineering Science.* 31(11), 593-601.

Mbarki F, Ammari F, Amor A.B.H, Meganem F. (2017). Functional groups grafted on poly(vinyl chloride) – evaluation of new modified polymers in metal ions adsorption. *Polimery*. 62, 109-117.

McCabe W.L., Smith J.C., Harrior P (2004). *Unit Operations of Chemical Reaction*. McGraw Hill Ed.

Meena A.J., Mishra G.K., Rai P.K., Rajagopal C., Nagar P.N. (2005). Removal of Heavy Metal Ions from Aqueous Solutions using Carbon Aerogel as an Adsorbent. *Journal of Hazardous Materials*. 122(1-2), 161-170.

Moradi. O (2016). Applicability comparison of different models for ammonium ion adsorption by multi-walled carbon nanotube. *Arabian Journal of Chemistry*. 9(2), 1170-1176.

Muataz A.A, Omer Y.B, Al-Tawbini B, Bukhari A.A, Abuilaiwi F.A, and. Fettouhi M.B. (2010). Effect of Carboxylic Functional Group Functionalized on Carbon Nanotubes Surface on the Removal of Lead from Water. *Bioinorganic Chemistry and Applications*. 2010, 1-9.

Mulu B.D. (2013). Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste. *Journal of Thermodynamics*. 2013, 1-6.

Mustapha A.A., Abdu N., Jibrin J.M. (2017). Adsorption of Cadmium, Copper, Lead and Zinc on Organically Amended Soil Fractions Using the Freundlich, Langmuir and Dubinin-Raduskevich Models. *International Journal of Soil Science.* 12, 43-53.

Nabi S.A., Naushad M., Ganai S.A. (2007) Use of Naphthol Blue–Black-Modified Amberlite Ira-400 Anion-Exchange Resin for Separation of Heavy Metal Ions. *Acta Chromatographica*. 18, 180-189.

Naidoo S, and Olaniran AO. (2014). Treated Wastewater Effluent as a Source of Microbial Pollution of Surface Water Resources. *International Journal of Environmental Research and Public Health.* 11(1), 249–270.

Namasivayam, C., Senthilkumar, S. (1999). Adsorption of Copper(II) by 'Waste' Fe(III)/Cr(III) Hydroxide from Aqueous Solution and Radiator Manufacturing Industry Wastewater. *Separation Science and Technology.* 34(2), 201-217.

Nasef, M.M. And Hegazy, E.S.A. (2004) Preparation And Applications Of Ion Exchange Membranes By Radiation-Induced Graft Copolymerization Of

Polar Monomers Onto Non-Polar Films. *Progress In Polymer Science*. 29, 499-561.

Nasef, M.M., Saidi, H., Mohd Dahlan, K.Z., (2009) Single-step Radiation Induced Grafting for Preparation of Proton Exchange Membranes for Fuel Cell. *Journal of Membrane Science.* 339(1), 115-119

Nasef, M.M., Saidi, H., Ujang, Z., Mohd Dahlan, K.Z., (2010). Removal of Metal Ions from Aqueous Solutions Using Crosslinked Polyethylene-GTMFJ-Polystyrene Sulfonic Acid Adsorbent Prepared by Radiation Grafting. *J. Chil. Chem. Soc*. 55(4), 421-427.

Nasef, M.M and Guven, O. (2012). Radiation-Grafted Copolymers for Separation and Purification Purposes: Status, Challenges and Future Directions. *Progress in Polymer Science.* 37, 1597– 1656.

Nasef, M.M., Ujang, Z. (2012), Introduction to Ion-Exchange Processes, in: *Ion-Exchange Technology: Theory, Materials and Applications,* Inamuddin Sediqi and Luqman, M. (Eds.), Springer Science, New York, USA, 1-39.

Nasef, M. M., Nallappan, M. and Ujang, Z. (2014) Polymer-based Chelating Adsorbents for the Selective Removal of Boron from Water and Wastewater: A Review. *Reactive and Functional Polymers*. 85, 54-68

Nasef M.M., Abbasi A., Ting T.M. (2014). New CO2 adsorbent containing aminated poly (glycidyl methacrylate) grafted onto irradiated PE-PP nonwoven sheet. *Radiation Physics and Chemistry*. 103, 72-74.

Nasef M.M., Alinezhad S.S. Mat R., Shabanzadeh P., Yusof R. Zakeri M., Farag H. (2016) Preparation Of Alkaline Polymer Catalyst By Radiation Induced Grafting For Transesterification Of Triacetin Under Neural Network Optimized Conditions. *Journal of Macromolecular Science Part A.* 53(9), 557-565.

Nasef M.M., Ting T.M., Abbasi A., Layeghi-MoghaddamA. Alinezhad, S.S. Hashim K. (2016). Radiation grafted adsorbents for newly emerging environmental applications. *Radiation Physics and Chemistry*. 118, 55-60.

Neumann, S. and Fatula, P. (2009): Principles of Ion Exchange in Wastewater Treatment. In: *Asian Water*. 14-19.

Nilchi A., Yaftian M., Aboulhasanlo G., Garmarodi S.R., (2009). Adsorption of Selected Ions on Hydrous Cerium Oxide. *Journal of Radioanalytical and Nuclear Chemistry*. 279(1), 65-74.

Nuengmatcha P., Mahachai R., Chanthai S. (2014). Thermodynamic And Kinetic Study Of The Intrinsic Adsorption Capacity Of Graphene Oxide For Malachite Green Removal From Aqueous Solution. *Oriental Journal Of Chemistry*. 30(4), 1463-1474.

Nwabanne, J. T. and Igbokwe, P. K (2012). Adsorption Performance of Packed Bed Column for the removal of Lead (ii) using oil Palm Fibre. *International Journal of Applied Science and Technology*. 2(5), 106-115.

Oliveira H. (2012). Chromium As An Environmental Pollutant: Insights On Induced Plant Toxicity. *Journal of Botany*. 2012, 7-15.

Pagnanelli F, Mosca E, Giuliano V And Toro L. (2004) Sequential Extraction of Heavy Metals in River Sediments of an Abandoned Pyrite Mining Area; Pollution Detection and Afnity Series. *Environmental Pollut*ion. 132, 189–201.

Patiha, Heraldy E., Hidayat Y. and Firdaus M. (2016). The langmuir isotherm adsorption equation: The monolayer approach. IOP Conference Series: *Materials Science and Engineering*. 107(1), 1-9.

Paul Chen J, Chua M.L., Zhang B., (2002) Effects of Competitive Ions, Humic Acid, and pH on Removal of Ammonium and Phosphorous from the Synthetic Industrial Effluent by Ion Exchange Resins. *Waste management.* 22(7), 711-719.

Pehlivan, E and Altun, T, (2006). The Study of Various Parameters Affecting the Ion Exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from Aqueous Solution on Dowex 50W Synthetic Resin. *Journal of Hazardous Materials*. 134(1-3), 149-156.

Pehlivan, E and Altun, T, (2007). Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} Ions from Aqueous Solution by Lewatit CNP 80. *Journal of Hazardous Materials*. 140, 299-307.

Pillay V, Seedat A, Choonara YE, du Toit LC, Kumar P, Ndesendo VMK.(2013). A Review of Polymeric Refabrication Techniques to Modify Polymer Properties for Biomedical and Drug Delivery Applications. *AAPS PharmSciTech*. 14(2), 692-711.

Rafatullah M., Sulaiman, O., Hashim A. Ahmad, A. (2009). Adsorption of Copper (II), Chromium (III), Nickel (II) and Lead (II) Ions from Aqueous Solutions by Meranti Sawdust. *Journal of Hazardous Materials.* 170(2-3), 969-977.

Rao, K.S., Anand, S., Venkateswarlu, P. 2011. Modelling the Kinetics of Cd(II) Adsorption on *Syzygium cumini L* Leaf Powder in a Fixed Bed Mini Column. *Journal of Industrial and Engineering Chemistry*. 17(2), 174-181.

Rengaraj S., Yeon J.W., Kim Y., Jung Y., Ha Y.K. Kim W.H (2007). Adsorption Characteristics of Cu(II) onto Ion Exchange Resins 252H and 1500H: Kinetics, Isotherms and Error Analysis. *Journal of Hazardous Materials*. 143, 469–477.

Rezaei F., and Webley P.(2010) Structured Adsorbents in Gas Separation. *Separation and Purification Technology.* 70, 243–56.

Rohani R., Nasef M.M., Saidi H., Dahlan K.Z.M. (2007). Effect of reaction conditions on electron induced graft copolymerization of styrene onto poly(ethylene-*co*-tetrafluoroethylene) films: Kinetics study. *Chemical Engineering Journal*. 132, 27-35.

Salamatinia B., Kamaruddin A.H., Abdullah A.Z., (2008) Modeling of the Continuous Copper and Zinc Removal by Sorption onto Sodium Hydroxide-Modified Iol Palm Frond in a Fixed-Bed Column. *Chemical Engineering Journal*. 145, 259-266.

Samiey B., Cheng C.H., Wu, J (2014). Organic-Inorganic Hybrid Polymers as Adsorbents for Removal of Heavy Metal Ions from Solutions: A Review. *Materials*. 7, 673-726 .

Sarkar B. (2003).Heavy Metal in the Environment . New York:Marcel Dekker Inc.

Sarkar S., Greenleaf, J. E. and SenGupta, A. K. (2009). Ion Exchange Technology. Encyclopedia of Polymer Science and Technology. John Wiley & Sons, Inc.

Sekhula, M.M., Okonkwo J.O., Zvinowanda C.M., Agvei, N. N., Chaudhary A.J. (2012). Fixed bed Column Adsorption of Cu (II) onto Maize Tassel-PVA Beads. *J Chem Eng Process Technology*. 3(2), 1-5.

Seko N, Tamada M, Yoshii F. (2005) Current Status of Adsorbent for Metal Ions with Radiation Grafting and Crosslinking Techniques. *Nuclear Instruments and Methods in Physics Research Section B*. 236, 21–9.

Seko N, Bang LT, Tamada M.(2007) Syntheses of Amine-Type Adsorbents with Emulsion Graft Polymerization of Glycidyl Methacrylate. *Nuclear Instruments and Methods in Physics Research Section B*. 265, 146–9.

Shahbazi A., Younesi H., Badiei A., 2011. Functionalized SBA-15 Mesoporous Silica by Melamine-Based Dendrimer Amines for Adsorptive Characteristics of Pb(II), Cu(II) and Cd(II) Heavy Metal Ions in Batch and Fixed Bed Column. *Chemical Engineering Journal*. 168, 505-518.

Shaidan N.H., Edemerdash U., Awad S. (2012). Removal of Ni(II) Ions from Aqueous Solutions Using Fixed Bed Ion Exchange Column Technique. *Journal of the Taiwan Institute of Chemical Engineers*. 43, 40-45.

Sharifnia S., Khadivi M.A., Shojaeimehr T. and Shavisi Y. (2016). Characterization, isotherm and kinetic studies for ammonium ion adsorption by light expanded clay aggregate (*LECA*). *Journal of Saudi Chemical Society*. 20(1), 342-351.

Sharma R. and Singh B., (2013). Removal of Ni(II) ions from aqueous solutions Using Modified Rice Straw in a Fixed Bed Column. *Bioresource Technology*. 146, 519-524.

Sharma S.K. (2015). Heavy Metals in Water : Presence, Removal and Safety. Royal Society of Chemistry. UK.

Shoji A, Kenichi S, Akinori J, Akio K, Takanobu S. (2001) Phosphoric Acid Fiber for Extremely Rapid Elimination of Heavy Metal Ions from Water. *Analytical Science.* 17, 205–208

Singare P.U. and Patange N. (2014). Ion-exchange reaction thermodynamics to study the selectivity behaviour of nuclear and non-nuclear grade anion exchange resins. International Letters of Chemistry, *Physics and Astronomy*. 6, 8-15.

Singha S. and Sarkar U. (2014). Analysis of the Dynamics of a Packed Column using Semi-Empirical Models: Case Studies with the Removal of Hexavalent Chromium from Effluent Wastewater. *Korean Journal of Chemical Engineering.* 32(1), 20-29.

Sivakumar P And Palanisamy P.N. (2009). Adsorption Studies Of Basic Red 29 By A Non- Conventional Activated Carbon Prepared From Euphorbia Antiquorum L . *International Journal of Chemtech Research*. 2(3), 502-510.

Strathmann H.(2004) *Ion-exchange Membrane Separation Processes*. Amsterdam: Elsevier.

Tanaka Y.(2007). *Ion Exchange Membranes: Fundamentals and Applications*. Amsterdam: Elsevier.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy Metals Toxicity and the Environment. *EXS*. 101, 133–164.

Ting T.M, Nasef M.M, Sithambaranathan P. (2017). Kinetic investigations of emulsion-and solvent-mediated radiation induced graft copolymerization of glycidyl methacrylate onto nylon-6 fibres. *Journal of Radioanalytical and Nuclear Chemistry*. 311(1), 843-857.

Ting T.M., Nasef M.M., Hashim K. (2015). Modification of nylon-6 fibres by radiation-induced graft polymerisation of vinylbenzyl chloride. *Radiation Physics and Chemistry.* 109, 54-62.

Ting T.M. (2015). *Preparation and characterization of radiation grafted fibrous adsorbent containing N-methyl-D-glucamine for boron removal*. PhD thesis, Universiti Teknologi Malaysia, Skudai.

Tongwen X.(2005). Ion Exchange Membranes: State of Their Development and Perspective. *Journal of Membrane Science*. 263, 1–29.

Tran T.H., Hirotake O., Yoshiki H., Kazuhiro H., (2017). Removal of Metal Ions from Aqueous Solutions using Carboxymethyl Cellulose/Sodium Styrene Sulfonate Gels Prepared by Radiation Grafting *Carbohydrate Polymers.* 157, 335–343.

Trgo M.,Medvidovic N.V., Peric J. (2011). Application of mathematical empirical models to dynamic removal of lead on natural zeolite clinoptilolite in a fixed bed column. *Indian Journal of Chemical Technology*. 18, 123-131.

Tripathi A, Ranjan MR (2015) Heavy Metal Removal from Wastewater Using Low Cost Adsorbents. *Journal of Bioremediation and Biodegradation.* 6, 315-320.

Turhanen P.A.,Vepsäläinen, Jouko J. Peräniemi, S. (2015). Advanced material and approach for metal ions removal from aqueous solutions. *Scientific Reports*. 5(8992).

United Nations Environment Programme East Asian Regional Coordinating Unit (UNEP/SCS) (2004) *National Report of Malaysia On the Formulation of a Transboundary Diagnostic Analysis And Preliminary Framework of a Strategic Action Programme for the Bay of Bengal*.

Verbych,S., Alpatova, A., Bryk, M., Nigmatullin, R., Hilal, N (2004) Ultrafiltration of Water Containing Natural Organic Matter: Heavy Metal Removing in the Hybrid Complexation-Ultrafiltration Process. *Separation and Purification Technology*. 40(2), 155-162.

Venkateswarlu S, S. Himagirish Kumar, N.V.V. Jyothi, (2015). Rapid removal of Ni(II) from aqueous solution using 3-Mercaptopropionic acid functionalized bio magnetite nanoparticle. *Water Resources and Industry*. 12, 1-7.

Vieira, M L G, Esquerdo, VM, Nobre, LR (2014) Glass beads coated with chitosan for the food azo dyes adsorption in a fixed bed column. *Journal of Industrial and Engineering Chemistry.* 20(5), 3387–3393.

Wang, J. Zhao L., Duan W., Han L., Chen Y. (2012). Adsorption of Aqueous Cr(VI) by Novel Fibrous Adsorbent with Amino and Quaternary Ammonium Groups. *Ind. Eng. Chem. Res.* 51(42), 13655–13662.

Wang, S., Vincent, T., Faur, C., & Guibal, E. (2017). Algal Foams Applied in Fixed-Bed Process for Lead(II) Removal Using Recirculation or One-Pass Modes. *Marine Drugs*. 15(10), 315-320.

Xu Z., Cai J G., Pan B.C. (2013). Mathematically modeling fixed-bed adsorption in aqueous systems. *Journal of Zhejiang University SCIENCE A*. 14(3), 155-176.

Yousef N.S., Farouq R., Hazzaa R. (2016). Adsorption kinetics and isotherms for the removal of nickel ions from aqueous solutions by an ion-exchange resin: application of two and three parameter isotherm models. *Desalination and Water Treatment.* 57(46), 21925-21938

Yu Z., Qi T., Qu J., Wang L., Shu J.(2009) Removal of Ca(II) and Mg(II) from Potassium Chromate Solution on Amberlite IRC 748 Synthetic Resin by Ion Exchange. *Journal of Hazardous Materials*. 167(1-3), 406-412.

Zafer Y.(2007) Salt Splitting with Cation-Exchange Membranes. *Desalination.* 212, 70–8.

Zagorodni AA.(2006). *Ion Exchange Materials, Properties and Applications*. Amsterdam: Elsevier.

Zare K., Sadegh H., Shahryarigoshekandi R., Asif M., Tyagi I., Agarwal S., Gupta V.K. (2016). Equilibrium and kinetic study of ammonium ion adsorption by Fe_3O_4 nanoparticles from aqueous solutions. *Journal of Molecular Liquids*. 213, 345-350.

Zhongxin J,Yiling B,Qingyang L.(2011). Removal of Copper Ions from Aqueous Solution with a Weak Cation Exchanger By Radiation-Induction Grafting Acrylic Acid Onto Polypropylene Fiber. *International Journal of Industrial Chemistry.* 2(1), 23–26.

Zu J, He S, Nho YC, Pyo JJ, Yan F. (2010). Preparation of Adsorbent for Palladium Ions by Amination of Acrylonitrile Grafted Polypropylene Nonwoven Fabrics. *Journal of Applied Polymer Science*.116, 1414–21.

Zwain H.M, Vakili M., Dahlan I. (2014). Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review. *International Journal of Chemical Engineering.* 2014, 1-13.