UNIVERSITI PUTRA MALAYSIA

PERFORMANCE OF AMIDOXIME-MODIFIED POLY (ACRYLONITRILE-CO-ACRYLIC ACID) FOR THE REMOVAL OF CADMIUM(II) AND LEAD(II) IONS IN AQUEOUS SOLUTION

NUR AMIRAH BINTI MOHD ZAHRI

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By

NUR AMIRAH BINTI MOHD ZAHRI

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

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The untreated heavy metal ions that were discharged as effluent waste had caused serious impact on the environment and human health. The adsorption process is an alternative way to remove heavy metal ions. The polymer-based adsorbent was chosen as material to remove heavy metal ions due to its economic cost, can be prepared with convenient method and excellent capability to make high adsorption towards metal ions. In this study, the synthesis and modification of amidoxime (AO) modified poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) was carried out. Next, the effect of adsorption parameters, equilibrium and kinetic studies of cadmium ion (Cd^{2+}) and lead ion (Pb^{2+}) were investigated. The optimisation of adsorption parameter was analysed using Response surface methodology (RSM).

The poly(AN-*co*-AA) was synthesised *via* redox polymerisation and was further chemically modified with hydroxylamine hydrochloride to produce AO modified poly(AN-*co*-AA) as adsorbent. Then, single batch system of adsorption experiments for each heavy metal ions of Cd^{2+} and Pb^{2+} were implemented by varying the pH, adsorbent dosage, initial metal ion concentration and contact time. The isotherm and kinetic studies were carried out by using single batch of experimental data. Lastly, the optimisation of adsorption conditions was employed using Central composite design of RSM.

The synthesis yield of poly(acrylonitrile) (PAN) was 73% and poly(AN-*co*-AA) 93:7 obtained the highest yield at 72%. The Fourier transform infrared (FTIR) spectra confirmed the successful of polymerisation due to the appearance of absorption peaks that were assigned to the C≡N and –COOH functional groups on the spectra. The microanalysis showed that the overall trend of elemental percentage for poly(AN-*co*-AA) copolymers were slightly decreased as the mole ratios of acrylic acid (AA) increased. The thermogravimetric (TG) analysis suggested that the thermal stability of poly(AN-*co*-AA) was lower as compared to the PAN. On the other hand, the FTIR spectra of AO modified poly(AN-*co*-AA) proved that the C≡N were successfully converted into amidoxime groups. The microanalysis showed that the increasing trend of nitrogen and hydrogen elements in amidoxime modified polymer. The amine capacity test confirmed the quantity of amidoxime functional groups in modified polymer.

The maximum removal percentage based on parameters effect for each Cd^{2+} and Pb^{2+} were with an initial adsorbate concentration of 100 $mg.L^{-1}$ at pH 9 with adsorbent dosage of 4 $g.L^{-1}$ (Cd^{2+}) and 8 $g.L^{-1}$ (Pb^{2+}). The Sips isotherms showed good agreement for the adsorption of Cd^{2+} (R^2 of 0.9997) with maximum adsorption capacities of 20 $mg.g^{-1}$. The adsorption of Pb^{2+} satisfied the Freundlich isotherms (R^2 of 0.9875) with maximum adsorption capacities of 125 $mg.g^{-1}$. The Lagergren pseudo-first order was observed to have better R^2 compared to the other models for both Cd^{2+} and Pb^{2+}.

The RSM shows the removal of Cd^{2+} (98.33%) was satisfied with predicted value (98.58%) at optimum conditions, 10 $mg.L^{-1}$ of Cd^{2+} initial concentration and the 4.66 $g.L^{-1}$ of adsorbent dosage at pH 9.31. The removal of Pb^{2+} was 99.41% that fitted well with the predicted value (99.80%) with the optimum conditions, 20 $mg.L^{-1}$ of Pb^{2+} initial concentration and 8.27 $g.L^{-1}$ of adsorbent dosage at pH 9.08.

The results suggested that the AO modified poly(AN-*co*-AA) sorbent is a potential material to capture high quantity of Cd^{2+} and Pb^{2+} from aqueous solution under certain conditions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PRESTASI POLI(AKRILONITRIL-KO-ASID AKRILIK) DIMODIFIKASI DENGAN AMIDOKSIM BAGI PENYINGKIRAN ION-ION KADMIUM(II) DAN PLUMBUM(II) DALAM LARUTAN AKUES

Oleh

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Logam berat yang tidak dirawat dan dilepaskan sebagai sisa perindustrian telah menyebabkan kesan yang serius terhadap alam sekitar dan kesihatan manusia. Proses penjerapan merupakan kaedah alternatif dalam menyingkirkan ion-ion logam berat. Penjerap berasaskan polimer telah dipilih untuk menyingkirkan ion-ion logam berat kerana kos yang rendah dan teknik penyediaan yang mudah dan mampu menjerap ion-ion logam berat dengan jayanya. Kajian mengenai sintesis dan modifikasi terhadap poli(akrilonitril-*ko*-asid akrilik) (poli(AN-*ko*-AA)) dimodifikasi dengan amidoksim (AO) telah dijalankan. Seterusnya, kesan penjerapan ion kadmium (Cd^{2+}) dan ion plumbum (Pb^{2+}) terhadap parameter-parameter penjerapan, keseimbangan dan kinetik telah dilakukan. Selain daripada itu, parameter-parameter penjerapan telah dioptimumkan melalui analisis dengan menggunakan Kaedah tindakbalas permukaan (RSM).

Sintesis poli(AN-*ko*-AA) dilakukan melalui pempolimeran redoks dan seterusnya diubahsuai melalui kaedah kimia dengan hidroksilamina hidroklorida dalam menghasilkan penjerap poli(AN-*ko*-AA) dimodifikasi dengan AO. Seterusnya, eksperimen tunggal penjerapan terhadap ion-ion logam berat Cd^{2+} dan Pb^{2+} telah dijalankan dengan mengubah pH, dos bahan penjerap, kepekatan awal bagi ion logam berat dan masa penjerapan. Kajian isoterma dan kinetik telah dilakukan dengan menggunakan data eksperimen tunggal. Akhir sekali, pengoptimuman kajian penjerapan telah dilakukan dengan kaedah RSM yang menggunakan Reka bentuk komposit tengah.

Hasil sintesis pempolimeran poli(akrilonitril) (PAN) ialah sebanyak 73% dan poli(AN-*ko*-AA) 93:7 telah memberi hasil pempolimeran tertinggi iaitu sebanyak 72%. Spektroskopi inframerah transformasi fourier (FTIR) mengesahkan kejayaan pempolimeran dengan kehadiran kumpulan berfungsi C≡N dan –COOH pada spektra. Mikroanalisis menunjukkan keseluruhan peratusan unsur-unsur untuk kopolimer bagi poli(AN-*ko*-AA) sedikit menurun sejajar dengan peningkatan nisbah asid akrilik (AA). Analisis termogravimetrik (TG) menunjukkan kestabilan haba bagi poli(AN-*ko*-AA) adalah lebih rendah berbanding dengan PAN. Manakala, analisis FTIR bagi poli(AN-*ko*-AA) dimodifikasi dengan AO membuktikan kumpulan berfungsi nitril telah berjaya ditukarkan kepada kumpulan AO. Mikroanalisis menunjukkan peningkatan bagi unsur nitrogen dan hidrogen yang terdapat pada polimer dimodifikasi dengan AO. Ujian kapasiti amina mengesahkan bilangan kumpulan berfungsi AO dalam polimer dimodifikasi dengan AO.

Peratusan penjerapan yang paling tinggi berdasarkan kesan parameter bagi Cd^{2+} dan Pb^{2+} ialah dengan kepekatan awal logam berat sebanyak 100 mg.L^{-1} pada pH 9 dengan kesan dos bahan penjerap sebanyak 4 g.L^{-1} (Cd^{2+}) dan 8 g.L^{-1} (Pb^{2+}). Model isoterma Sips merupakan paling sesuai dengan data kajian bagi Cd^{2+} (R^2=0.9997) dengan kapasiti penjerapan sebanyak 20 mg.g^{-1} manakala isoterma Freundlich bersetuju bagi data kajian Pb^{2+} (R^2=0.9875) dengan kapasiti penjerapan sebanyak 125 mg.g^{-1}. Data kinetik Cd^{2+} dan Pb^{2+} didapati sesuai dengan model Largergren aturan pertama-pseudo.

Kajian RSM menunjukkan sebanyak 98.33% penyingkiran Cd^{2+} selari dengan nilai ramalan (98.58%) dalam keadaan optima iaitu 10 mg.L^{-1} bagi kepekatan awal dan 4.66 g.L^{-1} bagi dos bahan penjerap pada pH 9.31. Penyingkiran bagi Pb^{2+} telah berjaya sebanyak 99.41% dengan nilai ramalan (99.80%) dalam keadaan optima iaitu 20 mg.L^{-1} bagi kepekatan awal dan 8.27 g.L^{-1} bagi dos bahan penjerap pada pH 9.08.

Keputusan data yang diperolehi menunjukkan poli(AN-*ko*-AA) dimodifikasi dengan AO merupakan bahan penjerap yang berkebolehan untuk menjerap Cd^{2+} dan Pb^{2+} dengan kuantiti yang tinggi dari larutan akues dengan keadaan yang tertentu.

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LIST OF NOTATIONS/SYMBOLS

AN	Acrylonitrile
AA	Acrylic acid
AO	Amidoxime
PAN	Poly(acrylonitrile)
Poly(AN-*co*-AA)	Poly(acrylonitrile-*co*-acrylic acid)
Pb^{2+}	Lead ions
Cd^{2+}	Cadmium ions
RSM	Response surface methodology
CCD	Central composite design
FTIR	Fourier transform infrared
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
SSE	Sum of squares errors
R^2	Correlation coefficient
PZC	Point zero charge
Qe (%)	Concentration amount of adsorbate being adsorbed by adsorbent at equilibrium
q_e (mg.g^{-1})	Amount of adsorbate adsorbed on per gram of adsorbent at equilibrium
C_o (mg.L^{-1})	Initial adsorbate concentration in solution
C_e (mg.L^{-1})	Adsorbate concentration in solution at equilibrium
W_s (g)	Weight of adsorbent
q_m (mg.g^{-1})	Maximum adsorption capacity
q_t (mg.g^{-1})	Adsorbate concentration being adsorbed on per gram of adsorbent at time *t* (min)

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CHAPTER 1

INTRODUCTION

1.1 Background

Water is a fundamental support in life either for food productions and population growth (Corcoran et. al., 2010). The water pollution existences interrupt the aquatic biodiversity and cause diseases to humans, animals and plants. One of the main causes of water pollution is due to the irresponsible and insensible of certain industrial sectoring authorities that failed to manage the industrial waste according to the standard requirement by the health organization (Moradi et al., 2009). The untreated industrial effluents may lead to huge disasters in the ecosystem life in a long run and the worst impact will be faced by the generations that inherit this land. The untreated effluents that were discharged into water had caused to the transportation of toxic and polluted waste throughout the water sources. The polluted water remains in water sources and leads to environmental problem for many generations as long as no effective action is taken out to solve this worldwide problem.

The industrial effluents may contain solid, chemicals and toxic waste that should be handled in efficient ways. The industrial effluents of heavy metals ions become a great concern nowadays due to their toxicity that influences the global health (Demirbas, 2008). Most of the heavy metal elements are very toxic such as arsenic, cadmium, lead and mercury even in low concentrations (Azelee et. al., 2012). The industries that produce massive amount of heavy metals waste are electroplating, metal finishing, printing circuit board and battery manufacturing plants (lead-acid battery and nickel-cadmium battery industries) (Wong et. al., 2014). Therefore, there are regulations for industries to meet a standard of effluent discharge. In Malaysia, the standard of effluent discharge was stipulated by the Department of Environment (DOE) in the Third Schedule Environmental Quality Act, 1974 as attached in Appendix A.

The development technologies on treating heavy metals have become a great interest and indirectly have increased research activities in this area. There are many innovation and techniques have been carried out for heavy metal ions uptake with better ways in term of simplicity, efficiency and production cost. Various techniques have been implemented for heavy metal ions treatment such as sedimentation, flocculation, absorption, co-precipitation, cation and anion exchanger, complexation, precipitation, oxidation/reduction, microbiological activity and plant uptake (Matagi et. al., 1998, Moradi et al., 2009; Geyikci et al., 2012). The heavy metal ions uptake techniques have many advantages and disadvantages that have been addressed from time to time. In this study, we have implemented adsorption technique to make heavy metal ions capture in aqueous solution. This is due to the simple, economic, feasible, and efficient ways provided by the adsorption technique for the wastewater treatment (Foo & Hameed, 2010).

1.2 Polymerisation

Polymerisation is a process of each molecule of monomers to link to two (or more) other molecules of a monomer by chemical reaction (Young & Lovell, 2011). There are various methods can be applied for synthesis techniques such as bulk, solution, suspension and emulsion polymerisation (Mittal, 2010). In present work, suspension polymerisation was applied to prepare polymer adsorbent. A redox method was selected due to water based synthesis that was carried out in mild reaction conditions at shorter time and yet produce high yield (Bhanu et. al., 2002).

Preparation of polymers has become an interesting topic for researchers by introducing monomers and comonomers into reactive polymer chains to form linear or crosslinked polymers (El-Newehy et. al., 2014). The groups and polymeric nature of polymers play important roles in large range of applications such as packaging, building and transportation construction, electrical and electronic equipment, agriculture, medical and sports equipment (European Chemical Agency, 2012). Besides, the polymers can be utilized in heavy metals adsorption applications. This is because the polymer can be copolymerised or grafted and then modified with metal-chelating functional groups (Chen et al., 2013). Hence, the polymer-based adsorbent through polymerisation process was studied on the removal of cadmium ion (Cd^{2+}) and lead ion (Pb^{2+}).

1.3 Problem statement

This study is focus on the removal of cadmium ion (Cd^{2+}) and lead ion (Pb^{2+}) using polymer-based adsorbent of amidoxime (AO) modified poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)).

The polymer-based adsorbent was studied because the existing adsorbent like activated carbon (AC)-based adsorbent needs a high energy in production. Solener et al. (2008) reported that AC was limited due to high operation cost and difficult in regeneration for the industrial scale application. The waste material of fly ash also has been studied in removing heavy metals. Based on Abdel Salam et al. (2011) article, the fly ash was proved as effective as activated carbon. However, the high dosages of fly ash needed were disadvantages and would lead to disposal problem. Apart from that, another type of adsorbent which is known as biosorbent requires plenty of time for culturing process prior to its usage. Moreover, Fu and Wang (2011) studied that the separation of biosorbent would be difficult after adsorption process, thus regeneration of sorbents are not convenient. The polymer-based adsorbent was an alternative way in adsorption due to large surface area, perfect mechanical rigidity, chemical modification on polymer surface and pore size distribution, and feasible regeneration under mild conditions (Pan et al., 2009). Hence, polymer-based adsorbents are useful for application in the removal of heavy metal ions in solution. This was proved by different studies on heavy metal removal such as chromium, copper, nickel and uranium using polymer-based adsorbent

(Chakraborty et al., 2014; Moradi et al., 2009; Shaaban et al., 2014; Zhang et al., 2005). Hence, the polymer-based adsorbent was chosen and studied in this work.

The polymer-based adsorbent is prepared by synthesising polymers using various methods. Most of the polymerisation methods consume a lot of energy, time and chemical solvents which tend to produce more chemical waste (Moghadam & Bahrami, 2005; Atta et al., 2011; Demir et al., 2004; Shan et al., 2006). Therefore, the more feasible condition of polymerisation with high recovery of poly(AN-*co*-AA) was studied. In this study, the toxic solvent that frequently used as reaction medium in suspension polymerisation was replaced with deionised water that is cheaper, none hazardous and omits the use of solvent recovery. The polymerisation time was shorter with less energy usage by using mild temperature but yet obtained high polymerisation yield.

The copolymerisation of AN and AA were carried out due to the poor characteristics of poly(acrylonitrile) (PAN) to act as adsorbents. PAN has high nitrile-nitrile dipolar interactions that lead to low moisture absorption, hydrophobicity and lack of active functionality (Mishra et al., 2011). Therefore, in order to overcome these problems, the copolymerisation of AN with AA was implemented. The AA was chosen as a monomer due to its potential to overcome the shortcoming of PAN by interupting the high nitrile-nitrile dipolar interactions along the PAN chains. The –COOH functional groups in AA was reported to improve the hydrophilicity and affinity of the polymer chains for adsorption applications in aqueous solution (Shan et al., 2006).

The poly(AN-*co*-AA) cannot be utilized in removing heavy metal ions because the available functional groups in the polymer chains were not capable to form strong coordination with cations. Thus, the modification with hydroxylamine hydrochloride was carried out to overcome the limitation in heavy metal ions adsorption applications. The hydroxylamine hydrochloride itself has the advantages which can act as reducing agent towards the poly(AN-*co*-AA) and convert the C≡N groups to amidoxime (AO) groups ($RCNONH_2$). The AO functional groups are capable to form coordination with heavy metal ions during adsorption process. Apart from that, most of the adsorption studies in producing adsorbents of AO modified polymer resins involved tedious methods with long reaction time that are not feasible to be applied in industrial scale (Liu et. al., 2010; Shaaban et. al., 2014; Horzum et. al., 2012). The current study in producing AO modified poly(AN-*co*-AA) however, makes several noteworthy contributions to the high recovery poly(AN-*co*-AA) with more feasible condition; synthesis at mild temperature and time with the consumption of deionised water as reaction medium. For instance, the chemical modification with hydroxylamine hydrochloride was carried out with less chemicals consumption and shorter modification time compared to any established method (Horzum et al., 2012; Saeed et al., 2008; Liu et al., 2010).

Heavy metals have become a public great concern due to its toxicity, non-biodegradable and tendency to accumulate in living organisms (Gherasim et al., 2013). The heavy metals of cadmium (Cd) and lead (Pb) were categorized as high toxic heavy metals compared to some heavy metals like zinc, copper and manganese that required for living organism but in low concentrations. The Cd and Pb also were widely produced as effluent waste in variety of industrial sectors. As shown in the Third Schedule Environmental Quality Act, 1974 (Appendix A), it has stipulated that Cd and Pb were among heavy metals that was permitted to presence at low concentration in industrial discharge wastewater. Hence, with the characteristic of AO modified poly(AN-*co*-AA) as adsorbent, the studies on removal of cadmium ions (Cd^{2+}) and lead ions (Pb^{2+}) were investigated.

The ability of AO modified poly(AN-*co*-AA) to remove heavy metal ions (Cd^{2+} and Pb^{2+}) with different effect of parameters were carried out. The adsorption study only consider the trend and statistical on heavy metal ions removal for each parameters. In current work, the adsorption study was extended by predicting the equilibriums and kinetics of the adsorption of heavy metal ions towards the AO modified poly(AN-*co*-AA) polymer.

Furthermore, previous study reported the parameters that influenced the adsorption process such as the initial pH of heavy metal ions, adsorbent dosage, initial concentration of heavy metal ions and contact time without optimizing the maximum removal of heavy metal ions. In the present work, the optimization of maximum removal of heavy metal ions was successfully employed by the response surface methodology (RSM). Besides, the RSM is capable to make condition optimization for each parameter, hence the interactions between the parameters were evaluated.

The limitation in this study was to compare the concentration of cadmium and lead in the experimental solution and the actual industrial effluent waste. Due to time constraint, the performance of the AO modified poly(AN-*co*-AA) in actual industrial effluent waste was not carried out. Hence, this work will be proposed as the objective in future studies.

Therefore, the preparation of AO modified poly(AN-*co*-AA) adsorbent *via* convenient and affordable method was carried out and the performance of the adsorbent to capture Cd^{2+} and Pb^{2+} were investigated. In addition, the optimization study was carried out using RSM.

1.4 Objectives

The objectives of this study are:

1. To synthesis poly(acrylonitrile) (PAN) and poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) *via* redox method and to modify the polymers with hydroxylamine hydrochloride.

2. To investigate the effect of initial pH, adsorbent dosage and initial concentration of metal ions and contact time during the adsorption of Cd^{2+} and Pb^{2+} onto amidoxime (AO) modified (poly(AN-*co*-AA) in aqueous solution.

3. To study the equilibrium and the kinetics of adsorption process of Cd^{2+} and Pb^{2+} onto amidoxime-modified poly(AN-*co*-AA) in aqueous solution.

4. To optimize the percentage removal of Cd^{2+} and Pb^{2+} by determining the optimum conditions of pH, adsorbent dosage and initial concentration of (adsorbate) using response surface methodology (RSM).

1.5 Scope of study

In this study, an endeavor was made to polymerise poly(acrylonitrile) (PAN) and poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) with different feed mole ratios of AN and AA. Then, all poly(AN-*co*-AA) undergo chemical modification with hydroxylamine hydrochloride to form amidoxime (AO) modified poly(AN-*co*-AA). The AO modified poly(AN-*co*-AA) with the highest amine capacity was selected as adsorbents for the removal of Cd^{2+} and Pb^{2+} from aqueous solution. The further adsorption study was implemented through equilibrium study, kinetic study and optimization percentage removal of Cd^{2+} and Pb^{2+}.

1.6 Thesis layout

This thesis consists of 5 chapters and has been organised as below:-

- Chapter 1: Introduction covers brief reviews about the related subject study, problem statement, objectives and scope of the study.

- Chapter 2: Literature reviews containing comprehensive review related to the preparation of amidoxime modified resin polymer and heavy metal ions removal from aqueous solution.

- Chapter 3: Material and methods describe the procedure of polymerisation and chemical modifications. The characterization and analysis that have been carried out in this study are described as well.

- Chapter 4: Result and discussions laying out all the observations, lists of data and analysis results with comprehensive discussion

- Chapter 5: Conclusions part that recap all findings that were obtained in this study. The recommendations for future works were included as well.

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