REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS USING POLY(VINYLBENZYL CHLORIDE)

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DEDICATION

Dedicated with love:

To my beloved daddy; Gamal Abdo Allozy

To my adore mom; Ashwaq

To my dear brother; Mohammed

To my pretty sisters

To my sweetheart; Sara

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ABSTRACT

Poly (vinyl benzyl chloride) (PVBC) was synthesized through Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerisation technique utilizing monomer, vinylbenzyl chloride (VBC), 4-cyano-4 (phenyl-carbonothioylthio pentanoic acid) (CPADB) as RAFT agent and 4,4'-Azobis (4-cyanopentanoic acid) (ACPA) as initiator. The aim of this study is to obtain PVBC polymer with higher conversion rate and higher molecular weight polymer and to test on its ability to remove copper ions from aqueous solution. In this study, the time and temperature of RAFT polymerisation of PVBC was varied while the mole ratio VBC: CPADB: ACPA of polymerisation reaction is kept constant. PVBC was successfully synthesized when reacted for 24 hours at 80°C. The PVBC was characterized by Proton Nuclear Magnetic Resonance spectroscopy (^{1}H NMR) and Attenuated Total Reflection (ATR-FTIR). The highest monomer conversion was 57.7 % at 80°C for 24 hours. To explore the ability of the PVBC, adsorption study was carried out using Cu (II) solution. The PVBC was evaluated for removal of Cu (II) ions from aqueous solution. Important adsorption parameters such as adsorbate concentration, adsorption dosage and contact time were studied. The maximum Cu (II) adsorption ability (Q_{max}) of PVBC was 263.15 mg/g with copper removal rate 95 % under the optimum conditions of initial concentration (160 ppm), adsorbent dosage (14mg) and contact time (3 hours). The experimental data fitted better into Langmuir adsorption isotherm model than Freundlich model and kinetics studies were correlated with pseudo-second-order kinetic model. The polymers adsorption ability was over than 90% level after five cycles of adsorption but the total adsorption ability of PVBC for Cu (II) ions started to decrease after other five cycles from 80% to 54%. In view of the outcomes acquired, PVBC can be an effective and potential adsorbent for removing Cu (II) ions from an aqueous solution. The adsorption study showed that the PVBC has affinity towards Cu (II) ions. The prepared of PVBC proved to be potentially good for applications in wastewater treatment.

ABSTRAK

Poly (vinyl benzyl chloride) (PVBC) disintesiskan menggunakan teknik pempolimeran Pemindahan Rangkaian Terpisah-Pertambahan Berbalik (RAFT) menggunakan monomer, vinylbenzyl chloride (VBC), 4-cyano-4 (phenyl-carbonothioylthio pentanoic acid) (CPADB) sebagai agen RAFT dan 4,4'-Azobis (4-cyanopentanoic acid) (ACPA) sebagai pemula. Tujuan kajian ini ialah untuk memperoleh lebih banyak polimer PVBC dengan kadar penukaran lebih tinggi dan polimer dengan berat molekular tinggi untuk menguji kebolehan PVBC menyingkirkan ion kuprum daripada larutan akueus. Dalam kajian ini, masa dan suhu pempolimeran RAFT untuk PVBC berubah apabila kadar mol reaksi pempolimeran VBC: CPADB: ACPA dimalarkan. PVBC berjaya disintesiskan apabila dibiarkan bertindak balas selama 24 jam pada suhu 80°C. PVBC dicirikan oleh spektroskopi Resonans Magnetik Nuklear Proton (^{1}H NMR) Jumlah Refleksi Atenuat (ATR-FTIR). Pertukaran monomer tertinggi ialah 57.7 peratus pada 80°C untuk 24 jam. Kajian jerapan dijalankan untuk mengukur keupayaan PVBC untuk menyingkirkan ion Cu (II) daripada larutan akueus. Parameter penting jerapan seperti kepekatan zat terjerap, dos jerapan, dan masa sentuh telah dikaji. Keupayaan jerapan maksimum Cu (II) (Q_{max}) PVBC ialah 263.15 mg/g dengan kadar penyingkiran kuprum 95% pada keadaan optimum iaitu kepekatan awal (160 ppm), dos bahan terjerap (14 mg) dan masa sentuh (3 jam). Data eksperimen lebih padan kepada model isoterma jerapan Langmuir berbanding model Freundlich dan kajian kinetik berkorelasi dengan model kinetik pseudo-second-order. Keupayaan jerapan polimer tersebut adalah lebih 90% selepas lima kitaran jerapan tetapi keupayaan jerapan PVBC untuk ion Cu (II) mula berkurangan selepas lima kitaran daripada 80% kepada 54%. Dapat disimpulkan daripada keputusan yang diperoleh bahawa PVBC mampu menjadi bahan penjerap yang efektif dan berpotensi untuk menyingkirkan ion Cu (II) daripada larutan akueus. Kajian jerapan menunjukkan PVBC mempunyai afiniti terhadap ion Cu (II). PVBC yang digunakan terbukti berpotensi untuk digunakan dalam aplikasi melibatkan rawatan air kumbahan.

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LIST OF ABBREVIATIONS

^{1}H NMR	-	Proton Nuclear Magnetic Resonance spectroscopy
ACPA	-	4,4 Azobis (4-cyanopentanoic acid)
AIBN	-	Azobisisobutyronitrile abbreviated
ATR-FTIR	-	Attenuated Total Reflection
ATR-FTIRP	-	Atom transfer radical polymerization
CLRP	-	Controlled/living radical polymerisation
CPADB	-	4-cyano-4 (phenyl-carbonothioylthio pentanoic acid)
CSIRO	-	Common Wealth Scientific and Industrial Research Organization
CTA	-	Chain transition agent
Cu (II)	-	Copper (II)
$CuSO_4.5H_2O$	-	Copper sulfate pentahydrate
DP	-	Degree of polymerization
HCl	-	Hydrochloric acid
M	-	Monomer
MeOH	-	Methanol
MN	-	Molecular weight number
Na_2EDTA	-	Disodium ethylenediaminetetraacetate dihydrate
NMP	-	Nitroxide-mediated radical polymerization
PVBC	-	Poly (vinyl benzyl chloride)
Qmax	-	Maximum adsorption capacity
R	-	Main radicals
RAFT	-	Reversible Addition-Fragmentation Chain Transfer
UV-vis	-	Ultraviolet absorption spectroscopy
VBC	-	Vinyl benzyl chloride

LIST OF SYMBOLS

%	-	Percentage
°C	-	Degree Celcius
ppm	-	Parts per million
h	-	Hour
mg / L	-	milligram/liter
mL	-	milliliter
M	-	Molarity
mg	-	Milligram
V	-	Volume
M	-	Monomer

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The organic free radical chemistry is a multi-purpose technique when it comes to reaction states and functionality. Therefore, it is an ideal technique for functional polymeric materials synthesis. On the other hand, chain length and final polymeric material chain end are hard to control, which makes common radical processes not the ideal approach for particular applications. In 1990s the living radical polymerisation was established, the synthesis of the polymer horizon was fundamentally altered, llowing the development of clearly defined polymers with preferred molecular weights with limited dispersion (< 1.5) and narrow complex structure (or as they are known as block copolymers) (Matyjaszewski and Davis, 2003) (Barner-Kowollik et al., 2012). The irreversibly terminated chains in the polymerisation of radical proportion can possibly be limited by utilizing the inactive state of the emerging radical of a propagating chain, and therefore controlling the produced polymeric chain structure.

The polymerisation technique of reversible addition fragmentation chain transfer (RAFT) is the on top, among other methods, when it comes to versatility. This versatility is most evident in the multiple reactions conditions and wide range functionality tolerance (Chiefari et al., 1998). RAFT technique utilizes a chain transfer agent (RAFT agent, or CTA). This agent is a result of a reversible transfer in a degenerative process from a propagating chain to another. RAFT agent quick exchange from one propagating chain to another makes sure all chains are growing in parallel during the polymerisation process and a fair polymer output molecular weight buildup is accomplished. Furthermore, according the amount of CTA initially incorporated, the final material molecular weight can be tuned. Radicals presence stimulates the degenerative process, which is conventionally produced from thermal or photoinitaitors. The initiator amount is maintained low (i.e. high CTA/initiator ratio) to reduce the proportion of resulting dead chains. Hence, it is fairly known that to get the average degree of polymerisation (DP, i.e., monomers count per a chain), monomer to RAFT agent ratio should be measured to obtain that (Graeme Moad et al., 2012). RAFT polymerisation is widely used in the production of materials such as nanomaterials, hybrid materials and polymeric architectures (Moraes et al., 2013) (Boyer et al., 2011).

Vinylbenzyl chloride (VBC) is one of those monomers that provides ready post-polymerization functionality through the chloride group. This monomer can go through nucleophilic substitution readily or be utilized in the atom transfer radical polymerisation as an initiating site (Moraes, et al., 2013). Thus, 4-vinylbenzyl has been applied as a precursor to glycopolymer stars in a diverse number of systems, triblock copolymers, graft abd star polymers, comb, nanofibers, and photo- and pH-responsive nanoparticles (Bayramoglu et al., 2009) (Y. Chen et al., 2010), (Feng et al., 2009), (Fu et al., 2009). Also, it has been reported that copolymerisation of VBC by RAFT method can also occur (Couture and Améduri, 2012) (Feng, et al., 2009). Because side reactions can be avoided (such as C-Cl bond dissociation), RAFT polymerisation is a very practical technique for VBC (Couture and Améduri, 2012) (Bhuchar, 2011).

The first genuine polymer was invented by Leo Baekeland in 1907. The polymer was a thermosetting phenol formaldehyde (Wampler, 2006). Traditionally, vinyl benzyl chloride has be used as a multi-purpose functional monomer in the reactive precursor production for the thiol functional copolymers. VBC can be polymerized via several RDRP as a comonomer, and the benzyl chloride side is very prone to a nucleophilic attack, producing an apparent replacement of chloride with a variety of strong nucleophiles (Faghihi and Hazendonk, 2017).

A clear example of how versatile RAFT polymerisation technique is evident in the ability of vinyl benzyl chloride (VBC) control (Moraes, et al., 2013).The first time RAFT polymerisation was discovered and documented was at CRITO by Rizzardo and coworkers in 1998 (G Moad and Chiefari, 2018). This technique has drawn special interest among researchers recently. Its works based on degenerative chain transfer process principle (Bai et al., 2008). Among the factors that decide the RAFT polymerisation process, the right selection of chain transfer agent is probably the most important. RAFT agents are thiocarbonylthio compounds can belong to one of these groups (based on the Z group): xanthates, dithiocarbamates, dithioesters and tri-thiocarbonates (G Moad and Chiefari, 2018).

RAFT insensitivity to the functional groups in the monomers polymerized made it a very promising technique. This is especially important when it is required to protect group chemistry. In this case RAFT can directly be used on the targeted monomer. This particular characteristic drew a substantial research focus on RAFT technique from the time it was introduced 2 decades ago (Quinn et al., 2007).

In view of the ability to produce high-molecular chains of polymer surface from the surface, high-molecular chains (approx. 20 to 100 kg / mole) are important. This enables us to increase the amount of functioning benzyl chloride groups. Moreover, with large quantities of polymers produced from the particle, the effective diameter of the particle is controlled by simple tuning of the polymerisation conditions in order to determine the size of the particle. Their relative contribution to the particle diameter is therefore insignificant and cannot be achieved if tiny molecular weights are targeted. For that, the molecular chain of the final material can be easily tuned depending on the amount of CTA (i.e., high ratio CTA/initiator) in order to minimise the fraction of dead chains produced and obtain a high- molecular chain at the end.

Heavy metals do not have biodegradable properties like organic contaminations. Heavy metals also tend to accumulate in living organisms with the potential if becoming toxic and carcinogenic. Certain types of heavy metals are of a particularly concern in industrial wastewater treatment. This includes: copper, mercury, zinc, lead, nickel, chromium and cadmium. Therefore, these toxic heavy metals have to be minimized in the environment to avoid catastrophic results on the living organisms including human beings. Several techniques have been used to remove heavy metals such as electrochemicals, ion exchange, membrane filtration, chemical precipitation and adsorption (Ge et al., 2012).

This study investigates the behavior of polymer for heavy metals removal from wastewater using PVBC through adsorption method. According to previous studies, it is obvious that the most commonly investigated methods for wastewater treatment are adsorption, ion-exchange and membrane filtration.

In this study focuses on RAFT polymerisation. First and foremost, it has used of RAFT polymerisation to synthesis of poly (vinylbenzyl chloride), polymerisation of the monomer in solution at particular temperature. Then use this polymer to remove the copper Cu (II) from the aqueous solution via adsorption process between the polymer and the heavy metal.

1.2 Problem Statement

There are several techniques used in wastewater treatment, some of them cost a lot of money, effort and time in the removal of heavy metals during water treatment. Many of the techniques used to remove heavy metal particles include electrochemicals, membrane filtration, ion exchange, chemical precipitation and adsorption.

There are few problems such as low microporosity, poor moulding performance, and low adsorption and regeneration efficiency in electrosorption techniques, when the activated carbon used as an electrode material. In electrochemical oxidation and electrochemical reduction is require addition of chemicals, and this causes chemicals to be heavily consumed (i.e. coagulants, flocculants, salts). For chemical precipitation techniques used for wastewater treatment, it also consume a lot of chemicals (i.e. lime, oxidants, H_2S) and in membrane filtration such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) investment costs are often too high for small and medium industries but in adsorption process, it is technologically simple (simple equipment) and adaptable to many treatment formats and no need for consume a lot of chemicals.

Nowadays, contamination of heavy metals such as Cu(II) has become one of the worst environmental problems. Due to its environmental resistance and persistence, the treatment of Cu(II) is very important. Various methods have been extensively studied in recent years on the removal of Cu(II) ions from waste water and drinking water. Cu(II) is atomicly significant element 63.5; Cu(II) is increasingly discharged directly or indirectly into the ecosystem with the rapid development of industries. Cu(II) ions does not have biodegradable properties like organic contaminations, and are generally deposited in live organisms and are known to be toxic.

Today, heavy metals are a pollutant of environmental priority and one of the most serious environmental issues. These toxic heavy metals should therefore be removed from wastewater to protect the environment and human beings.

This study examines the polymer used to remove Cu(II) from aqueous solution by adsorption using PVBC. Past study shows that adsorption is the most frequently studied treatment for heavy metal wastewater.

1.3 Objective of Study

I. To synthesize the PVBC from VBC by using RAFT polymerisation method.

II. To evaluate the performance of the polymer in the removal of copper ions from aqueous solutions.

III. To characterize the adsorption of Cu (II) by PVBC using isotherm and kinetic studies.

1.4 Scope of Study

This study focused on the removal of Cu(II) ion from the aqueous solution via adsorption process utilizing poly(vinylbenztl chloride) as adsorbent , which has synthesized via reversible additional chain transfer (RAFT) method using vinylbenzyl chloride monomer and 4 4'-azobis (4-cyanopentanoic acid) as initiator. Optimization of the following parameters such as temperature, amount of initiator, monomer and reaction time were carried out to maximize the percentage polymer. Thereafter, properties of the polymer were characterized using Proton Nuclear magnetic resonance (^{1}H NMR) spectroscopy. ^{1}H NMR spectra recorded in the presence of $CDCl_3$ to determine the highest percentage mass yield through calculating the conversion rate and to check the presence of functional group of poly(vinylbenzyl chloride). In the Attenuated total reflectance (ATR-FTIR) spectrum of the polymer sample, it had used Attenuated total reflectance (ATR-FTIR) to characterizing and studying the chemical structure of the polymer such as present of the functional groups of the polymer.

Finally, Polymer adsorption ability that has prepared was evaluated using heavy metal of Cu(II) in aqueous media.

1.5 Significance of Study

Nowadays, with the increasing human population and industrialization, the need for treatment of effluents bearing hazardous substances before their discharge into the environment is becoming more pronounced. This is best done right at the source of the pollutants before they enter the complex ecosystems in which they are often very difficult to remove. A wide variety of hazardous substances, particularly heavy metals such as copper, aromatic molecules and dyes, has become a serious environmental issue globally. Unlike organic compounds, soluble heavy metal ions are not biodegradable and are toxic even at low concentration levels. Therefore, there is a need to develop low-cost, recyclable adsorbent to remove toxic materials from environmental and industrial wastewater. Findings from this research work will present potential adsorbent to removal copper metal from water by using adsorption process. The prepared adsorbent could be an alternative inexpensive for the removal of the target pollutants from water sources, particularly for the treatment of industrial effluents. It is expected that this research study would reveal vital information on the adsorption ability and adsorption mechanism of the prepared adsorbent and the reusability for this adsorbent. Moreover, it could also help to remove another contaminant from water. For this study, UV-Vis spectroscopy was used to determine the amount of copper concentration that will be removed from aqueous solution.

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