

POLY(METHACRYLAMIDE) AND POLY(*N*-VINYL-2-PYRROLIDONE)
GRAFTED CROSSLINKED CHITOSAN FOR REMOVAL OF ORANGE G AND
SELECTED HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

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I dedicate this work to my beloved Ibu, Ayah and family

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ABSTRACT

Natural biopolymers such as chitosan have high potential as sorbents for a wide range of applications. However, these materials present significant limitations that require appropriate modifications. In this study, chitosan was modified by crosslinking and grafting and the newly prepared grafted copolymers were evaluated as sorbents for the removal of a selected dye, Orange G (OG) and several heavy metal ions (Pb(II), Cu(II) and Cd(II)) from aqueous solutions. Chitosan beads were produced from their commercial form and crosslinked with glutaraldehyde to enhance their stability in acidic medium. The crosslinked chitosan beads were then grafted separately with two different monomers, namely methacrylamide and *N*-vinyl-2-pyrrolidone by conventional free radical polymerization using ammonium persulfate as an initiator. The modified chitosan beads were characterized using Fourier transform infrared (FTIR) spectroscopy, solid state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and CHN analysis to provide evidence of successful crosslinking and grafting. The solubility and swelling of the grafted copolymers and chitosan beads were investigated. The optimum percentage grafting (263.5%) for the preparation of crosslinked chitosan-graft-poly(methacrylamide) (cts(x)-g-PMAm) was obtained at reaction temperature of 60°C , reaction time of 3 h, $2.63 \times 10^{-1} \text{ mol L}^{-1}$ of ammonium persulfate, $17.62 \times 10^{-1} \text{ mol L}^{-1}$ of methacrylamide and 1 g of crosslinked chitosan beads. Meanwhile, the optimum percentage grafting (138%) for the preparation of crosslinked chitosan-graft-poly(*N*-vinyl-2-pyrrolidone) (cts(x)-g-PNVP), was achieved using reaction temperature of 60°C , reaction time of 2 h, $2.63 \times 10^{-1} \text{ mol L}^{-1}$ of ammonium persulfate, $26.99 \times 10^{-1} \text{ mol L}^{-1}$ of *N*-vinyl-2-pyrrolidone and 1.5 g of crosslinked chitosan beads. It was found that (cts(x)-g-PMAm) and (cts(x)-g-PNVP) beads showed significantly higher maximum adsorption capacities, q_{max} , for OG (25.8 mg g^{-1} and 63.7 mg g^{-1} , respectively) as compared to that of unmodified chitosan beads (1.7 mg g^{-1}). It was also proven that the Langmuir model fitted very well with the experimental adsorption data for OG and the selected heavy metal ions with R^2 of nearly unity, while the adsorption kinetics were well described by the pseudo-second order kinetic model. In addition, the adsorbent-adsorbate interactions were elucidated by means of FTIR and X-ray photoelectron spectroscopy (XPS). This study concludes that both cts(x)-g-PMAm and cts(x)-g-PNVP beads are potentially useful as sorbents for the removal of pollutants from water and wastewater.

ABSTRAK

Biopolimer semula jadi misalnya kitosan mempunyai potensi tinggi sebagai penyerap untuk pelbagai aplikasi. Walau bagaimanapun, bahan ini mempunyai had keupayaan ketara yang memerlukan pengubahsuaian yang sesuai. Dalam kajian ini, kitosan telah diubahsuaikan secara perangkaian silang dan cangkukan dan kopolimer cangkuk yang baru disediakan itu telah dinilai sebagai penyerap untuk menyingkirkan pewarna terpilih, jingga-G (OG) dan beberapa logam berat (Pb(II), Cu(II), Cd(II)) daripada larutan akueus. Manik kitosan telah diperbuat daripada bentuk komersialnya dan dirangkai silang menggunakan glutaraldehid untuk meningkatkan kestabilannya di dalam medium berasid. Manik kitosan yang berangkaian silang kemudiannya dicangkuk secara berasingan dengan dua monomer yang berbeza, iaitu metakrilamida dan *N*-vinil-2-pirolidon dengan pemolimeran radikal bebas konvensional menggunakan ammonium persulfat sebagai pemula. Manik kitosan yang diubahsuaikan telah dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi ^{13}C resonans magnet nukleus keadaan pepejal (^{13}C NMR), analisis termogravimetri (TGA), kalorimetri imbasan pembezaan (DSC), mikroskopi imbasan elektron (SEM) dan analisis CHN untuk membuktikan kejayaan perangkaian silang dan cangkukan. Keterlarutan dan pembekakan kopolimer cangkuk tersebut dan manik kitosan telah dikaji. Peratus cangkukan optimum (263.5%) bagi penyediaan kitosan berangkaian silang-cangkuk-poli(metakrilamida) (cts(x)-g-PMAM) telah diperolehi pada suhu tindak balas 60°C , masa tindak balas 3 jam, ammonium persulfat $2.63 \times 10^{-1} \text{ mol L}^{-1}$, metakrilamida $17.62 \times 10^{-1} \text{ mol L}^{-1}$ dan 1 g manik kitosan berangkaian silang. Sementara itu, peratus cangkukan optimum (138%) bagi penyediaan kitosan berangkaian silang-cangkuk-poli(*N*-vinil-2-pirolidon) (cts(x)-g-PNVP) telah dicapai dengan menggunakan suhu tindak balas 60°C , masa tindak balas 2 jam, ammonium persulfat $2.63 \times 10^{-1} \text{ mol L}^{-1}$, *N*-vinil-2-pirolidon $26.99 \times 10^{-1} \text{ mol L}^{-1}$ dan 1.5 g manik kitosan berangkaian silang. Manik (cts(x)-g-PMAM) dan (cts(x)-g-PNVP) didapati menunjukkan kapasiti penyerapan maksimum, q_{max} , bagi OG yang jauh lebih tinggi (masing-masing, 25.8 mg g^{-1} dan 63.7 mg g^{-1}) berbanding dengan manik kitosan yang tidak diubahsuaikan (1.7 mg g^{-1}). Ia juga membuktikan bahawa model Langmuir sangat bersesuaian dengan data penyerapan eksperimen untuk OG dan ion logam berat terpilih dengan R^2 menghampiri satu, sementara kinetik penyerapan telah diterangkan dengan baik oleh model kinetik pseudo-tertib kedua. Sebagai tambahan, interaksi antara penyerap-terapan telah dicirikan dengan spektroskopi FTIR dan spektroskopi fotoelektron sinar-X (XPS). Kajian ini menyimpulkan bahawa kedua-dua manik cts(x)-g-PMAM dan cts(x)-g-PNVP berpotensi sebagai penyerap yang berguna bagi penyingkiran bahan pencemar daripada air dan air sisa.

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LIST OF ABBREVIATIONS

APS	-	Ammonium persulfate
ATRP	-	Atom transfer radical polymerization
BET	-	Brunauer-Emmett-Teller theory
BPO	-	Benzoyl peroxide
CA	-	Caffeic acid
CHN	-	Carbon hydrogen and nitrogen analysis
cs(x)-g-PNVP	-	Crosslinked chitosan-grafted-poly(<i>N</i> -vinyl-2-pyrrolidone)
cts(x)-g-PMAm	-	Crosslinked chitosan-grafted-poly(methacrylamide)
DD	-	Deacetylation degree
DMF	-	Dimethylformide
DSC	-	Differential scanning calorimetry
ECH	-	Epichlorohydrin
FA	-	Ferulic acid
FTIR	-	Fourier transforms infrared spectroscopy
<i>g</i>	-	Graft
G(%)	-	Grafting percentage
GA	-	Glutaraldehyde
HCl	-	Hydrochloric acid
KBr	-	Potassium bromide
KPS	-	Potassium persulfate
MAA	-	Methacrylic acid
MAm	-	Methacrylamide
MB	-	Methylene blue
MeSO ₃ H	-	Methanesulfonic acid
NMR	-	Nuclear magnetic resonance
NVP	-	<i>N</i> -vinyl-2-pyrrolidone

OG	-	Orange G
PMAM	-	Poly(methacrylamide)
PNVP	-	Poly(<i>N</i> -vinyl-2-pyrrolidone)
SEM	-	Scanning electron microscopy
T _g	-	Glass transition temperature
TGA	-	Thermogravimetric analysis
TPP	-	Tripolyphosphate
UV	-	Ultraviolet
XPS	-	X-ray photoelectron spectroscopy
Y(%)	-	Yield percentage

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Rapid development of industrialization, agricultural activities and exploitation of natural resources together with the growth of human population over the past few decades have inevitably resulted in raising pollution on Earth (Kiliç *et al.*, 2013). Pollution of water resources by harmful substances such as dyes and heavy metals is one of the most significant environment problems worldwide. These harmful substances are of increasing public concern due to their detrimental effect on a variety of living species.

The main cause of water pollution always correlates to the effluents from textile and dyeing industries. These industries consume large quantities of water with various chemical and coloring substances. The presence of dye in such wastewater is highly visible and undesirable. It can destroy aquatic environment by preventing the penetration of sunlight and oxygen (Crini and Badot, 2008).

Wastewaters containing heavy metals mainly originate from industries such as metal plating, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides (Yang *et al.*, 2013). They are often discharged directly or indirectly into water bodies without proper treatment process. Besides contaminating surface water (i.e. rivers, lakes, ponds and reservoirs), this pollutant can also contaminate underground water by leaking from soil after rain events. Heavy metals of particular interest in treatment of industrial wastewater include copper (Cu),

cadmium (Cd), nickel (Ni), lead (Pb), zinc (Zn), silver (Ag), chromium (Cr(III)), mercury (Hg), iron (Fe), cobalt (Co) and arsenic (As) (Meena *et al.*, 2008). Unlike organic wastes, metal compounds are of considerable concern because they are non-biodegradable and toxic even at low concentration. Exposure to elevated levels of heavy metals can adversely affect water resources, endangering the ecosystems and human health.

Removal of dyes as well as heavy metals from wastewater is very important for the sake of public health and environmental remediation. Various methods for removing the pollutants from contaminated water have already been applied years ago including chemical precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. Most of these methods may show some economical and technical disadvantages (Mehdinia *et al.*, 2015). For examples, chemical precipitation has been widely used to remove dye or heavy metal from inorganic effluent by increasing the pH of the solution in order to convert the soluble substances into an insoluble form. Even though the process is simple, it generates a large quantity of sludge which requires further treatment and high cost. Chemical precipitation is also not effective to remove trace level of pollutants from aqueous solutions. In ion exchange method, the resin, either synthetic or natural solid, exchanges its cations with the unwanted substance in the wastewater. The problem is drawn when the ion exchanger is quickly polluted and thus, reduces the exchange capacity. In addition, this method usually consumes high capital and operational costs. Coagulation-flocculation has been capable of removing pollutants from solution, but the process can destabilize colloidal particles by adding a chemical agent (coagulant) which resulting in sedimentation (O'Connell *et al.*, 2008; Abas *et al.*, 2013). Adsorption is established as the most effective method for water decontamination applications and analytical separation purposes. It offers advantages over the other options such as simplicity in terms of design and operation, uses less chemicals, requires low initial costs and can remove different types of pollutants (Bhatnagar and Minocha, 2006; Fu and Wang, 2011).

The most important factors that determine adsorption, especially for large scale treatment applications are efficiency and treatment cost. In recent years, the

development of adsorbent containing biopolymer origin has been considered as one of the most favorable option for the removal of dye and heavy metal from aqueous solutions. Biopolymers such as cellulose, starch, alginate, chitin and chitosan were intensively studied due to their fascinating features such as cheap, abundance, renewable, non-toxic and highly selective towards contaminants (Crini, 2005; Chauhan, 2015).

Chitosan is an amino polysaccharide produced from chitin and can be found naturally in some fungi. It is the most versatile biopolymer for a broad range of applications because of its biocompatibility, biodegradability and antibacterial property. Furthermore, this material is regarded as an ideal adsorbent. The presence of $-NH_2$ and $-OH$ groups on the polymeric backbone can serve as chelating and reaction sites towards pollutants (Wan Ngah and Fatinathan, 2008). Despite its fascinating properties, chitosan has severe drawbacks that restrict its application in water treatment and purification. Chitosan is commonly available in powder or flake form as the end product in the production process. It has crystallized structure and presents poor acid resistance and low porosity. In view of this limitations, pure chitosan is not suitable to be used in adsorption process without further modifications (Poon *et al.*, 2014).

Modification of chitosan in adsorption study has two main goals. The first goal is to increase the chemical stability of the polymer in wide pH-range aqueous media. The second goal is to improve the sorption performance such as sorption capacity and pollutant selectivity (Wang and Chen, 2014). The modification of chitosan can be carried out by either physical or chemical techniques or both.

Preparation of new chitosan-based materials may include impregnation, crosslinking, internal hydrogen bonding formation, graft polymerization and composite formation (Vakili *et al.*, 2014). In particular, crosslinking is one of the common modifications performed on chitosan mainly to prevent its dissolution in acidic media. This technique involves the formation of covalent bonds between two polymer chains by using bifunctional reagents containing reactive end groups that react with functional groups of chitosan (i.e. NH_2).

Another important modification is graft copolymerization. This approach has gained considerable interest among researchers and has become a vital technique in polymer chemistry. Grafting reaction provides various molecular designs leading to novel types of hybrid materials, which are composed of bio- and synthetic-polymers. Chitosan has two types of reactive groups; $-\text{NH}_2$ and $-\text{OH}$ groups for grafting to occur. Different functional groups have been successfully grafted onto chitosan by covalent bond onto the chitosan backbone. As a result, graft copolymers have broad applications in many fields including water treatment, toiletries, medicine, agriculture, food processing and separation (Zohuriaan-mehr, 2005).

1.2 Problem Statement

In recent years, extensive works have been undertaken with the aim of finding alternatives in view of economic adsorbents for water treatment. Natural polymer, in particular chitosan, has high potential as sorbent in removing a wide range of contaminants, yet this material presents significant limitations which requires appropriate modifications.

Chitosan, in its native state, is characterized as a crystallized polymer due to strong inter- and intramolecular hydrogen bonding in the structure. Since adsorption process usually takes place only at the amorphous region of the crystal, advancement has been made to prepare chitosan hydrogel beads in order to reduce the crystallinity of the polysaccharide through a gel formation process (Lee *et al.*, 2001). Additionally, the shape of adsorbent particle indeed plays an important role in adsorption capacity of either organic or inorganic pollutants. Cahyaningrum *et al.* reported the comparison between chitosan powder and chitosan beads for the removal of mercury ions (Cahyaningrum *et al.*, 2010). The results revealed that the adsorption capacity of the metallic ion by chitosan beads ($17.39 \times 10^{-4} \text{ mol g}^{-1}$) was much higher than that of chitosan powder ($7.20 \times 10^{-4} \text{ mol g}^{-1}$).

Pure chitosan has a major limitation of being highly soluble in most dilute mineral and organic acid solutions by protonation of the amine groups. This makes it even more difficult to evaluate its application as sorbent in the treatment of industrial effluents. Crosslinking process has been found to be an effective method to reinforce chemical stability of chitosan under acidic conditions. Several chemical crosslinking agents such as glutaraldehyde, epichlorohydrin, sodium tripolyphosphate and ethylene glycol diglycidyl ether have been employed for this purpose. This reaction, somehow, decreases the adsorption capacity slightly because amine groups of chitosan, which is known to be the main sites for target analytes, are usually bound with the crosslink agent to form a stable covalent bond (i.e. imine group). Hence, grafting copolymerization on crosslinked chitosan beads with vinyl monomers is necessary to increase the number of adsorption sites and thus, the adsorption capacity.

In this study, chitosan was suitably converted to chitosan beads and crosslinked using chemical crosslink agent, glutaraldehyde. The beads were then grafted for the first time with methacrylamide (MAM) and *N*-vinyl-2-pyrrolidone (NVP) separately, using ammonium persulfate as free radical. MAM and NVP monomers were chosen as side chain with expectation of increasing the amino group onto the surface of the chitosan beads as well as enhancing adsorptive capacities of chitosan beads for the removal of Orange G and metal ions (Pb(II), Cu(II) and Cd(II)) from aqueous solutions. The newly modified chitosan beads were characterized and evaluated as adsorption material with improved or enhanced properties. Moreover, the adsorption factors such as pH, initial concentration and contact time were studied.

1.3 Objectives of Study

The objectives of this study are;

- i. To prepare new chitosan-based sorbents by grafting crosslinked chitosan beads with methacrylamide and *N*-vinyl-2-pyrrolidone, separately, using ammonium persulfate as initiator.
- ii. To optimize the parameters of graft copolymerization and characterize the prepared graft copolymers.
- iii. To evaluate the adsorption performance of the grafted copolymers in removing selected dye and heavy metal ions from aqueous solution.
- iv. To study the adsorption kinetics and isotherms of the grafted copolymers using Langmuir and Freundlich models.

1.4 Scope of Study

In the present study, chitosan was physically modified by conversion into chitosan gel beads. The prepared chitosan beads were crosslinked using glutaraldehyde as a crosslinking agent and incorporated with two different functional groups, namely methacrylamide and *N*-vinyl-2-pyrrolidone by grafting method. The graft copolymerization was adopted via free radical mechanism in the presence of ammonium persulfate as initiator.

The effect of grafting parameters, namely temperature, time of reaction, concentration of initiator, monomers and weight of crosslinked chitosan beads were investigated in order to obtain the optimum values of grafting and yield percentages. The modified chitosan beads were characterized using Fourier transform infrared (FTIR) spectroscopy to elucidate the chemical structure changes after modifications. The carbon bonds formed in crosslinking and grafting reaction were confirmed by Solid state ^{13}C nuclear magnetic resonance analysis (^{13}C NMR). The surface morphologies of chitosan and the modified beads were observed at different magnifications using scanning electron microscopy (SEM). Thermogravimetric

analysis (TGA) was used to evaluate the thermal stability of graft copolymers by measuring the continuous change in weight of materials as a function of temperature. Meanwhile, glass transition temperature (T_g) was determined by differential scanning calorimeter (DSC) that measured endothermic and exothermic heat flows as a function of temperature/time. CHN analysis was carried out to determine the percentage elemental composition of carbon, hydrogen and oxygen. The prepared chitosan beads were also characterized in terms of their solubility and swelling behavior.

In the last part of the study, laboratory batch experiments were performed to investigate adsorption capacities of the modified chitosan beads for Orange G and selected heavy metals, namely Pb, Cd and Cu in aqueous solutions. Herein, FTIR and X-ray photoelectron (XPS) analyses were used to elucidate the mechanisms involved in the adsorption processes.

1.5 Significant of Study

This study focuses on the modifications of chitosan in order to prepare new hybrid materials that serve as effective sorbents with desired properties to overcome its limitations. These materials are potentially useful for the extraction and removal of targeted pollutants from aqueous solution.

The presence of hazardous substances, in particular dyes and heavy metals in the environment has received extensive attention as a result of their wide industrial uses. These kinds of pollutants are known to be toxic or carcinogenic. They are often discharged as effluent or wastewaters into water bodies; thus detrimental to human health and ecosystem stability. Therefore, it is necessary to develop an appropriate method to remove or minimize the amount of these pollutants from the environment. Findings from this research work can potentially contribute to green chemistry and new sustainable sorbents.

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