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Removal of copper (II) ion using chitosan-graft-poly(methyl methacrylate) as adsorbent

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ABSTRACT

Synthesis of the poly(methyl methacrylate) (PMMA) from methyl methacrylate monomer has been successfully carried out by reversible addition-fragmentation chain transfer polymerization (RAFT) techniques using 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) initiator and 4-Cyanopentanoic acid dithiobenzoate (CPADB) as RAFT agent with mole ratio of MMA: CPADB: ACPA fixed at 148: 3: 1. The obtained PMMA macro RAFT was used as initiator together with N,N-dicyclohexylcarbodiimie (DCC) and 4-dimethylaminepyridine (DMAP) as coupling agent and catalyst respectively in synthesis of CS-g-PMMA. The effect of reaction hours on grafting percentage was investigated by manipulating the reaction time to 2, 8, 14 and 22 hours. The CS-g-PMMA obtained at 22 hours showed the highest grafting percentage and efficiency which 72% and 36% respectively. All the homopolymers and grafted copolymers were then used to fabricate electrospun using electrospinning techniques. However, only PMMA electrospun was successfully obtained whereas chitosan and CS-g-PMMA were unsuccessful in electrospinning due to the instrument setup and solubility restriction. The grafted copolymers and PMMA electrospun was characterized by using ATR-FTIR and SEM. The adsorption efficiency of powdered-form CS-g-PMMA and homopolymers was investigated and analysed using F-AAS. It has been proven that longer hour grafted copolymers have high adsorption efficiency as compare to shorter hour grafted copolymers. The highest adsorption efficiency obtained was 86.18% shown by 22 hours CS-g-PMMA. Thus, it expected CS-g-PMMA electrospun will provides maximum adsorption as compared to powdered-form copolymers due to its high surface area, high permeability and porosity of the membrane.

Keywords: chitosan ,poly(methyl methacrylate), RAFT polymerization, graft copolymer, adsorption.

1. INTRODUCTION

Water pollution was highlighted as a major environmental issue to the world concern due to contamination of heavy metals discharge in wastewater. This urged the researchers to develop new technique in the fields of environmental protection. The water contains heavy metals such as chromium (Cr), cadmium (Cd), mercury (Hg), and zinc (Zn) with above certain limit can cause carcinogenic effect to health of human, hence, several treatment methods have been used to remove contaminants which include coagulation, precipitation, ion exchange, adsorption, filtration, reverse osmosis, biodegradation, membrane separation and solvent extraction [1].

Among those techniques, adsorption seems to be best method due to its low-cost, ease operation, regeneration capacity and environmental friendly. Adsorption behaviour of heavy metal ion of chemical cross-linked chitosan beads grafted using different polymer has been studied, where removal increased with decreasing pH. For advance in its utilization, vinyl grafting onto chitosan will be a key point, which can introduce desired properties and broaden the field of its potential applications by choosing various types of side chains [2].

Graft polymerization is one of the well-known methods for alteration of the physical and chemical characteristics of the polymers. Although several strategies such as oxidation, esterification, etherification, and silylation have been used in chemical modification, polymer grafting is still a great interest as the wide application in the industry. This graft polymerization is done using the reversible addition-fragmentation chain transfer (RAFT) polymerization technique as it is tolerant to foreign impurities and can carried out in a wide range of temperatures and applicable for wide range of monomers. [3]. These copolymer material electrospun adsorbent is then prepared using the unique method which known as electrospinning technique.

Electrospinning has become many researchers focus and interest due to development of nanotechnology. It is an efficient and progressive technique and enables fabrication of polymer electrospun with unique properties and characteristics [4]. Electrospinning is a process that uses high voltage to create an electric field between a droplet of polymer solution or polymer melt at the tip of a needle and a collector plate to produce a thread-like fibre of various diameters in order of some hundred nanometres. Recently years, electrospinning is widely been used in many polymeric related field as due to it certain advantages such as simple and easy to use, has possibility of scaling the process, possibility to control fiber morphology and all kind of polymers with high molecular weight can used to processes by electrospinning. To obtain a uniform electrospun with reproducible morphology, the parameters such as processing parameters and essential properties of solutions should be carefully optimized [5].

It has been very challenging for environmentalists to remove heavy metal from effluents due to the complicated steps. Hence, researchers focused in developing an efficient adsorbent to dispose heavy metals and they recognized activated carbon as one of the good adsorbents due to its high surface area and adsorption capacity. However, high cost and the difficulty to separate them have been the drawbacks of activated carbon and restricted from being applied [6]. Therefore, the focus of this study is to develop polymer material made of chitosan-grafted-poly(methyl methacrylate) (CS-g-PMMA) as compatible and competent adsorbent for removal of contaminants in water.

2. EXPERIMENTAL

2.1 Material

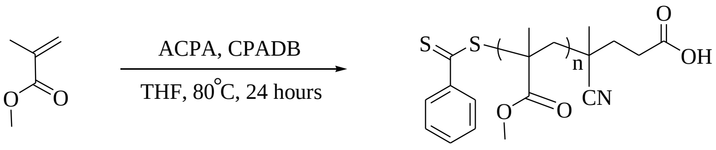
Chitosan flakes with medium molecular weight, methyl methacrylate (MMA), 4,4-azobis(4-cyanopentanoic acid) (ACPA) and 4-cyanopentanoic acid dithiobenzoate (CPADB) were all purchased from Sigma-Aldrich Co. (St. Louis, USA). Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloromethane (DCM), acetic acid (CH_3COOH) and chloroform ($CHCl_3$) were all purchased from QRëC (Selangor, Malaysia), standard solution of copper, Cu(II), (1,000 mg/L), methanol (MeOH), 4-dimethylaminopyridine (DMAP) were purchased from Merck (Darmstadt, Germany) whereas activated aluminium oxide (Al_2O_3) and N,N-dicyclohexylcarbodiimie (DCC) were purchased from Univar (USA) and Acros Organics respectively. All the experiments were conducted in laboratory scale and the reagents were analytical grade and used without further purification.

2.2 Removal of inhibitors from monomer

MMA was purified by passing through a column packed with an activated alumina to remove its inhibitor. A small burette was packed with glass wool and followed by activated alumina. The burette then attached to the retort stand and MMA was filled up through a conical funnel and allow to flow through the burette. The activated alumina change its colour from white to pink when the inhibitor were trapped. Finally, the purified MMA was collected in a reagent bottle, sealed and kept in a refrigerator below 10^{o}C. The purified monomer solution was analysed by ^1H NMR using $CDCl_3$ as solvent.

2.3 Synthesis of poly(methyl methacrylate)(PMMA) homopolymer

MMA (1 g), ACPA (0.0189 g) and CPADB (0.0614 g) were first dissolved in a 10 mL THF in 100 mL two-necked round bottom flask. The solution was then degassed using nitrogen for 30 minutes. The polymerization was then carried out by placing the flask into preheated oil bath at 80^{o}C for 24 hours. The reaction mixture was cooled to room temperature and air was introduced into the flask. The polymer solution from flask was precipitated using cold methanol and the resultant pink solid powders were dried in vacuum oven at 40^{o}C for 24 hours. The purified polymer was analysed by ^1H NMR using $CDCl_3$ as solvent and ATR infrared spectroscopy.



MMA

PMAA macro RAFT agent

2.4 Graft polymerization of chitosan-grafted-PMMA

Chitosan (0.1 g) with 10 mL of acetic acid was added to a 50 mL beaker together with a magnetic stirrer and was stirred for 30 minutes. In the meantime, DCC (0.1 g) and DMAP (0.034 g) were dissolved together in 4 mL of THF while PMMA (0.5 g) was dissolved in 5 mL of THF in two different 50 mL beakers. Then, the prepared DCC/DMAP solution was added dropwise followed by PMMA solution into the chitosan solution. The solutions were added dropwise with rate 1 drop/min. This prepared solution was transferred into a 100 mL of three-necked flask and was degassed using nitrogen for 30 minutes. The polymerization was then carried out by placing the flask into preheated oil bath at 60°C for 2 hours with stirring rate of 200 rpm. Immediately, after the reaction, the flask was exposed to the ambient atmosphere. The polymer solution was precipitated using cold methanol and the resultant solid powders were dry in vacuum oven at 40°C for 24 hours. This experiment was repeated by optimizing the reaction time to 8, 14 and 22 hours. All the purified polymer was characterized using ATR infrared, ^{1}H NMR using $CDCl_3$ as solvent and SEM. The percentage and efficiency of grafting were calculated as below:

$$\% \text{ Grafting: } \frac{W_1 - W_2}{W_2} \times 100 \qquad \text{(Equation 2.1)}$$

$$\% \text{ Efficiency: } \frac{W_1 - W_2}{W_3} \times 100 \qquad \text{(Equation 2.2)}$$

where $W1$,$W2$ and $W3$ denote respectively, the weight of the grafted copolymer, the weight of chitosan and weight of homopolymer used.

2.5 Electrospinning of PMMA

PMMA (2.0 g) was dissolved in 10 mL of $CHCl_3$. The concentration of PMMA in electrospinning solution was made to 0.2 g/mL. The electrospinning of PMMA was carried out on a single-spinneret electrospinning setup. Solution was loaded into a 10 mL syringe with a blunt-ended stainless steel needle which was mounted on a pump. The voltage was adjusted to 15 kV with flow rate of 1.2 mL/hour and the distance between the needle and the collector was fixed to 15 cm. The voltage was supplied by power was applied between the needle tip and the grounded aluminium foil collector, and the power supply was connected to the syringe needle via an alligator clips. The experiment was carried out on a horizontal electrospinning set-up at room temperature. The obtained electrospun was analysed using the SEM.

2.6 Adsorption Study of Cu(II).

Standard stock solution of Cu(II) (1000 ppm) was diluted with deionized water to obtain the desired concentrations Batch experiment was conducted by placing 50 mg of chitosan, PMMA and different grafting percentage copolymer powders in 50 mL beakers containing 15 mL of aqueous solution of Cu(II) (0.8 mg/L). The mixture was stirred using a magnetic stirrer for 3 hours at room temperature. The mixture was separated by filtration and the residual metal concentration was measured using the Flame-AAS.

3. RESULTS AND DISCUSSION

3.1. Characterization of Poly(methyl methacrylate)(PMMA)

Figure 1 shows that there was a distinct absorption band between 1140 cm^{-1} to 1240 cm^{-1} in both infrared spectra of (a) MMA and (b) PMMA, which attributed to C-O-C stretching vibration. The band at 1735 cm^{-1} in MMA spectrum and

1724.14 cm^{-1} in PMMA spectrum confirms the presence of C=O of ester. The two bands appeared between 3000 cm^{-1} and 2900 cm^{-1} in both spectra assigned to –CH sp^3. It can be observed that the absorption band of -CH sp^3 in MMA was weaker compared to PMMA due to there was only one –CH sp^3 bond present in MMA before polymerization. Besides, the infrared spectrum of MMA shows the absorption of C=C (vinyl) and =CH sp^2 (vinyl) at about 1670 cm^{-1} and 3100 cm^{-1} respectively. However, these absorption bands were not seen in infrared spectrum of PMMA. The disappearance of this two functional group suggested that MMA was successfully polymerized to PMMA by RAFT polymerization.

In Figure 2 (a), there were two peaks signal arise at 5.85 ppm and 5.31 ppm showed the presence of vinyl in MMA whereas peak signal around 3.49 ppm indicates the presence of methoxy protons. The peak signal at 1.60 ppm indicates that the methyl proton of the MMA present. However, in Figure 2 (b), it proved that PMMA macro RAFT compound was successfully synthesized via RAFT polymerization method. The peak signal appeared between 7.45 ppm to 7.90 ppm assigned to the protons of phenyl. The two peak signal at 3.75 ppm and 1.86 ppm corresponds to the methoxy and methylene protons of PMMA main chain whereas the peak signal arise at 1.49 ppm to 2.19 ppm are relative to the protons from CPADB RAFT agent. Besides, the two signals around 0.85 ppm and 1.23 ppm are assigned to the methyl group. The absence of the peak signal at around 5.90 ppm and 5.40 ppm confirms that PMMA is pure without any unreacted MMA monomers. This indicates that the PMMA chains are able to act as macro RAFT agent and to be used in further polymerization process.

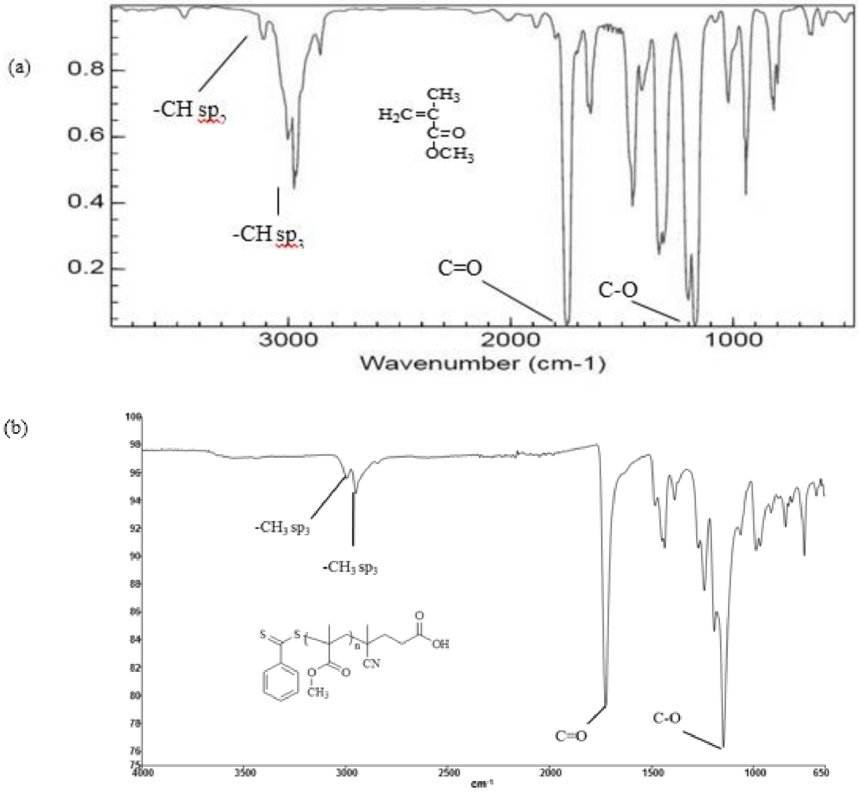


Figure 1 IR spectrum of (a) MMA and (b) PMMA

3.2 Characterization of Chitosan-*g*-PMMA

As the step for confirmation that grafting process has occurred, infrared spectroscopy was used to analyse and compare the grafting sample spectrum with the chitosan and PMMA spectrum. Figure 3 displays the combined ATR spectrum of the chitosan, PMMA macro RAFT agent and CS-g-PMMA.

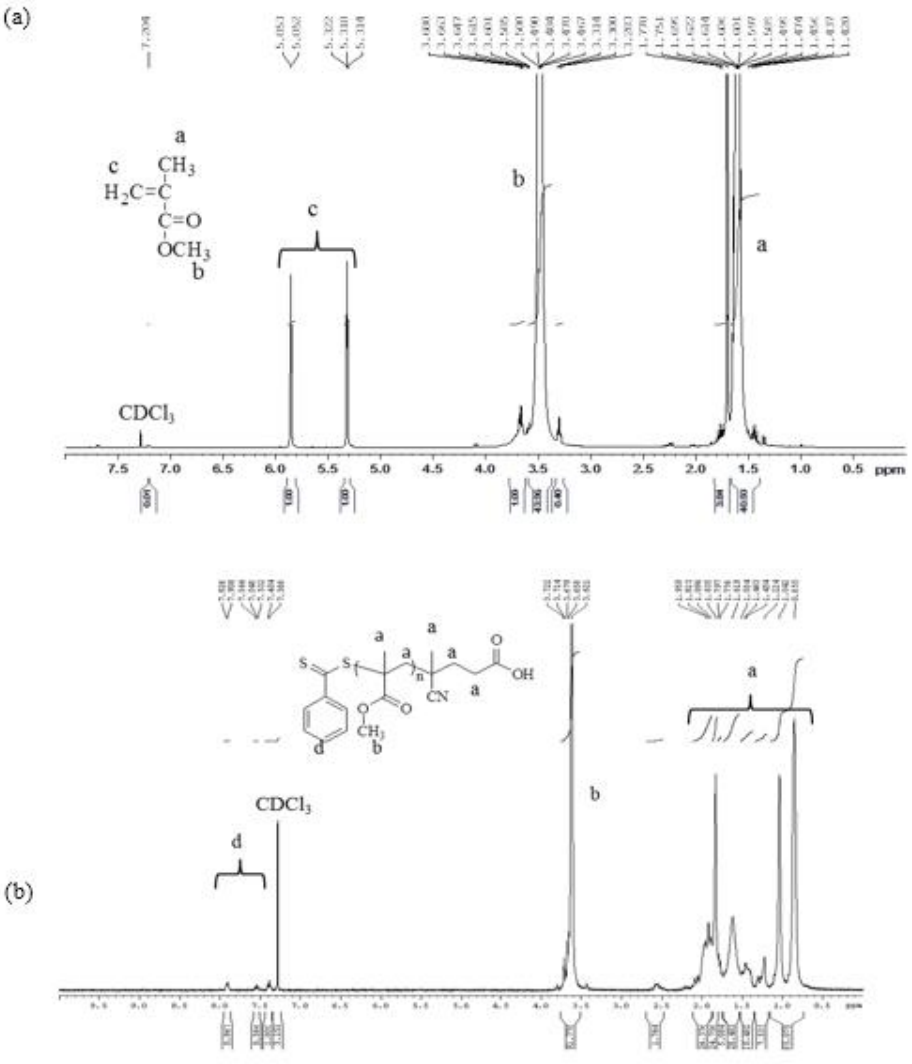


Figure 2 ^{1}H-NMR spectrum of (a) MMA and (b) pure PMMA

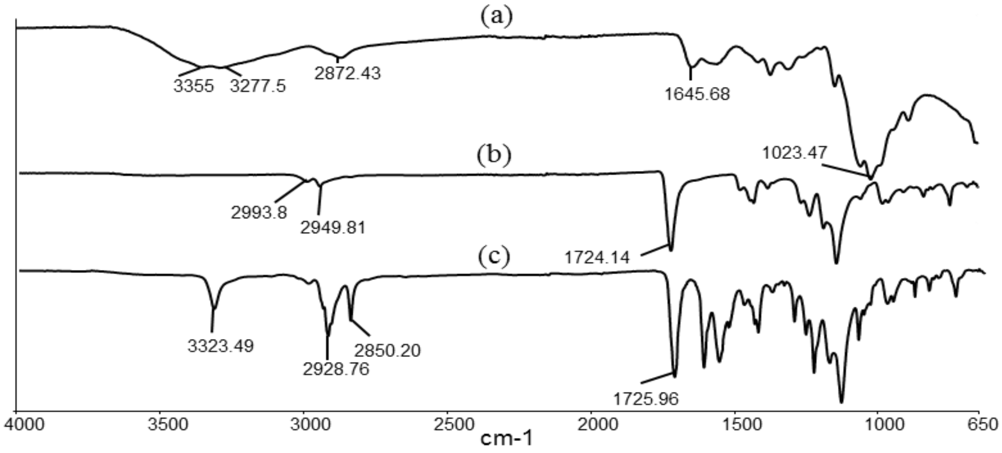
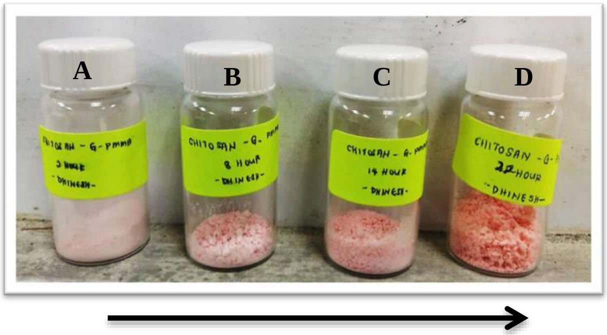


Figure 3 The ATR spectrum of (a) chitosan, (b) PMMA macro RAFT agent and (c) CS-g-PMMA**.**

The spectrum of chitosan showed a broad band with two spike peak at range of 3200 - 3400 cm^{-1} which is assigned to a typical hydroxyl (O-H) and amine (N-H) stretching vibration on polysaccharide backbone. A band representing C-H is seen at 2872.43 cm^{-1} whereas stretching of C=O group seen at 1644.68 cm^{-1}. This band is due to the acetamide group in chitosan. Besides, the PMMA spectrum showed two weak bands for C-H at 2949.81 cm-1 and 2993.80 cm^{-1} and signal band at 1724.14 cm^{-1} for C=O ester. Meanwhile, the spectrum of CS-g-PMMA proves that grating process has taken place with the presence and absence of certain characteristics peak. The spectrum clearly shows that there was absence of broad O-H absorption band of chitosan at around 3300 cm^{-1} and presence of N-H absorption band of PMMA at 3322 cm^{-1}. Besides, the increased in the intensity of C-H sp^3 stretching at ranging from 2850 -2930 cm^{-1} can be associated to a large number of methyl groups from graft copolymer. This has confirmed that PMMA has been successfully grafted onto chitosan surface.

3.2.1 Effect of Reaction Time of Graft Copolymerization

Figure 4 displays the product of grafted copolymer obtained at different time. It can be observed the pink colour intensity increase gradually from 2 hour to 22 hour reaction time. These physical changes were explained by the models in Figure 5 below which shows that the increase in reaction time enables more PMMA macro RAFT to interact and bind on the hydroxyl group of chitosan and resulting the colour intensity increases. This is due to the ester exchange reaction which is a reversible process. Thus, from the observation it can be proven that longer grafting time gives an increase in grafting. From spectrum in Figure 6, it can be seen that there were changes in the intensity of peaks for different reaction hours. The increase in C-H and C=O ester peak intensity from 2 hours to 22 hours indicates that high number of PMMA has been grafted onto the chitosan backbone.



Changes in color intensity of polymer

Figure 4 The product obtained from grafting of PMMA on chitosan at 2 hour (**A**), 8 hour (**B**), 14 hour (**C**) and 22 hour (**D**).

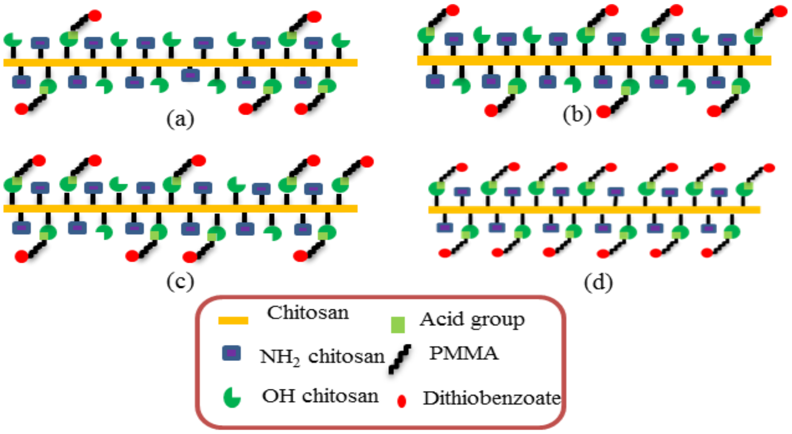


Figure 5 The quantities of PMMA homopolymers grafted on chitosan at (a) **A**, (b) **B**, (c) **C** and (d) **D**.

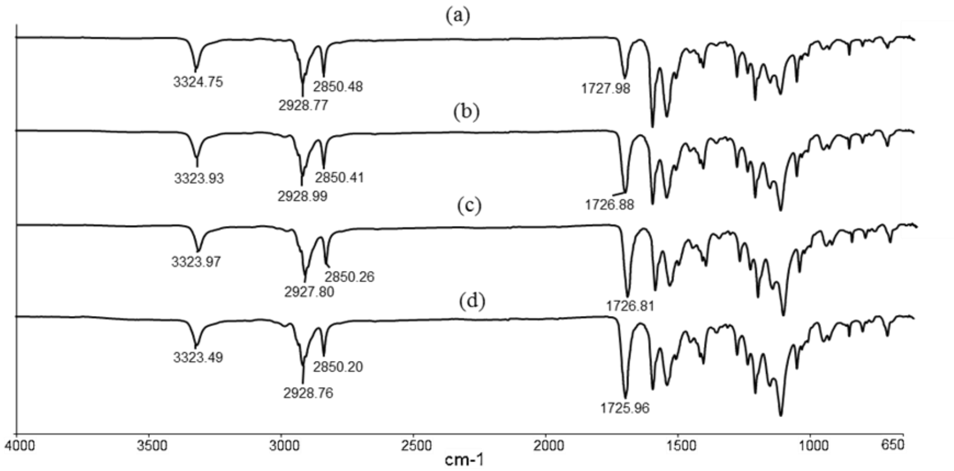


Figure 6 Graft copolymerization of CS-g-PMMA at reaction time of (a) **A**, (b) **B**, (c) **C** and (d) **D.**

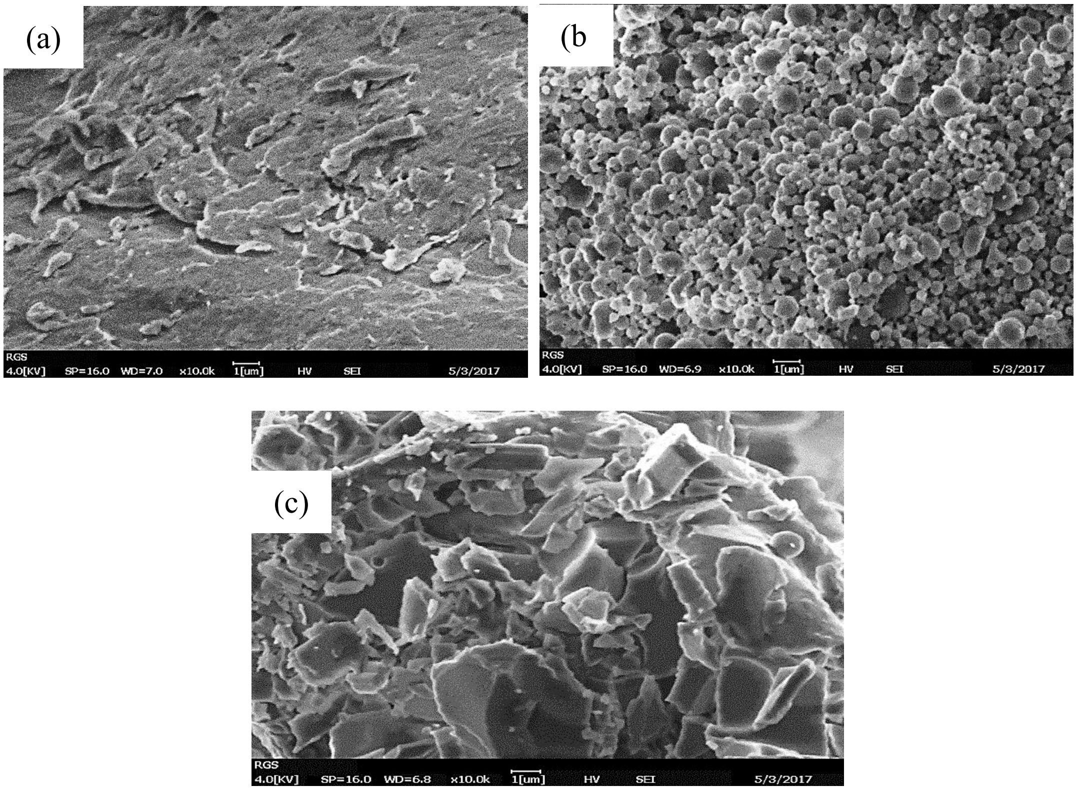


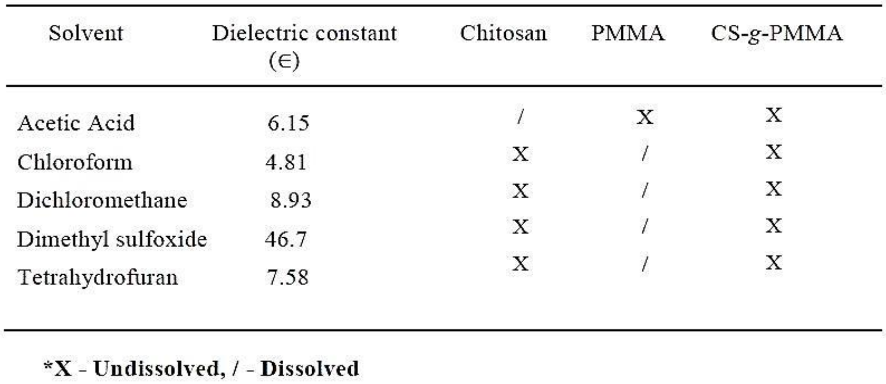
Figure 7 SEM micrographs of (a) CS (x 10), (b) PMMA (x 10) and (c) CS-g-PMMA (x 10).

In Figure 7(a), SEM image of pure chitosan exhibited smooth and nonporous surface whereas Figure 7(b) for pure PMMA surface morphology shows a rough surface with micro pore structure. Besides, it can be seen that grafted chitosan as in Figure 7(c), it was almost covered by PMMA after grafting process. Thus, the surface of modified chitosan appeared to be denser and rougher with more pores structure as compared to the pure chitosan and PMMA. Therefore, it can be proven that these changes may be due to the strongly attached PMMA onto the surface of chitosan.

3.3 Solubility Test for CS, PMMA and Cs-*g*-PMMA

Solubility test for chitosan, PMMA and CS-g-PMMA were done to choose the best solvent for electrospinning. All this polymer and copolymer were dissolved in a series of solvent as shown in Table 1. PMMA shows good solubility in all the organic soluble solvents whereas chitosan was only soluble in water soluble solvent. However, CS-g-PMMA shows negative solubility result for all the tested solvent and this made CS-g-PMMA to be unsuccessful for electrospinning. In electrospinning, the dielectric constant and conductivity of the solutions influence the electrospinning solutions and it is highly depend on the solvents used [6].

Table 1 Solubility of chitosan, PMMA and CS-g-PMMA in series of solvents



Solvent	Dielectric constant (ϵ)	Chitosan	PMMA	CS-*g*-PMMA
Acetic Acid	6.15	/	X	X
Chloroform	4.81	X	/	X
Dichloromethane	8.93	X	/	X
Dimethyl sulfoxide	46.7	X	/	X
Tetrahydrofuran	7.58	X	/	X

***X - Undissolved, / - Dissolved**

As from table above, DMSO solvent has the high dielectric constant value but is not suitable to be used as the electrospinning solvent because it is not volatile to evaporate quickly during the process, thus, we could not achieve a dry fibre on the collector. Besides, DCM and THF also were proven to be less suitable as good solvents in electrospinning process due to the formation of solid skin on the jet surface, caused by the partial diffusivity of polymer molecule from jet surface to the liquid core [8]. Thus, $CHCl_3$ was chosen as best solvent in this study although it has low dielectric constant value and lead to uniform yet thick fibre in the microscale range instead of nanoscale range.

Also, chitosan was also unable to be electrospin using the typical laboratory instrument in this study although the solubility test shows a positive result. This was due to the required for modification of the electrical charge terminals in the electrospinning instrument setup. Additionally, pure chitosan is a cationic bio-polymer, thus, this affects the rheology of the solution which could result of hindered or no fibre formations [9].

3.4 Electrospinning of Polymer

In this study, electrospun absorbent with smooth morphological structures were fabricated using electrospinning technique to understand and compare the adsorption efficiency between electrospun and powder. Nevertheless, only PMMA electropun was successfully electrsopinned whereas chitosan and CS-g-PMMA was unsuccessful to electrospinned due to its instrument setup and solubility restrictions. Figure 8 displays the comparison between PMMA in powdered-form and electrospun-form obtained via electrospinning technique.

3.5 Adsorption of Cu(II) ion

The adsorption study was conducted for 3 hours to allow the adsorbent to have maximum interaction with the copper (II) ions in the aqueous solution. As can be seen from the illustration, the hydroxyl groups of the chitosan were fully grafted by PMMA while the amino groups were freely available. Hence, those amino groups serve as the active site for the binding of metal ion.

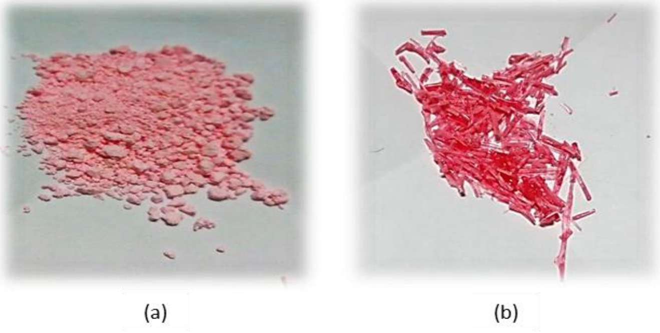

(a) (b)

Figure 8 Comparison on physical property of PMMA in (a) powdered-form and (b) electrospun-form obtained via electrospinning technique.

According to Bryan et al., amino group attributes largely for the natural adsorption of chitosan as compared to hydroxyl groups [9]. Chui et al. also proven that amino sugar is an effective binding site for metal ions to form stable complexes by co-ordination through dative bonding [10]. Besides, the dangling ester group at the grafted chitosan sites seems to be also responsible for the adsorption. Therefore, it is noticeable that grafted copolymer show high adsorption efficiency as compared to the homopolymers. Figure 9 illustrates the adsorption mechanism of Cu(II) ion on the CS-g-PMMA adsorbent.

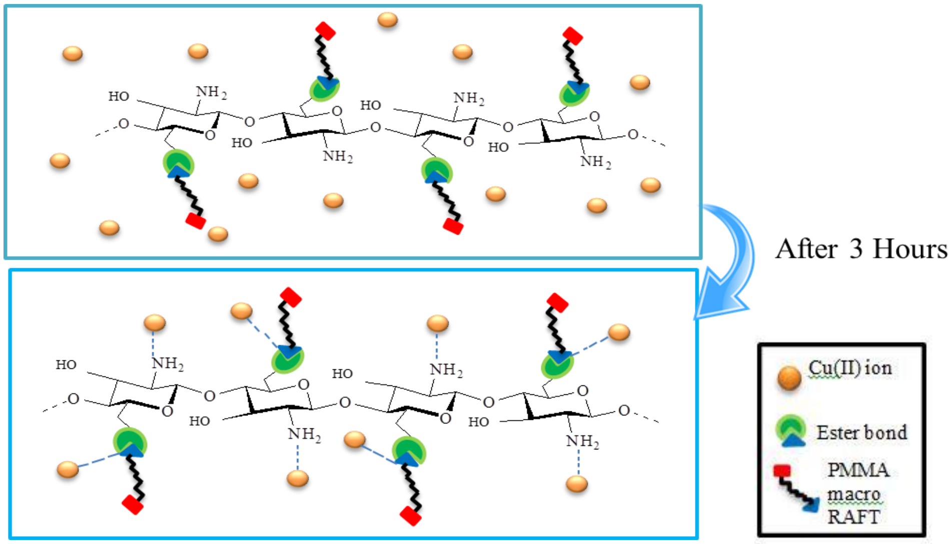


Figure 9 Illustration of Cu(II) adsorption mechanism using CS-g-PMMA as an adsorbent.

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3.5.1 Effect of Grafting Percentage

This study has proven that hompolymers has low adsorption efficiency and it is less suitable to be use as an adsorbent as compared to grafted copolymers. Also, the longer hours of grafting copolymer provides better adsorption efficiency compare to the shorter hour grafting copolymer. Thus, grafting plays an important role in increasing the adsorption efficiency of the grafted adsorbent. The increase of grafting percentage results in increase in adsorption efficiency as there are more ester group available which is primarily responsible for the adsorption of metal ion process.

Table 2 Adsorption efficiency of adsorbent for Cu(II)

Adsorbent	Solution pH	Initial concentration (ppm)	Final concentration (ppm)	Adsorption percentages (%)
Chitosan	6.0	0.275	0.073	73.45
PMMA	6.0	0.275	0.066	76.36
PMMA Electrospun	6.0	0.275	0.045	83.64
CS-g-PMMA				
A	6.0	0.275	0.068	75.27
B	6.0	0.275	0.060	78.18
C	6.0	0.275	0.038	86.18
D	6.0	0.275	0.035	87.27

Table 2 displays the data of absorption efficiency of Cu(II) on chitosan, PMMA, PMMA electrospun and each different CS-g-PMMA adsorbent whereas Figure 10 illustrate the bar chart of percentage of adsorption of Cu(II) using various adsorbents. The data shows that CS-g-PMMA at D reaction time has best adsorption efficiency as compared to other adsorbents.

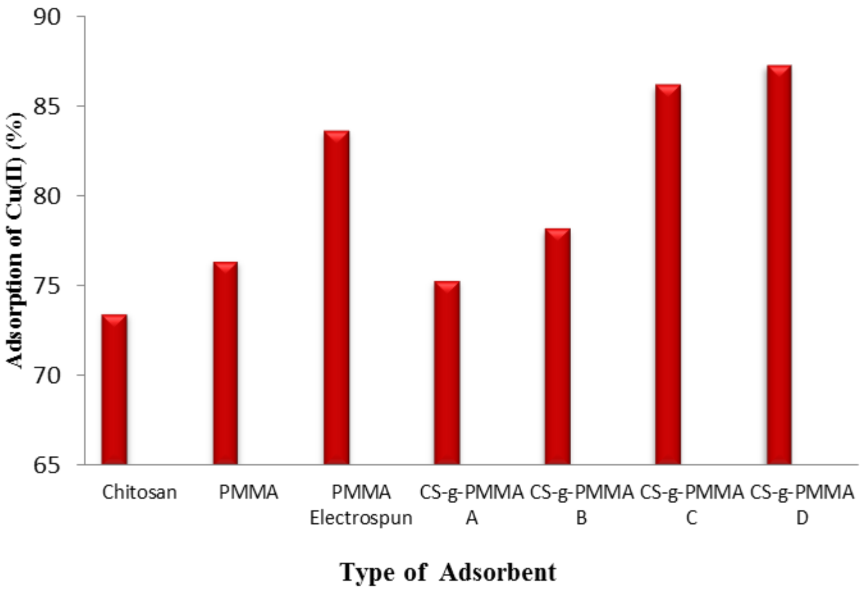

Figure 10 Percentage of adsorption of Cu(II) using various adsorbents

From the study, it can be expected that grafted copolymer electrospun will show much better adsorption efficiency as compared to other adsorbents. This because the overall adsorption test results have proven that grafted copolymer has good adsorption efficiency. Besides, PMMA homopolymer in electrospun-form shows a good performance in adsorption efficiency as compared to its powdered-form.

As according to Shouzhu Li et al., electrospun membrane is good candidates as an adsorbent for heavy metal ions adsorption from aqueous solution due to its high permeability, high surface area and small pore sizes that allow them to appropriate for wide range of filtration. Moreover, powdered materials are less suitable for recycling in the field of water treatment [12]. Besides, Zhengyang et al. proven that CS-g-PMMA nanofiber membrane achieved high adsorption efficiency of Cr(VI) compared to pure PMMA and pure chitosan membrane. This is due to the larger specific surface area which has provided enough space for the metal ion to adsorb [13]. Hence, it can prove that grafted copolymer electrospun will show a maximum adsorption efficiency when compare to the powder-form copolymers, thus, it will be more suitable to be used as an adsorbent for adsorption of heavy metal ion in wastewater treatments.

4. CONCLUSION

Methyl methacrylate was successfully polymerized to poly(methyl methacrylate)(PMMA) using 4-cyanopentanoic acid dithiobenzoate (CPADB) RAFT agent and 4,4-azobis(4-cyanopentanoic acid)(ACPA) initiator by RAFT polymerization technique and readily used as a macro initiator in the copolymer synthesis. Chitosan-g-PMMA was successfully synthesized using the N,N-dicyclohexylcarbodiimie (DCC) initiator and 4-dimethylaminepyridine (DMAP) catalyst and the presence of PMMA on the chitosan surface was confirmed by IR and SEM analysis.

However, CS-g-PMMA obtained was unsuccessful to form electrospun due to its electrospinning solubility restriction. Conversely, grafted copolymer and homopolymer powder was used to test and compare its adsorption efficiency and it has proven that grafted copolymer has the good adsorption ability compared to homopolymer. Besides, PMMA homopolymer in electrospun-form shows a good performance in adsorption efficiency as compared to its powdered-form, Thus, it can be concluded that grafted electrospun could show a better adsorption performance than a powdered-form copolymer due to its large surface area and high stability of membrane which has proven by previous study.

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