

## Biobased Chitosan/Polyester Crosslinked Polymer: Preparation and Characterization of Novel Polymeric Spheres

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### Abstract

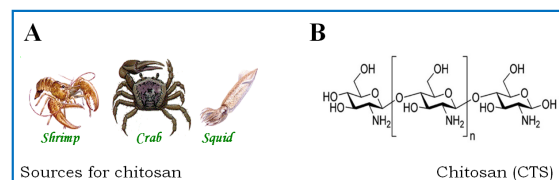
Neat chitosan spheres retain the solubility in dilute acids; therefore, it lacks to be used in various applications. This solubility is typically overcome by presence of crosslinking. A conventional chitosan crosslinking reaction involves dialdehydes, diethers or epoxides. In this study, chitosan spheres were crosslinked with esters-based crosslinker agents. A novel class of crosslinked biomacromolecule spheres has been prepared from chitosan (CTS), and maleic anhydride-based polyester. Two polyesters were synthesized maleic anhydride (MA), 1,4-butadiol (But) and (MA), (But) and glycerine (Gly). The structures of the esters (MA-But) and (MA-But-Gly) were confirmed by Fourier transform infrared spectroscopy (FT-IR). Crosslinking of CTS spheres were carried out with polyester in ethanol solution (5 wt%). The reaction between primary amine in CTS and carboxylic acid in polyester forming amid bond was confirmed using FTIR. In particular, the stability of CTS-based spheres was significantly enhanced with crosslinking in aqueous media. The effects of crosslinking on hydrophilicity of CTS were investigated. The results indicated that the obtained spheres are good candidates for hydrogel applications such as water purification and gas dehydration.

**Keywords:** Maleic anhydride; chitosan; polyester; crosslinked polymer; polymeric spheres.

### 1. Introduction

Porous organic materials are attractive products which are used for a wide range of applications, such as sorbents, thermal insulators, environmental protection, catalyst supports, ion-exchange membrane, swelling, resins for column packing, due to their unique properties such as high surface compared to the others dense polymers [1]. In recent years, the major challenge of research is the development of advanced porous spheres from natural, biodegradable and biocompatible polymeric materials. One of the biodegradable polymers are chitosan (see Figure 1.1b) which has been found to be a good natural chemical for developing ecofriendly-based porous spheres because of its high ability for crosslinking due to the presence of functional

groups [2].



**Figure 1.1:** Sources and chemical structures of chitosan (CTS). (Adapted from Ref. 2).

Chitosan (CTS) is a modified version of a high molecular weight branched polysaccharide produced by deacetylation of chitin obtained from prawns, krill, shrimp shells and crabs. Chitin reported to

be the second most abundant natural polymer on earth after cellulose [3]. The hydroxyl and amino functional groups in CTS generates hydrophilicity and excellent chelating properties for heavy metal ions [4]. Chitosan is a polar biopolymer with good physical properties and have unique chemical interactions due to the presence of (-NH<sub>2</sub>) and hydroxyl (-OH) functional groups that can easily react with various groups [3, 5, 6]. In addition, chitosan is attractive to dissolve in dilute acidic medium [7]. However, it is insoluble in water and common organic solvents. Because of its high chemical reactivity, low cost and environmental friendliness, it has wide applications in water treatment, chemicals, textiles, and medical fields [3, 5, 8, 9]. Nonetheless, CTS is a brittle material and has several problems, such as insolubility in organic solvents as well as poor thermo-mechanical properties. These weaknesses are commonly mitigated by grafting or crosslinking CTS chain with other polymers, such as cellulose, starch, genipin [9], aldehydes, polyamide [10], poly(acrylic acid), polyamide, agar/poly(vinyl alcohol) [9], acrylamide, polyaniline, poly(vinyl alcohol), and poly-(acrylic acid-co-acrylamide) [3]. It has not been reported that hyperbranched polyester is used as a crosslinker for chitosan. In this work, a kind of alcohol-soluble hyperbranched polyester was synthesized from semi-commercially available chemicals and was used as a crosslinking agent of CTS; the properties and application of CTS/polyester were investigated.

## 2. Experimental

### 2.1. Materials

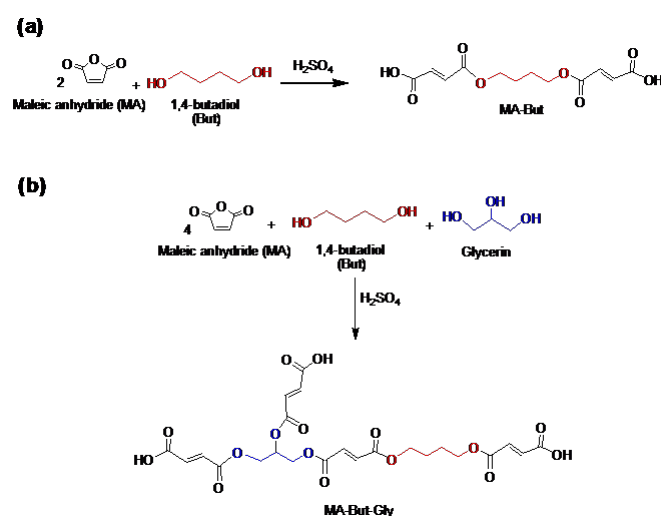
Chitosan, CTS, (was used without further purification) from Acros Reagent Co, Maleic anhydride (98 wt%) was purchased from Alfa Aesar Reagent Co. (USA), 1,4-butadiol (But) (99 wt%) was purchased Reagent Plus, and Glycerin (Germany) was purchased from Riedel-deHaen Reagent Co, (Germany).

### 2.2. Synthesis polyesters

#### 2.2.1. Synthesis of MA/But-based polyester

MA/But-based polyester were synthesized by reaction of MA and But and abbreviated as Polyester-Gly<sub>0</sub> (see Scheme 1a). In 250 mL a three-necked glass reactor flask fitted with a gas inlet pipe for N<sub>2</sub>, 1,4-Butadiol (But), (22.1 mmol, 2.02 gm) and

malice-anhydride (MA) (220 mmol, 2.22 g) were dissolved in 25 mL of xylene with 1 vol % sulfuric acid under vigorous magnetic stirring at 140 °C for 2 h. The produced water was removed using continuous vacuum distillation. The resultant liquid product was colored as sepia likes honey, which was washed several times and dried at 40 °C in oven.



**Scheme 1:** Preparation of polyester from reaction of: (a) malic anhydride (MA) and 1,4-butadiol (But) and (b) malic anhydride (MA) and 1,4-butadiol (But) and Glycerine (Gly).

#### 2.2.2. Synthesis of MA/But/Gly-based polyester

Two different polyesters were synthesized by reaction of MA and But with 5 wt% and 10 wt% glycerine (Gly) and abbreviated as Polyester-Gly<sub>5</sub> and Polyester-Gly<sub>10</sub>, respectively (see Scheme 1b). For example Polyester-Gly<sub>5</sub>, glycerine solution (1.1 mmol, 0.25 mL) was added dropwise to 250 mL three-necked glass reactor flask fitted with a gas inlet pipe for N<sub>2</sub>, containing But (20.9 mmol, 1.903 g) and MA (440 mmol, 4.32 g) were dissolved in 25 mL xylene in presence of in 1 vol % sulfuric acid. The solution was thoroughly stirred using magnetic stirrer at 140 °C for 2 h. The solid product was filtered and washed several times with distilled water. The obtained product was yellowish color.

### 2.3. Fabrication of CTS-Polyester crosslinked spheres

Two different CTS-Polyester crosslinked spheres were fabricated from reaction of CTS with the obtained esters Polyester-Gly<sub>0</sub>, Polyester-Gly<sub>5</sub> and

Polyester-Gly<sub>10</sub>, which were abbreviated as CTS-Polyester-Gly<sub>0</sub>, CTS-Polyester-Gly<sub>5</sub>, and CTS-Polyester-Gly<sub>10</sub>, respectively. 2.5 g of CTS powder was dissolved in 100 mL of H<sub>2</sub>O (in 1 vol % acetic acid) using magnetic stirring for 2 hr. Then, the solution was left at atmosphere for about 4 hr until all air bubbles were released from the CTS gel. The neat CTS beads were formed as the gel spheres dropped into 150 mL of 1.0 M NaOH aqueous solution at room temperature using a syringe under continuously stirring with a magnetic stirrer to prevent bead agglomeration. In order to maintain a constant size and shape of the beads, the height of the syringe tip from the surface of aqueous solution and the rate of dropping were kept a constant throughout the bead fabrication [11]. The gel beads were then left for 24 h without any stirring in order to obtain the complete formation of CTS gel beads. The CTS beads were then collected and washed several times with distilled water (100 mL). For crosslinking of CTS beads, a 0.6 g beads were added to a polyester solution containing 0.2 g of one of the previously obtained polyesters (Polyester-Gly<sub>0</sub>, Polyester-Gly<sub>5</sub> or Polyester-Gly<sub>10</sub>) in 25 mL of ethanol at 80 °C for 8 h. Finally, the obtained spheres were washed three times with distilled water and dried in oven at 40 °C for 24 h.

#### 2.4. Characterization

The structure of the polyester and CTSP crosslinked polymers were confirmed by Fourier a Bruker Vertex infrared spectroscopy (FT-IR), resolution 3 cm<sup>-1</sup>, in the range of 4000-500 cm<sup>-1</sup> using the KBr pellet technique. Dry spheres were crushed into powder in a mortar and an amount of the sample was about 6-8 mg in each pellet. The contact angle was measured using the static sessile drop method by capturing an image of a drop of liquid sitting on the surface at ambient conditions. For each sample, 3 measurements were taken to obtain reproducible results. Atomic absorption spectrometer (Perkin-Elmer AAnalyst 400) was used to measure the concentration of heavy metal ions in water. The concentrations of the adsorbed ions onto surfaces were determined through a calibration curve for the known ions concentration in the individual aqueous solution.

#### 2.5. Water uptake

Water absorption behavior of the obtained spheres was studied by the conventional gravimetric procedure. The samples were first placed into a vac-

uum at 50 °C for 24 h to make sure that completely dried. Then, the samples were immersed completely in different distilled water at room temperature for 48 h. The percentage of water absorption was measured as shown in Equation 2.1. [1, 4, 12].

$$\text{Water absorption \%}(W\%) = \frac{(W_t - W_0)}{W_0} \times 100 \quad (2.1)$$

where  $W_0$  and  $W_t$  are the mass of the sample in dried state and at time ( $t$ ), respectively. The adsorption values were obtained as the average of three measurements.

#### 2.6. Equilibrium adsorption experiments

Metal adsorption experiments were carried out by the batch equilibrium procedure [4, 13]. A weighed sample of the adsorbents was put into a 50 mL conical flask containing 25 mL of stock solution (80 mg L<sup>-1</sup> metal ion solution) and allowed to adsorb at room temperature for a contact time of 24 h under constant shaking rate of 160 rpm room temperature. The pH value of the solutions was adjusted to the desired value with 1 M HCl or 0.5 M NaOH. Each supernatant aliquot was diluted with distilled water, and then flame atomic absorption spectrometry was used to determine the concentration of the metal ions in the supernatant using a standard calibration curve. The adsorption capacity was calculated according to Equation 2.2.

$$q_e = \frac{(C_o - C_e)V}{W_d} \quad (2.2)$$

where  $q_e$  (mg g<sup>-1</sup>) is the adsorption capacity of the adsorbent (mg g<sup>-1</sup>) and  $C_o$  and  $C_e$  (mg·L<sup>-3</sup>) are the initial and final concentrations of metal ions in aqueous solution, respectively.  $V$  (L) is the volume of the aqueous solutions, and  $W_d$  (g) is the mass of the adsorbent.

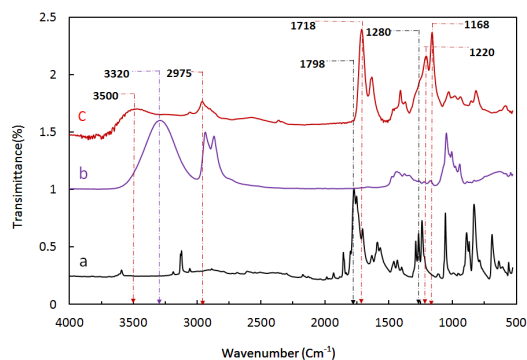
### 3. Results and Discussion

#### 3.1. Confirmation of polyester synthesis

##### 3.1.1. 1,4-Butadoil and Malice anhydride polyester

The structure of MA-But-based ester was confirmed by Fourier transform infrared spectroscopy (FT-IR). The FTIR spectra of starting materials (But and MA) and the obtained polyester are shown in

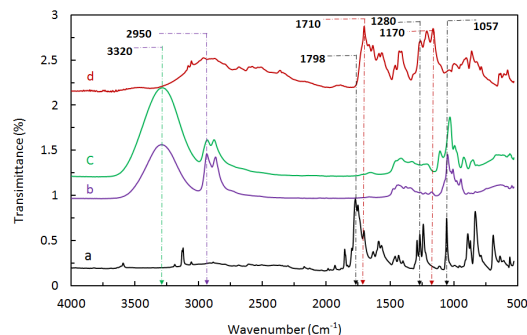
Figure 2.1. The strong band at  $1718\text{ cm}^{-1}$  is clearly presents a corresponding to ester groups ( $\text{C}=\text{O}$ ), which confirms the formation of ester bond. The peaks assigned at  $1220\text{ cm}^{-1}$  and  $1168\text{ cm}^{-1}$  is due to C-O stretching of acid [14], while the peak centered at  $2975\text{ cm}^{-1}$  was assigned to methylene ( $-\text{CH}_2$ ) stretching from (But). FT-IR results of the product also show absorption broadened peaks at  $3,500\text{ cm}^{-1}$ , which may be due to the hydrogen bond formed between the many terminal hydroxyl groups of the product [3].



**Figure 3.1:** FT-IR spectra of (a) = (MA), (B)= (But), (C) = poly(MA -But).

### 3.1.2. But-MA-Gly polyester

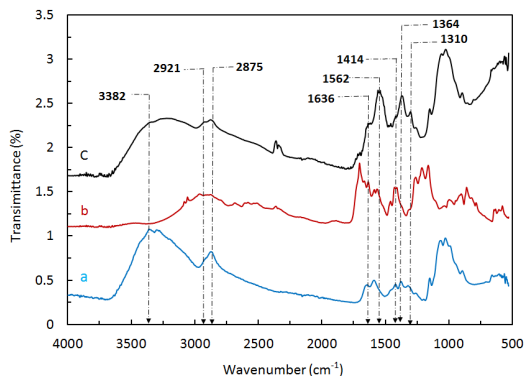
The FTIR spectra of the synthesized polyester in Figure 3.2, the absorption of carbonyl groups ( $\text{C}=\text{O}$ ) had happened to her displacement in the direction of the Supreme Energy from  $1798\text{ cm}^{-1}$  to  $1710\text{ cm}^{-1}$ , which indicates a carboxylic acids. The disappearance of (O-H) polyester as a result of interaction with the carboxylic group in the MA and Gly, and the peak assigned at  $1170\text{ cm}^{-1}$  and  $1280\text{ cm}^{-1}$  due to (C-O) stretching of acid and indicates to overlap an ester with carboxylic acids. The peaks assigned at  $1050\text{ cm}^{-1}$  in Gly and  $1057\text{ cm}^{-1}$  in MA and But indicates to alcohols group were disappearance in polyester. Absorption of methylene groups ( $-\text{CH}_2$ ) at ( $2850\text{--}2950\text{ cm}^{-1}$ ) was evident in both (But) and (GLY) were decrease in polyester absorbance became more widely distributed. Which shows that this group has been associated with chemical groups in a different order, resulting in a deformation of the surrounding environment in this group.



**Figure 3.2:** FT-IR spectra of: (a) MA, (b) But, (c) GLY, (d) Polyester-Gly<sub>5</sub>.

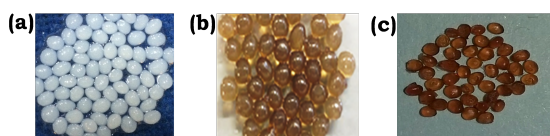
### 3.1.3. Chitosan /polyester crosslinked spheres

Crosslinking of CTS-based spheres for applications in water medium is necessary to form stable materials in order to prevent dissolution of the polymer chains in an aqueous environment [15]. Therefore, FT-IR was used to investigate the proposed interactions of primary amine groups ( $-\text{NH}_2$ ) in CTS backbone with carboxylic acid ( $-\text{COOH}$ ) on the obtained polyesters. Figure 3.3a, b and c show the FT-IR spectra of the CTS, CTS-Polyster-Gly<sub>0</sub>, and CTS-Polyster-Gly<sub>5</sub>, respectively. The FT-IR spectrum of CTS exhibits a strong peak at  $3382\text{ cm}^{-1}$  which corresponds to axial stretching vibration of O-H superimposed to the N-H stretching band and the inter hydrogen bonds of the polysaccharide [3]. The two absorption bands at  $2921$  and  $2875\text{ cm}^{-1}$  attributed to asymmetric and symmetric vibration of  $-\text{CH}_2$  groups. The shoulder peak at  $1636\text{ cm}^{-1}$  and strong absorption band located at  $1562\text{ cm}^{-1}$  are attributed to C-O bond (amide I) and the NH bending of vibration in  $\text{NH}_2$  groups (amide II), respectively, in the acetamido groups in the CTS matrix, due to reaction of primary of amine groups ( $-\text{NH}_2$ ) on CTS backbone and carboxylic acid ( $-\text{COOH}$ ) on polyester [16]. Furthermore, the peaks located at  $1414$ ,  $1364$ , and  $1310\text{ cm}^{-1}$  are ascribed to the C-N stretching vibration (amide III). Some optical images are presented in Figure 3.4 to investigate the differences between the obtained spheres as a function of the synthesis conditions. According to the color of spheres, different colors were observed for neat CTS and CTS-Polyster-Gly<sub>5</sub> spheres, which attributed to reaction of CTS with polyester ( see Scheme 1). As seen in Figure 3.4, CTS-Polyster-Gly<sub>5</sub> spheres in wet and dry states



**Figure 3.3:** FT-IR spectra of (a) = (CTS), (b) = Poly (5%Gly), (C) = CTSP (5%GLY) crosslinked spheres.

being almost light brown (see Figures 3.4b and 3.4c) owing to the content of polyester as compared to the neat CTS spheres that are in white (see Figure 3.4a). In addition, the color of the CTS-Polyesters spheres in dry state becomes browner.



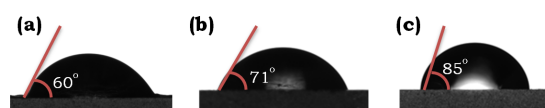
**Figure 3.4:** Optical images of the obtained spheres: (a) neat CTS, (b) CTS-Polyester-Gly<sub>5</sub> in wet state, and (c) CTS-Polyester-Gly<sub>5</sub> in dry state.

### 3.2. Hydrophyllicity of CTS/polyester spheres

#### 3.2.1. Analysis of contact angle

CST-based materials have hydrophilic nature; however, crosslinking of CTS with other polymers decreases of its hydrophilicity [3]. Among of these polymers, polyester can react with CTS and form crosslinked polymers as shown in Scheme 1. Contact angle analysis was used to investigate the hydrophilicity of the CTS-Polyester crosslinked polymers. Figure 3.5 shows the results of contact angle of the spheres. The results indicated that the presence of Gly decreases the degree of hydrophilicity of spheres, which ascribed to the increase in crosslinking density. For example, the contact angle of Gly-free spheres (CTS-Polyester-Gly<sub>0</sub>) was increased from 60° to 70° and 85° with Gly content

of 5% and 10%, respectively, (CTS-Polyester-Gly<sub>5</sub>, and, CTS-Polyester-Gly<sub>10</sub>). Therefore, the modified CTS spheres were less hydrophilic nature. On the other hand, the increase of polyester content led to a more crosslinking and subsequently, it leads good mechanical properties.



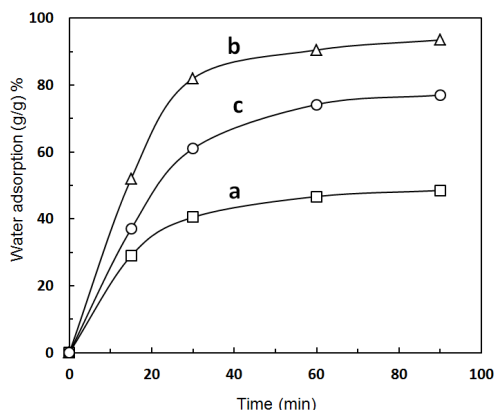
**Figure 3.5:** Water contact angle images of (a) CTS-Polyester-Gly<sub>0</sub>, (b) CTS-Polyester-Gly<sub>5</sub>, and (c) CTS-Polyester-Gly<sub>10</sub>.

#### 3.2.2. Water adsorption

The hydrophilicity of the obtained spheres was also studied using measurement of water adsorption. Percentage of quantity adsorption of water versus time at 25 °C was plotted as a function of Gly content. Figure 3.6 showed variation of the water adsorption degree of CTS-Polyester spheres with different Gly contents. It is observed that the degree of water adsorption decreased with increasing Gly in the sample. When the concentration of Gly was 5 wt%, the adsorbed quantity of water was more than the Gly-free sample. This indicated that presence of Gly improves hydrophilicity of CTS-Polyester compared to Gly-free sample, which ascribed to the increase of carboxylic acid groups in the polymer matrix. However, the efficiency of adsorption was reduced with increasing Gly content (10 wt%), which may be due to the interaction between the carboxyl groups on polyester and hydroxyl groups or amino groups on chitosan chains [17]. These imply that interactions performed high crosslinking polymeric spheres. In addition, the hydrogen bond interaction among chitosan chains and polyesters may be reduces the adsorption ability of CTS-based spheres.

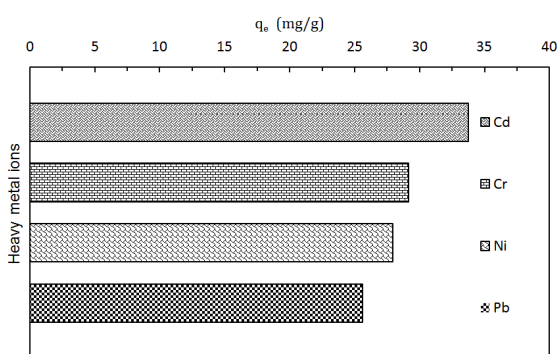
### 3.3. Applications of CTS-polyester polymeric spheres

Treatment of metal-contaminated wastewater has always been a serious issue in mining, electroplating, and the chemical and electronic industries. The impact of toxic heavy metal ions on health and on the environment has been widely reported. Adsorption is the current technology that has attracted



**Figure 3.6:** Variation of water adsorption degree with different glycerine concentrations in the CTS-Polyester crosslinked spheres: (a) CTS-Polyester-Gly<sub>0</sub>, (b) CTS-Polyester-Gly<sub>5</sub>, and (c) CTS-Polyester-Gly<sub>10</sub>.

considerable attention for removal of heavy metal ions due to their high efficiencies and economic feasibility [1]. Chemically or physically modified Chitosan (CTS), a low-cost non-toxic natural biomaterial, has been considered as a green adsorbent for the removal of metal ions because it contains various chelating groups such as amino and hydroxyl groups.



**Figure 3.7:** Variation of water adsorption degree with different glycerine concentrations in the CTS-Polyester crosslinked spheres: (a) CTS-Polyester-Gly<sub>0</sub>, (b) CTS-Polyester-Gly<sub>5</sub>, and (c) CTS-Polyester-Gly<sub>10</sub>.

The efficiency of the obtained polymeric spheres for removal of several heavy metal ions has been evaluated. The effect of metal types on the adsorption capacity at equilibrium using CTS-Polyester-Gly<sub>5</sub>

was investigated and the results are presented in Figure 3.7. The results indicated that removal of metal ions by using the CTS-Polyester sphere as a ligand was in the following order: Cd<sup>2+</sup>, Cr<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>. The observed results imply that Cd<sup>2+</sup> has the highest tendency to form a complex with the polymer matrix, which may be the Cd<sup>2+</sup> has the lowest enthalpy of hydration ( $\Delta H^\circ$ ). In addition, the Van der Waals radius had significant effects on the sorption of the metal ions onto the polymer-based sorbents [18]. These results are in agreement with that reported for CTS-based sorbents [19-22].

#### 4. Conclusion

A new class of CTS-Polyester crosslinked spheres been successfully fabricated with two different polyesters. Effect of glycerine content on the hydrophilicity of CTS-Polyester has been studied in details. Results indicated that 5% Gly improves the hydrophilicity of resulting polymer that obtained by reaction of CTS with polyester that prepared via reaction of malic anhydride with 1,4-butadiol (CTS-Polyester-Gly<sub>0</sub>). The application of the obtained polymeric spheres was evaluated for wastewater treatment. The adsorption of heavy metal ions were investigated and the results indicated that the sample of CTS-Polyester-Gly<sub>5</sub> showed the highest metal adsorption. This study demonstrated that CTS-Polyester was a good candidate for adsorption of Cd<sup>2+</sup>, Cr<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solutions.

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