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Synthesis and Characterization Pectin-Carboxymethyl Chitosan crosslinked PEGDE as biosorbent of Pb(II) ion

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Abstract Pectin and chitosan are biodegradable polymers, potentially applied as a heavy metal adsorbents. Unfortunately both biosorbents pectin and chitosan have a weakness in acidic media. For this purpose required modified pectin and chitosan. The modified adsorben is intended to obtain a stable adsorbent and resistance under acid. The research was done by experimental method in laboratory. The stages of this research are the synthesis of carboxymethyl chitosan (CMC), synthesis of Pec-CMC-PEGDE film adsorbent, stabily test under acid, the characterization of active group using FTIR, stability characterization of Pec-CMC-PEGDE powder adsorbent using XRD, termo stability using DTA- TGA. The results of the research have shown that: pectin and CMC can be cross-linked using PEGDE crosslinking agent, the film adsorbent was stable under HCl 1 M, the film adsorbent have active group comprise of carboxylate and amine groups. The result of characterization using XRD, shows that the adsorbent is semi-crystalline. Base on termo stability, the film adsorbent Pec-CMC-PEGDE stable up to 600°C. The film can be applied as an adsobent of Pb (II) ion remediation. The optimum pH of pec-CMC-PEGDE in adsorbed of Pb(II) was reached at pH 5 with 99.99% absorbent adsorbed and of and adsorption capacity was 46.11 mg/ g.

1. Introduction

Waters contaminated by waste materials from industrial processes containing hazardous and non-biodegradable materials such as Cu, Ni, Zn, Cr, Hg, Cd, Pb will disrupt the dynamic relationship of the balance of nutrient component composition, organic matter and biomass which are very important for the stability of aquatic ecosystems. The existence of input materials that are toxic will reduce the potential of biological resources in addition to increasing cases of poisoning and public health disorders [1]. Thus it is necessary to have a simple technology capable of dealing with aquatic environmental problems, particularly with regard to methods for dealing with heavy metals contamination.

The adsorption is a simple method, economical, and naturally occurring, but highly effective method used to overcome wastewater problems in the aquatic environment. Methods for dealing with heavy metals by means of adsorption are generally based on the interaction of metals with functional groups present on the surface of the adsorbent through complex forming interactions and usually occur by involving groups such as -OH, -NH, -SH and -COOH.

Various biomaterials have been applied as adsorbents, and Pectin is one of those compounds which is applied as metals absorbent. Pectin is an anionic plant cell wall polysaccharide based on α-(1–4)

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linked D-galacturonic acid [2]. Pectin widely available in the middle lamella of plant cell walls. Pectin has many active groups. The main functional groups contained in the pectin are hydroxyl, carboxyl, amide and methoxy [3]. Lately the pectin was widely used in pharmaceuticals and cosmetics, in the food industry and as adsorbent to remove heavy metal ion [4,5]. Pectin contains a lot of active groups, that can be used as a source biosorbent. These functional groups can be used to bind heavy metals, especially hydroxyl groups [6]. Another biomaterials that capable of acting as biosorbents are well known are chitosan. Chitosan containing the active group -OH and $-NH_2$ or in neutral state $-NH_3$ is able to adsorb heavy metal ions well, either by ion formation mechanism and / or ion exchanger.

However, chitosan is easily soluble in acetic acid, it also partially soluble in dilute acid, such as HNO_3, HCl, $HClO_4$, and others, so that the direct use of chitosan as an adsorbent will be less effective. In a acidic conditions, the number of amine group which is an active group that capable to bind a metal ions will be reduced. So to solve this problem, chitosan chains must be crosslinked in order to improve the stability and hold up with acid condition. Several chitosan cross-linker agents suitable for chitosan such as Glutaraldehyde, epichlorhidrin chloromethyl oxirane, poly ethylene glycol (PEG), ethylene diamine diglycidyl ether (EDGE) and so on. Cross-linked chitosan is insoluble acids condition because it is very stable [7].

Chitosan can be modified into carboxymethyl chitosan (CMC). CMC is one derivative of chitin obtained by a carboxymethylation process of chitosan alkalis with monochlororoacetic acid. This CMC powder has the advantages of chitin and chitosan because CMC powder is easily soluble in water compared with chitin powder and chitosan powder, in addition it is biodegradable, biocompatible and non-toxic [8]. Carboxymethyl chitosan contains more active groups than chitosan so carboxymethyl chitosan can adsorb Pb (II) more than chitosan.

In this research, crosslinking between pectin and carboxymethyl chitosan was studied. The crosslinking agent to be used is Poly (ethylene glycol) Diglycidyl Ether (PEGDE). The presence of a cyclic ether group in both ends of PEGDE is expected to bind the -OH group of pectin and chitosan. This research synthesizes CMC-Pectin-PEGDE film to adsorb heavy metals Pb based on pH variation, contact time, and concentration.

2. Experimental section

2.1. Material

Chitosan with the deacetylation degree in the range of 75-85% and Poly ethylene glycol diglycidyl ether (PEGDE) were purchased from Sigma Aldrich (Germany). Chloroacetic acid, acetone, HCl 37 % v/v, HNO_3, $Pb(NO_3)_2$ were purchased from E. Merck (Germany).

2.2 Procedure

2.2.1. Preparation of adsorbent

Chitosan (3.0 g) was dispersed in 80 mL isopropanol (0.2 M) and stirred for 30 min. NaOH 40% (28 mL) was then added dropwise for 30 min and followed by dropwise addition of chloroacetic acid in isopropanol. The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered and washed with ethanol and then dried on oven to obtain CMC. The next step, 0.2 g pectin and 0.2 g CMC was dispersed in 10 mL acetic acid 5% respectively and then 1.78 ml PEGDE in 25 mL ethanol was added and stirred for 2 h. The mixture was poured in a petri dish and dried in oven. The film was than immersed in an aqueous solution of sodium hydroxide (1 mol/L) for 12 h, and then washed with distilled water.

2.2.2. Adsorption of Pb(II) ion

10 mg Pec-CMC-PEGDE adsorbent was contacted with 10 mL of 50 ppm Pb (II) solution at pH 2,3,4,5, and 6, then stirred with shaker for 3 hours. Then Filtering the mixture using Whatmann filter paper and measure the absorbance of the filtrate by using Atomic Absorption Spectrophotometry (AAS).

3. Result And Discussion

3.1. FTIR Characterization

In order to prove that the -COOH group is the dominant active group in pectin, the $-NH_2$ group is the dominant active group on the chitosan while the dominant active group in the CMC are the $-NH_2$ and -COOH groups. Furthermore, the Polyelectrolyte membrane Pectin-CMC tested its functional group using infrared spectrophotometer. FTIR spectra results are presented in Figure 1.

From the FTIR spectra of pectin there is a wide absorption band at 3387 cm^{-1} which shows the stretch vibration of the -OH group. The band at 1065 cm^{-1} is the vibration of the -C-O-. The uptake at 1628 cm^{-1} is the absorption of the -COOH group and at the 1751 cm^{-1} is wave number of C=O ester.

The IR spectra of Pec-CMC-PEGDE adsorbent have the same adsorption as the the constituent compounds Pectin, CMC, and PEGDE. The constituent compounds of pectin, CMC, and PEGDE show the characteristic peaks. The peak of 1628 cm^{-1} which indicates for the -COOH group, whereas the –OH group at 3449 cm^{-1} and 1034 cm^{-1} indicate the –C–O group. The peak on wave number 1597 cm^{-1} indicates COOH group of CMC, and at wave number 3464 show the peak of –OH group. Increasing of peak intensity at wave number 1095 cm^{-1} which is –C–O– group of adsorbent Pec-CMC-PEGDE indicates increasing of ether on the Pec-CMC adsorbent. The increasing peak on 2908 and 1411 cm^{-1} indicates an increasing of CH_2 groups after cross-linking.

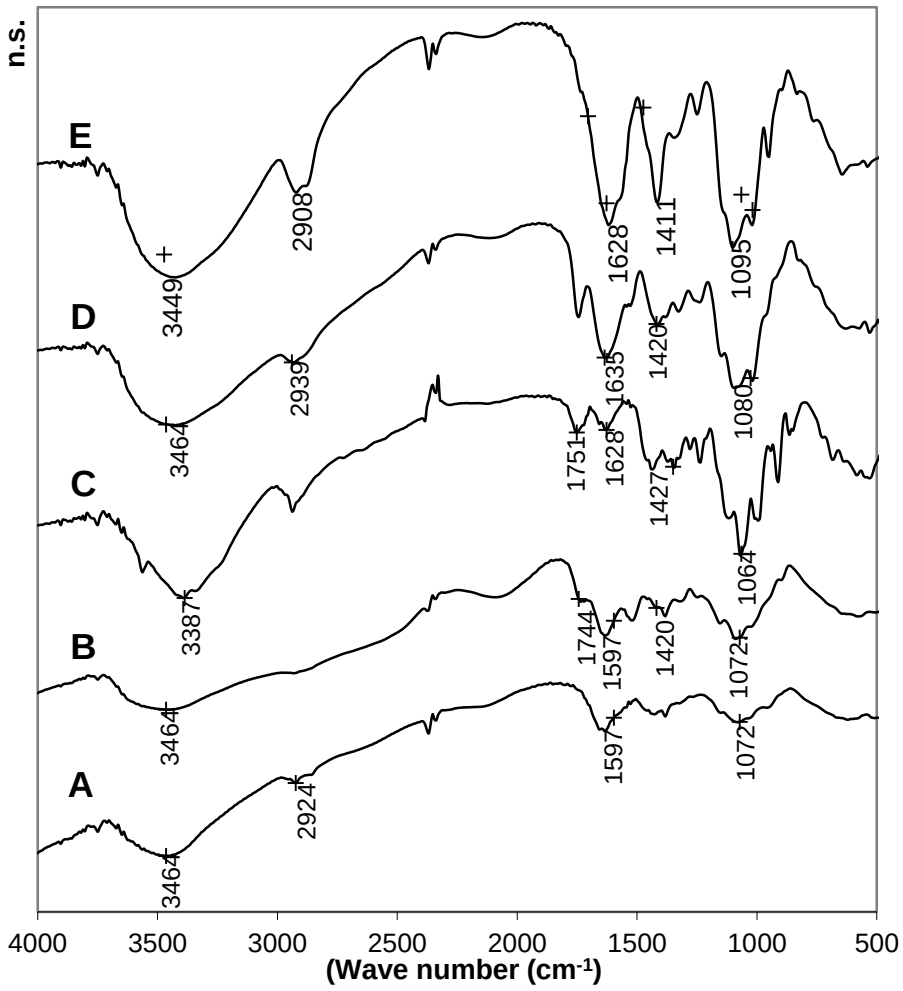

Figure 1 FTIR Spectra of: (A) Chitosan; (B) CMC; (C) Pectin; (D) Pec-CMC; and (E) Pec-CMC-PEGDE

3.2. Analysis of Pec-CMC-PEGDE adsorbent by XRD

Analysis with XRD spectrometry is intended to determine the crystallinity of the material after modification. Diffractogram Pectin, Chitosan, CMC, Pec-CMC and Pec-CMC-PEGDE shown in Figure 2. Initial chitosan showed peak at 2Θ = 10° and 20° degree showed chitosan was crystalline. Furthermore, in the CMC a wider peak is indicated at 2Θ = 10 ° and 20 °(Zang et al, 2011). This is due to a decrease in crystallinity degree due to the transplant process. The structure of chitosan crystals is strongly influenced by hydrogen bonds that occur in one chain (intra) and between chains (inter) chitosan. The grafting process to form the side group by changing hydrogen atom with acetic acid so make the hydrogen bond weaken. The difractogram pattern pectin shows only one sharp peak at an angle of 2Θ = 25 ° degrees while peak of Pec-CMC- PEGDE adsorbent doesn't found in XRD difractogram. This may indicate that after chemical modification the ability to form hydrogen bonds has decreased and the Pec-CMC- PEGDE adsorbent becomes amorphous. It shows Pec-CMC-PEGDE adsorbent is more stable.

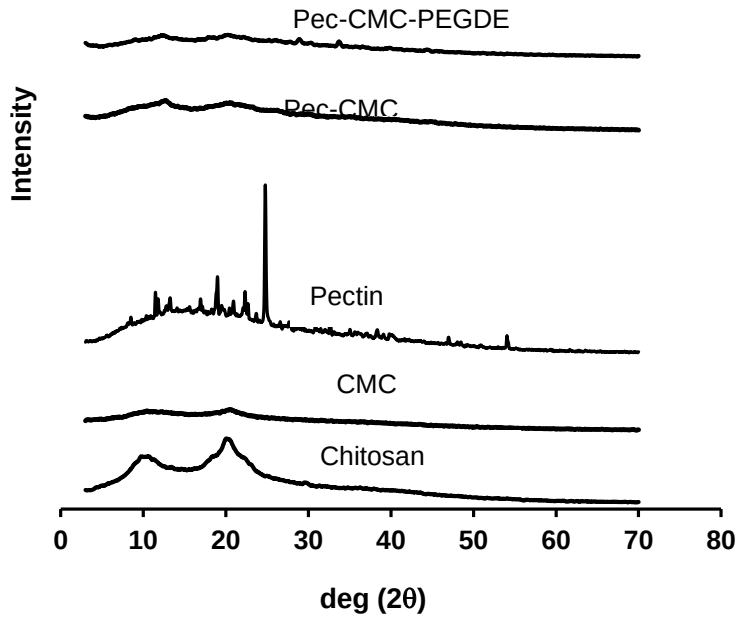

Figure 2. The diffractogram of Pectin, Chitosan, CMC, Pec-CMC and Pec-CMC-PEGDE

3.3 Thermal Analysis

DTA-TGA analysis aims to identify of the thermal caracteristic of chitosan, CMC, pectin and Pec-CMC-PEGDE adsorbent. The DTA-TGA termogram of CMC-Pec-PEGDE were shown in Figure 3.

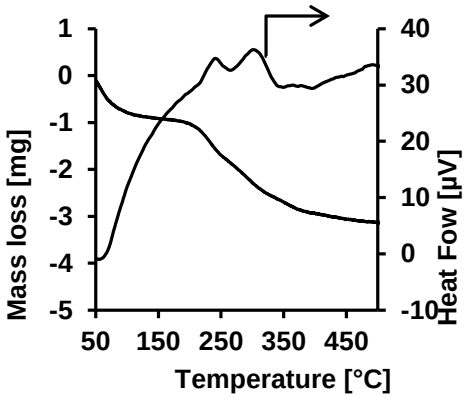

Figure 3. DTA termogram of: (a) chitosan; (b) CMC; (c) Pectin: and (d) CMC-Pec-PEGDE

DTA-TGA Thermogram of Pec-CMC-PEGDE adsorbent shows that two process stages are involved as temperature increase. The first stage at temperature range of 60° to 110° C is a weight loss of 8% which is loss of absorbed water due to the breaking of hydrogen bonds between water and adsorbent. The second stage is an initial degradation of the adsorbent with weight loss of 44% which is an exothermic reaction at temperature range of 150° to 370°C. This stage is an initial degradation, especially the side group of CMC and pectin. The third stage at temperature range of 370-500°C is an exothermic reaction from degradation of main chain of pec-CMC and continued degradation with weight loss of 5%. At this stage the degradation product of water, CO_2 and other small molecules are produced.

3.4 The aplication of Pec-CMC-PEGDE as adsorbent

Pec-CMC-PEGDE adsorbent was contacted with Pb(II) by varying of pH solution that show in figures 4. It show that the optimum condition of Pb(II) ion adsorption on carboxymethyl chitosan (CMC) occurs at pH 5, where the percentage absorbent in adsorpt Pb(II) was 91.12% with an adsorption capacity was 42.01 mg/g. The optimum condition of Pec-CMC-PEGDE in adsorpt of Pb(II) occurred on pH 5 with percentage absorbent was 99.99% with adsorption capacity was 46.11 mg/g.

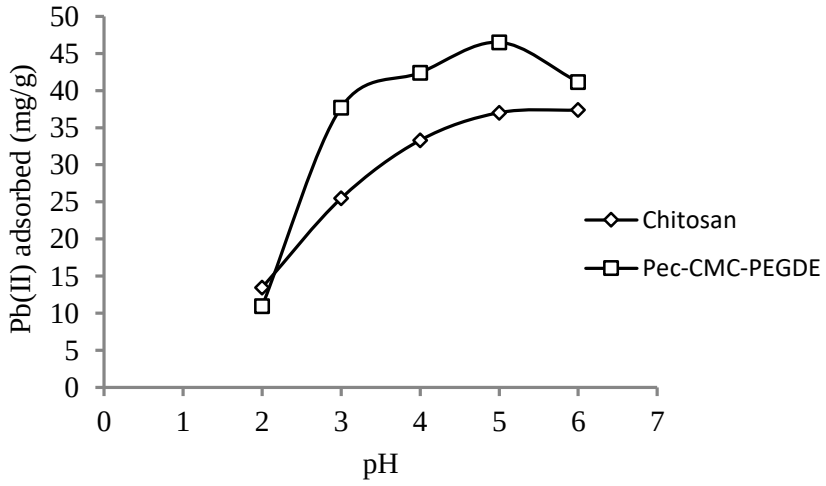

Figure 4. Effect of solution pH on adsorption capacity of Pb(II): Chitosan (upper) and Pec-CMC-EGDE (lower)

4. Conclusion

Pec-CMC-PEGDE were prepared by combine both polysaccharides Pectin and Chitosan with PEGDE as a crosslinker agent. Chitosan was grafted with acetate to form a carboxymetyl chitosan (CMC). Base on the analysis of XRD, DTA-TGA and photo SEM, the modified adsorbent Pec-CMC-PEGDE show that it stable. Based on FTIR spectroscopy, the adsorbent have active group comprise of carboxylate and amine groups. The result of characterization using XRD, shows that the adsorbent is semi-crystalline. Base on termo stability, the film adsorbent Pec-CMC-PEGDE stable up to 600°C. The modified adsorbent can be applied as an adsobent of Pb (II) ion remediation.

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