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Preparation of Cu(II) ion-imprinted based on carboxymethyl chitosan and application as adsorbent of Cu(II) ion

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Abstract. Preparation of Cu(II) template carboxymethyl chitosan (CMC) cross-linked with Bisphenol A Diglycidyl Ether (BADGE) (CMC-BADGE-t) have done. The synthesis has been done through four step i.e. synthesis carboxymethyl chitosan, adsorption Cu(II) on CMC, crosslinking with BADGE, and desorption Cu(II) from adsorbent. The adsorbent was insoluble in acetic acid solution. FTIR spectrum and SEM-EDX analysis showed that the synthesis has been successfully done. Application of the adsorbent for adsorption Cu(II) ions has optimum pH at 6 and contact time of 60 min. Adsorption kinetics followed pseudo-second order equation, and adsorption isotherms followed Langmuir isotherm adsorption. Maximum adsorption capacity of Cu(II) ions on CMC-BADGE-t was 0.276 mmol/g. The relative selectivity factor (α_T) value of Cu(II)/Zn(II), Cu(II)/Cd(II) and Cu(II)/Pb(II) were 50.55, 1.48, and 7.85 respectively that were greater than 1. This adsorbent could be used for several times without loss of adsorption capability.

Keyword: chitosan, template (Cu(II)), cross-linked, BADGE, adsorbent

1. Introduction

Pollution is one of the most concern in modern industries. Metals ion was released in to the environment by industries through their waste water. Some of metal ions are extremely toxic elements for living organism especially human, therefore their removal from waste water is important [1]. Copper (Cu(II)) is a metal ion that has attracted wide attention of environmentalist as one of the most toxic heavy metals. The major source of Cu(II) ion is industries of the metal coating, the smelting of iron and steel, colour/textile, paint, and electrical wiring [2]. Current treatments to remove metals ion from contaminated water are mostly based on reversed osmosis, ion-exchange, electrolysis, liquid extraction, adsorption, complexation, and precipitation. Among the others, adsorption is a process which get increasingly attention because it is inexpensive, generally simple, and able to reduce metal ions until a very low concentration [3].

Chitin is a biopolymer that is contained in the exoskeleton of crustaceae, shrimp, insect and mushrooms. Chitosan (CTS) is a deacetylation product of chitin through reflux of chitin in sodium hydroxide. Chitosan has biological and chemical properties such as non-toxic, biocompatible, high chemical reactivity, chelation and adsorption properties. Chitosan has high sorption capacity for several metal ions because it possesses a number of functional groups such as amines and hydroxyls groups that can bind metal ions by chemical and physical adsorption. However, chitosan has several disadvantages when used as an adsorbent directly such as because its solubility in acidic medium, prone to swelling, unsatisfactory mechanical properties and small adsorption capacity for certain metal ions. To make chitosan stable in acid and has good mechanical properties, it can be done by cross-linked,



immobilization and blending. There are some cross-linkers that has been used by researchers such as epichlorohydrin (ECH), glutaraldehyde and EGDE. Cross-linking can reduce the adsorption capacity, but it increase the stability of the polymer [4-6].

Ion imprinted polymers (IIPs) is a synthetic approach to produce functionalized materials that have the ability to recognize the specific template on cross-linked macro molecule polymers. These are highly cross-linked polymers synthesized in the presence of an ion as the template. Ionic imprinted adsorbent based on chitosan has been prepared as an effective adsorbent for metals ion. The procedure of IIPs preparation consists of the formation of a ligand-metal complex followed by a crosslinking in the presence of a crosslinking agent. After that, the template ion is released by washing. This process will produce three-dimensional polymer network recognition cavities with a predetermined orientation according to their stereochemical interaction with the template metal ion. This material will bind selectively only the template ions [7-10].

In this paper explain synthesized a new type Cu(II) ion imprinted adsorbent and applied as Cu(II) ion sorbent. Chitosan was grafted using chloroacetic acid produced carboxymethyl chitosan (CMC). CMC was used as sorbent Cu(II) ion followed by cross-linking using bisphenol A diglycidyl ether (BADGE), and then the sorbed Cu(II) was released using acidic solution. The used of CMC instead of chitosan increased the number of active groups thus increasing the adsorption capacity for Cu(II) ions. BADGE are bifunctional reagent having two benzene ring and two epoxide groups, that reacted both amine and hydroxyl groups on CMC [8]. Bisphenol The material was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometry (EDS), and solubility studies. The adsorption behaviour of Cu(II) from water solutions with the materials membrane was evaluated.

2. Methods

2.1. Material.

Chitosan flakes (DD>85) and BADGE were obtained from Sigma-Aldrich Germany, chloroacetic acid, isopropanol, acetic acid glacial, ethanol absolute, NaOH pellet, HCl 37%, Cu(NO₃)₂·4H₂O, Pb(NO₃)₂·4H₂O, Zn(NO₃)₂·4H₂O, Cd(NO₃)₂·4H₂O were obtained from E Merck Germany, Whatman no 42 filter paper, and distilled water obtained from Central Laboratory, Sebelas Maret University.

2.2. Procedure

2.2.1. Preparation of adsorbent. Synthesis of CMC was followed Chen, 2006 methods [11] with modification. Chitosan (1.0 g) was dispersed and stirred in 20 mL isopropanol for 30 min. Sodium hydroxide 40% (6.3 mL) was added to this solution and followed by addition of 31.2 mL chloroacetic acid in isopropanol (0,2 M). This mixture was stirred at room temperature for 20 hours. The precipitate was filtered and washed with ethanol and distilled water. The product was dried in the oven at 100°C for 24 hours and named as CMC.

The CMC was added to a 112 mL solution of Cu(II) 0.02 M, and stirred for 20 hours. The product was filtered and washed with distilled water until no Cu(II) ion in the filtrate and detected used sodium sulphide solution. The product was dried on oven at 105°C for 24 hours and named as CMC-Cu.

The CMC-Cu was put in a round flask containing 37 mL of distilled water, 1 mL of 1 M NaOH and 1 g BADGE. The mixture was refluxed for 6 hours. The product was filtered and washed by ethanol and distilled water until pH of filtrate neutral. The product was named CMC-Cu-BADGE

CMC-Cu-BADGE was dispersed in to 113 mL HCl 1 M and stirred for 20 hours. The product was filtered and the process was repeated until Cu(II) was undetectable in the filtrate. The product was washed using distilled water, dried in the oven at 105°C for 24 hours and was named CMC-BADGE-t.

2.2.2. Adsorption experiment. The effect of pH on adsorption ability were performed. Initial pH solution was controlled used NaOH and HCl. The adsorbent 10,0 mg and 25.0 mL Cu(II) (25 mg/L) solution was shook for 6 hours at 160 rpm. The mixture was filtered and concentration of Cu(II) in filtrate was analysed using Atomic absorption spectrophotometer (AAS). The contact times was varied by 0 to 350

min for determination of adsorption kinetics. Varying the concentration Cu(II) solution was carried out for the determination of adsorption isotherm. Selectivity ion adsorption for Cu(II)/Zn(II), Cu(II)/Cd(II) and Cu(II)/Pb(II) was evaluated based on the data of binary. Reusability adsorbent was done by desorption Cu(II) from sorbent using HCl 1 M.

3. Result and Discussion

3.1. Characterization Materials

Chitosan and CMC-BADGE-t was characterized their solubility, functional group using FTIR and surface photograph using SEM-EDX. Fig. 1 was showed the spectrum FTIR which were characteristic of chitosan. Vibration of -OH and -NH groups was showed at peaks 3335 cm^{-1} . The peak at 2868 cm^{-1} is due to -CH stretching vibration of methylene and ethylene groups. Vibration of C=O from amide characterized at 1635 cm^{-1} , that was overlapped with NH vibration from amine groups at 1592 cm^{-1} . Modification of chitosan using chloroacetic acid changed the adsorption peaks at 3335 cm^{-1} became widened and weakened. The carboxylic groups was observed at 1600 and 1412 cm^{-1} which was the characteristic absorption bands of the asymmetric and symmetric stretching vibrations of COO^- [5]. Adsorption Cu(II) on to CMC showed the new peak at 1381 cm^{-1} of COO-Cu . Decreasing the peak at 1600 cm^{-1} showed interaction between COO^- with Cu(II) ions. Crosslinking adsorbent using BADGE showed new peak at 1242 and 1512 cm^{-1} . This peak indicated C=C stretching from aromatic groups from BADGE. A new peak at 825 cm^{-1} indicated the symmetry and asymmetry stretching vibration of para-substituted benzene [9]. The spectrum of CMC-BADGE-t showed that peak at 1743 and 1381 cm^{-1} disappeared due to desorption Cu(II) ion from adsorbent. Releasing Cu(II) from carboxylate groups is showed from increasing peak at 1600 cm^{-1} .

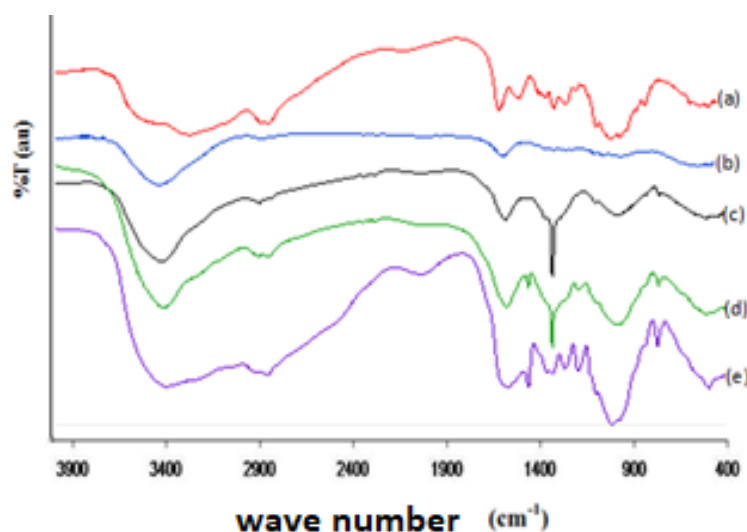


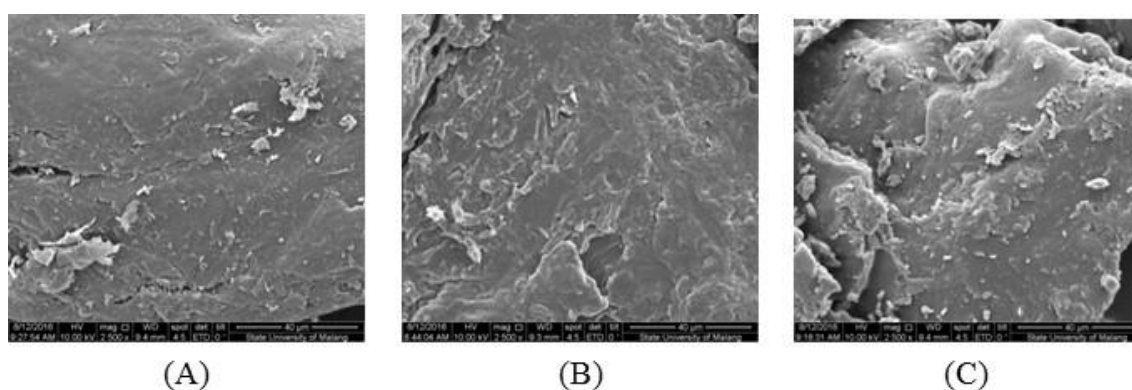
Figure 1. FTIR spectrum of a) CTS, b) CMC c) CMC-Cu, d) CMC-Cu-BADGE, and e) CMC-BADGE-t.

Adsorbent were characterized using scanning electron microscopy (SEM) (Fig. 2) and elemental analysis analysed using EDX. SEM image of chitosan and CMC-Cu-BADGE showed the smooth surface, fibrous and non porous appearance. While on the SEM CMC-BADGE-t showed smoother surface than chitosan. The elemental composition from EDX analysis is presented in Table 1. The data showed that the adsorbed Cu(II) ion in CMC was not released during crosslinking of CMC using BADGE. The elemental percentage of Cu in CMC-Cu-BADGE was 18.85%. Desorption of Cu(II) from adsorbent using HCl 1.0 M can release Cu(II) from material and there are no Cu on the adsorbent. This data showed that the imprinting process of Cu(II) into the adsorbent material was successfully done.

Table 1. Elemental composition for CTS, CMC-Pb-BADGE, and CMC-BADGE-t

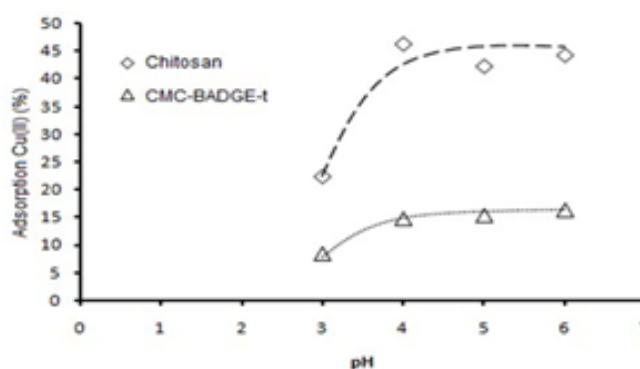
Adsorbent	Element (%)			
	C	O	Cl	Cu
Chitosan	41.84	36.16	0.00	0.00
CMC-Cu-BADGE	53.20	27.95	0.00	18.85
CMC-BADGE-t	56.77	34.40	8.84	0.00

Solubility test showed that both of chitosan and CMC-BADGE-t insoluble in distilled water, but chitosan soluble in acetic acid 2% produced viscous solution. However, CMC-BADGE-t insoluble in acetic acid. This result showed that modification of chitosan increased adsorbent stability on acid medium.

**Figure 2.** SEM image of CTS (A), CMC-Pb-BADGE (B), and CMC-BADGE-t (C).

3.2. The effect of pH on Cu(II) adsorption

The effect of pH on the adsorption of Cu(II) by chitosan and CMC-BADGE-t. was studied in the pH range between 2 to 6. The result is shown in Fig. 3, the adsorption of Cu(II) ion was highly dependent on the pH because it can affect both on the solubility of the metal ions and ionization state of the functional groups on adsorbent. In the lower pH, adsorption capacity of adsorbent is very low since more proton was available and functional groups from adsorbent was protonated. Chitosan has amine and hydroxyl groups as the active site, and CMC-BADGE-t has amine, hydroxyl and carboxylate groups. Around pH 4, 5 and 6, the acidity increased, inhibitory effect of H^+ decreased, which led to increase in the Cu(II) adsorption. At pH more than 7, concentration of hydroxide ion in solution increased and copper hydroxide formed precipitate [12].

**Figure 3.** Effect of pH on adsorption capacity of Cu(II) ion by CTS and CMC-BADGE-t.

3.3. Adsorption kinetics

The effect of contact time on adsorption of Cu(II) was shown in Fig. 4. Initially, when contact time increased, Cu(II) removal efficiency increased rapidly due to the availability of more active surface of the adsorbents, which led to fast adsorption of the Cu(II) ions from the solution. Later, the slower rate of Cu(II) ions adsorption probably occurred due to the lesser availability of active site on the surface of adsorbent. Optimum contact time for adsorbent was found to be 120 min. From the data, kinetics equation was applied to investigate the potential rate-determining step of the adsorption process. In this paper we used two kinetic models, which are pseudo-first order (Lagergren) and pseudo-second order (Ho) [13].

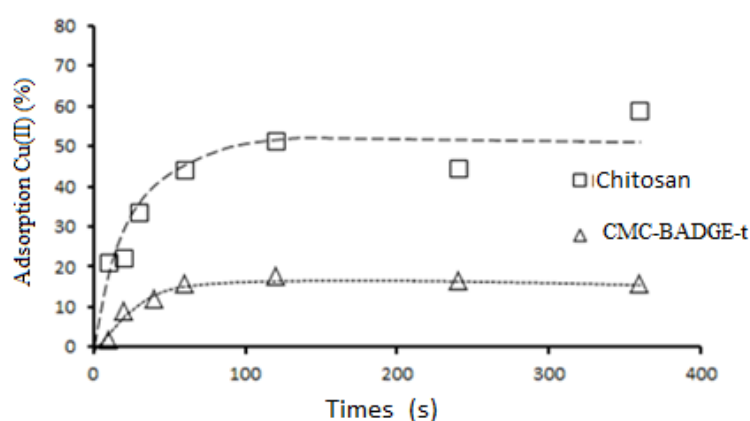


Figure 4. Effect of contact time on adsorption capacity of Cu(II) ion by Chitosan and CMC-BADGE-t

The linear form of the pseudo first-order equation is given by eq. (1) and pseudo second order kinetics is given by eq. (2)

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t (min), respectively, k_1 is the rate constant of the first-order adsorption, and k_2 (g/(mmol.min)) is a pseudo second order constant.

Data of kinetics adsorption Cu(II) on chitosan and CMC-BADGE-t is showed in Table 2. The adsorption data has a very low correlation for the pseudo-first order equation. The adsorption Cu(II) on chitosan and CMC-BADGE-t followed pseudo-second order equation kinetics, as shown by high R^2 value ($R^2 > 0.94$).

Table 2. Kinetic parameter for Pb(II) adsorption onto CTS and Pb-IIP

Adsorbent	Pseudo orde-1		Pseudo orde-2	
	$K_1 (\times 10^{-2})$ (1/min)	R^2	$K_2 (\times 10^{-2})$ (g/mmol min)	R^2
Chitosan	0.71	0.775	0.41	0.969
CMC-BADGE-t	0.11	0.401	0.29	0.941

3.4. Adsorption Isotherm

The effect of concentration variation of Cu(II) ions on adsorption capacity is shown in Fig. 5. This data was measured at pH 5 and contact time of 120 min. Langmuir and Freundlich adsorption isotherms were used to describe the interaction between Cu(II) ion on the adsorbent.

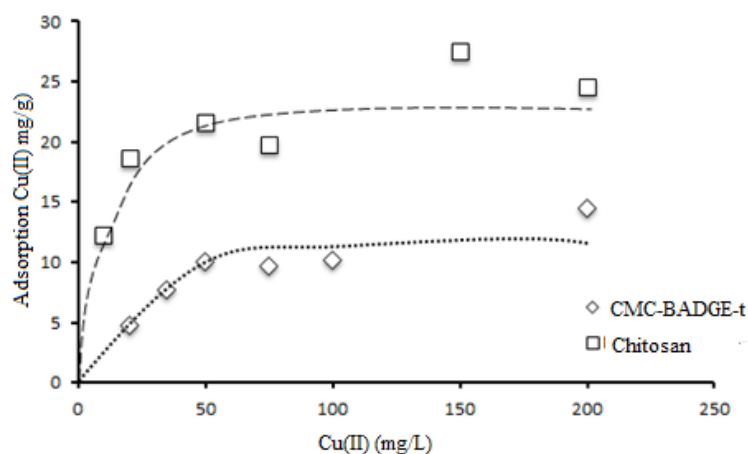


Figure 5. Effect of initial concentration on adsorption capacity of Cu(II) ion by Chitosan and CMC-BAGE-t

The Freundlich isotherm equation is given on eq.3. This isotherm is an empirical equation that was used for adsorption on heterogeneous surfaces.

$$\log m = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where m is the number of metal ions adsorbed (mg/g), K_f (L/g) is the adsorption distribution coefficient related to Freundlich adsorption capacity, and n is the Freundlich constants indicating heterogeneity of the surface.

The Langmuir adsorption isotherm equation describes an adsorption that occurring on the surface that has a finite number of sites with similar energy levels. This models based on the assumptions that homogeneous adsorption was occurring on a monolayer surface coverage and without net interaction between the adsorbed species. The linearized Langmuir isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{bK} + \frac{1}{b} C_e \quad (4)$$

where q_e is the amount of adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mg/L), b is the Langmuir adsorption capacity (mg/g), K (L/mol) is the Langmuir adsorption equilibrium [3].

Table 3 showed the parameters of Freundlich and Langmuir isotherm adsorption. Based on Table 3, the adsorption Cu(II) using the chitosan and CMC-BADGE-t shows a good fit to the Freundlich due to its high R^2 value ($R^2 > 0.95$). This fact showed that grafting and cross-linking onto chitosan produce homogeneous active sites in the surface that dominated by carboxylate groups. The adsorption capacity of CMC-BADGE-t is decrease than chitosan cause surface of adsorbent covered by crosslinker (5).

Table 3. Parameters of Langmuir and Freundlich isotherm

Adsorbent	Langmuir			Freundlich	
	b (mg/g)	K (L/mmol)	R^2	K_f (mg/g)	R^2
Chitosan	6.484	7.813	0.991	22.039	0.829
CMC-BADGE-t	17.539	1.393	0.959	1.677	0.908

3.5. Adsorption selectivity

The adsorption selectivities were studied by adding 10.0 mg adsorbent to 25.0 mL of solution containing ion pairs: Cu(II)/Zn(II), Cu(II)/Cd(II), and Cu(II)/Pb(II), with the concentration of 0.5 mmol/L Cu(II) and 0.5 mmol/L of the metal ion pairs. The adsorption was carried out in batch system using magnetic stirrer at pH 5. Selectivity coefficient (α) was determined using equation 7 [14]

$$\alpha_{(M1/M2)} = D_{M1}/D_{M2} \quad (6)$$

Where distribution ratio $D = Q/C_e$, Q is adsorption capacity (mmol/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mmol/L), and α is selectivity coefficient.

Table. 4 showed selectivity coefficient (α) Cu(II) toward Zn(II), Cd(II) and Pb(II). Adsorption selectivity are influenced by metal ions size and properties of metal ions and functional groups. Based on the hard and soft acid and bases principle (HSAB) by Pearson, carboxylate and amine groups are hard base, whereas Cu(II), Pb(II) and Zn(II) are intermediate and Cd(II) is soft acid. This data showed that both of chitosan and CMC-BADGE-t selective for Cu(II) ion than Zn(II), Cd(II) and Pb(II).

Table 4. Selectivity coefficient adsorption Cu(II) on Chitosan and CMC-BADGE-t

Adsorbent	Cu(II)/Cd(II)	Cu(II)/Zn(II)	Cu(II)/Pb(II)
Chitosan	264.42	2.31	6.14
CMC-BADGE-t	60.55	1.48	7.85

3.6. Reusability

Determination of reusability on the adsorbent was carried out by adsorption and desorption sequentially. Initially Cu(II) ion was adsorbed by CMC-BADGE-t followed desorption process using HCl solution 1M. There are no data for chitosan adsorbent because during desorption process, chitosan dissolved and can't be filtrated from this solution. This process was repeated 5 times and the result was showed at Fig. 6.

Fig. 6. showed that adsorption capability of CMC-BADGE-t was not change significantly to the fourth usage. In the fifth desorption, adsorption capability decreased 10.6% due to damage to the adsorbent structure.

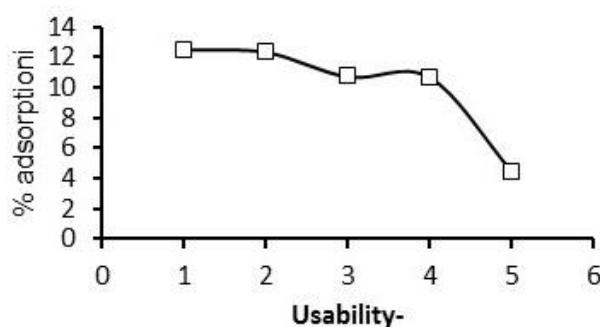


Figure 6. Reusability adsorption Cu(II) on CMC-BADGE-t.

4. Conclusion

Ionic imprinted polymer from chitosan (CMC-BADGE-t) was prepared using Cu(III) as the imprinted ion, CMC as a polymers and BADGE as a cross-linker. CMC-BADGE-t is not soluble in acid and base. The adsorption process could be best described by pseudo-second order kinetic model and Langmuir isotherm adsorption. The adsorbents have high selectivity for Cu(II) than Pb(II), Cd(II) and Zn(II). Modified chitosan can be regenerated with desorption processes using HCl 1 M.

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