Preparation of Fully Deacetylated Chitosan for Adsorption of Hg(II) Ion from Aqueous Solution

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Abstract
In this work, the fully deacetylated chitosan (FCS) was obtained from the deacetylation process of chitosan (= 31\%) in 5% NaOH solution. The structure of FCS was characterized by nuclear magnetic resonance (NMR) spectroscopy, X-Ray diffraction and Bruaer – Emment – Teller (BET) analysis. The FCS was used to adsorb Hg(II) ion from aqueous solutions. The influences of various operating parameters such as pH, temperature, initial concentration of Hg(II) ion and contact time on the adsorption capacity of FCS have been investigated. The results showed that the adsorption capacity of FCS for Hg(II) ion rapidly reached equilibrium within 60 min and strongly depended on pH and temperature. Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm kinetics. It was shown that the FCS had given good correlation with Langmuir isotherm model and the adsorption kinetics of Hg(II) ion could be best described by the pseudo-second-order model.

Keywords: Chitosan; Deacetylation; Heavy metal ion; Adsorption isotherm; Kinetics

Introduction
Contamination of aquatic media by heavy metals is a serious environmental problem, mainly due to the discharge of industrial waste. The presence of heavy metal ions from transition series, viz., Cu, Pb, Fe, Mn, etc. in the environment is of major concern due to their toxicity of many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into any harmless end products. One of the most toxic heavy metals commonly found in the global environment including lithosphere, hydrosphere, atmosphere and biosphere and its toxic nature has been known for centuries is mercury (Hg). Symptoms of mercury poisoning are mainly neuronal disorders but also damage to the cardiovascular system, kidney, bones, etc. The three major sources of Hg emissions are natural, anthropogenic and re-emitted sources. Urban discharges, agricultural materials, mining and combustion and industrial discharges are the principal anthropogenic sources of Hg pollution in the environment. In order to minimize the adverse effects of Hg in the environment, it is desirable to find ways to capture it before it becomes a problem [1,2]. For these reasons, recently, many technologies have been established for the recovery of metals from wastewater, which include chemical precipitation, flotation, biosorption, electrolytic recovery, membrane separation, removal by adsorption on minerals, activated carbon adsorption, etc. Among all the treatments proposed, adsorption using sorbents is one of the most popular methods. Many materials of biological origins have been studied as adsorbents to remove various heavy metal ions from water and industrial effluents. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation to analytical purpose [3-6]. Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Polysaccharides which are abundant, renewable and biodegradable resources have the capacity to associate by physical and chemical interaction with a wide variety of molecules. But much attention was focused on chitin, starch and cyclodextrin [7].

Chitin is a naturally abundant polymer like cellulose and is distributed in the shell of crustacean such as crabs and shrimps, and the cuticle of insects and also in the cell wall of some fungi and microorganisms. Chitin consists of 2-acetamido-2-deoxy-(1-4)-β-D-glucopyranose residues (N-acetyl-D-glucosamine units) which has intra- and inter-molecular hydrogen bonds and is water-insoluble due to its rigid crystalline structure. Chitosan ideally consists of 2-amino-2-deoxy-(1-4)-β-D-glucopyranose residues (D-glucosamine units) and has no or a small amount of N-acetyl-D-glucosamine units, and is water-soluble as the salt with various acids on the amino group of D-glucosamine unit [8]. The possibility of extending the use of chitosan to immobilize biologically active species of to remove metal ions from wastewater has been regarded as an area worthy of further investigation. Because of its coarse porous structure, low toxicity, and the presence of free amino groups, chitosan has been considered an excellent candidate as a support for such purposes. The amine groups on chitosan chain have been already shown to serve as a selective chelating site for transition metal ions [9-14].

Up to now, many approaches on using chitosan for adsorption of heavy metal ions from aqueous solutions have been reported. However, the use of chitosan with low degree of acetylation for these aims has not been showed. With low degree of acetylation, chitosan possesses numerous free amino groups, which facilitate for complexation of chitosan with many heavy metal ions, so that the adsorption capacity might be enhanced. Therefore, in this work, the fully deacetylated chitosan was prepared from chitosan (\(\overline{D}\overline{A}=31\%\)). The structure of fully deacetylated chitosan was improved by NMR spectra and X-ray diffraction. Physical properties of initial chitosan and fully deacetylated chitosan were also measured. The adsorption behaviors and the effects of adsorptive conditions such as pH medium, contact time and initial concentration of Hg(II) ions to adsorption behavior of fully deacetylated...
chitosan were also investigated. The characterizations of isothermal adsorption and adsorption kinetics were also studied in order to provide a new method and theoretical evidences for wastewater treatment.

**Experimental**

**Materials**

The β-chitosan with a 31% degree of acetylation (DAA=31%) was received from the deacetylation of chitin (squid pen). Sodium hydroxide and hydrochloric acid were purchased from Merck (Germany). The metal salt chosen HgCl₂ was analytical reagent grade. All other chemicals and reagents used were of analytical grade.

**Preparation of fully deacetylated chitosan**

The fully deacetylated chitosan was prepared through two steps described as follows:

**Decrystallization of chitosan:** β-chitosan (1 g) was dissolved in 500 ml of 0.1M hydrochloric acid with stirring (200 rpm) at 25°C for 24 h. The deacetylated solution was obtained after filtering the mixture through a textile cloth to remove any insoluble components. Then the chitosan solution (100 ml) was drop-wise into 500 ml of 90% (v/v) ethanol with stirring vigorously. The forming precipitate was filtered out, washed with the excess amount of distilled water to remove any impurities and dried for obtaining decrystallized chitosan.

**Deacetylation of decrystallized chitosan:** 1 g of decrystallized chitosan was added into 100 ml of 5% sodium hydroxide solution. The deacetylation of chitosan was carried out at 80°C for 3 h with stirring vigorously in air atmosphere. After that, chitosan was separated and washed many times by distilled water to remove any impurities. It was then dried at 60°C in an oven or lyophilisation for obtaining the fully deacetylated chitosan.

**Characterizations of fully deacetylated chitosan**

¹H- and ¹³C NMR spectra of the initial chitosan and fully deacetylated chitosan were recorded on the 500 MHz Bruker Avance spectrometer. The sample concentration was about 10 g/l for ¹H NMR and 70 g/l for ¹³C NMR in 1% CD₂COOD/D₂O.

Degree of acetylation (DA) was estimated from the formula:

$$\text{DA} = \frac{I_{\text{CH}_3}}{3 \times I_{\text{CH}_2}} \times 100\%$$

Where I₃CH₃ was the integral of the hydrogen atom in -COCH₃ group and I₃CH₂ was total integral of the hydrogen atom linked to C1 atom of D-glucosamine units.

X-ray diffraction patterns for initial chitosan, decrystallized chitosan and fully deacetylated chitosan were analyzed using a Siemens D5000 (Japan) diffractometer equipped with a CuKα target at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 2θ=0° to 2θ=60°.

Teller (BET) surface area was measured using Micromeritics ASAP 2010 gas adsorption surface analyzer.

**Measurement of Hg(II) ion**

The solutions of HgCl₂ salt using for experimental were prepared by dissolving the salt in distilled water. The pH value of these solutions was adjusted by using dilute sodium hydroxide or hydrogen chloride solutions. In a typical experiment, 0.02 g of FCS was added to 50 mL of Hg(II) ion solution (initial concentration, 2.5 mM), shaking 2 h at 30°C, then filtered out. The concentration of Hg(II) ion in aqueous solution was determined by atomic adsorption spectrophotometer with a Perkin Elmer atomic adsorption spectrophotometer (AAS-3300). The adsorption capacity of metal ion was calculated based on the difference of Hg(II) ion concentration in aqueous solutions before and after adsorption, according to the following equation:

$$Q = \frac{V \times (C_0 - C)}{W}$$

Where Q was the adsorption capacity (mmol/g), C₀ and C were, respectively, the initial and solution phase metal ion concentration at equilibrium (mmol/L), V was the solution volume (L), and W was the mass of sorbent (g).

**Adsorption kinetics**

For kinetic measurements, 0.02 g of FCS was added into 50 mL solution containing Hg(II) ion with the initial concentrations 2.5 mM under the condition of pH 6.0 with stirring vigorously. Then 0.5 mL of the supernatant was withdrawn at a given time interval by using a 1 mL pipette and used for the residual metal analysis and the pH was measured. In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first- and second-order equations were used to fit the experiment data. The first-order kinetic equation and second order kinetic equation were expressed as equation (3) and (4), respectively [15].

$$\ln(q_e - q_t) = \ln q_e - k_1t$$

$$t = \frac{1}{k_2q_e} + \frac{t}{q_e}$$

where qₑ and qₜ were the amounts of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at time t, respectively, and k₁ was the rate constant of first-order adsorption (min⁻¹). The straight-line plots of ln(qₑ−qₜ) against t were used to determine the rate constant k₁; k₂ was the rate constant of second-order adsorption (g mg⁻¹ min⁻¹), it could be obtained from the straight-line plots of t/qₑ against t.

**Adsorption isotherms**

Keeping the other conditions constant and changing the Hg(II) initial concentration, adsorption behavior of Hg(II) ion onto FCS surface was described by Langmuir isotherm plots and Freundlich isotherm plots. The equations were shown as Equation (5) and (6), respectively [16,17].

$$\frac{C_e}{q_e} = \left( \frac{1}{k_fq_m} \right) + \left( \frac{C_e}{q_m} \right)$$

$$ln Q_e = ln k_f + \left( \frac{1}{n} \right) ln C_e$$

where Cₑ was the equilibrium concentration of the metal ion in solution (mg/L), Qₑ was the equilibrium adsorption capacity (mg/g), qₑ was the monolayer saturated adsorption capacity (mg/g), and kᵢ, kᵢ, n were the constants.

**Results and Discussion**

**Preparation and characterization of fully deacetylated chitosan**

**Decrystallization of chitosan:** The crystalline of polymer could play a restrictive role on its metal sorption capacity and also on
Chitosan is a product which resulted from the deacetylation of chitin in alkaline medium. The origin of chitosan influences the arrangement of polymer chains, and three different types of chitosan obtained by deacetylation of three kinds of chitin have been identified: α-chitosan results from α-chitin (shrimp and crab shells), β-chitosan from β-chitin (squid pen) and γ-chitosan from γ-chitin (stomach cuticles of cephalopodan), corresponding to parallel, anti-parallel, and alternated arrangements of polymer chains, respectively. In the crystal state, chitosan has a tight structure due to the strong hydrogen linkages among hydroxyl and amine groups. This was one of main reasons that limited the ability application of chitosan [18-25]. In order to decrease the crystallinity of chitosan or produce chitosan with amorphous chitosan, finding methods were necessary. According to the methods described in experimental part, by dissolving chitosan in dilute solution and stirring vigorously, the crystal structure of chitosan was broken and formed amorphous structure (Scheme 1).

After precipitation or lyophilisation, this structural state was still maintained, so amorphous chitosan was obtained. Due to the processes for obtaining amorphous chitosan were carried out completely in water, so it could be given a conclusion that the above method used for obtaining amorphous chitosan was quite simple, cheap and easily doing. The decrystallized chitosan prepared by the above method have promising applications in many fields such as film, complexion or loading medicine etc.

Preparation of fully deacetylated chitosan: Chitosan with a very low degree of acetylation (DA ≈ 1%) approaching nearly total deacetylation, was rarely prepared due to the difficulty of deacetylation and risks of degradation. Therefore, in industry, many methods for deacetylation of chitosan have been reported such as the deacetylation of chitosan using highly concentrated sodium hydroxide (40-50%) and even with organic solvents (N-methyl pyrrolidone or propan-2-ol) to increase the swelling capacity of chitosan, several successive treatments were required. For example, starting with a chitosan having a initial DA of 25%, to obtain chitosan with a final DA of 1%, the deacetylation had to be repeated three times. In comparison, decrystallized chitosan (suspension of chitosan in water due to gradually precipitation of chitosan from aqueous solution) having an initial DA of 31% required only one deacetylation treatment in 5% aqueous NaOH to give a product with DA = 1%, no toxic organic solvent being used [26]. The deacetylation of chitosan occurred as follows (Scheme 2).

NMR characterizations: The 1H NMR spectrum (Figure 2) with lower intensity in the N-acetyl peak at about 2.55-2.57 ppm than that of the initial chitosan (Figure 1) and in the (Figure 3) with the absence of peaks at 22.45 ppm and 174.69 ppm corresponding to carbon of CH, and C=O of NHCOCH, group, respectively. The value of DA calculated was 1.13% indicating that the deacetylation was nearly completed.

The evidence of the deacetylation of chitosan could be seen in the 1H NMR spectrum (Figure 2) with lower intensity in the N-acetyl peak at about 2.55-2.57 ppm than that of the initial chitosan (Figure 1) and in the (Figure 3) with the absence of peaks at 22.45 ppm and 174.69 ppm corresponding to carbon of CH, and C=O of NHCOCH, group, respectively. The value of DA calculated was 1.13% indicating that the deacetylation was nearly completed.

X-ray diffractions: The X-ray curves of chitosan, decrystallized chitosan and fully deacetylated chitosan were shown in (Figure 4). It could be seen that, there were two strong and sharp peaks in the diffractogram of chitosan at 2θ at 10° and 19.5°. The peak at 2θ about 22° was attributed to the allomorphic tendon form of chitosan, which resulted in a strong decrease in sorption capacities. Meanwhile, no clear sharp peak was found in the diffractograms of decrystallized chitosan and fully deacetylated chitosan obtained from deacetylation of chitosan. Besides, the peak intensity in the diffractogram of initial chitosan was also highest that of both decrystallized chitosan and fully deacetylated chitosan. These indicated that the crystal structure of the chitosan has been destroyed and replaced by amorphous structure after the process of deacetylation of chitosan. In amorphous state, the functional groups typical for chitosan such as amine (–NH2) and hydroxyl (–OH) groups become more active and flexible, these lead the chitosan easily react with other reagents for forming derivatives of chitosan or complex with many metal ions.

BET characterization: The BET surface area for chitosan and fully deacetylated chitosan was measured from N2 adsorption isotherms. The values were computed and shown in (Table 1). According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores could be divided in broad terms according to diameter (d) into macropores (d>50 nm), mesopores (2<d<50 nm) and micropores (d<2 nm). As shown in Table 1, chitosan (27%31%) corresponded to micropores and that of fully deacetylated chitosan was to mesopores. In addition, comparison to initial chitosan, the surface area of fully deacetylated chitosan was increased strongly, from 0.1698 m2 g−1 of initial chitosan to 5.5156 m2 g−1 of fully deacetylated chitosan. Chitosan had a high surface area that would make its functional groups such as amine (–NH2) and hydroxyl (–OH) groups become more active and flexible so that these functional groups would be easily available for doing. The decrystallized chitosan prepared by the above method have promising applications in many fields such as film, complexion or loading medicine etc.
Figure 1: $^1$H-NMR spectrum of initial chitosan.

Figure 2: $^1$H-NMR spectrum of fully deacetylated chitosan.
Figure 3: $^{13}$C-NMR spectra of initial chitosan (A) and FCS (B).
interaction with metal ions and as results of this the fully deacetylated chitosan might have a promising for adsorption of metal ions.

**Adsorption of FCS for Hg(II) ion**

**Effect of initial concentration of Hg(II) ion:** The relationship between the initial concentration of Hg(II) and the adsorption capacity of the fully deacetylated chitosan was shown in (Figure 5). It could be seen that the adsorption capacity of FCS to Hg(II) increased with increasing of initial concentration of metal ions from 0.05 to 5 mM before equilibrium was reached. The maximum adsorption capacity in the studied range of the FCS for Hg(II) was about 5.07 mmol/g. This value was higher than the results reported by MCKay et al., that the adsorption capacity of the chitosan for Hg(II) ion was about 4.05 mmol/mg [27].

**Temperature effect:** The influence of temperature on adsorption capacity of FCS for Hg(II) ion was shown in (Figure 6). As seen from the Figure 6, the adsorption capacity and adsorption efficiency of Hg(II) ion appeared to decrease as the temperature was raised from 25 to 100°C. It was found that the high temperature was to the disadvantage of adsorption and that the adsorption was an exothermic reaction. Furthermore, it should be noted that excessively high temperature could result in solvent evaporation or some desorption, which affect the content of Hg(II) ion in solutions.

**Effect of pH value:** Indeed, the precipitation occurrence under different pH value for the different metals could lead to the misunderstanding and inaccurate interpretation of adsorption. Moreover, the comparison of adsorption performance would require an optimum pH value for adsorption of the different metals before a well-founded conclusion could be reached. In the case of the sorption of metal ion, the chelation is very sensitive to pH value and usually adsorption does not occur at low pH value of the solution. The relationship between pH value of the original solution and adsorption capacity of FCS for Hg(II) ion was shown in (Figure 7). As seen in the Figure 7, it was observed that the adsorption capacity of FCS for the Hg(II) ion increased with increasing the pH value of the solution until a maximum and then decreased with an increase in pH value. This could be explained as follows: At acidic pH, a decrease in the adsorption was attributed to the increase in ionic strength of solution and to the protonation of complications sites. At alkaline pH, the Hg(II) ion in solution could form precipitate of mercury(II) hydroxide, which decreased the adsorption capacity. The experimental result suggested that the optimal pH for Hg(II) ion adsorption of FCS was around 6.0-6.5.

**Langmuir and Freundlich equilibrium adsorption isotherms**

An adsorption isotherm, the relation between the amounts of solute adsorbed (q) and the remaining concentrations in the aqueous phase (Cₑ), is basically important to describe how adsorbate interacts with adsorbent and so is critical in optimizing the use of sorbents. Therefore, correlation of equilibrium data by a theoretical equation is necessary to practical operation. For these aims, the Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The Langmuir isotherm model assumes that adsorption occurs in a monolayer or that adsorption may only occur at a fixed number of localized sites on the surface with all adsorption sites identical and energetically equivalent. The linear correlation coefficient (R²) values
equation employed to describe heterogeneous systems characterized by the heterogeneity factor 1/n. Therefore, a plot of \( \ln q \) vs. \( \ln C_{eq} \) gives reversible adsorption and it is not restricted to the formation of a monolayer. This isotherm model is the most important multi-site adsorption isotherm for heterogeneous surfaces and it is another form of Langmuir’s approach of adsorption on an amorphous surface. The amount of adsorbed material is the summation of adsorption on all sites [28]. Table 2 summarized the characteristic parameters of these isotherms. It could be seen that the Langmuir isotherm has a better fitting model than Freundlich as the former have higher correlation regression coefficient than the latter, thus indicating to the applicability of monolayer coverage of the Hg(II) ion on the surface of adsorbent.

**Adsorption kinetics:** The effect of contact time on the amount of adsorption has been investigated over the range from 0 to 180 min with three initial Hg(II) ion concentrations of 0.5; 1.0 and 2.5 mmol/l, and the results were shown in (Figure 8). The uptake amount of Hg(II) increased with increasing of contact time but increased slightly after 60 min of contact time, indicating that the equilibrium was almost reached after 60 min. Therefore, the optimum contact time for adsorption of Hg(II) ion was about 60 min.

In order to examine the controlling mechanism for the adsorption process, kinetic models are used to assess the experimental data. The Langelier rate equation is one of the most widely used equations for the adsorption of a solute from a liquid solution [15]. The fitting validity of these models is traditionally checked by the pseudo first order and pseudo second order models to interpret the experimental data. A good correlation of the kinetics data explains the adsorption mechanism of the metal ion on the solid phase. The results of the first-order and second-order adsorption rate constants, calculated \( q_{e,cal} \) and experimental values \( q_{e,exp} \) for different initial Hg(II) concentrations were given in (Table 3).

It could be seen from Table 3, that the values of regression coefficient for pseudo-second-order model were closely unity (>0.999) for all initial Hg(II) concentrations. The calculated values \( q_{e,cal} \) were very close to obtained \( q_{e,exp} \) values. Hence, the adsorption of Hg(II) onto the fully decetylated chitosan could be by the pseudo-second-order kinetic model. This indicated that chemical sorption was the rate-limiting step of adsorption mechanism and not involving a mass transfer in solution.

**Conclusion**

The fully decetylated chitosan (with \( \overline{D_A}=1.13\% \), amorphous structure and high surface area) has been easily obtained from the deacetylation of chitosan (\( D_A=31\% \)) using only 5% sodium hydroxide solution, at 80°C for 3 h. Adsorptive behaviors of FCS for Hg(II) ion from aqueous solutions have been investigated. The results shown that: the adsorption capacity of fully decetylated chitosan was higher than that of initial chitosan in experimental ranges; the high temperature was to the disadvantage of adsorption and that the adsorption was an exothermic reaction; the optimal pH for adsorption was about 6.0-6.5, the adsorption capacity rapidly reached equilibrium within 60 min and

| Metal ion | \( K_L \) (L/g) | \( q_m \) (mmol/g) | \( R^2 \) |
|-----------|-----------------|------------------|--------|
| Hg(II)    | 15.672          | 5.071            | 0.9995 |
| Metal ion | \( n \) (g/L)   | \( K_F \) (mmol/g) | \( R^2 \) |
| Hg(II)    | 1.852           | 4.635            | 0.8952 |

**Table 2:** Langmuir and Freundlich isotherm parameters for Hg(II) with FCS.
the maximum adsorption capacity of FCS for Hg(II) ion was about 5.07 mmol/g. The adsorption isotherms could be well fitted by the Langmuir equation and the kinetics mechanism followed a pseudo-second-order model.

Acknowledgement

This study was supported by the Vietnam’s National Foundation for Science and Technology Development (NAFOSTED, 104.04-2010.64).

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