Preparation of chitosan composite film using activated carbon from oil palm empty fruit bunch for Cd2+ removal from water

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Abstract. Preparation of chitosan composite film using activated carbon had been successfully conducted. Activated carbon was produced by pyrolysis process of oil palm empty fruit bunch. The chitosan composite films were prepared by varying activated carbon content. The obtained chitosan composite films were characterized by tensile test, Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD) and Scanning Electon Microscope (SEM). Tensile test results showed content of activated carbon influenced the tensile strength of chitosan film. Adsorption study was conducted with various contact time, pH and initial concentration of Cd2+. Langmuir and Freundlich isotherm models were used to describe the mechanism of Cd2+ adsorption by chitosan composite film. The maximum adsorption capacity based on Langmuir isotherm model (Q) was 333.33 mg/g. Regeneration study showed the chitosan composite film exhibited higher performance than pure chitosan film.

1. Introduction
The presence of heavy metal ions in water has a negative impact on ecosystems and human health. Therefore wastewater treatment has become an important concern. Several methods of wastewater treatment have been performed such as ion exchange method [1], precipitation [2], membrane filtration, electrodialysis and photocatalysis [3], however these methods require high operational costs. The adsorption method is the preferred method of wastewater treatment because it is simple, effective, efficient and easy to operate. Chitosan is one of the adsorbents that get most attention because its biodegradability, availability, high adsorption capacity and easy to modified. Chitosan is a deacetylation form of chitin which is the second most abundant biopolymer after cellulose. Chitin is a major component of arthropod shells such as shrimp, lobster and crabs [4]. Chitosan has a very high efficiency and effectiveness in heavy metal ions adsorption because it contains amino group (-NH2) and hydroxyl group (-OH) that serve as the side of coordination and electrostatic interaction with heavy metal ions [5].

Chitosan is generally used as fine powder. It is difficult to separate chitosan from the solution after adsorption. Chitosan is easily soluble in acid solutions [6] and has weak mechanical properties. To overcome these drawbacks, some modifications have been conducted, such as the addition of filler to polymer that can improve the properties of the polymer. This method is easy, biodegradable and does not require additional chemicals. Addition of activated carbon on chitosan polymer has been reported by Karaer [7] and Sharififard [8]. However, the activated carbon used was commercially activated carbon that will resulting high-cost materials. Therefore, in this work we used activated carbon...
prepared from oil palm empty bunch which is low cost material. Oil palm empty bunch is the waste of palm oil industry that easily found in Aceh and has not been utilized optimally. Activated carbon was obtained by pyrolysis process of oil palm empty bunch. Preparation of chitosan composite films were conducted with various content of chitosan and oil palm empty bunch activated carbon. The obtained chitosan composite film was characterized with tensile test, FTIR, XRD and SEM. The adsorption performance was evaluated for Cd$^{2+}$ adsorption. The adsorption experiments were performed with various contact time, pH and initial concentration of Cd$^{2+}$.

2. Materials and methods

2.1. Materials
Oil palm empty fruit bunch was collected from Aceh, Indonesia. Chitosan, derived from deacetylated shrimp shell, was purchased from Tokyo Chemical Industry Co., Ltd. Japan (degree of deacetylation: 75.0-85%).

2.2. Preparation of activated carbon
Oil palm empty fruit bunch was cleaned with distilled water and cut to be small pieces and pyrolyzed at 500°C for 2 hours. After pyrolysis process, it was grounded into powder using ball milling machine at 300 rpm for 10 hours to obtained activated carbon particles. The resulting activated carbon was characterized by BET (Table 1), XRD, FTIR, and SEM.

| Parameter         | Value     |
|-------------------|-----------|
| Average pore radius | 1.295 nm  |
| Surface Area      | 127.862 m²/g |

2.3. Preparation of chitosan composite films
Chitosan was added to 100 mL acetic acid solution 2% (v/v) and stirred for 3 hours in order to get chitosan solution. Activated carbon particles were mixed with chitosan solution and stirred for 2 hours. The mixture was poured onto PET plastic container and dried at 40°C for 20 hours. The obtained chitosan composite films were characterized by tensile test, XRD, FTIR and SEM. Preparation of chitosan composite film was conducted by various activated carbon content. Chitosan was added to 100 mL acetic acid solution 2% (v/v) and stirred for 3 hours in order to get chitosan solution. Activated carbon particles were mixed with chitosan solution and stirred for 2 hours. The mixture was poured onto PET plastic container and dried at 40°C for 20 hours. The obtained chitosan composite films were characterized by tensile test, XRD, FTIR and SEM. Preparation of chitosan composite film was conducted by various activated carbon content.

2.4. Adsorption studies
The adsorbent (0.05 g) was added to the erlenmeyer flask containing 25 mL Cd$^{2+}$ solution. The mixture was shaked with a constant speed of 150 rpm for 20 minutes. After adsorption, final cadmium concentration was examined with UV-Vis spectrophotometer. Adsorption studies were done with various contact time (20, 25, 30, 35, 40, and 50 minutes), pH (2, 3, 4, 5, 6, 7, 8, and 9 which were adjusted using 0.1 M NaOH and 0.1 M HCl) and Cd$^{2+}$ initial concentration (15, 25, 35, 45, 55, and 65 ppm). Regeneration experiments were conducted using HNO$_3$ (0.001 M).

3. Results and discussion

3.1. Characterization
In this work, activated carbon prepared from oil palm empty fruit bunch was used as a filler of chitosan film resulting chitosan composite films. In order to study the mechanical properties, tensile
test was conducted to every chitosan composite films which contained different activated carbon content. Based on figure 1, chitosan composite films showed higher tensile strength than chitosan film without activated carbon. The results indicated that activated carbon reinforced chitosan film. Tensile strength of chitosan film without loading with activated carbon was 12.30 kgf/mm². It increased after activated carbon loading and the highest value was obtained at chitosan composite film containing 25% of activated carbon. Tensile strength value of chitosan film improved almost twice after filled with activated carbon. Activated carbon prevented the movement of chitosan molecules and improved the mechanical properties.

Figure 1. Tensile strength of chitosan composite films with various contents of activated carbon.

Figure 2 showed FTIR spectra of chitosan film (a), activated carbon from oil palm empty fruit bunch (b) and chitosan composite film (c). Figure 2a exhibited the characteristics bands of chitosan, such as the band at 3230 cm⁻¹ which was attributed to stretching vibration of OH and band at 1575 cm⁻¹ which corresponded to bending vibration of N-amide II [9]. Figure 2b showed typical bands of activated carbon. The bands at 1035 cm⁻¹ and 874 cm⁻¹ corresponded to ether vibration and stretching vibration of alkene, respectively. The bands appeared on chitosan composite film spectrum (figure 2c) were combination of chitosan and activated carbon bands. Compared with FTIR spectrum of chitosan, the band of stretching vibration of OH of chitosan composite film became broader and shifted to higher wave number. The band of bending vibration of N-amide II of chitosan shifted to lower wave number on chitosan composite film.

Compared with activated carbon spectrum, the band of ether vibration of chitosan composite film shifted to lower wave number and the band of stretching vibration of alkene shifted to higher wave number. These results confirmed interaction between chitosan and activated carbon that leaded a good adhesion between matrix and filler.

XRD analysis was performed on chitosan film (a), activated carbon (b) and chitosan composite film (c). The obtained results were shown in figure 3. Figure 3a showed diffractogram of chitosan and it exhibited typical peak of chitosan at 2θ = 20°. This result is in accordance to chitosan used as a bioactivity of polyester reported by Ali [10]. The diffractogram of oil palm empty fruit bunch activated carbon (figure 3b) showed the amorphous structure. The amorphous structure of activated carbon was also reported by [11], where the activated carbon was prepared from coconut. Addition of activated carbon on chitosan film resulting an amorphous chitosan film as shown in figure 3c. It was not exhibited typical peak of chitosan. This amorphous phase is favorable for adsorption due to the active sites are more accessible for adsorbate.
Figure 2. FTIR spectra of chitosan film (a), activated carbon (b) and chitosan composite film (c).

Figure 3. XRD patterns of chitosan film (a) activated carbon particles (b) and chitosan composite film (c).

SEM was performed to study the morphology of materials. Figure 4 showed SEM image of chitosan film (figure 4a), activated carbon particles (figure 4b) and chitosan composite film (figure 4c) where the magnification was 500x. The average particle size of activated carbon particles was 0.7 μm (figure 4b). The surface of chitosan film was smooth comparing with the surface of chitosan composite film due to the existence of activated carbon in the composite film. The distribution of activated carbon in chitosan film was confirmed by figure 3c. It also confirmed activated carbon covered by chitosan film.
3.2. Adsorption study
In this work, adsorption study was performed with various contact time, pH and initial concentration of Cd\(^{2+}\). Adsorption capacity (Q) was calculated based on the difference of Cd\(^{2+}\) concentration in aqueous solution before and after adsorption (Equation 1).

\[
Q = \frac{(C_0 - C_f)V}{W}
\]

Where \(C_0\) and \(C_f\) are initial and final concentration, respectively. W is the weight of adsorbent and V is the volume of Cd\(^{2+}\) solution. % Removal was calculated based on equation 2.

\[
\% \text{ Removal} = \left(\frac{C_0 - C_f}{C_0}\right) \times 100\%
\]

The effect of contact time on adsorption of Cd\(^{2+}\) by chitosan composite film was examined for 20-50 minutes. The initial concentration of Cd\(^{2+}\) was 10 ppm. The results were shown in figure 5a.

![SEM analysis](image)

Figure 4. SEM analysis of (a) chitosanSn film, (b) activated carbon and (c) chitosan composite film.

Figure 5a showed adsorption capacity of Cd\(^{2+}\) by chitosan composite film increased significantly on the beginning adsorption and tended to be constant after reach 40 minutes. The increase in adsorption capacity was due to a large number of empty active sites of the chitosan composite film. By increasing of contact time, the active sites of the chitosan composite film decrease and adsorption reached equilibrium when active sites have been saturated.

One of the factors affecting the adsorption capacity is pH. In order to study the effect of pH on adsorption capacity of Cd\(^{2+}\) by chitosan composite film, experiments were performed at pH 2, 3, 4, 5,
6, 7, 8 and 9. The experiments were conducted for 40 minutes and initial concentration of Cd$^{2+}$ was 10 ppm. The pH was adjusted using NaOH 0.1 N and HCl 0.1 N. The results were shown in figure 5b.

Based on figure 5b, adsorption capacity of Cd$^{2+}$ by chitosan composite film at low pH was low and increased by increasing the pH. The highest adsorption capacity was found at pH 5. In acidic solutions, the amino group (-NH$_2$) of chitosan was protonated to NH$_3^+$ [12]. Protons will occupy most of adsorbent active sites and the amount of Cd$^{2+}$ adsorbed was low due to electrostatic repulsion. While by increasing the pH, amino group was free from protonation due to the decrease in hydrogen ion concentration. The competition between H$^+$ and Cd$^{2+}$ on binding with adsorbent active sites was decreased. However, the precipitation of the cadmium may cause a decrease in adsorption capacity at above pH 8. Cadmium in an aqueous solution will be hydrolyzed by the formation of various compounds depending on the pH of the solution [12].

![Figure 5](image)

**Figure 5.** Effect of contact time (a) and pH (b) on adsorption capacity (Q) of Cd$^{2+}$ by chitosan composite film.

Langmuir and Freundlich isotherm models were used to study the adsorption behavior of Cd$^{2+}$ by chitosan composite film. The experiments were conducted with various initial concentration of Cd$^{2+}$ solution (15, 25, 35, 45, 55, 65 and 200 ppm) at pH 5 for 40 minutes. The results were shown in Table 2.

Table 2 showed correlation coefficient ($R^2$) of Langmuir adsorption isotherm model of Cd$^{2+}$ by chitosan composite film was 0.985. Base on equation of Langmuir adsorption isotherm model (equation 3), the value of maximum adsorption capacity of Cd$^{2+}$ by chitosan composite film was 333.33 mg/g. This value was higher than other adsorbents as shown in Table 3. This indicates that the adsorbent in this study is highly potential to be used as an adsorbent for Cd$^{2+}$.

$$\frac{1}{Q_t} = \frac{1}{Q_{max}K_L} + \frac{1}{Q_{max}}$$ (3)

The linearized Freundlich adsorption isotherm model is shown equation 4. Correlation coefficient $R^2$ for Freundlich adsorption isotherm model was 0.921. It indicated that Langmuir and Freundlich adsorption isotherm models were fit to adsorption of Cd$^{2+}$ by chitosan composite film, where $R^2$ values for both models were higher than 0.9. However, Langmuir adsorption isotherm model showed a better fitting.

$$\log Q_t = \log K_f + \frac{1}{n} \log C_t$$ (4)
Langmuir adsorption isotherm model basically describes a homogeneous adsorption surface and Freundlich adsorption isotherm model describes a heterogeneous adsorption surface. The interaction between the adsorbent and adsorbate can be expressed using n value of Freundlich adsorption isotherm model. If n <1, it indicates the physisorption and n > 1 for chemisorption [13]. In this study, the value of n obtained was 0.811 which lower than 1. It showed adsorption of Cd$^{2+}$ by chitosan composite film was physisorption.

Table 2. Comparison data of Langmuir and Freundlich adsorption isotherm models.

| Langmuir     | Freundlich  |
|--------------|-------------|
| $Q_m$ (mg/g) | $K_L$       |
| 333.33       | 0.009       |
| $R^2$        | $K_f$ (mg/g) |
| 0.985        | 0.161       |
| $n$          | $R^2$       |
| 0.811        | 0.921       |

The regeneration process is one of the important factors in the industry because wastewater treatment becomes more economical where adsorbent can be used several times. The regeneration process was done by immersing the adsorbent into HNO$_3$ 0.001 N solution. The regenerated adsorbent was separated from the solution and washed until the neutral pH. The adsorbent was then dried and reused for adsorption process. In this work, regeneration was done for chitosan and chitosan composite film. The results obtained were shown in figure 6.

Figure 6. Regeneration efficiency of chitosan film and chitosan composite film.

Figure 6 showed adsorption capacities of chitosan composite film were higher than chitosan film for all cycles. It confirmed that activated carbon content in chitosan film improved the performance of chitosan film on adsorption of Cd$^{2+}$. The improvement is important for application in wastewater treatment of industry.

4. Conclusions
Activated carbon prepared from oil palm empty fruit bunch has been produced and used as filler on chitosan composite film preparation. Results showed activated carbon loading was a good reinforcement of chitosan film. Chitosan composite film was applied as an adsorbent of Cd$^{2+}$. The highest adsorption capacity was found at pH 5 with a contact time of 40 minutes. Langmuir and Freundlich adsorption isotherm models were used to study the adsorption equilibrium. The maximum adsorption capacity ($Q_{max}$) was 333.33 mg/g. Based on regeneration studies, chitosan composite film showed higher performance than chitosan film.

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