Adsorption of HA (humic acid) using sulfuric acid-crosslinked chitosan/pectin polyelectrolyte complex film

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Abstract. A sulphuric acid-crosslinked chitosan/PEC film had been synthesized and applied for adsorption of HA from aqueous solution. The parameters for adsorption study were an optimum ratio of chitosan/pectin composition, contact time, the effect of the solution pH, and HA concentration. The model for adsorption kinetics and isotherm adsorption as well as desorption study were also conducted. The result showed that the film was durable in water at pH 2 to 12. The analysis using FTIR indicated a shift of absorption peak at 1527 cm$^{-1}$ (bending vibration N–H in $\text{NH}_3^+$). Analysis with SEM showed the morphological differences of the film before and after adsorption and after desorption. Adsorption reached its optimum capacity in the film with a ratio of chitosan and pectin composition 70:30, at pH 6, contact time of 480 mins and HA concentration of 450 mg L$^{-1}$. The kinetic model of HA adsorption could be explained by the second-order kinetic model of Ho & McKay and the adsorption isotherm follows the Langmuir isotherm model with a maximum adsorption capacity of 50.0 mg g$^{-1}$, the Langmuir constant ($K_L$) of 1.49×10$^5$ L mol$^{-1}$ and the adsorption energy was found to be 29.7 kJ mol$^{-1}$. The highest desorption was 82.5% using 1 M NaOH.

1. Introduction

Water is a very important component of human survival and is needed sustainably. Efforts were required to provide clean water that meets health requirements such as removal of compounds that cause water to become smelly, taste and color. According to the World Health Organization [1], the color in raw water for drinking water is usually due to the presence of colored organic matter (mainly humic acid (HA) and fulvic acid (FA)) which is combined with the humus fraction on the soil. The density of colors derived from humic compounds can also indicate a high tendency to produce side products from the disinfection process.

Trihalomethane is an example of Disinfection By-Products (DBPs) as a result of the reaction of humic substances with chlorine in water treatment. Humic substances also play a significant role in increasing the transport of hydrophobic or heavy metal organic contaminants which bind to HA, causing bacterial growth in water distribution systems due to their role as providers of food sources and causing unpleasant and colored taste in drinking water[2]. The presence of HA certainly can reduce the quality of water to be consumed and endanger the health. Its effects on human health must be prevented by removing organic compounds from water before being supplied for the chlorination process [3].

Various techniques for removing HA in water have been carried out such as coagulation [4], photocatalysis [5-6] and adsorption using activated carbon [7]. The disadvantage of the coagulation technique is that it produces large volumes of mud and requires high operational costs [2]. Photocatalytic techniques require photocatalysts whose prices are relatively expensive and relatively simple equipment.
Another technique is Fenton oxidation and photocatalysis with TiO$_2$ which is also efficient in decomposing HA but requires the addition of several Fenton reagents or nanomaterial into the water to initiate chemical reactions that might provide secondary pollution as micro-pollutants of water sources [8].

The adsorption process is considered the best method because of its simplicity, high efficiency and ease of operation [9]. Adsorption also does not produce DBPs or large volumes of mud so that it can be used as an alternative technique for removing HA from the water. Adsorption with activated carbon which has been recommended by the USA Environmental Protection Agency turned out to be inefficient and practical for large molecular organic compounds such as natural organic substances [3]. The adsorbent is quite expensive and for higher quality, the cost is also greater. Therefore, to date, a number of studies have been conducted to develop cheaper and more effective adsorbents including natural polymers such as chitosan [10].

Chitosan is a natural polymer and is obtained from deacetylation of chitin which is the second most abundant biopolymer in nature. Chitosan shows chemical stability and high reactivity, but has several disadvantages such as swelling on acidic media, tends to agglomerate, low specific surface area, poor mechanical properties [11], less hydrophilic and low degradability [12] thus limiting its application as an adsorbent. However, the weakness of chitosan (low hydrophilicity and degradability) and pectin (very good solubility in water) can be overcome through the formation of PEC so that it can be used for various applications. Furthermore, the modification of chitosan membranes by adding crosslinking agents can increase swelling property and mechanical strength in the application[13].

In this study, we developed a sulfuric acid-crosslinked chitosan/pectinPEC film as an adsorbent for HA in a batch system. Good hydrophilicity and free protonated amine groups that can interact with the adsorbate become the main active sites so that the adsorption capacity increases. The parameters studied in the film-making process are the mechanical properties and stability of the film in the acid-base medium. The adsorption study includes the effect of chitosan/pectin composition ratio, contact time, solution pH and HA concentration on the adsorption ability of chitosan/pectinPEC films. The desorption aspect studied was the effect of NaOH concentration on percent desorption of films.

2. Experimental Section

2.1. Material

The materials used in this study were pro analytical quality including chitosan with 87% deacetylation (produced by Bogor Agricultural University) and pectin from Chemix Yogyakarta.CH$_3$COOH solution, 96% H$_2$SO$_4$ solution, NaOH, KCl, NaCl, Na$_2$HPO$_4$, KH$_2$PO$_4$ (Merck), HA sodium salt (Sigma Aldrich) were used as received.

2.2. Instrumentation

FTIR spectrophotometer (Shimadzu FTIR PRESTIGE 21) and Scanning Electron Microscope/SEM (JEOL JSM-6510LA) were used for characterization of the film. UV-Vis Spectrophotometer (Thermo Scientific Evolution 201) was used for determination of HA concentration. Other instruments include pH meter (BNQ PH-777) and a sonicator (Branson 3210).

2.3. Procedure

2.3.1 Synthesis of the film. Pectin was dissolved with a mass of 0.03 g using 4 mL of distilled water and stirred to obtain an homogeneous solution. About 0.07 g of chitosan was added and stirred vigorously until the chitosan was dispersed in the solution, then an acetic acid solution (0.4 M, 16 mL) was added to the mixture with stirring. The solution was sonicated to ensure that chitosan and pectin were mixed
homogeneously. The solution was poured into a petri dish and dried in an oven at 70 °C overnight. The film formed was immersed in 1 M NaOH solution for 4 hours until it was peeled off, washed using distilled water and phosphate buffer. The film was then immersed in 0.1 M H₂SO₄ solution for 2 hours and dried. The same procedure was performed for film synthesis with the ratio of 80:20 chitosan-pectin (0.08 g chitosan and 0.02 g pectin) and 90:10 (0.09 g chitosan and 0.01 g pectin).

2.3.2 Characterization of chitosan/pectin PEC films crosslinked sulfuric acid. Functional groups in the film were characterized by FTIR spectrophotometer at 4000-400 cm⁻¹. Surface morphology of the film was analyzed by SEM for the film before and after adsorption and after desorption. The swelling property of the films was examined by weighing the film after immersed in water for 2 h, and % swelling was calculated relative to the weight of the dry film. The resistance of films in acid and the alkaline medium was tested by soaking the film in the solution of various pH (2-12) for 24 h.

2.3.3 Adsorption study. Films (0.04 g) were put into a 30 mL of HA solution (100 mg L⁻¹) and shaken out for 6 h. The film was separated from the solution and the remaining concentration of the HA solution was measured using a UV-Vis spectrophotometer at its maximum wavelength. The variables examined were the mass composition of chitosan/pectin, optimum contact time, optimum pH, and HA concentration.

2.3.4 Desorption Study. The desorption process was studied using NaOH solution of 1.0, 0.1 and 0.05 M. The film that had adsorbed HA was soaked in NaOH solution at various concentrations with a volume of 30 mL and was shaken for 6 h. The HA concentration in the filtrate obtained was determined by a UV-Vis spectrophotometer to estimate the concentration of the remaining HA in the film.

3. Discussion

3.1. Film Characterization

Qualitative analysis using FTIR indicating functional groups of chitosan, pectin, and chitosan/pectinPEC films crosslinked sulfuric acid are shown in figure 1. The main absorption peak of chitosan is shown at 1651 cm⁻¹ (C=O amide) and 1605 cm⁻¹ (N–H). For pectin, the absorption peaks at 1743 cm⁻¹ (C=O carboxylate methyl ester) and 1635 cm⁻¹ (–COO⁻) were observed. After crosslinking using H₂SO₄, some shifted peaks were observed at 1527 cm⁻¹ (N–H of–NH₃⁺), 1628 cm⁻¹ (–COO⁻) and 1720 cm⁻¹ (C=O carboxylate methyl ester).

Figure 1. FTIR spectra of chitosan, pectin and sulphuric acid-crosslinked chitosan/pectin PEC film
The shift is in accordance with the results of Chen et al. (2010) that showed the peaks of 1564 cm\(^{-1}\) (chitosan) and 1611 cm\(^{-1}\) (pectin) shifted to 1598 cm\(^{-1}\) on chitosan/pectin composite material. The peak shift was explained as the result of a strong ionic interaction of the amine group from chitosan with the carboxyl group of pectin so the C = O peak to be covered. Peaks at 1103 and 617 cm\(^{-1}\) were the contributions of \(\text{SO}_4^{2-}\) ions that confirm the effectiveness of the crosslink reactions and are consistent with previous studies [14-15].

3.2 The surface morphology of chitosan/pectin PEC films crosslinked sulfuric acid

The morphological analysis of the surface of the film using SEM was carried out on films that before and after HA adsorption as well as after the desorption process. The results of the SEM analysis of the film are presented in Figure 2. The surface of the film after the adsorption was smoother than before the adsorption which indicates that the film has successfully absorbed HA. The film after HA desorption (Figure 2.c) contains particles scattered almost throughout the surface of the film that probably was NaOH crystals formed after the desorption process.

3.3 Swelling of sulfuric acid-crosslinked chitosan/pectin PEC films

The swelling test was conducted to determine the hydrophilicity properties of the film based on the ratio of the composition of chitosan and pectin and the results are presented in figure 3. The result shows that
the greater the composition of chitosan the lower the water absorption ability of the film as the 
hydrophilicity of the film is also lower.

![Graph showing swelling percentage with Chitosan:Pectin mass ratio](image)

**Figure 3.** Effect of the ratio of film composition on the results of the film development test

Pectin plays an important role related to film hydrophilicity because of the abundant content of the carboxyl group (–COO⁻) [12], that may be responsible for binding of water molecules. Therefore, the water absorption capacity in sulfuric acid-crosslinked chitosan/pectinPEC films is mainly influenced by the presence of pectin in the film.

3.4 The resistance of films in acid-base medium
Testing of the acid to alkaline medium aims to determine the stability of the film. Overall, sulfuric acid-crosslinked chitosan/pectin PEC films are resistant to acid-base medium. The chitosan amine group (–NH₂) will be protonated to be –NH₃⁺ group at pH <6.4 [16] and will interact electrostatically with the pectin carboxyl group (–COO⁻) to form a strong PEC. According to Ngah et al. Ionic bonds formed between chitosan protonated amines (–NH₃⁺) and SO₄²⁻ ions improve chemical stability [15]. This makes the film stable at acidic pH. At pH 7-10, even though the protonated amine group is in a lesser amount, the film is still stable. However, at pH 11-12, the film start to partially dissolve because of weakening the interaction between –NH₃⁺ and –COO⁻ groups.

3.5. Adsorption Study of Films against HA Solutions

3.5.1 Determination of film composition ratio. The effect of the ratio of the composition of chitosan and pectin of the film on the adsorption of HA was examined and the result is shown in Figure 4. The highest adsorption capacity of 32.8 mg g⁻¹ was observed for the film with a composition ratio of chitosan : pectin 70:30. The result proves that the more mass of chitosan or the less mass of pectin, the lower the adsorption capacity of the film. The effect of the chitosan/pectin mass ratio on the film on the adsorption of HA can be attributed to its ability to absorb water. The adsorption process of HA from an aqueous solution into an adsorbent was assumed to consist of 3 steps, namely migration of HA molecules from
solution to the surface of the adsorbent, diffusion through the boundary layer to the inside of the adsorbent (interior) and adsorption site [17]. The high composition of pectin causes more anionic groups and more water absorption capacity [18] that will facilitate the process of diffusion of HA into the adsorbent. Therefore, there is a positive correlation between water absorption (swelling) and HA adsorption capacity.

3.5.2 Determination of optimum contact time and adsorption kinetics. The optimum contact time between the adsorbate and the adsorbent was recorded to determine the kinetic model of HA adsorption onto the sulfuric acid-cross linked chitosan/pectinPEC film. The results are presented in Figure 5. The main active sites (–NH$_3^+$) may be responsible for the most adsorption of HA through electrostatic interaction with the –COO$^-$ group of HA. In addition, weak interaction such as physisorption may also contribute to the HA adsorption. The data were examined for the pseudo-first-order and pseudo-second-order kinetic models and the result was summarized in Table 1. Based on $R^2$ value, the pseudo-second-order kinetic model that obtained by plotting the $t$ versus $t/q_e$ showed the best linearity and the calculated $q_e$ was comparable to experimental value (33.1 vs 33.7 mg g$^{-1}$). This result supports the assumption that the adsorption of HA in chitosan/pectinPEC films should be a chemisorption.

| Kinetic Model      | Parameter              | $R^2$    | $k_1$ (min$^{-1}$) | $q_e$ (mg g$^{-1}$) |
|-------------------|------------------------|----------|-------------------|---------------------|
| Pseudo-first order| $R^2$                  | 0.4908   |                   |                     |
|                   | $k_1$ (min$^{-1}$)     | 2.40 $\times$ 10$^{-3}$ |         |
|                   | $q_e$ (mg g$^{-1}$)    | 5.96     |                   |                     |
| Pseudo-second order| $R^2$                  | 0.9917   |                   |                     |
|                   | $k_2$ (mg g$^{-1}$ min$^{-1}$) | 1.64 $\times$ 10$^{-3}$ |         |
|                   | $q_e$ (mg g$^{-1}$)    | 33.1     |                   |                     |

**Figure 4.** Effect of the mass ratio of the chitosan/pectin composition to the HA adsorption capacity.

**Figure 5.** Effect of contact time on the adsorption of HA.
3.5.3 Determination of optimum pH. The HA adsorption on the sulfuric acid-crosslinked chitosan/pectin PEC films was examined in a pH range of 4 to 10 and the results are presented in Figure 6. The highest adsorption capacity of 37.1 mg g\(^{-1}\) was observed at pH 6. The adsorption capacity of HA solution increases at acidic pH and decreases at neutral to basic pHs. A solution with a low pH (3–6) produces a protonation of the amine group on which produces strong electrostatic interaction between the –NH\(_3^+\) group of the chitosan and the RCOO\(^-\) group of HA, and this resulted in a significant increase in the amount of HA adsorbed. The optimum pH value for adsorption of HA on chitosan/pectin film occurs at pH 5–7.5. Meanwhile, the carboxylic group begins to dissociate at pH 4-6 so it suggests that at pH 6 the electrostatic attraction between the deprotonated carboxylic group from HA and the protonated amine group from chitosan is the strongest so that the maximum adsorption capacity of HA is observed at that pH value [10].

![Figure 6](image1.png)  
**Figure 6.** Effect of pH on the adsorption of HA onto sulfuric acid-crosslinked chitosan/pectin PEC films.

![Figure 7](image2.png)  
**Figure 7.** Effect of initial concentration of HA on the adsorption of HA onto sulfuric acid-crosslinked chitosan/pectin PEC films.

3.5.4 Determination of optimum HA concentration. The effect of the initial HA concentration on the HA adsorption capacity of the sulfuric-acid crosslinked chitosan/pectin PEC film was examined to determine the appropriate adsorption isotherm model. The result is shown in Figure 7 that indicated the increase of the adsorption capacity until it reaches its optimum point. The saturation point occurs when all the active sites of the adsorbent have bonded to the adsorbate and the adsorption capacity reaches its optimum point. Adsorption isotherms are related to how HA interacts with chitosan/pectin PEC films crosslinked with sulfuric acid. Table 2 shows the Freundlich and Langmuir isotherm models for the data obtained in this experiment. As the value of \(R^2\) in the Langmuir isotherm model is greater than that of the Freundlich isotherm model, the HA adsorption the sulfuric-acid crosslinked chitosan/pectin PEC film may follow the Langmuir isotherm model. The chitosan/pectin PEC film adsorbent has a homogeneous adsorption site (–NH\(_3^+\)). and adsorption of HA on this adsorbent is assumed to be a monolayer adsorption as the result of the interaction of the protonated amine group (–NH\(_3^+\)) from the chitosan and carboxylic group (–COO\(^-\)) from HA.
Table 2. Parameters of the Freundlich and Langmuir adsorption isotherm models.

| Isotherm Model | Parameter       | Value   |
|---------------|----------------|---------|
| Langmuir      | $R^2$          | 0.9861  |
|               | $q_{\text{max}}$ (mg g$^{-1}$) | 50.0    |
|               | $K_L$ (L mol$^{-1}$) | 1.49×10$^5$ |
|               | $E$ (kJ mol$^{-1}$) | 29.7    |
|               | $R_L$        | 7.48×10$^{-5}$ |
| Freundlich    | $R^2$          | 0.9329  |
|               | $K_F$ (L g$^{-1}$) | 11.6    |
|               | $n$           | 4.25    |

The maximum adsorption capacity obtained in this study is compared with the results of previous studies and presented in Table 3. The data show that the sulfuric acid-crosslinked chitosan/pectinPEC film exhibited a high HA adsorption capacity compared to the other reported adsorbent. The film has the potential as a good performance adsorbent for HA removal applications in waters.

Table 3. Comparison of the adsorption capacity of HA on different adsorbents

| Adsorbent                  | $q_{\text{max}}$ (mg g$^{-1}$) | Reference                                      |
|----------------------------|---------------------------------|------------------------------------------------|
| Activated carbon from husk ash | 45.5                            | (Daifullah et al., 2004)                       |
| Chitosan-epichlorohydrin bead | 44.84                           | (Ngah et al., 2008)                           |
| Activated sludge           | 2.78                            | (Jonglertjunya and Lertchutimakul, 2012)       |
| ZnO nano particles         | 0.82                            | (Oskoei et al., 2016)                         |

3.5.5. Desorption study. Desorption test is related to the film regeneration to be reused as an adsorbent. Good desorption performance of an adsorbent is important in relation to the potential for practical application [16]. The desorption process at this stage was done by interacting the chitosan/pectinPEC film crosslinked sulfuric acid that had adsorbed HA under optimum conditions with NaOH solution at various concentration. The result on the effect of NaOH concentration on percent desorption is presented in Figure 8. The highest percent desorption of 82.5% was observed when 1 M NaOH solution was used as a desorbant solution. Lin and Zhan [17] reported that the low adsorption capacity of chitosan/zeolite against HA solution at high pH implies that HA adsorbed on the adsorbent might be de-absorbed in alkaline solutions. The desorption efficiency is relatively high which might be related to the fact that in
alkaline solutions, the positive charge in the amine group is deprotonated and the attraction between chitosan/zeolite and HA molecules becomes weaker.

Figure 8. Effect of NaOH concentration on desorption of HA.

4. Conclusion

The sulfuric acid-crosslinked chitosan/pectinPEC film showed good stability in water at wide range medium acidity (pH 2–10). The best film composition was films with chitosan to pectin mass ratio of (70:30). The adsorption isotherm pattern suitable for HA adsorption in chitosan/pectinPEC film crosslinked sulfuric acid is a Langmuir isotherm model with maximum adsorption capacity value of 50.0 mg g⁻¹, Langmuir constant (K_L) 1.49×10⁵ L mol⁻¹ and the adsorption energy is 29.7 kJ mol⁻¹. Desorption of HA from the chitosan/pectinPEC film can be achieved by using a 1.0 M NaOH solution with a percent desorption value of 82.5%.

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