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Synthesis of Glutaraldehyde Crosslinked Superporous Chitosan with Polyvinyl Alcohol Addition for Peat Water Humic Acid Adsorption

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ABSTRACT

This research aims to synthezise the superporous adsorbent from chitosan using glutaraldehyde as a cross linker, $NaHCO_3$ as a porogen, and polyvinyl alcohol (PVA) as a reinforcing agent. Generally, the reaction of adsorbent synthesis was carried out through four steps: (1) the addition of PVA to the chitosan solution, (2) the addition of porogen, (3) the crosslinking of chitosan, and (4) the releasing of porogen. The obtained adsorbents were characterized by Fourier Transform Infra Red (FTIR) Spectroscopy, photograph of Digital Microscope (DM), and Scanning Electron Microscopy (SEM) to measure the porosity. The adsorbent was then be applied to adsorb of HA for adsorption capacity determination. The results showed that the addition of PVA and porogen during adsorbent synthesis has produced adsorbent with more compact and flexible physical properties and greater porosity. The adsorption test showed that the adsorption capacity of KPG is 33.07 mg/g. However, if the amount of used adsorbent is larger (based on the chitosan mass 1 g), the capacity adsorption of KPG is 141.74 mg/g. The initial concentration of HA contained in peat water was 45.64 mg/L, KPG can adsorb of HA as much as 95%.

Key words: adsorption; chitosan; humic acid

INTRODUCTION

In Indonesia, one of the water resources which is still abundant are peat water. Qualitatively water peat in Indonesia is very potential to be managed as a water resource that can be processed into clean water or drinking water. However the water treatment plants in Indonesia generally use methods of chlorination at disinfection stage. The use of chlorination methods in water without removing peat humic compounds can lead to a reaction between chlorine and humic compounds, forming carcinogenic compounds trihalomethane (Deborde & von Gunten, 2008). Obviously, it will have impact on the health of water users.

One of the methods which is most commonly used to remove humic acid (HA) from the water is by adsorption method. Various adsorbents have been reported by several investigators such as natural zeolite (Wang et al., 2008), cetylpyridinium bromide-modified zeolite (Zhan et al., 2010), iron-coated activated carbon (Godini et al., 2011), activated sludge (Moura et al., 2007), polyaniline (Wang et al., 2011), and Mg/Al hydrotalcite (Santosa et al., 2008), but those adsorbents still have relatively low adsorption capacities. The results of an intensive review of the literature showed that chitosan in the form of gel beads have adsorption capacity of HA which is higher than the other adsorbents that is equal to 262.0 mg/g (Chang & Zuang, 2004). These data indicate that chitosan has good prospects to be used as a binding agent for HA.

However, since chitosan is soluble in a slightly acidic medium, the chitosan can not be applied directly as an adsorbent for HA in peat water has a pH of about 4,5. Some

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researchers has modified chitosan to increase its stability so that it is not easily soluble in acidic medium. Modifications was made by adding a crosslinker agent to form a cross-binding between the polymer chitosan molecules. Cross-binding process using glutaraldehyde, epichlorohydrin, ethylene glycol diglycidyl ether, or other cross-binding agent has been proven to increase the stability of chitosan in acid medium (Wan Ngah et al., 2005). Polyvinyl alcohol (PVA) can acts as interpenetrating network agent (IPN) so that the addition of PVA can repair chitosan gel by decreasing the gelation time and increase the mechanical strength of the gel (Wang et al., 2004). The binding of cross-reaction between the polymer chitosan using glutaraldehyde occurs between the primary amino groups of chitosan and two aldehyde groups on glutaraldehyde. This binding resulted a formation of Schiff bases. However, the cross-binding treatment can result a decreased porosity of chitosan. While on the other hand, the size of HA macropolymer is relatively very large (Torres et al., 2007). Addition of porogen as a pore mold can prevent or decrease the pore shrinkage during cross-binding process (Annabi et al., 2010).

Based on the description above, it is interesting to study the synthesis of a chitosan-based adsorbent superporous by using a cross-binding agent, and adding PVA as a reinforcing agent along with the porosity control treatments. This study used glutaraldehyde as a cross-linking agent and $NaHCO_3$ as porogen. This study aims to obtain scientific data on the effect of adding glutaraldehyde, PVA, and porogen on the characteristics of chitosan-based superporous adsorbent, and examine its adsorption ability on humic acid.

MATERIALS AND METHODS

Materials

Chitosan (Aldrich), polyvynil alcohol, humic acid (Yaco), and chemicals with pro analysis grade such as HNO_3, HCl, NaOH, CH_3COOH, glutaraldehyde, and $NaHCO_3$ as porogen.

Instrumentation

The adsorbent were characterized by fourier transform infra red (FTIR) Spectroscopy (Shimatzhu), photograph of digital microscope (DM) (Olympus CX22), and scanning microscope electron (SEM) (JEOL JSM-35C). Concentration of residual HA in solution (unbound) were analyzed by UV-Vis spectrophotometer (LGS 53).

Procedure

Synthezise *the Superporous Adsorbent*

The synthesis of superporous adsorbent through binding of crosslinked chitosan with the addition of polyvinyl alcohol (PVA) and porogen has been conducted. The synthesis was conducted by adopting the method proposed by Gupta and Shivakumar (2010), where the method was modified by adding PVA. In this study, the cross-bonding agent (crosslinker) used was glutaraldehyde, and sodium bicarbonate was used as porogen agent. In general, the synthesis of superporous adsorbents was conducted through 4 stages of research, i.e. PVA addition, porogen addition, crosslinker addition, and porogen release. The chitosan used in this study was obtained from Aldrich with a medium molecular weight.

Effect of PVA Addition on Adsorbent Porosity

The influence of PVA addition was conducted by mixing of concentration of chitosan solution (3% w/v) and the concentration of PVA stock solution (10% w/v) with a volume ratio of chitosan : PVA as (6 : 0); (4 : 2); (3 : 3); (2 : 4); and (0 : 6). As much as 0.6 grams of $NaHCO_3$ was added into each solution. After stirring for 30 seconds, 2 ml of 10 % glutaraldehyde was added into the solution and stirred until evenly distributed. The mixture was then put into the bath enclosed and heated in an oven at ± 90°C. After 3 hours, the product was decantered, and reheated in the oven for 2 hours with an open bath. The product obtained was rinsed with distilled water until neutral pH. The porosity and stability of the product was then measured.

Effect of Porogen Addition on Adsorbent Porosity

In order to study the influence of porogen addition it was conducted by the same way as the above study. In this experiment, the chitosan : PVA ratio used was the ratio that gave the best porosity. Sodium bicarbonate ($NaHCO_3$) as porogen was added to the solution with a variation of 0 ; 0.2 ; 0.4 ; 0.6 ; and 0.8 grams. Each mixture was cross linked by adding 2 ml of 10 % glutaraldehyde. Products that gave the best porosity and stability were then used for the next procedure, which was varying the amount of glutaraldehyde.

Effect of Glutaraldehyde Concentration as Crosslinker for Adsorbent Porosity

In this step, the volume variations of 10% glutaraldehyde added into the mixture were 0.5 ; 1.0 ; 1.5 ; 2.0 ; and 2.5 ml. Product that gave the best porosity from this procedure was then analyzed by using FTIR spectroscopy, along with analyses of its swelling ratio, HA adsorption and regeneration capability. The porosity measurements were performed by using the software JMicrovision 1.2.7 version of the photo with the observation Digital Microscope (DM).

Evaluating Humic Acid Binding Capacity and Its Regeneration

Evaluating the capacity of the synthesized products in binding humic acid (HA) was conducted by mixing the adsorbent with HA solution with different initial concentrations. The concentration of residual HA in solution (unbound) was measured by UV-Vis spectrophotometric method at a wavelength of 390 nm. The amount of bound HA would be equal to the difference between the initial and residual amount of HA after the adsorption. The HA adsorption capacity of the adsorbent was equal to the amount of HA per weight of adsorbent used (mg/g). The obtained data was then interpolated into the Langmuir isotherm, Freundlich, and/or the Langmuir-Freundlich isotherm in order to determine the maximum adsorption capacity.

Desorption of HA was also conducted in order to study the regeneration of the adsorbent regeneration. Desorption process was conducted by immersing the adsorbent which has HA bond on it in a solution with a pH of 10. The volume of the solution in this desorption step was the same volume as the volume used during the steps on evaluating HA binding ability. The HA concentration in the solution as a percentage represented the percentage of HA being desorbed. In the same way, testing the ability of the adsorbent to bind HA was also performed on water samples of peat.

RESULTS AND DISCUSSION

Caracterization of Superporous Adsorbent using Fourier Transform Infra Red (FTIR) Spectroscopy

Figure 1a which is the FTIR spectra of chitosan before synthesized into superporous adsorbent, showed a broad absorption peaks at wave numbers around 3425 cm^{-1} due to the symmetric stretching vibration absorption of N-H amine or hydroxyl groups experiencing hydrogen bonds (Costa-Junior et al., 2009). Typical group of chitosan is also reinforced by the appearance of absorption peaks at wavenumber 1658 cm^{-1} which is a primary amide vibration absorption. Sharp absorption band at wavenumber 1381 cm^{-1} and a weak absorption band at wave number 1419 cm^{-1} respectively as the absorption of deformation symmetric and asymmetric CH_3 (Costa-Junior et al., 2009). Absorption band at wavenumber 1033 cm^{-1} and 1049 cm^{-1} is the absorption of stretching vibration of C-O-C on the frame chitosan (Zhao et al., 2008) and the C-OH stretching vibration alcohol (Sastrohadjojo, 2001).

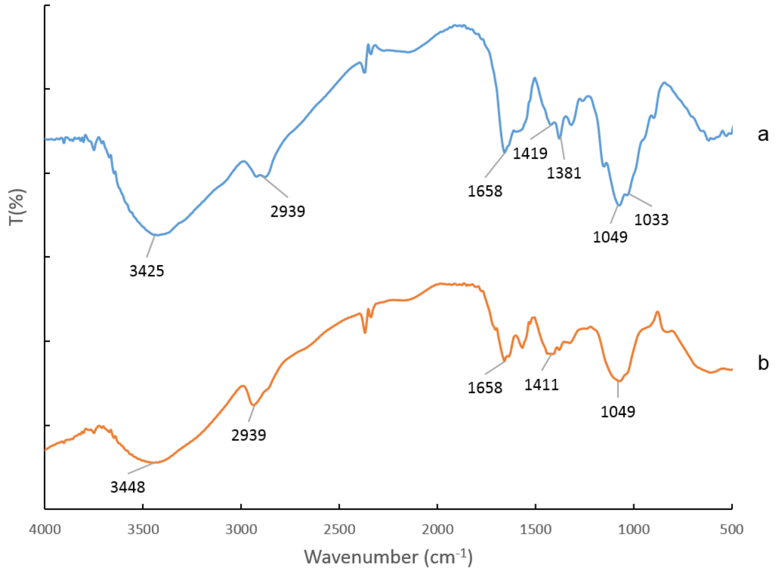


Figure 1. FTIR spectra of chitosan (a) and adsorbent with the addition of glutaraldehyde crosslinked PVA (b)

Figure 1b is an FTIR spectra superporous adsorbent glutaraldehyde crosslinked. The reaction between chitosan with glutaraldehyde probably can be happened in two ways. The first reaction between an aldehyde group of glutaraldehyde with hydroxyl groups on the chitosan to form a hemiasetal or acetal. Secondly, the reaction between the aldehyde group of glutaraldehyde with the amine group of chitosan to form an imine. Absorption peak increased at numbers 2939 cm^{-1} indicate an increasing number of groups C─H derived from glutaraldehyde or PVA (Silverstein et al., 1991). According to Silverstein et al. (1991), C═N stretching vibration of the imine group can be interpreted from the absorption at wave numbers 1689 to 1471 cm^{-1} so that the formation of the imine group (C═N) results glutaraldehyde reaction with the amine group of chitosan should be verified in this area. However, the peak absorption in this area overlaps with the absorption band of the carboxylate anion group from chitosan solvents which is appeared around 1650 - 1550 cm^{-1} and primary amides around 1650-1515 cm^{-1} .Although the characterization of the type of bond that is formed on a glutaraldehyde crosslinked adsorbent cannot provide specific data but the binding reaction by glutaraldehyde cross-linking chitosan can be observed from the color change of chitosan samples that initially colorless turn into tawny.

Effect of PVA Addition on Adsorben Porosity

In this study, the adsorbent was synthesized by adding a solution of PVA to a solution of chitosan by varying the volume of chitosan : PVA. The effect of PVA addition was studied by using glutaraldehyde as a crosslinker agent. A qualitative results of adsorbent porosity measurements is presented in Figure 2.

Based on Figure 2, it can be seen that the addition of PVA to chitosan and PVA ratio of 1 : 1 (3 ml + 3 ml chitosan PVA) hardly reduces the porosity of the adsorbent. But when the addition of PVA has been greater than chitosan, there is a tendency that the porosity of the adsorbent reduces. This reduction in porosity when more PVA is added indicates that the addition of PVA will increase the amount of cross-bonding occurring when the adsorbent is being formed. A bond can be formed either between chitosan and PVA, or between PVA with crosslinker. However, the main purpose of PVA addition is to increase the mechanical strength of adsorbent through formation of fiber on the adsorbent.

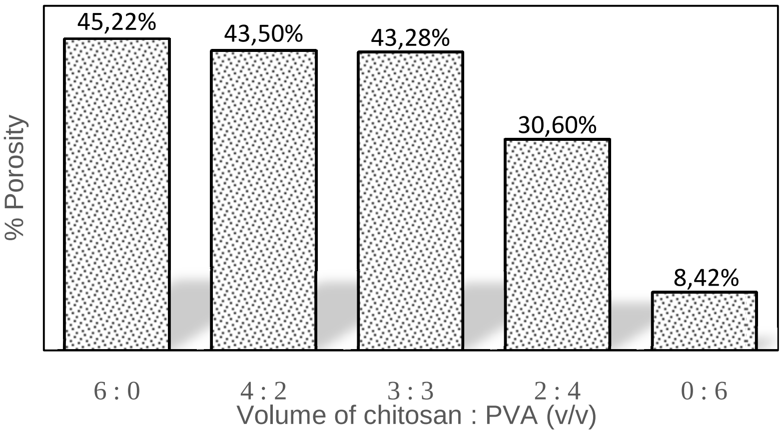


Figure 2. Influence of PVA addition to the porosity of glutaraldehyde crosslinked adsorbent.

Based on Figure 2, it can be seen that the addition of PVA to chitosan and PVA ratio of 1 : 1 (3 ml + 3 ml chitosan PVA) hardly reduces the porosity of the adsorbent. But when the addition of PVA has been greater than chitosan, there is a tendency that the porosity of the adsorbent reduces. This reduction in porosity when more PVA is added indicates that the addition of PVA will increase the amount of cross-bonding occurring when the adsorbent is being formed. A bond can be formed either between chitosan and PVA, or between PVA with crosslinker. However, the main purpose of PVA addition is to increase the mechanical strength of adsorbent through formation of fiber on the adsorbent.

Based on the observations of the physical adsorbent and touch by hand, some comparisons can be drawn between the adsorbent without the addition of PVA and with the addition of PVA, which are presented in Table 1 below.

Table 1. Comparison between the adsorbent with and without the addition of PVA

Adsorbent without PVA	Adsorbent with PVA
- In the wet state, the adsorbent is rigid	- In the wet state, the adsorbent is springy and elastic
- Dry adsorbent is fragile, thus easily broken and very easily smoothed	- Dry adsorbent is clay / chewy, thus it is not easily broken and difficult to be smoothed
	- Smaller pore diameter and fibrous
- A larger pore diameter and not fibrous	
- Less number of pores	- More number of pores

Based on Table 1 can be reported that the addition of PVA gel can reduce the formation time of the cross-binding reactions, and also adds mechanical strength. However the addition of PVA resulted in reduction of the pore.

Effect of Porogen Addition on Adsorbent Porosity

In this study, porogen is added to a PVA-chitosan solution before binding reaction to form the pore. The Porogen used was sodium bicarbonate ($NaHCO_3$), a foaming agent which is cheap and readily available and is relatively easy to be released after the pore has formed in the synthesized adsorbents.

Sodium bicarbonate is a chemical compound with the formula $NaHCO_3$ and often commonly known as baking soda (sodium bicarbonate). This compound is often used to make bread because it releases carbon dioxide gas easily, causing the bread to expand.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \uparrow$$

To produce more CO_2, the adsorbent is heated in an oven at a temperature of ±90°C.

$$Na_2CO_3 \longrightarrow Na_2O + CO_2 \uparrow$$

Besides to produce more CO_2 gas, heating also serves to accelerate the reaction. The heating is carried out in two stages, the first heating is carried out in a sealed vessel so more pores are formed along with more CO_2 being produced. The second heating is carried out in an open vessel in order to release the CO_2 gas that has formed pore. The Digital Microscope (MD) images in glutaraldehyde crosslinked adsorbent without and with the addition of $NaHCO_3$ 0.6 grams can be observed in Figure 3.

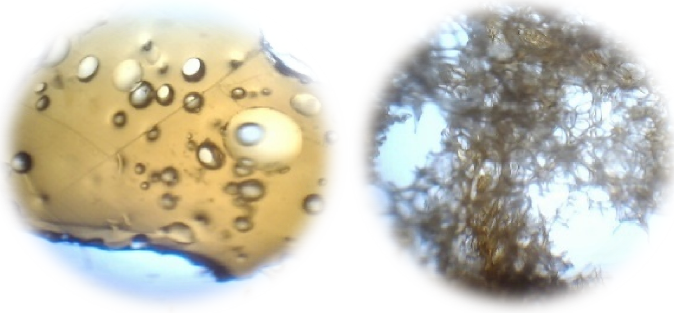
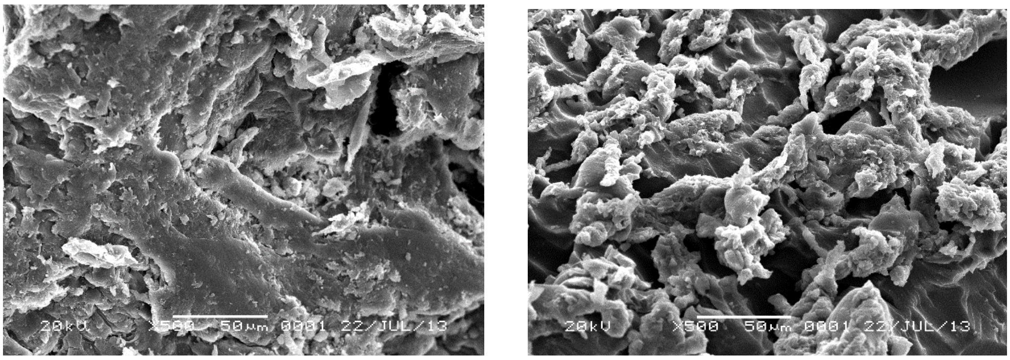

(a) (b)

Figure 3. Photo MD glutaraldehyde crosslinked adsorbent without the addition of porogen (a) and with the addition of porogen (b)

The effect of $NaHCO_3$ addition can also be seen from Figure 4 where SEM photographs of the adsorbents are being presented.



(a) (b)

Figure 4. Adsorbent SEM glutaraldehyde crosslinked without the addition of $NaHCO_3$ (a) and with the addition of $NaHCO_3$ (b)

Based on morphological analysis of SEM photos, it is apparent that addition of $NaHCO_3$ led to a more porous adsorbent compared to without $NaHCO_3$. Adsorbent with $NaHCO_3$ addition formed pores with diameters ranging between 5-20 μm. A pore diameter between 0.5 to 1000 μm is categorized as superporous (Larsson, 1999). Thus, the resulting adsorbent can be categorized as an superporous adsorbent which has a diameter larger than the pore size of HA molecules (ranging between 1-2 μm) (Chen et al., 2007). To study the effect of $NaHCO_3$ addition towards the porosity of the adsorbent, various weight of $NaHCO_3$ (0, 0.2, 0.4, 0.6, and 0.8 g) were added to a mixture of 3 ml chitosan and 3 ml PVA, and then crosslinked with a fixed concentration of glutaraldehyde (2 ml of 10 % glutaraldehyde). The results of the porosity analysis can be seen in Figure 5.

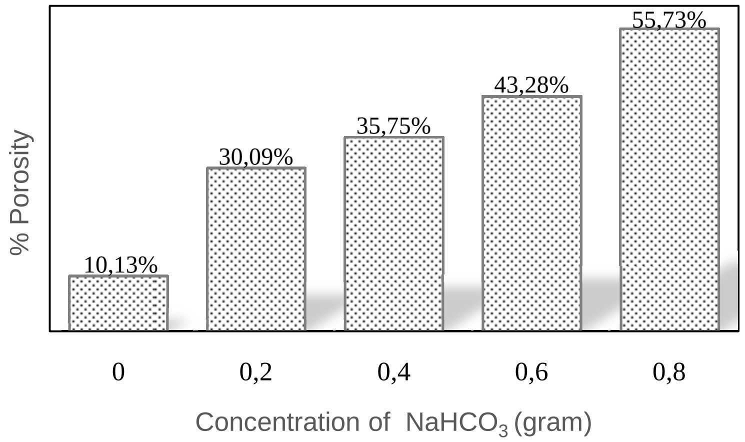


Figure 5. Influence of $NaHCO_3$ addition of porosity on glutaraldehyde crosslinked adsorbent

Figure 5 shows that a higher concentration of $NaHCO_3$ produces greater porosity of the adsorbent. Even when the concentration has exceeded 0.6 grams of $NaHCO_3$, the increase in porosity is higher than the increase obtained erenow. This is likely to happen because the glutaraldehyde crosslinked adsorbent is able to maintain the pore walls, due to longer carbon chain that it has.

Effect of Glutaraldehyde Concentration as Crosslinker for Adsorbent Porosity

The amount of crosslinker can affect the amount of the crossbonding points, while the number of cross-ties can also affect the porosity. With this consideration, it is very likely that crosslinker concentration will also affect the porosity of the adsorbent. In this study, various concentrations of glutaraldehyde were added to a mixture of 3 ml of chitosan and PVA, along with the addition of 3 ml of 0.8 grams of $NaHCO_3$. The results of porosity analysis are presented in Figure 6.

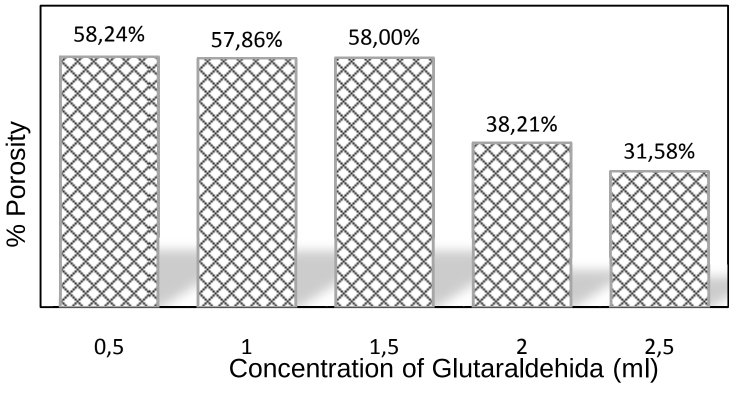


Figure 6. Effects of addition of glutaraldehyde (GLA) to the porosity of the adsorbent

Based on Figure 6, the addition of 0.5 to 1.5 ml GLA hardly decreases the adsorbent porosity. However, at a certain point more addition of GLA can lead to a more significant decrease in the adsorbent porosity. A higher amount of crosslinker being added up to a certain concentration is needed in order to increase the mechanical strength of adsorbent, along with the increasing number of cross-bonding points. However, if the amount of crosslinker added becomes too much, there is a possibility that it can decrease the porosity. The adsorbent with a porosity of 0.10 – 0.33 from the total volume can be categorized as superporous adsorbent (Gustavsson et al., 1997). Thus, the adsorbent obtained in this study can be categorized as superporous adsorbent.

Glutaraldehyde Cross-Linked Adsorbent (KPG) Ability of Binding Humic Acid (HA)

The test on the ability of the KPG adsorbent to bind HA is also determined by assessing the isotherm equation models that fit the experimental data of HA adsorption. The experiment of HA adsorption by the KPG adsorbent was carried out with various initial concentration, i.e. 10, 30, 50, 100, 150, and 600 mg/L. The amount of adsorbed HA was determined by using UV-Vis spectrophotometer, and the results of experimental data are presented in Table 2.

Table 2. Capability of KPG adsorbent in adsorbing HA with different initial concentrations from HA solution (HA concentration is measured by using the UV-Vis method)

Initial concentration HA (mg/L)	Adsorbed HA		
	(mg/L)	(mg/g) wet	(mg/g)dried
10	3.434	0.103	0.859
30	5.000	0.150	1.250
50	14.646	0.439	3.662
100	27.020	0.811	6.755
150	56.566	1.697	14.141
600	142.172	8.143	30.465

The adsorption data were than transformed into appropriate variables to be plotted into the Langmuir and Freundlich isotherm model of a linear equation. The plot of *Ce/qe* versus *Ce*, and the plot of *log qe* versus *log Ce* which was derived from the data of HA adsorption by KPG adsorbent is presented in Figure 7.

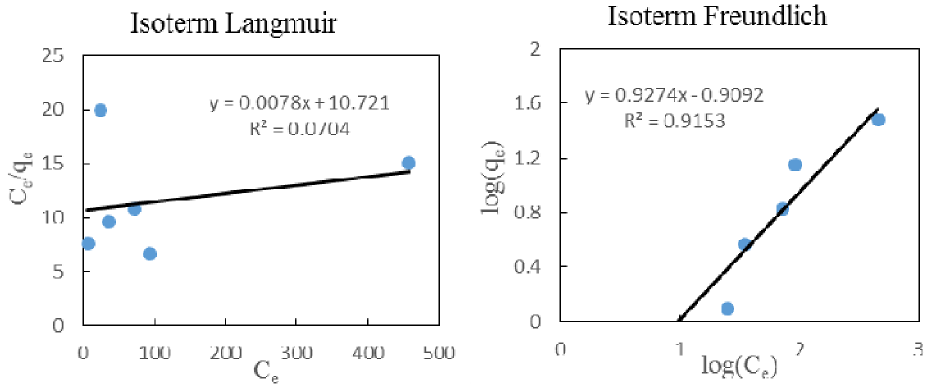


Figure 7. Plots of UV-Vis analysis data of HA adsorption on KPG adsorbent by using linear Langmuir isotherm and Freundlich isotherm model.

Figure 7 shows that HA adsorption by KPG adsorbent tends to follow the Freundlich isotherm than the Langmuir isotherm, and as a consequence the adsorption capacity should not be determined based on the Langmuir isotherm. The adsorption capacity of the adsorbent can also be determined using a Freudlich-Langmuir isotherm model, which is a developed model by merging Langmuir isotherm and Freundlich isotherm together (Santoso et al., 2008). Mathematically, Freundlich-Langmuir isotherm model is written in a linear form as follow:

$$\frac{C_e^{1/n}}{q} = \frac{1}{q_m K_a} + \frac{1}{q_m} \cdot C_e^{1/n}$$

The above equation is worth to try, considering that although HA adsorption by KPG adsorbent does not fully in compliance with the Langmuir isotherm, it is close enough to comply with the Freundlich isotherm. The plot for Langmuir-Freundlich isotherm for HA adsorption data on KPG adsorbent by measuring HA concentration using the UV-Vis spectrophotometer is presented in Figure 8.

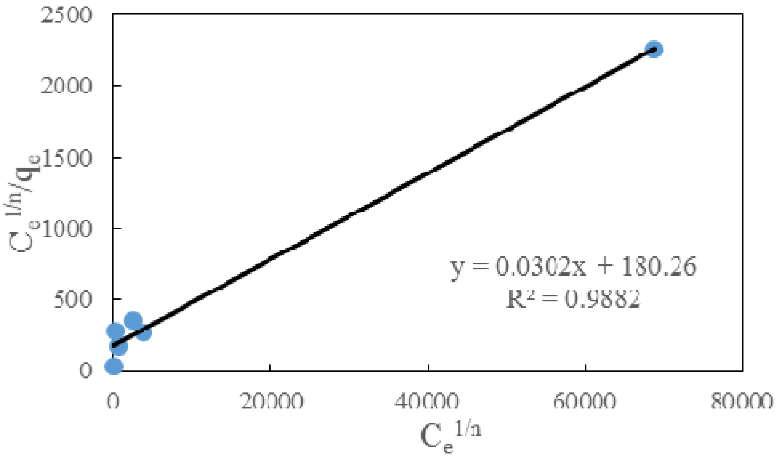


Figure 8. Plots of UV-Vis analysis of data on HA adsorption on KPG adsorbent with Langmuir – Freundlich isotherm linear model

Based on the above data plot, it can be determined that the maximum adsorption capacity (*qm*) adsorbent is equal to 33.07 mg/g.

To evaluate the adsorption capacity of KPG adsorbents in large numbers, the adsorbent was then made from as much as 1 gram of chitosan. With the same reaction conditions of synthesis, the results showed that the chitosan-based adsorbent which was made from 1 gram of material has a higher adsorption capacity compared to the adsorbent which was made with a smaller amount of material. The HA adsorption capacity of the KPG adsorbent reached up to 141 mg/g.

Figure 9. Interactions that can occur between the carboxyl group of HA and the hydroxyl group of KPG adsorbent through the formation of hydrogen bond (a) and the formation of ester (b).

The adsorption capacity of KPG adsorbent is still relatively smaller than chitosan beads (Zhan et al. 2010), carboxymethyl chitosan (Zhao et al., 2008), and chitosan beads crosslinked epichlorohydrin (Wan Ngah et al., 2008). Presumably because in the glutaraldehyde crosslinked adsorbent, the number of amine groups is reduced, due to the crosslinking reaction between the amine group with the aldehyde group of glutaraldehyde forming imine. This led to the dominance of carboxyl ─HA group in interacting with ─OH group on the KPG adsorbent. These interactions can occur through the formation of hydrogen bonds or the formation of an unstable ester bond. Schematic of reaction between HA and KPG adsorbent is presented in Figure 9.

Test of Adsorbent Ability to Bind Humic Acid in Peat Water

In this study, the test of adsorbent ability in binding HA in peat water was carried out within a laboratory scale before it is being applied to environment. Peat water samples used in this ability test was taken in the dry season on June 21, 2013, in Gambut country, KM. 22. Peat water samples was made in contact with 1 gram of KPG adsorbent overnight, and then filtered. The filtrate was used to determine the concentration of HA which remains in the water, to determine adsorption capacity of KPG adsorbent in peat water. The adsorbent ability to bind HA was evaluated by analyzing the concentration of HA using UV-Vis spectrophotometer with the standard addition method. From the analysis, the initial concentration of HA in water peat samples is 45.64 mg/L while the concentration of HA being adsorbed is 43.75. This demonstrates the ability of KPG adsorbent on HA peat water reaches 95%, which indicates that this adsorbent has a high ability to bind HA and can be applied to environment.

CONCLUSION

Porosity of superporous adsorbent from chitosan which crosslinked by glutaraldehyde tends to decrease with the increasing concentration of PVA and glutaraldehyde, but can be increased by the increasing concentration of $NaHCO_3$. KPG adsorbent can adsorb HA with an adsorption capacity of 33.07 mg/g. But if the adsorbent is made with greater amount of material, (in this study, 1 gram of chitosan was used as a comparison), the adsorption capacity of KPG adsorbent can reach up to 141.74 mg/g. From an initial concentration of 45.64 mg/L HA in peat water, KPG adsorbent able to adsorb up to 43.75 mg/L of HA, demonstrating the ability of KPG adsorbent to adsorb HA from peat water reaches 95% . It also indicates that this adsorbent has a high ability to bind HA and can be used for environmental application.

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