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# Synthesis of Chitosan-Coated Magnetic Microparticle Using Glutaraldehyde as Crosslinker and PEG as Spacer Arm and Its Application as Adsorbent of Peat Humic Acid

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## ABSTRACT

A simple procedure for synthesis of chitosan-coated magnetic microparticle (CMMP) using glutaraldehyde as a cross-linker and polyethylene glycol (PEG) as a spacer arm has been developed. The functionalized microparticle were prepared using an inexpensive, simple, rapid, one-pot process, based on the heating of chitosan, PEG, and ferrous sulfate mixture at high pH. X-ray diffraction results indicated that the surface-modified $Fe_3O_4$ microparticle did not lead to phase change unlike the pure $Fe_3O_4$. Magnetic chitosan adsorbent has been evaluated for removal of peat humic acid from its aqueous solution.

**Keywords : chitosan, magnetic, microparticle, adsorption, humic acid, peat**

## INTRODUCTION

It is well known that the most extended tropical peatlands occur in Southeast Asia and most (22.5 million ha or 65%) of which are located in Indonesia (Hooijer *et al*. 2010). However, there is a scarcity of potable water on peatland areas. Water resources from this region contain humic substances (HS) in large amount. HS can act as a source of methyl groups and thus can react with hypochlorite ion which is used as a biocide in water treatment plants, produce disinfectant by-products such as trihalomethanes, haloacetic acids, and other chlorinated compounds and nitriles. Some of them are suspected to be carcinogenic (Van Duuren et al., 1986; Carlsen & Lassen, 1992; Nikolaou et al., 2004). To prevent adverse effects on human health, HS should be eliminated from water in drinking water treatment process. Although various treatment techniques are available for removing HS, adsorption method has shown to be a promising technique to remove these organic matters from aqueous solution due to the ease of operation and relatively low cost of application in the adsorption process. Among the adsorbents, chitosan has been shown to be the most promising alternatives due to its high ability to bind HS, biocompatible and biodegradable material. However, the fast biodegrading rate and the low mechanical strength of the chitosan scaffolds pose crucial problems and limit the use of this material in applications as an adsorbent.

Cross-linking the chitosan using exogenous cross-linkers is an effective method to tune the rate of biodegradation and the mechanical property of the scaffolds. Cross-linkers such as glutaraldehyde were reported for chitosan, but crosslinking process causes reducing the ability of chitosan to bind HS. On the other hand, the low specific gravity of chitosan makes itself separated

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difficultly from aqueous solution and limits its use in either batch or column modes. Hence, we prepared a chitosan-coated iron magnetic microparticle as a new chitosan based adsorbent that can be separated easily. The chitosan magnetic microparticle was synthesized using glutaraldehyde as crosslinker and PEG as spacer arm. Its applicability has been tested by humic acid (HA) adsorption experiment in laboratory scale. For study the adsorbent capacity and its surface properties of adsorbent, the equilibrium data were fitted with Langmuir and Freundlich isotherm models.

## METHODS

### Materials

Chitosan powders was isolated from shrimp shells, peat HA was isolated from peat soil. All the other chemicals used were analytical grade. Distilled water was used throughout the study. Stock solution of 500 mg/L was prepared by dissolving appropriate amounts of HA in distilled water. Working solutions ranging from 20 to 100 mg/L of HA were prepared by diluting the stock solution.

### Preparation of Chitosan-Coated Magnetic Microparticle

The chitosan-coated magnetic microparticle (CMMP) were prepared by procedures as follows: one gram of chitosan was dissolved in 250 mL of 5% (v/v) acetic acid solution under stirring with a mechanical overhead stirrer. After chitosan dissolution, 250 mL of water was added, followed by 100 mL of 3.6% (w/v) solution of $FeSO_4 \cdot 7H_2O$. Then 10% (w/v) NaOH was added dropwise under intense stirring until the pH of the suspension was at least 10 and a dark precipitate was formed. The suspension was heated at 80ºC for 10 minute. The magnetically responsive chitosan microparticle formed were repeatedly washed with water.

### *Batch Adsorption Experiments*

Batch adsorption experiments were performed using conventional bottle-point method at room temperature (~30°C). A series of 0.2 g of CMMP were dispersed into 50 mL of HA solution contained in a 150-mL Erlenmeyer flask at concentrations 20, 40, 60, 0, and 100 mg/L. The flasks were sealed and then shaken for 2 h and let stand for a night. After the attainment of equilibrium, the suspension was separated by an external magnet. The concentration of HA remaining in solution was measured by UV-Vis spectrophotometer at wave length of 400 nm. The amount of adsorbed HA was calculated by analyzing the difference between initial and final HA concentrations and was expressed in mg of HA per g of CMMP (expressed as mg/g).

In this study, Langmuir and Freundlich models were employed to describe the adsorption characteristics between adsorbent and HA. The linear forms of the Langmuir and Freundlich equations are expressed as follows (Xu *et al*, 2011):

$$\text{Langmuir equation}: \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \qquad \text{(eq 1)}$$

$$\text{Freundich equation}: \ln q_e = \frac{\ln C_e}{n} + \ln K_F \qquad \text{(eq 2)}$$

Where:

$C_e$ = the equilibrium concentration of HA solution (mg $L^{-1}$),

$q_{max}$ = the maximum adsorption capacity (mg $g^{-1}$),

$q_e$ = the amount of HA adsorbed per unit weight of adsorbents at equilibrium (mg $g^{-1}$),

$b$ = the equilibrium constant of Langmuir equation (L $mg^{-1}$),

$K_F$ = the Freundlich constants related to the adsorption capacity ($mg^{(1-1/n)}$ $g^{-1}$ $L^{1/n}$), and

$n$ = the Freundlich constants related to intensity.

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## RESULTS AND DISCUSSIONS

### Adsorbent Characterization

A simple and one-pot procedure has been used for the preparation of magnetically responsive chitosan microparticles with typical diameters of these adsorbents ranged from 30 to 120 µm (**Fig. 1**). The production of these particles is rapid, and they can be easily removed using an appropriate magnetic separator. X-ray diffraction results indicated that the surface-modified $Fe_3O_4$ microparticle did not lead to phase change unlike the pure $Fe_3O_4$ (**Fig. 2**).

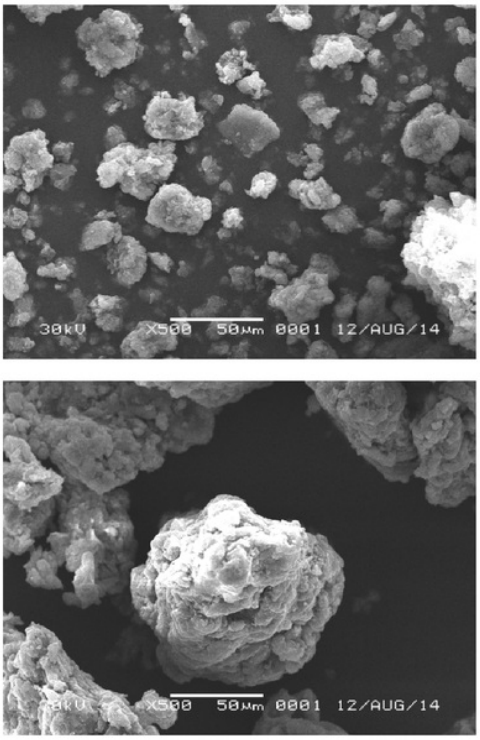



**Fig. 1**. SEM photograph of chitosan-PEG-$Fe_3O_4$ adsorbents with chitosan/$FeSO_4$×$H_2O$ weight ratio are: 1/3.6 (up) and 3/3.6 (down).

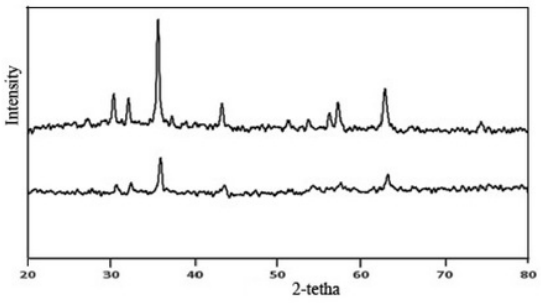
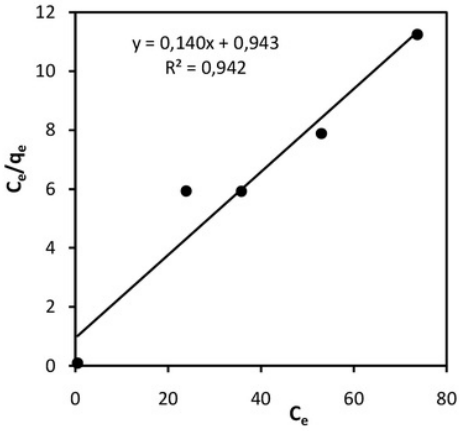



**Fig. 2**. X-ray diffraction patterns of: $Fe_3O_4$ (top) and chitosan-coated $Fe_3O_4$ with chitosan/$FeSO_4$×$H_2O$ weight ratio is 3/3.6.

### Adsorption Studies

Application of Freundlich and Langmuir isotherm linear equation to the experimental data points of adsorption of HA on the adsorbent-1 and adsorbent-2 are shown in **Fig. 3** and **Fig. 4**, respectively.



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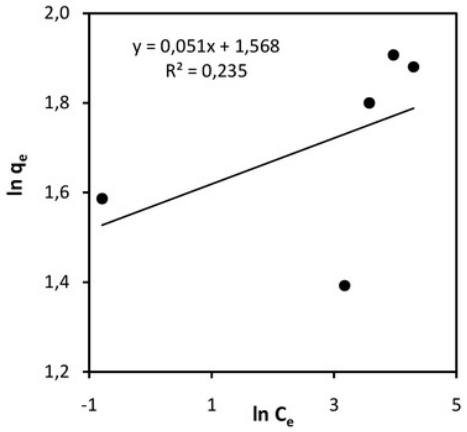


**Fig. 3**. Application of Langmuir (up) and Freundlich (down) isotherm linear equations to the experimental data points for the adsorption of HA on the adsorbent-1 (chitosan/$FeSO_4 \cdot H_2O$ weight ratio is 1/3.6).

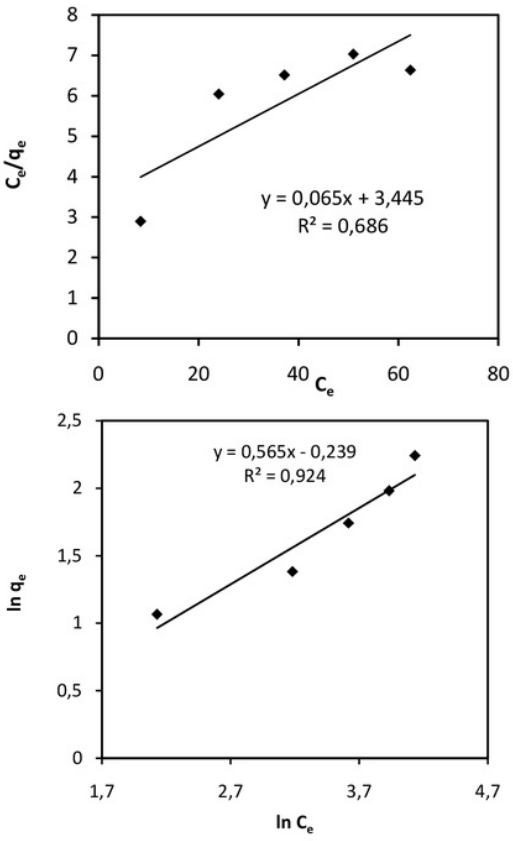


**Fig. 4**. Application of Langmuir (up) and Freundlich (down) isotherm linear equation to the experimental data points for the adsorption of HA on the adsorbent-2 (chitosan/$FeSO_4 \cdot H_2O$ weight ratio is 3/3.6).

**Table 1** shows the adsorption experimental data that was fitted to Langmuir and Freundlich isotherm models. Compared with the Langmuir and Freundlich correlation coefficients (r) presented in **Table 1**, the adsorption process of the HA on the adsorbent-1 was more consistent with the Langmuir isotherm equation model but the HA adsorption on the adsorbent-2 was more consistent with the Freundlich isotherm equation model. The fact that the data was better fitted to the Langmuir isotherm suggest that a monolayer adsorption process occurred dominantly on the surface of the adsorbent-1 whereas the fact that the data better fitted to the Freundlich isotherm suggest that multilayers adsorption process occurred dominantly on the surface of the adsorbent-2.

The constant $q_m$ in the Langmuir isotherm which represents a practical limiting adsorption capacity can be used for comparing adsorption performance of the adsorbents. From the slope value of the linearized plot of $c_e/q_e$ versus $c_e$ presented in **Fig. 3** and **Fig. 4**, as shown in **Table 1**, the $q_m$ values are 7.094 mg/g and 15.385 mg/g, respectively. This result indicates that the adsorption performance of the adsorbent-2 was higher than the adsorbent-1.

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**Table 1**
Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of HA on adsorbent-1 and adsorbent-2

| Adsorbent | Langmuir Constants | | | | Freundlich Constants | | |
|---|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | $b$ (L/mg) | $r$ | $R_L$ | $n$ | $K_F$ ($L^{1/n}$ $mg^{1/n-1}$/g) | $r$ |
| 1 | 7.097 | 0.150 | 0.971 | 0.063 | 19.569 | 4.797 | 0.485 |
| 2 | 15.385 | 0.019 | 0.829 | 0.346 | 1.769 | 0.787 | 0.961 |

Furthermore, the Langmuir constant $b$ can be used to determine the suitability of the adsorbent for the adsorbate using the Hall separation factor ($R_L$) as follows (Hall *et al*, 1966, Santoso, *et al*, 2010):

$$R_L = \frac{1}{1+bC_m} \quad \text{(eq 3)}$$

where $C_m$ is the highest initial HA concentration (mg/L). $R_L$ is the constant separation factor (dimensionless) and can be used for the interpretation of the sorption type as follows:

$R_L > 1$ unfavorable
$R_L < 0$ unfavorable
$R_L = 1$ favorable (linear)
$0 < R_L < 1$ favorable
$R_L = 0$ irreversible

Based on the linearized plot of $c_e/q_e$ versus $c_e$ presented in **Fig. 3 and Fig. 4**, the $b$ values were 0.150 and 0.019 for adsorbent-1 and adsorbent-2, respectively. Therefore, the value of $R_L$ for HA adsorption on the adsorbent-1 and adsorbent-2 were 0.063 and 0.346, respectively. These $R_L$ values indicate a favorable adsorption of HA on both the adsorbent-1 and adsorbent-2.

The adsorption parameter $n$ in the Freundlich isotherm can be used as an indicator of preferential adsorption of one adsorbate to other. The slope ranges ($1/n$) between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process where $1/n$ above one is an indicative of cooperative adsorption (Foo and Hameed, 2010).

As observed from **Table 1**, the equilibrium data fitted well to both the Langmuir and Freundlich adsorption isotherm models. The value of the Freundlich constant, $K_F$ represents a function of adsorption energy and temperature related to the adsorption capacity. The higher of $K_F$ values at adsorbent-2 than at adsorbent-1 suggests that the adsorption energy at adsorbent-1 was higher than that of adsorbent-2.

## CONCLUSIONS

This paper demonstrates a fast, easy and inexpensive method for the preparation of magnetically responsive chitosan microparticle and its examination to be use as an adsorbent for humic acid removal. In this study both Freundlich and Langmuir isotherms have been used to describe and illustrate adsorption process of HA removal on two types of adsorbents with the different weight ratio between chitosan and Fe(II). The application of the constants in the evaluation and comparison of quality and capacity of humic acid adsorption was also demonstrated. The experimental data in the adsorption studies were fitted to Langmuir and Freundlich equations to determine the extent and degree of favorability of adsorption.

## ACKNOWLEDEMENTS

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