A New Type of Adsorbent Based on the Immobilization of Humic Acid on Chitin and Its Application to Adsorb Cu(II)*

Sri Juari Santosa,† Siti Sundari, and Sri Sudiono
Department of Chemistry, Fac. of Mathematics and Natural Sciences, Gadjah Mada University, Sekip Utara Kotak Pos Bls. 21, Yogyakarta, Indonesia

W. H. Rahmanto
Department of Chemistry, Fac. of Mathematics and Natural Sciences, Diponegoro University, Jl. Prof. Sudarto, Semarang, Indonesia
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Synthesis of a new type of adsorbent has been conducted by immobilizing peat soil humic acid (HA) on chitin isolated from crab shell waste. The adsorbent was then applied to adsorb Cu(II) in aqueous medium. The HA was extracted from peat soil of Gambut District, South Kalimantan, Indonesia; while the chitin was isolated from marine crab shell waste of seafood restaurants. The extraction of HA was performed by the commonly used alkaline extraction in NaOH 0.1 M solution, and the isolation of chitin was conducted through deproteinization using NaOH 3.5%(w/v) and followed by removal of inorganic impurities using HCl 1 M. The extracted HA and the isolated chitin were characterized by Fourier Transform Infra Red (FT-IR) spectroscopy. Parameters investigated in this study consisted of method of HA immobilization on chitin, stability test of the immobilized HA, as well as rate, capacity, and energy of adsorption. The FT-IR spectra revealed the presence of main functional groups of COOH and OH (phenolic- and alcoholic-OH) in HA, and those of NH, C=O, CH and energy of adsorption. The FT-IR spectra revealed the presence of main functional groups of COOH and OH (phenolic- and alcoholic-OH) in HA, and those of NH, C=O, CH

I. INTRODUCTION

Humic acid (HA) is a natural organic compound ubiquitously spread-out in terrestrial and aquatic environments. Along with fulvic acid and humin, humic acid composes organic compound known as humic substances.

HA is a complexing agent having multi-ligand property because it possesses many complexing functional groups on its molecule. The functional groups on humic acid possess different ability in binding metal ion through complex bond formation. The decrease of affinity of functional groups on humic acid in complexing metal ion follows the order of -O- (enolic) > -NH2 (amine) > -N=N (azo) > -N- (ring) > -COOH (carboxyl) > -O- (ether) > -C=O (carbonyl) [1]. Similar to the finding of Aiken et al. [1], McBride [2] and Sevenson [3] have also pointed out that among functional groups of humic acid, oxygen containing functional group such as -OH and -COOH are the most reactive to bind metal cation. For that reason, phenolic-OH and -COOH groups are the most important in complex formation. Infra red spectroscopy study has confirmed that carboxyl group plays its important role in complexing metal cations [4–9].

Based on the fact above, it is a primary concern in context of environmental preservation to utilize HA as a decontamination agent of metal cations. Many reports have shown that in the form of solid material, HA can be utilized as adsorbent that effectively remove various metal cations from aqueous medium. However, the existence of HA as a solid material can only be maintained at the medium acidity equivalent to pH 2 or lower[3–5, 8–11]. At medium acidity with pH higher than 2, HA gradually dissolves and its rate of dissolution reaches maximum at pH 5. At pH 7, approximately 90% of HA has already dissolved [4, 9].

To maintain the stability of HA toward dissolution at pH higher than 2, many efforts have been conducted through a variety of immobilization methods. We have successfully immobilize HA on chitin and the immobilized HA is stable against dissolution up to pH 11 [12]. The use of chitin as support material for HA results better stability than that of alumina [13], various aluminum and iron oxides [14], TiO2 and ZnO [15]. To evaluate the performance of the material resulted from the immobilization of HA on chitin, we have utilized the material as adsorbent for the adsorption of Cu(II) from aqueous medium. The result is now reported here.

II. EXPERIMENTAL

A. Sampling and Sample Preparation

Sample of peat soil as source of HA was taken in Gambut District of South Kalimantan, Indonesia. The sample
FIG. 1: FT-IR spectra of sodium humate (Na-Humate) from Merck (above), and humic acid (HA) extracted from peat soil of Gambut District, South Kalimantan, Indonesia (below).

was taken using a Teflon pipe dipped in weak and partly submerged peat soil. Peat soil trapped inside the Teflon pipe was pouring out and collected in a black plastic bag. After transportation and returning to the laboratory, peat soil was dried in room condition under the flow of nitrogen gas to prevent oxidation by oxygen in the atmosphere.

Sample of crustacean shell waste as a source of chitin was collected from traditional market and sea-food restaurant in Semarang, Central Java, Indonesia. The crustacean shell was dried under sun light and then crushed and sieved to the size of 80 mesh.

B. Extraction of Humic Acid and Isolation of Chitin

HA was extracted from the peat soil sample according to the procedure of IHSS (International Humic Substances Society) [16] while chitin was isolated through deproteination and followed by demineralization processes according to the method of Hong et al. [17]. Both HA and chitin were then characterized using Fourier Transform Infra Red (FT-IR) spectroscopy.

C. Materials

All reagents in analytical grade i.e. CuCl$_2$−2H$_2$O, HCl, HF, and NaOH, were obtained from Merck Co Inc. (Germany) and used without further purification. Standard chitin and sodium humate (Na-Humate) were purchase from Sigma Chemical (USA).

D. Preparation of Chitin Humic Acid (Chitin-HA) Adsorbent through Immobilization of Humic Acid on Chitin

As described in our previous paper [12], the immobilization of HA on chitin was done by reacting gelatinous chitin (40 g) in 250 mL of HCl 0.5 M and solution of HA (2 g) in 250 mL of NaOH 0.5 M. Chitin (40 g) was first dispersed in 250 mL of HCl 0.5 M and stirred con-
timuously to form gelatinous solution. Into the gelatinous chitin solution, 250 mL of the humic acid solution (0.008 g/mL) in NaOH 0.5 M was poured and mixed by stirring for 24 hours. The mixed solution was filtered, and the precipitation was washed with water and dried in oven at 50–60°C. After crushing and filtering to the size of 80 mesh, the resulted powder of chitin containing HA was then applied as adsorbent for Cu(II).

E. Stability Test of Humic Acid Contained in Adsorbent

Five hundred mg of adsorbent was added to 50 mL of distilled water and the acidity was then adjusted to pH of 1, 3, 5, 7, 9, 11, and 13 by using either HCl or NaOH solution. The mixture was stirred for 30 minutes and followed by standing for 24 hours. After separating supernatant from the solid, the content of dissolved humic acid in supernatant was determined spectrophotometrically at 400 nm by using standard addition method.

F. Adsorption Kinetics

The kinetic experiments were carried out using a batch-type reactor using a 100-mL Erlenmeyer in a water bath at 25±0.01°C. The effective volume of the solution of the reacting suspension was 25 mL, the initial metal ion concentration was 100 mg/L, the acidity was adjusted at pH 4.0 (the optimum acidity for chitin-HA adsorbent) and 6.0 (the optimum acidity for chitin adsorbent), and to each solution, 50 mg of adsorbent was added and then stirred continuously. At selected interaction time, the sample was immediately filtered through 0.45-µm membrane filter and the concentration of Cu(II) in the supernatant was analyzed by using atomic absorption spectrometry (AAS). Sample and blank solutions were analyzed under the same condition. The amount of Cu(II) adsorbed was then calculated based on the assumption that the adsorption obeyed Langmuir isotherm model with first order adsorption reaching equilibrium [18, 19].

G. Capacity and Energy of Adsorption

The experiments were also conducted using a batch-type reactor at 25±0.01°C. As much as 50 mg of adsorbents was interacted with and stirred in 25 mL of solutions containing the various concentrations of 5, 15, 30, 50, 60, 90, 120, and 180 mg/L of Cu(II) for as long as 2 hours and then aged for 24 hours. After separating the supernatants, the concentration of Cu(II) in the supernatant was determined by AAS. Under the same condition with the sample solution, the blank solution was also analyzed. Based on the data obtained, the capacity and equilibrium constant (K) of adsorption was calculated based on the Langmuir isotherm adsorption model, and the energy (E) of adsorption was then calculated from the equation of \( E = RT \ln K \).

III. RESULTS AND DISCUSSION

A. Characterization of Humic Acid and Chitin

FT-IR spectra of the extracted HA from peat soil of Gambut District, South Kalimantan, Indonesia (Fig. 1) is closely resemble with those of HA extracted from Rawa Pening, Central Java, Indonesia [12]. As a comparison, the FT-IR spectra of Na-Humate purchased from Merck is also given in Fig. 1.

Both the extracted HA and the purchased Na-Humate showed remarkable absorption bands at wavelength number 3380, 2930, and 1620 cm\(^{-1}\), and broaden absorption band at 2600 cm\(^{-1}\). The absorption bands at 3380 and 2930 cm\(^{-1}\) were for stretching of –OH and asymmetric stretching of aliphatic CH in CH\(_2\) [19]. In the case of absorption band at 1620 cm\(^{-1}\), it was assumed to be the absorption bands of stretching of aromatic C=C and asymmetric stretching of COO\(^{-}\). The broad absorption band at 2600 cm\(^{-1}\) was resulted from the asymmetric stretching of O-H from OH group in –COOH. The broad absorption bands at 2600 and also 3380 cm\(^{-1}\) were because of hydrogen bonding that was experienced by –OH and –OH group in COOH.

In addition to the absorption bands at 3380, 2930, 1620, and 2600 cm\(^{-1}\), the extracted HA, but not the purchased Na-Humate, had absorption band at 1720 cm\(^{-1}\). This absorption band at 1720 cm\(^{-1}\) was attributed to the stretching of C=O in COO\(^{-}\) [20]. As commonly known that COO\(^{-}\) in HA is the most responsible functional group interacting with metal cations [6, 7, 21]. As a result, in the form of Na-Humate, the functional group of COO\(^{-}\) was not free. It interacted with Na(I), and therefore absorption band of C=O stretching in free COO\(^{-}\) at wavelength 1720 cm\(^{-1}\) was disappeared and it was replaced with a new absorption band of COO\(^{-}\) Na\(^+\) at wavelength 1380 cm\(^{-1}\). This is why that the FT-IR spectra of Na-Humate showed a new absorption band at 1380 cm\(^{-1}\) but the absorption band at 1720 cm\(^{-1}\) was absent.

In the case of the isolated chitin, its characterization result is presented in Fig. 2. In Fig. 2, the FT-IR spectra of standard chitin is also presented as a comparison. Both the isolated chitin and the standard chitin showed very similar spectra with the main absorption bands at 3450, 3270, 3100, 2900, 2890, 1660, 1630, 1560, 1415, 1377, and 1070 cm\(^{-1}\). From those absorption bands, the absorption band at 3450 cm\(^{-1}\) was characteristic for –OH, at 3270, 3100, and 1630 cm\(^{-1}\) was for N-H stretching, symmetric stretching N-H, and N-H bending, respectively [20]. Carbonyl (C=O) stretching of acyl group (CH\(_2\)CO) appeared at 1660 cm\(^{-1}\), while asymmetric and symmetric bending of C-CH\(_2\) appeared at 1415 and 1377 cm\(^{-1}\), respectively. The other absorption bands at 2900, 2890, and 1070 cm\(^{-1}\) were characteristic for asymmetric and symmetric stretching of C-H of CH\(_2\), and stretching of C-O, respectively [20].
B. Characterization of Adsorbents

Characterization using FT-IR toward the adsorbents (chitin-HA and chitin itself) resulted in very similar spectra (Fig. 2). The only difference between the spectra of chitin-HA and chitin was the presence or absence of absorption band at 2600 cm$^{-1}$. Before immobilization, the absorption band at 2600 cm$^{-1}$ was absent, and after the immobilization of humic acid, the absorption band appeared.

As described before, the absorption band at 2600 cm$^{-1}$ was the asymmetric stretching of O-H from OH group in $\text{COOH}$. Since chitin contains no $\text{COOH}$ group, the FT-IR spectra of chitin lack of the absorption band at 2600 cm$^{-1}$, but after humic acid stacks on chitin, the resulted adsorbent contains $\text{COOH}$ group and therefore, the adsorption band at 2600 cm$^{-1}$ is appeared.

Instead of broad absorption band as shown in Fig. 1, the adsorption band at 2600 cm$^{-1}$ in Fig. 2 was small but very sharp. The broad absorption spectra for O-H in $\text{COOH}$ group is attributed to the presence of intense hydrogen bonding in humic acid. After immobilization on chitin, humic acid may be stretched on the surface of chitin and the inter- and intra-molecular hydrogen bonding involving the OH in COOH may be reduced drastically so the appearance of its absorption band was very sharp.

C. Stability Test of Humic Acid Contained in Adsorbent

Before investigating the stability of humic acid contained in the adsorbent, the total amount of humic acid in the adsorbent is determined first. One hundred mg of the adsorbent was dissolved in 50 mL of NaOH 0.05 M to result clear solution. By using standard addition method,
the content of humic acid released from the adsorbent to the solution was then determined by ultraviolet-visible spectrometer at wavelength of 400 nm [12]. The determination resulted the content of humic acid on the adsorbent of 1.98% (w/w). By the same method we successfully immobilized HA extracted from Peat Soil of Rawa Pening as much as 2.22%. The content of 1.98% was then used as a base to calculate the stability of immobilized humic acid at various medium acidities. The stability of HA on chitin was calculated by comparing the eluted amount of HA in each medium acidity relative to the total amount of HA in the adsorbent.

The immobilization greatly improved the stability of HA toward dissolution (Fig. 3). Without immobilization, HA was gradually dissolved from pH 1 to 3, and then dissolved sharply from pH 3 to 5, and at acidities lower than pH 5, HA was only slowly dissolved. On the contrary, the dissolution of immobilized HA on chitin was small. After initial small dissolution from pH 2 to 3, the immobilized HA was then stable at the value of about 90% from pH 3 to 11. The same evidence was also observed in our previous paper by using HA extracted from another peat soil [12].

### D. Adsorption Kinetics

Applying a kinetic model for first order metal adsorption reaching equilibrium with the mathematical expression as follow [18, 19]:

\[
\frac{\ln(C_{A0}/C_A)}{C_A} = k_1 \frac{t}{C_A} + K,
\]

where $C_{A0}$ is the initial concentration of metal ion, $C_A$ is the remaining concentration of metal ion after adsorption at $t$ adsorption time, $k_1$ is first order adsorption constant, and $K$ is adsorption-desorption equilibrium constant. The resulted linear relationship between $\ln(C_{A0}/C_A)/C_A$ and $t/C_A$ as shown in Fig. 4. From the relationship shown in Fig. 4, the obtained $k_1$ for the adsorption of Cu(I) on chitin-HA and chitin was 4.6 and $3.7 \times 10^{-4}$ min$^{-1}$, respectively. It is clear that the presence of HA on chitin enhances the $k_1$. The presence of HA on chitin increases the amount of active site for adsorption since HA contains huge functional group like carboxyl group that is suitable for adsorbing metal cation.
TABLE I: Capacity (b), equilibrium constant (K) and energy (E) for the adsorption of Cu(II) on humic acid immobilized on chitin (chitin-HA) and chitin.

| Adsorbent  | Adsorption parameters |              |              |
|------------|-----------------------|--------------|--------------|
|            | b (mol/g)             | K (mol/L)^{-1} | E (kJ/mol)   |
| Chitin-HA  | 2.82 × 10^{-2}        | 3490         | 20.4         |
| Chitin     | 1.96 × 10^{-2}        | 8416         | 22.5         |

Carboxyl is the most responsible functional group in HA that binds Cu(II) [3, 9].

E. Capacity and Energy of Adsorption

The Langmuir isotherm adsorption model with the mathematical expression given below was used to determine the capacity (b) and equilibrium constant (K) of adsorption, and the energy (E) of adsorption was then calculated according to the equation $E = RT \ln K$.

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b},$$

where $C$ is the concentration of metal ion remaining in solution at equilibrium, $m$ is adsorbed metal ion on 1 g adsorbent, $K$ is equilibrium constant of adsorption, and $b$ is adsorption capacity. The resulted relationship between $C/m$ and $C$ for the adsorption of Cu(II) on chitin-HA at pH 4 and chitin at pH 6 is presented in Fig. 5.

From the relationship given in Eq. 5, the adsorption capacity (b) can be obtained from the slope, and the equilibrium constant (K) can be calculated based on the intercept and the value of b. The resulted b, K and E for the adsorption of Cu(II) on chitin-HA and chitin were summarized in Table 1.

It is clear that the presence of HA on chitin enhances the adsorption capacity of Cu(II) on chitin. As mentioned before that HA on chitin will adds significant amount of functional group especially carboxyl group on the surface of chitin. As a result, the amount of active site increases and it leads to the higher adsorption capacity.

In contrast to adsorption capacity, the adsorption energy tends to decrease with presence of carboxyl group on chitin. According to hard soft acid base (HSAB) principle that initially proposed by Pearson [22], Cu(II) is belong to intermediate acid, while the carboxyl functional group in HA belongs to hard base and as a base it is harder than the N-acetyl (NHOCH$_2$) group in chitin. The affinity of harder base of carboxyl group in the surface of chitin will be less suitable for intermediate acid like Cu(II). Therefore, the presence of HA on chitin decreases the adsorption energy of Cu(II). The same evidence is also observed for soft acid like Ag(I) [23].

IV. CONCLUSIONS

It was proved that the immobilization of HA on chitin resulted the great enhancement on the stability of HA toward dissolution. The HA immobilized on chitin was stable in wide medium acidity range from pH 3 to 11. The presence of HA on chitin add the active site for Cu(II) and hence enhanced the adsorption rate and capacity. In term of adsorption energy, the presence of HA on chitin was, however, decreased the adsorption energy of Cu(II). This evidence was in accordance with the result of previous study that showed the presence of HA on chitin decreased the adsorption energy of soft metal cation Ag(I) [22] but relatively enhanced that of hard metal cation such as Cr(III) [12].

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