A new type of adsorbent based on the immobilization of humic acid (HA) extracted from tropical peat soil taken in Sambutan village, East Kalimantan, Indonesia, on silica gel (SG) was synthesized and then applied as an adsorbent for the selective adsorption of Cu(II) in the presence of Ca(II). The extraction of HA was performed by the recommended procedure of International Humic Substances Society (IHSS). The immobilization was begun with purification of SG in HCl 1:1 and followed by activation at temperature 110°C for 24 hours. The activated silica gel (4 g) was suspended into 40 mL of NaOH 0.01 M, and into this suspension, 60 mL of NaOH 0.01 M containing 4 g HA was then poured and stirred for 24 hours to allow immobilization of HA on SG. This immobilization produced an adsorbent (SG-HA) with the content of HA was 13.05%(w/w), and this immobilized HA was stable in the acidity range of pH 1.0 to 8.0. The application of SG-HA to selectively adsorb Cu(II) from the solution containing Ca(II) could be achieved at medium acidity that equivalent to pH 4.0 to 5.0. At pH 5, the adsorption rate constant of Cu(II) on SG-HA was 0.027 min⁻¹, while that of Ca(II) on SG-HA was only 0.004 min⁻¹. Similar to the adsorption rate constant, the adsorption capacity and energy of SG-HA for Cu(II), i.e. 0.21 mmol/g and 26.63 kJ/mol, respectively, were also higher than those for Ca(II), i.e. 0.07 mmol/g and 24.87 kJ/mol, respectively. Compared to SG, the immobilization of HA on SG resulted enhancement of the rate constant, capacity, and energy of adsorption. By using SG, the rate constant, capacity, and energy of adsorption of Cu(II) were 0.001 min⁻¹, 0.10 mmol/g, and 21.34 kJ/mol, respectively. [DOI: 10.1380/ejssnt.2006.602]

Keywords: humic acid; silica gel; immobilization; copper; selective adsorption

I. INTRODUCTION

Humic substances are considered as the end product of the decomposition of plant material in soil [1]. They are chemically homogenous in their compositions, but very heterogeneous in their molecular weights. Based on their solubility in acid and alkaline solutions, humic substances can be differentiated into 3 fractions namely (i) humic acid, fraction of insoluble humic substances in acidic water (pH<2), but soluble in water having higher pH, (ii) fulvic acid, fraction of humic substances soluble in all pH range, and (iii) humin, fraction of humic substances that are insoluble in water in all pH conditions.

Humic acid is a very good adsorbent in term of capacity and rate of adsorption for various metal cations. In comparison to the commonly used adsorbent such as metal oxides [2, 3], bentonite [4, 5], and active carbon [6, 7], humic acid generally possesses higher capacity and energy of adsorption, and also has faster rate of adsorption. Unfortunately, the existence of humic acid as an adsorbent can only be maintained at the medium acidity which is equivalent to pH 2 or lower [8, 9].

Realizing the stability of solid humic acid as adsorbent can only be maintained at medium pH 2 or lower, many efforts have been conducted to stabilize it through various methods of immobilization. Tombacz, et al. [10] interacted humic acids and alumina. This interaction was only stable at the medium pH range of 4 to 10. Other kinds of aluminum and iron oxides have also been tried to be associated with humic acids [11]. All of the oxides (geothite, hematite, gibbsite, and bochmite) could only give stable association at pH range of about 7.0 to 8.0.

For many purposes, semiconductors such as TiO₂ and ZnO ever been used together with humic acid. From the work of Sell, et al. [12], it was clear that ZnO was only stable at medium pH 7 to 10, and another result using TiO₂ [13] showed that the stability of the semiconductor of TiO₂ was only in the pH range of 3 to 7. These evidences clearly indicate that both ZnO and TiO₂ are not the proper candidates for the support material of humic acids.

Compared to the oxides described above, silica gel may possess higher stability towards the change of medium acidity [14, 15], and its interaction with humic acid may result stable immobilization. As a result the main objective of this paper is to report the preparation of an adsorbent based on the immobilization of HA on SG, the application of the adsorbent for the adsorption of Cu(II) and for the selective adsorption of Cu(II) in the presence of Ca(II).

II. EXPERIMENTAL

A. Sampling and Sample Preparation

Peat soil as source of HA was taken in Sambutan village of Samarinda Ilir subdistrict, East Kalimantan, Indonesia. The peat soil was taken using a Telton pipe dipped in weak and partly submerged peat soil. Peat soil trapped inside the Telton pipe was poured-out and collected in a black plastic bag containing nitrogen gas. 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. During this drying period, the contaminants such rocks, root, etc. must be separated from the soil sample. HA was then extracted from the peat soil sample according to the procedure of IHSS (International Humic Substances Society) [16].

B. Materials

All reagents in analytical grade i.e. CuCl$_2$-2H$_2$O, CaCl$_2$, HCl, HF, and NaOH, were obtained from Merck Co Inc. (Germany) and used without further purification. SG use as support material was also purchase from Merck Co Inc. (Germany).

C. Preparation of Adsorbent through Immobilization of Humic Acid on Silica Gel

SG was first purified with immersing and stirring in HCl solution 1:10 for 24 hours. The purified SG was activated at 110°C for as long as 24 hours and then suspended into NaOH 0.001 M. Into the suspension of SG, the solution of HA in NaOH 0.01 M was poured and gently shaken for 24 hours. The resulted adsorbent (SG-HA) was washed and rinsed with water until the supernatant was free from chloride. After rinsing, the adsorbent was dried in oven at 60°C to constant weight. The obtained adsorbent and also the SG were then characterized using FTIR Spectroscopy.

D. Determination of Total Amount of Humic Acids Contained in Adsorbent

One hundred mg of the adsorbent was dissolved on 50 mL of NaOH 0.05 M to obtain clear solution. By using standard addition method, the content of HA released from the adsorbent to the solution was then determined by ultraviolet-visible spectrometer at wavelength of 400 nm.

E. Solubility Test of Humic Acid Contained in Adsorbent

Five hundred mg of adsorbent was added to 50 mL of destilled water and the acidity was then adjusted to pH of 1, 3, 5, 7, and 9 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 HA in supernatant was determined spectrometrically at 400 nm by using standard addition method.

F. Effect of Medium Acidity on the Speciation of Cu(II)

A series of 50 mL of Cu(II) solutions at concentration of 15 mg/L was prepared and their acidity was adjusted to pH 2.0, 4.0, 5.0, 6.0, and 7.4 by adding HCl or NaOH solutions. Into every solution, 100 mg of adsorbent was poured and then stirred for 2 hours. After filtering through 0.45-um membrane filter, the concentrations of Cu(II) in the supernatant were analyzed by using atomic absorption spectrometry (AAS) and Ion Selective Electrode (ISE). Sample and blank solutions were analyzed under the same condition. The amount of adsorbed Cu(II) was considered to be the difference between the initial amount and the amount remaining in supernatant determined by AAS, while the amount remaining in supernatant determined by ISE was defined as hydrated Cu(II). In the case of the difference between the amount remaining in supernatant determined by AAS and by ISE for every time a sample was analyzed, was attributed as complexed Cu(II).

G. Adsorption Kinetics of Metal Ions Cu(II) and Ca(II) on Adsorbent

The kinetic experiments were carried out using a batch-type reactor using a 300-mL Erlenmeyer in a water bath at 25±0.01°C for specified time period. The effective volume of the solution of the reacting suspension was 250 mL.
FIG. 2: Effect of medium acidity on the stability of pure humic acid (HA) and HA immobilized on silica gel (SG-HA) toward dissolution.

The initial metal ion concentration was 4 mmol/L, the acidity was adjusted at pH in which the adsorbent was stable for dissolution. To each solution, 150 mg/L adsorbent was added and stirred continuously. At selected time periods, 10-mL sample was taken from the reactor with a syringe and immediately filtered through 0.45-µm membrane filter to 30-mL beaker glass.

The concentration of Cu(II) and Ca(II) in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same condition. The amount of ion metal adsorbed was considered to be the difference between the initial and the amount remaining in the reacting solution each time a sample was analyzed.

From the data obtained, the value of $k_1$ (first order rate constant) for the metal adsorption were then calculated based on the assumption that the adsorption obeyed Langmuir isotherm model with first order adsorption reaching equilibrium (FOA) [17, 18].

H. Capacity and Energy of Adsorption

The experiments were also conducted using a batch-type reactor at 25±0.01°C. As much as 100 mg of adsorbent was interacted with and stirred in 10 mL of solutions containing the various concentrations of 2, 5, 10, 25, 50, 100, 200, 400, 1000, 2000, 5000 mg/L of Cu(II) or Ca(II) for as long as 2 hours. After separating the supernatants, the concentrations of Cu(II) and Ca(II) in the supernatant were determined by AAS. Under the same condition with the sample solution, the blank solution was also analyzed. Based on the data obtained, the adsorption capacity ($K$) for Cu(II) and Ca(II) was determined according to the Langmuir isotherm adsorption model. From the $K$ value, the adsorption energy ($E$) for the metal ions investigated was then calculated according to the equation $E = -RT \ln K$.

I. Adsorption Selective of Cu(II) in the Presence of Ca(II)

Experiments were conducted the same as experiments in section 2.6, but Cu(II) is coexist with Ca(II) in the adsorption medium. Three different mole ratio of Cu(II) to Ca(II), i.e. 1.60, 1.00, and 0.63 was performed and the adsorption data of Cu(II) and Ca(II) on SG-HA adsorbent were examined.

III. RESULT AND DISCUSSION

A. Characterization of Silica Gel, Humic Acid, and Humic Acid Immobilized on Silica Gel

The purified SG showed remarkable absorption bands at wavelength number 3412, 1618, 1113, 804, 598, and 470 cm$^{-1}$ (Fig. 1). The absorption bands at 3412 cm$^{-1}$ is due to the presence of –OH group. This –OH group is attributed to silanol group and H$_2$O trapped in SG. The presence of H$_2$O trapped in SG is proved by the appearance of absorption band at 1618 cm$^{-1}$ [19]. The absorption bands at 1113 and 804 cm$^{-1}$ are attributed to Si-O stretching and bending vibrations, respectively, of siloxane bond. In the case of adsorption bands at 400 to 700 cm$^{-1}$, they may indicate the presence of Si-Cl bond, since those bands are absent in the FT-IR spectra of SG.
FIG. 4: Effect of contact time on the adsorption of Cu(II) and Ca(II) on silica gel (SG) and humic acid (HA) immobilized on SG (SG-HA).

before purification with HCl (the spectra of SG without purification is not shown).

In the case of the spectra of HA, the presence of O-H stretching is shown at 3435 cm$^{-1}$. The broadness of this band is attributed to the effect of hydrogen bonding due to the statistical distribution in the extent of hydrogen bonds in polimeric association. The presence of O-H stretching of COOH group results the appearance of absorption band around 2340 cm$^{-1}$. The absorption band around 2940 and 2860 cm$^{-1}$ superimposed on the shoulder of the broad O-H stretching and are contributed by the symmetric and symmetric stretching vibration of aliphatic C-H bands in methyl and/or methylene groups [20]. The absorption bands of 1706 and 1624 cm$^{-1}$ are for C=O of COOH stretching and COO$^-$ asymmetric stretching vibrations that superimposed with C=C stretching vibration. Peaks emerging around 1541 cm$^{-1}$ are attributed to aromatic C-H stretching.

The immobilization of HA on SG resulted small but remarkable modification on the FT-IR spectra of SG. Before the immobilization, the spectra of SG was lack of absorption bands at 2940, 2345, 1541 cm$^{-1}$; but after the immobilization, those absorption bands appeared. It qualitatively indicates that HA is indeed present on SG.

B. Stability Test of Humic Acid Contained in Adsorbent

Before the stability test, the determination of the total amount of HA immobilized on SG resulted the content 13.05%(w/w). This content of HA immobilized on SG was then used as base for the determination of stability of HA toward dissolution at various medium acidities.

The stability of HA toward dissolution greatly improved by the immobilization (Fig. 2). Without immobilization, HA was gradually dissolved from pH 1 to 4, and then dissolved sharply from pH 4 to 5, and at acidities lower than pH 5, HA was again dissolved gradually. On the contrary, the dissolution of immobilized HA on SG was significantly small from pH 1 to pH 8. Dissolution became significant at pH higher than 8. The instability of HA at pH higher than 8 may also caused by the fact that SG itself is dissolved at pH higher than 8 [1].

C. Effect of Medium Acidity on the Speciation of Cu(II)

The medium acidity clearly affects the ability of the adsorbent (SG-HA) in adsorbing Cu(II) and also affects the chemical form of Cu(II) species remaining in the supernatant (Fig. 3). The adsorbed Cu(II) significantly increases from pH 2 to 5 and relatively constant from pH 5 to 7.4. From pH 5 to 7.4, The adsorbed Cu(II) is more than 93%.

As has been commonly known that carboxyl group in HA is the main and the most reactive group in attracting metal cations [8, 21, 22]. The amount of ionized carboxyl functional group in HA gradually increases from pH vely low typically pH 2 to pH 4 and rapidly increases from pH 4 to 5. At pH 5, approximately 90% of carboxyl group in HA has been ionized [23, 24]. As a result, the increase of adsorbed Cu(II) on the adsorbent is accordance with the increase of the portion of the ionized carboxyl group in the adsorbent. The contribution of remaining functional groups in SG such as siloxan and silanol in adsorbing Cu(II) is predicted to be limited as described in the next section.

In contrast to the adsorbed Cu(II), the amount of hydrated Cu(II) in the solution decreases with increasing pH, while that of complexed Cu(II) is significantly low and relatively constant at the whole pH range. As has been shown before that the adsorbent is stable from pH 1 to 8. It means that in the pH range applied here (pH 2 to 7.4), the dissolution of HA from the adsorbent is minimum and therefore the formation of Cu(II)-humate complex in the remaining solution is also consistently small. Since the amount of complexed Cu(II) in the solution is relatively constant and that of adsorbed Cu(II) on the adsorbent increases with increasing pH, so the amount of hydrated Cu(II) in the solution decreases with increasing pH. As a summary, if maximum adsorption of Cu(II) with minimum interference from the formation of complex Cu-Humate is desired, so the adsorption should be performed at pH around 6.

D. Adsorption Kinetics of Metal Ions (Cu(II) and Ca(II)) on Adsorbent

The adsorption of Cu(II) and Ca(II) on SG-AH and SG adsorbents as a function of contact time is given in Fig. 4. At the initial stage of contact time, the adsorbed amount of all metal cations increased as the contact time increased. The increase of the adsorbed amount of metal cations caused by SG-HA adsorbent was observed faster than that caused by SG adsorbent. It is an indication that
the adsorption rate of metal cations on SG-HA adsorbent is higher than that on SG adsorbent. It can also be seen in Fig. 4 that SG-HA adsorbent resulted more adsorbed amount of metal cations than SG adsorbent. Thus, in addition to adsorption rate, the adsorption capacity of SG-HA for the metal cation studied will be also higher.

Applying a kinetics model that obeyed Langmuir isotherm model with first order adsorption reaching equilibrium (FOA) as shown in the equation below [17, 18], the k1 will be obtained from the slope of the relationship between ln(Ceq/Cfa)/Cfa and t/Cfa. The resulted k1 and correlation coefficient (R) of the plot ln(Ceq/Cfa)/Cfa vs. t/Cfa for the two metal cations is summarized in Table I.

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

where \( C_{fa} \) is the initial concentration of metal ion, \( C_f \) is the remaining concentration of metal ion after adsorption at t adsorption time, \( k_1 \) is first order adsorption rate constant, and \( K \) is adsorption-desorption equilibrium constant, \( i.e \) ratio of the first order adsorption rate constant relative to the first order desorption rate constant \( k_1/k_{-1} \).

As predicted from Fig. 4, it is confirmed in Table I that the presence of HA on SG increases the adsorption rate of both Cu(II) and Ca(II). The presence of HA on SG enhances the amount of active site for adsorption on SG since HA contains various functional group like carboxyl group that is suitable for adsorbing metal cation. Many studies has shown that carboxyl is the most responsible functional group in HA that binds metal cations especially for relatively hard metal cations [8, 21]. Since the affinity of carboxyl group toward metal cations is high, so it presence on SG enhances the adsorption rate of cations.

As occur for \( k_1 \), the enhancement of active sites of adsorption on SG due to the presence of HA gave higher \( b \) for both Cu(II) and Ca(II). Compared to Ca(II), Cu(II) was more adsorbed by the adsorbents. This evident may be caused by the nature of Cu(II) that is more ready to complex with carboxyl group in HA than Ca(II). In case of Ca(II), its interaction with carboxyl group is more ionic and its hydration energy is also higher than Cu(II). As a result, harder competition with water will occur for the adsorption of Ca(II) than that of Cu(II). This is why the adsorption energy for Cu(II) consistently higher than that for Ca(II).

### E. Capacity and Energy of Adsorption

Application of various initial concentration of Cu(II) and Ca(II) resulted profiles between the adsorbed metal cations and the concentration of metal cations remaining in the solution (Ceq) as shown in Fig. 5. On the application of low initial concentration of metal ions, the increase of metal ion concentration resulted highly increase on the adsorbed metal cations. This increase of the adsorbed metal cations became smaller on the application of higher initial concentration of metal cations.

From the profiles shown in Fig. 5, the capacity (b) of adsorption is then determined according to the Langmuir isotherm adsorption model with the mathematical expression given below. For the energy (E) of adsorption, it is calculated from equilibrium constant of adsorption (K) according to the equation \( E = RT \ln K \). The resulted b and K from the Langmuir adsorption model along with the calculated E are presented in Table II.

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

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.

As occur for \( k_1 \), the enhancement of active sites of adsorption on SG due to the presence of HA gave higher \( b \) for both Cu(II) and Ca(II). Compared to Ca(II), Cu(II) was more adsorbed by the adsorbents. This evident may be caused by the nature of Cu(II) that is more ready to complex with carboxyl group in HA than Ca(II). In case of Ca(II), its interaction with carboxyl group is more ionic and its hydration energy is also higher than Cu(II). As a result, harder competition with water will occur for the adsorption of Ca(II) than that of Cu(II). This is why the adsorption energy for Cu(II) consistently higher than that for Ca(II).
TABLE I: First order rate constant ($k_1$) and correlation coefficient ($R$) of the plot $\ln(C_{A_0}/C_A)/C_A$ vs. $t/C_A$ for the adsorption of Cu(II) and Ca(II) on silica gel (SG) and humic acid immobilized on silica gel (SG-HA).

| Metal cation | Adsorbent    | $k_1$ (min$^{-1}$) | $R$  |
|--------------|--------------|-------------------|------|
| Cu(II)       | SG-HA        | 0.0271            | 0.930|
|              | SG           | 0.0011            | 0.992|
| Ca(II)       | SG-HA        | 0.0040            | 0.927|
|              | SG           | 0.0008            | 0.948|

TABLE II: Capacity ($b$), equilibrium constant ($K$) and Energy ($E$) for the adsorption of Cu(II) and Ca(II) on silica gel (SG) and humic acid immobilized on silica gel (SG-HA).

| Metal cation | Adsorbent    | $b$ ($10^{-5}$ mol·g$^{-1}$) | $K$ (mol·L$^{-1}$)$^{-1}$ | $E$ (kJ·mol$^{-1}$) |
|--------------|--------------|------------------------------|--------------------------|-------------------|
| Cu(II)       | SG-HA        | 20.97                        | 39032                    | 26.63             |
|              | SG           | 10.43                        | 4765                     | 21.34             |
| Ca(II)       | SG-HA        | 7.23                         | 19368                    | 24.87             |
|              | SG           | 4.58                         | 2061                     | 19.22             |

F. Adsorption Selective of Cu(II) in the Presence of Ca(II)

For all mole ratios of Cu(II) to Ca(II) applied, i.e. 1.60, 1.00, and 0.63, the adsorption of Cu(II) on SG-HA was not affected by the coexistence of Ca(II) if the adsorption is performed at pH 4.0 or 5.0. As shown in Fig. 6, for the mole ratio of Cu(II) to Ca(II) 0.63, the adsorption of Cu(II) at pH 4.0 to 7.4 was nearly complete, while the adsorption of Ca(II) occurred at pH 6 or higher. As a result, the selective adsorption of Cu(II) can be simply conducted at pH 4 to 5.

IV. CONCLUSIONS

The immobilization of HA on SG improved the stability of HA toward dissolution. The HA immobilized on SG was stable in wide medium acidity range from pH 1 to 8. The presence of HA on SG add the active site for Cu(II) and Ca(II) and hence enhanced the adsorption rate, capacity, and energy. Compared to Ca(II), Cu(II) was adsorbed on SG-HA faster and with higher capacity and energy of adsorption. The presence of Ca(II) in the adsorption medium gave negligible effect on the adsorption of Cu(II) if the adsorption is performed at pH 4 to 5.

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