Article

Adsorption Kinetics of Cu(II) Species on Silica Gel in the Presence of Humic Acid

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Abstract

The adsorption kinetics and mechanism of two dissolved Cu(II) species, i.e. hydrated Cu(II) (Hy-Cu(II)) and its humic acid complexed (HA-Cu(II)), on silica gel (SG) have been studied. The adsorption medium containing both Hy-Cu(II) and HA-Cu(II) was first prepared by introducing humic acid (HA) previously immobilized on SG into aqueous solution containing Hy-Cu(II). The acidity of the solution was adjusted to pH 4.0 in order the Hy-Cu(II) to be proportionally distributed to HA-Cu(II). The adsorption of the Cu(II) species on SG showed that Hy-Cu(II) was adsorbed much faster than HA-Cu(II), with adsorption rate constant (k_{ad}) of 0.48 min^{-1} for Hy-Cu(II) and 0.05 min^{-1} for HA-Cu(II). Since HA-Cu(II) complex should be anionic in nature, strong adsorption of the species on SG could not be expected. The adsorption energy (E) of $24.82 \text{ kJ mol}^{-1}$ for HA-Cu(II) complex which is significantly higher than that of $12.56 \text{ kJ mol}^{-1}$ for Hy-Cu(II) suggests that HA-Cu(II) complex is chemically adsorbed through ligand exchange after the rapid electrostatic interaction through outer-sphere complexation of Hy-Cu(II) on SG. This evidence indicates that the adsorption of the Cu(II) species proceeds sequentially, where the Hy-Cu(II) is adsorbed first and it then acts as a bridge for the adsorption of HA-Cu(II).

Key words: adsorption kinetics, Cu(II) species, silica gel, humic acid

1 Introduction

Metals in the aquatic environment may exist as hydrated metal ions, hydroxyl species, and metal complexes. The chemical speciation of metals controlling their toxicity and mobility depends largely on the nature of the metals and the surrounding substances.[1] Dissolved humic substances such as humic and fulvic acids are ubiquitous in the environment. They exist as natural weak polyelectrolytes that are very active in complexing cations.[2] The ability to complex cations is due to their unusual high content of oxygen-containing functional groups, which include COOH, phenolic-, enolic-, alcoholic OH, and C=O.[2,3] Humic acid as a complexing agent has been known to have ability to solubilize metals.[4,5] Spark et al. [5] found that the formation of insoluble $M(OH)_2$ species at higher pH value in the presence of dissolved humic acid is considerably less than that without the presence of humic acid.

For many years efforts have been spent to minimize the risk of metal leaching to groundwaters and to limit the uptake of the contaminants by crops.[6] This may be achieved by immobilizing metallic species through adsorption. Although the adsorption for contaminant removal from water has extensively been conducted, a novel adsorption process is always investigated due to lack of adequate knowledge of adsorption kinetics and especially adsorption mechanism.[7,8] Instead of kinetics and mechanism, capacity and energy are two parameters which are commonly determined in the adsorption.[9-11] Therefore, it is necessary to study adsorption kinetics and mechanism of metal species on particular adsorbent in which the system can represent the natural water system. However, adsorption study of metals in natural water is very complicated considering the metal speciation that may occur. In this study, an aqueous solution system was

prepared to contain two species of Cu(II), i.e. hydrated Cu(II) {hy-Cu(II)} and humic acid complexed Cu(II) {HA-Cu(II)}. The adsorbent chosen was silica gel (SG) due to its reactive surface functional groups such as silanol, relatively low cost, and does not need any special complicated pretreatment.[12] The aim of this paper is therefore to study the adsorption kinetics and mechanism of Hy-Cu(II) and HA-Cu(II) on SG.

2 Experimental

2.1 Material

All reagents in analytical grade i.e. $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, KOH, KCl, CaCl_2 , HCl, HF, and NaOH, were obtained from Merck Co Inc. (Germany) and used without further purification. Silica gel type G-60 used as support material for HA was also purchase from Merck Co Inc. (Germany), while three buffer solutions at pH 4.00, 7.00, and 10.00 for pH calibration were purchased from Fisher Scientific Co (Germany).

Humic acid was isolated from peat soil taken in Siantan Subdistrict, Pontianak, West Kalimantan, Indonesia, according to the procedure of International Humic Substances Society (IHSS).[13] The region in which the peat soil was collected was an area that has not been exposed by agricultural treatment and far from human intervention.

2.2 Immobilization of HA on SG (HA-SG)

Before immobilization, SG was first ultrasonically purified in HCl solution 1:10 for 15 min. This ultrasonic assisted purification greatly reduces the purification time, since the purification of SG by stirring in HCl solution 1:10 without the assistance of ultrasonic wave consumes 24 h.[12] After purification, 66.7 g dm^{-3} HA solution in 0.01M ($M = \text{mol dm}^{-3}$) NaOH was then interacted with a suspension of 100 g dm^{-3} the purified SG in 0.01 M NaOH according to the procedure described in our previous paper. [12] The resulted HA-SG contained 13.05 % (w w⁻¹) HA.

2.3 Speciation of Cu(II) as a Function of Medium Acidity

The speciation of Cu(II) in aqueous solution containing HA-SG was carried out as follows. Into every 50 cm^3 of 20 mg dm^{-3} Cu(II) solution, 50 mg HA-SG was added. The acidity of the mixtures was adjusted to pH 2, 4, 6, and 7.5 using either HNO_3 or NaOH solution and aged overnight. The mixtures were then centrifuged at 10,000 rpm and followed by filtering to separate supernatants. The Hy-Cu(II) in the supernatant was analyzed using Cu(II) ion selective electrode (ISE), while the total concentration of Cu(II) species was quantified using atomic absorption spectrometry (AAS). The concentration of HA-Cu(II) was obtained by subtracting the concentration of Hy-Cu(II) from the total concentration of Cu(II) species.[14]

2.4 Preparation of Sample Containing Hy-Cu(II) and HA-Cu(II)

Sample containing both Hy-Cu(II) and HA-Cu(II) was prepared through the interaction between 50 mg of HA-SG and 50 cm^3 of 20 mg dm^{-3} Cu(II) solution. The acidity of the mixture was adjusted to pH 4 using HNO_3 solution and aged for 24 h. After centrifuging at 10,000 rpm and followed by filtering, the supernatant was then analyzed using Cu(II) ISE and AAS to quantify its Hy-Cu(II) and total Cu(II) species contents, respectively. As performed above, the content of HA-Cu(II) was obtained by subtracting the concentration of Hy-Cu(II) from the total concentration of Cu(II) species.[14]

2.5 Adsorption Kinetics of Hy-Cu(II) on SG

Into 35 cm^3 of the prepared sample above, the tip of the electrode of ISE was appropriately immersed and 35 mg SG was then added. The signal of ISE was recorded continuously as a function of time for 2 h. The concentration of Cu(II) adsorbed on SG as a function of time was calculated by subtracting the remaining concentration of Hy-Cu(II) in solution from the initial concentration of Hy-Cu(II) in the prepared sample. Based on the obtained data, the adsorption rate constant (k_{ad}) and adsorption-desorption equilibrium constant (K) of Hy-Cu(II) on SG was then determined using the formulation of first order adsorption reaching equilibrium,[15] and the energy of adsorption (E) was calculated according to the equation $E = RT \ln K$. [10,11]

2.6 Adsorption Kinetics of HA-Cu(II) on SG

The prepared samples were interacted with SG for 5, 10, 15, 20, 30, 60, and 120 min, the mixtures were then centrifuged at 10,000 rpm and followed by filtering. The total concentration of Cu(II) species in the supernatant was analyzed using AAS. At corresponding interaction time, the difference between the concentration of Cu(II) analyzed using

AAS and that using ISE is the remaining concentration of HA-Cu(II) in solution, while the difference between the remaining concentration of HA-Cu(II) at corresponding interaction time and the initial concentration of HA-Cu(II) gives the concentration of adsorbed HA-Cu(II). As conducted for Hy-Cu(II), the adsorption parameters (k_{ad} , K , and E) of HA-Cu(II) on SG were then determined.

3 Results and Discussion

3.1 Speciation of Cu(II) as a function of medium acidity

The presence of HA-SG in Cu(II) solution caused Cu(II) to be distributed into three kinds of Cu(II) species, i.e. the remaining Hy-Cu(II), the complex of HA-Cu(II), and the adsorbed Cu(II) (Fig. 1). The distribution among these Cu(II) species was pH dependence. The Hy-Cu(II) was the dominant species at pH 2, and its portion was continuously reduced with decreasing the medium acidity. On the contrary, the portion of the adsorbed Cu(II) increased rapidly from its negligible portion at pH 2 to become dominant species at pH higher than 5.5. In case of HA-Cu(II), its portion slightly increased from pH 2 to 4 and then gradually decreased at lower medium acidity.

Although the stability of HA toward dissolution improves substantially with the immobilization on SG, but close inspection shows that the dissolution of the immobilized HA still tends to increase with decreasing medium acidity from pH 2.0 to 7.0. [12] Considering this increase of dissolution for the immobilized HA with decreasing medium acidity, it was surprising that above pH 4, the portion of HA-Cu(II) decreased with decreasing medium acidity (Fig. 1). This evidence may be interpreted that above pH 4, the soluble HA-Cu(II) is re-immobilized on Cu(II)-coated SG to form SG-Cu(II)-HA-Cu(II).

3.2 Preparation of sample containing Hy-Cu(II) and HA-Cu(II)

For studying kinetics of simultaneous adsorption of Hy-Cu(II) and HA-Cu(II) on SG, it is necessary to prepare first a sample containing both Hy-Cu(II) and HA-Cu(II) based on the results of Cu(II) speciation above. As shown in Fig. 1, Hy-Cu(II) and HA-Cu(II) existed on their closest concentration when the medium acidity was at pH 4.0. For that reason, the preparation of sample solution containing both Hy-Cu(II) and HA-Cu(II) for the study of their simultaneous adsorption on SG was done at pH 4.0.

3.3 Adsorption kinetics of Hy-Cu(II) and HA-Cu(II) on SG

Fig. 2 showed clearly that the adsorption of Hy-Cu(II) on SG was much faster to reach equilibrium than the adsorption of HA-Cu(II). Maximum adsorption of Hy-Cu(II) was reached before the adsorption proceeded 1 min. Compared to Hy-Cu(II), the adsorbed HA-Cu(II) on SG was substantially slower. The adsorption still processed when the adsorption time reached 60 min.

The less percentage of the adsorbed Hy-Cu(II) than that of the adsorbed HA-Cu(II) was due to the relatively higher initial concentration of Hy-Cu(II) than HA-Cu(II) in the prepared sample. The difference in their initial concentration could be seen at Fig. 1 where the pH was 4.0.

Fig. 1 Effect of pH on the distribution of Cu(II) species in aqueous solution of Cu(II) containing HA-SG

Parameters used to study the adsorption are the adsorption rate constant (k_{ad}) and adsorption-desorption equilibrium constant (K) which are specific for a reaction and has particular dimension depending on the order of reaction.[16] The k_{ad} and K of Hy-Cu(II) and HA-Cu(II) were separately determined using the formulation of the first order adsorption reaching equilibrium as shown below.[15] By plotting $\ln(C_0/C)/C$ versus t/C , a linear line will be obtained where the slope is k_{ad} and the intercept is K . The application of the formulation to the adsorption data of Fig. 3 gave adsorption parameters as summarized in Table 1.

Fig. 2 Effect of contact time on the adsorption of Cu species on SG at pH 4.0

In the prepared sample where the pH is 4, the SG surface is coated with negative charges since its isoelectric point is about 3.[17,18] These negative charges tend to interact with positively charged species. Therefore, the excess of Hy-Cu(II), which is smaller in size, would be adsorbed first on the surface of SG with high value of k_{ad} . In addition to the much bigger in size, the slow adsorption of HA-Cu(II) could be due to rearrangement within HA-Cu(II) itself, which is initially considered spherical within boundaries hydrated with solvent,[19] while interact with the adsorbent surface. The overall adsorption reaction lead to the adsorbed Hy-Cu(II) as cation bridge between negative charges of SG and HA-Cu(II) as mentioned before.

The magnitude of K which is thermodynamic term does not relate to k_{ad} which is kinetic term.[20] In this study, although the k_{ad} of Hy-Cu(II) was higher than that of HA-Cu(II), but Hy-Cu(II) has K approximately 140 times lower than the K of HA-Cu(II) (Table 1). Therefore, the surface complexes formed from HA-Cu(II) and the surface of SG are more stable.

The relation between K and energy of adsorption (E) which is the energy changing during the adsorption (ΔG^0) is given by $E = -\Delta G^0 = RT \ln K$. [10,11] According to this relationship, the energy evolved during the adsorption on SG was 12.6 kJ mol⁻¹ for Hy-Cu(II) and 24.8 kJ mol⁻¹ for HA-Cu(II). The adsorption of Hy-Cu(II) forming less stable complexes

$$\frac{\ln\left(\frac{C_0}{C}\right)}{C} = k_{ad} \frac{t}{C} + K$$

where C_0 is the initial concentration of adsorbed species (mol dm⁻³), C is the remaining concentration of adsorbed species after sorption at t sorption time (mol dm⁻³), t is adsorption time (min), k_{ad} is adsorption rate constant (min⁻¹), K is adsorption-desorption equilibrium constant (mol⁻¹ dm³).

The adsorption rate constant of Hy-Cu(II) was more than ten fold higher than that of HA-Cu(II) (Table 1). This result leads to the assumption that the adsorption may proceed sequentially. Hy-Cu(II) and HA-Cu(II) have different size and charge property which in turn will influence their rate of adsorption on SG. The size of Hy-Cu(II) can be expected much smaller than that of HA-Cu(II) but it is more positively charged.

Table 1 Adsorption parameters and correlation coefficient (R^2) of the plot of $\ln(C_0/C)/C$ vs t/C for the adsorption of Hy-Cu(II) and HA-Cu(II) on SG at pH 4.0

Adsorbed species	Adsorption parameters			
	k_{ad} (min ⁻¹)	K (mol ⁻¹ dm ³)	E^* (kJ mol ⁻¹)	R^2
Hy-Cu(II)	0.49	159	12.6	0.980
HA-Cu(II)	0.05	22,353	24.8	0.986

* $E = RT \ln K$

on SG. In attracting Hy-Cu(II), the active site of SG, which is mainly composed negatively charged oxygen from the ionized silanol group, will be hindered by water molecules surrounding Cu(II). Therefore, the adsorption of Hy-Cu(II) on SG is dominantly directed by electrostatic interactions through outer-sphere complexation of Cu(II) on negatively charged ionized silanol group. In this electrostatic interaction to form an outer-sphere complexation, both ionized hydroxyl group and Cu(II) maintain their hydration sheath. Electrostatic interaction through outer-sphere complexation is typically rapid and the interaction is relatively weak in nature.[21]

In the second step of adsorption, the degree of electrostatic interaction between Cu(II)-coated SG and HA-Cu(II) is not as large as that between Cu(II) and the negatively charged ionized hydroxyl group on SG surface. It can be understood since part of the negative charges of the dissolved HA has been neutralized by Cu(II) to form complex substance. Therefore, the adsorption is assumed to be favored by ligand exchange between bound water molecule on the adsorbed Cu(II) on SG and oxygen on the remaining ionized carboxyl groups of HA-Cu(II). In this mode of interaction, the hydration sheath has no longer been maintained, and consequently a strong chemical bond is formed.

The above suggestions were in agreement with the results obtained from the kinetic study of selenite adsorption on goethite surface.[22] Two steps of adsorption were involved, i.e. rapid formation of outer-sphere surface complex through electrostatic interaction was in the first step and followed by the slower formation of inner-sphere complex for the second step.

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