The Determination of Active Site, Capacity, Energy and Rate Constant on the Adsorption of Zn(II) and Cd(II) on Chitin

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Abstract

Active sites, capacity, energy, and rate constant on the adsorption of Zn(II) and Cd(II) on chitin isolated through deproteination followed by demineralization processes of crab (Portunus pelagicus Linn) shell have been investigated. The chitin possessed acetamide functional group that was suggested to exist in two different chemical forms of NHC(O)CH₃ and NHC(OH)=CH₂. It means that one hydrogen ion in CH₃ in the acetamide can be conjugated to oxygen carbonyl to form C-OH. The active site responsible for the adsorption of Zn(II) and Cd(II) would be nitrogen on the acetamide functional group. The adsorption data for both metal ions were fit quite well with the Langmuir isotherm model, resulting the adsorption capacities of 3.2 × 10⁻⁴ and 2.8 × 10⁻⁴ mol g⁻¹ for Zn(II) and Cd(II), respectively, and adsorption energies of 15.1 kJ mol⁻¹ for Zn(II) and 17.9 kJ mol⁻¹ for Cd(II). It was also revealed that Zn(II) was adsorbed slightly faster than Cd(II) with first order adsorption rate constants of 2.7 × 10⁻³ min⁻¹ for Zn(II) and 2.6 × 10⁻³ min⁻¹ for Cd(II).

1 Introduction

Discharge of industrial wastes containing heavy metals continuously degrades the environmental quality in especially many developing countries. This is the reason why effort to eliminate or at least to minimize the metal content in the environment always receives much attention. One effort to minimize the metal content in the industrial wastes and environment can be performed through adsorption. To achieve this purpose, various types of adsorbent have already been applied. These include the utilization of invaluable material such as tropical soils,[1] peat soil,[2] diatomae earth,[3] chitin,[4,5] chitosan,[6,7] bentonite,[8,9] and so on. Compared to other techniques, this adsorption technique in minimizing the metal content possesses the advantages in term of simplicity and relatively low cost of operation.

In the case of chitin as an adsorbent, it is predicted that the adsorption of metal ions on the adsorbent may proceed through the combination of ion exchange and complexation processes.[7] The ion exchange mechanism usually plays a dominant role in adsorption of alkali earth metal ions like Ca²⁺, while complexation mechanism is dominant on the adsorption of transition metal ions. In the complexation mechanism, -NHCO- (amide) group of chitin is said to act as active site for the adsorption.[7] Since –NHCO- group on chitin contains N and O elements with one and two lone pair electrons, respectively, both may be able to interact with a metal ion. Unfortunately, it is still unclear which element, N, O or both of them, that is really responsible for the adsorption. For that reason, more detailed study is necessary. Zinc(II) and Cd(II) were selected to study this aspect. In addition, the determination of kinetic and thermodynamic parameters such as capacity, rate constant and energy of adsorption are also presented.
2 Experimental

2.1 Materials

Chitin was prepared from crab (*Portunus pelagicus* Linn) shell through deproteination followed by demineralization processes according to the method of Hong *et al.*[10] All reagents in analytical grade *i.e.* ZnCl₂, CdCl₂, HCl, and NaOH, were obtained from Merck Co Inc. (Germany) and used without further purification.

2.2 Active site identification

The identification of the functional group acted as active sites responsible for the adsorption of Zn(II) and Cd(II) was performed by using Fourier Transform Infra Red (FTIR) spectroscopy after interacting for 2 hours 100 mg chitin with 50 cm³ of 10,000 mg dm⁻³ Zn(II) and 10,000 mg dm⁻³ Cd(II), respectively. As a control, the identification of the functional group of chitin was also conducted.

2.3 Adsorption rate

The evaluation of the adsorption rate of metal ion on chitin was based on the assumption that the adsorption obeyed Langmuir isotherm model with first order adsorption reaching equilibrium. Based on this assumption, the first order adsorption rate constant (k₁) is determined from the slope of the plot of \( \frac{\ln(C_0/C)}{C} = k_1 \frac{t}{C} + K \) from the following equation:[11]

\[
\frac{\ln(C_0/C)}{C} = k_1 \frac{t}{C} + K
\]

Where \( C_0 \) is the initial concentration of metal ion in the solution, \( C \) is the concentration of metal ion after \( t \), \( t \) is adsorption time, and \( K \) is adsorption equilibrium constant.

2.4 Capacity and energy of adsorption

Capacity and energy of adsorption of Zn(II) and Cd(II) on chitin was calculated based on the Langmuir isotherm model according to the equation:

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

Where \( C \) is the metal ion concentration in the solution after adsorption reaches equilibrium, \( m \) is mol metal ion adsorbed on 1 g chitin, \( K \) is equilibrium constant, and \( b \) is maximum amount of metal ion adsorbed on chitin (adsorption capacity).

By plotting \( C/m \) against \( C \), the values of \( b \) and \( K \) can be obtained from the slope and intercept, respectively. After obtaining \( K \), the adsorption energy was then calculated according to the equation \( E = -RT \ln K \).

3 Results and Discussion

3.1 Active site identification

Chitin is a natural polysaccharide containing N-acetyl-D-glucosamine as repeating unit which is held together with β 1→4 bond.[7] As a result, the two-dimensional visualization of chitin always shows the presence of NHCOCH₃ group (Fig. 1).

In this study, FTIR spectroscopy revealed the main absorption bands of chitin at the region of 1031.8 (C-O stretching), 1448.4 (C-H deformation of CH₃, C-H bending of CH₂, and C=O stretching), 1629.7 (O-H stretching of C=O conjugated and N-H bending),
2895.0 (C-H stretching of CH$_2$), and 3448.5 cm$^{-1}$ (O-H stretching of aliphatic and phenolic –OH). The presence of the 1031.8 (C-O stretching) and 2895.0 cm$^{-1}$ (C-H stretching of CH$_2$) bands seem to be disagree with the chemical structure of the N-acetyl group in the form of NHCOCH$_3$ (Fig. 1). If it is assumed that in addition to C-H deformation of CH$_3$ and C=O stretching, C-H bending of CH$_2$ also contributes to the generation of the 1448.5 cm$^{-1}$ band, and in addition to N-H bending, O-H stretching of C=O conjugated also contributes to the appearance of the 1629.7 cm$^{-1}$ band, so it is reasonable to think that N-acetyl group in chitin may be present in an equilibrium condition between two different chemical forms of NHCOCH$_3$ and NHCO=CH$_2$ (Fig. 2).

After adsorption of Zn(II) or Cd(II), the intensity of the 1031.8, 2895.0, and 3448.5 cm$^{-1}$ bands increased, that of the 1448.4 cm$^{-1}$ band highly increased, while the intensity of the 1629.7 cm$^{-1}$ band was relatively unchanged. The strong increase on the intensity of the 1448.4 cm$^{-1}$ absorption band after adsorption may be interpreted as a result of the overlapping of the original band (before adsorption) and a new band generated after the adsorption.

By examining the elements composing the N-acetyl group of chitin, it is predicted that the active site for the adsorption of Zn(II) and Cd(II) may be either N or O element. Considering that O element in the N-acetyl group is involved in conjugation to form the chemical structure of NHCOH=CH$_2$ as described above (Fig. 2), so N becomes the most possible element which acts as the active site of the adsorption.

Considering the Hook’s equation, the interaction between Zn(II) and Cd(II) with N element in N-acetyl group must result the shift of N-H bending band to lower wave number. Before the adsorption, N-H bending band appears at 1629.7 cm$^{-1}$; and after adsorption Zn(II) and Cd(II), this 1629.7 cm$^{-1}$ band may shift to the region of 1448 cm$^{-1}$, overlaps and consequently enhances the intensity of the original 1448.4 cm$^{-1}$ band that has already existed. Unfortunately, the shift of N-H bending band from 1629.7 to the region of 1448 did not cause the decrease of the intensity of the 1629.7 cm$^{-1}$ band. Therefore, there will be an additional evidence that the adsorption of Zn(II) and Cd(II) may result the intensity enhancement of the 1629.7 cm$^{-1}$ band and also the enhancement of the 1031.8, 2895, and 3448.5 cm$^{-1}$ bands. The intensity enhancement of these bands can only be explained if the adsorption results the shift of equilibrium in Fig. 2 to the right. As a result, the intensity of C-O stretching, C-H bending of CH$_2$, O-H stretching of C=O conjugated, C-H stretching of CH$_2$, and O-H stretching of aliphatic –OH, respectively at 1031.8, 1448.4, 1629.7, 2895.0, and 3448.5 cm$^{-1}$ increased. The intensity increase at 1629.7 cm$^{-1}$ caused by the higher amount of O-H stretching of C=O conjugated may approximately balance the intensity decrease caused by the shift of N-H bending band to the region of 1448 cm$^{-1}$.

### 3.2 Capacity, energy, and rate of adsorption

Plotting $\ln(C_0/C)/C$ against $t/C$ of the equations (1), and $C/m$ against $C$ of the equation (2) results, respectively, the first order rate constant ($k_1$), and capacity ($b$), and equilibrium constant ($K$) of adsorption as shown in Table 1.

It is clear that Zn(II) and Cd(II) were adsorbed at the relatively same adsorption rate. If the small difference on the adsorption rate constant of both metal ions is assumed to be significant, it may be caused by the difference on the size of the ions and the nature of their interaction with the active sites on chitin. Zn(II) is smaller than Cd(II), and as mentioned before that its interaction with active sites on chitin is more polar. These two aspects may contribute to
the relatively faster adsorption of Zn(II) than Cd(II). The smaller size of Zn(II) than Cd(II) must also be the main reason for the higher adsorption capacity of chitin for Zn(II) than for Cd(II).

The adsorption of Zn(II) and Cd(II) on chitin was performed in polar (aqueous) medium, and as has already been described above, the interaction of Zn(II) with the active sites was more polar than that for Cd(II) with the active sites. Since the more polar interaction for Zn(II) with the active sites exists in polar medium, its interaction will be weakened and therefore its interaction energy becomes smaller than the interaction energy of the less polar interaction between Cd(II) and the active sites. This argument must be the main reason for the smaller adsorption energy for Zn(II) compared to Cd(II).

References