

## SORPTION-DESORPTION MECHANISM OF Zn(II) AND Cd(II) ON CHITIN

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### ABSTRACT

This study reports the results of the elucidation of the sorption-desorption mechanism of Zn(II) and Cd(II) on chitin through the determination of capacity, energy, and rate constant of sorption as well as the investigation of their desorption properties in NaCl and Na<sub>2</sub>EDTA solutions. The chitin was isolated through deproteinization followed by demineralization of crab (*Portunus pelagicus* Linn) shell using NaOH solutions. The sorption of both metal ions followed the Langmuir isotherm model, resulting the sorption capacities of  $3.2 \times 10^{-4}$  and  $2.8 \times 10^{-4}$  mol g<sup>-1</sup> for Zn(II) and Cd(II), respectively, and sorption energies of 15.1 kJ mol<sup>-1</sup> for Zn(II) and 17.9 kJ mol<sup>-1</sup> for Cd(II). It was also observed that Zn(II) was sorbed slightly faster than Cd(II) with first order sorption rate constants of  $2.82 \times 10^{-3}$  min<sup>-1</sup> for Zn(II) and  $2.61 \times 10^{-3}$  min<sup>-1</sup> for Cd(II). The result of the desorption experiment showed that Cd(II) and especially Zn(II) could only be exchanged by Na(I) after desorbing those metal ions by strong chelating agent of EDTA<sup>2-</sup>. The easier desorption of Zn(II) than Cd(II) by EDTA<sup>2-</sup> must be attributed by the smaller sorption energy of Zn(II) and by harder acid property of Zn(II) than Cd(II) as EDTA<sup>2-</sup> contained hard electron donor elements.

**Keywords:** sorption, desorption, chitin, Zn(II), Cd(II).

### INTRODUCTION

Because of the widespread pollution of water by human activity, water treatments have been the subject of numerous investigations. Chemical precipitation, membrane separation, and sorption are the major techniques applied to minimize the metal content in waters [1]. Compared to the sorption technique, chemical precipitation and reverse osmosis become inefficient when metal ions are present in trace concentrations [1,2]. Moreover, membrane process including reverse osmosis and electrodialysis is generally expensive in its application [3]. For that reason, sorption technique becomes promising alternative available [1].

Various types of sorbent materials have already been applied to remove metal ions. These include the utilization of activated carbon [4,5], metal oxides [6,7], bentonite [8,9], chitin [10], chitosan [10,11], exchange resins [12,13], and invaluable materials such as tropical soils [14], diatomeae earth [15], and peat soil [16]. Some of those materials such as ion exchange resins are highly effective but expensive. In contrast, other materials such as tropical soils, and activated alumina, diatomeae earth, and bentonite are inexpensive but ineffective. Activated carbon and humic acids in peat soil seem to be very effective in removing metal ions, but these materials are readily soluble under high pH condition [17].

In the case of chitin, this material is very cheap in the countries like Indonesia with the longest coastal line

in the world, because it is isolated from invaluable crustacean shell waste produced largely in many areas. As a sorbent, it is predicted that the sorption of metal ions on chitin may proceed through the combination of ion exchange and complexation processes [18]. The ion exchange mechanism usually plays a dominant role in sorption of alkali earth metal ions like Ca(II), while complexation mechanism is dominant on the sorption of transition metal ions. In the complexation mechanism, acetamide group in chitin is believed to act as active site for the sorption [18]. Since the acetamide group on chitin contains N and O elements with one and two lone pair electrons, respectively, both atoms may be able to interact with a metal ion. At present, it is still unclear which element, N, O or both of them, is really responsible for the sorption. Chui *et al.* [19] pointed out that nitrogen in the acetamide group was the responsible element interacting with transition metal ions, while Lerivrey *et al.* [20] stated that oxygen of the acetamide group and -OH group in chitin were involved in the complexation. For that reason, more detailed study is necessary to be done. Zinc(II) and Cd(II) were selected to study this aspect. In addition, the determination of some sorption parameters such as capacity, rate constant and energy, as well as evaluation on the contribution of cation exchange and chelating mechanisms on the desorption of Zn(II) and Cd(II) from chitin are also presented.

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## EXPERIMENTAL SECTION

### Materials

Chitin was prepared from crab (*Portunus pelagicus* Linn) shell through deproteination followed by demineralization processes according to the method of Hong *et al.*[21]. All reagents in analytical grade i.e. ZnCl<sub>2</sub>, CdCl<sub>2</sub>, HCl, NaOH, NaCl, and Na<sub>2</sub>EDTA were obtained from Merck Co Inc. (Germany) and used without further purification.

### Experimental Section

#### Capacity and Energy of Sorption

Experiments for the determination of capacity and energy of sorption were carried out using a batch-type reactor of a 50-mL Erlenmeyer in a water bath at 25 ± 0.1 °C. The effective volumes of the metal ion solutions were 10 mL, and the concentrations of metal ion in the solutions were varied from 2 to 5,000 mg/L. Into each metal solution, 100 mg chitin was added and followed by continuous stirring for 2 hours. After stirring, the solutions were immediately filtered through 0.45-µm membrane filter.

The concentration of Zn(II) and Cd(II) in the supernatant was analyzed by using atomic absorption spectrometer (AAS). Sample and blank solutions were analyzed under the same conditions. The amount of ion metal sorbed was calculated by the difference between the initial and the amount remaining in the reacting solution.

#### Sorption Rate

Experiments for the determination of sorption rate were also carried out using a batch-type reactor of a 50-mL Erlenmeyer in a water bath at 25 ± 0.1 °C. The initial volume and metal ion concentration were 10 mL and 100 mg/L, respectively. To each solution, 100 mg chitin was added and stirred continuously. At selected time periods, a sample is immediately filtered through 0.45 µm membrane filter.

In every selected time period, the concentration of Zn(II) and Cd(II) in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same conditions. The amount of ion metal sorbed was calculated by the difference between the initial and the amount remaining in the reacting solution.

#### Sorption Mechanism

The sorption mechanism for Zn(II) and Cd(II) on chitin was evaluated based on the desorption data of the sorbed metal ions which are desorbed using desorption reagents of NaCl and Na<sub>2</sub>EDTA. The experiment was carried out as follow: One gram chitin was first interacted with 15 mL of 500 mg L<sup>-1</sup> Zn(II) or 500 mg/L Cd(II) for 2

hours using a batch-type reactor of a 50-mL Erlenmeyer in a water bath at 25 ± 0.1 °C. The sorbed amounts of Zn(II) and Cd(II) on chitin was calculated by the difference between the initial amount of Zn(II) and Cd(II) in the solution and their remaining amounts in the solution after interaction. The sorbed metal ion on 100 mg chitin was then desorbed in the batch-type reactor using 0.1 M Na<sub>2</sub>EDTA or 0.1 M NaCl solution. The content of metal ion on the filtrate after desorption was determined using AAS.

## RESULT AND DISCUSSION

### Capacity and Energy of Sorption

The sorption profiles of Zn(II) and Cd(II) on chitin as a function of the initial metal ion concentrations are given in Fig. 1. The sorption of both metal ions was non-linear and the sorption rapidly increased at low level of initial concentration of metal ions from 0 to 0.03 mol L<sup>-1</sup> for Zn(II) and from 0 to 0.018 mol L<sup>-1</sup> for Cd(II). Then, the sorption only increased slightly when the applied metal ion concentration was higher than 0.03 mol L<sup>-1</sup> for Zn(II) and 0.018 mol L<sup>-1</sup> for Cd(II). Since the weight of sorbent used in this experiment is 100 mg, it seems that the application of 0.03 mol L<sup>-1</sup> Zn(II) or 0.018 mol L<sup>-1</sup> Cd(II) results in the nearly saturated sorption of Zn(II) or Cd(II) on 100 mg chitin.

From the data in Fig. 1, capacity and energy of sorption of Zn(II) and Cd(II) on chitin are calculated based on the Langmuir isotherm model according to the equation (1)

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \quad (1)$$

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

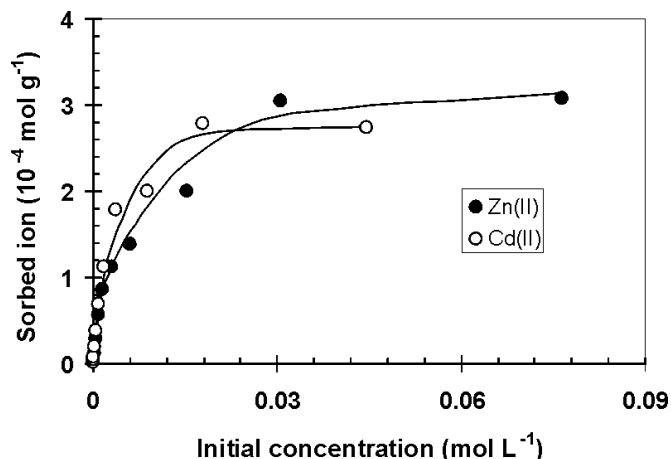
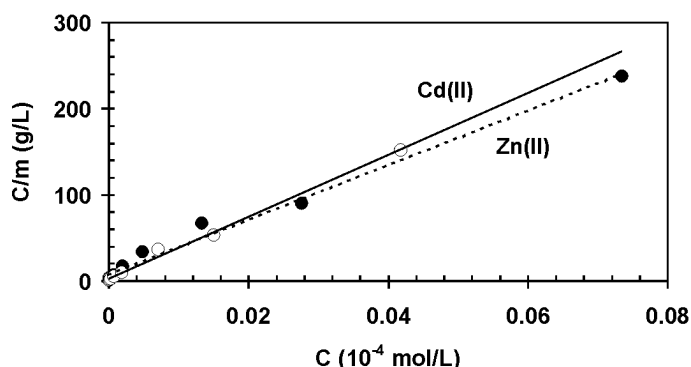


Fig 1 Adsorption isotherm (25 °C) of Zn(II) and Cd(II) on chitin



**Fig 2** Plot of  $C/m$  against  $C$  from the Langmuir adsorption isotherm of Zn(II) and Cd(II).

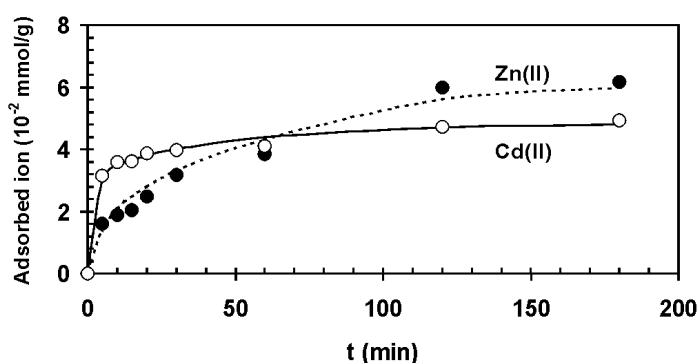
By plotting  $C/m$  against  $C$  (Fig. 2), the values of  $b$  and  $K$  can be obtained from the slope and y-intercept, respectively. After obtaining  $K$ , the sorption energy is then calculated according to the equation  $E_{\text{sorp}} = -\Delta G^0_{\text{sorp}} = RT \ln K$ . The resulted values of  $b$ ,  $K$  and  $E$  for the sorption of Zn(II) on chitin were  $3.2 \times 10^{-4} \text{ mol g}^{-1}$ ,  $428 \text{ (mol dm}^{-3}\text{)}^{-1}$ , and  $15.1 \text{ kJ mol}^{-1}$ , respectively. In the case of Cd(II), those values were  $2.8 \times 10^{-4} \text{ mol g}^{-1}$ ,  $1300 \text{ (mol dm}^{-3}\text{)}^{-1}$ , and  $17.9 \text{ kJ mol}^{-1}$ , respectively. The linearity ( $R^2$ ) of the plot was 0.988 and 0.996 for Zn(II) and Cd(II), respectively.

It is clear that the sorption capacity of chitin for Zn(II) is higher than that for Cd(II). This fact may be caused by the difference on the size of the ions and the nature of their interaction with the active sites of chitin. In coordination number 4, for example, zinc(II) with the radius of  $0.74 \text{ \AA}$  is smaller than Cd(II) ( $0.94 \text{ \AA}$ ) [22], and its interaction with active sites on chitin is more polar, since the electronegativity of Zn, i.e. 1.6 is smaller than that of Cd, i.e. 1.7 [23]. With smaller size, more Zn(II) than Cd(II) will be able to be accommodated by chitin. With more polar interaction with the active sites of chitin, Zn(II) is more flexible in adjusting its position around the active sites.

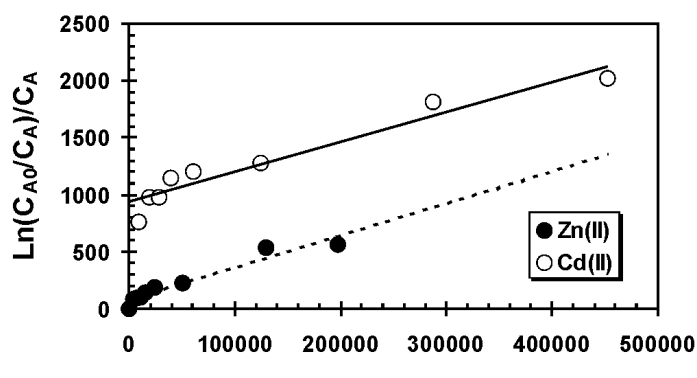
The sorption of Zn(II) and Cd(II) on chitin is performed in polar (aqueous) medium, and as it has already been described above, the interaction of Zn(II) with the active sites is more polar than that of Cd(II) with the active sites. Since the more polar interaction for Zn(II) with the active sites exists 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 sorption energy for Zn(II) as compared to that for Cd(II).

### Rate of Sorption

The sorption profiles of Zn(II) and Cd(II) as a function of interaction time is presented in Fig. 3. The sorption is initially rapid and then goes slower. The initial



**Fig 3** Sorption of Zn(II) and Cd(II) on chitin as a function of interaction time.



**Fig 4** Plot of  $\ln(C_{A0}/C_A)/C_A$  against  $t/C_A$  for the determination of sorption rate constant of Zn(II) and Cd(II) on chitin.

rapid sorption was observed for the first 10 min for both Zn(II) and Cd(II). After the first 10 min, Cd(II) was then slowly sorbed, while Zn(II) was still relatively sorbed rapidly. Although the sorbed Zn(II) was smaller than Cd(II) in the early step of sorption, but it became higher after the sorption was longer than 60 min.

The calculation of the sorption rate is based on the assumption that the sorption obeyed Langmuir isotherm model reaching equilibrium as expressed in eq. 2 [24].

$$\ln\left(\frac{C_{A0}}{C_A}\right) = k_1 \frac{t}{C_A} + K \quad (2)$$

Plot of  $\frac{\ln(C_{A0}/C_A)}{C_A}$  versus  $t/C_A$  give, a straight line with the slope is equal to the sorption rate constant ( $k_1$ ). For Zn(II) and Cd(II), plotting  $\frac{\ln(C_{A0}/C_A)}{C_A}$  against  $t/C_A$  of

the equations (2) (Fig. 4) resulted in linear relationship with linearity ( $R^2$ ) as high as 0.932 and 0.933, respectively. Based on the slopes of the plots, the

obtained sorption rate constants ( $k_1$ ) for Zn(II) and Cd(II) were relatively the same, i.e.  $2.82 \times 10^{-3}$  and  $2.61 \times 10^{-3} \text{ min}^{-1}$ , respectively. If the small difference on the sorption rate constant of both metal ions is assumed to be significant, it may be due to the fact that Zn(II) is smaller than Cd(II), and as already mentioned before that its interaction with active sites on chitin is more polar. These two aspects considered to contribute to the relatively faster sorption of Zn(II) than Cd(II).

### Sorption Mechanism

Results on the desorption of Zn(II) and Cd(II) sorbed on chitin using NaCl and Na<sub>2</sub>EDTA solutions are summarized in Table 1. Upon the employment of NaCl at the concentration of Na(I) 208 times higher than that of the sorbed Zn(II) on chitin, the desorbed Zn(II) from chitin was only 11.61%. This desorbed Zn(II) increased only to 20.32% if the applied concentration of Na(I) in NaCl solution was enhanced to 1040 times higher than that of the concentration of sorbed Zn(II). The relatively similar trends was also observed for Cd(II). The use of NaCl solution at the concentration of Na(I) 258 and 1286 times higher than that of the sorbed Cd(II) on chitin resulted in desorption of Cd(II) from chitin only as high as 16.53 and 26,62%, respectively. Therefore, it is evident that Na(I) in NaCl form is not strong enough in replacing Zn(II) and Cd(II) from their positions in the active sites of chitin.

Contrary to Na(I) in the form of NaCl, Na(I) in the form of Na<sub>2</sub>EDTA is much powerful in replacing Zn(II) and Cd(II) from the active sites of chitin. The use of Na<sub>2</sub>EDTA at the concentration of Na(I) that was only 21 times higher than that of the sorbed Zn(II) resulted in 95.79% desorption of Zn(II). In the case of Cd(II), the employment of Na<sub>2</sub>EDTA at the concentration of Na(I) 24 times higher than that of the sorbed Cd(II) resulted in 73.80% desorption of Cd(II).

**Table 1** Desorption test for Zn(II) and Cd(II) sorbed on chitin using NaCl and Na<sub>2</sub>EDTA solutions for 2 hours

Desorption agent	Mol ratio		Desorption (%)	
	Na(I) / sorbed Zn(II)	Na(I) / sorbed Cd(II)	Zn(II)	Cd(II)
NaCl	0	-	0.00	-
	208	-	11.61	-
	1040	-	20.32	-
	-	0	-	0.00
	-	258	-	16.53
	-	1286	-	26.62
Na <sub>2</sub> EDTA	21	-	95.79	-
	-	24	-	73.80

The significantly higher ability of Na(I) in the form of Na<sub>2</sub>EDTA solution than Na(I) in the form of NaCl solution in exchanging the sorbed Zn(II) and Cd(II) from the active sites of chitin must be associated with the different ability of EDTA<sup>2-</sup> and Cl<sup>-</sup> anions in attracting the adsorbed metal ions. EDTA<sup>2-</sup> is a good chelating agent for various metal cations, while Cl<sup>-</sup> is very poor complexing agent. As a result, EDTA<sup>2-</sup> has higher ability to compete with the active sites of chitin in fighting the targeted metal ions than Cl<sup>-</sup>. In Na<sub>2</sub>EDTA solution, therefore, the interaction of Zn(II) and Cd(II) with the active sites of chitin is weakened and leads to the easier replacement by Na(I).

As has been mentioned that the employment of Na<sub>2</sub>EDTA at the concentration of Na(I) 21 times higher than that of the sorbed Zn(II) on chitin resulted in 95.79% desorption of Zn(II), while the employment of Na<sub>2</sub>EDTA at the concentration of Na(I) 24 times higher than that of the sorbed Cd(II) resulted in 73.80% desorption of Cd(II). Therefore, it is reasonable to conclude that Na(I) in Na<sub>2</sub>EDTA solution is able to desorb more Zn(II) than Cd(II). The ability of Na(I) in Na<sub>2</sub>EDTA solution to desorb more Zn(II) than Cd(II) is in accordance with the difference ability of EDTA<sup>2-</sup> in chelating the both metal ions.

The functional group in EDTA<sup>2-</sup> that is responsible for binding metal cation is carboxyl group. According to HSAB principle, carboxyl group belongs to hard base [25]. Since Zn(II) with smaller size than Cd(II) is harder acid than Cd(II), so compared to Cd(II), Zn(II) interact with the carboxyl group of EDTA<sup>2-</sup> more favorably and hence the interaction is stronger. Indeed, Zn(II) belongs to intermediate acid, while Cd(II) is soft acid [25]. In addition, as has been mentioned above that the sorption energy of Zn(II) on chitin was smaller than that of Cd(II). This fact should also contribute to the easier attraction of Zn(II) than Cd(II) by EDTA<sup>2-</sup> from its interaction with the active sites of chitin.

### CONCLUSION

The sorption of Zn(II) and Cd(II) on chitin is non-linear and follows quite well the Langmuir isotherm model. Since the size of Zn(II) is smaller than that of Cd(II), the sorption capacity of chitin for Zn(II) is higher than that for Cd(II). In addition, due to the smaller electronegativity of Zn(II) than that of Cd(II), the interaction of Zn(II) with the active sites on chitin is more polar. With more polar interaction and smaller size, the relatively faster sorption of Zn(II) than Cd(II) may result. Another consequence for the more polar interaction for Zn(II) than Cd(II) is that the energy for the sorption of Zn(II) in aqueous solution onto chitin is smaller than that of Cd(II). This lower sorption energy for Zn(II) should contribute to the easier attraction of Zn(II) than Cd(II) by EDTA<sup>2-</sup> from its interaction with the active sites of chitin. Besides that, compared to Cd(II),

the ability of EDTA<sup>2-</sup> itself to attract Zn(II) is higher because the hard base character of the carboxyl group in EDTA<sup>2-</sup> is more suitable to harder acid of Zn(II) than to Cd(II).

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