Comparison of Adsorption Models for Cd and Zn in the Berau Delta: Water–Sediment System

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Abstrak

Perbandingan Model Penyerapan Cd dan Zn di Delta Berau: Sistem Perairan-Sedimen

Adsorpsi merupakan proses penting dalam mengontrol transfer logam dari larutan ke padatan. Cd dan Zn merupakan logam yang banyak digunakan manusia sehingga berpotensi banyak dibuang ke lingkungan. Penelitian ini membandingkan model adsorpsi Cd dan Zn dalam sistem air laut-sedimen di delta Berau, Kalimantan Timur. Sampel air dan sedimen didapat di 12 stasiun. Untuk mendapatkan konsentrasi Cd dan Zn, sampel air dianalisis menggunakan metode back extraction yang menggunakan bahan kimia organik (Amonium pirolidinditio karbamat dan metili sobutil keton) dan anorganik (asam nitrat). Sampel sedimen dianalisis menggunakan distruksi asam yang mengacu metode dari USEPA 3050b. Data yang didapat dikalkulasi berdasar model adsorpsi yaitu: Model partisi, Freundlich Model dan Langmuir Model. Dalam perhitungan di studi ini, Delta Berau dibagi menjadi dua bagian: bagian utara dan bagian selatan. Dari kedua bagian ini, Model isotermis langmuir merupakan model yang paling cocok untuk proses adsorpsi dalam sistem air sedimen. Di sungai bagian utara, hasil perhitungan linearitas memberikan angka R^2=0.949 untuk Cd dan R^2=0.838 untuk Zn, sedangkan, untuk sungai bagian selatan nilai R^2=0.575 untuk Cd dan R^2=0.944 untuk Zn. Kapasitas adsorpsi maksimum Cd adalah 0,5-0,6 mg.kg^{-1} sedangkan kapasitas adsorpsi maksimum untuk Zn adalah 12-43 mg.kg^{-1}. Prediksi kapasitas maksimal sedimen menggambarkan total kapasitas sedimen sebagai Cd dan Zn deposit. Penambahan Cd dan Zn akan menyebabkan logam-logam tersebut tidak teradsorpsi dan berpotensi racun bagi organisme perairan.

***Kata kunci**: delta Berau, adsorpsi, air, sedimen, model isotermis langmuir*

Abstract

Adsorption is important process for controlling metals transfer from dissolved phase to solid phase. Cd and Zn become trace metal which generally used in human activity and the release of those trace metals into aquatic environment cannot be evaded.The purpose of this work was to compare adsorption models of Cd and Zn in water-sediment system in Berau Delta, East Kalimantan. Sediment and water sample were collected at 12 stations. Measuring Cd and Zn concentration, water sample analysis was conducted using organic chemicals (Ammonium Pyrrolidine Dithio Carbamate and Methyl Isobutyl Ketone) and inorganic chemicals (nitric acid) based on back extraction procedure. On the other hand, sediment analysis was conducted using acid destruction according to USEPA method 3050b. The data would be calculated in some different adsorption model: Partition model, Freundlich model and Langmuir model. In this study, Berau Delta was divided into two groups: North river stream (N) and South river stream (S). In both groups,Langmuir isotherm model was the most representative model for adsorption process in water-sediment system. In North stream, the linearity of data gave R^2=0.949 for Cd and R^2=0.838 for Zn, whereas, R^2=0.575 for Cd and R^2=0.944 for Zn calculated in the South stream. Maximum adsorption capacity of Cd was 0.5-0.6 mg.kg^{-1} and maximum adsorption capacity of Zn was 12-43 mg. kg^{-1}. Those maximal adsorption capacities illustrated the total capability of sediment as Cd and Zn deposit. Another Cd and Zn input will not be adsorbed and probably become bioavailable for aquatic life.

***Keywords**: Berau delta, adsorption, water, sediment, langmuir isotherm model*

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Introduction

Trace metals like Cd and Zn are essential, however, in particular concentration level, metals can potentially become endanger organisms (Lane *et al*., 2005). Below an inorganic zinc concentration of about 2 pmol.kg^{-1}, some species of phytoplankton become growth limited (Ellwood, 2004). Having Zn-limited content in environment, phytoplankton will uptake Cd instead of Zn to maintain its growth rate although Cd cannot completely replace Zn. Cd is toxic metal for human and it can cause lung and kidney damage, decalcification of bone as well (Fernández *et al*., 2010).

Anthropogenic activities, in most locations, alter trace metals concentration via riverine runoff and atmospheric fallout (Luoma and Rainbow, 2008; Hosono *et al*., 2010; Wang *et al*., 2011). Metals input in aquatic ecosystem can be absorbed/ adsorbed by seston (plankton and inorganic particle) (Hendry *et al*., 2008) or sink into bottom sediment (Sakellari *et al*., 2011). Adsorption in sediment is important process for decreasing dissolved trace metals concentration in the water column (Dali-Youcef *et al*., 2006; Apeti *et al*., 2009), however, benthic organisms are treated by sediment enriched metals (Lepland *et al*., 2010).Ecological risk of metal isnot determined by total metal content alone, the adsorption ability of metals to particulate phase is also important (Luoma and Rainbow, 2008).

There were three models generally used to predict adsorption process: Partitioning model, Freundlich model and Langmuir model (Muzakky, 2008). Partitioning model is the relative concentration of each contaminant in each phase and become useful parameter to compare the sorptive capacities of different materials for any particular ions (Luoma and Rainbow, 2008; Seo *et al*., 2008). On the other hand, Langmuir and Freundlich model were used in both riverine (Jain *et al*., 2004) and estuarine system (Gerringa *et al*., 1995) and usefull to predict sorption capacity of particle (Kozar *et al*., 1992; Holmes *et al*., 2012). Freundlich equation is used for heterogenous surface energy term and widely use to model adsorption of pollutant from aqueous medium (Dahiya *et al*., 2008). Langmuir equation can be used not only in adsorption of gases to solids but adsorption of subtances, in solution form, on an insoluble adsorbent also (Ghabbour and Davies, 2011).

Estuarine environment is dynamic ecosystem influenced by terrestrial and oceanic area (Sanusi, 2006). Human activities have greatly influenced Berau Delta causing ecological pressure (Pemkab Berau, 2012). The purpose of this work was to compare adsorption models of Cd and Zn in the Berau Delta that perhaps demonstrate sediment role in controlling pollution.

Material and Methods

Sediment and water samples were collected from Berau Delta at 12 stations, along geographycal area 117^0 41' 7" E - 117^0 53' 59" E and 2^0 1' 28"N - 2^0 12' 27" N (Figure1). In each station, water sample was collected using van dorn water sampler.About 1 L of the water sample was filtered using 0.45 µm nitrate-celloluse Whatmann filter and acidify to pH<2. The preserved water samples were transferred into pre-cleaned polyethylene box. Whereas, surface sediment sample, 0-10 cm beneath water column-bed sediment interface, was taken using stainless steel grap. Homogenous sediments was stored in polyethylene box under cool temperature (Hutagalung *et al*., 1997). To ensure clean method, all glasswares and polyethylene boxes were rinsed for 24 hours in HNO_3 (1+1) before used (Standard Method, 1992).

In Inorganic Chemistry Laboratory-Research Center for Oceanography, Cd and Zn in sediment analyses were conducted using USEPA (1996) 3050b method. Acid digestions of dried sediment (1 g) with mixtures of concentrated HNO_3, H_2O_2 30% and concentrated HCl were performed for almost 5 hours on hotplate reflux. Cd and Zn in water samples were extracted using organic solvent according to back-extraction procedure (Standard Method, 1992) that was first developed by Magnusson and Westerlund (1981). APDC 4% and MIBK, as organic solvent, was used in first step of extraction. Cd and Znwere back-extracted, from organic phase to inorganic phase, by ultra pure water then be digested using concentrated HNO_3 under room temperature. Determination of Cd and Zn contents in both sediment and water sample was performed with Flame Atomic Absorption Spectrophotometer Varian SpectrAA 20 type. After the measurement of Cd and Zn in all sea water and sediment samples, the data would be calculated in order to model adsorption of Cd and Zn in the sea water and sediment. The detail formula for each model was described as below:

Partitioning model

Partitioning behaviour/ partitioning model can be expressed as distribution coefficients, K_D.K_D can be expressed as:

$$K_d = \frac{C\,metals\,on\,sediment\,mg\,kg^{-1}}{C\,metals\,in\,waters\,mg\,l^{-1}}$$

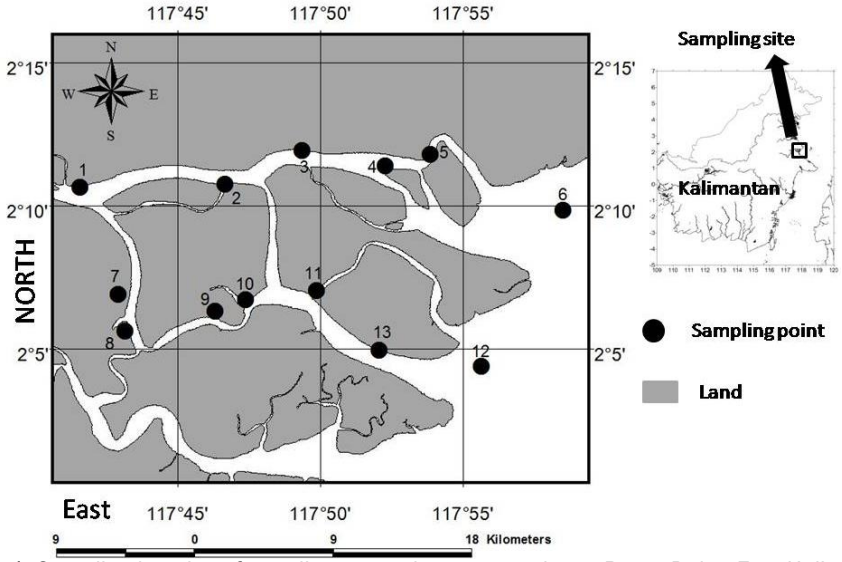

Figure 1. Sampling locations for sediments and water samples at Berau Delta, East Kalimantan

Freundlich model

The original form of the Freundlich equation (Dahiya *et al*., 2008; Seo *et al*., 2008) can be written as:

$$q = KCe^{\frac{1}{n}}$$

q represent adsorption capacity (mg.kg^{-1}), the metal concentration in the sorbent material, K is constants incorporating all factors affecting the adsorption capacity, Ce is the concentration of solution (mg.L^{-1}) and n is empirical parameter related to the intensity of sorption. This original form of Freundlich equation can be re-arranged in logarithmic form as:

$$log\ q = log\ K + \frac{1}{n} logCe$$

Langmuir model

The original form of Langmuir equation (Seo *et al*., 2008) can be written as:

$$q = \frac{abCe}{1 + bCen}$$

Where Ce (mg.L^{-1}) and q (mg.kg^{-1}) represent the concentration of metal in solution and the mass b are the maximum adsorption capacity of metals and constant related to the binding strength of metal adsorbed on sediment, respectively. a and metal, respectively. Equation 4 can be re-arranged as:

$$\frac{Ce}{q} = \frac{1}{ab} + \frac{1}{a} Ce$$

Results and Discussion

Stations could be devided into 2 group due to difference of point source, north stream (N) and south stream (S). Stations 1-6 were grouped in N and stations 7-12 were categorized in S. Closed to and point source of south main stream, station 7 was clustered in S although its river basically flow from same point source with N (Figure 1). The reason of this classification was the difference of main river stream flowing in the delta. The anthropogenic activities along those two main streams probably difference, as a result, the composition of sediment and metal released by human may be difference. In order to minimize the bias of calculation, those two main river streams were separated.

The distribution coefficient (K_D; l kg^{-1}) of Zn (10^2-10^4) was greater than that Cd (up to 10^1) (Table 1). Having 100 to 1000 fold ofK_D value above Cd, Zn tend to bind strongly onto sediment. These values less than another report, Feng *et al*. (1999) found that K_D value of Zn was greater Cd did in magnitude of ($10^{3.4}$-$10^{6.2}$) for Zn and (10^3-10^4) for Cd and there was an agreement of partitioning behaviour of the elements. This phenomenon was derived by metals character and the presence of interference. Cd forms very strong complex with chlorine than Zn Neither Cd nor Zn indicated the lowest determination coefficient (Figure 2 and Figure 3). This result implied that partition model/distribution coeficient could not demonstrate natural adsorption processes precisely.

Freundlich model could not interprate adsorption process for Cd (R^2<1), however, it described transfer process of Zn onto surface

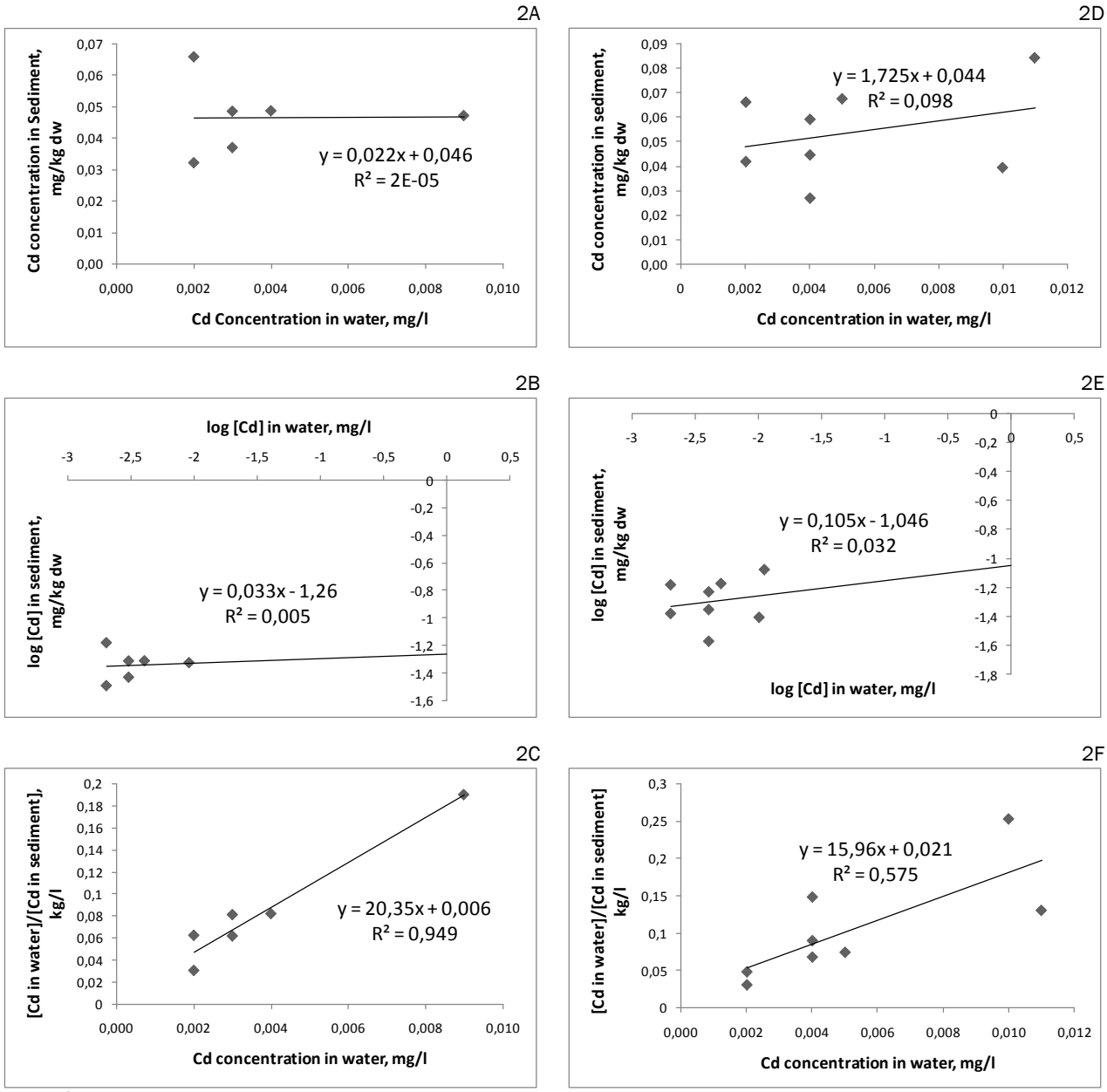

Figure 2. Different adsorption model for Cd in north stream (N) and south stream (S): 2A) N Partition model; 2B) N Freundlich model; 2C) N Langmuir model; 2D) S Partition model; 2E) S Freundlich model and 2F) S Langmuir model.

Table 1. K_D Value for Cd and Zn

	stations	K_D Cd; l kg^{-1}	K_D Zn; l kg^{-1}
north stream	ST. 1	30	8x10^3
	ST. 2	20	5x10^3
	ST. 3	20	1x10^3
	ST. 4	5	1x10^4
	ST. 5	10	6x10^3
	ST. 6	10	2x10^4
south stream	ST. 7	8	1x10^4
	ST. 8	10	1x10^4
	ST. 9	7	9x10^2
	ST. 10	4	2x10^4
	ST. 11	10	8x10^3
	ST. 12	10	2x10^3
	ST. 13	20	4x10^3

particle (R^2>0.5) (Figure 2B, Figure 2E, Figure 3B and Figure 3E). Langmuir model was the most representative model for both Cd and Zn, 0.949 and 0.575 in R^2 value of Cd for N and S, respectively, 0.838 and 0.944 in R^2 value of Zn for both N and S, respectively (Figure 2C, Figure 2F, Figure 3C, Figure 3F). Cdmaximum adsorption capability did not show significant differentiation, 0.05 mg.kg^{-1} for N and 0.06 mg.kg^{-1} for S. Whereas, Zn showed different character, Zn in the N has 12.7 mg kg^{-1} in maximum adsorption capability and Zn in S has 43.5 mg.kg^{-1} in maximum adsorption capability. Dissolved Cd and Cd in the sediment showed insignificant correlation, interprated by low R^2 value in S (R^2=0.575), eventhough high R^2 value showed in the N

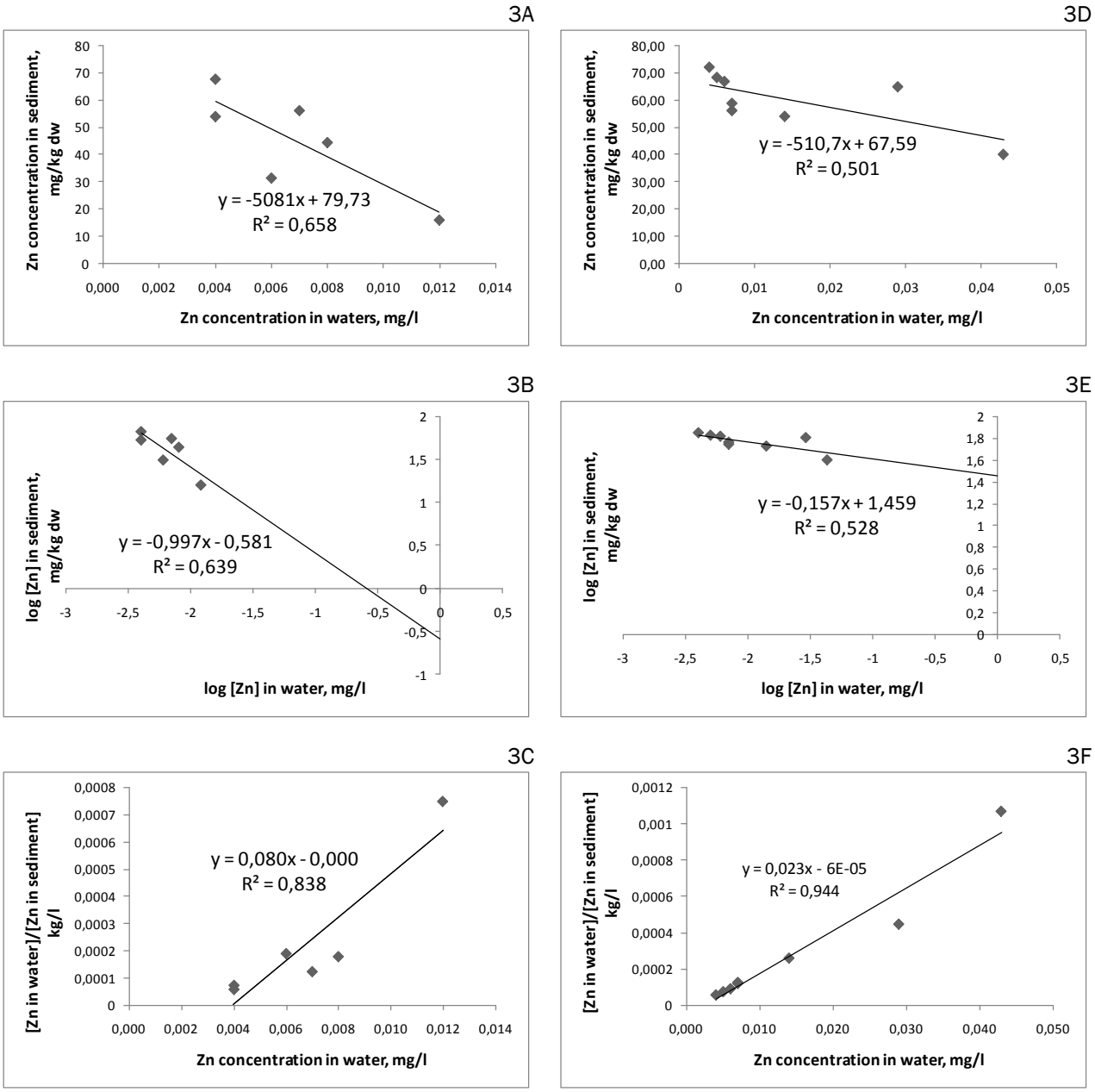

Figure 3. Different adsorption model for Zn in north stream (N) and south stream (S): 3A) N Partition model; 3B) N Freundlich model; 3C) N Langmuir model; 3D) S Partition model; 3E) S Freundlich model and 3F) S Langmuir model.

(R^2=0,949). Sanusi (2006) and Luoma and Rainbow (2008) explained that cadmium will bind in anionic element, like Cl^-, and make chloride-cadmium complex. This complex will inhibit cadmium adsorption to particulate surfaces or Fe/Mn Oxide. This cadmium behavior influenced cadmium adsorption capability, as a result, particulate matter could not adsorp cadmium optimally. Different phenomenon showed by Zn, Zn have greatly influenced by particulate/sediment condition. Dali-Youcef *et al*. (2006) discovered that Zn adsorption performances were strongly affected by their initial concentration and carbonate phase concentration. This sediment condition would affect adsorption capability, different location should have different sediment/particulate condition.

Conclusion

Langmuir isotherm model was the most representative model to interprate Cd and Zn transfer from water column to bed sediment. Maximum adsorption capability of Cd was 0.05 mg. kg^{-1} for N and 0.06 $mg.kg^{-1}$ for S. Whereas, maximum adsorption capability of Zn in the N was

12.7 mg kg^{-1} in and Zn in S was 43.5 mg kg^{-1}. Cadmium behavior to make complex in soluble form inhibit its adsorption onto particulate surface and Zn adsorption was greatly influenced by sediment condition. This study represented the maximum adsorption of Cd and Zn concentration in sediment in order to illustrate the maximum capacity of sediment as contaminant deposit. Another input of Cd and Zn to this system will not be adsorbed and tend to endanger aquatic life due to abundance of ambient Cd and Zn.

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