

# Biosorption of Lead (II)-containing Sasirangan Textile Wastewater using Nanocomposites of *Eleocharis dulcis* Fibers with Iron (III) Nanoparticles as Adsorbent

Chairul Irawan<sup>1\*</sup>, Iryanti F. Nata<sup>1</sup>, Meilana D.Putra<sup>1</sup>, Yuli Ristianingsih<sup>1</sup>

<sup>1</sup> Chemical Engineering Study Program, Engineering Faculty, University of Lambung Mangkurat, Banjarbaru, South Kalimantan 70714, Indonesia.

**Abstract.** This research focuses on the study of biocomposite nanoparticles of *Eleocharis dulcis* (ED) as potentials biosorbent to reduce the concentration of lead (II) ion containing Sasirangan textile industry wastewater. *Eleocharis dulcis*, locally named as Purun Tikus, has been developing becomes the biocomposites nanomaterial and valuables material in this research. Batch experiments were carried out to considering the kinetic of biosorption of lead onto the adsorbent, evaluating the effects of lead ion equilibrium concentration, equilibrium pH, and temperature on the adsorption of lead (II). Kinetic data of lead (II) biosorption onto EDB and EDB-MH revealed that equilibrium time was reached within 2 h, and the isotherm data showed that the Langmuir maximum adsorption capacity of the EDB-M and EDB-MH at  $pH_e$  of  $6 \pm 0.2$ , room temperature were 150.43 mg/g and 180.92 mg/g, respectively. The thermodynamic of lead (II) biosorption onto the adsorbent implied the biosorption was spontaneous and endothermic indicating by increased in temperature would increased in adsorption capacity.

## 1 Introduction

Heavy metals are present harmful, carcinogenic and non-biodegradable characteristics when they appeared in the aquatic environment. Recently, from the point of view the heavy metals categories, lead has gained an increasing attention due to its numerous occurrence in wastewaters and its high toxicity impacts to human health [1, 2]. Lead (Pb) is considered detected in outflow approaching from smelters industry and refineries, battery manufacturing, glass manufacturing, alloy steel industry, and textile industry even from dyestuff and printing process [3, 4]. Then, lead is considered detected in Sasirangan textile wastewater. In Sasirangan textile wastewaters, Pb-ion concentrations approach of 2–5 mg/L. This concentration is quite high in relative to provisional guidelines value, and Pb-ion concentration of the wastewaters must be decreased to below of 0.01 mg/L before its discharging into water ways body.

A number of technologies already used prior to diminish Pb-ion concentration in textile wastewater including chemical precipitation, coagulation–flocculation, electrochemical methods, ion exchange, membrane separation, reduction, adsorption, etc [5]. In recent years, biosorption method, a part category of

adsorption, has gain concern for treatment lead-containing wastewater due to its high efficiency, easy operation, low cost, abundant amount in nature, mitigating heavy metal removal in low metal concentration ( $< 100$  mg/L), reduced quantity of chemical and sludge handling.

Nowadays, biosorption using agricultural biomass-derived magnetic as adsorbent offer various attractive features, such as highly adsorption capacity, porous, inexpensive, non-toxic, biodegradable and biocompatible [6]. Sugarcane bagasse [7], oak wood and oak bark [8], pine bark [9], bagasse [10], and pine wood [11] are a samples of agricultural biomass-derived magnetic for lead adsorption. The agricultural biomass-derived magnetic as adsorbent would be easy separated after adsorption process from solution by using magnet kits. This research proposed *Eleocharis dulcis* (ED), locally named as Purun Tikus, becomes the biocomposites nanomaterial with magnetic modifiers and valuables material as an adsorbent for treating lead-containing Sasirangan textile wastewater. The contact time effect, equilibrium pH, equilibrium Pb-ion concentration, and temperature, related to kinetic and isotherm adsorption models, and thermodynamic parameters, such as enthalpy, free energy change, and entropy were considered in batch model experiment for a more appropriate understanding of the mechanism of

\* Corresponding author: [cirawan@unlam.ac.id](mailto:cirawan@unlam.ac.id)

biosorption process of lead (II)-containing Sasirangan textile wastewater.

## 2 Experimental Details

### 2.1 Materials

Lead containing Sasirangan textile wastewater samples of the typical high density of dyes were collected from the factory discharge point without any treatment in Banjarmasin, South Borneo, Indonesia. The samples were kept stored at below 4°C.  $Pb(NO_3)_2 \cdot 4H_2O$  as an artificial lead solution. HCl and NaOH were utilized to adjust the pH value of the solution, used in the present work were obtained from MERCK. All others chemicals employed in this work were of pure grade analytical without any further treatment. EDB-M and EDB-MH as adsorbent were prepared by author according to [12].

### 2.2 Batch model adsorption experiments of Lead containing Sasirangan textile wastewater

Batch model adsorption experiments were accomplished by placing 50 mL solution of certain amount of lead containing Sasirangan textile wastewater into 100 mL glass bottle and arranging its pH value using 1M NaOH or 1M HCl. Afterwards, weighed amount of the biosorbent, EDB-M and EDB-MH was taking into glass bottle, respectively. The mixtures was then placed in a water bath shaker (Firstek Scientific) at 150 rpm at room temperature for a desired contact time. The adsorption was carried out while shaking at room temperature for 6 hours. Afterward, besides separation of the solution from adsorbent assisted by using magnet kits. At the last of the experiment, the mixed solution are centrifuged and filtered through 0.2  $\mu m$  PVDF membrane (Advantec). Finally, the lead concentration in the initial and filtrate solution were measured by using inductively coupled plasma optical emission spectrophotometer (HORIBA Jobin Yvon 2000-2 ICP-OES). Adsorbed Pb-ion was determined from the difference between the initial and equilibrium adsorbate concentrations. The batch adsorption experiments were done triplicate, where as the average value was taken.

The equilibrium adsorption capacity,  $q_e$  (mg/g) was determined by the following equation:

$$q_e = (C_o - C_e)V/M \quad (1)$$

Where  $C_o$  (mg/L) was the initial lead concentration,  $C_e$  (mg/L) was the effluent or equilibrium lead concentration,  $V$  (L) was the volume of the lead solution and  $M$  (g) was the mass of the biosorbent used.

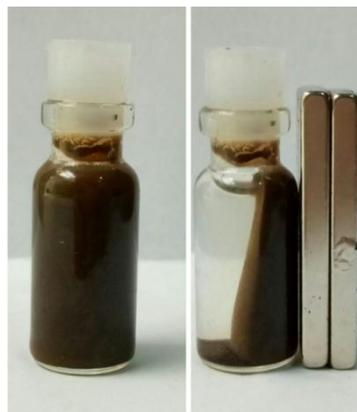
The biosorbent, EDB-M and EDB-MH, were used to investigate the factor affecting lead adsorption such as pH, initial lead concentration, and temperature. The adsorbent was separately used for adsorption isotherm studies and finding out the correlation between the adsorbent content that has a major role in the lead adsorption mechanism.

In addition, to regenerated the adsorbent by suitable desorption proses, the EDB-M and EDB-MH loaded metal ions were desorbed by shaking in 0.1 N HCl for 24 hours for repeated uses. After washing properly with deionized water, the regenerated adsorbent was charged for the next cycle of lead adsorption process. The cycles of such adsorbent were repeated for three times in triplicate analysis.

## 3 Results and Discussion

### 3.1 Biosorption of Lead containing Sasirangan textile wastewater by using ED as biosorbent

The ED biocomposite with iron (III) nanoparticles (EDB-M) with diameter size around 30–50 nm is a promising precursor to be used in the biosorption process for the reduction of lead from Sasirangan industrial textile wastewater. Clearly as shown in Fig. 1, the adsorbent easily separate from the solution after adsorption process by using magnet kits.



**Fig. 1.** The samples of lead adsorption onto EDB-M a. before separate adsorbent from the solution, b. separate adsorbent assisted by using magnet kits

### 3.2 Kinetic studies of biosorption of Lead-containing Sasirangan textile wastewater

The contact time effect on the Pb-ion adsorption onto EDB-M was conducted at room temperature,  $pH_e$  of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, initial Pb-ion concentration of ca. 100 mg/L, and dose of biosorbent of 2.5 g/L.

Fig. 2 shows that during the first 15 minutes, Pb-ion uptake capacity significantly increased from 0 mg/g to 21.90 mg/g, which was apparently due to the diffusion taking place into the vacant pores and or adsorption onto the surface of the adsorbent. Initially, the Pb-ion concentration gradient was quite high diffusing into and through the vacant porous of the adsorbent, then the lead uptake capacity are increased slightly to lead uptake capacity of 24.56 mg/g and being constant until reached equilibrium condition within 2 hours. The equilibrium adsorption experiments were conducted within 2 h of reaction time.

The kinetic models of pseudo-first-order and pseudo-second-order are adapted to fit the adsorption reaction model of lead adsorption onto the EDB-M. The Lagergren pseudo-first-order expression is given as [13]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

where  $q_e$  and  $q_t$  are the amount of Pb-ion adsorbed onto biosorbent per mass unit of the biosorbent (mg/g) at equilibrium and contact time  $t$ , respectively, and  $k_1$  is the rate constant of biosorption (1/min). Integrating of equation (2) for boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  resulted in the following:

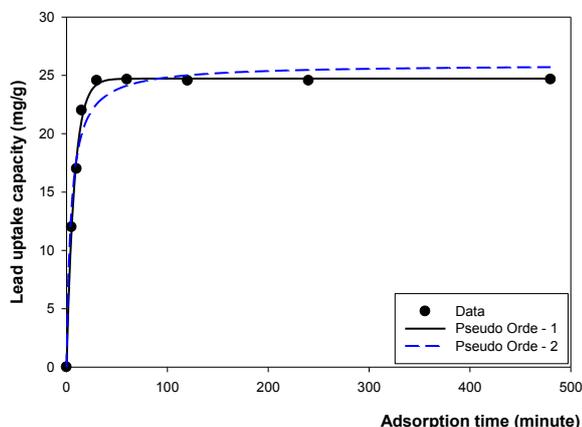
$$q_t = q_e(1 - \exp(-k_1t)) \quad (3)$$

The model of pseudo-second order is considered as [14]

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

where  $q_e$  is the maximum adsorption capacity (mg/g);  $k_2$  the rate constant of the pseudo-second order equation (g /mg.min);  $q_t$  are the amount of lead adsorbed onto biosorbent per unit mass of the biosorbent (mg/g). Integrating the equation for boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives:

$$q_t = q_e \left( \frac{q_e k_2 t}{1 + q_e k_2 t} \right) \quad (5)$$



**Fig. 2** Kinetic plot of lead biosorption onto the EDB-M at room temperature,  $pH_e$  of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, initial Pb-ion concentration of ca. 100 mg/L, and dose of biosorbent of 2.5 g/L.

The comparison figure of the different kinetic model for lead adsorption onto the EDB-M was shown in Fig. 2. The resulting of the parameter and the correlation coefficients achieved by using non-linear regression was calculated and listed in Table 1. The values of the coefficient related to the Lagergren kinetic model for pseudo-first order was found to be 0.997, which was more representative fitted than the kinetic model for pseudo-second order. Based on the composition of EDB-M, it was likely several reaction type or mechanisms are

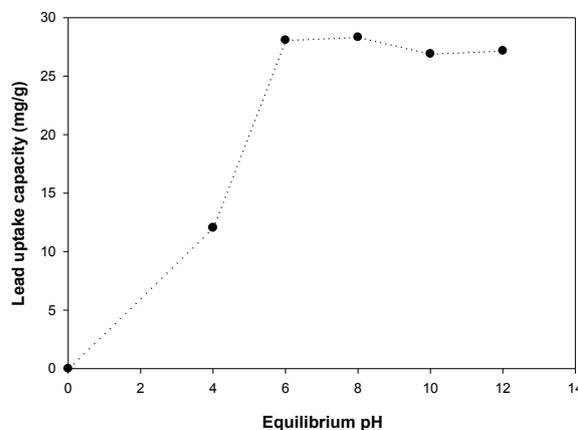
involved in the fixation of lead onto EDB-M. However, uses of the kinetic models tend to suggest that the rates of this reaction could be adjacent to pseudo-first-order kinetic model. A better correlation of kinetic reaction rate data in this model justified the physical biosorption mechanism occurred.

**Table 1.** Kinetic parameters of lead biosorption onto the EDB-M at room temperature

Kinetic Model	Parameter	Value
Pseudo-first order	$q_e$ (mg/g)	24.722
	$k_1$ (1/min)	0.1293
	$R^2$	0.9969
Pseudo-second order	$q_e$ (mg/g)	25.948
	$k_2$ (g/(mg.min))	0.0085
	$R^2$	0.9756

### 3.3 Equilibrium pH studies of biosorption of Lead-containing Sasirangan textile wastewater

Plotted in Fig. 3 shown that the lead adsorption envelopes for the adsorbent was bell-shaped like typical oxyanions sorption curves. The lower value of lead adsorption capacity when the pH was low (pH around 4) could be due to the excess of hydrogen ions surrounding the binding sites making adsorption process was unfavorable. Lead and  $H^+$  ions compete with the active adsorption site and account for the lower adsorption uptake capacity.

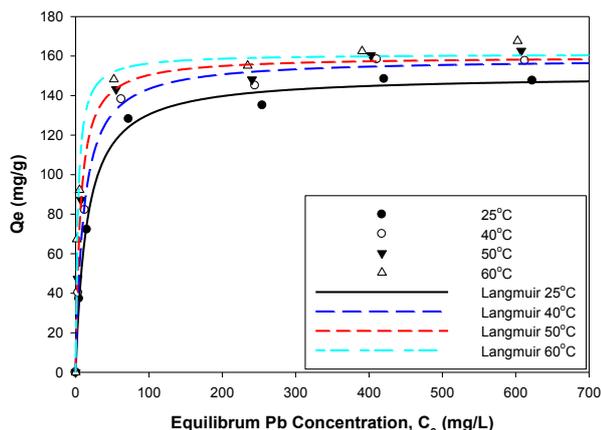


**Fig. 3** The equilibrium pH effect on lead biosorption onto the EDB-M at equilibrium adsorption time of 2 h, room temperature, shaking rate of 150 rpm, initial Pb-ion concentration of ca. 100 mg/L, and dose of biosorbent of 2.5 g/L.

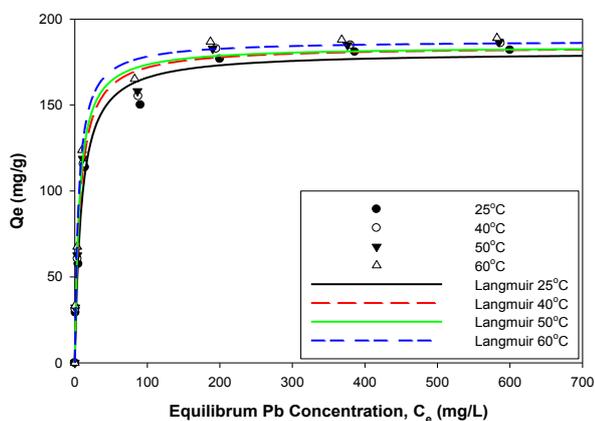
Thus, lead biosorption capacity will increase with increasing pH around 6–8 up to 27.18 mg/g for EDB-M as biosorbent. The increase in lead uptake capacity as equilibrium pH increases can be interpreted by a decrease in competition between protons ( $H^+$ ) and positively charged metal ions at the surface sites. At higher pH ( $pH > 8$ ) due to metal solid hydroxide precipitation of the lead, several hydroxyl low-soluble such as  $Pb(OH)_2$  maybe form, then the lead uptake capacity seems remaining constant [15].

### 3.4 Effect of temperatures studies of biosorption of Lead-containing Sasirangan textile wastewater

The effect of temperature on lead adsorption was investigated in order to figure out the behavior of lead biosorption process, and also used to predict the thermodynamic parameters. The temperature effect was studied by varying the temperature from ambient temperature up to 60°C at equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L.



**Fig. 4** Langmuir isotherm model plot at various temperatures for lead biosorption onto the EDB-M at equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L.

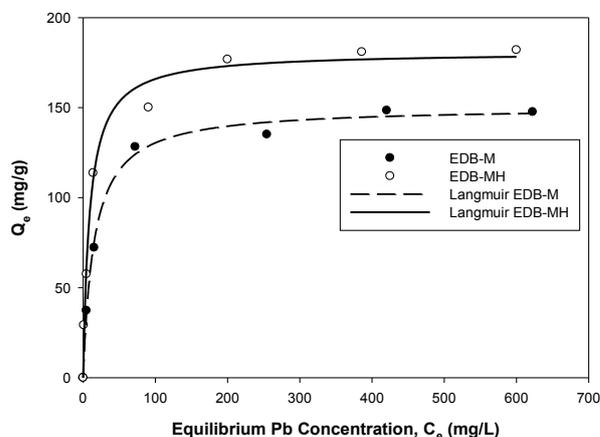


**Fig. 5** Langmuir isotherm model plot at various temperatures for lead biosorption onto the EDB-MH at equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L.

Fig. 4 shows that lead uptake capacity was slightly increased with increasing temperature. Lead adsorption onto the surface of the EDB-M seems was favored at higher temperature. The Langmuir isotherm model was illustrated to predict the thermodynamic parameters. The linearity of the data was derived from regression analysis and it was found that the correlation coefficient are average better than 0.996 at temperature 25, 40, 50, and 60°C. The tendency was also same shown in Fig. 5.

### 3.5 Adsorption isotherm models studies

The adsorption isotherm model studies were conducted by varying initial lead concentration of c.a. 50 to 1000 mg/L at room temperature, equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L.

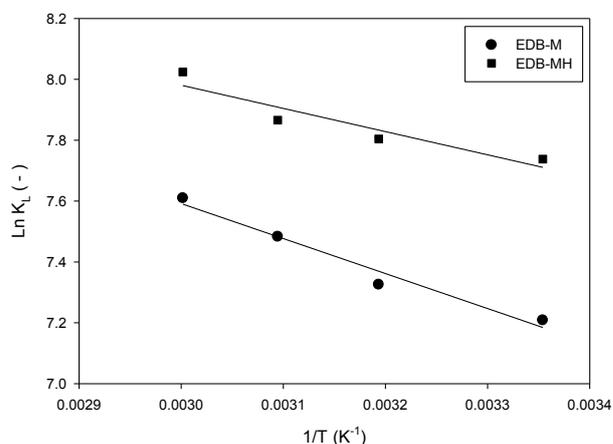


**Fig. 6** Langmuir isotherm plot for lead adsorption onto EDB-M and EDB-MH at room temperature, equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L.

Fig. 6 shown that lead adsorption density increased up to 147.72 mg/g using EDB-M, then up to 179.51 mg/g using EDB-MH as adsorbent. The Langmuir model described the adsorption data satisfactorily ( $R^2$  value average = 0.996), and the batch maximum adsorption capacities were found as 150,43 and 180,92 mg/g using EDB-M and EDB-MH, respectively at pH value of  $6.2 \pm 0.2$ . The maximum adsorption densities compared with previously reported adsorbents shown in Table 2.

### 3.6 Thermodynamic biosorption studies

Enthalpy, Gibbs free energy and entropy changes are considerations into the thermodynamic biosorption studies, Its should be taken into account to determine which process will take place spontaneously.



**Fig. 7** Van't Hoff plots at different temperature, equilibrium adsorption time of 2 h,  $pH_e$  value of  $6.2 \pm 0.2$ , shaking rate of 150 rpm, and dose of biosorbent of 2.5 g/L for EDB-M and EDB-MH as biosorbents, respectively.

The values of thermodynamic parameters are substantial indicator for practically of process applied, where the thermodynamic parameters should be calculated at various temperatures [2]. For this reason, the amounts of lead adsorbed capacity at 25, 40, 50, and 60°C were calculated to obtain the thermodynamic properties such as enthalpy change ( $\Delta H^\circ$ ), Gibbs free energy change ( $\Delta G^\circ$ ), and entropy change ( $\Delta S^\circ$ ). The molar free energy change of the adsorption process is related to the equilibrium constant ( $K_L$ ) and calculated from the following equation is shown below :

$$\Delta G^\circ = -RT \ln K_L \quad (6)$$

where R is the gas constant in the ideal gas equation (8.314 J/mol.K), T is the absolute temperature, and the free energy change is calculated at 25°C.  $K_L$  is Langmuir constant (L/mol)

Enthalpy change value,  $\Delta H^\circ$ , and entropy change value,  $\Delta S^\circ$ , of biosorption of lead can be predicted by using the Van't Hoff equation is shown below:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

A plot of  $\ln K_L$  against  $1/T$  renders a straight line, as shown in Fig. 6. The slope of the plot is equal to  $-\Delta H^\circ/R$  and its intercept value is equal to  $\Delta S^\circ/R$ . It was well known that these parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction [2].

The thermodynamic parameters were calculated and tabulated in Table 2. The general explanation accounts for the thermodynamic study of lead adsorption onto EDB-M and EDB-MH were probably generally accompanied by release of energy, that is, most adsorption processes are endothermic in nature [2]. This adsorption process was favor under high temperature condition. The negative values of  $\Delta H^\circ$  (9.56 and 6.34 kJ/mol) confirmed the endothermic nature of biosorption of lead. The  $\Delta H^\circ$  value is quite high (9.56 and 6.34 kJ/mol), suggesting it was physical adsorption and chemical reaction mechanism, since the change of enthalpy value in physical adsorption process was usually of 5–40 kJ/mol [16]. Biosorption of lead was a spontaneous process, therefore its the change of free energy value is negative ( $\Delta G < 0$ ). The positive values of  $\Delta S^\circ$  (91.79.15 and 85.38 J/mol K) show the increased randomness at the solid/liquid interface during lead biosorption onto the biosorbent, which was accorded with fact that the mobility of adsorbates on adsorbent surface become more restricted as compared with that of those in the solution, and also reflect the affinity of the adsorbent material for lead removal.

**Table 2.** Langmuir adsorption isotherm model constants for the lead biosorption onto the EDB-M at various temperature

Isotherm Model	25°C	40°C	50°C	60°C
<b>Langmuir</b>				
$q_{max}$ (mg/g)	150.43	160.79	165.72	170.75
$K_L$ (L/mg)	0.0652	0.0928	0.1598	0.3228
$R_L^2$	0.996	0.997	0.996	0.988

**Table 3.** The maximum lead adsorption capacity and pH optimum of some bioadsorbent as reported in the literature.

Adsorbent	Max. adsorption capacity (mg/g)	pH Optimum	References
Rapeseed biomass	21.29 (20°C)	around 5	[2]
Phytolacca americana L.	10.83 (PAL) 12.66 (HPAL)	6	[17]
Flax fibres	10.741	6	[18]
Peanut shell	38.91	5.5±0.2	[15]
Cyclosorus interruptus	46.25	5.5	[19]
Magnetic Co-Fe NP	44.58 (25°C)	-	[20]
EDB-M	150.43 (25°C)	6.2±0.2	Present study
EDB-MH	180.92 (25°C)	6.2±0.2	Present study

## 4. Conclusions

The study of biocomposite nanoparticles of *Eleocharis dulcis* (ED) as promising biosorbent for the treatment of lead (II) ion containing Sasirangan textile industry wastewater was investigated. Kinetic data of lead (II) biosorption onto EDB and EDB-MH revealed that equilibrium time was reached within 2 h, and the isotherm data showed that the Langmuir maximum adsorption capacity of the EDB-M and EDB-MH at  $pH_e$  of  $6 \pm 0.2$ , room temperature were 150.43 mg/g and 180.92 mg/g, respectively. The thermodynamic of lead (II) biosorption onto the adsorbent implied the biosorption was spontaneous and endothermic indicating by increased in temperature would increased in adsorption capacity. Even the  $\Delta H^\circ$  value is quite high (9.56 and 6.34 kJ/mol), suggesting it was physical biosorption since the value of enthalpy change in physical adsorption process was usually of 5–40 kJ/mol, but chemical reaction mechanism probably included that indicating by favorable in high temperature.

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