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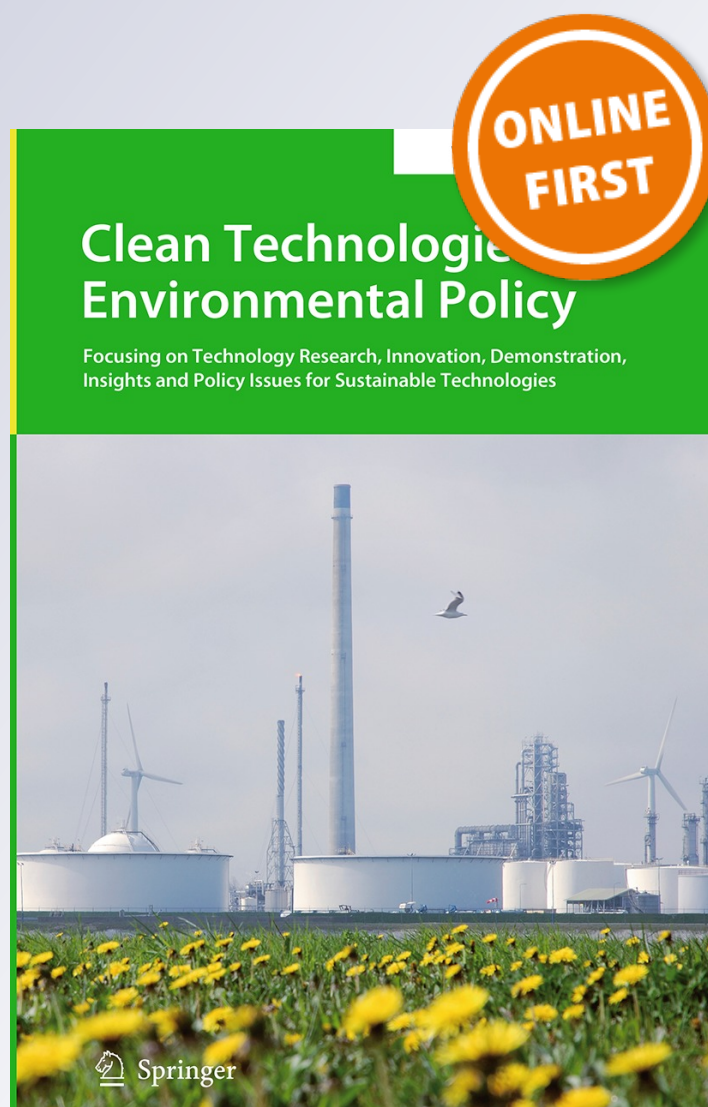
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The half saturation removal approach and mechanism of Lead (II) removal using eco-friendly industrial fish bone meal waste biosorbent

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Abstract Lead (II)-laden wastewater from lead acid battery and printed wire board industries are hazardous to human health and environment due to their toxicity and persistent characteristics. This study focuses on eco-friendly industrial *Lutjanus erythropterus* fish bone meal waste as biosorbent for Lead (II) removal. In this study, the effects of optimization of biosorption, isotherm, kinetic, thermodynamic, characterization of biosorbent were investigated, and the characteristics of biosorbent were compared with those of commercial resins. The half saturation removal of biosorbent amount was determined at 0.09 g in order to represent the excessive metal in real industrial wastewater condition compared to biosorbent and to minimize the consumption of chemicals and biosorption operation time. Such approach is supported by optimization results and Langmuir isotherm. Results obtained were better with Freundlich than with Langmuir isotherm, confirming the presence of heterogeneous monolayer with reversible binding sites. The biosorption mean energy inferred that chemisorption occurred in Lead (II) biosorption, and pseudo-second-order kinetics implied that chemisorption mechanism is the rate-limiting factor.

Thermodynamic described an endothermic non-spontaneous reaction with reversible bonding between Lead (II) ions and binding sites. Characterization analysis further confirmed a macroporous surface morphology with multi-binding sites of hydroxyl, carboxyl, and amide groups which contributed to reversible bonding in chemisorption mechanism. The 85 % of recovery supported reversible binding in chemisorption. The biosorbent is at least 70 times cheaper than resins. Hence, this developed biosorbent is a potential candidate to replace resins and can be used in the pretreatment of industrial wastewater application due to cost effectiveness and low environmental impacts. This study successfully gains an insight into green technology by converting waste to a useable product and zero waste concept by minimizing environmental solid management and pollution control.

Keywords Biosorption · Chemisorption · Fish bone meal waste · Half saturation · Lead (II) · Mechanism

Introduction

Environmental impact of inorganic heavy metal from rapid industrialization is gaining global attention. Lead (II) is one of the three most toxic heavy metals that causes acute human health effect although in low concentration. Its persistent toxicity and non-biodegradable characteristics lead to acute and chronic diseases. Lead (II) from lead acid battery and printed wire board industries which mainly contributes to wastewater containing Lead (II) even though in low concentration 1–25 mg/L is becoming a great concern. Consequently, wastewater heavy metal has a stringent permissible limit in regulations in order to safeguard the human health and environment. Nowadays, the most wide

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applied technology for Lead (II) removal is ion exchange process using petrochemical-based resins (Ozacar et al. 2008) and adsorption using coal-based activated carbon (Agwaramgbo et al. 2013) or mineral-based zeolite (Remenarova et al. 2014; Wang and Peng 2010). These materials have certain drawbacks of being ineffective in removing heavy metals when present in low concentrations, less cost effective, and not eco-friendly (Mahdavi et al. 2015). In addition, a lot of researches focus on the modification of these materials to improve their effectiveness by means of a chemical approach, but an eco-friendly perspective is not taken into consideration (Ucar et al. 2015; Zafar et al. 2015). Therefore, a search of alternative materials from waste and eco-friendly perspective of biosorbent for heavy metal treatment through biosorption technology is emphasized.

Biosorption is a passive process using metabolically inactive non-living biological-based materials to bind with contaminants of heavy metal. Generally, high amount of biosorbent and long operation time have been considered for optimization study in order to understand the performance and mechanism of biosorption (Abbas et al. 2014; Tay et al. 2011). Furthermore, no attempt has been made on integration of results to explain biosorption mechanism. To overcome this issue, the half saturation removal of Lead (II) from aqueous solution has been investigated and evaluated in this study. This study also relates the experimental and evaluated results with characterization results in order to elucidate the mechanism involved in Lead (II) biosorption.

Generally, waste materials locally available from agriculture and industries are selected as biosorbent materials for biosorption technology (Choudhary et al. 2015; Venkatesan et al. 2014). Industrial *Lutjanus erythropterus* fish bone meal waste is chosen as a biosorbent in this study as it is easily and abundantly available from local fish-based product industries and is of low cost, but it has limited applications as a low-value supplementary feedstock in aquaculture industries. The industrial fish bone meal waste is a promising potential biosorbent as it contains high chitosan. As known, chitosan has high capability of heavy metal biosorption through amino and hydroxyl groups (Goto and Sasaki 2014; Won et al. 2014; Yong et al. 2015). According to Kizilkaya and Tekinay (2014), fish bone biosorbent was reported to effectively remove Lead (II) from aqueous solution. To the authors' knowledge, there is a lack of study on industrial *L. erythropterus* fish bone meal waste biosorbent in Lead (II) removal. Hence, it can be hypothesized that the industrial *L. erythropterus* fish bone meal waste is a potential biosorbent for Lead (II) removal which is in line with sustainable concept. It not only converts waste to a product in solid-waste management but also contributes a role in wastewater treatment.

In the present study, biosorption optimization batch experiment as well as evaluation of isotherm, kinetic, and thermodynamic equations were investigated through the half saturation removal of Lead (II) in order to minimize the consumption of chemicals and operation time. To gain an insight into mechanism, a characterization analysis was conducted and integrated with experimental and evaluated data. The characteristics of the developed biosorbent and resins were also compared.

Methodology

Biosorbent and Lead (II) solution preparation

Industrial *L. erythropterus* fish bone meal waste biomass was collected from food industrial area around Pulau Pinang, Malaysia. First, the biomass was washed in hot water (100 ± 3 °C) and followed by pretreatment by 0.1 M sodium hydroxide at 60 °C for 2 h and stirred at intervals. The pretreatment procedure was carried out at a solid-to-liquid ratio of 1:10. The sample was washed thoroughly with ultrapure water till the color of the washing water was clear with pH 7 and then dried in an oven at 60 °C to a constant weight. Next, it was milled into powder and passed through a sieve of size 710 μm . The prepared sample was kept in the desiccator as biosorbent.

A stock solution of 1000 mg/L was prepared using 0.7994 g of metal salt Lead (II) nitrate, $\text{Pb}(\text{NO}_3)_2$ (Merck, Germany), in a 500-mL volumetric flask. The stock solution was diluted to the desired concentration using ultrapure water.

Biosorption optimization batch experiment

A solution of 50 mL 50 mg/L Lead (II) was added into 250-mL Erlenmeyer flask containing biosorbent at a range of 0.005–0.600 g. The flasks were placed on incubator shaker which was agitated at 125 rpm for 60 min at a temperature of 25 °C. The samples were then separated by filtration using filter paper. The final filtrates were analyzed using ICP-OES (Perkin Elmer, Optima 7300DV). The initial pH of 5.00 ± 0.03 was measured using pH meter. The percentage of Lead (II) removal and their uptake were calculated using Eqs. 1 and 2. The biosorbent amount at the half saturation removal of Lead (II) removal was chosen for further studies.

$$\text{The percentage of Lead(II) removal, \%} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \quad (1)$$

$$\text{The uptake of Lead(II) removal, \%} = \frac{(C_{\text{initial}} - C_{\text{final}})V}{W}, \quad (2)$$

where $C_{initial}$ is the initial concentration of Lead (II) solution, mg/L; C_{final} the final concentration of lead (II) solution, mg/L; V the volume of solution, L; and W is the weight of biosorbent, g.

Experiment was repeated with parameters of pH of 1–6, contact time of 1–75 min, Lead (II) concentration of 10–60 mg/L, and temperature of 4–45 °C. The optimum parameters were selected for subsequent experiment. All samples were prepared in duplicates and the standard deviation was less than 3.

Isotherm, kinetic, and thermodynamic equations' evaluation

The results from Lead (II) concentration optimization biosorption batch experiment were fitted to linearized Langmuir and Freundlich equations as shown in Eqs. 3 and 4, and the mean energy of biosorption through the Dubinin–Radushkevich constant was calculated using Eq. 5.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln q_e \quad (4)$$

$$E = \frac{1}{\sqrt{-2K}}, \quad (5)$$

where q_e is the equilibrium Lead (II) biosorption uptake (mg/g), q_{max} the maximum Lead (II) biosorption uptake (mg/g), C_e the Lead (II) concentration at equilibrium (mg/L), b the Langmuir constant, K_F and n the Freundlich constant, E the mean free energy (kJ/mol), and K is the constant related to the mean free energy of biosorption per mol of biosorbent (mol^2/kJ^2).

The contact time was used to fit the pseudo-first-order kinetic and pseudo-second-order kinetic equations (Eqs. 6 and 7):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{t}{q_e}, \quad (7)$$

where q_e and q_t are, respectively, the Lead (II) biosorption uptake at equilibrium and at time (mg/g), t the time (min), and k_1 and k_2 are, respectively, the constant of pseudo-first-order and pseudo-second-order kinetics.

The obtained results from temperature optimization were evaluated by thermodynamic equations using Eqs. 8 and 9. Thermodynamic parameters of Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated.

$$\log K_c = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (8)$$

$$\Delta G = \Delta H - T\Delta S, \quad (9)$$

where K_c (L/g) is the distribution coefficient; q_e (mg/g) and C_e (mg/L) the biosorption capacity and Lead (II) concentration at equilibrium, respectively; T the temperature in Kelvin, and R is the gas constant. ΔG is free energy (kJ/mol). ΔH and ΔS were obtained from the slope and intercept of the plots of $\log K_c$ versus $1/T$.

Biosorbent characterization

Characterization study of industrial fish bone meal waste biosorbent was analyzed using BET surface area (BELSORP-MINI-II), SEM/EDX (Quanta FEG 650), zero point charge (pH_{pzc}), and Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Electron Corporation Nicolet 380) in order to understand the surface characteristic and functional groups of industrial fish bone meal waste biosorbent.

Biosorbent comparison experiment

Commercial resin products of Amberlite IRC-86 and Dowex 50 W X8 were used in this biosorbent comparison experiment. Similar amounts of biosorbent and resins were applied under similar selected optimal parameters of biosorption batch study. The obtained results were evaluated and compared. Cost estimation of biosorbent preparation per kg was estimated and desorption of loaded Lead (II) on the biosorbent was conducted using 0.1 M nitric acid.

Results and discussion

Biosorption optimization batch experiment

Figure 1a–e shows effects of investigated parameters on biosorption batch experiment, such as biosorbent amount, pH, contact time, Lead (II) concentration, and temperature. The half saturation removal was found to be at 0.09 g of biosorbent amount from experimental result as shown in Fig. 1a. The half saturation removal was selected over 100 % removal because excessive Lead (II), compared to biosorbent amount, minimizes consumption of chemicals and materials, experimental time, as well as human power requirements. In addition, this selected parameter also serves as a reference point in subsequent optimization experiments. Such half saturation removal is also supported by the Sigmoidal curve with r^2 of 0.9973 (Eq. 10).

$$y = \frac{93.8112}{1 + e^{\frac{x+0.0833}{0.0508}}}, \quad (10)$$

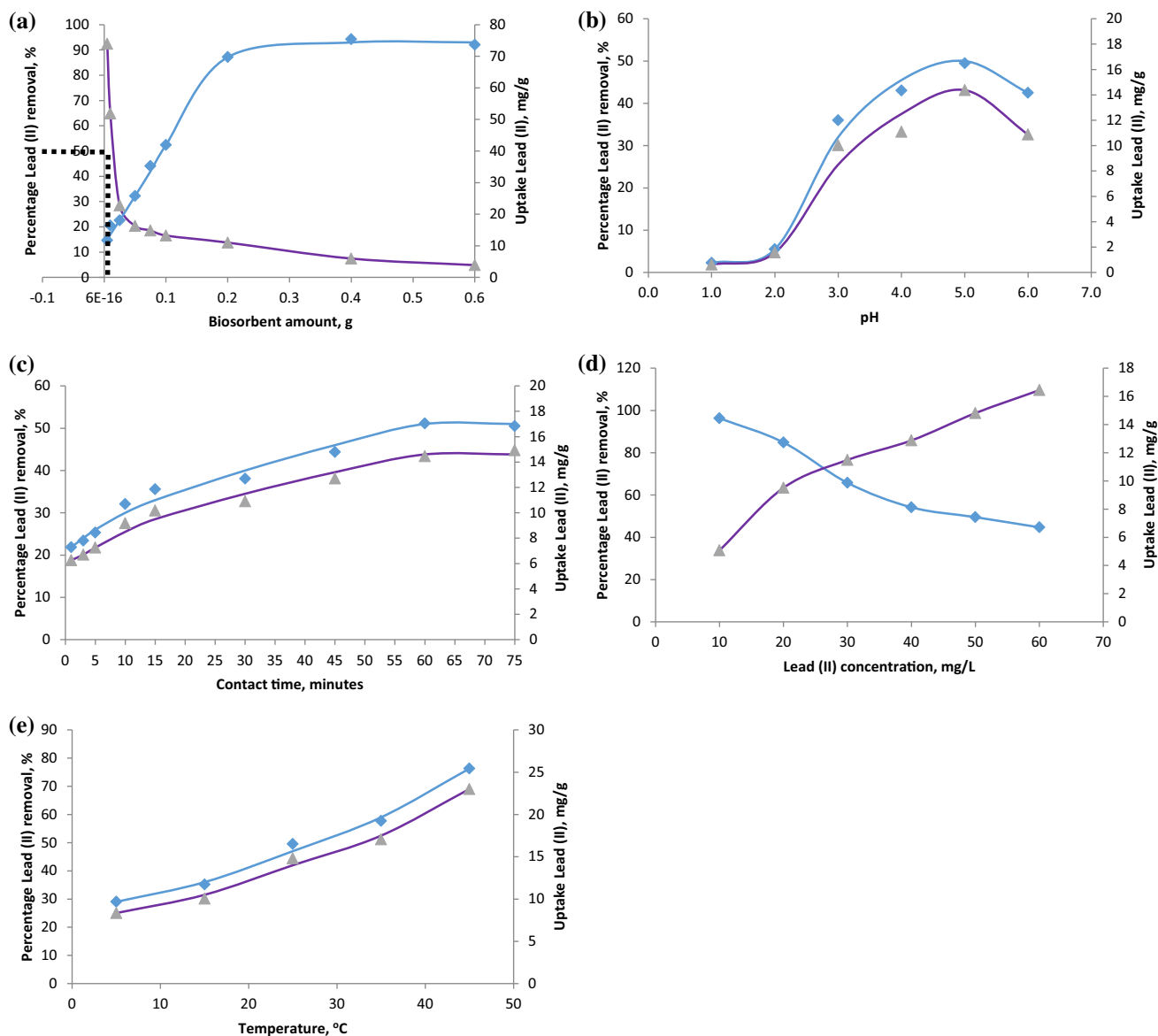


Fig. 1 Effects of optimization of parameters on biosorption batch experiment: (a) biosorbent amount, (b) pH, (c) contact time, (d) Lead (II) concentration, (e) temperature

The optimum pH was observed at unadjusted pH of 5 since it corresponds to the maximum removal condition and reduces chemicals consumption as well as labor requirements (Fig. 1b). As illustrated in Fig. 1c, the saturation condition was achieved at 60 min of contact time which supported the experimental design of the half saturation removal approach which minimized the chemicals, materials, and time for further evaluation (Tay et al. 2012). The inverse relationship between percentage of Lead (II) removal and Lead (II) concentration was attributed to the increase ratio of Lead (II) ions to biosorbent (Fig. 1d). The removal of Lead (II) increased with the increasing temperature as shown in Fig. 1e. This suggested that Lead (II)

biosorption using industrial fish bone meal waste is an endothermic reaction and needs to be confirmed through thermodynamic evaluation.

The average Lead (II) removal and uptake for selected biosorbent amount of 0.09 g at unadjusted pH of 5 for 50 mL and 50 mg/L Lead (II) solution, operation conditions of 60 min, 125 rpm agitation, and temperature 25 °C were 50 ± 0.43 % and 14.49 ± 0.34 mg/g, respectively. This also indicated that the developed half saturation removal approach is reliable and consistent as standard deviation is low. The uptake Lead (II) showed an increasing trend with the increasing Lead (II) concentration. The comparison of uptake capacity with other studies

should be referred to Langmuir maximum uptake in the following section (Table 2).

Isotherm, kinetic, and thermodynamic equations' evaluation

Table 1 shows the comparison between the Langmuir and Freundlich isotherm using industrial fish bone waste biosorbent. The obtained data were better interpreted with Freundlich with R^2 of 0.9853 compared to Langmuir with R^2 of 0.9776. The results of the present study are consistent with those of Wang et al. (2015), where Freundlich isotherm better fitted than Langmuir isotherm. Based on calculation, the maximum uptake value as determined experimentally (16.44 mg/g) corresponded excellently with the maximum uptake value as calculated using Langmuir equation (16.72 mg/g). These fittings deduced that biosorption is governed by a complete monolayer heterogeneous surface at multiple binding sites. The high value of b inferred that the industrial fish bone meal waste biosorbent has a high selectivity towards Pb(II) and therefore can be used as an effective treatment in industrial wastewater application. Meanwhile, the high n value revealed that a weak bond is formed between the Pb(II) ions and binding sites, suggesting the possibility of chemisorption mechanism. In addition, the calculated mean biosorption energy was found to be 40.82 kJ/mol, implying chemisorption mechanism (Crini and Badot 2008).

Table 2 compares the uptake of Lead (II) by Industrial fish bone meal waste with that by other biosorbents. In view of abundantly local available and cheapness, this industrial waste is a good candidate for biosorption. Table 2 also shows the time taken for biosorption process is comparable with other Lead (II) biosorption studies with advantages of using less biosorbent amount. Hence, this supported that the credibility of half saturation removal approach is highly reliable and contributes towards sustainability.

Regression analysis of linearized pseudo-second-order kinetic ($R^2 = 0.9833$) has a higher fit than pseudo-first-order kinetic ($R^2 = 0.9676$), as shown in Fig. 2a, b. The value of maximum uptake of Lead (II) as determined experimentally (14.93 mg/g) well fitted to that calculated

using pseudo-second-order kinetic (15.46 mg/g) than that using pseudo-first-order kinetic (7.84 mg/g). Hence, Lead (II) biosorption of industrial fish bone meal waste biosorbent was better fitted by pseudo-second-order kinetic than pseudo-first-order kinetic, describing that chemisorption mechanism is the rate-limiting factor in biosorption process. It signified and confirmed that chemisorption is a major mechanism in biosorption process. Kizilkaya and Tekinay (2014) also concurred that pseudo-second-order kinetic has a higher coefficient and reliable maximum Lead (II) uptake value by fish bone-based biosorbent.

The calculated values of the thermodynamic parameters of ΔG , ΔH , ΔS , and R^2 are summarized in Table 3. The negative ΔG indicated non-spontaneous reaction and an increase of spontaneous biosorption process as environmental temperature increased. The positive ΔH exhibited endothermic reaction and supported the result of Fig. 1e. The negative ΔS inferred weak and reversible bonds were formed, and supported by Freundlich high n value in Table 1. This implied chemisorptions through valence force due to sharing of electrons. This also specified that chemisorption meddles in Lead (II) biosorption mechanism, and such biosorbent is a potential candidate for regeneration and reuse after metal recovery. Coelho et al. (2014) and Yuvaraja et al. (2014) also reported endothermic reaction for Lead (II) removal using *Solanum melongena* leaf powder and cashew nut shell *Anacardium occidentale* L. as biosorbent, respectively.

Biosorbent characterization

BET surface area analysis

The surface area and BET surface area were 1.4292 and 1.5504 m²/g, respectively. Meanwhile, the pore volume was 0.0027 cm³/g and pore size was 70.4113 Å. Table 4 compares BET surface area and particle size of industrial fish bone meal waste biosorbent with those used in other studies. This indicated that industrial fish bone meal waste biosorbent is a macroporous biomaterial and has a high surface area. High surface area and pore volume contributed to biosorption process and implied that this industrial fish bone meal waste is a potential biosorbent (Subbaiah et al. 2011). However, this result needs to be investigated and supported by SEM/EDX analysis.

SEM/EDX analysis

Figure 3a, b shows the SEM micrographs of the industrial fish bone meal waste biosorbent before and after biosorption. Before biosorption, the biosorbent surface was clear with macroporous structures. After biosorption, changes in the morphology of the biosorbent surface were observed:

Table 1 Comparison of Lead (II) Langmuir and Freundlich isotherms using industrial fish bone meal waste biosorbent

Langmuir		Freundlich	
q_{exp} (mg/g)	16.44	K_F	0.15
q_{max} (mg/g)	16.72	n	4.18
b (L/mg)	0.33	R^2	0.9853
R^2	0.9776		

Table 2 Comparison of the amount of Lead (II) uptake by biosorbents in recent studies

Biosorbent	q_{max} (mg/g)	Contact time (min)	Biosorbent amount per 50 mL (g)	Operation pH and Pb(II) concentration (mg/L)	References
Sugarcane bagasse	7.297	120	0.5	pH 5, 1–220 mg/L	Martin-Lara et al. (2010)
<i>Adononsia digitata</i> fruit shells	7.65	120	0.45	pH 6, 10–100 mg/L	Chigondo et al. (2013)
Plant <i>Acacia nilotica</i> leaves	2.51	50	2.0	pH 5, NA	Waseem et al. (2014)
Nanocellulose fibers	9.42	40	0.125	pH 6, 1–50 mg/L	Kardam et al. (2014)
Maize stover	19.65	60	0.5	pH 5, 10–50 mg/L	Guyo et al. (2015)
Industrial fish bone meal waste	16.72	60	0.09	pH 5, 10–60 mg/L	This study

NA not available

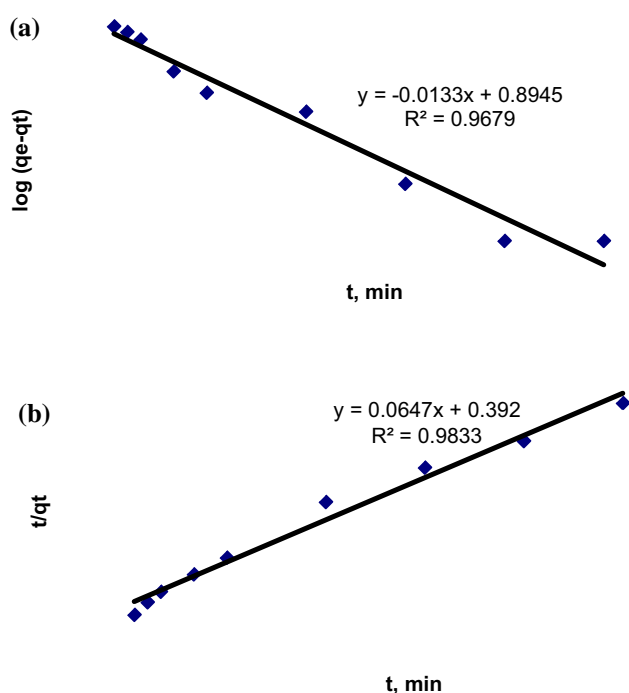


Fig. 2 Lead (II) kinetic for industrial fish bone meal waste biosorbent: (a) pseudo-first-order kinetic, (b) pseudo-second-order kinetic

the surface became rough due to the deposition of Lead (II) ions. This may be due to clear opening pores which provided easy accessibility of Lead (II) ions into the internal

part of the biosorbent and enhanced chemisorption process that changed in eternal bulk fluid thus creating an impact on surface morphology. Figure 4a, b depicts the EDX spectrum of industrial fish bone meal waste biosorbent before and after biosorption. The presence of calcium, carbon, magnesium, oxygen, phosphorus, and sodium was observed in industrial fish bone meal waste biosorbent before biosorption (Kizilkaya and Tekinay 2014). The additional peaks of Lead (II) that emerged after biosorption indicated that Lead (II) has been attached on the surface of industrial fish bone meal waste biosorbent. This observation supported the macroporous surface of industrial fish bone meal waste biosorbent as reported in BET analysis. This result was consistent with the previous studies conducted by Wen et al. (2011) and Lim et al. (2012).

Zero point charge (pH_{pzc}) analysis

Figure 5 illustrates an inverse relationship between pH difference (ΔpH) and initial pH (pH_i). The pH_{pzc} was determined at pH 7.5 which implied the maximum Lead (II) removal. When the pH of solution was lower than the pH_{pzc} value, the acidic solution donated more protons causing the biosorbent surface to become positively charged. The result demonstrated that the increase of pH (Fig. 1b) increased the biosorbent affinity towards cations and hence increased the efficiency of Lead (II) removal. Based on the biosorption study, Lead (II) removal

Table 3 Calculated thermodynamic parameters of Lead (II) biosorption using industrial fish bone meal waste biosorbent

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol/K)	R^2
278	+3.426	+36.848	-0.1190	0.9539
288	+2.870			
298	+1.503			
308	+0.711			
318	+1.535			

Table 4 Comparison properties of industrial fish bone meal waste biosorbents with those used in other studies

Biosorbent	BET surface area (m ² /g)	Particle size (μm)	References
Fungus <i>Trametes versicolor</i>	3.103	200–300	Subbaiah et al. (2011)
Wheat straw <i>Triticum aestivum</i>	8.17	<100	Farooq et al. (2011)
Sisal fiber <i>Agave sisalana</i>	0.0233	152	dos-Santos et al. (2011)
Iodine (20 %)-pretreated chitosan	0.29	<150	Dongre (2014)
Industrial fish bone meal waste	1.5504	≤710	This study

Fig. 3 SEM of industrial fish bone meal waste biosorbent (a) before and (b) after Lead (II) biosorption

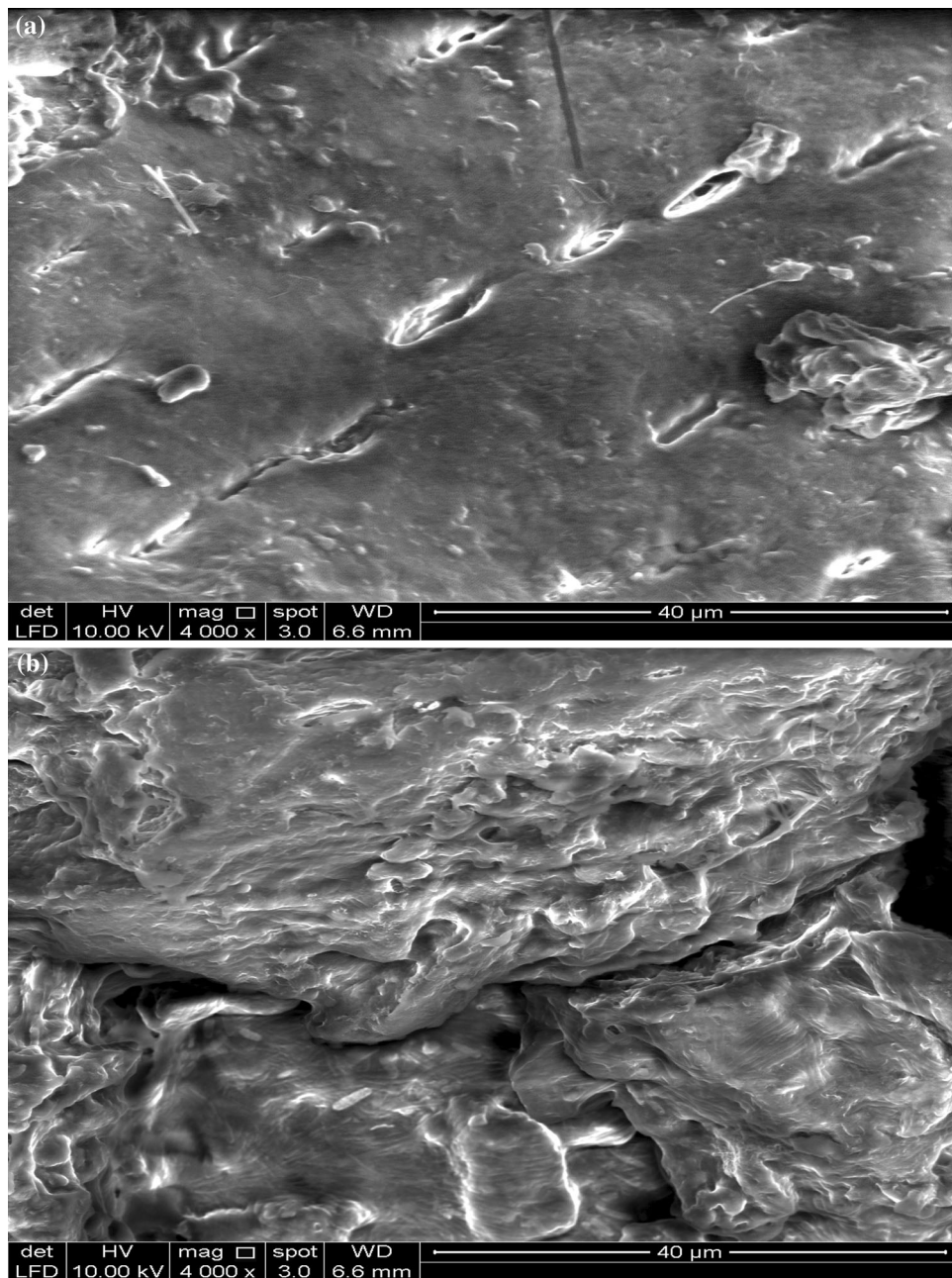
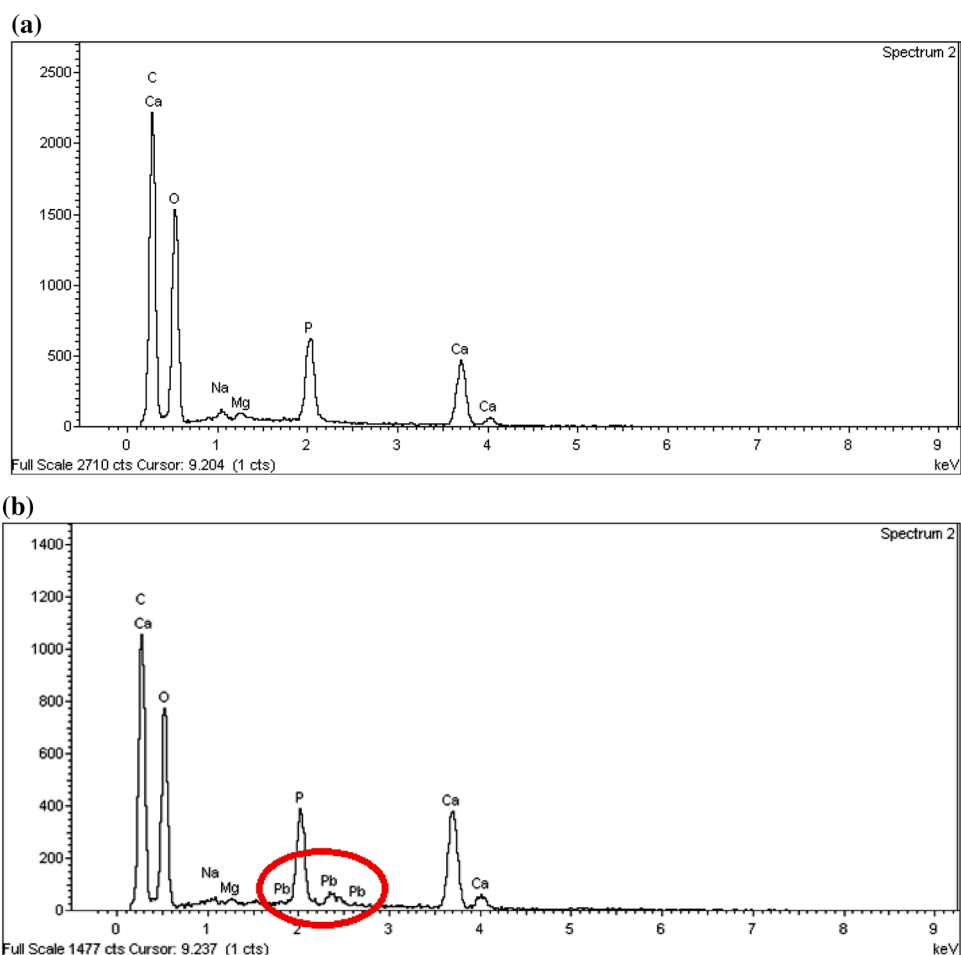


Fig. 4 EDX of industrial fish bone meal waste biosorbent (a) before and (b) after Lead (II) biosorption



decreased after pH 5, not as predicted by pH_{pzc} due to the precipitation of the metal. A similar pH_{pzc} was reported by Trakal et al. (2014). In addition, this observation also deduced that the weak acidic functional groups such as carboxyl, hydroxyl, and amide interact with Lead (II) ions

during biosorption process. However, this needs to be further investigated through FTIR analysis.

FTIR analysis

Table 5 and Fig. 6 illustrate the shifted peaks and assignment of biosorbent before and after biosorption. The changes of wavelength signified the functional groups involved in biosorption. The spectrum of biosorbent shifted from $3281.77\text{--}3282.77\text{ cm}^{-1}$, assigning to --NH and --OH stretching. The C=O and C--O--C stretchings appeared at 1643.66 and 1018.23 cm^{-1} with the increased intensity in biosorbent, respectively. The --NH band intensity at 1537.67 cm^{-1} reduced to 1537.48 cm^{-1} when lead (II) chelated on the biosorbent surface. In conclusion, the functional groups involved in Lead (II) biosorption were --NH , --OH , C=O , and C--O--C which are consistent with the study conducted by Wen et al. (2011) and Lim et al. (2012). This result also confirmed the heterogeneous weak acidic binding sites of industrial fish bone meal waste biosorbent as suggested by Freundlich isotherm and pH_{pzc} analysis.

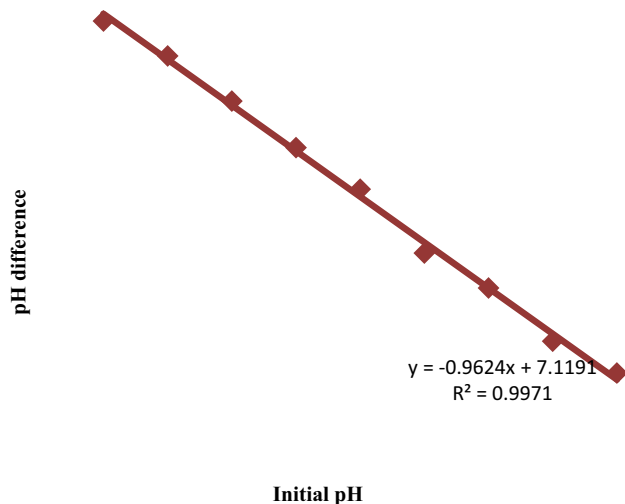


Fig. 5 The pH_{pzc} of industrial fish bone meal waste biosorbent

Table 5 The shifted peaks and assignation of biosorbent before and after biosorption

Wavenumber before biosorption (cm ⁻¹)	Wavenumber after biosorption (cm ⁻¹)	Assignations	References
3281.77	3282.77	-NH/-OH	Lim et al. (2012)
1643.66	1644.00	C=O	Khan et al. (2011)
1537.67	1537.48	-NH	Wang and Chen (2014); Wen et al. (2011)
1018.23	1018.98	C-O stretching of -OH and COOH	Yipmantin et al. (2011)

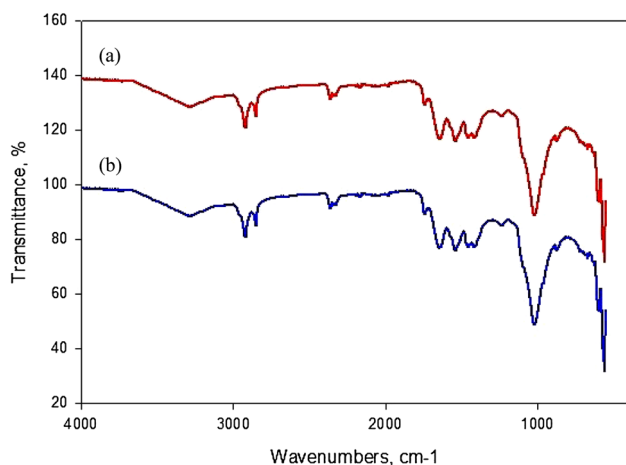


Fig. 6 FTIR spectrum of industrial fish bone meal waste biosorbent (a) before and (b) after Lead (II) biosorption

Biosorbent comparison experiment

The performance of Lead (II) biosorption between biosorbent and commercial resins is summarized in Table 6. The percentage removal and uptake by industrial fish bone meal waste biosorbent was 40 % lower than that by Resin Amberlite IRC-86 and Dowex 50 W X8. In terms of cost estimation, this developed biosorbent is 70 and 240 times more cost effective than Resin Amberlite IRC-86 and Resin Dowex 50 W X8, respectively. Details of calculation for cost estimation of industrial fish bone meal waste are shown in Table 7. Therefore, the biosorbent is a potential competitive material to commercial resins. Furthermore,

this biosorbent can be used to desorb Lead (II) using 0.1 M nitric acid with Lead (II) recovery of 85 %, due to reversible binding sites in chemisorption mechanism as suggested in the previous sections. These situations shed light for replacement of resin or pretreatment application in industrial wastewater which reduce the consumption of chemicals and disposal problem of toxic sludge or resin materials. In short, this developed biosorbent is a cost-effective eco-friendly product which contributes to zero waste concept by recovery the metal from biosorbent and final discarded material could be used for composite filler or organic compost material in downstream industries.

Conclusion

Industrial fish bone meal waste, which is a cost-effective and eco-friendly biosorbent, was evaluated as a potential biosorbent for Lead (II) removal. An amount of 0.096 g biosorbent was found at the half saturation removal of Lead (II) in order to reduce operation time and the consumption of chemicals. This approach is supported by optimization results and Langmuir equation. The chemisorption mechanism is supported by the mean energy value of 40.82 kJ/mol and SEM analysis of surface morphology changes. Pseudo-second-order kinetic aptly described that chemisorption is the rate-limiting factor in biosorption process. The pH_{pzc} and FTIR analysis revealed heterogeneous surface functional groups as suggested by Freundlich isotherm. Functional groups of Hydroxyl, carboxyl, and amides serve as multi-binding sites of Lead (II) ions which contributed to reversible bonding of chemisorption

Table 6 Comparison performance of industrial fishbone meal waste biosorbent with other commercial resins

Characteristics	Industrial fish bone meal waste biosorbent	Resin amberlite IRC-86	Resin dowex 50 W X8
Percentage removal (%)	50	77	79
Uptake (mg/g)	14.65	23.78	24.39
Estimated cost (RM/kg)	10.00 [2.50 USD]	700.00* [175 USD] (70×)	2400.00* [600 USD] (240×)
Desorption	Yes (85 %)	Yes	Yes

* Estimated price obtained from suppliers and industries operators

Table 7 Cost estimation for industrial fish bone meal waste from sample collection to biosorbent

Activities	Estimated cost (RM/kg)
Sample collection and transportation	3.00
Washing in hot 100 ± 3 °C water	
Water	0.0012 ^a
Heating 100 ± 3 °C	$2.2 \text{ kW} \times 0.05 \text{ h} \times \text{RM}0.50^* = 0.055$
0.1 M sodium hydroxide pretreatment at 60° C for 2 h	
0.1 M sodium hydroxide	$\text{RM}54/\text{kg} \times 0.054 = 2.92$
Ultrapure water system	$0.15 \text{ kW} \times 24 \text{ h} \times \text{RM}0.50^* = 1.80$
Water for ultrapure water system	0.2 ^a
Water for sodium hydroxide	0.04 ^a
Heating 60° C	$0.15 \text{ kW} \times 2 \text{ h} \times \text{RM}0.50^* = 0.15$
Ultrapure water for washing	0.08 ^a
Drying sample in an oven at 60 °C	$0.3 \text{ kW} \times 10 \text{ h} \times \text{RM}0.50^* = 1.50$
Grinding and sieve of sample	$1.5 \text{ kW} \times 0.17 \text{ h} \times \text{RM}0.50^* = 0.125$
Total cost	9.87→10.00

* Estimated cost for electricity for 1 kWh = RM0.50

^a Estimated cost for water per 1000 kg/1 m³ = RM4.00

mechanism. In addition, thermodynamic revealed that Lead (II) biosorption is endothermic and non-spontaneous in nature with reversible weak bonding formed during the biosorption process due to sharing of electrons in chemisorption mechanism. The developed biosorbent is cheap, with an estimated cost of RM10.00/2.50 USD per kg that is at least 70 times cheaper than commercial resins. Furthermore, Lead (II) could be recovered from biosorbent for downstream applications with the efficiency of 85 % and this supported reversible bonding in chemisorption mechanism. In application, this biosorbent could be considered to replace resin or used in pretreatment process in industrial wastewater application as it is cost effective and eco-friendly. Therefore, this study sheds light on waste-to-wealth green technology and zero waste eco-friendly concept.

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