

## Isothermal, kinetics and thermodynamics studies of the biosorption of Pb(II) ion from aqueous solution using the scale of croaker fish (*Genyonemus lineatus*)

Mojisola O. Nkiko, Abideen I. Adeogun, N. A. Adesola Babarinde and Oluwabunmi J. Sharaibi

### ABSTRACT

Biosorbent prepared from the scale of croaker fish (*Genyonemus lineatus*) has been used for the removal of Pb(II) ion from aqueous solution in a batch system. The effects of some important parameters such as pH, initial metal concentration, temperature and biosorbent dosage on biosorption capacity were investigated. Equilibrium time for the biosorption process is 20 and 30 min at lower and higher concentrations, respectively. The process at 28 °C is in agreement with a pseudo-second-order kinetics model. The equilibrium data obeyed the Langmuir adsorption isotherm with a maximum monolayer adsorption capacity of 14.58 mg g<sup>-1</sup>. The study showed that the sorption process depends on biomass dosage, temperature, pH and initial metal ion concentration. The calculated thermodynamics parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) indicated that the biosorption of the metal ion onto fish scale is feasible, spontaneous and exothermic in nature.

**Key words** | biosorption, croaker fish, isotherms, kinetics, scale

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### INTRODUCTION

Heavy metals are natural components of the Earth's crust and as such cannot be degraded or destroyed. They have long been recognized as hazardous substances and their chronic toxicities as well as accumulation abilities in living organism have been of great research interest in the past (Naimo 1995). The advanced technologies for industrialization and urbanization have also substantially enhanced the degradation of the environment especially the aquatic, through the discharge of industrial waste waters and domestic wastes (Senthilkumar *et al.* 2000; Amini *et al.* 2008). Industrial processes such as mining operations, sludge disposal, metal plating and the manufacture of electrical equipment are responsible for the release of metal ions, such as Mn(II), Cr(III) and Pb(II) which pollute the environment. The toxic nature of these pollutants has caused increased concern for their removal from industrial effluents. According to the United States Environmental Protection Agency, lead (Pb) is one of the metals that is extremely toxic to organisms even at low

concentrations (Ramos *et al.* 2002). It can damage the nervous system, gastrointestinal track, encephalopathy with pretreatment damage, kidneys and reproductive system particularly in children (Senthilkumar *et al.* 2000; Amini *et al.* 2008). Therefore, the removal of heavy metals from waters and wastewaters is important to protect public health and wildlife alike.

Heavy metals can be recovered successfully from solution by precipitation as hydroxides or carbonates, or membrane filtration or capture on synthetic ion exchangers. However, these methods are not efficient at lower metal concentration, can be prohibitively expensive and can even fail to achieve tolerable limits. As an alternative, especially at very low concentrations of metal ion contaminant, it is preferable to use sorption techniques (Akar & Tunali 2005). The adsorption technique, being very effective and economical, is one of the preferred methods for removal of toxic contaminants from water.

Biosorption has been found to be an efficient and effective alternative technology at little or no cost when compared with conventional methods (which are rather expensive with associated demerits) of removing toxic metal ions from effluents. Different agricultural wastes have been investigated for their potential to remove these metal ions from solution in order to determine their possible usage in treating industrial effluents (Bello *et al.* 2008; Adeogun *et al.* 2010, 2012; Babarinde 2011).

This study exploits the fact that the scales from different fish species contain significant portions of organic protein (collagen) and other functional groups, such as phosphate, carboxyl, amine and amide, that are involved in the biosorption of heavy metals (Mustafiz *et al.* 2003). Croaker fish scales were used to prepare biosorbent for the removal of Pb(II) ion from aqueous solution. The effects of operational factors such as pH, adsorbent dose, contact time, and initial concentration were investigated. The kinetics of Pb(II) ion biosorption was analyzed by fitting with pseudo-first and pseudo-second-order, and intraparticle diffusion models. Adsorption data were also fitted using the Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm equations.

## MATERIALS AND METHODS

### Biosorbent preparation and characterization

Croaker fish was obtained from the local fish market at Oke Aje in Ijebu Ode, Ogun State, Nigeria. The scales were soaked in distilled water for 24 h and washed several times with distilled water to remove any surface contaminants. The scales were air dried and pulverized using a household blender. The biomaterial was sieved to obtain a particle size range of 150–500  $\mu\text{m}$ , this was stored in clean air-tight containers. The concentrations of Pb(II) ion in the biosorbent was determined by placing 1 g of the adsorbent in 10 mL de-ionized water for 2 h with continuous agitation, after which it was centrifuged at 2,000 rpm. The supernatant was analyzed using a flame atomic absorption spectrophotometer (FAAS) Buck Scientific 310 VGP. The biomaterial was later characterized using Fourier transform infrared (FTIR) spectroscopic analysis. This was performed

using an FTIR spectrometer (FTIR-2000, Perkin–Elmer). The spectra were measured from 4,000 to 400  $\text{cm}^{-1}$ .

### Preparation of aqueous solution of metal ions

The aqueous solution of Pb(II) ion was prepared from analytical grade of lead(II) nitrate,  $\text{Pb}(\text{NO}_3)_2$ . 1,000  $\text{mg L}^{-1}$  aqueous solution of the salt was prepared with de-ionized water in 1%  $\text{HNO}_3$  solution as the stock solution and was further diluted with de-ionized water to obtain the working standard solutions. The pH of the solutions were adjusted with aliquots of 1.0  $\text{mol L}^{-1}$  of HCl and NaOH. The pH of the solution was checked on a Radiometer PHM 85 Research pH meter, which had earlier been standardized with standard buffer solutions pH 4.00 and 7.00.

### Equilibrium studies

Equilibrium adsorption isotherms were performed in a batch process as described earlier (Adeogun *et al.* 2010). The amount of metal ion adsorbed by the biosorbent at equilibrium,  $Q_e$  ( $\text{mg g}^{-1}$ ), was calculated using Equation (1) below:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration and  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration of the metal ion at equilibrium in the liquid-phase.  $V$  is the volume of the solution (L), and  $W$  is the mass of dry adsorbent used (g).

### Batch kinetics studies

The procedures for the kinetics studies were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of the metal ions were similarly determined. The amount of metal ion adsorbed at time  $t$ ,  $Q_t$  ( $\text{mg g}^{-1}$ ), was calculated using Equation (2):

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where  $C_0$  and  $C_t$  ( $\text{mg L}^{-1}$ ) are the liquid-phase concentrations of the metal ion at initial and at time  $t$ , respectively.  $V$  is the volume of the solution (L), and  $W$  is the mass of dry adsorbent used (g).

## RESULTS AND DISCUSSION

### Characterization of biosorbent

Figure 1 shows the FTIR vibrational spectra of croaker fish scale before and after the biosorption processes. It is gratifying to note that some bands initially present in the spectrum of the biosorbent before the biosorption process were either missing or shifted to higher or lower frequency after the biosorption process. This is an indication of metal ion sorption onto the biosorbent. The wide band with maxima at 3,441, 3,342 and 3,306  $\text{cm}^{-1}$  were assigned to the stretching of O–H and N–H groups of macromolecular association, the band at 2,858 and 2,929  $\text{cm}^{-1}$  were assigned to –CH– bond of the methylene group presented in the structure of the croaker fish scale. The strong peaks that appear at 1,658 and 1,654  $\text{cm}^{-1}$  were assigned to the C–O stretching vibration of a carboxylic acid that exists with intermolecular hydrogen bonding. In addition, the band at 1,413  $\text{cm}^{-1}$  confirms the presence of C=C of aromatic rings. Several bands ranging from 1,338 to 1,030  $\text{cm}^{-1}$  refer to the C–O bonding in phenols. The FTIR data confirm the functional

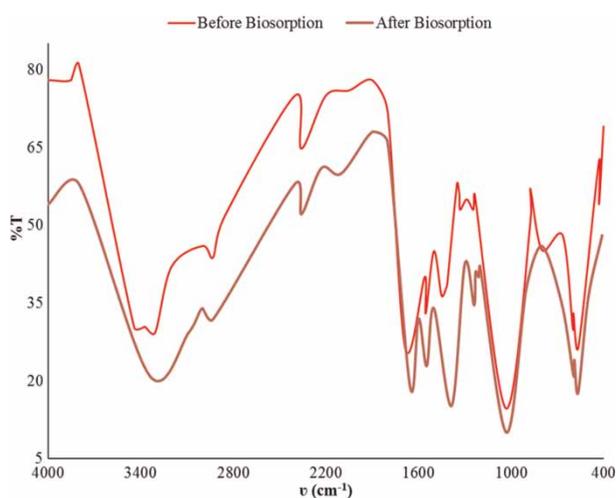


Figure 1 | FTIR spectra of croaker fish scale before and after biosorption.

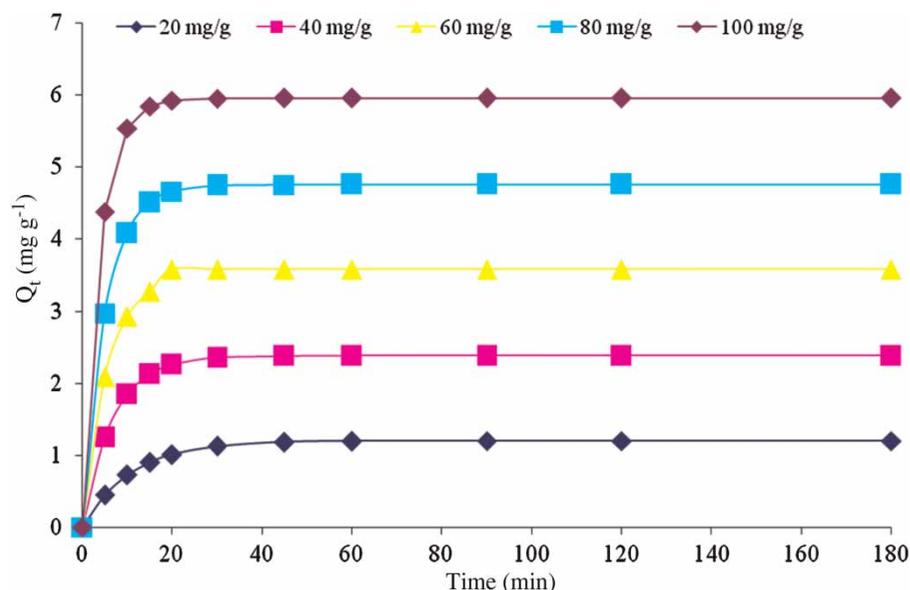
groups in the biosorbent and their ability to form a chelate with the Pb(II) ion in aqueous solution (Huang *et al.* 1991).

### Effect of agitation time and initial metal concentration

The effect of agitation time and initial concentration on the uptake of Pb(II) ion by biosorbent is shown in Figure 2 for various ion concentrations at 28 °C. The process showed rapid biosorption of Pb(II) ion in the first 10 min for all the concentrations studied, and thereafter, the increase became gradual until a point where there is no change in the amount adsorbed, i.e. a constant value when the amount desorbed is proportional to the amount adsorbed on the biosorbent, inferring a dynamic equilibrium (at around 15–20 min). The biosorption capacity at equilibrium increases from 1.01 to 5.84  $\text{mg g}^{-1}$  with an increase in the initial concentration from 20 to 100  $\text{mg L}^{-1}$ . As there is no significant difference in the biosorption values after 20 min of contact, a steady-state approximation was assumed and a quasi-equilibrium situation was reached. The biosorption curves were single, smooth, and continuous, leading to saturation, and indicated the possible monolayer coverage on the surface of biosorbent by the Pb(II) ion molecules (Langmuir 1918; Saha & Sanyal 2010).

### Effect of pH

pH plays an important role in the biosorption capacity by influencing the chemistry of both the Pb(II) ion and the biosorbent in aqueous solution. The adsorption capacities of the biosorbent for Pb(II) ion at different pH levels is shown in Figure 3. From the figure, it is noted that at pH 2, about 99.8% of initial metal ion is removed from the solution. However, as acidity decreases, the amount of the Pb(II) ions biosorbed decreased drastically. The pH dependency of biosorption efficiency may be attributed to the functional groups involved in metal uptake. At low pH and high acidity, protons occupy most of the biosorption site on the biomass surface so a small concentration of the Pb(II) ions is absorbed due to electric repulsion between the protons and biomass. As the pH increases and acidity decreases, the biosorbent surface becomes more negatively charged and biosorption of the positive metal ion occurs with maximum biosorption at pH of 2, above pH 2 soluble



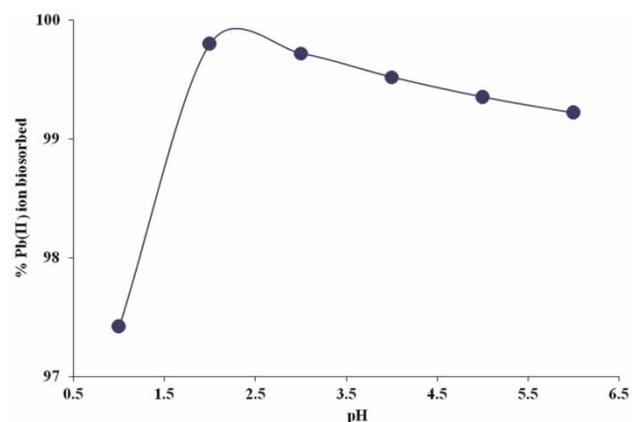
**Figure 2** | Effect of agitation time and initial metal ion concentrations on biosorption of Pb(II) ion on croaker fish scale (pH = 2.0, temperature = 28 °C, biosorbent dosage = 0.5 g).

hydroxyl complexes of Pb(II) ions capable of competing with the active sites are formed, consequently the retention of the metal ion by the biomass decreases as acidity decreases and pH increases (Galun *et al.* 1987).

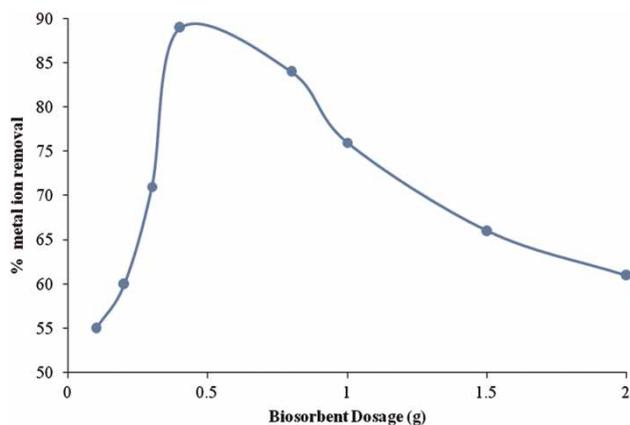
### Effect of biosorbent dosage

The effect of biosorbent dosages for removal of Pb(II) ions from aqueous solution was investigated at different adsorbent doses ranging between 0.20 and 2.0 g using

100 mg L<sup>-1</sup> of the metallic ion in solution. It was observed that highest quantitative removal of the metallic ion was attained at biosorbent dosages of about 0.5 g (Figure 4). This observation implies that the number of adsorption sites has increased due to the increase in surface area of adsorption. The initial increases in the percentage of metallic ion removal with biosorbent dosages could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption. At biosorbent dosages higher than the optimum dosage value, decrease in the percentage metal ion



**Figure 3** | Effect of pH on the percentage adsorption of the metal ion (conditions: initial concentration = 100 mg L<sup>-1</sup>; time = 60 min; temperature = 28 °C, biosorbent dosage = 0.5 g).



**Figure 4** | Effect of biosorbent dosage on the percentage adsorption of the metal ion (conditions: initial concentration = 100 mg L<sup>-1</sup>; time = 60 min; temperature = 30 °C).

biosorbed may be attributed to the concentration gradient between adsorbate and biosorbent. Increasing biomass concentration may cause a decrease in the amount of metallic ion adsorbed per gram of biomass (Lin et al. 2011).

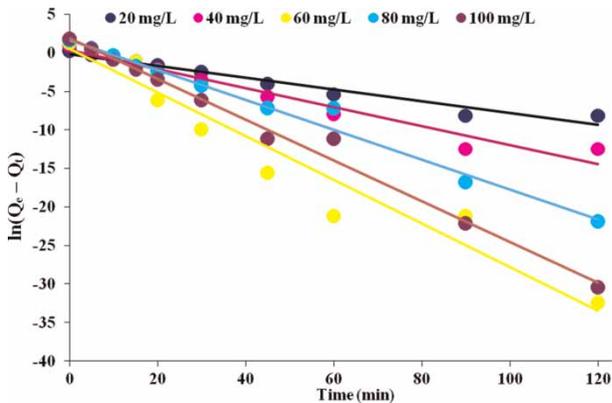
## Biosorption kinetics

### The pseudo-first-order kinetics model

A simple kinetics analysis of adsorption under the pseudo-first-order assumption is given by Equation (3) below (Adeogun et al. 2011; Lin et al. 2011):

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \quad (3)$$

where  $Q_e$  and  $Q_t$  are the concentrations of Pb(II) ion biosorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  the adsorption rate constant ( $\text{min}^{-1}$ ),



**Figure 5** | Pseudo-first-order kinetics model for the biosorption of Pb(II) ion by the biosorbent prepared from croaker fish scale (conditions: pH = 2, temperature = 28 °C, biosorbent dosage = 0.5 g).

**Table 1** | Comparison of the pseudo-first- and pseudo-second-order adsorption rate constants, and calculated and experimental  $q_e$  values for different initial Pb(II) ion concentrations at 25 °C

Initial concentration ( $\text{mg L}^{-1}$ )	$Q_e$ (exp.) ( $\text{mg g}^{-1}$ )	$Q_e$ (cal.) ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	%SSE	$Q_e$ (cal.) ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g (mg g}^{-1})^{-1}$ )	$R^2$	%SSE
20	1.198	0.848	0.077	0.961	0.035	1.411	2.439	0.997	0.018
40	2.380	1.370	0.123	0.961	0.101	2.451	0.173	0.999	0.0059
60	3.577	1.684	0.283	0.945	0.189	3.652	0.036	0.999	0.0063
80	4.753	5.165	0.194	0.983	0.041	4.829	0.012	0.999	0.0062
100	5.952	6.468	0.264	0.980	0.052	6.002	0.003	0.999	0.0042

and  $t$  is the contact time (min). The integration of Equation (3) with initial concentrations,  $Q_t = 0$  at  $t = 0$ , and  $Q_t = Q_t$  at  $t = t$ , yields Equation (4) below:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

Values of  $k_1$  were calculated from the plots of  $\ln(Q_e - Q_t)$  versus  $t$  (Figure 5) for different concentration of Pb(II) ion. The correlation coefficient values ranged between 0.93 and 0.98. Table 1 shows the experimental  $Q_e$  values does not in agree with the calculated ones. This implies that the biosorption process is a pseudo-first-order kinetics, however, the disparity in the values of experimental and calculated  $Q_e$  contradicts this kinetic theory. Hence, a pseudo-second-order kinetics model was employed.

### The pseudo-second-order kinetics model

A pseudo-second-order kinetics model is based on equilibrium adsorption (Adeogun et al. 2010, 2011) and it is expressed as shown in Equation (5) below:

$$t/Q_t = 1/k_2 Q_e^2 + (1/Q_e)t \quad (5)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rates constant of pseudo-second-order adsorption, or

$$Q_t/t = \frac{h}{1 + k_2 Q_e t} \quad (6)$$

where  $h$  can be regarded as the initial sorption rate as  $Q_t/t$ , when  $t$  approaches 0. Hence,

$$h = k_2 Q_e^2 \quad (7)$$

If pseudo-second-order kinetics is applicable, the plot of  $t/Q$  versus  $t$  should show a linear relationship, Equation (5).  $Q_e$  and  $k_2$  are determined from the slope and intercept of the plot. The linear plots of  $t/Q$  versus  $t$  (Figure 6) show a good agreement between experimental and calculated  $Q_e$  values (Table 2). The correlation coefficient of greater than 0.99 obtained from the plot shows that the second-order kinetics model is more suitable. Therefore, the biosorption process of Pb(II) ion on croaker fish scale is best described by pseudo-second-order kinetics model.

### Statistical test for the kinetics data

Although, the square of the correlation coefficients  $R^2$  was used to compare the data, the models were also evaluated further by the percentage error function which measures the differences (% SSE) in the amount of the metallic metal ion taken up by the adsorbent predicted by the models, ( $Q_{cal}$ ) and the actual, i.e.  $Q_{exp}$  measured experimentally (Langmuir 1918; Naimo 1995). The validity of each

model was determined by the sum of error squares (SSE, %) given by:

$$\%SSE = \sqrt{\frac{(Q_{(exp)} - Q_{(cal)})^2}{N}} \quad (8)$$

$N$  is the number of data points. The higher is the value of  $R^2$  and the lower the value of SSE; the better fitted the data to the pseudo-second-order kinetics model as shown in Table 1.

### Intraparticle diffusion model

Due to the fact that the diffusion mechanism cannot be obtained from the kinetics model, the intraparticle diffusion model (Lin et al. 2011) was also tested. The initial rate of the intraparticle diffusion is given by the following expression:

$$Q_t = K_{id}t^{0.5} + C_i \quad (9)$$

where  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ) and  $C_i$  is intercept and a measure of surface thickness. Figure 7 shows that the biosorption of Pb(II) ion on biosorbent prepared from croaker fish scale is multilinear in nature with a two-step diffusion process. The first is represented by a sharper portion which depicts the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. In other words, the external surface adsorption is completed very rapidly and the second stage of intraparticle diffusion rate control (stage 2) is attained within the first 16 min. Pb(II) ions are slowly transported via intraparticle diffusion into the particles and are finally retained in the micropores. Figure 7

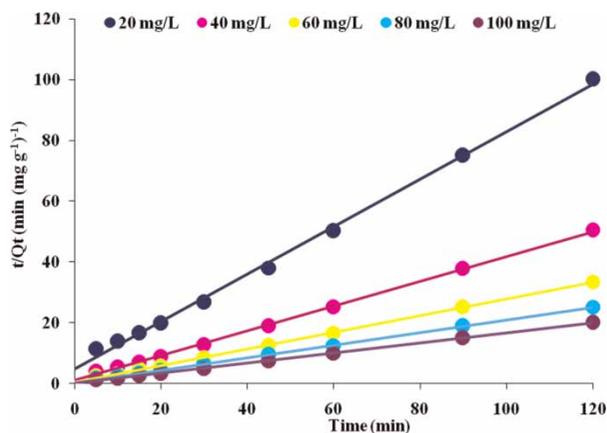
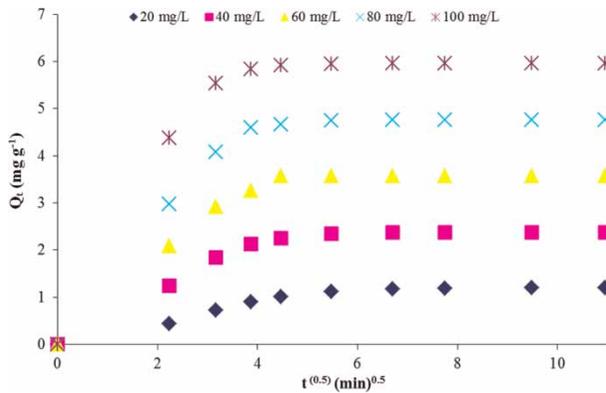


Figure 6 | Second-order kinetics model for the biosorption of Pb(II) ion by the biosorbent prepared from croaker fish scale.

Table 2 | Pseudo-second-order rate and diffusion coefficient parameters for sorption of Pb(II) ion on croaker fish scale

Initial concentration ( $\text{mg L}^{-1}$ )	$h_o$ ( $\text{mg (g min)}^{-1}$ )	$k_{id}$ ( $\text{mg g}^{-1} \text{min}^{0.5}$ )	$C_1$	$R^2$	$k_{2d}$ ( $\text{mg g}^{-1} \text{min}^{0.5}$ )	$C_2$	$R^2$
20	0.207	0.232	0.021	0.992	0.050	0.787	0.753
40	0.960	0.558	0.008	0.998	0.058	1.966	0.714
60	2.092	0.866	0.060	0.992	0.086	3.059	0.463
80	3.446	1.215	0.094	0.992	0.025	4.543	0.663
100	8.489	1.575	0.289	0.965	0.014	5.837	0.482



**Figure 7** | Intraparticle diffusion model for the biosorption of Pb(II) ion by the sorbent prepared from croaker fish scale.

shows the plot passes through the origin at the initial stage, Table 2 shows the parameter for the mechanism of diffusion in the two stages with higher values of  $R^2$  for  $K_{id}$  of the first stage, which implies that the intraparticle diffusion is the rate-determining step.

### Adsorption isotherms

Langmuir, Freundlich or Redlich–Peterson adsorption models can be used to describe the equilibrium between adsorbed metal ions and metal ions in solution.

### Langmuir isotherm

The Langmuir isotherm equation is based on the following assumptions: (i) all the surface for the adsorption has the same activity for adsorption; (ii) there is no interaction between adsorbed molecules and all the adsorption occurs by the same mechanism; and (iii) the extent of adsorption is less than one complete monomolecular layer on the surface. The Langmuir equation is given by Equation (10):

$$Q_{eq} = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (10)$$

where  $Q_o$  is the maximum amount of the metal ion per unit weight of the microorganism to form a complete monolayer on the surface bound at high  $C_{eq}$  ( $\text{mg g}^{-1}$ ) and  $K_L$  is biosorption equilibrium constant ( $\text{dm}^3 \text{mg}^{-1}$ ).  $Q_o$  represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison

of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during the experiments (Veglio & Beolchini 1997; Donmez *et al.* 1999; Matheickal *et al.* 1999; McKay *et al.* 1999). The shape of the Langmuir isotherm can be used to predict whether a sorption system is favorable or unfavorable in a batch adsorption process. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor ( $R_L$ ) that can be defined by the following relationship (Anirudhan & Radhakrishnan 2008):

$$R_L = \frac{1}{1 + C_i K_L} \quad (11)$$

where  $C_i$  is the initial concentration ( $\text{mg L}^{-1}$ ) and  $K_L$  is the Langmuir equilibrium constant ( $\text{L mg}^{-1}$ ). The value of separation parameter  $R_L$  provides important information about the nature of adsorption. The value of  $R_L$  indicates the type of Langmuir isotherm to be irreversible if  $R_L = 0$ , favorable when  $0 < R_L < 1$ , linear when  $R_L = 1$  and unfavorable when  $R_L > 1$ . However, it can be explained apparently that when  $K_L > 0$ , a sorption system is favorable (Chen *et al.* 2008).

### Freundlich isotherm

The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface. It is commonly presented as:

$$Q_{eq} = K_F C_e^{1/n} \quad (12)$$

where  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively (Bello *et al.* 2008; Adeogun *et al.* 2012).

### Redlich–Peterson isotherm

A three parameter Redlich–Peterson equation has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by Equation (13):

$$Q_{eq} = \frac{Q_o K_R C_e}{1 + K_R C_e^\beta} \quad (13)$$

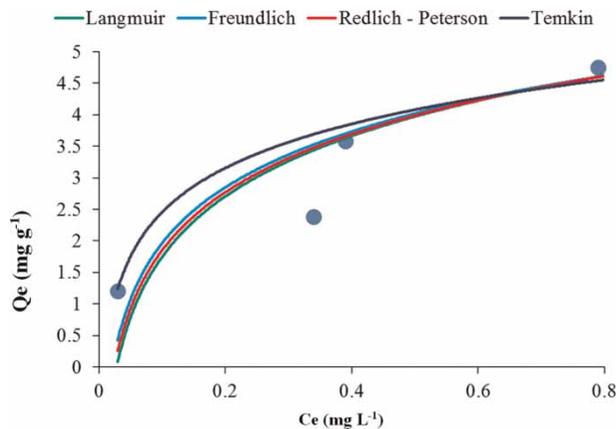
where  $K_R$  and  $\beta$  are the Redlich–Peterson parameters,  $\beta$  lies between 0 and 1 (Vaghetti et al. 2009). For  $\beta = 1$ , Equation (13) converts to the Langmuir form. The adsorption model constants were obtained by non-linear regression analysis method using a program written on Micro Math Scientist software (Salt Lake City, Utah) and the isotherms are shown in Figure 8. The parameters used for fitting the isotherms are shown in Table 2.

### The Temkin isotherm model

The Temkin isotherm model was also used to fit the experimental data. Unlike the Langmuir and Freundlich equations, the Temkin isotherm takes into account the interaction between adsorbents and metal ion to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage (Chen et al. 2008). The linear form of the Temkin isotherm is represented in Equation (14):

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \quad (14)$$

where  $C_e$  is concentration of the adsorbate at equilibrium ( $\text{mg L}^{-1}$ ),  $q_e$  is the amount of adsorbate adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $T$  is the temperature (K), and  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $a_T$  and  $b_T$  are constants. The constant,  $b_T$ , is related to the heat of adsorption and also related to bonding energy. The parameter,  $a_T$ ,



**Figure 8** | Biosorption isotherms for Pb(II) ion by the biosorbent prepared from croaker fish scale.

is the equilibrium binding constant ( $\text{L min}^{-1}$ ) corresponding to the maximum bonding energy. The typical binding energy reported for an ion exchange mechanism is between 8 and  $16 \text{ kJ mol}^{-1}$ . Bonding energy of up to  $-20 \text{ kJ mol}^{-1}$  indicates physisorption due to electrostatic interaction between the charged particle, whereas more negative than  $-40 \text{ kJ mol}^{-1}$  indicates a chemisorption process (Chen et al. 2008). The value  $b_T$  in this study (Table 3) shows that the process is not purely chemisorption (Langmuir 1918).

### Biosorption thermodynamics

The distribution of the metal ion between the solution and the biosorbent at equilibrium is written as:

$$K_D = \frac{M_{\text{solution}}^{n+}}{M_{\text{Biosorbed}}^{n+}}$$

$$K_D = \frac{C_e}{Q_e}$$

**Table 3** | Adsorption isotherm parameters for the biosorption of Pb(II) ion on croaker fish scale

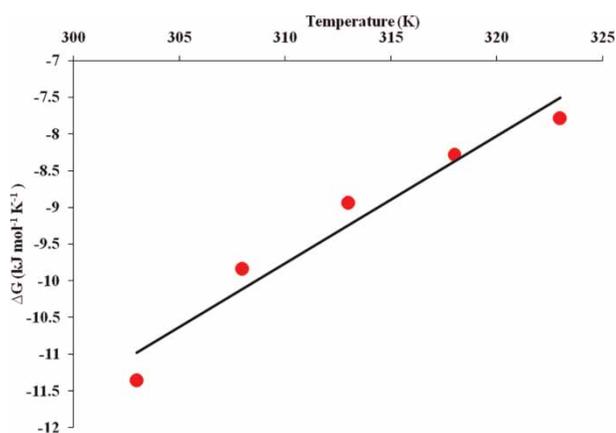
Langmuir isotherm	
$Q_o$ ( $\text{mg g}^{-1}$ )	14.58
$K_L$ ( $\text{L}^{-1} \text{ mg}^{-1}$ )	0.73
$R_L$	0.03
$R^2$	0.976
Freundlich isotherm	
$K_F$ ( $\text{mg g}^{-1}$ )( $\text{mg L}^{-1}$ ) <sup>n</sup>	6.12
$N$	1.55
$R^2$	0.98
Redlich–Peterson isotherm	
$Q_o$ ( $\text{mg g}^{-1}$ )	31.87
$K_R$ ( $\text{L}^{-1} \text{ g}^{-1}$ )	4.12
$\beta$ ( $\text{g cm}^{-3}$ )	0.4
$R^2$	0.979
Temkin isotherm	
$a_T$ (L/mg)	5.44
$b_T$ (kJ/mol)	0.66
$R^2$	0.978

The equilibrium constant  $K_D$  is temperature dependent and it is used in determining the thermodynamics parameters. The thermodynamics parameters i.e.  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were estimated using the following relation:

$$\Delta G^\circ = -RT \ln K_D \quad (15)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (16)$$

A plot of  $\Delta G^\circ$  against the temperature, (Figure 9) gives a straight line graph with intercept as  $\Delta H^\circ$  and slope as  $\Delta S^\circ$ . The thermodynamics parameters are shown in Table 4. The values of  $\Delta G^\circ$  are negative which implies that biosorption is thermodynamically feasible and spontaneous in nature. The  $\Delta G^\circ$  values increases, i.e. less negative, as the temperature increases which implies that the process becomes less feasible as temperature increases. The  $\Delta H^\circ$



**Figure 9** | Thermodynamics of Pb(II) ion biosorption by the biosorbent prepared from croaker fish scale.

**Table 4** | Thermodynamic parameters for the biosorption of Pb(II) ion on croaker fish scale

Temperature (K)	ln $K_D$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$R^2$
303	4.51	-11.36	-0.174	-63.67	0.95
308	3.84	-9.84			
313	3.43	-8.94			
318	3.14	-8.29			
323	2.90	-7.79			

parameter was also found to be negative indicating the exothermic nature of the biosorption processes. The negative  $\Delta S^\circ$  value implies a decrease in the randomness at the solid/solution interface during the biosorption process.

## CONCLUSION

This study revealed the feasibility of scale of croaker fish as a biosorbent for the removal of Pb(II) ions from its aqueous solution using batch sorption technique. The adsorption process depends on numerous factors such as the solution pH, adsorbent dosage, temperature, stirring rate, initial Pb(II) concentration and contact time. The percentage removal of lead ions decreased with pH, as pH of 2 was exceeded, while it increased with increase in contact time and adsorbent dose up to 0.5 mg. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of Pb(II) ions with a monolayer adsorption capacity of 14.58 mg g<sup>-1</sup> at 301 K. The adsorption kinetics is explained using a pseudo-second-order kinetics model, square of the correlation coefficient close to unity (Table 3). Intra-particle diffusion was not the sole rate controlling factor. The thermodynamics parameter obtained indicates the exothermic nature of lead adsorption. Therefore, the present findings suggest that scale of croaker fish be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of lead ions from aqueous solutions.

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