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Biosorption of lead(II) onto pine cone powder: Studies on biosorption performance and process design to minimize biosorbent mass

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ABSTRACT

Biosorption kinetic modeling is frequently performed on both raw and modified biosorbents and changes in model parameters observed. Comparative studies on the relationship between best fitting model parameters and biosorption performance for raw and modified is scares in literature. In the present study, the effect of surface modification on the kinetic parameters of the best fitting kinetic model (pseudo-second order) for biosorption of lead(II) ions onto Raw and NaOH modified pine cone powder was examined and related with biosorption performance for each sample. Equilibrium biosorption studies performed showed that the Langmuir-1 isotherm gave a better fitting of the equilibrium data for all samples indicating that biosorption sites are homogenous regardless of surface modification. Based on the Langmuir-1 isotherm, a two-stage batch adsorber was designed to predict the minimum biosorbent amount to achieve a specified percentage lead(II) removal.

1. Introduction

Plant fibres, rich in cellulosic and lignin materials, show a strong tendency to attract and remove heavy metal ions from aqueous solution (Conrad, 2008; Demirbas, 2008; Ngah & Hanafiah, 2008; Ofomaja & Ho, 2007). These components of plant fibre are usually compose of groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups which are known to bind heavy metals by the donation of an electron pair from these functional groups to form complexes or exchange hydrogen ions for heavy metal ions in solution (Ho, 2005; Ofomaja & Ho, 2007; Ofomaja, Naidoo, & Modise, 2010a; Pagnanelli, Mainelli, Veglio, & Toro, 2003; Sud, Mahajan, & Kaur, 2008). Heavy metal binding on plant materials therefore involves complex processes that comprise a number of mechanisms like adsorption, complexation, chelation and entrapment in capillaries and spaces within polysaccharide network, due to concentration causing diffusion through the cell walls and membrane (Farooq, Kozinski, Khan, & Athar, 2010). Lignin in plant materials serve two major purpose: (1) to strengthen the cell walls and (2) to protect the microfibrils of the cell wall from chemical, physical, and biological attack (Goodwin & Mercer, 1986; Ofomaja, Naidoo, & Modise, 2009). Therefore, these properties of lignin may help to explain the low total negative charge, low biosorption capacities and low carboxyl group content displayed by agricultural wastes with high lignin concentrations. Various researchers have observed that high lignin contents have resulted in low porosity, low CEC and capacity (Marshall, Wartelle, Boler, Johns, & Toles, 1999; Ofomaja et al., 2009; Wartelle & Marshall, 2000). Extraction of lignin and other plant base soluble fractions using acids (organic or inorganic) solutions, base solutions, or oxidizing agents have been shown to improve these properties and also impart or increase the quantity and types of functional groups on the material surface (Ngah & Hanafiah, 2008; Ofomaja et al., 2009) thereby increasing the complex nature of the metal removal process.

Several kinetic models have been applied to the biosorption of heavy metals by agricultural wastes. Of these models the frequently used are: the pseudo-first order and pseudo-second order (Jacques, Lima, Dias, Mazzocato, & Pavan, 2007; Panda et al., 2006; Schiewer & Patil, 2007; Singh, Talat, & Hasan, 2006; Zulkali, Ahmad, & Norulakmal, 2006), modified pseudo-first order model (Ofomaja, Naidoo, & Modise, 2010a; Unuabonah, Adebowale, & Ofomaja, 2009; Unuabonah, Adie, Onah, & Adeyemi, 2009; Yang & Al-Duri, 2005) and the Elovich model (Ho & McKay, 1998a, 1998b, 1998c; Örnek, Özacar, & Şengil, 2007; Özacar & Şengil, 2005). The kinetic parameters for these models have been reported for the various biosorbents in literature but little or nothing is mentioned about how these kinetic parameters predict the biosorption performance of the biosorbent or how modification of these biosorbent affect the biosorption performance. Secondly, most biosorption studies do not consider the practical application of the biosorption material in-terms of amount needed to purify a given volume of waste water which is a critical issue.

This study is aimed at investigating the best fitting kinetic model for the biosorption of lead(II) onto pine cone powder and

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base treated pine cone powder and the relationship between the kinetic parameters and the biosorption performance at different initial lead(II) concentration. The equilibrium uptake will also be determined and a design procedure will be attempted using the Langmuir isotherm to design a two-stage biosorption system to minimize the amount of pine cone and base modified pine cone powder required and compare the optimized minimum for each biosorbent type.

2. Materials and methods

2.1. Materials

Pine tree cones were obtained from a plantation in Sasolburg, Free State South Africa. Pine tree cones were collected between August and September 2007. The cones were washed to remove impurities such as sand and leaves, and the washed cones were then dried at 90 °C for 48 h in an oven. The scales on the cones were then removed and blended in a food processing blender. The resultant powder was sieved and particles below 300 μm were collected and used for analysis.

The stock solution of lead nitrate ($Pb(NO_3)_2$) was prepared by dissolving an accurately weighed amount of the salt in deionized water. The experimental solutions were prepared by diluting the stock solution with distilled water where necessary.

2.2. Methods

2.2.1. Sample preparation

A weighed amount (50 g) of the powder was contacted with 0.01 and 0.15 mol dm^{-3} separately of 0.5 dm^{-3} NaOH solutions and the slurry stirred overnight. The powder was then rinsed with distilled water to remove excess NaOH. This procedure was repeated two more times to ensure removal of NaOH from the powder. The residue was then dried overnight at 90 °C. The original samples were coded, PCP Raw, while the treated samples were coded PCP 0.01 and PCP 0.05 according to the concentration of NaOH was for the treatment process.

2.2.2. Bulk density determination

Bulk density measurement was carried out in a 25 cm^3 density bottle. The dry pine cone powder was added to the density bottle with gentle tapping to ensure that the particles settle to the bottom and all air spaces are filled. The mass of the density bottle containing the pine cone powder was then determined. The mass of pine cone powder that occupied 25 cm^3 was then obtained from the mass of the bottle and pine cone powder minus the mass of empty bottle.

Mass of PCP which occupies 25 cm^3 volume = (mass of bottle + pine cone powder) − mass of empty bottle.

$$\text{Bulk density} = \text{Mass of PCP occupying } 25\,\text{cm}^3\ \text{volume}/25\,\text{cm}^3 \quad (1)$$

2.2.3. Point of zero charge

The pH at point zero charge (pH_{PZC}) of the pine cone powder was determined by the solid addition method (Mall, Srivastava, & Agarwal, 2006). To a series of 100 cm^3 conical flasks, 45 cm^3 0.01 mol dm^{-3} of KNO_3 solution of known concentration was transferred. The pH_i values of the solution were roughly adjusted from pH 2 to 12 by adding ether 0.10 mol dm^{-3} HCl or NaOH on a pH meter (Crison Basic 20+). The total volume of the solution in each flask was made up to 50 cm^3 by adding the KNO_3 solution of the same strength. The pH_i of the solution was accurately noted, and 0.10 g of pine cone powder was added to the flask, which was securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquids were noted. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve at which $\Delta pH = 0$ gave the pH_{PZC}.

2.2.4. Determination of acid and basic groups on pine cone powder surface

Acidic and basic sites on both raw and modified pine cone powder were determined by the acid–base titration method proposed by Boehm (1994). The total acid sites matching the carboxylic, phenolic and lactonic sites were neutralized using a 0.10 mol dm^{-3} NaOH solution while the basic sites were neutralized with a 0.10 mol dm^{-3} HCl solution. The carboxylic and lactonic sites were titrated with a 0.05 mol dm^{-3} Na_2CO_3 solution and the carboxylic sites were determined with a 0.10 mol dm^{-3} $NaHCO_3$ solution, and the phenolic sites were estimated by difference (Boehm, 1966).

2.2.5. Iodine number determination

A 25 cm^3 of iodine solution of 0.05 mol dm^{-3} was added to flasks, which contained different amount of pine cone powder ranging from 0.031 to 0.500 g. The flasks were then shaken for 24 h to assure equilibrium adsorption of iodine onto pine cone powder. The iodine number (mg g^{-1}) (or adsorption capacity) was determined from the titration of the residual solution of 10 cm^3 with 0.10 mol dm^{-3} sodium thiosulfate in the presence of 1 cm^3 of 1.00 wt% starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration.

2.2.6. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of pine cone powder before and after base washing were recorded on a Fourier transform infrared spectrometer (Perkin-Elmer infrared spectrophotometer) to elucidate the functional groups present on the pine cone powder before and after base washing.

2.2.7. Scanning electron microscope

SEM images were obtained on a LEO 1430 instrument that has a tungsten filament as electron source. Imaging was done at 3 kV to further alleviate charge build-up. On each sample about 10 images were obtained at 75× magnification and a further 5 images at 150× magnification in order to provide a representative overview of each sample.

2.2.8. Effect of initial lead(II) concentration

Kinetic experiments were carried out by agitating 100 cm^3 of lead(II) solution of concentration ranging from 60 to 120 mg dm^{-3} with 0.40 g of pine cone and base modified pine cone powder in a 250 cm^3 beaker at 291 K at an optimum pH of 5.0 and at a constant agitation speed of 160 rpm for 15 min. Samples (3.0 cm^3) were pipette out at different time intervals, centrifuged and the concentration of lead(II) analyzed using a Perkin-Elmer model 2100 atomic absorption spectrometer (AAS).

2.2.9. Equilibrium studies

A volume of 100 cm^3 of lead(II) solution with a concentration ranging from 60 to 120 mg dm^{-3} was placed in a 250 cm^3 conical flask and set at pH 5.0. An accurately weighed amount (0.40 g) of the pine cone and base modified pine cone powder were added to the solutions. The conical flask was then shaken at a constant speed of 160 rpm in a shaking water bath with temperatures 291 K. After shaking the flasks for 1 h, the pine cone and base modified pine cone powders were separated by filtration. The filtrate was analyzed for the remaining lead(II) concentration by a Perkin-Elmer model 2100 atomic absorption spectrometer (AAS).

3. Results and discussion

3.1. Results on NaOH pretreatment

The effect of NaOH pretreatment on the properties of pine cone powder was determined by measuring the changes in properties such as bulk density, surface acid groups, pH at point zero charge and iodine number after pretreatment with two concentrations of NaOH solutions. The bulk densities of the samples were measured and obtained to be 0.499 for PCP Raw, 0.444 for PCP 0.01 and 0.418 for PCP 0.05. A reduction in bulk density indicates that a fraction of constituents of the biosorbent has been leached out and this leaching increases with increasing NaOH concentration. The colour of the liquid at the end of the experiment was dark brown indicating that plant pigments and lipids were removed. Wartelle and Marshall (2000) attributed the decrease in bulk density of almond hulls from 0.63 to 0.25 after pretreatment with 0.1 M NaOH to be largely due to the removal of soluble sugars and lignin fraction, which comprise 27% of the unextracted almond hull.

The effect of leaching out of plant component materials and pigments was also reflected in the amounts of acid and basic groups on the biosorbent, before and after pretreatment. The PCP Raw was shown to contain 0.80 mmol/g of carboxylic group, 1.33 mmol/g of lactone group, 1.07 mmol/g of phenolic group and a total acidity and total basicity of 3.20 and 4.27 mmol/g, respectively. The predominant acid group in pine cone is the Lactone group. It was observed that the carboxylic and phenolic content of the pine cone powder reduced as the concentration of NaOH in the wash solution increased. Reduction in carboxylic (PCP 0.01: 0.65 mmol/g and PCP 0.05: 0.55 mmol/g) and phenolic content (PCP 0.01: 0.84 mmol/g and PCP 0.05: 0.68 mmol/g) may be attributed to the extraction of resin acids as they are converted to their sodium salt and phenolic content may decrease due to the slight solubility of lignin that contains phenolic compounds. A reduction in total acidity was observed with increasing NaOH concentration (PCP 0.01: 3.08 mmol/g and PCP 0.05: 3.00 mmol/g) which is in line with the extraction of sugars and resin acids from the biosorbent material. There was also a change observed in the total basic groups due to pretreatment, the values of total basicity was PCP 0.01: 1.60 mmol/g and PCP 0.05: 0.08 mmol/g. Such changes in total acidity and basicity are bound to affect the pH at point zero charge of the biosorbent materials. The $\mathrm{pH_{PZC}}$ for pine cone powder was determined to be 7.49. The results of the $\mathrm{pH_{PZC}}$ for the pretreated PCP samples show that there was a large drop in the $\mathrm{pH_{PZC}}$ values. The $\mathrm{pH_{PZC}}$ for PCP 0.01: 2.62 and for PCP 0.05: 2.58, showing a reduction with NaOH pretreatment and with increase in NaOH concentration. The fall in $\mathrm{pH_{PZC}}$ can be attributed to the sharp reduction in basic functional groups due to NaOH washing of the pine cone powder making the amount of negative charges much higher than the positive charges. The total surface area of an adsorbent is made up of both external and internal surface. The iodine number gives information on the internal surface of an adsorbent (Daifullah, Girgis, & Gad, 2003). Iodine number for PCP was obtained to be 15.46 mg g^{-1}. The pretreatment of PCP with NaOH solution increased the iodine number (PCP 0.01: 16.7 mg/g and PCP 0.05: 17.0 mg/g). The iodine number is found to increase with increasing NaOH concentration in the wash solution. The trend was found to be in line with the trend in bulk density, suggesting that the extraction of plant components would have opened up pore spaces and increased internal surface area of the pine cone.

Fig. 1 shows the FTIR spectra's of PCP Raw (a), PCP 0.01 (b) and PCP 0.05 (c). Several peaks were observed from the spectra indicating that pine cone is composed of various functional groups. The broad intense spectra bands observed at 3418.47 cm^{-1} are indicative of unbounded–OH (Perez-Marıın, Meseguer-Zapata, Ortuno, Aguilar, & Llorens, 2007) and the peak observed at 2925.90 cm^{-1} represents the aliphatic C–H group. The peak at 1647.08 cm^{-1} coresponds to the C=O stretch. The peaks between 1058.81 and 559.32 cm^{-1} may be assigned to the –C–C– and –CN stretching, respectively (Malkoc, 2006).

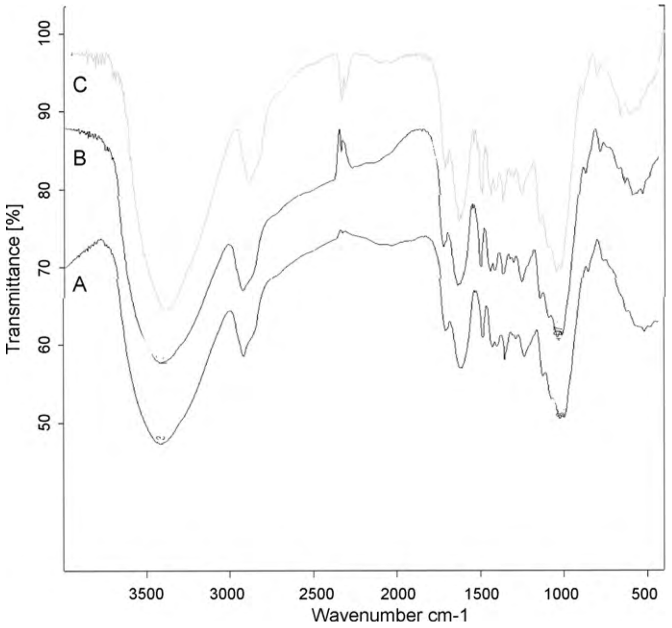

Fig. 1. FITR spectra's of (A) PCP Raw, (B) PCP 0.01 and (C) PCP 0.05.

Comparing the FTIR spectra's of the raw pine cone and NaOH modified pine cone powder sample, it will be observed that though the spectra's are similar but some difference can be seen in the intensity of the broad band at 3418.47 cm^{-1}, the peak at 2925.90 and 1647.08 cm^{-1}.

All these peaks tend to decrease slightly as the concentration of NaOH in the wash solution increases. The results supports the reported reduction in carboxylic acid function as observed in the results from Boehm titration.

The surface morphology of pine cone powder (PCP Raw) determined by SEM is shown in Fig. 2a. The PCP Raw is made up of a rough flat multilayer surface. This surface can be seen to contain little amounts of small pores indicating that this material presents good characteristics to be employed as a natural adsorbent for metallic ion uptake, as previously reported (Can, Kaya, & Algur, 2006). It is believed that these pores provide ready access and large surface area for the sorption of metals on the binding sites.

With NaOH pretreatment, the surface became smooth and pores were seen to develop (Fig. 2b and c). It is considered that increasing the NaOH concentration increased the smoothness of the surface and reduced the loosened the particles as can be seen in Fig. 2a–c.

3.2. Effect of initial copper(II) concentration

3.2.1. Theory

The pseudo-first order kinetic model equation is written as (Lagergren, 1898):

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \tag{2}$$

where q_t and q_e are the amount sorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo-first order sorption process. The integrated rate law, after applying the initial conditions of $q_t = 0$ at $t = 0$ is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{3}$$

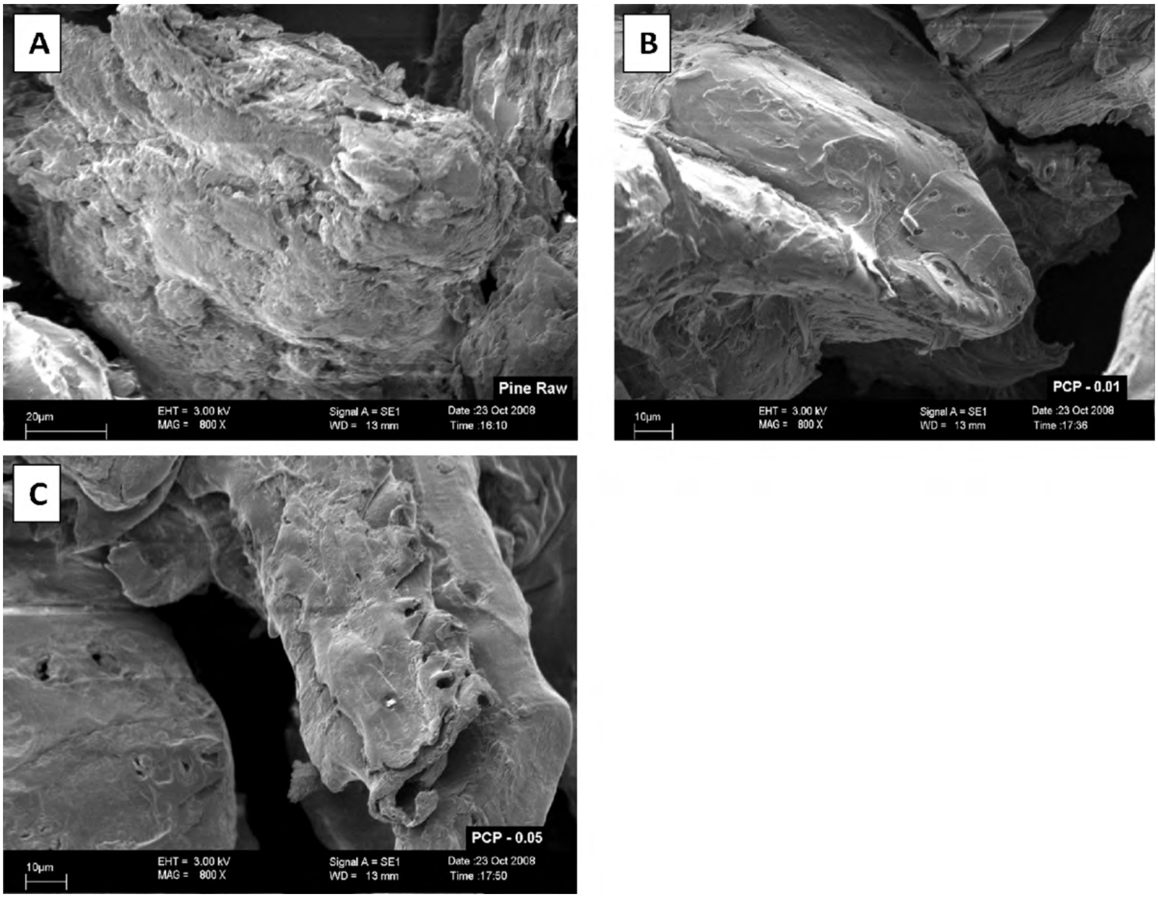

Fig. 2. (a–c) SEM of (A) PCP Raw, (B) PCP 0.01 and (C) PCP 0.05.

Plots of $\log(q_e - q_t)$ versus t gives a straight line for pseudo-first order kinetics, which allows computation of the biosorption rate constant, k_1. If the experimental results do not follow Eqs. (2) and (3) they differ in two important aspects: (i) $k_1(q_e - q_t)$ does not represent the number of available sites, and (ii) $\log(q_e)$ is not equal to the intercept of the plot of $\log(q_e - q_t)$ against t.

To set up the new model for the pseudo-first order kinetics Eq. (1) was modified by Yang and Al-Duri (2005), through the modification of its rate constant, k_1. The rate constant in the modified pseudo-first order kinetic model (MPFOM) was denoted by K_1 and the following equation was proposed:

$$k_1 = K_1 \frac{q_e}{q_t} \tag{4}$$

As $q_t < q_e$, the above equation implies that the rate constant k_1 is minimum when equilibrium is reached. The modified pseudo-first order rate equation can be derived as follows:

$$\frac{dq_t}{dt} = K_1 \frac{q_e}{q_t}(q_e - q_t) \tag{5}$$

Eq. (5) can be rearranged into

$$-dq_t + \frac{q_e dq_t}{(q_e - q_t)} = K_1 q_e d_t \tag{6}$$

Integrating Eq. (6) over time t during which the solid-phase concentration increases from zero to q_t, the following algebraic equation can be obtained:

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{7}$$

If the biosorption process follows the modified pseudo-first order kinetic model represented by Eq. (7), a plot of $q_t/q_e + \ln(q_e - q_t)$ against t should be a straight line.

The pseudo-second order chemisorption kinetics may be expressed as (Ho & McKay, 1998a, 1998b, 1998c):

$$\frac{-d(q_e - q_t)}{dt} = 2K(q_e - q_t)^2, \tag{8}$$

where k_2 is the rate constant of sorption, q_e and q_t have the same definition as above. This can be separated and integrated to the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t. \tag{10}$$

On rearrangement Eq. (10) gives:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{11}$$

were the initial sorption rate h, can be represented by

$$h = 2Kq_e^2. \tag{12}$$

The constant can then be determined experimentally by plotting of t/q_t against t.

3.2.2. Pseudo-first and modified pseudo-first order models

The pseudo-first order model was applied to study the effect of initial lead(II) concentration on the removal of lead(II) by PCP raw, PCP 0.01 and PCP 0.05. The pseudo-first order model parameters for the effect of initial lead(II) concentration were calculated for the three biosorbents and are shown in Table 1. The values

Table 1
Parameters of kinetic models for lead(II) biosorption on Raw PCP and NaOH treated PCP at different lead(II) concentrations.

Sample	Parameter	60 mg dm^{-3}	70 mg dm^{-3}	80 mg dm^{-3}	90 mg dm^{-3}	100 mg dm^{-3}	110 mg dm^{-3}	120 mg dm^{-3}
PCP Raw								
Pseudo-first	$q_{e,1}$ (Exp)	5.78	6.56	7.20	7.68	8.09	8.39	8.46
	$q_{e,1}$ (Cal)	2.85	3.61	4.30	4.90	5.43	5.86	6.04
	k_1	0.3178	0.3086	0.3017	0.2971	0.2925	0.2879	0.2856
	r^2	0.983	0.986	0.988	0.990	0.991	0.992	0.998
Modified pseudo-first	$q_{e,m,1}$ (Cal)	5.32	6.47	7.43	8.23	8.90	9.41	9.60
	K_1	0.280	0.270	0.257	0.252	0.243	0.237	0.234
	r^2	0.9964	0.9976	0.9980	0.9970	0.9969	0.9960	0.9954
PCP 0.01								
Pseudo-first	q_e (Exp)	11.37	12.95	14.22	15.22	15.91	16.05	16.16
	$q_{e,1}$ (Cal)	1.62	2.54	3.87	5.16	6.35	7.21	7.86
	k_1	0.3685	0.3455	0.3478	0.3316	0.3293	0.3201	0.3155
	r^2	0.965	0.962	0.971	0.973	0.978	0.981	0.983
Modified pseudo-first	$q_{e,m,1}$ (Cal)	3.18	5.10	7.62	10.41	13.17	15.53	16.87
	K_1	0.367	0.344	0.333	0.327	0.316	0.304	0.296
	r^2	0.9678	0.9683	0.9740	0.9812	0.9860	0.9896	0.9918
PCP 0.05								
Pseudo-first	q_e (Exp)	11.93	13.57	14.90	16.10	16.73	17.16	17.29
	$q_{e,1}$ (Cal)	1.37	2.33	3.52	4.89	5.98	7.11	7.88
	k_1	0.3593	0.3478	0.3408	0.3362	0.3339	0.3276	0.3201
	r^2	0.958	0.960	0.965	0.970	0.975	0.979	0.981
Modified pseudo-first	$q_{e,m,1}$ (Cal)	3.40	5.49	7.91	10.44	12.03	13.96	15.07
	K_1	0.349	0.333	0.322	0.311	0.306	0.295	0.285
	r^2	0.9662	0.9712	0.9788	0.9854	0.9895	0.9932	0.9995

for equilibrium biosorption capacity as predicted by the pseudo-first order kinetics for a particular initial concentration was higher for PCP 0.05 than for PCP 0.01 and least for PCP raw and the values increased with increasing initial copper(II) concentration. The trend with increasing equilibrium biosorption capacity with initial concentration was similar to the trend in experimental equilibrium capacity with initial concentration. The predicted values were not close to the experimental and it was observed that the difference in the values increased with base pretreatment. This can also be seen by observing the values of correlation coefficient, r^2.

The pseudo-first order model considers the rate of occupation of biosorption sites to be proportional to the number of unoccupied sites. A deviation was observed in the experimental data from the straight line at about 5 min of contact for all initial lead(II) concentrations, this deviation increased with NaOH pretreatment. This means that the proportionality of between occupied and unoccupied biosorption site theory is not obeyed after 5 min of biosorption, but only between 0 and 5 min where initial biosorption rate is fast. That is to say, mass transfer was more predominant for PCP than it is for PCP 0.01 and PCP 0.05 at the initial stage of biosorption. The difference in the samples as seen from the surface characterization in Section 3.1 are the lower pH_{PZC}, the larger internal surface and higher amount of total acidity. The higher internal surface and acidity will definitely increase the initial sorption of metal ions on the biosorbent making the mass transfer rate stronger and faster for PCP 0.01 and PCP 0.05. The rate constant for the pseudo-first order model, k_1, was found to be higher for PCP 0.01 and PCP 0.05 than for PCP raw. The constant, k_1, was also observed to decrease with increasing initial lead(II) concentration, indicating that resistance to mass transfer of lead(II) ions to biosorbent surface reduces as concentration increases may be due to difference in concentration driving force.

To minimize the observed deviation in the data from the straight line a modified form of the pseudo-first order model was proposed (Yang & Al-Duri, 2005). The modified Pseudo-first order model parameters for the effect of initial lead(II) concentration on the biosorption of lead(II) onto the prepared biosorbent are compared in Table 1 against the pseudo-second order parameters. The deviation in the data from the straight line was actually minimized. The predicted values of equilibrium constant, q_e, for the modified pseudo-first order model were found to be higher than the pseudo-first order, but not very close to the experimentally determined values. Like the pseudo-first order model, the correlation coefficient, r^2, values where higher for PCP raw than for PCP 0.01 and PCP 0.05 confirming the importance of mass transfer in PCP raw than for the other samples. The rate constant, K_1, were lower than the constant, k_1, and reduces with increasing initial lead(II) concentration as seen in Table 1. According to Yang and Al-Duri (2005), the physico-chemical properties of the adsorbate and the adsorbent have an important role to play in determining adsorption equilibrium and adsorption kinetics. Therefore, it is expected that the biosorption performance of the three different biosorbents on the removal of lead(II) ions can be related to the kinetic parameters. Fig. 3 shows the plot of pseudo-first order model rate constants, k_1 (solid lines), and modified pseudo-second order rate constant,

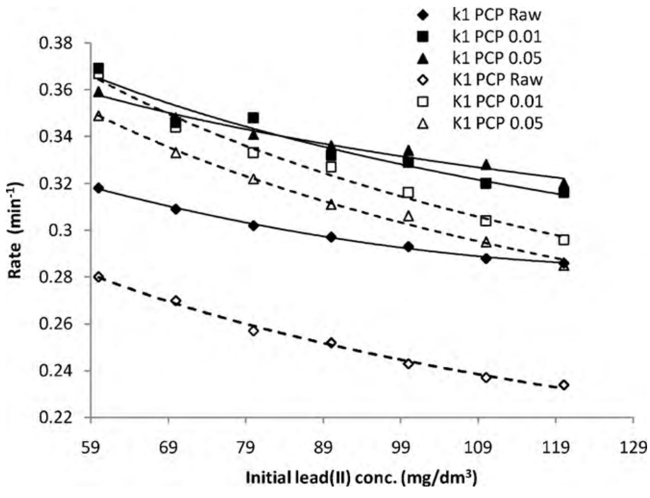

Fig. 3. Relationship between the pseudo-first and modified pseudo-first order rate constant with the initial lead(II) concentration.

Table 2
Parameters of kinetic models for lead(II) biosorption on Raw PCP and NaOH treated PCP at different lead(II) concentrations.

Sample	Parameters	60 mg dm^{-3}	70 mg dm^{-3}	80 mg dm^{-3}	90 mg dm^{-3}	100 mg dm^{-3}	110 mg dm^{-3}	120 mg dm^{-3}
Raw PCP	q_e (Exp)	5.78	6.56	7.20	7.68	8.09	8.39	8.46
	$q_{e,2}$ (Cal)	6.07	6.96	7.71	8.30	8.82	9.22	9.34
	h	8.12	7.63	7.25	6.90	6.54	6.23	6.01
	k_2	0.2204	0.1575	0.1220	0.1001	0.0841	0.0733	0.0689
	r^2	0.996	0.993	0.998	0.995	0.999	0.998	0.993
PCP 0.01	q_e (Exp)	11.37	12.95	14.22	15.22	15.91	16.05	16.16
	$q_{e,2}$ (Cal)	11.48	13.13	14.51	15.65	16.48	16.75	16.95
	h	82.45	62.33	46.83	36.81	30.93	25.93	23.04
	k_2	0.6252	0.3615	0.2224	0.1503	0.1139	0.0924	0.0802
	r^2	0.999	0.997	0.998	0.992	0.994	0.999	0.993
PCP 0.05	q_e (Exp)	11.93	13.57	14.90	16.10	16.73	17.16	17.29
	$q_{e,2}$ (Cal)	12.02	13.73	15.16	16.49	17.24	17.81	18.05
	h	106.76	76.45	57.23	45.12	37.87	31.54	27.34
	k_2	0.7389	0.4055	0.2490	0.1659	0.1274	0.0994	0.0839
	r^2	0.992	0.997	0.998	0.997	0.998	0.996	0.995

$q_{e,2}$ = mg g^{-1}; k_2 = g mg^{-1} min^{-1}; h = mg g^{-1} min^{-1}.

K_1 (broken lines) versus initial lead(II) concentration, C_0. It was observed that the rate constants decreased gradually with increasing concentration for both kinetic models, indicating that increase in driving force of caused by higher lead(II) concentration influences the rate of removal at the initial biosorption period. This trend was also observed by Yang and Al-Duri (2005) with initial concentration. The results also revealed that the values of modified pseudo-first order rate constant, K_1, for PCP raw where were quite small compared to the other samples and that PCP 0.01 had higher K_1 values than PCP 0.05 for higher concentrations. For the rate constant, k_1, the separation between the values for PCP Raw and the pretreated samples where much smaller and k_1, for PCP 0.01 only increased above that for PCP 0.05 at high concentrations.

3.2.3. *Pseudo-second order model*

The kinetic data obtained were plotted using the pseudo-second order kinetic models and the kinetic parameters for lead(II) biosorption were calculated and given in Table 2 for all three biosorbents. From Table 2, it will be observed that the model lines were quite close to the experimental data throughout the biosorption period for all initial concentrations with all the biosorbent materials. The equilibrium capacity values for the pseudo-second order model were higher than for the pseudo-first order and the modified pseudo-first order kinetic models and increased with increasing lead(II) initial concentration, C_0. The equilibrium capacities were higher for PCP 0.05 than for PCP 0.01 and least for PCP Raw. The closeness to the pseudo-second order model equilibrium capacity to the experimentally determined equilibrium capacity indicates the ability of the pseudo-second order model to describe the kinetics of lead(II) uptake on all three biosorbents in the range of initial concentration examined. The pseudo-second order rate constant, k_2, were found to increase with NaOH pretreatment and with NaOH concentration. The values of k_2 were much higher for the pretreated PCPs than for the PCP raw and they decreased with increasing initial lead(II) concentration. The initial biosorption rate, h, was also found to follow the same trend as the biosorption rate constant, k_2. The values of h were far higher for the pretreated PCPs than for the PCP raw and they decreased as the initial lead(II) concentrations increased (Table 2). Similar results have been obtained by Ofomaja, Naidoo, and Modise (2010b) in the biosorption of lead(II) and copper(II) onto KOH pretreated pine cone powder.

3.2.4. *Relationship between pseudo-second order parameters and biosorption performance*

A relationship described as the approaching equilibrium factor, R_W, between the pseudo-second order model constants and the characteristic kinetic curve was proposed by Wu, Tseng, Huang, and Juang (2009).The approaching equilibrium factor, R_W, is defined as:

$$R_W = \frac{1}{1 + k_2 q_e t_{ref}} \tag{13}$$

$$k_2 q_e t_{ref} = \frac{R_W - 1}{R_W} \tag{14}$$

where t_{ref} is the longest operation time (based on kinetic experiments) in a biosorption system, q_e is the amount of biosorption calculated from Eq. (11). The pseudo-second order model can be rewritten as:

$$\left(\frac{t_{ref}}{q_{ref}}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t_{ref} \tag{15}$$

where q_{ref} is the amount of adsorption at time t_{ref} (g/kg).

A family of curves for R_W = 0.01–1.00 can then be produced. When R_W = 1, the kinetic curve is called linear (zone 0), meaning that $k_2 q_e t_{ref} \ll 1$ in Eq. (13). The possible causes of this effect are: (i) it does not facilitate biosorption when the pseudo-second order rate constant (k_2) is very small, (ii) the equilibrium amount of biosorption (q_e) is very small, and (iii) the longest time (t_{ref}) of the biosorption process is too short. All these factors indicate an ineffective biosorption system where equilibrium cannot be reached. The curvature of biosorption curve increases as R_W reduces. The characteristic biosorption curve is called approaching equilibrium in the range $1 > R_W > 0.1$ (zone I); called well approaching pseudo equilibrium in the range $0.1 > R_W > 0.01$ (zone II); and called drastically approaching equilibrium when $R_W < 0.01$ (zone III).

The calculated values for the approaching equilibrium factor, R_W, for lead(II) removal using all three biosorbents are shown in Table 3. For the biosorption of lead(II) onto PCP Raw, PCP 0.01 and PCP 0.05 at concentrations ranging from 120 to 60 mg/dm^3, the values for R_W were found to range from 0.047 to 0.093 for PCP Raw, 0.009 to 0.047 for PCP 0.01 and 0.007 to 0.042 for PCP 0.05. These values for PCP Raw lie in zone II under largely curved and well approaching equilibrium level; for PCP 0.01 and PCP 0.05, the systems of 60 mg/dm^3 lies in zone III (PCP 0.01: 0.009 and PCP 0.05: 0.007) under pseudo-rectangular and drastically approaching equilibrium, while the other systems (70–120 mg/dm^3) lies within zone II under largely curved and well approaching equilibrium level. These results indicate that the approach of the biosorption process to equilibrium is higher for pretreated biosorbents than for the untreated and the approach to equilibrium increases with lower lead(II) concentration. With the 60 mg/dm^3 lead(II) concentration using PCP 0.01 and PCP 0.05, the equilibrium is drastically approached and the shape of the curve is different. Therefore the

Table 3
Pseudo-second order model parameters to determine biosorption performance.

Parameter	60 mg dm^{-3}	70 mg dm^{-3}	80 mg dm^{-3}	90 mg dm^{-3}	100 mg dm^{-3}	110 mg dm^{-3}	120 mg dm^{-3}
Raw PCP							
R_w	0.047	0.57	0.066	0.074	0.082	0.090	0.093
k_2q_e (min^{-1})	1.34	1.10	0.94	0.83	0.74	0.68	0.64
$t_{0.5}$	0.75	0.91	1.06	1.20	1.35	1.48	1.55
PCP 0.01							
R_w	0.009	0.014	0.020	0.028	0.034	0.041	0.047
k_2q_e (min^{-1})	7.18	4.75	3.23	2.35	1.88	1.55	1.36
$t_{0.5}$	0.14	0.21	0.31	0.43	0.53	0.65	0.74
PCP 0.05							
R_w	0.007	0.011	0.017	0.024	0.029	0.036	0.042
k_2q_e (min^{-1})	8.88	5.57	3.77	2.74	2.20	1.77	1.51
$t_{0.5}$	0.11	0.18	0.26	0.37	0.46	0.56	0.66

pretreated biosorbents are likely to remove more lead(II) ions at low concentrations and reach equilibrium levels than the untreated biosorbent.

Another parameter in the pseudo-second order model that can define kinetic performance is the k_2q_e (min^{-1}) (Wu et al., 2009). This parameter can be obtained by rearranging Eq. (8):

$$\frac{d(q_t/q_e)}{dt} = k_2q_e\left[1-\left(\frac{q_t}{q_e}\right)\right]^2 \tag{16}$$

Eq. (16) reveals that the time changes in dimensionless solid-phase concentration, $d(q_t/q_e)/dt$, which is another form of biosorption rate, is proportional to the square of the residual amount of biosorption, $1-(q_t/q_e)$. Consequently, the proportionality constant k_2q_e can be defined as the second order rate index. On the other hand, Eq. (8) can be rewritten as:

$$\left(\frac{1}{q_t}-\frac{1}{q_e}\right)t = \frac{1}{k_2q_e^2} \tag{17}$$

and

$$t = \frac{[q_t/(q_e-q_t)]}{k_2q_e} \tag{18}$$

At the half-life of the biosorption process (i.e., $t = t_{0.5}$), we have $q_t = 0.5q_e$ and

$$t_{0.5} = \frac{1}{k_2q_e} \tag{19}$$

It is evident that k_2q_e is the only parameter of Eq. (19). The k_2q_e value is equal to the inverse of the half-life of biosorption process, describing the actual meaning of pseudo-second order biosorption parameter better. The results of the calculated k_2q_e parameter values are shown in Table 3. The rate parameter where found to be higher for the pretreated biosorbents than for the untreated and were also found to increases with decreasing concentration (PCP Raw: 1.34–0.64 min^{-1}; PCP 0.01: 1.36–7.18 min^{-1}; PCP 0.05: 1.51–8.88 min^{-1}) as concentration of lead(II) ions decreases from 120 to 60 mg/dm^3. A plot of the rate constant, k_2q_e, versus the initial concentration is shown in Fig. 4. From Fig. 4 it can be observed that the curve for the PCP Raw was gentler than those of PCP 0.01 and PCP 0.05 which were more curved. The reason for this difference in curvature may be related to the properties of the biosorbents. PCP Raw had the least surface area and total negative charge of the three samples, therefore a large change in the initial lead(II) concentration did not affect the rate of lead(II) removal by PCP Raw since the amount of internal surface and negative charge (biosorption sites) are small. On the other hand, the pretreated samples had higher values of internal surface, and lower values of pH$_{\mathrm{PZC}}$. Therefore these samples will contain larger surface for biosorption and more biosorption sites than PCP Raw; this will explain the curved nature of the plots in Fig. 4. The trend in the values of k_2q_e is also similar to the initial biosorption rate of the pseudo-second order, h, which also increase with decreasing concentration of lead(II) ions concentration.

The half-life of the biosorption process, $t_{0.5}$, which is the time for half the amount of biosorbate to be removed by the biosorbent (Table 3) was found to decreased with decreasing lead(II) concentration from 1.55 to 0.75 min (PCP Raw), from 0.74 to 0.14 min (PCP 0.05) and from 0.66 to 0.11 min (PCP 0.05) as lead(II) concentration decreased from 120 to 60 mg/dm^3. These results indicate again that the pretreated samples removed lead(II) at much shorter times than the untreated and that the half-life reduced with decreasing initial lead(II) concentrations. The half-life were far shorter for the pretreated samples than for the untreated which is the same trend as the rate constant, k_2, the initial biosorption rate, h, and the constant k_2q_e. The half-life reduces by up to half when initial lead(II) concentration is reduced from 120 to 60 mg/dm^3 for PCP Raw, and up to 5 times for PCP 0.01 and up to 6 times for PCP 0.05 when initial lead(II) concentration is reduced from 120 to 60 mg/dm^3.

The relationship between operating time and amount of biosorption is an important factor in engineering practice. Eq. (17) can be rewritten as:

$$t_x = \frac{W}{k_2q_e} \tag{20}$$

where $W = q_t/(q_e - q_t)$.

The fractional adsorption X is define as $X = q_t/q_e$ and $W = X/(1 - X)$. At equilibrium, $q_t/q_e = 1$, W = infinite, and t_x = infinite. As X equals 1, W approaches infinite. When X is gradually approaching 1, W and t_x increases rapidly.

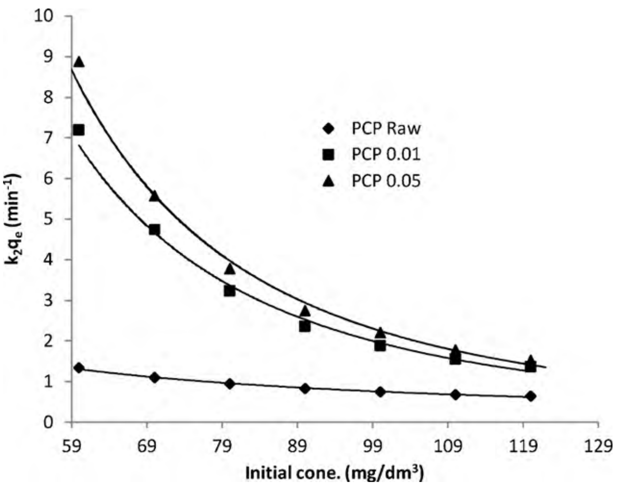

Fig. 4. Relationship between the rate constant, k_2q_e, of the pseudo-second order model with the initial lead(II) concentration.

Table 4
Relationship between the operating time and the amount of biosorption of copper(II) onto Mansonia sawdust.

Conc. (mg/dm^3)	k_2q_e	$X=0.6t_{0.6}$ (min)	$X=0.8t_{0.8}$ (min)	$X=0.9t_{0.9}$ (min)	$X=0.95t_{0.95}$ (min)	$X=0.97t_{0.97}$ (min)
Raw PCP						
120	0.64	2.34	6.25	14.06	39.69	50.52
110	0.68	2.21	5.88	13.24	27.94	47.55
100	0.74	2.03	5.41	12.16	25.68	43.69
90	0.83	1.81	4.82	10.84	22.89	38.96
80	0.94	1.60	4.26	9.57	20.21	34.40
70	1.10	1.36	3.64	8.18	17.27	29.39
60	1.34	1.12	2.99	6.72	14.18	24.13
Raw 0.01						
120	1.36	1.10	2.94	6.62	13.97	23.77
110	1.55	0.97	2.58	5.81	12.26	20.86
100	1.88	0.80	2.13	4.79	10.11	17.20
90	2.35	0.64	1.70	3.83	8.09	13.76
80	3.23	0.46	1.24	2.79	5.88	10.01
70	4.75	0.32	0.84	1.89	4.00	6.81
60	7.18	0.21	0.56	1.25	2.65	4.50
Raw 0.05						
120	1.51	0.99	2.65	5.96	12.58	21.41
110	1.77	0.85	2.26	5.08	10.73	18.27
100	2.20	0.68	1.82	4.09	8.63	14.70
90	2.74	0.55	1.46	3.28	6.93	11.80
80	3.77	0.40	1.06	3.89	5.04	8.58
70	5.57	0.27	0.72	1.62	3.41	5.80
60	8.88	0.17	0.45	1.01	2.14	3.64

The relationship between the operating time, t_x, and the metal ion biosorbed at each lead(II) concentration was determined and the results are displayed in Table 4. This information can be used to make decisions on scale up and design purposes. It will be noticed that operating time, t_x, reduces with initial lead(II) ion concentration for all the biosorbent materials. For example, to achieve fractional biosorption of 0.6, the operating times will be 2.34 min (PCP Raw), 1.10 min (PCP 0.01) and 0.99 min (PCP 0.05) for initial lead(II) concentration of 120 mg/dm^3. A rapid increase can also be observed as the fractional biosorbed amount increases over 0.9, indicating that equilibrium is closely approached and the operating times are lower for the pretreated samples and for lower lead(II) concentrations.

3.3. Equilibrium biosorption

3.3.1. Langmuir isotherm

At constant temperature, metal ions held onto the biosorbent will be in equilibrium with metal ions in bulk solution. The saturated monolayer isotherm can be represented as (Langmuir, 1916):

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{21}$$

where C_e is the equilibrium concentration (mg/dm^3); q_e is the amount of metal ion biosorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is biosorption equilibrium constant (dm^3/mg).

3.3.2. Freundlich isotherm

The empirical Freundlich isotherm (Freundlich, 1906) based on biosorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of biosorption with the increase in the fraction of occupied sites and is given by:

$$q_e = K_F C_e^{1/n} \tag{22}$$

where K_F and $1/n$ are the Freundlich constants characteristics of the system, indicating the biosorption capacity and biosorption intensity, respectively. Eq. (22) can be linearized in logarithmic form to give Eq. (22) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{23}$$

Equilibrium biosorption studies were conducted for the removal of lead(II) ions from solution of concentrations ranging from 60 to 120 mg/dm^3 by PCP Raw, PCP 0.01 and PCP 0.05 agitated at 160 rpm, solution pH 5.0 and biosorption temperature 291 K and the equilibrium data fitted to the isotherm models and the parameters shown in Table 5. The Freundlich isotherm constants, n and K_F were found to increase with NaOH pretreatment. Freundlich constants K_F indicate the biosorption capacity of the biosorbent and the values of K_F at equilibrium for the biosorbents were: PCP Raw (2.282 dm^3/g), PCP 0.01(5.724 dm^3/g) and PCP 0.05 (6.510 dm^3/g) for lead(II) biosorption. The constant K_F was lower for PCP Raw indicating that base pretreatment improved biosorption capacity. The Freundlich constant n is a measure of the deviation from linearity of the biosorption or the biosorption affinity of the biosorbent for a metal ion in solution and the numerical values of n for the biosorbents were PCP Raw (2.538), PCP 0.01 (3.115) and PCP 0.05 (3.058). The values for n are always greater than unity, indicating that lead(II) ions are favorably biosorbed by PCP Raw and the NaOH pretreated PCP. The Freundlich constants were much higher than for the biosorption of copper(II) on NaOH pretreated treated sawdust (*Acacia arabica*) which were n: 1.000 and K_F: 1.00 (Meena, Kadirvelu, Mishraa, Rajagopal, & Nagar, 2007).

The Langmuir-1 constants, q_m and K_a were calculated and the values show that the monolayer capacities of the different biosorbents were PCP Raw (16.34 mg/g), PCP 0.01 (22.78 mg/g) and PCP 0.05 (24.75 mg/g). These results indicate that monolayer capacity increases with NaOH pretreatment and concentration of NaOH. The Langmuir-1 constant, K_a, known as the heat of biosorption is a measure of the strength of the bonds formed during biosorption. The value of K_a was found to increase with NaOH pretreatment and with NaOH concentration. The bonds formed between lead(II) ions and the functional groups on the biosorbent surface are stronger for the pretreated biosorbents. The Langmuir constants were much higher than for the biosorption of copper(II) on NaOH pretreated rubber leaves powder which were q_m: 14.90 mg/g and K_a: 0.412 dm^3/g (Ngah & Hanafiah, 2008). The Langmuir-2 isotherm parameters

Table 5
Minimum total amount of PCP, PCP 0.01 and PCP 0.05 needed to achieve various percentage removals for a series of two-stage and single-stage biosorption systems.

% Lead(II) removal	Biosorbent	Two-stage biosorption process				Single-stage biosorption process
		System number	S_1 (kg)	S_2 (kg)	S_{Total} (kg)	Biosorbent mass (kg)
99.9	PCP Raw	5	2.45	1.87	4.32	3910.94
	PCP 0.01	5	1.63	1.21	2.84	1047.31
	PCP 0.05	5	1.10	1.10	2.20	785.77
99.0	PCP Raw	5	2.00	1.80	3.82	672.01
	PCP 0.01	5	1.28	102	2.30	93.48
	PCP 0.05	5	0.67	0.90	1.57	68.63
85.0	PCP Raw	5	1.35	1.73	3.08	13.11
	PCP 001	5	0.96	0.96	1.93	2.45
	PCP 0.05	5	0.50	0.41	0.91	1.61
80.0	PCP Raw	5	1.10	1.34	2.44	3.08
	PCP 0.01	5	0.18	0.11	0.28	0.61
	PCP 0.05	5	0.13	0.08	0.21	0.39

shows that the trends in the parameters, q_m and K_a are similar to those of the Langmuir-1 isotherm, but that values of q_m and K_a are higher than those of the Langmir-1 parameters.

The correlation coefficient, r^2, for the equilibrium isotherm models applied in this study showed that the Langmuir-1 isotherm had the highest r^2 values followed by the Langmuir-2 and Freundlich isotherms. The Langmuir-1 isotherm is therefore the best fitting of the three models; this indicates that biosorption is monolayer coverage of the biosorbate on the biosorbent and homogeneity of the actives sites on the biosorbent surface.

3.4. Optimization of biosorbent mass

The amount of biosorbent required for the biosorption process for each stage is critical both in the design of the biosorption equipment and its application on a large scale. Applying the data gathered so far, let us consider the minimum biosorbent mass required for the removal of 99% lead(II) from 2.5 m^3 of 120 mg/dm^3 of the metal in two stages of a batch biosorption process.

A schematic diagram for an *n*-stage biosorption system is shown in Fig. 5. The solution to be treated contains L dm^3 solution and the lead(II) concentration is reduced for each stage from C_0 to C_1 mg/dm^3 (Ho & McKay, 1998b; Unuabonah, Adebowale, et al., 2009; Unuabonah, Adie, et al., 2009) C_1 to $C_2,\ldots,C_m - C_n$ where C_m is equilibrium concentration of the biosorbate (lead(II)) in previous biosorption stage (mg/dm^3) and C_n is final concentration of the biosorbate in aqueous solution at final adsorption stage (mg/dm^3). The amount of biosorbent added is S g with solid-phase biosorbate concentration being q_0 (mg/g). Thus, the biosorbate concentration on the biosorbent increases from q_0 to q_1 mg/g adsorbent. The mass balance equation gives:

$$L(C_{i-1} - C_i) = S_i(q_{t,i} - q_0) \tag{24}$$

The lead(II) loading on the biosorbent for each stage increased from q_0 to $q_{t,i}$ (mg/g). When fresh biosorbent was used, $q_0 = 0$, and the mass balance at each stage in a multi-stage adsorption system in Eq. (24) can be expressed as:

$$L(C_{i-1} - C_i) = S_i q_{ti} \tag{25}$$

where i is the sequence number of adsorption stage ($i = 1, 2, 3,\ldots,m$). Therefore, Eq. (25) can be rewritten as

$$q_{t,i} = \frac{L}{S_i}(C_{i-1} - C_i) \tag{26}$$

When the biosorption comes to equilibrium, C_i is the lead(II) solution equilibrium concentration at the ith stage, S_i and $q_{t,i}$ are the biosorbent amount and the lead(II) equilibrium loading on the biosorbent, respectively, at the ith stage, namely $C_i = C_{e,i}$ and $q_{t,i} = q_{e,t,i}$. From the previous section (Section 3.3), the relation of q_e and C_e was best described by the Langmuir-1 isotherm, therefore the adsorption equilibrium at ith stage is:

$$q_{ti} = \frac{q_m K_a C_i}{1 + K_a C_i} \tag{27}$$

Combining Eqs. (26) and (27), the following is obtained:

$$\frac{L}{S_i}(C_{i-1} - C_i) = \frac{q_m K_a C_i}{1 + K_a C_i} \tag{28}$$

$$(C_{i-1} - C_i) = \frac{S_i q_m K_a C_i}{L(1 + K_a C_i)} \tag{29}$$

The total amount of lead(II) removal can be evaluated as follows:

$$\sum_{i-1}^{m}(C_{i-1} - C_i) = \sum_{i-1}^{m}\frac{S_i q_m K_a C_i}{L(1 + K_a C_i)} \tag{30}$$

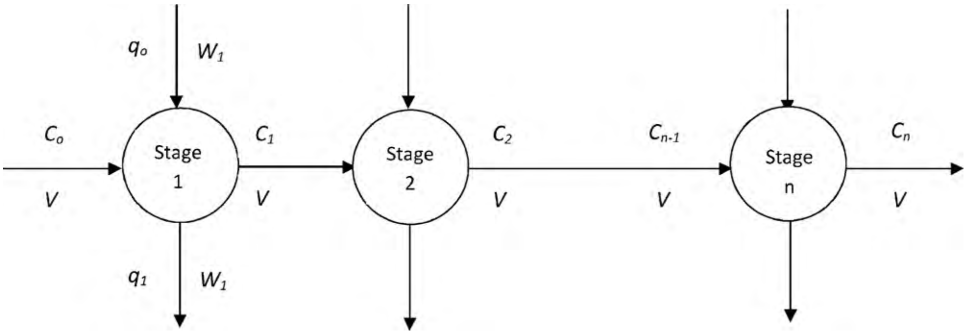

Fig. 5. Schematic diagram for a multi-stage batch adsorber.

The lead(II) removal percentage in each biosorption stage, R_i, can be calculated from the equation:

$$R_i = \frac{(C_{i-1} - C_i)}{C_o} = \frac{S_i q_m K_a C_i}{L(1 + K_a C_i)} \tag{31}$$

So, the total lead(II) removal percentage is obtained from the following equation:

$$\sum_{i-1}^{m} R_i = \frac{1}{C_0 L} \sum_{i-1}^{m} \frac{q_m S_i K_a C_i}{(1 + K_a C_i)} \tag{32}$$

For the ith stage, the relationship between C_i and C_0 can be written as:

$$C_i = \left(1 - \sum_{i-1}^{m} R_i\right) C_0 \tag{33}$$

And substituting Eq. (33) into Eq. (32) we obtain:

$$\sum_{i-1}^{m} R_i = \frac{1}{C_0 L} \sum_{i-1}^{m} \frac{q_m S_i K_a \left(1 - \sum_{i-1}^{m} R_i\right) C_0}{1 + K_a \left(1 - \sum_{i-1}^{m} R_i\right) C_0} \tag{34}$$

Applying Eqs. (31), (33) and (34), the removal percentage of lead(II) at any given initial lead(II) concentration can be predicted and the biosorbent amount needed for multi-stage systems can also be evaluated. If the solution is treated using a number of batch

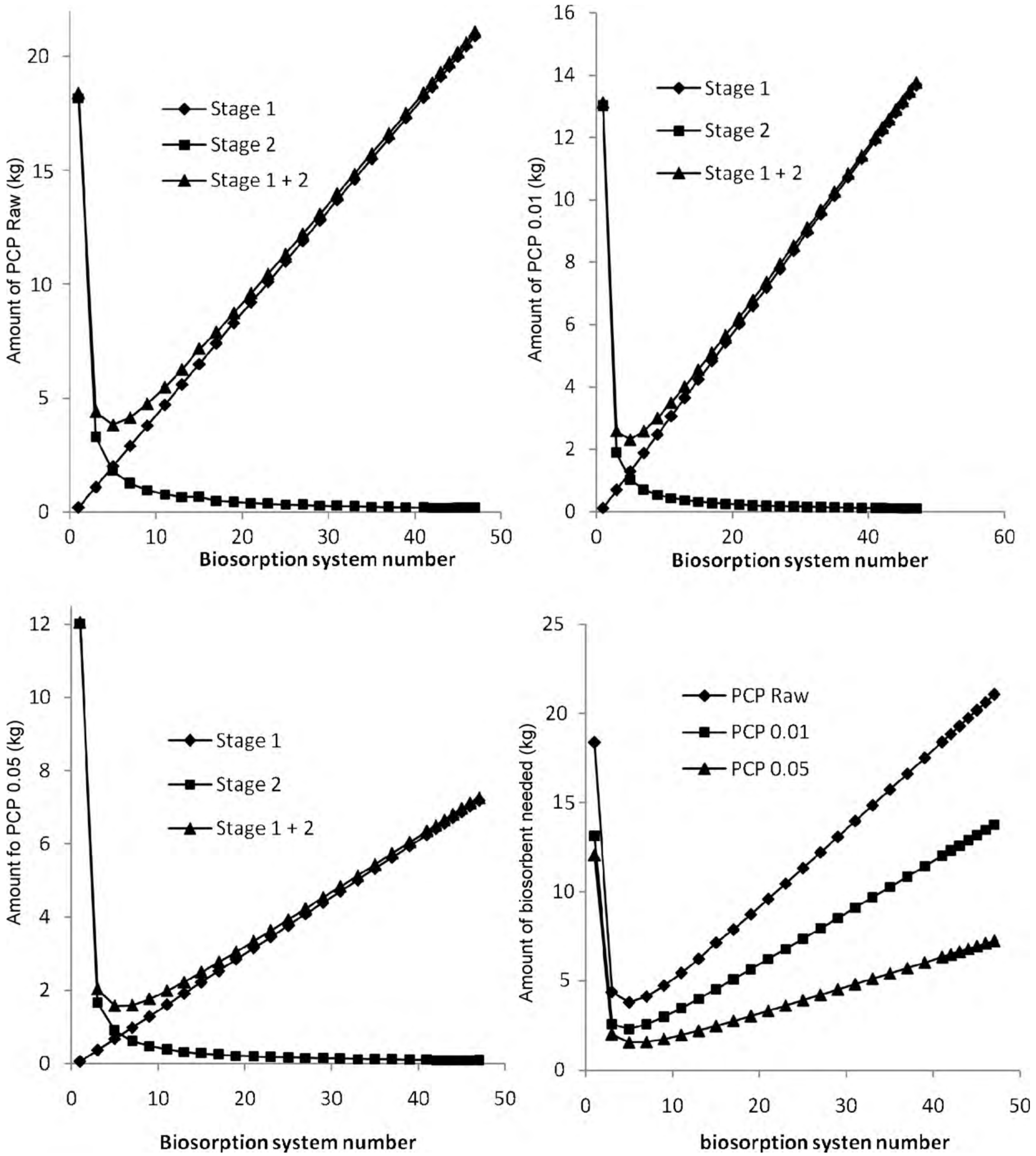

Fig. 6. Comparison of the amounts of (A) PCP Raw, (B) PCP 0.01, (C) PCP 0.05 and (D) minimum amounts of biosorbents required for 99% lead(II) removal from a 2.5 m^3 solution of lead(II) concentration of 120 mg/dm^3, initial pH 5, biosorption time 15 min and temperature 299 K.

biosorption stages rather than a single-stage batch, the efficiency of solute removal can be improved (Ozacar, 2006). Analytically, if the total solute removal efficiency is fixed, an increased number of stages in the multi-stage biosorption process reduce the adsorbent consumption. A typical example is considered for the case of a two-stage batch biosorption, where the treated lead(II) ion solution volume is 2.5 m^3 and the initial lead(II) concentration entering the first stage is 120 mg/dm^3. At stage 1 of the two-stage batch biosorption system for 99% lead(II) removal, a series of added amounts of the biosorbent: for PCP Raw, from 0.2 up to 20.9 kg (0.45 kg increment); for PCP 0.01, from 0.1 up to 13.7 kg (0.3 kg increment) and for PCP 0.05 from 0.05 up to 7.18 kg (0.16 kg increment) was proposed. So, each system numbered from 1 to 47 is based on a 0.20 kg (PCP Raw), 0.10 kg (PCP 0.01) and 0.05 kg (PCP 0.05), respectively, biosorbent amounts interval at stage 1 of the two-stage biosorption system. For the system numbered N, the PCP Raw amount in the first stage S_i, is

$$S_1 = 0.20 \text{ kg} + (N-1) \times 0.45\,\text{kg} = N\,\text{kg} \tag{35}$$

For the system numbered N, the PCP 0.01 amount in the first stage S_i, is

$$S_1 = 0.10 \text{ kg} + (N-1) \times 0.30\,\text{kg} = N\,\text{kg} \tag{36}$$

And for the system numbered N, the PCP 0.05 amount in the first stage S_i, is

$$S_1 = 0.05 \text{ kg} + (N-1) \times 0.16\,\text{kg} = N\,\text{kg} \tag{37}$$

Then the lead(II) removal efficiency at the first stage (R_1) for each two-stage adsorption system can be determined by Eqs. (31) and (33). Consequently, the biosorbent amount needed in the second stage S_2 can be calculated using Eq. (34), for a fixed total percentage of lead(II) removal. And the total biosorbent amount needed for each two-stage adsorption system, S_{total}, is expressed as:

$$S_{\text{total}} = S_1 + S_2 \tag{38}$$

For a fixed percentage of lead(II) removal, the S_{total} values are plotted against the system number, N, and the minimum total biosorbent amount needed for the biosorption system to achieve the fixed lead(II) removal percentage can be determined by minimum point on the plot. In the two-stage batch biosorption process of PCP Raw, PCP 0.01 and PCP 0.05 for lead(II) removal at a fixed percentage of 99%, the data of biosorbent amount can be plotted for the $N = 47$ systems for stage 1, stage 2 and stage 1 + 2 as shown by the three curves in Fig. 6a–c for the different biosorbents, and the minimum total biosorbents amount for 99% dye removal can be identified. The values of minimum total biosorbents amount needed for the three biosorbents at four removal percentages (99.9, 90, 85 and 80%) are listed in Table 5.

The results of this analysis shows that the amount of biosorbent amounts required were higher at higher percentages of lead(II) removal. For each percentage removal, PCP 0.05 was required in smaller amounts than PCP 0.01 and PCP raw and the required amount decreased with decreasing percentage removal. For example, 4.32 kg of PCP Raw is required to achieve 99.9% lead(II) removal from 120 mg/dm^3 of 2.5 m^3 of lead(II) solution, while 3.82 kg of the biosorbent is required for 99% removal, 3.08 kg for 85% removal and 2.44 kg for 80% removal of lead(II) from the same solution in a two-stage operation. The optimum system numbers for the biosorbents for a particular percentage removal were found to be the same. Comparing the optimum biosorbent mass required for single-stage and two-stage operation in Table 5, it will be observed that the trends in the single-stage operation are similar to those of the two-stage operation. The single-stage operation requires more biosorbent amounts than the two-stage operations for each percentage removal (Qian, Qin-Yan, Yuan, Bao-Yu, & Hong-Jian, 2010). The differences between the amounts of biosorbent required are larger for higher percentage removal and smaller for lower percentage removal.

4. Conclusion

Effect of modification on the parameters of kinetic models applied for biosorption of lead(II) onto pine cone powder was related to biosorption performance. The pseudo-second order parameters: approaching equilibrium factor, R_w, biosorption half-life, $t_{0.5}$ rate parameter, k_2q_e, and operating time, t_x, were analyzed to determine the biosorption performance. Isotherm analyses were carried out and the best fitting isotherm observed to be the Langmuir-1 model. It was observed that for two stages a total of 3.82, 2.30 and 1.57 kg of PCP Raw, PCP 0.01 and PCP 0.05 is required to remove 99% of 120 mg/dm^3 lead(II) from 2.5 m^3 solution.

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