



Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo)—A comparative study

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ABSTRACT

Melocanna baccifera (Poaceae) is the most abundant and economically important non-timber product in state of Mizoram, India. The communities of the region use this potential resource in many ways, charcoal production is one of them. Bamboo charcoal has application in food, pharmaceutical and chemical industries. Activated charcoal was prepared from *M. baccifera* charcoal by chemical pretreatment in order to make better use of this abundant biomass material. Batch experiments were conducted under varying range of pH (2.0–6.0), contact time (15–360 min) and metal ion concentrations (50–90 mg L⁻¹). The optimum conditions for lead biosorption are almost same for *M. baccifera* raw charcoal (MBRC) and *M. baccifera* activated charcoal (MBAC)—pH 5.0, contact time 120 min, adsorption capacity q_{\max} 10.66 mg g⁻¹ and 53.76 mg g⁻¹, respectively. However, the biomass of MBAC was found to be more suitable than MBRC for the development of an efficient adsorbent for the removal of lead(II) from aqueous solutions. FTIR analysis revealed that –OH, C–H bending, C=O stretching vibration and carbonyl functional groups were mainly responsible for Pb(II) biosorption. Thus, this study demonstrated that both the charcoal biomass could be used as adsorbents for the treatment of Pb(II) from aqueous solution.

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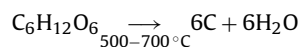
1. Introduction

Heavy metal ions such as lead, cadmium, mercury, chromium, nickel, zinc and copper are non-biodegradable, can be toxic and carcinogenic even at very low concentrations, and hence, usually pose a serious threat to the environmental and public health [1]. The traditional methods for the treatment of lead and other toxic heavy metal contaminated in wastewaters include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation and coagulation, nevertheless these techniques have disadvantages including incomplete metal removal, high consumption of reagent and energy, low selectivity, high capital and operational cost and generation of secondary wastes that are difficult to be disposed off [2,3]. For these reasons, cost-effective alternative technologies for treatment of metals contaminated waste streams are needed.

According to the ranking of metal interested priorities referred by Volesky [4], Pb(II) is one of the most interesting heavy metal for removal and/or recovery considering the combination of environmental risk and reserve depletion. This metal is widely used in many industrial applications, such as storage battery manufac-

turing, painting pigment, fuels, photographic materials, explosive manufacturing, coating, automobile, aeronautical and steel industries [5–8]. Lead pollution results from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations [9]. Lead is a highly toxic and cumulative poison, accumulates mainly in bones, brain, kidney and muscles. Lead poisoning in human causes severe damage to kidney, nervous and reproductive systems, liver and brain [10]. In drinking water, even at a low concentration may cause anemia, encephalopathy, hepatitis and nephritis syndrome [11]. The permissible limit for Pb(II) in waste water as set by Environmental Protection Agency (EPA) is 0.05 mg L⁻¹ and that of Bureau of Indian Standard (BIS) is 0.1 mg L⁻¹ [12] and in drinking water intended for drinking, as set by EU, USEPA and WHO are 0.010, 0.015 and 0.010 mg L⁻¹, respectively [13,14]. It is therefore, essential to remove Pb(II) from wastewater before disposal.

Charcoals biomass is popular adsorbents for air and water purification [15,16]. Charcoal is manufactured initially by thermal decomposition according to the following reaction:



The use of activated carbon is considered to be the best currently available technology for removing low-solubility contaminants in water treatment, including trace metals [17,18]. Charcoal was a carbonaceous material that has highly developed porosity and internal surface area.

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Melocanna baccifera belongs to a family of Poaceae. The bamboo forest area of Mizoram constitutes 14% of the total of India's bamboo area. *M. baccifera* is the most abundant, contributing about 95% of the growing stock of bamboo. The communities of the region use this potential resource for food, shelter, furniture, handicraft, medicines, charcoal production etc.

Bamboo charcoal application includes environment protection, food, pharmaceutical, chemical and metallurgical industries. A surface area of pores of bamboo charcoal is wider than wood charcoal. So ability of cleaning water of bamboo charcoal is more than wood charcoal.

So, the present study was performed to compare and evaluate *M. baccifera* raw charcoal (MBRC) and *M. baccifera* activated charcoal (MBAC) as adsorbents for the removal of Pb(II) from aqueous solution by systematic evaluation of the parameters involved such as pH, Pb(II) concentration and time. Furthermore, the Redlich–Peterson, Langmuir–Freundlich, Langmuir, Freundlich adsorption isotherms and pseudo-first-order and pseudo-second-order reaction were applied to calculate isotherm parameters and to study the kinetics of adsorption. Fourier transform infrared spectroscopy (FTIR) was also used to elucidate the adsorption.

2. Experimental

2.1. Biosorbent

M. baccifera charcoal was collected from the state of Mizoram (North-East India). This bamboo charcoal was produced by stacking of many bamboo culms (usually 2–3 feet in length) inside the charcoal kiln. Thermal decomposition of *M. baccifera* culm was carried out inside the charcoal kiln. During charcoal production, a small opening of air ventilation was made at the charcoal kiln for oxygen circulation. The oxygen supply should be reduced so that the culm will not burn away. Under reduced oxygen supply, charring of the culm was take place. The charring operation can take between 2 and 4 h. The charcoal biomass was milled with a blender and sieved to a particular size.

2.2. Activation of *M. baccifera* charcoal

Chemical activation was carried out using phosphoric acid (Qualigens) and potassium hydroxide (Himedia) at various concentrations (20, 40, 60 and 80%, w w⁻¹). In the activation system, the charcoal powder with a mass concentration of 40 g L⁻¹ was in contacted with the above various concentrations of chemical reagents, respectively, for 24 h by shaking on an orbital shaker with a speed of 150 rpm. Centrifugation was done at a speed of 10,000 rpm for 10 min using Remi centrifuge C20 in order to separate activated charcoal from the chemical solutions. The activated charcoal was thoroughly washed with deionised water, oven-dried at 110 °C for 24 h, cooled at room temperature and stored in an air-tight container. 0.1 g of the MBRC and the MBAC pretreated by the above various concentrations of potassium hydroxide and phosphoric acid were mixed with 70 mg L⁻¹ of Pb(II) solution for 6 h on the orbital shaker at 29 ± 1 °C. The supernatants were separated from the biomass by centrifuging at 10,000 rpm for 8 min. The concentrations of metal in the solutions were analyzed.

2.3. Preparation of stock solution of metal

All chemicals used in this study were analytical grade. Stock solution of lead was prepared using Pb(NO₃)₂ in double distilled water. Different desire concentrations of Pb(II) were prepared by diluting 1000 mg L⁻¹ of the stock solution. Standard solution of Pb(II) (1000 mg L⁻¹) for atomic adsorption spectrophotometer was

obtained from Sisco Research Laboratories (India). Acid and base solutions (1N HNO₃ and 1N NaOH) were used for pH adjustments.

2.4. Scanning electron microscope (SEM) analysis

In order to characterize the surface structure of activated charcoal and raw charcoal, SEM (XL30 ESEM, Philips, USA) analysis was carried out.

2.5. Batch mode adsorption studies

The biosorption of Pb(II) ions on the MBRC and MBAC of *M. baccifera* was investigated in batch mode sorption equilibrium experiments. All batch experiments were carried out in 250 mL conical Erlenmeyer flasks containing 100 mL metal solution.

The effect of pH on the sorption capacity of MBRC and MBAC for Pb(II) was evaluated in the range of 2.0–6.0. The pH of each metal solution was adjusted to the required pH value by using 1N HNO₃ or 1N NaOH. Then 0.1 g of dried adsorbent was added to the metal solution. The reaction mixture was shaken on an orbital shaker for at 150 rpm, 29 °C for 6 h, which was enough to attain adsorption equilibrium. Similarly, adsorbent dosage (0.1–0.5 g), Pb(II) concentration (50–90 mg L⁻¹), contact time (15–360 min) and for raw and activated charcoals were also conducted. At the end of the experiment, the solutions were separated from the biomass by centrifuging at 10,000 rpm for 8 min. The concentrations of metal in the solutions were analyzed using Flame Atomic Adsorption Spectrometer (GBC 932 plus, Australia). The wavelength of 283.3 nm was used for the analysis of the metal. The instrument was calibrated with a standard solution within a linear range and a correlation coefficient (R²) of 0.995–1.0 was obtained. In order to reproduce the results, the experiments were conducted in triplicate and the average values were used in this data analysis.

2.6. Desorption experiments

For the desorption study, 0.1 g biomass was in contacted with 100 mL of Pb(II) solution (60 mg L⁻¹). After adsorption experiment, the biomass was collected by filtration and washed with deionised water for two times to remove excess Pb(II) residual on the surface. Then it was in contacted with 100 mL of 0.1 M HCl. The mixture was shaken for 6 h and then centrifuged at 10,000 rpm for 8 min. supernatant was collected and metal analysis was carried out. The experiment was carried out five cycles.

The percentage of desorption values were obtained as

$$\% \text{ of Desorption} = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100$$

2.7. FTIR analysis

In order to determine the functional groups involved in metal adsorption, the unloaded biomass, MBRC-Pb(II) loaded and MBAC-Pb(II) loaded with 50 mg L⁻¹ Pb(II) ions were analyzed using Fourier Transform Infrared Spectroscopy (JASCO FTIR-5300) in a range of 400–4000 cm⁻¹.

3. Results and discussion

3.1. Properties of charcoal

Composition of bamboo charcoal is carbon 44.40%, hydrogen 5.17%, oxygen 43.00% and ash 7.43%. Ash in the charcoal powder was not required. The pH of the bamboo charcoal was 7.85. The average diameter of the pores was 6.77 μm and 11.72 μm for raw

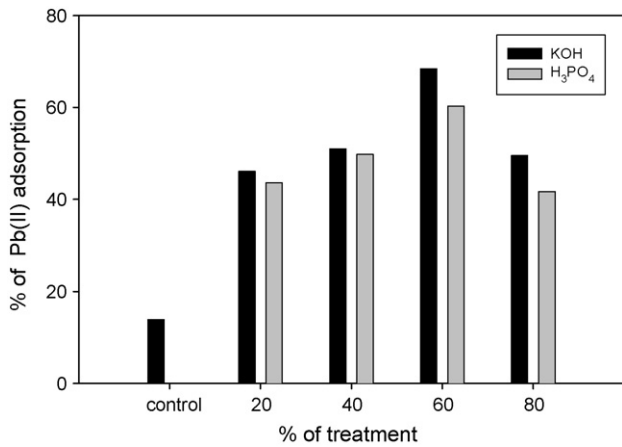


Fig. 1. Effect of pretreatment on *M. baccifera* charcoal by different concentrations of phosphoric acid and potassium hydroxide for the removal of Pb(II) ions.

and activated charcoal, respectively, and the particular size of raw and activated charcoals powder was 100 meshes.

3.2. Activation of *M. baccifera* charcoal

Changes in the sorption capacity of the biomass which was chemically pretreated with different concentrations of KOH and H₃PO₄ were investigated. The effect of chemical pretreatment on the adsorption of Pb(II) ions by MBRC and MBAC was shown in Fig. 1. Data obtained from activation studies showed that 60% KOH pretreatment shows highest percentage of adsorption, i.e. 68.42% in 70 mg L⁻¹ of Pb(II) solution.

In case of pretreatment with acidic solutions of H₃PO₄, percentage of adsorption capacity was slightly decreased in comparison with that of alkali activation, 60.27% was the highest percentage of adsorption obtained with 60% phosphoric acid pretreatment. 60% KOH treated activation was used for further experiments since it shows highest percentage of adsorption.

Some researchers reported that alkali pretreatments of biomass enhanced the adsorption capacity in comparison with raw biomass [19–22]. Remaining alkalinity can cause hydrolysis of various metals, which may improve adsorption capacity of biomass. In case of pretreatment with an alkali solution, hydrolysis reactions can occur. The hydrolysis reactions can lead to the formation of more carboxylate (–COO) and alcohol (–OH) groups in the pretreated biomass, which enhances the cationic biosorption [23].

An increased in biosorption capacity was observed in case of pretreatment with an acidic solution, which cause protonation of biomass surface, may be attributed to the exchange of bound hydrogen ions with heavy metal ions.

3.3. Scanning electron microscope (SEM) analysis

SEM micrographs of the charcoal biomass revealed that the surface was highly porous in nature; this increased the surface area for metal adsorption. The pore size of Pb(II) loaded activated charcoal was larger in size than the raw charcoal as shown in Fig. 2.

3.4. Effect of pH

Many studies showed that pH is an important factor affecting biosorption of heavy metals [24,25]. The adsorption pH was examined in a range of 2–6 to avoid the formation of lead hydroxide precipitation and the results were presented in Fig. 3. The maximum biosorption of Pb(II) was found 16.26% for MBRC whereas for MBAC 84.89% was observed at pH 5 in 60 mg L⁻¹ of Pb(II) solu-

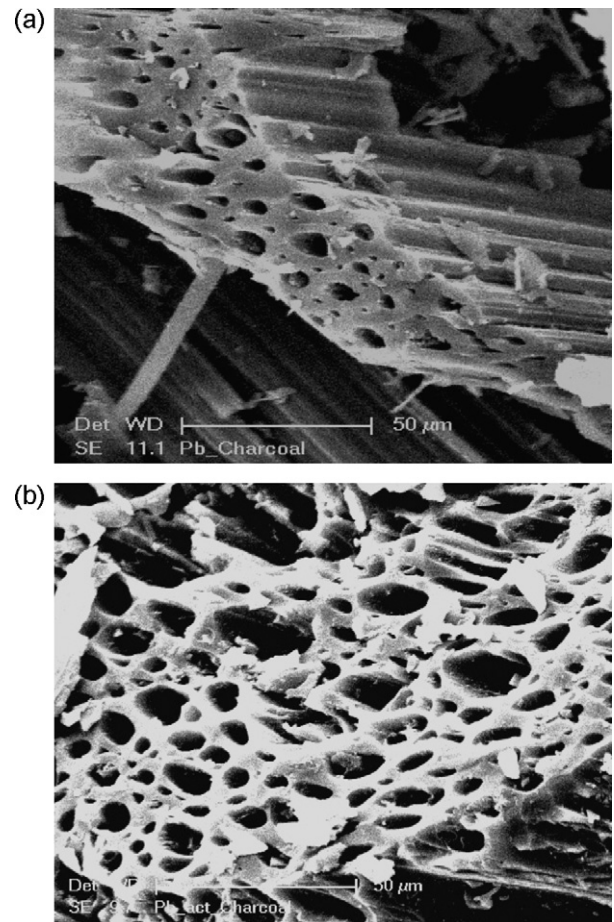


Fig. 2. Scanning electron microscope (SEM) micrograph: (a) Pb(II) loaded *M. baccifera* raw charcoal and (b) Pb(II) loaded *M. baccifera* activated charcoal.

tion. At pH 6, the adsorption yield for Pb(II) was slightly decreased in MBRC and MBAC. Therefore, all the biosorption experiments were carried out at pH 5. The increased in sorption of metal with increased in pH value can be explained using the analogy between the reaction of metal hydrolysis and the reaction between binding sites of the sorbent and the metal, where in both reactions, the bond for hydrogen is broken and hydrogen ions are released and substituted by the metal [26,27]. Therefore, the electrostatic attraction plays an important role in metal adsorption [28]. As the pH increases, metal adsorption increased since ion exchange is more

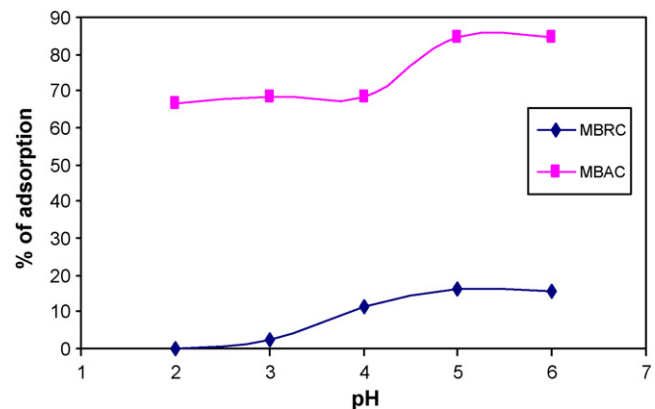


Fig. 3. Effect of pH on Pb(II) removal by *M. baccifera* raw charcoal (MBRC) and *Melocanna baccifera* activated charcoal (MBAC).

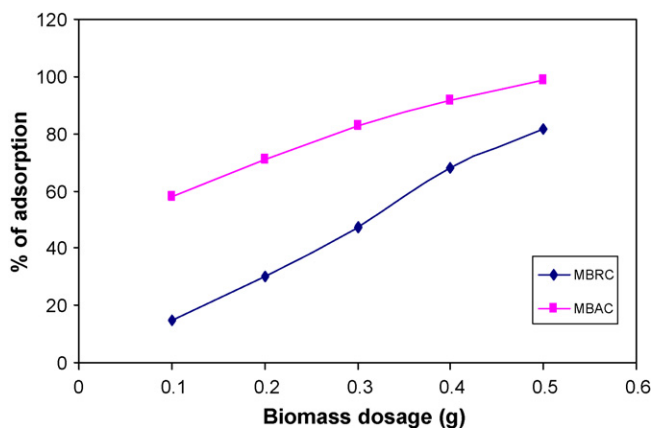


Fig. 4. Effect of adsorbent dosage on Pb(II) removal by *M. baccifera* raw charcoal (MBRC) and *M. baccifera* activated charcoal (MBAC).

effective when fewer protons are available to compete with the metal for binding sites onto the adsorbent. At low pH, there was a high concentration of H^+ ions, which competed with Pb(II), resulting in decreased of Pb(II) adsorption. At higher pH, more divalent cation forms disappear, and more soluble or insoluble hydroxylated forms of lead increases [29], the formation of hydroxylated complexes of the metal would also compete with the active sites and as a consequence, the retention would decrease again [30].

3.5. Effect of adsorbent dosage

Adsorption of Pb(II) at different adsorbent doses (0.1–0.5 g/100 mL) was analyzed at a constant concentration of metal solution. The percentage of adsorption of Pb(II) was increased from 14.731 to 81.695% for MBRC. Similarly, the percentage of adsorption was increased from 58.81 to 98.76% for MBAC with increased in adsorbent dose as shown in Fig. 4. This can be explained as adsorbent dose increased, more and more surface area will be available which exposed more active sites for binding of metal ions. A similar trend for the effect of adsorbent concentration was also observed and discuss in some literatures [31,32].

3.6. Effect of initial metal concentration

Adsorption experiments of Pb(II) concentration from 50 to 90 $mg L^{-1}$ with a fixed adsorbent doses (0.1 g/100 mL) at pH 5 for MBRC and MBAC were performed. For MBRC, Pb(II) removal range from 19.46 to 11.22% whereas for MBAC, Pb(II) removal range from 95.74 to 59.87%. As shown in Fig. 5, the percentage of Pb(II) adsorption decreased with increased in Pb(II) ions concentration and showed little decreased or almost constant in percentage(%) of adsorption at higher concentration. This can be explained that all the biosorbents has a limited number of active sites, which would has become saturated at a certain concentration. Although decreased in percentage (%) of adsorption, the equilibrium adsorption capacity of the biomass increased with increasing Pb(II) ions concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases, hence a higher initial concentration of metal ion may increase the adsorption capacity [33]. The data obtained from effect of initial concentration were further used to determine the isotherms of Pb(II) biosorption.

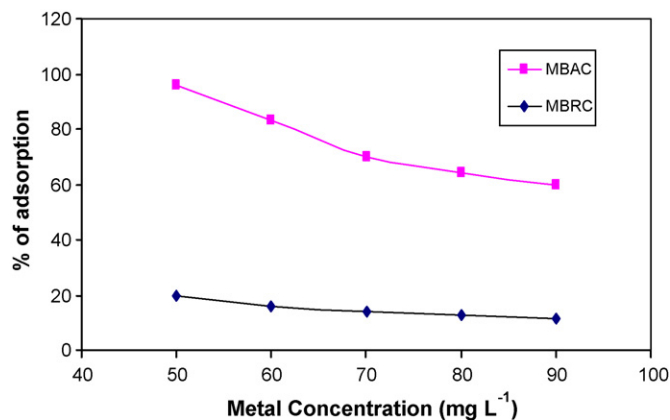


Fig. 5. Effect of initial concentration of Pb(II) concentration 50, 60, 70, 80 and 90 $mg L^{-1}$ onto the *M. baccifera* raw charcoal (MBRC) and *M. baccifera* activated charcoal (MBAC).

3.7. Effect of contact time

The effect of contact time (15–360 min) on the biosorption of lead (60 $mg L^{-1}$) onto MBRC and MBAC (0.1 g) in the solution of pH 5 at 29 °C was shown in Fig. 6. The lead percent adsorption increases with contact time until the equilibrium was attained. Studies conducted on the adsorption kinetics of Pb(II) removal revealed that the majority of metals ions were removed within the first 60–120 min contact with the adsorbents. The equilibrium state was attained at 360 min. It can be seen that the biosorption yield of Pb(II) increases with rise in contact time up to 120 min for MBRC and MBAC. Percentage of maximum biosorption was 13.63% for MBRC and 83.01% for MBAC. Afterwards, there was no a significant increase in Pb(II) adsorption. The fast adsorption at the initial stage is probably due to the increased concentration gradient between the adsorbate in solution and adsorbate in adsorbent as there must be increased number of vacant sites available in the beginning [34]. The initial fast uptake of Pb(II) is through physical adsorption since adsorption phenomenon tends to attain instantaneous equilibrium. As contact time was increased, more and more functional groups participated in adsorption of the metal ions until it reached equilibrium. After it reached the equilibrium, there was no a significance changes in lead concentration in the solution. The data obtained from effect of contact time were further used to determine the kinetics of Pb(II) biosorption.

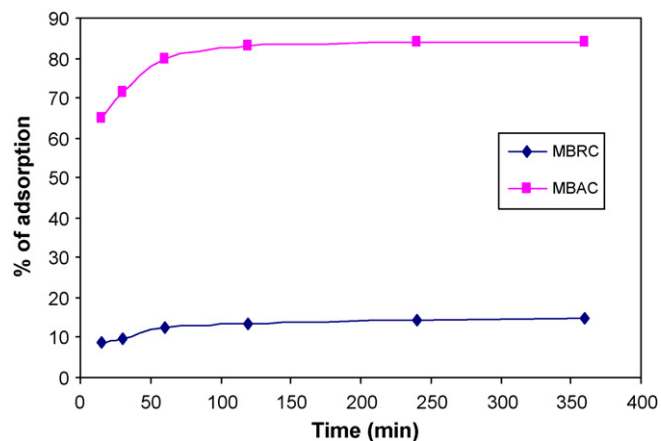


Fig. 6. Effect of contact time on Pb(II) removal by *M. baccifera* raw charcoal (MBRC) and *M. baccifera* activated charcoal (MBAC).

Table 1

Comparison of the pseudo-first-order and pseudo-second-order adsorption rate, the experimental and calculated q_e values of MBRC and MBAC.

Adsorbent	Experimental value	First-order-kinetic model			Second-order-kinetic model		
	q_e (mg g ⁻¹)	q_e cal. (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e cal. (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
MBRC	8.99	3.786	11.515×10^{-3}	0.963	9.363	6.605×10^{-3}	0.998
MBAC	50.49	10.146	17.042×10^{-3}	0.921	51.282	4.345×10^{-3}	1.00

3.8. Kinetics studies

The several kinetic models are needed to determine the data to examine the mechanism of adsorption process. Pseudo-first-order and pseudo-second-order were used to explain the kinetics of adsorption to investigate the mechanism of biosorption. The Pseudo-first-order Lagergren model [35] for solid/liquid systems of adsorption is expressed as

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \tag{1}$$

where q_e and q_t (mg g⁻¹) are the amounts of lead adsorbed on the biomass at equilibrium and at any time t , in mg g⁻¹, respectively. k_1 (min⁻¹) is the rate constant of pseudo-first-order biosorption. The model is based on the assumption that the rate is proportional to the number of unoccupied sites.

The slopes and intercepts of plot of $\log(q_e - q_t)$ versus t were used to calculate the first-order rate constant k_1 and equilibrium adsorption capacity q_e . The adsorption kinetics data were further analyzed using Ho and McKay's pseudo-second-order kinetic model [36]. The model is based on the assumption that the rate of sorption is proportional to the square of the number of unoccupied sites. It is expressed as

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

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). The slopes and intercepts of plots t/q_t versus t were used to calculate the pseudo-second-order rate constants k_2 and q_e .

The comparison of the results with the correlation coefficients for both MBRC and MBAC were presented in Table 1. The correlation coefficients of the pseudo-second-order kinetics model for MBRC and MBAC were 0.998 and 1.0 respectively and the experimental q_e values were also agreed well with the calculated data. On the other hand, the correlation coefficients of the pseudo-first-order kinetics model were lower than pseudo-second-order kinetics model in MBRC and MBAC. Therefore, it can be concluded that this adsorption system followed a pseudo-second-order reaction rather than pseudo-first-order reaction.

3.9. Isotherms studies

Adsorption isotherms of Pb(II) concentration from 50 to 90 mg L⁻¹ with a fixed adsorbent doses (0.1 g/100 mL) at pH 5 of MBRC and MBAC were studied. Redlich–Peterson (R–P), Langmuir–Freundlich, Freundlich and Langmuir adsorption isotherms were applied to describe the equilibrium relationships between sorbent and sorbate in solution. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is dynamic balance with that of the interface [37].

The R–P equation contains three parameters and incorporates the features of the Langmuir and Freundlich isotherms [38]. The R–P isotherm can be described as follows:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \tag{3}$$

where K_{RP} , a_{RP} and β are the R–P parameters. β lies between 0 and 1. For $\beta = 1$, the R–P equation convert to Langmuir form. When K_{RP} and a_{RP} are much greater than unity, the equation can transform Freundlich form.

The Langmuir–Freundlich isotherm equation is characterized by the heterogeneity factor, n , and employed to describe the heterogeneity system. The isotherm can be expressed as

$$q_e = \frac{K_{LF} C_e^n}{1 + a_{LF} C_e^n} \tag{4}$$

where K_{LF} is the Langmuir–Freundlich constant (L mg⁻¹). a_{LF} is the affinity coefficient (L mg⁻¹) and n is the heterogeneity coefficient.

The Freundlich isotherm [39] assumes that a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. Its mathematical formula is given as

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{5}$$

where C_e (mg L⁻¹) is the equilibrium concentration, q_e (mg g⁻¹) is the amounts of metal ions adsorbed per specified amount of adsorbent at equilibrium, K_f (mg g⁻¹) and ' n ' are constants which are adsorption capacity and intensity of adsorption, respectively. A graft was plotted $\log q_e$ versus $\log C_e$. The graft gives a straight line with correlation coefficient (R^2) of 0.855 and 0.679 for MBRC and MBAC, respectively. The slopes and intercepts of the graft were used to calculate the n and K_f values (Table 2).

The Langmuir [40] isotherm assumes that solid surface has a finite number of identical sites which are energetically uniform. According to this model, there is no interaction between adsorbed species, which mean that the amount adsorbed has no influence on the rate of adsorption. A monolayer was formed when the equilib-

Table 2

Redlich–Peterson, Langmuir–Freundlich, Freundlich and Langmuir isotherms parameters for the adsorption of Pb(II) onto MBRC and MBAC.

	Adsorbent	
	MBAC	MBRC
Experimental value		
q_e (mg g ⁻¹)	53.883	10.104
Redlich–Peterson		
K_{RP} (L g ⁻¹)	30.03	4.374
a_{RP} ((L mg ⁻¹) β)	-1.5	-0.319
β	0.849	0.828
R^2	0.9987	0.9993
Langmuir–Freundlich		
K_{LF}	106.382	14.771
a_{LF}	0.789	1.024
n	0.043	0.1704
R^2	0.6322	0.6063
Freundlich		
K_f (mg g ⁻¹)	46.320	7.730
n	31.153	16.556
R^2	0.679	0.855
Langmuir		
q_{max} (mg g ⁻¹)	53.760	10.66
b (mg ⁻¹)	1.317	0.231
R^2	0.996	0.998

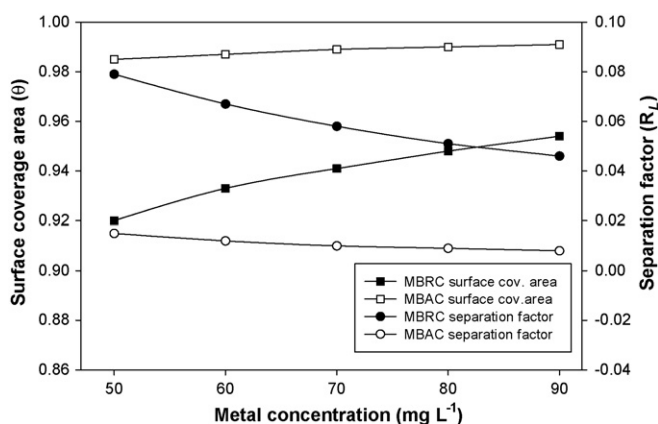


Fig. 7. The calculated separation factor (R_L) and surface coverage (θ) for Pb(II) adsorption plot against Pb(II) ions concentrations (mg L^{-1}).

rium was attained. Its mathematical form is as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \quad (6)$$

where C_e is the concentration of Pb(II) in solution (mg L^{-1}) at equilibrium, q_{\max} (mg solute g^{-1} adsorbent) is the maximum adsorption capacity corresponding to complete monolayer coverage and b (mg^{-1}) is a parameter related to the energy of adsorption, respectively. A graft was plotted C_e/q_e versus C_e gives a straight line with correlation coefficient (R^2) of 0.998 and 0.996 for MBRC and MBAC respectively. The slopes and intercepts of the graft were used to calculate the q_{\max} and b (Table 2). Further the obtained q_{\max} compared with other biosorbents and found to be MBAC is efficient biosorbent (Table 3).

Further, the Langmuir isotherm was used to calculate a dimensionless constant called separation factor or equilibrium parameter (R_L) which tell the favorability of adsorption of Pb(II) onto the biomass. Its mathematical formula was given as:

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

where R_L is a dimensionless separation factor or equilibrium parameter, b is the Langmuir isotherm constant and C_i (mg L^{-1}) is the initial concentration of Pb(II) ions. The R_L values between 0 and 1 indicated a favorable isotherm. The values of R_L at different concentrations of Pb(II) were calculated for MBRC and MBAC. The calculated R_L values at a different concentrations of Pb(II) fall within a favorable range. A graft was plotted R_L versus C_i (Fig. 7). The graft showed that, with increasing initial concentration of metal ion, the R_L values were decreasing. This indicated that adsorption of Pb(II)

ions at higher concentration were also still favorable for both the biomass.

To account for the adsorption behaviour of the metal ions onto the MBRC and MBAC, the Langmuir type equation related to surface coverage (θ) was used. The equation is given as

$$KC_i = \frac{q}{1 - \theta} \quad (8)$$

where K is the adsorption coefficient, C_i is initial concentration of lead ions and θ is the surface coverage. The fraction of biomass surface covered by metal ions was studied by plotting the surface coverage values (θ) versus Pb(II) ions concentration (Fig. 7). As shown in the figure the increase in initial metal ion concentration for Pb(II) increased the surface coverage on the MBRC and MBAC until the surface was nearly fully covered with a monomolecular layer. This indicates that both the biomass will be highly effective in removing Pb(II) ions in aqueous effluent.

R-P parameter (Table 2) describes the adsorption of metal ions. The values of β were closer to unity than 0, which implied that the isotherm was more approaching the Langmuir than the Freundlich isotherm. The Langmuir–Freundlich isotherm confirm the heterogeneity of sorbent surface since $0 < n < 1$. The correlation coefficients of the R-P and Langmuir isotherm model were higher than Freundlich isotherm model for MBRC and MBAC and the experimental q_e values were also agreed well with the calculated data in Langmuir isotherm model rather than Freundlich isotherm model for MBRC and MBAC, respectively. The maximum adsorption capacity (q_{\max}) value of MBAC was higher than MBRC; this is attributed by larger surface area of MBAC which had exposed several active binding sites and functional groups for metal ions binding. Therefore, the monolayer coverage process of heavy metal onto charcoals powder was approved by the best fit of equilibrium data in R-P and Langmuir rather than Freundlich isotherm expressions.

3.10. Desorption/reused studies

Adsorption-desorption cycle of Pb(II) was repeated five times in order to show the reusability by saturation of MBRC and MBAC with Pb(II) ions (60 mg L^{-1}) at each cycle. The Pb(II) ions was desorbed from the adsorbents with 0.1 M HCl. More than 77% and 63% were desorbed from MBAC and MBRC respectively. The adsorption capacities of the adsorbents did not noticeably change (only a maximum of 7% and 8% changes was observed) during the repeated adsorption-desorption process (Fig. 8). This result showed that the test adsorbent could be reused without significant losses in its initial adsorption capacity.

Metalliferous adsorbent from different experiments has been pooled (a few milligrams only) and sent to local hazardous waste disposal site.

Table 3
Comparison of biosorption capacity of Pb(II) by MBRC and MBAC and other found in the literatures.

Adsorbent	Biosorption capacity (mg g^{-1})	pH	Reference
<i>Penicillium simplicissimum</i>	76.90	5.0	[46]
<i>Melocanna baccifera</i> act. charcoal	53.76	5.0	This study
Crushed concrete fines	37.0	–	[47]
<i>Cephalosporium aphidicola</i>	36.91	5.0	[48]
Mustard husk	30.48	6.0	[49]
<i>Caulerpa lentillifera</i>	28.7	5.0	[50]
Coconut shell activated carbon	21.88	–	[51]
Powder activated carbon	20.7	5.0	[52]
Coir (<i>Coco nucifera</i>)	18.9	–	[53]
Waste bakers yeast in ethanol	17.49	5.0	[54]
Fly ash	15.08	6.0	[55]
Lichen (<i>Cladonia furcata</i>)	12.3	5.0	[56]
<i>Melocanna baccifera</i> charcoal	10.66	5.0	This study

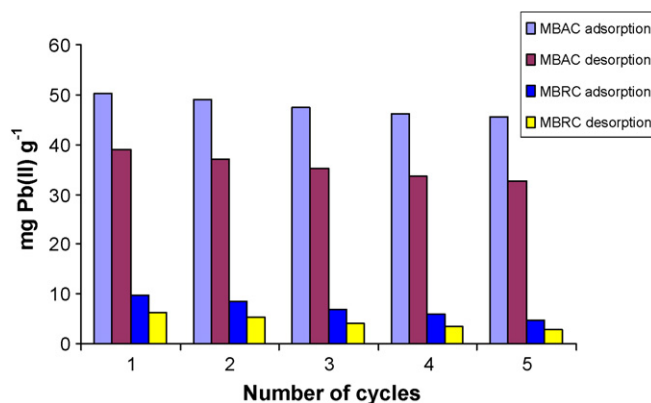


Fig. 8. Adsorption-desorption study of Pb(II) removal.

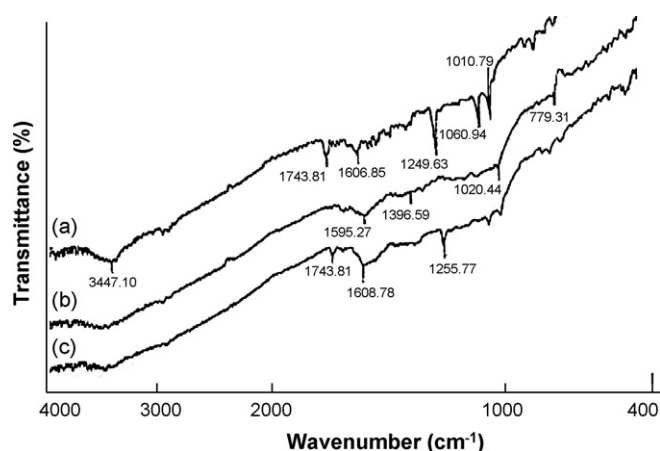


Fig. 9. FTIR spectra of (a) Pb(II) unloaded charcoal, (b) Pb(II) loaded *M. baccifera* activated charcoal and (c) Pb(II) loaded *M. baccifera* raw charcoal.

3.11. FTIR analysis

The FTIR spectral analysis is important to identify some characteristic functional groups which are responsible of adsorbing metal ions [41–44]. The FTIR spectra of dried unloaded charcoal, Pb(II)-loaded charcoal and Pb(II)-loaded activated charcoal were examined to determine the possible interactions between the functional groups and the metal ions and presented in Fig. 9. The FTIR spectra of the adsorbents were recorded in the range of 400–4000 cm^{-1} to obtain the information regarding stretching and bending vibrations of the functional groups which are involved in the adsorption of metal ions. The spectrum of dried unloaded charcoal exhibits a broad band at 3447.10 cm^{-1} due to the presence of hydroxyl groups on the biomass surface. The peak located 1743.21 cm^{-1} is due to the presence of carbonyl functional group. The peak at 1606.85 cm^{-1} is due to stretching vibration of C=O. The adsorption peak at 1259.63–1010.79 cm^{-1} are due to C–H bending and C–O stretching vibration.

Comparing Pb(II) unloaded charcoal with Pb(II) loaded *M. baccifera* raw charcoal and Pb(II) loaded *M. baccifera* activated charcoal. The peak at 3447.10 cm^{-1} was disappeared in Pb(II) loaded activated charcoal and Pb(II) loaded raw charcoal. 1743.21 cm^{-1} peak was disappear in Pb(II) loaded activated charcoal and the peak size was reduced in Pb(II) loaded raw charcoal. The peak at 1606.63 cm^{-1} was shifted to 1595.27 cm^{-1} in Pb(II) loaded activated charcoal and 1608.78 in Pb(II) loaded raw charcoal. The peak at 1259.63 cm^{-1} was shifted to 1396.59 cm^{-1} in Pb(II) loaded activated charcoal and 1255.77 in Pb(II) loaded raw charcoal, also greatly reduced in size. The peak at 1010.79 cm^{-1} was shifted to 1020.44 cm^{-1} in Pb(II) loaded activated charcoal and reduced in size in Pb(II) loaded raw charcoal. The region below 1000 cm^{-1} is the ‘fingerprint zone’ and the adsorption can not clearly be assigned to any particular vibration because they correspond to complex interacting vibration systems [45]. The relevance explanation of a shift in the spectra, reduction and disappearance of the peaks were that there is an effect of chemical pretreatment and metal biosorption on the functional groups.

4. Conclusion

The effect of chemical pretreatment on the adsorption of Pb(II) ions by MBRC and MBAC showed that 60% KOH pretreatment shows highest percentage of adsorption. The maximum biosorption of Pb(II) was found at pH 5. Maximum adsorption capacity was 10.66 mg g^{-1} for MBRC and 53.76 mg g^{-1} for MBAC. Maximum biosorption was attained at 120 min for MBRC and MBAC. After-

wards, there was no a significant increase in Pb(II) adsorption. The rate of adsorption was best described by pseudo-second-order reaction. The adsorption isotherm was best described by Langmuir isotherm. The FTIR analysis of MBRC and MBAC showed that different functional groups are involved in the adsorption of the metal ions. From these results, MBRC and MBAC can be efficiently used for the removal of Pb(II) from the aqueous solution.

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