Pb(II) sorption by pyrolysed *Pongamia pinnata* pods carbon (PPPC)

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ABSTRACT

Experiments employing pyrolysed *Pongamia pinnata* pods carbon (PPPC) to delineate the effects of environmental variables like pH, sorbent dosage, sorbate concentration, contact time and physicochemical pretreatments on Pb(II) sorption were conducted. Maximum adsorption capacity 170.6 mg g^{-1} was observed at pH 3.5. Pb(II) sorption data was fitted to Langmuir, Fruendlich, Dubnin–Radushkevich and Tempkin isotherms while time dependent study was well described by pseudo-second-order kinetic model. The equilibrium data suited well the Langmuir isotherm with q_{max} value of 370 mg g^{-1}. FTIR spectroscopic analysis of PPPC revealed the existence of various alkane, aromatic C=C and oxygen functionalities along with aromatic NO_2 and surface SO_2 complexes. The surface modification by various physicochemical approaches markedly influenced the chemical structure of PPPC. FTIR spectra confirmed that the basic pretreatment caused an increase in the hydroxyl group contents; acidic treatment increased the amount of single bonded oxygen functional groups along with bond cleavage while significant changes took place in the spectrum of boiled PPPC.

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1. Introduction

Pb(II) is among one of the most toxic metals found in the environment and a cumulative poison. It can trigger both acute and chronic symptoms of poisoning. Its high affinity for proteins leads to inhibition of the red blood cells and the vital transport of oxygen. Such intoxication leads to encephalopathies in the central nervous systems, necrosis in kidney, damage to the reproductive organs, anaemias and many metabolic deficiency symptoms. The drinking water guideline value recommended by World Health Organization and Ministry of Health Pakistan is 0.01 and 0.01–0.05 mg L^{-1} respectively [1] while the legal discharge limit for Pb(II) into inland surface water/sewers and sea is 0.5 mg L^{-1} [2]. The presence of metal ions in natural or industrial wastewater, their potential, and sequestration has been a subject of great importance in environmental resortation areas over the past two decades [3,4]. Various treatment technologies have been developed for removing toxic metals, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process, biosorption and adsorption [5–8]. The usage of activated carbons and biosorbents has been intensively studied as an effective means to mitigate a wide variety of soluble heavy metals from aqueous solution [9–11].

But attention has been corroborated on identifying natural biomaterials that are available in large quantities or certain wastes from agricultural or industrial operations such as distillery sludge, rice bran, corn cob, rose distillation biomass, and spent grains have potential to be used as low cost adsorbents [12–16].

Pongamia pinnata Linn Pierre (Leguminosae) is a large deciduous fast growing nitrogen fixing, ever green tree widely distributed in humid subtropical regions of Asia, including Pakistan, India and throughout South Asia. It is also naturalized in Fiji, Australia, Japan, Malaysia, and humid environments around the world including Egypt, Florida and Hawaii. Different parts of this plant have traditional medicinal uses [17]. Oil is the most important product of the *P. pinnata* tree in some parts of the world. Oil from seeds is used as a lubricant, varnish, water paint binder, in soap making and for leather dressing in tanning industries. Pods are collected and seeds are winnowed out. It has been found that 2 kg of mature pods yield about 1 kg of husked kernels. The pods containing seed husk are discarded as waste. Preliminary reports exist on work to produce carbonaceous porous solids (active carbons, chars and composites) from waste seed husks and pods of the tropical multipurpose tree and unmitigated agro forestry wastes [18,19] demonstrating active carbons can be prepared by pyrolysis at temperatures in the range 600–900 °C in the absence of air, making unwanted natu-

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ral biopolymers ash/chars/carbons industrially attractive because of their capability of lowering transition metal ion concentrations to parts per billion levels [9,20]. In recent years development of surface modified carbon has generated a diversity of activated carbon with far superior adsorption capacity [21,22].

In this study we prepared a sorbent with an improved and simple preparative strategy, from *P. pinnata* pods carbon (PPPC) for an efficient Pb(II) removal from aqueous solutions under the influence of different environmental parameters like pH, adsorbent dose, initial Pb(II) concentration and contact time, similarly investigated the sorption equilibrium and kinetics through batch experiments and modeling to develop a cost effective, low cost adsorbent from a natural waste biomass, which in turn would assist in environmental decontamination processes.

Some key objectives of this study were:

(i) To investigate the extent to which manipulation of experimental parameters influences the Pb(II) binding by PPPC.
(ii) To identify the nature of functional groups present on the PPPC and their relative contribution to Pb(II) binding.
(iii) The effect of surface functionalities on PPPC was intensified by carefully modifying the surface chemistry of carbon by various acids, bases and physical pretreatments, viz., heating, boiling and autoclaving, also confirmed by FTIR spectroscopy.

2. Experimental

2.1. Preparation of pyrolysed carbon from P. pinnata pods biomass

P. pinnata Linn Pierre trees were identified in the nearby area of National Institute for Biotechnology and Genetic Engineering (NIBGE), Faisalabad and Government Officer Residence (II), Sargodha. Dropping pods borne in high quantities which often litter the ground were collected from the target plants during August–September, 2006. Pods were washed thoroughly with distilled water to remove adhering dirt, sun dried, seeds were removed by hands. *P. pinnata* pods were firstly incinerated in open air. Then pyrolysis was carried out in a horizontal temperature controlled furnace (EYELA Electric furnace, TMF-2100, Japan). About 100 g of the sample was placed in a Tin container, and pushed into the hot zone of the furnace. During pyrolysis, the furnace temperature was increased at a rate of 10 °C/min from room temperature to 550 °C and was held at this temperature for 4 ± 0.5 h. The pyrolysed sample thus obtained was crushed into powder form and sieved into three different sizes, viz., 40, 63 and 150 μm through octagon siever (OCT-DIGITAL 4527-01). These samples were stored at room temperature in separate airtight containers.

2.2. Materials

All solutions were prepared using distilled and deionized water. Hydrochloric acids, sulphuric acid, phosphoric acid, sodium hydroxide, calcium hydroxide, aluminum hydroxide were obtained from Fisher Scientific and lead nitrate from BDH (England). All chemicals were of ACS reagent grade and used as received. The stock solution of 1000 mg L^{-1} Pb(II) was prepared by dissolving lead nitrate in deionized water. All the working solutions were prepared by diluting the stock solution with distilled water.

2.3. Modification approaches of P. pinnata pods carbon

The *P. pinnata* pods carbon (PPPC) was treated by various approaches, subsequently washed with generous amount of deionized water until constant pH of the washed liquid was achieved and dried in an Eyle oven at 110 °C for 24 h. The carbons were stored in sealed containers at room temperature.

2.3.1. Chemical approach

In chemical modification, PPPC was treated by 0.1 M (HCl, H$_2$SO$_4$, H$_3$PO$_4$, NaOH, Ca(OH)$_2$, and Al(OH)$_3$ at a ratio of 1 g/15 mL. These chemicals–carbon suspensions were shaken at 100 rpm, 30 °C for 2 h.

2.3.2. Physical approach

For the physical modification PPPC sample was heated at 100 °C for 24 h, boiled for 30 min and autoclaved at 121 °C, 15 psi for 15 min at a ratio of 1 g/15 mL of distilled water.

2.4. Equipment

The metal concentration in solution was determined using Atomic Absorption Spectrophotometer (PerkinElmer A Analyst 300, AA Win Lab Software, flame mode). The spectra were collected using PerkinElmer Spectrum BX FTIR system (Beaconsfield Bucks, England) equipped with diffuse reflectance accessory. The samples were ground in an agate mortar (Merck, for spectroscopy), immersed in small amount of doubled distilled water, vortexed for 5 min. A small amount of sample was transferred to diffuse reflectance rods in the form of thin film. The samples were dried for 6 h in a heating oven. The background obtained from a scan of empty rod was automatically subtracted from the sample spectra.

2.5. Batch experimental systems

Adsorption experiments were conducted in a batch reactor system. An orbital shaker (IFS-1-W Kuhner, Switzerland) was used for the experiments at 200 rpm under controlled temperature of 30 °C. Experiments were performed to study the adsorbent capacity of PPPC by varying the pH of Pb(II) solution, the adsorbent dosage, adsorbate concentration, and contact time. Pb(II) solutions at different pHs were prepared by adjusting the pH with 0.1 M NaOH or 0.1 M H$_2$SO$_4$. A known amount of the adsorbent of the appropriate particle size (150 μm) was added to the batch reactor system and kept in the shaker for 24 h to attain equilibrium. To understand the maximum uptake of the adsorbent and its behavior at high metal concentrations, the solutions of various concentrations ranging from 25 to 800 ppm were prepared in separate 100 mL conical flasks. The standardized adsorbent dosage and particle size was transferred to each of the conical flasks. These flasks were placed in the orbital shaker, which provided gentle end over end agitation for 24 h, after which the suspensions were centrifuged and then filtered through a 0.45 μm nylon filter. The Pb(II) remaining in the solution was analyzed using AAS. Control samples without adsorbent were run in parallel. The concentration of adsorbed Pb(II) on PPPC was calculated by difference from the control and test solution concentrations. The sorption density of Pb(II) onto the PPPC, q_e, was calculated by,

$$q_e = \frac{C_i - C_e}{M} \times V \tag{1}$$

where C_i and C_e are initial and equilibrium concentrations. The sorption kinetic experiments were performed for 24 h under conditions of pH (3.5), initial Pb(II) concentration (100 mg L^{-1}), particle size (150 μm). At each predetermined time point, a 2 mL solution was collected through Millipore and analyzed for Pb(II) contents. The effect of sorbent loading (0.0025–0.2 g L^{-1}) was also examined. All the experiments were performed at least in triplicate. Average and standard deviation values were calculated using Microsoft Excel, version Office XP, software. The error bars in the figures represent the standard deviation values. Linear regression analysis was used to determine slope and intercepts of linear plots for statistical analysis of the data.

2.6. Sorption isotherms

The equilibrium sorption isotherms express the relationship between the concentration of the sorbate and its degree of accumulation onto sorbent surface at constant temperature and are important to understand the mechanism of biosorption. The Langumir isotherm [23] can be explained in the following linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max \cdot b}} + \frac{C_e}{q_{max}} \tag{2}$$

where q_{max} is the monolayer sorption capacity and b (L mg^{-1}) is the Langumir constant related to the free energy of sorption, independent of temperature.

The Freundlich sorption isotherm assumes that the uptake of sorbate occurs on a heterogeneous surface by multilayer sorption. This model can be adopted in the following linearized form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where q_e is the amount of Pb(II) adsorbed per unit weight of the adsorbent (mg g^{-1}), C_e is the equlibrium concentration of solute in the bulk solution (mg L^{-1}), K_F is the multilayer sorption capacity and $1/n$ is the characteritic constant indicative of the intensity of the adsorption. The slope of the linear plot of $\log q_e$ against $\log C_e$ gives the value of $1/n$ and the intercept yields the value of K_F.

Debnin–Radushkevich isotherm is used to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. This isotherm postulates a fixed volume or sorption space close to the sorbent surface where sorption takes place. This model assumes the heterogeneity of sorption energies within this space. The Debnin–Radushkevich isotherm equation is

$$q_e = q_m e^{-\beta \varepsilon^2} \tag{4}$$

It is applied to the sorption data in the following linearized form:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{5}$$

where q is the amount of sorbate sorbed onto sorbent surface (mg g^{-1}), q_m (mg g^{-1}) is theoretical sorption capacity. The Polanyi sorption potential ε, the amount of energy required to pull a sorbed molecule from its sorption site to infinity is independent of temperature which is equal to

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{6}$$

R is the gas constant (8.314 J mol^{-1} K^{-1}), T (K) is absolute temperature, C_e is the equilibrium concentration of sorbate in solution (mg L^{-1}). The constant β is related to mean free energy, E (kJ mol^{-1}) of sorption per mole of the sorbate as it migrates to the surface of

the solid from infinite distance in the solution and can be computed using the relationship [24,25]:

$$E = \frac{1}{(2\beta)^{1/2}} \tag{7}$$

This parameter gives the information about sorption mechanism as chemical ion exchange or physical biosorption. The magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process follows chemical ion exchange while for the values of $E < 8$ kJ mol^{-1}, the biosorption process is of a physical nature [26].

Tempkin isotherm contains a factor that, explicitly takes into account adsorbing species–adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate repulsions and the adsorption is characterized by distribution of maximum binding energy, up to some maximum binding energy [27]. Commonly, it has been written in the following form:

$$q_e = \frac{RT}{b} \ln(K_t C_e) \tag{8}$$

Linear form of Tempkin isotherm can be expressed as:

$$q_e = B \ln K_t + B \ln C_e \tag{9}$$

The plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_t and B. where $B = RT/b$ represents heat of adsorption, T is absolute temperature in Kelvin and R is universal gas constant, $1/b$ indicates the adsorption potential of the adsorbent while K_t is the equilibrium binding constant corresponding to the maximum binding (L mg^{-1}) energy.

3. Results and discussion

A surface phenomenon called "sorption" is greatly affected by various environmental parameters like pH, amount of the adsorbent, sorbate concentration and equilibrium time between the two phases which were subsequently optimized one by one, keeping all other constant.

3.1. Effect of pH

Effect of pH was studied in the range of 3.5–5.5 because the metal precipitation occurs above and below this range. In Fig. 1A maximum adsorption capacity 170.86 mg g^{-1} was obtained at pH 3.5, it remained nearly constant at pH 4.0 and 4.5 and decreased up to 18.36% at pH 5. pH affects the surface properties of the sorbent, i.e. the surface charge of the cells present in the sorbent. The potential binding sites in the cells of agricultural/forestry waste may be carbohydrates, amine, hydroxyl, carboxyl and fiber carbonaceous
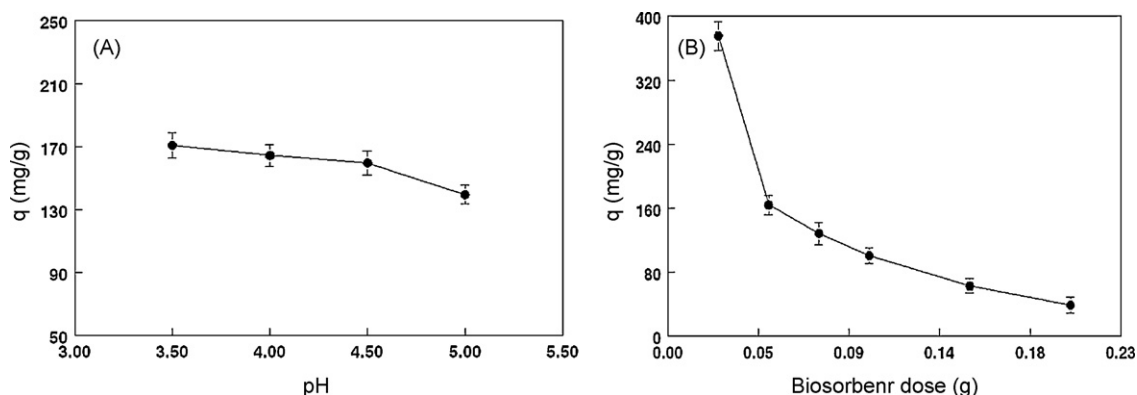

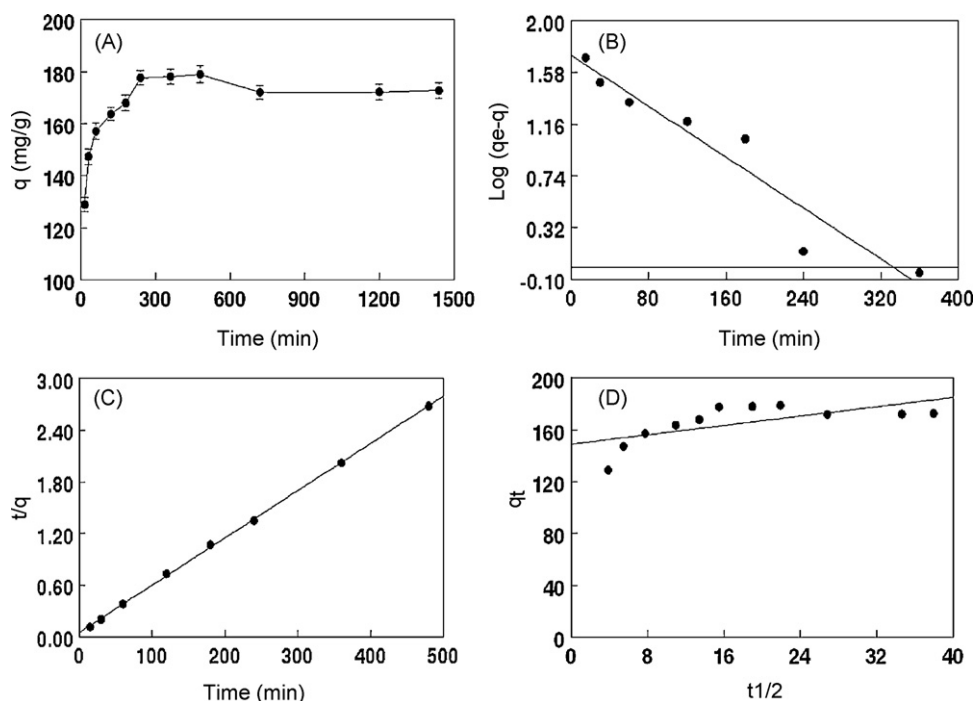**Fig. 1.** Effect of pH (A) and sorbent dose (B) on Pb(II) sorption using PPPC.

Fig. 2. (A) Effect of time interval on Pb(II) sorption using PPPC, (B) kinetic rate study using pseudo-first-order, (C) pseudo-second-order and (D) intraparticle diffusion models.

C_xOH [28]. Thus the ionic state of cell wall functional groups can be used to explain the pH dependence of the biosorption [29].

3.2. Influence of PPPC dosage

Effect of PPPC amount (0.025–0.200 g/100 mL) on the adsorption capacity for Pb(II) was studied. It is an important parameter, which determines the capacity of sorbent for given concentration of the sorbate. The results are shown in Fig. 1B. The adsorption capacity of the sorbate decreases with an increase in the mass of the sorbent presenting about 90% decline with regular increments in the amount of sorbent. This may be recognized that at higher doses of PPPC the sorbent–sorbent interactions are more dominating than sorbate–sorbent interactions [30,31]. For further investigations, 0.05 g sorbent was chosen as an optimized dose.

3.3. Effect of contact time on adsorption

The results of adsorption experiment for different contact times are presented in Fig. 2A. It was observed that percentage of Pb(II) removal was enhanced with increase in contact time. Maximum amount of Pb(II) was removed within 30 min (60–85% of total Pb(II) adsorbed) and thereafter the adsorption proceeds at slower rate till equilibrium after 8 h and a steady decrease in adsorption capacity was noticed after 12–24 h [32].

3.4. Kinetic studies

The kinetics of Pb(II) sorption onto PPPC was examined using Morris–Weber Lagergren pseudo-first-order and pseudo-second-order equations. The Pb(II) sorption rate constants were evaluated by subjecting the kinetics data to the linear form of Lagergren equation [33]:

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \tag{10}$$

where K_1 is the first order rate constant of sorption while q_e and q_t are the maximum sorbed concentrations at equilibrium and at time t. The linear plots of $\log(q_e - q_t)$ versus t in Fig. 2B and the value of K_1 computed from the slope of the linear plots (Table 1) suggests that the rate of removal is faster. The correlation coefficient (R^2) is low, moreover the experimental q_e (q_{exp}) value disagree with the calculated ones. This suggests that the adsorption of Pb(II) onto PPPC is not the first order reaction.

The pseudo-second-order kinetic model of Ho and McKay [34,35] is,

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \tag{11}$$

The integrated form of Eq. (11) becomes

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where K_2 is the rate constant of pseudo-second-order adsorption ($g\,mg^{-1}\,min^{-1}$) and $h = K_2 q_e^2$ where h is initial sorption rate ($mg\,g^{-1}\,min^{-1}$). The initial sorption rate (h), the equilibrium adsorption capacity q_e and K_2 were obtained from the slope and intercepts of plots of t/q_t against t (Fig. 2C) for PPPC and are presented in Table 1. Since the correlation coefficient (R^2) is 0.999 and the q_{exp} value is consistent with calculated one. These results imply that the adsorption system studied could well be explained by pseudo-second-order kinetic model at all time intervals.

Table 1
Kinetic parameters for the Pb(II) sorption by PPPC.

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model				Intraparticle diffusion model			Experimental value
q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (mg g^{-1})	K_2 (mg g^{-1} min^{-1})	R^2	h	R^2	C	K_{id} (min^{-1})	q_{exp} (mg g^{-1})
52.49	1.19×10^{-2}	0.9211	181.82	5.89×10^{-4}	0.9996	1695.89	0.448	149.03	0.9011	179

The rate parameters of intra particle diffusion are determined using following form of Morris–Weber relationship [36]:

$$q_t = K_{id}t^{1/2} + C \tag{13}$$

where C is intercept K_{id} is the intraparticle transport rate constant. q_t is sorbed concentration (mg g^{-1}) at time t [37] and indicated in Fig. 2D.

In Table 1 the intercept C, gives an idea about the boundary layer thickness, i.e. the larger the intercept the greater is the boundary layer effect [38].

3.5. Effect of initial Pb(II) concentration

Metal solutions of varying concentrations of lead ranging from 25 to 800 mg L^{-1} adjusted to optimum pH 3.5 were treated with 0.05 g of PPPC for 20 h at 30 °C. Experimental data points obtained for the Pb(II) sorption by PPPC at several Pb(II) concentrations are presented in Fig. 3A. These results depict that specific metal uptake increased with an increase in the sorbate concentration. The highest uptake of the PPPC was around 331.9 mg g^{-1} at an initial Pb(II) concentration of 800 mg L^{-1}. The enhancement in metal sorption could be due to an increase in electrostatic interactions involving the sites

of progressively lower affinity for metal ions [39]. However, with an augmentation of Pb(II) concentration a corresponding decrease in percent sorption was observed suggesting limiting number sorption sites available for sorption at higher Pb(II) concentrations. This effect may also be interpreted that at low sorbate ion/sorbent ratios, sorbate ion sorption takes into account the higher energy sites. As the sorbate ion/sorbent ratio increases, the higher energy sites are saturated and sorption begins on lower energy sites, resulting in a decrease in removal efficiency [40]. It is appropriate to note that sorption by sorbents in literature has been projected at low metal concentrations for metal sequestration, particularly in the range 1–100 mg L^{-1}. So all the sorption experiments were carried out at 100 mg L^{-1} of Pb(II) concentration.

3.6. Sorption isotherms

Among several existing isotherms, sorption data was analyzed by four isotherms, i.e. Langmuir, Fruendlich, Debnin–Radushkevich and Tempkin to evaluate the maximum saturation capacity of PPPC. The main reason for the extended use of these models is that they incorporate constants that are easily interpretable. The
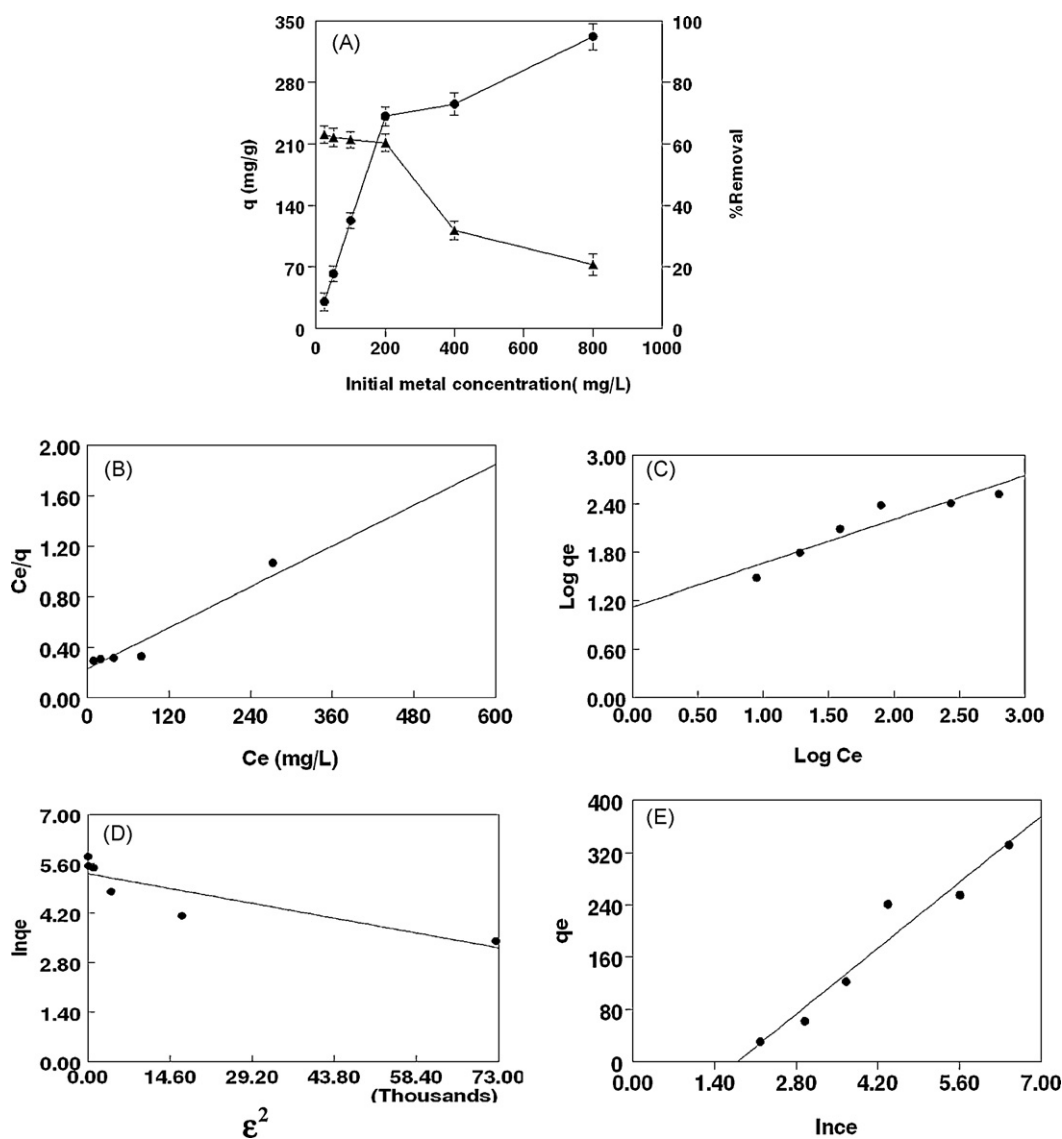

Fig. 3. (A) Effect of initial metal ion concentration (q, ● and %removal, ▲) on Pb(II) sorption and equilibrium modeling of sorption data using Langmuir (B), Freundlich (C), Dubinin (D) and Temkin (E) models.

Table 2
Comparison of the coefficients isotherm parameters for Pb(II) sorption by PPPC.

Equilibrium model	Parameter	Value	q_{exp} (mg g^{-1})
Langmuir isotherm	q_{max} (mg g^{-1})	370.37	
	K_L (L mg^{-1})	0.012	
	R^2	0.9877	
Freundlich isotherm	q_{max} (mg g^{-1})	438.68	
	K (mg g^{-1})	13.243	
	$1/n$	0.5425	
	R^2	0.8738	
Dubinin−Radushkevich isotherm	β (kJ^2 mol^{-2})	3×10^{-5}	331.9
	q_e (mg g^{-1})	203.69	
	E (kJ mol^{-1})	129.2	
	R^2	0.7687	
Temkin isotherm	K_t (L mg^{-1})	6.00	
	b (J mol^{-1})	34.911	
	B (L g^{-1})	72.1589	
	R^2	0.9438	

Langmuir, Fruendlich, Debnin–Radushkevich and Tempkin sorption isotherms of Pb(II) sorption onto PPPC are presented in Fig. 3B–E respectively and their respective constants along with correlation coefficients are enlisted in Table 2. These results predict that Langmuir sorption isotherm is followed by the sorption data very well.

The Langmuir capacity, q_{max}, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that PPPC had a mass capacity 370 mg g^{-1} for Pb(II) cation, which is close to the experimental value 331.9 mg g^{-1}. The values of q_{max} computed from, Fruendlich and Debnin–Radushkevich sorption isotherms are 438.7 and 203.7 respectively, far away from the experimental value. Moreover, when R^2 values of the models are compared, indicate, Langmuir model better fits the Pb(II) sorption process onto PPPC due to high correlation coefficient.

3.6.1. Separation factor

Favorability of sorption of Pb(II) on PPPC waste biomass was tested using the essential feature of the Langmuir isotherm, expressed in terms of a dimensionless constant, R_L referred as separation factor [13] which can be calculated as:

$$R_L = \frac{1}{1 + bC_i} \tag{14}$$

where C_i = initial concentration of sorbate, b = Langumir constant. The parameter R_L represents the shape of isotherm and nature of the sorption process as given below:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable isotherm
$R_L = 1$	Linear isotherm
$R_L = 0$	Irreversible isotherm
$0 < R_L < 1$	Favorable isotherm

Fig. 4 shows that Pb(II) sorption on PPPC increased concomitantly as the initial metal concentration increased from 25 to 800 mg L^{-1} indicating that adsorption is even favorable for higher Pb(II) concentration.

3.6.2. Surface coverage

The adsorption behavior of Pb(II) onto PPPC can be accounted using Langmuir type equation related to surface coverage, expressed as [15],

$$KC_i = \frac{\theta}{1 - \theta} \tag{15}$$

where θ is the surface coverage, C_i initial concentration and K is an adsorption coefficient. Fig. 4 reveals that, surface coverage on the
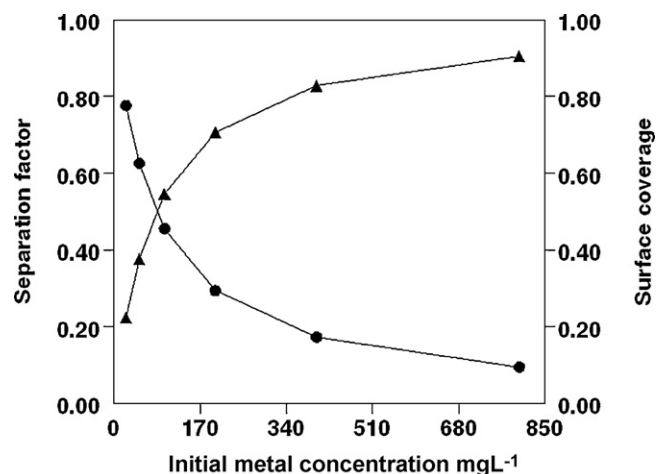

Fig. 4. A plot of separation factor (●) and surface coverage (▲) against initial Pb(II) concentration.

biomass increases with increase in initial metal concentration until the surface was nearly fully covered with a monomolecular layer.

3.6.3. Distribution coefficient

Distribution coefficient (D) can be defined as "the ratio of metal concentration in the adsorbent phase, to the concentration in the aqueous phase". The biomass relativeness in sequestration of Pb(II) ion from aqueous solution can be evaluated in terms of distribution coefficient. The values of D computed for a range of Pb(II) concentrations are recorded in Table 3. It is quite obvious from these results that the concentration of Pb(II) at the sorbent–water interface is higher than the concentration in the continuous aqueous phase. This suggests that the PPPC is effective in mitigation of Pb(II) removal. The sorbed species nature may be deduced from the fact that the metal ion is divalent. This indicates that two molecules of biomass were associated with Pb(II). So the composition of sorbed complex and the probable mechanism may be presented as follows [41,42]:

$$M^{2+} + 2B{-}OH \leftrightarrow M(BO)_2 + 2H^+ \tag{16}$$

where M^{2+} is divalent metal ion, B is biomass (PPPC), OH is hydroxyl group and H$^+$ is proton.

3.6.4. Gibbs free energy

The thermodynamic of exchange process depends on the number of water molecules (n) replaced by the Pb(II). The apparent Gibbs free energy of the adsorption process (ΔG_{ads}°) regarding the Pb(II) on PPPC is evaluated using the Bockris–Swinkel's adsorption isotherm equation [43], Gibbs free energy equation is represented as:

$$\Delta G_{ads}^\circ = -2.303RT \log \times \left[\left\{ \frac{55.4\theta}{C_i(1-\theta)} \right\} \left\{ \frac{\theta + n(1-\theta)^{n-1}}{n^n} \right\} \right] \tag{17}$$

Table 3
Apparent Gibbs free energy ΔG_{ads}° (kJ mol^{-1}) and distribution coefficient, D, of Pb(II) between aqueous phase and PPPC.

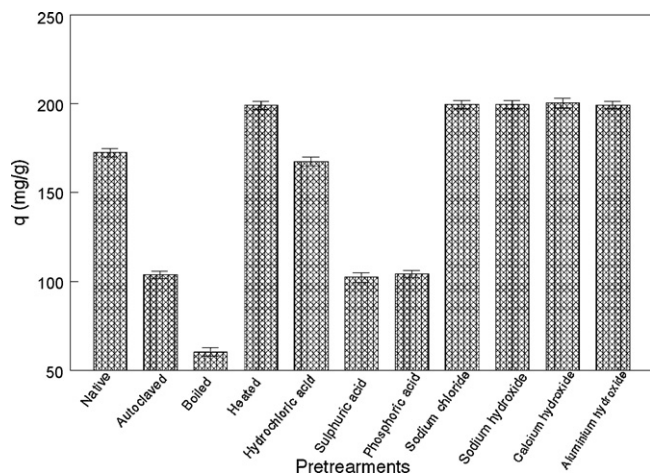| C_i (mg L^{-1})	ΔG_{ads}° (kJ mol^{-1})	D
24	−31.1264	0.630833
50	−30.7085	0.6202
100	−30.0435	0.6132
200	−29.0695	0.60325
400	−27.8131	0.319
800	−26.3494	0.207438

Fig. 5. Effect of pretreatments of PPPC on Pb(II) sorption.

where C_i is initial concentration of Pb(II) in the solution, θ = surface coverage and $n = 2$ since the most probable value of n is 2. The values of ΔG_{ads}° at various initial Pb(II) concentrations were predicted and documented in Table 3. The negative values of ΔG_{ads}° represent the spontaneous nature of Pb(II) sorption onto PPPC suggesting strong adsorption of Pb(II) ions onto biomass surface. Generally, it is considered that up to −20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and biomass surface representing physisorption while more negative than −40 kJ mol^{-1} indicate chemisorption, whereas values between −20 and −40 kJ mol^{-1} expressing that both physisorption and chemisorption responsible for sorption process. In the present study, the order of magnitude of ΔG_{ads}° values indicates a physical as well as chemical mechanism for Pb(II) adsorption onto PPPC.

3.7. Effect of chemical pretreatment

Effect of different chemical pretreatments on the sorption capacity of PPPC was studied at the optimized conditions of sorption, i.e. 0.05 g PPPC/100 mL Pb(II) of 100 mg L^{-1}, pH 3.5, temperature 30 °C, shaker speed 200 rpm, agitation time 20 h.

Different pretreatments of PPPC affected the sorption capacity (mg g^{-1}) in the following order: 200.2 Ca(OH)$_2$ > 199.42 NaCl ≈ NaOH > 198.99 Al(OH)$_3$ > 198.92 heated > 172.22 native > 167.38 HCl > 104.36 H$_3$PO$_4$ > 103.8 autoclaved > 102.36 H$_2$SO$_4$ > 60.42 boiled (Fig. 5). A considerable increase in the percent sorption was noticed 13.98–13.64% by Ca(OH)$_2$, NaCl, NaOH, Al(OH)$_3$ and heat pretreatments. Pretreatments using acids HCl, H$_2$SO$_4$, H$_3$PO$_4$ and physical pretreatments, i.e. autoclaved and boiling greatly reduced the Pb(II) sorption capacity (from 167.38 to 60.42 mg g^{-1}).

It can be seen, among all the pretreatments methods, alkali chemicals, salt and heat treatments resulted in an improvement in Pb(II) sorption capacity compared with different acids, autoclave and boiling pretreatments.

These findings predict that an increase in the Pb(II) sorption as a result of alkali pretreatment could be due to chemical modification of PPPC cell wall component, removal of surface impurities and exposure of available binding sites may be the cause of Pb(II) sorption capacity enhancement. In acid modification, H$^+$ ions alter the cross linkages which cause dissolution of organic groups, while the reduction in sorption capacity of autoclaved and boiled PPPC may be attributed to the loss of intracellular uptake [44] and heavy loss of biomass after boiling, respectively which was confirmed by FTIR studies.

3.8. FTIR characterization of PPPC

The FTIR spectra of PPPC and differently pretreated PPPC were scanned before and after Pb(II) exposure (Fig. 6a–v). In all the recorded spectra, 4000–3000 cm^{-1} the bands of stretching O—H vibrations are revealed which can be attributed to surface hydroxylic groups and physically adsorbed water [45]. The weak absorption peaks in 2250–2400 cm^{-1} can be assigned to double bonded carbon oxygen groups. The strong adsorption bands in 1500–1600 cm^{-1} are suggested for the overlapping of aromatic ring stretching vibrations with the bands of carboxylate moieties [46]. In this regard sharp distinctive peak at 1598 cm^{-1} in all spectra is assigned to C=C skeletal stretch in condensed aromatic system (such as diketones, keto esters and keto enols).

Narrow bands observed at 1350 and 1450 cm^{-1} present in all spectra correspond to C—H in-plane vibrations in various alkane bonds [19]. The two characteristic bands at 878 and 834 cm^{-1} are assigned to aromatic C—H out of the plane bending vibrations [47]. The small and broad peaks in 1000–1300 cm^{-1} region for all the carbon samples can be attributed to C—O stretching and O—H bending modes of alcohols, phenols, ethers, carboxlic acids and lactones [45,48,49]. Diffuse reflectance FTIR spectra of PPPCs depict low intensive bands over 1000–450 cm^{-1} indicating the various oxides. 766 and 702 cm^{-1} peaks represent NO$_2$ bending vibrations (out of plane) in aromatic nitro groups. In the spectrum, 700–610 cm^{-1} absorption band of PPPC can be ascribed to symmetrical stretching vibration of S—O groups, confirming the presence of surface SO$_2$ complexes [22]. The extent of band shifting gives an indication of the degree of interaction of functional groups on PPPC with Pb(II) (Fig. 6b). The observable change in the spectrum of lead exposed PPPC was in symmetrical stretch of the carboxylate groups, which shifted from 1389 to 1352 cm^{-1}. This shift can be correlated to a change in the counter ion associated with the carboxylate anion, suggesting that acidic groups, especially carboxylate, contribute to the metallic ion (Pb(II)) uptake.

3.8.1. Effect of NaCl and basic pretreatment

Fig. 6c–j shows the spectra of PPPC after NaCl, NaOH, Ca(OH)$_2$, as well as Al(OH)$_3$ treatments. These FTIR spectra show the strong broad overlapping bands between 4000 and 3000 cm^{-1}, since basic pretreatments suggest the relative increase of hydroxyl groups corresponding to this region which may be due to surface reaction occurring to lactone groups [50] as following equation (Eq. (18)),

$$\text{NaOH} + \quad\quad\quad \longrightarrow \quad\quad\quad + \text{Na}^+ \qquad (18)$$
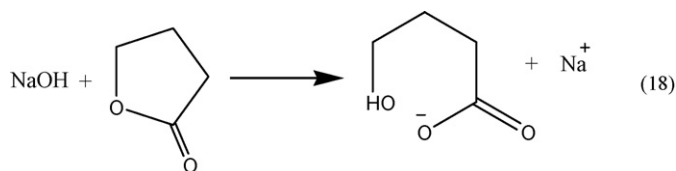
In the presence of a base, "hydrolysis" can lead to the formation of more carboxylic (−COOH), carboxylate (−COO$^-$) and alcoholic (−OH) groups which enhance the cationic sorption dominating a very clear sharp peak at 1047.38, 1042.46, 1043.20 cm^{-1} for NaOH, Ca(OH)$_2$ and NaCl treatments respectively after Pb(II) exposure.

3.8.2. Effect of acidic pretreatment

The spectrum of PPPC impregnated with HCl, H$_2$SO$_4$ and H$_3$PO$_4$ is shown in Fig. 6k–p. Several changes took place through the acid treated spectra compared with untreated PPPC spectrum. The acidic treatment increases the relative concentration of the peaks at 1000–1200 cm^{-1}. This implies a relative increase in single bonded oxygen functional groups such as phenols, ethers and lactones [45]. It displayed a sharp absorption peak at 1068, 1073 and 1063 cm^{-1} in HCl, H$_2$SO$_4$ and H$_3$PO$_4$ treated PPPC respectively. When an acid is

involved in modification it breaks many bonds in aliphatic and aromatic species present in the precursor material leading to liberation and elimination of many light and volatile products such as water, acetic acid, methanol and furan derivatives causing partial aromatization and recombination of species to form a stronger cross linked solid [51,47]. This behavior is consistent with the disappearance of C=C at 1598 and C—H at 1386 cm^{-1} in the PPPC spectrum accompanied by the appearance of new bands at 1490 and 1413 cm^{-1} (in HCl treatment) 1581 and 1403 cm^{-1} (in H$_2$SO$_4$ treatment) and 1586 cm^{-1} after H$_3$PO$_4$ modification.

3.8.3. Effect of physical pretreatment

Fig. 6q–v includes FTIR spectra that show the surface changes occurring in heat treated, autoclaved and boiled PPPC. Some similarities for heat treated and autoclaved samples to native PPPC's were observed with a broad region of absorption involving overlapping bands in the range 4000–3000 cm^{-1} existed but slightly shifted in the location and intensity leading to the decrease in aliphaticity in the PPPC by heat treatment [22] while in the autoclaved sample slight changes in the N and S containing oxides region were observed. After autoclave treatment the band at 1388 cm^{-1} showed effective increase in its intensity and was shifted to slightly higher position (1450 cm^{-1}). This includes the band at 1450 cm^{-1} resulting in a broad overlapping band at 1291.4 cm^{-1} after Pb(II) exposure. However, pretreatment of PPPC using heat increased Pb(II) sorption while autoclave pretreatment inhibited to some extent.
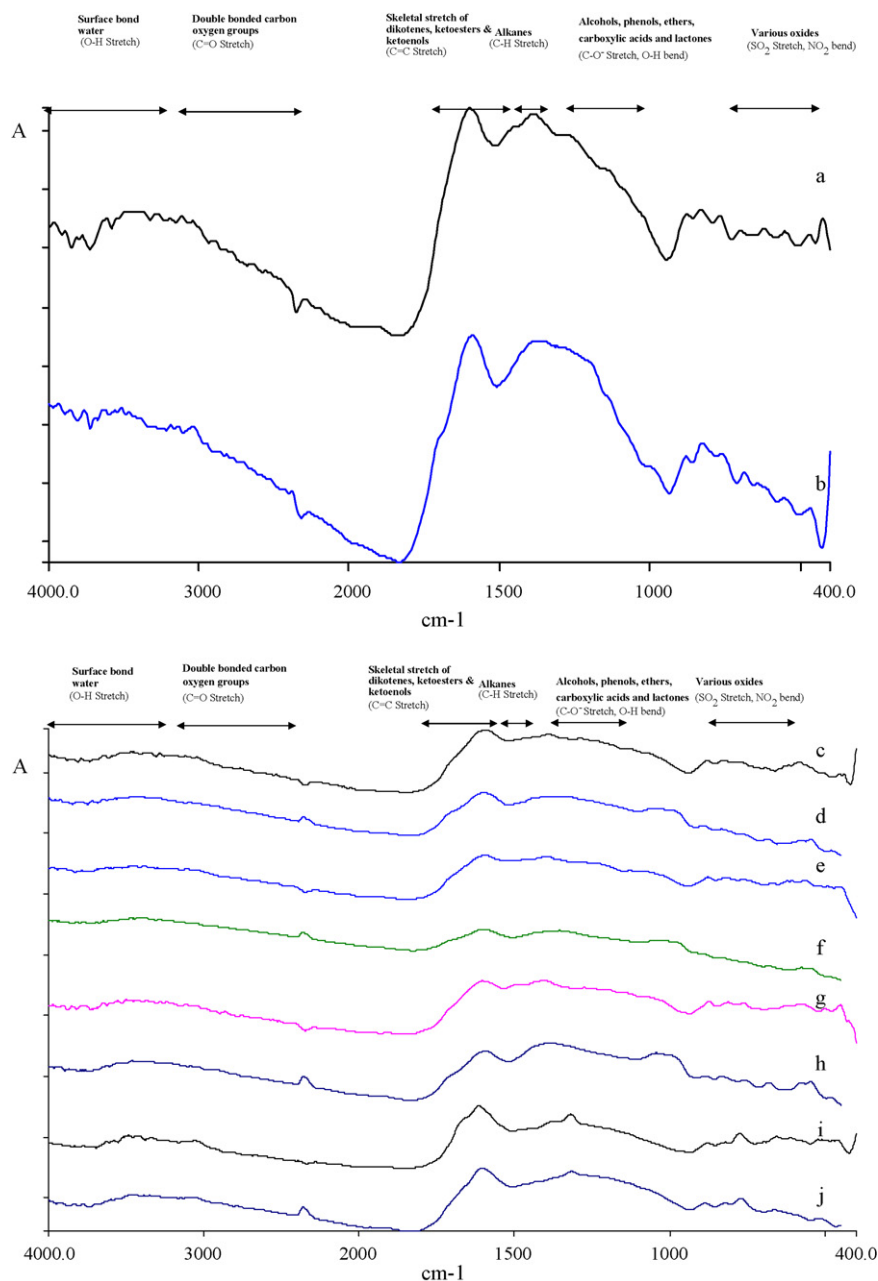

Fig. 6. (a–v) FTIR spectra observed for PPPC. (a) Non-treated PPPC, (b) Pb(II) loaded non-treated PPPC, (c–j) effect of NaCl and basic pretreatment on PPPC, (c) NaCl treated PPPC, (d) Pb(II) loaded NaCl treated PPPC, (e) NaOH treated PPPC, (f) Pb(II) loaded NaOH treated PPPC, (g) Ca(OH)$_2$ treated PPPC, (h) Pb(II) loaded Ca(OH)$_2$ treated PPPC, (i) Al(OH)$_3$ treated PPPC, (j) Pb(II) loaded Al(OH)$_3$ treated PPPC, (k–p) effect of acidic pretreatment on PPPPC, (k) HCl treated PPPC, (l) Pb(II) loaded HCl treated PPPC, (m) H$_2$SO$_4$ treated PPPC, (n) Pb(II) loaded H$_2$SO$_4$ treated PPPC, (o) H$_3$PO$_4$ treated PPPC, (p) Pb(II) loaded H$_3$PO$_4$ treated PPPC, (q–v) effect of physical pretreatment on PPPPC, (q) heat treated PPPC, (r) Pb(II) loaded heat treated PPPC, (s) boiled PPPC, (t) Pb(II) loaded boiled PPPC, (u) autoclaved PPPC and (v) Pb(II) loaded autoclaved PPPC.
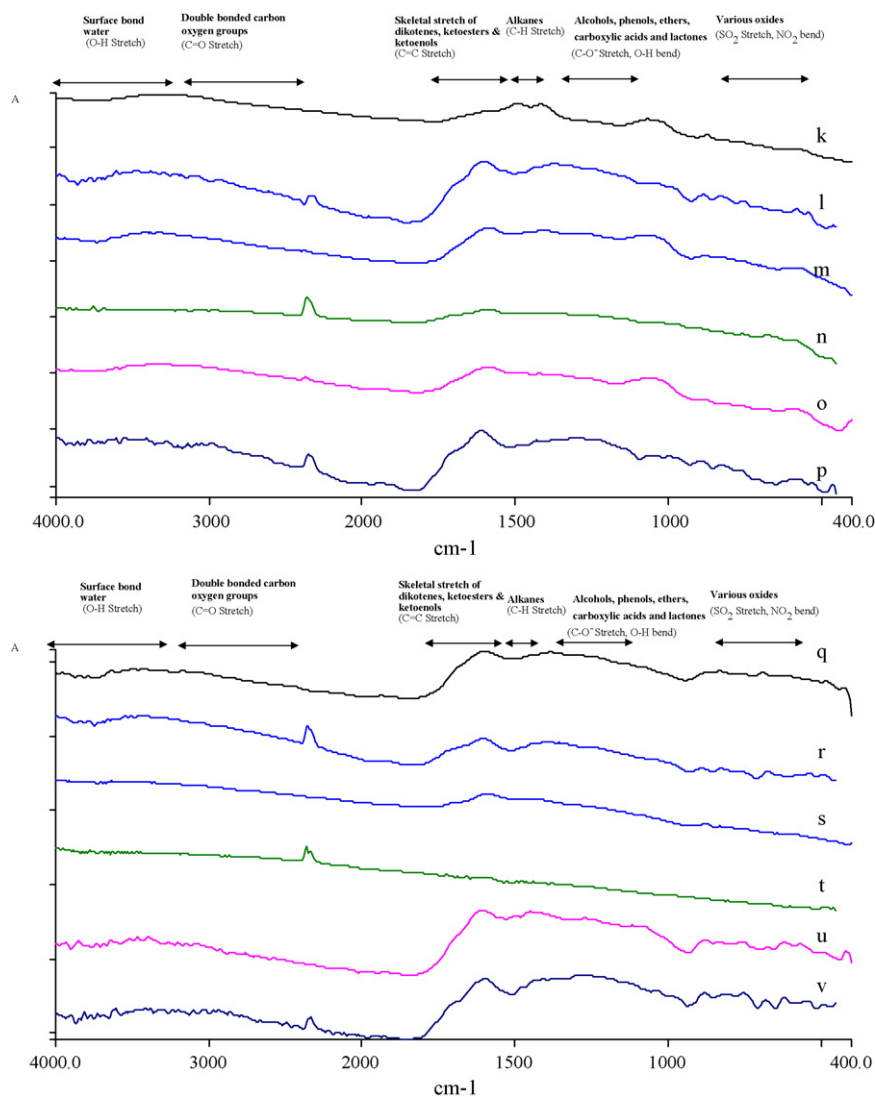
Fig. 6. (*Continued*)

Significant changes took place in the spectrum of boiled PPPC compared with native PPPC spectrum. It displayed only three overlapping bands in the higher region at 3989, 3640, 3472 cm^{-1} and two distinct peaks at 1587 and 878 cm^{-1} bands in the lower wave number region, attributed to C=C stretch and C—H aromatic stretch (out of plane). These bands appeared at relatively higher frequencies than their counterpart bands in the PPPC. This finding is apparently due to the heavy loss of biomass from boiling [52] which resulted in a significant reduction of adsorption capacity of Pb(II) in comparison with heat treated and autoclaved PPPC.

4. Conclusions

To eradicate the Pb(II) cation from aqueous solution *P. pinnata* pods carbon (PPPC) prepared by simple heat pyrolysis strategy was employed. The results of this study can be summarized as follows:

- Batch studies clearly suggest that, initial pH, sorbent dosage, initial sorbate concentration and contact time highly affect the sorption process.

- The sorption data has been fitted to linear form of Langmuir, Fruendlich, Dubnin–Radushkevich and Tempkin isotherms, but the Lagmuir model gives better fitting to the Pb(II) sorption than others.

- Pb(II) sorption onto PPPC follows the pseudo-second-order model which provides the best correlation of the data and the experimental q_{exp} agrees with the calculated one.

- Thermodynamic assessment of the Pb(II)–PPPC system depict the feasibility and spontaneous nature of the process and ΔG°_{ads} was calculated ranging from −31.1264 to −26.3494 kJ mol^{-1} in the concentration range 25–800 mg L^{-1} indicating physical as well as chemical mechanism for sorption.

- The Pb(II) sorption capacity follows a descending order of Ca(OH)$_2$ > NaCl ≈ NaOH > Al(OH)$_3$ > heated > native > HCl > H$_3$PO$_4$ > autoclaved > H$_2$SO$_4$ > boiled pretreatment.

- FTIR analysis of native PPPC proved the presence of various alkane, aromatic C=C and oxygen functionalities along with aromatic NO$_2$ and surface SO$_2$ complexes which are involved in Pb(II) sorption.

- Various physicochemical modifications bring about substantial variations in the PPPC chemical structure confirmed by FTIR spectroscopy.

Acknowledgments

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