



Sorptive removal of lead (II) from water using chemically modified mulch of *Madhuca longifolia* and *Polyalthia longifolia* as novel biosorbents

Rabia Rehman*, Jamil Anwar, Tariq Mahmud

Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan

Tel. +92 42 99230463, Ext: 870; Fax: +92 42 99230998; email: rabia.chem@pu.edu.pk

Received 16 February 2012; Accepted 9 September 2012

ABSTRACT

In this study, dried leaves (mulch) of *Madhuca longifolia* and *Polyalthia longifolia* have been used for removing Pb(II) from aqueous media. Their biosorption capacities were enhanced by chemical treatment using dipping methodology. It is found that formalin modified *M. longifolia* leaves and acetone modified *P. longifolia* leaves have greater biosorption capacity as compared to non-modified leaves. After optimizing operational parameters, Langmuir, Freundlich, and Temkin isotherms were applied to equilibrium data for determining maximum biosorption capacities, heat of biosorption, and biosorption intensities. The maximum biosorption capacity “ q_m ” values were 17.18, 25.77, 14.11, 4.50, 8.99, and 6.99 mg/g using simple *M. longifolia* leaves, base modified *M. longifolia* leaves, formalin modified *M. longifolia* leaves, simple *P. longifolia* leaves, base modified *P. longifolia* leaves, and acetone modified *P. longifolia* leaves correspondingly. Thermodynamic revealed that biosorption using these biosorbents occur spontaneously due to larger negative values of ΔG° and kinetic investigations suggested that pseudo-second order of reaction could be applied for explaining the mechanism of biosorption. Nitric acid was found as suitable desorbent for recycling of biosorbents.

Keywords: *Madhuca longifolia*; *Polyalthia longifolia*; Leaves; Pb(II); Biosorption; Isotherms; Thermodynamics; Kinetics; Desorbent

1. Introduction

Heavy metals are a constant threat for living creatures of earth because most of them are cumulative toxins capable of being stored, assimilated, and concentrated by organisms that are exposed to their low concentration for long periods [1]. Lead is one of the notorious examples of heavy metals. Basically it is used as a raw material in many industries like leaded

glass, pigments, photographic materials, solder, storage batteries, fuels, and steel products [2]. It is mostly unavailable to plants and animals due to its tendency of being strongly adsorbed by sediments and soil particles. Mostly lead in the form of oxides, sulfides, or chlorides is not readily soluble in water. That's why it is sequestered in soil sediments. In aqua-systems, its uptake by planktons is influenced by several environmental parameters like temperature, pH, salinity, and availability of organic matter [3,4]. It is a very toxic pollutant even in very low concentrations. Due to

*Corresponding author.

fat-soluble nature of organic lead compounds, they are more toxic than its other forms. Even lower concentration of lead in drinking water can cause anemia, liver and brain damage, hepatitis, and nephritic syndrome along with severe damage to nervous and reproductive system [5]. The maximum permitted levels of lead (II) in waste water and potable water are 0.1 and 0.015 mg/L, respectively, according to the United States Environmental Protection Agency [6].

Conventionally precipitation, flocculation, cation exchange, membrane processes, oxidation, and reduction are adopted for the removal of lead (II) from water [7]. These are expensive methodologies and often produce chemical sludge, whose disposal is itself challenging and problematic. Biosorption is an alternative of these conventional and painstaking methodologies. It is a process that applies low-cost biosorbents for sequestering toxic heavy metals and pollutants from aqueous media. It has distinctive advantages over these conventional ways that include: selectivity for specific pollutant, low operating cost, reusability of biosorbents, less time interval, and no chemical sludge [8]. Recently various biosorbents of agricultural origin have been used for heavy metal removal from water like rice husk, wheat husk, coconut husk and shell, hazelnut shell, peanut hull, banana peel, coffee beans, almond shell, sea weeds, bagasse ash, tree fern, black gram husk, maize leaf, maize, sun flower waste, leaves of olive tree, wheat bran, etc. [9–34].

In this research work, the leaves of *Madhuca longifolia* (Mawa or Mahua) and *Polyalthia longifolia* (Ulta ashok) were used as biosorbents for removing Pb (II) metal ion from aqueous media. *M. longifolia* (Family: Sapotaceae) is an economically important oilseed tree growing throughout the subtropical region of the Indo-Pak subcontinent. Due to its stimulant, demulcent, emollient, and astringent properties, it has many medicinal applications. There are numerous edible and medicinal applications of “mahua butter” or “mowrah butter” which is produced from its seed having high quantity of fat. Its fat is used as an alternative of cocoa butter and ghee, which is used in cooking and manufacturing chocolates. Due to its emulscent nature, it has several medicinal applications in skin disease, headache, laxative, rheumatism, etc. It is also employed in manufacturing of laundry soaps and lubricants. Its seed cake has insecticidal and pesticidal tendency and used as organic manure [35]. Whereas *P. longifolia var. pendula*, (Family: Annonaceae) is 25–30 foot tall, ever green, ornamental tree with markedly drooping, short branches, and soft leaves with columnar appearance. It is usually cultivated in gardens and avenues all over Pakistan [36].

The main aim of this study was to investigate the Pb(II) metal ion biosorption from aqueous solution by *M. longifolia* and *P. longifolia* leaves. Their biosorption capacity was enhanced by chemical treatment and all the operational parameters were optimized for evaluating equilibrium data by isothermal, thermodynamical, and kinetic studies.

2. Experimental work

2.1. Reagents

Following analytical grade chemicals were purchased from Merck (Germany): i.e. $\text{Pb}(\text{NO}_3)_2$, HNO_3 , H_2SO_4 , HCl , CH_3COOH , NaOH , $\text{K}_2\text{Cr}_2\text{O}_7$, ethanol, methanol, *iso*-propanol, *iso*-butanol, formalin, acetone, urea, thiourea, and tartaric acid for this study. All glassware used was immersed in chromic acid overnight and rinsed with double distilled water. For pH adjustment during batch biosorption experiments, 0.01 mol/L solutions of NaOH and HCl were used.

2.2. Instrumentation used

Following instruments are used in this research work. Balance ER-120A (AND) was used for weighing chemicals, electric grinder (Ken Wood) was used for grinding leaves into fine powder, orbital shaker (Model OS-752) was used for proper and equalized shaking of Pb(II) solutions during biosorption experiments, pH meter (HANNA pH 211) was employed for monitoring pH of the solutions, atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) with air-acetylene flame was used for estimating Pb(II) determination in filtrate, and FT-IR spectrophotometer (Perkin Elmer RX-I) was used to characterize the surface of biosorbents.

2.3. Preparation of biosorbents

The leaves of *M. longifolia* and *P. longifolia* were collected from plants grown at parent institute. After washing, they were dried in sunlight for a week. Then they were ground and sieved through 60 mesh (ASTM). This powdered mulch of *M. longifolia* and *P. longifolia* was stored in air tight glass jars separately till further treatments.

2.4. Synthetic waste water preparation

Synthetic waste water solutions were prepared by dissolving analytical grade $\text{Pb}(\text{NO}_3)_2$ in double distilled water to obtain 1,000 mg of metal/L solution. The solution was diluted to the required concentration for further experiments. The pH of these solutions was measured and observed as 6.0 ± 0.5 [25].

2.5. Chemical modification of biosorbent

The biosorbent was modified with different chemicals like 10.0 mmol HCl and NaOH, organic solvents (methanol, ethanol, *iso*-propanol, *iso*-butanol, formalin, and acetone), and 10% aqueous solution of various chelating agents (urea, thiourea, citric acid, and tartaric acid). Equal amount of *M. longifolia* and *P. longifolia* leaf powder was dipped in equal volume of all these solution separately in the beakers and after covering with aluminum foils, they were kept for two hours. After filtering and drying, 1.0 g of all the modified biosorbents were soaked in 50 mL of 50 mg/L Pb(II) ion solution separately. After agitating at 100 rpm for 15 min, all the solutions were filtered and remaining Pb(II) ion concentration was determined to calculate % biosorption, as shown in Fig. 1.

2.6. Biosorption experiments

The biosorption experiments were carried out by contacting precisely weighed samples of biosorbents with 50 mL of Pb(II) solutions in the sealed 250 mL Erlenmeyer flasks. The suspensions were agitated at room temperature ($25 \pm 1^\circ\text{C}$) on orbital shaker (Optima OS-752) at 100 rpm. After 20 min, suspensions were filtered and concentrations of Pb(II) ions in the filtrates were determined by AAS (Perkin Elmer AAnalyst100), working at 261.42 nm resonance wavelength. The effects of various parameters on the rate of biosorption process were investigated by varying: contact time (5–60 min), biosorbent amount (0.2–2.0 g), pH of the solution between 1 and 6, agitation speed (75–200 rpm), and temperature (10–80°C). For the isothermal studies, optimized quantity of biosorbent samples was stirred with Pb(II) solutions of different concentrations (50–150 mg/L) for optimized contact interval duration. In order to investigate thermodynamics, suspensions consisting of optimized quantity of biosorbent samples and 100 mL of Pb(II) solutions

containing 50 mg/L were stirred at variable temperatures (10–80°C) for 10 min. For studying kinetic parameters, solutions containing optimized quantity of biosorbent samples and 100 mL of 50 mg/L Pb(II) solutions were stirred from 5 to 60 min. The Pb(II) ion biosorption at any instant of time was determined by using following Eq. (1):

$$\% \text{ age biosorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Here C_0 and C_e are the concentrations of Pb(II) ion before and after biosorption process, respectively [36]. For ensuring the reproducibility and reliability of the results, each set of experiments was conducted in triplicate and the given data representing the mean of three independent sets of experiments within error range of ± 0.5 .

2.7. Regeneration of adsorbents

The used biosorbents were regenerated using 50 mL of 10.0 mmol solutions of HCl, HNO_3 , H_2SO_4 , and CH_3COOH separately in 250 mL Erlenmeyer flasks, while stirring at 100 rpm for 30 min at room temperature. After that, regenerated biosorbents were dried in an oven at 70°C for 2 h and then reused. Desorption % was calculated by Eq. (2):

$$\% \text{ desorption} = \frac{q_{\text{des}}}{q} \times 100 \quad (2)$$

where " q_{des} " is Pb(II) desorbed and " q " is the Pb(II) biosorbed in mg/g of biosorbent used. The value of q_{des} was determined by Eq. (3), using the concentration of Pb(II) desorbed (C_{des}) in the filtrate.

$$q_{\text{des}} = C_{\text{des}} \frac{V}{m} \quad (3)$$

here " V " is the volume of the desorbent used in liters and " m " is weight of the biosorbent in grams [37].

3. Results and discussion

3.1. Surface characterization

The FT-IR spectra were taken for characterization of *M. longifolia* and *P. longifolia* leaves to confirm the presence of functional groups like –OH, –CO, –CHO, –NH, and –COOH that can act as possible active sites for biosorption of Pb(II) using FT-IR spectrometer (Perkin Elmer BX Model). The resulting FT-IR graphs are given in Figs. 1 and 2. The vibrational frequencies band at 3275.91, 3267.54, 1616.06, 1646.15, 1026.08, and

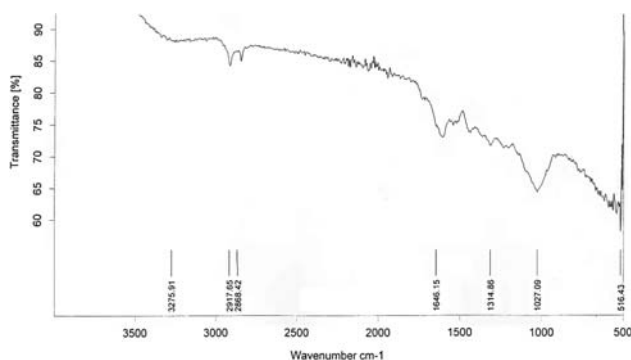


Fig. 1. FT-IR spectrum of *M. longifolia* leaves.

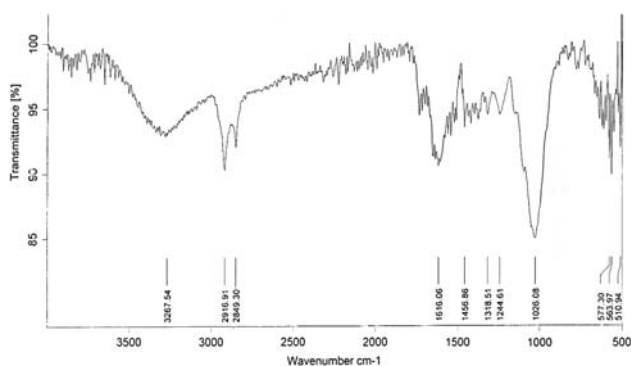


Fig. 2. FT-IR spectrum of *P. longifolia* leaves.

1027.09 cm^{-1} indicated the presence of amino and hydroxyl functional groups in biosorbents. The bands at 2917.65 , 2916.91 , 2864.42 , and 2849.30 cm^{-1} represented the presence of C–H bond of aldehydic functional group. The presence of aromatic compounds in these leaves was confirmed by the peak at 1456.86 cm^{-1} .

The vibrational frequency peaks at 1314.86 , 1318.51 , and 1244.61 cm^{-1} corresponded to carbonyl groups, indicating the presence of carboxylic and ester functional groups in leaves. The peaks between $2,000$ and $2,300\text{ cm}^{-1}$ in the spectra were due to $-\text{NCS}$, $-\text{NCO}$, or $-\text{CN}$ groups. Finger print region below $1,000\text{ cm}^{-1}$ is not used to represent any particular functional group [18,23].

3.2. Effect of chemical modification of biosorbent

The effect of chemical modification of biosorbent is shown in Fig. 3. From this graph, it is clear that base

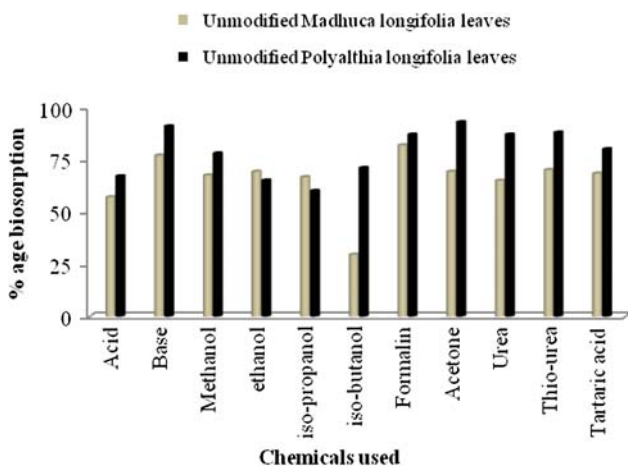


Fig. 3. Graph showing effect of chemical modification of biosorbents on % biosorption of Pb(II) ion.

and formalin modified *M. longifolia* leaves (F.M.L) show maximum biosorption capacity whereas in case of *P. longifolia* leaves, maximum biosorption was observed when base and acetone modified biosorbents were employed. So, in further experiments of Pb(II) biosorption, simple *M. longifolia* leaves (S.M.L), base modified *M. longifolia* leaves (B.M.L), F.M.L, simple *P. longifolia* leaves (S.P.L), base modified *P. longifolia* leaves (B.P.L), and acetone modified *P. longifolia* leaves (A.P.L) were used and results were compared.

Base treatment of leaves results in destruction of autolytic enzymes present in biomass that cause its putrefaction and remove lipids/proteins that mask reactive sites. Rupturing of cell membrane and removal of impurities from biosorbent surface resulted in improved biosorption efficiency of base modified biosorbents (B.M.L and B.P.L). Usually the resinous and colored components along with moisture contents of leaves were removed by oxygen containing organic solvents like formalin and acetone which resulted in enhanced biosorption capacity of *M. longifolia* and *P. longifolia* leaves for biosorption of Pb(II) ion [27,29].

3.3. Optimization of operational conditions

Various operational conditions of biosorption like biosorbent dose, pH of solution, agitation rate, contact time, and temperature were optimized during this study, because all of them have effect on each other during biosorption process. Their details are as followed.

3.3.1. Biosorbent dose

Effect of biosorbent dose on biosorption capacity of *M. longifolia* and *P. longifolia* leaves was investi-

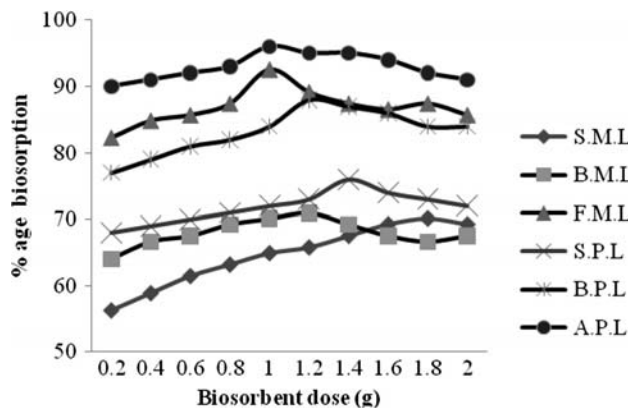


Fig. 4. Effect of biosorbent dose on % biosorption of Pb(II) ion.

gated in the range of 0.2–2.0 g biosorbent dose and results are compared as shown in Fig. 4.

The optimized biosorbent dose for maximum removal of Pb(II) ion from water were 1.8 g of S.M.L, 1.2 g of B.M.L, 1.0 g of F.M.L, 1.4 g of S.P.L, 1.2 g of B.P.L, and 1.0 g of A.P.L. For biosorbent quantities higher than these values, the metal ion removal remained more or less constant. Maximum biosorption capacity of Pb(II) was observed when A.P.L and F.M.L were used. Improvement in biosorption capacity with increased biosorbent doses was due to enhancement in surface areas, increasing the number of biosorption sites available for biosorption [15–18].

3.3.2. Contact time interval

Contact intervals between biosorbents and Pb(II) ion solution effect on biosorption capacity were studied and results are compared, as shown in Fig. 5.

The maximum removal of Pb(II) ion occurred when contact interval was 35, 30, 25, 35, 35, and 25 min in case of S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, and A.P.L, respectively. The results revealed the fact that chemical treatment of *M. longifolia* leaves with base and formalin enhanced its biosorption capacity to remove Pb(II) ion from water. Similarly chemical treatment of *P. longifolia* leaves with base and acetone enhanced its biosorption capacity by exposing more binding sites for biosorption. After the establishment of equilibrium, the biosorption rates gradually lower down to a constant value because all available binding sites were used to chelate Pb(II) ion and no more active site available for biosorption. At initial stage, more vacant surface sites are available for biosorption. But after equilibrium time, the remaining vacant surface sites are difficult to be occupied by Pb(II) ions

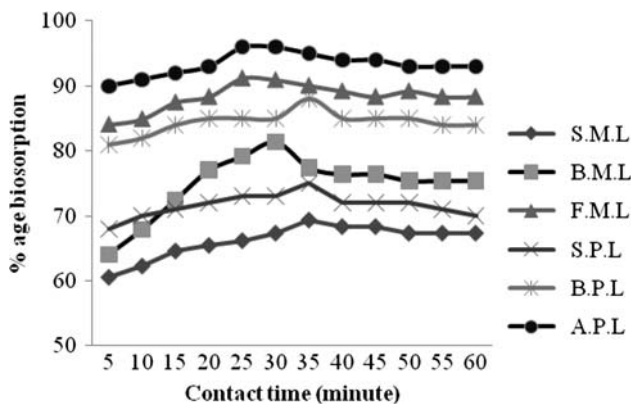


Fig. 5. Effect of various contact intervals of biosorbent with Pb(II) ion solution on % biosorption.

due to repulsive forces between the solute particles on the biosorbent surface and in solution phases [24].

3.3.3. pH

The pH of the metal ion solution is very crucial to consider during any waste water treatment, because it is directly related with the solubility of metal ion species and chelating processes. The pH value, in case of Pb(II) biosorption, is also important because of the fact that alkaline conditions result in precipitation of Pb(II). The results of pH effect on biosorption of Pb(II) are shown in Fig. 6.

Maximum biosorption % values were found at pH 3.0, 6.0, 5.0, 3.0, 6.0, and 5.0 in case of S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, and A.P.L, respectively. The maximum biosorption % obtained when F.M.L and A.P.L were used, i.e. 91.06 and 93.01% correspondingly. Chemical treatment of biosorbents has not only improved the biosorption efficiency of leaves, but also improved the working pH range [24].

3.3.4. Agitation rate

Agitation of solution usually results in better contact between biosorbent and adsorbate species by effecting the distribution of the ions in the solution phase and external boundary film formation around biosorbent mass.

The effect of variation in the agitation speed on the biosorption of Pb(II) ion was studied and graphically presented in Fig. 7. Maximum removal of Pb(II) ions occurred at 150 rpm agitation speed using simple leaves and at 125 rpm using chemically modified leaves. The degree of agitation minimizes the boundary layer resistance and enhances the mobility of system. With agitation, the external mass transfer coefficient increases resulting in quicker biosorption of the Pb(II) ions. By increasing speed more than 150 rpm, there

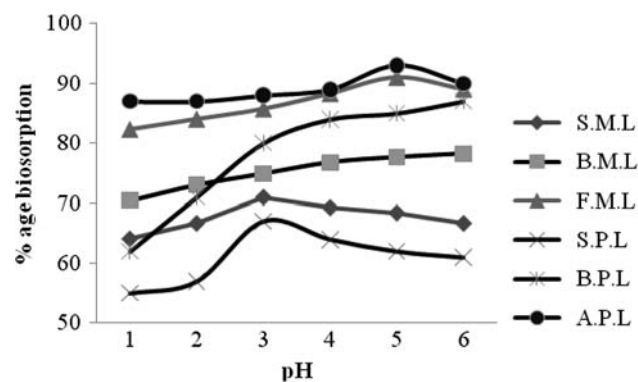


Fig. 6. Effect of pH of Pb(II) ion solution on % biosorption.

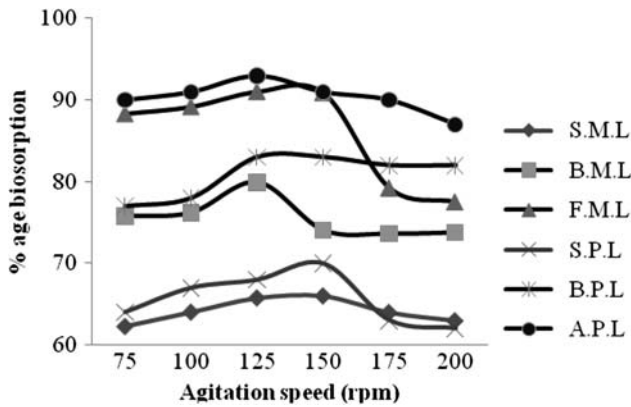


Fig. 7. Effect of agitation rate on % biosorption of Pb(II).

was no further enhancement in biosorption because all active sites had been already consumed [24].

3.3.5. Temperature

It has a distinct effect on the biosorption processes. Its effect was investigated in the range of 10–80°C and results are shown in Fig. 8.

The maximum removal of Pb(II) ions occurred at temperature 40, 40, 30, 50, 40, and 50°C using S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, and A.P.L, respectively. The maximum biosorption % values were 66.76, 80.18, 90.06, 67.01, 87.03, and 97.02% using S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, and A.P.L correspondingly. Chelation is a temperature-dependent phenomenon. Chemical treatments of leaves cause the structural changes in the surface morphology and results in the exposure of various functional groups, which can chelate adsorbate species at various temperatures more efficiently. Since biosorption is an exothermic process usually, it could be anticipated that increasing temperature of the adsorbate–adsorbent system would have negative impact on biosorption capacity of leaves [24].

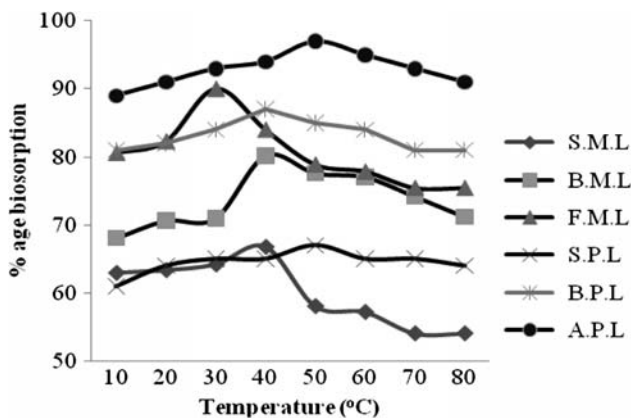


Fig. 8. Effect of temperature on % biosorption of Pb(II).

3.3.6. Isothermal Studies

The degree of the biosorbent affinity for the adsorbate determines its distribution between the solid and the liquid phases, in turns equilibrium mode. Several isothermal models are often employed to interpret the equilibrium data. In this study, Langmuir, Freundlich, and Temkin models were applied on experimental data for optimizing biosorption system design and relevant parameters are given in Table 1.

Langmuir isotherm was plotted by using Eq. (4)

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (4)$$

here “ q ” (mg/g) is the quantity of metal ion adsorbed, “ C_e ” (ppm) is the remaining metal ion concentration after biosorption, and “ q_m ” (mg/g) and b (L/g) are Langmuir isotherm parameters which were regression analysis of linear graph of “ $1/q$ ” vs. “ $1/C_e$ ”. The value of q was calculated by Eq. (5):

$$q = \frac{(C_0 - C_e)V}{m} \quad (5)$$

Here “ V ” (L) is the volume of metal ion solution and “ m ” (g) is the mass of leaf powder used [24]. The correlation coefficient value (R^2) is approaching to unity, which clearly suggested that Langmuir isotherm holds good to explain biosorption of Pb(II) metal ion on *M. longifolia* and *P. longifolia* leaves, i.e. there is a fixed number of binding sites which are regularly dispersed over the adsorbent surface, who have the same affinity for single molecular layer biosorption with no interaction between adsorbed species.

The maximum biosorption capacity “ q_m ” values were 17.18, 25.77, 14.11, 4.50, 8.99, and 6.99 using S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, A.P.L, A.M.L, and P.M.L correspondingly. Literature review regarding lead adsorption indicated that these modified leaves are moderate biosorbent for lead wastewater treatment as clear from Table 2 [38,39].

$$S = \frac{q_m NA}{M}$$

The biosorption capacity of biosorbents is enhanced by chemical modification can be estimated from Langmuir specific surface area “ S ” calculations using the formula given in Eq. (6) [5]:

$$S = \frac{q_m NA}{M} \quad (6)$$

Table 1
Isothermal parameters for biosorption of Pb(II)

Biosorbent	Langmuir isotherm parameters				
	Slope	Intercept	R^2	q_m (mg/g)	b (L/g)
S.M.L	4.65	0.06	0.99	17.18	0.012
B.M.L	3.11	0.04	0.99	25.77	0.012
F.M.L	5.41	0.07	0.99	14.11	0.013
S.P.L	6.51	0.22	0.94	4.50	0.034
B.P.L	6.02	0.11	0.98	8.99	0.018
A.P.L	2.92	0.14	0.92	6.99	0.049

Biosorbent	Freundlich isotherm parameters				
	Slope	Intercept	R^2	K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	n
S.M.L	0.76	-0.46	0.99	0.347	1.32
B.M.L	0.76	-0.28	0.99	0.521	1.32
F.M.L	0.69	-0.44	0.99	0.366	1.44
S.P.L	0.43	-0.29	0.98	0.513	2.33
B.P.L	0.61	-0.41	0.99	0.388	1.63
A.P.L	0.39	0.02	0.98	1.036	2.53

Biosorbent	Temkin isotherm parameters				
	Slope	Intercept	R^2	K_T (L/mg)	B_T (kJ/mol)
S.M.L	2.84	-4.92	0.987	0.18	2.84
B.M.L	4.27	-7.39	0.987	0.18	4.27
F.M.L	3.37	-7.45	0.964	0.11	3.37
S.P.L	1.19	-1.82	0.955	0.22	1.19
B.P.L	2.38	-4.89	0.96	0.13	2.38
A.P.L	1.81	-2.095	0.946	0.32	1.81

Table 2
Maximum biosorption capacities of some reported biosorbents used for Pb(II)

Biosorbents	q_m (mg/g)	Biosorbents	q_m (mg/g)
Apricot stone	0.0013	<i>Caulerpa lentillifera</i>	29
Cocoa shells	33.0	Bagasse fly ash	2.5
Oak stem	0.75	Tea waste	2.0
Rice husk	4.0	Hazelnut shell	1.78
Bagasse	2.5	Coir	18.90
Apple residues	17.76	Sawdust	3.0
Peach stone	0.0023	<i>Aspergillus niger</i>	10.13

Table 3
Separation factor for Pb(II) biosorption system and specific surface area of *M. longifolia* and *P. longifolia* leaves

Biosorbents	Specific surface area (m^2/g)	Separation factor R_L
S.M.L	2.78	0.63
B.M.L	4.17	0.63
F.M.L	2.28	0.61
S.P.L	0.73	0.37
B.P.L	1.45	0.53
A.P.L	1.13	0.29

Here “ N ” is Avogadro number, “ A ” is the cross-sectional area of metal ion whose value for Pb(II) is 5.56 Å, and “ M ” is molar mass of the adsorbate species which is 207 for lead. It is obvious from the Table 3 that spe-

cific surface area of *M. longifolia* and *P. longifolia* leaves is increased after chemical modification, which in turn results in better biosorption efficiency.

Langmuir parameter “ b ” is used for determining a dimensionless separation factor constant “ R_L ” by using Eq. (7) [16–22]:

$$R_L = \frac{1}{(1 + bC_0)} \quad (7)$$

The value of “ R_L ” is an indication of favorability of biosorption process. If it lies between 0 and 1, then biosorption process is favorable using that biosorbent, while $R_L > 1$ represents unfavorable process. As it is clear from Table 3 that R_L values for all types of biosorbent used is less than 1, so biosorption of Pb(II) by simple and chemically modified *M. longifolia* and *P. longifolia* leaves is a favorable process.

The Freundlich model is applicable to heterogeneous surfaces biosorption equilibrium along with interaction between adsorbed metal ions and is not limited to monolayer formation, rather favored multi-layered biosorption involving physiosorption. It was plotted by using Eq. (8):

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

Here “ K_F ” and “ n ” are Freundlich model constants. Their value can be determined from regression analysis of linear plot of “ $\log q$ ” vs. “ $\log C_e$ ”. The value of “ n ” lies in the range 2–10 shows good biosorption, whereas in 1–2 corresponds to moderately difficult biosorption. But its value less than 1 is the characteristic of poor biosorption. As it is clear from Table 1, simple and A.P.L show more value of “ n ” as compared to others. Greater values of K_F in case of B.M.L, S.P.L, and A.P.L indicated that Pb(II) ions are effectively bonded on biosorbent surfaces, which was an indication of constant partitioning of the biosorption mechanisms, where Pb(II) ions penetrated in the biosorbent and therefore showed good biosorption [34].

The Temkin isotherm model predicted an equal distribution of binding energies over the number of the active binding sites on biosorbent surface. The linearized form of Temkin model is in Eq. (9):

$$q = B_T \ln C_e + B_T \ln K_T \quad (9)$$

Here $B_T = RT/b$, “ T ” is absolute temperature in Kelvin, “ R ” is universal gas constant (8.314 J/mol), “ K_T ” is the equilibrium binding constant (L/mg), and “ B_T ” is related with heat of adsorption. The Temkin constants are obtained from the regression analysis of linear plots of “ q ” vs. “ $\ln C_e$ ” [16,18,24]. B_T values lesser than 8 point out weaker interaction between Pb(II) and leaf powder, favoring physiosorption mode of biosorption of Pb(II) ions. Comparison of B_T values in

Table 1 shows that for chemically modified leaves, it has higher values. That is a clear signal of the presence of relatively stronger cohesive forces in between biosorbent active binding sites and Pb(II) ions.

3.3.7. Biosorption mechanism

By isothermal modeling of equilibrium data of biosorption along with characterization of biosorbent surface and pH studies, it is found that various functional groups present in leaf material effectively chelate Pb(II) ions from water. By the chemical medication of leaves, their surface becomes more heterogeneous and porous due to removal of lignin material, either by its hydrolysis by base or its extraction into organic solvents like acetone or formalin or alcohols. This in turns enhances physiosorption along with chemisorptive removal of Pb(II) ions. This mechanism is also supported by regression coefficient (R^2) values of Langmuir, Freundlich, and Temkin isothermal models. It was observed that Freundlich isotherm model was more applicable as compared to other two, referred to multi-layered physiosorption is a predominant mode of Pb(II) ions biosorption on heterogeneous biosorbent surfaces [40,41].

3.3.8. Thermodynamical studies

For studying thermodynamic behavior of the biosorption of Pb(II) by *M. longifolia* and *P. longifolia* leaves, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated using Eqs. (10)–(12):

$$\Delta G^\circ = -RT \ln K_D \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

$$\ln K_D = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (12)$$

Table 4
Thermodynamical parameters for biosorption of Pb(II)

Biosorbent	Thermodynamical parameters			
	R^2	ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)
S.M.L	0.98x	−0.09	0.036	−10.71
B.M.L	0.97	−0.10	0.031	−9.31
F.M.L	0.98	−0.10	0.029	−8.72
S.P.L	0.98	−0.06	−0.004	1.16
B.P.L	0.98	−0.07	0.005	−1.52
A.P.L	0.99	−0.07	0.004	−1.27

Here ΔH° and ΔS° parameters were determined by the regression analysis of linear plots of $\ln K_D$ vs. $1/T$ and then employed for evaluation of ΔG° values. All these parameters are summed up in Table 4.

Negative values of ΔH° indicate the exothermic nature of biosorption process and negative values of ΔG° indicate the spontaneous nature of this process when chemically modified by *M. longifolia* and *P. longifolia* leaves were used for Pb(II) biosorption. The negative values of ΔS° indicated that the biosorption is stable when S.P.L were used, whereas the positive value of ΔS° shows that the bonding forces between biosorbent and Pb(II) impart randomness to the system when chemically modified *M. longifolia* and *P. longifolia* leaves were used [30–34].

3.3.9. Kinetic studies

Biosorption processes usually followed pseudo-second-order kinetic model. Therefore kinetic studies were carried out for kinetic modeling of equilibrium data using Eq. (13):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e t} \quad (13)$$

where " q_e " (mg/g) is sorption capacity at equilibrium, " q_t " (mg/g) is sorption capacity at time " t ", and " k_2 " is rate constants of pseudo-second-order adsorption model ([g/mg]/min). " q_e " and " k_2 " can be determined from regression analysis of the linear plot of " t/q_t " against " t ". The suitable applicability of this model was confirmed by the regression coefficient (R^2) values which were closer to one in all cases studied. Initial sorption rate " h " (mg/g min) can be calculated using Eq. (14):

$$h = K q_e^2 \quad (14)$$

Half biosorption time " $t_{1/2}$ " (min) can be calculated by Eq. (15):

$$t_{1/2} = 1/k_2 q_e \quad (15)$$

From Table 5, it is clear that rate of biosorption is more using simple *M. longifolia* and *P. longifolia* leaves, but it is decreased to lower values when chemically modified *M. longifolia* and *P. longifolia* leaves were used, showing the availability of more binding sites due to chemical modification. This fact is also supported by initial sorption rate and half biosorption time of S.M.L, B.M.L, F.M.L, S.P.L, B.P.L, A.P.L, A.M.L, and P.M.L [30–34].

3.3.10. Desorption studies

The regeneration of used biosorbents using different acids was quantified and the results are shown in Fig. 9.

It was found that as compared to other acids, HNO_3 is a good desorbent for desorption of Pb(II) from all biosorbents. The regenerated biosorbent can be reemployed for biosorption. Chemical treatment is applied similarly as described before, after desorption and prior to their reuse for biosorption of Pb(II). Table 6 is showing the results of reusability of these biosorbents for three cycles. It is clear from this data that biosorption capacity of regenerated biosorbents decreases as number of recycling increases. As *M. longifolia* and *P. longifolia* leaves can be easily biodegradable, so they can be disposed off as soil conditioner after recovering Pb(II).

3.3.11. Real wastewater treatment

Various results obtained from optimization experiments were employed for conducting a batch experiment with real industrial effluents from an electronics

Table 5
Kinetics parameters for biosorption of Pb(II)

Biosorbent	Pseudo-second-order kinetics parameters				
	R^2	k_2 ([g/mg]/min)	q_e (mg/g)	h (mg/g min)	$t_{1/2}$ (min)
S.M.L	0.99	0.15	1.11	0.19	7.21
B.M.L	0.97	0.09	1.98	0.36	21.71
F.M.L	0.98	0.09	2.48	0.54	27.98
S.P.L	0.98	0.12	2.16	0.57	17.71
B.P.L	0.97	0.07	1.97	0.26	29.56
A.P.L	0.95	0.06	1.75	0.17	31.53

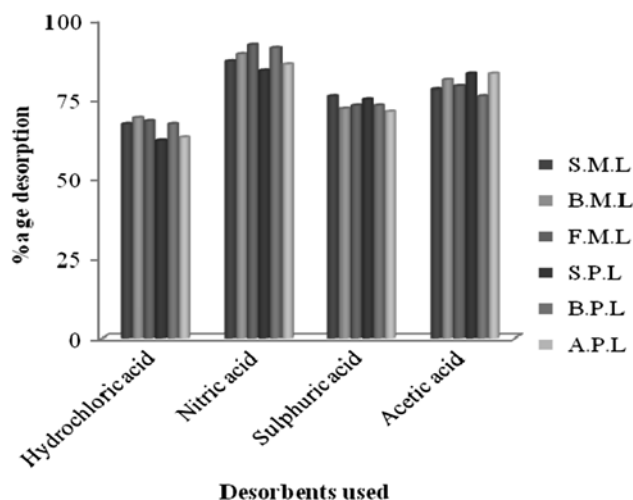


Fig. 9. Effect of different desorbents on % desorption of Pb(II).

Table 6
Recycling of *M. longifolia* and *P. longifolia* leaves

Biosorbent	% removal of Pb(II) after recycling		
	1st time reuse	2nd time reuse	3rd time reuse
S.M.L.	45.21	40.37	36.29
B.M.L.	58.9	52.31	48.23
F.M.L.	61.23	59.37	51.39
S.P.L.	47.36	41.69	39.26
B.P.L.	62.52	60.27	55.36
A.P.L.	68.52	58.34	51.27

assembly operation plant at Lahore (Pakistan), where the source of Pb(II) ions is solder flux cleaning aqueous parts washers that have a high level of lead from cleaning parts (100–150 mg/L). There was slight decrease in % biosorption efficiency when the biosorbents were used for real waste water treatment. The maximum removal of Pb(II) was 16.15, 22.46, 12.12, 3.13, 7.32, and 5.89 mg/g using S.M.L, B.M.L, F.M.L, S. P.L, B.P.L, A.P.L, A.M.L, and P.M.L correspondingly. Moderate decrease observed in removal capacity is linked to the presence of several other contaminants which can compete for binding sites on the biosorbents.

4. Conclusions

It is obvious from the results of this research work that *M. longifolia* and *P. longifolia* leaves are effective biosorbent for the removal of Pb(II) ions from aqueous

media. Their chemical modification increases their biosorption efficiencies, which is clear from “ q_m ” values. S.M.L. had removed 17.18 mg/g of Pb(II) ions, whereas base modified and F.M.L had removed 25.77 and 14.11. Same trend was found in *P. longifolia* leaves, where non-modified sample shows less biosorption, i.e. 4.50 mg/g and B.P.L and A.P.L had removed 8.99 and 6.99 mg/g of Pb(II) ions, respectively. The equilibrium data followed pseudo-second-order kinetics and isothermal modeling indicated that physiosorption mode of biosorption occurred more as compared to chemisorption. Desorption studies revealed that dilute nitric acid can efficiently desorb Pb(II) ions from used biomass, by breaking chelation between biosorbent and adsorbate and converting insoluble Pb(II) ions into soluble nitrates, which in turn can easily desorb. So, these leaves can be used on industrial scale for removing Pb(II) ions effectively using indigenous sources.

List of abbreviations

S.M.L	–	simple <i>M. longifolia</i> leaves
B.M.L	–	base modified <i>M. longifolia</i> leaves
F.M.L	–	formalin modified <i>M. longifolia</i> leaves
S.P.L	–	simple <i>P. longifolia</i> leaves
B.P.L	–	base modified <i>P. longifolia</i> leaves
A.P.L	–	acetone modified <i>P. longifolia</i> leaves

References

- [1] Q. Li, S. Wu, G. Liu, X. Liao, X. Deng, D. Sun, Y. Hu, Y. Huang, Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of *Phanerochaete chrysosporium*, Sep. Purif. Technol. 34 (2004) 135–142.
- [2] D.M. Vieira, A.C.A. da Costa, C.A. Henriques, V.L. Cardoso, F.P. de França, Biosorption of lead by the brown seaweed *Sargassum filipendula*—batch and continuous pilot studies, E. J. Biotech. 10 (2007) 368–375.
- [3] L. Wadanambi, B. Dubey, T. Townsend, The leaching of lead from lead-based paint in landfill environments, J. Hazard. Mater. 157 (2008) 194–200.
- [4] N. Perveen, M.A. Hanif, S. Noureen, T.M. Ansari, H.N. Bhatti, Phytoremediation of Pb(II) by *Jasminum sambac*, J. Chem. Soc. Pak. 33 (2011) 592–597.
- [5] E.O. Aluyor, I.O. Oboh, K.O. Obahiagbon, Equilibrium sorption isotherm for lead (Pb) ions on hydrogen peroxide modified rice hulls, Int. J. Phy. Sci. 4 (2009) 423–427.
- [6] S. Tangjuank, N. Insuk, J. Tontrakoon, V. Udeye, Adsorption of Lead(II) and Cadmium(II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells, WASET. 52 (2009) 110–116.
- [7] R. Say, A. Denizli, M.Y. Aroca, Biosorption of cadmium (II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*, Bioresour. Technol. 76 (2001) 67–70.
- [8] A. Ozer, D. Ozer, Comparative study of the biosorption of Pb (II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: Determination of biosorption heats, J. Hazard. Mater. B100 (2003) 219–229.

- [9] M.K. Mondal, Removal of Pb(II) ions from aqueous solution using activated tea waste: Adsorption on a fixed-bed column, *J. Environ. Manage.* 90 (2009) 3266–3271.
- [10] Z.R. Holan, B. Volesky, Biosorption of lead and nickel by biomass of marine algae, *Biotechnol. Bioeng.* 43 (1994) 1001–1009.
- [11] V. Emongor, Biosorption of lead from aqueous solutions of varied pH by kale plants (*Brassica oleracea var acephala*), *J. Agric. Food Environ. Sci.* 1 (2007) 1–8.
- [12] N.T. Abdel-Ghani, R.M. El-Nashar, G.A. El-Chaghaby, Removal of Cr(III) and Pb(II) from solution by adsorption onto *Casuarina glauca* tree leaves, *Elect. J. Env. Agricult. Food Chem.* 7 (2008) 3126–3133.
- [13] Y. Chen, L. Ding, J. Nie, Isotherm and thermodynamic studies of the biosorption of lead, cadmium and copper from aqueous solutions by rice bran, *Desalin. Water Treat.* 44 (2012) 168–173.
- [14] C. Hong, P. Shan-shan, Bioremediation potential of spirulina: Toxicity and biosorption studies of lead, *J. Zhejiang Univ. Sci.* 6B (2005) 171–174.
- [15] J.L. Gardea-Torresdey, J.H. Gonzalez, K.J. Tiemann, O. Rodriguez, G. Gamez, Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa), *J. Hazard. Mater.* 57 (1998) 29–39.
- [16] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhir, Adsorption of Pb(II) from aqueous solutions using activated carbon developed from Apricot stone, *Desalination* 276 (2011) 148–153.
- [17] U.A. Gilbert, I.U. Emmanuel, A.A. Adebajo, G.A. Olalere, Biosorptive removal of Pb²⁺ and Cd²⁺ onto novel biosorbent: Defatted *Carica papaya* seeds, *Biomass Bioenergy.* 35 (2010) 2517–2525.
- [18] G. Blazquez, M.A. Martini-Lara, G. Tenorio, M. Calero, Batch biosorption of lead(II) from aqueous solutions by olive tree pruning waste: Equilibrium, kinetics and thermodynamic study, *Chem. Eng. J.* 168 (2011) 170–177.
- [19] C.M. Futralana, C.C. Kanb, M.L. Dalidac, K.J. Hsienb, C. Pascuad, M.W. Wan, Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite, *Carbohydr. Polym.* 83 (2011) 528–536.
- [20] V.K. Gupta, S. Agarwal, T.A. Saleh, Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal, *J. Hazard. Mater.* 185 (2011) 17–23.
- [21] M.A. Martín-Lara, I.L. Rodríguez, G. Blázquez, M. Calero, Factorial experimental design for optimizing the removal conditions of lead ions from aqueous solutions by three wastes of the olive-oil production, *Desalination* 278 (2011) 132–140.
- [22] M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, M. Randelović, Kinetic study on lead (II) ion removal by adsorption onto peanut hull ash, *J. Taiwan Inst. Chem. Eng.* 42 (2011) 166–172.
- [23] V. Hernandez-Montoya, D.I. Mendoza-Castillo, A. Bonilla-Petriciolet, M.A. Montes-Moran, M.A. Pérez-Cruz, Role of the pericarp of *Carya illinoensis* as biosorbent and as precursor of activated carbon for the removal of lead and acid blue 25 in aqueous solutions, *J. Anal. Appl. Pyrolysis* 92 (2011) 143–151.
- [24] S.W. Liao, C.I. Lin, L.H. Wang, Kinetic study on lead (II) ion removal by adsorption onto peanut hull ash, *J. Taiwan Inst. Chem. Eng.* 42 (2011) 166–172.
- [25] Y. Liu, Q. Zhao, G. Cheng, H. Xu, Exploring the mechanism of lead(II) adsorption from aqueous solution on ammonium citrate modified spent *Lentinus edodes*, *Chem. Eng. J.* 173 (2011) 792–800.
- [26] J.Z.H. Chen, G. Dai, J. Wu, H. Yan, Adsorption characteristics of Pb(II) from aqueous solution onto a natural biosorbent, fallen *Cinnamomum camphora* leaves, *Desalination* 262 (2010) 174–182.
- [27] S. Chakravarty, A. Mohanty, T.N. Sudha, A.K. Upadhyay, J. Konar, J.K. Sircar, A. Madhukar, K.K. Gupta, Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*), *J. Hazard. Mater.* 173 (2010) 502–509.
- [28] L. Huang, C. Xiao, B. Chen, A novel starch-based adsorbent for removing toxic Hg(II) and Pb(II) ions from aqueous solution, *J. Hazard. Mater.* 192 (2011) 832–836.
- [29] S. Liang, X. Guo, Q. Tian, Adsorption of Pb²⁺ and Zn²⁺ from aqueous solutions by sulfured orange peel, *Desalination* 275 (2011) 212–216.
- [30] W.J. Liua, F.X. Zeng, H. Jiang, X.S. Zhang, Adsorption of lead (Pb) from aqueous solution with *Typha angustifolia* biomass modified by SOCl₂ activated EDTA, *Chem. Eng. J.* 170 (2011) 21–28.
- [31] R. Ayyappan, A.C. Sophia, K. Swaminathan, S. Sandhya, Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes, *Process Biochem.* 40 (2005) 1293–1299.
- [32] A. Hammami, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, Biosorption of heavy metals by activated sludge and their desorption characteristics, *J. Environ. Manage.* 84 (2007) 419–426.
- [33] S. Doyurum, A. Celik, Pb(II) and Cd(II) removal from aqueous solutions by olive cake, *J. Hazard. Mater.* B138 (2006) 22–28.
- [34] D.H.K. Reddy, Y. Harinatha, K. Seshaiaha, A.V.R. Reddy, Biosorption of Pb(II) from aqueous solutions using chemically modified, *Moringa oleifera* tree leaves, *Chem. Eng. J.* 162 (2010) 626–634.
- [35] S. Yadav, P. Suneja, Z. Hussain, Z. Abraham, S.K. Mishra, Prospects and potential of *Madhuca longifolia* (Koenig) J.F. Macbride for nutritional and industrial purpose, *Biomass Bioenergy* 35 (2011) 1539–1544.
- [36] J. Anwar, U. Shafique, W. Zaman, Z. Nisa, M.A. Munawar, N. Jamil, M. Salman, A. Dar, R. Rehman, J. Saif, H. Gul, T. Iqbal, Removal of chromium on *Polyalthia longifolia* leaves biomass, *Int. J. Phytoremed.* 13 (2011) 410–420.
- [37] A. Javaid, R. Bajwa, U. Shafique, J. Anwar, Removal of heavy metals by adsorption on *Pleurotus ostreatus*, *Biomass Bioenergy.* 35 (2011) 1675–1682.
- [38] S. Qaiser, A.R. Saleemi, M. Umar, Biosorption of lead(II) and chromium(VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study, *E. J. Biotech.* 12 (2009) 1–17.
- [39] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chem. Eng. J.* 132 (2007) 299–309.
- [40] A.H. Sulaymon, D.W. Abbood, A.H. Ali, Removal of phenol and lead from synthetic wastewater by adsorption onto granular activated carbon in fixed bed adsorbers: Prediction of breakthrough curves, *Desalin. Water Treat.* 40 (2012) 244–253.
- [41] C. Xiong, X. Chen, C. Yao, Study on the adsorption of Pb²⁺ from aqueous solution by D113-III resin, *Desalin. Water Treat.* 41 (2012) 62–71.