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Gardenia jasminoides: an ornamental plant for the biosorption of lead and cadmium ions

Moniba Rafiq, Umar Farooq*, M. Athar, M. Salman, M. Aslam, H.M. Hamid Raza

Institute of Chemistry, University of the Punjab, Lahore, Pakistan, Tel. +92 42 99230463; Fax: +92 42 99230998; emails: monibahunan@yahoo.com (M. Rafiq), umar.chem@pu.edu.pk (U. Farooq), atharmakshoof@gmail.com (M. Athar), salmanchemist@gmail.com (M. Salman), Muhammadaslam546@yahoo.com (M. Aslam), hamidthechemist@gmail.com (H.M.H. Raza)

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ABSTRACT

The present study is about the removal of lead and cadmium ions by biodegradable powdered biomass from an ornamental plant *Gardenia jasminoides* (GJB). The characterization by Fourier transformed infrared showed that the biomass consists of amino, hydroxyl, carbonyl, and halide functional groups. The pH_{pzc} and the concentration of acidic sites (10.5 mmol/g) and basic sites (7 mmol/g) were also determined. The effects of environmental parameters (varying initial Pb(II) and Cd(II) ions concentrations, time of contact, and pH) were studied. At contact times of 20 and 30 min, the sorption of Pb(II) and Cd(II) ions onto GJB was found to be maximum at pH 5 and 6, respectively. The pseudo-second-order kinetic model was followed by the biosorption of both metal ions. Non-linear equilibrium modeling showed that Langmuir model was suitable to describe the equilibrium with a $q_{\max}$ for Pb(II) ions as 131.6 mg/g and for Cd(II) as 48.54 mg/g, respectively. Thus, the biomass can be used effectively for the removal of lead and cadmium ions from aqueous solutions.

Keywords: *Gardenia jasminoides*; Langmuir model; Pseudo-second-order; Non-linear; Metal ions

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1. Introduction

With the developments in the industrial field, water pollution has become one of the major problems of the present era. Water pollution is caused due to variety of waste materials among which heavy metals are one of them. The metals which are commonly found in industrial wastewater include lead, cadmium, mercury, arsenic, chromium, bismuth, aluminum, zinc, etc. These metals also become a component of groundwater supply as contaminated water percolates through the soil [1–3]. Few metals have various physiological functions in human beings. However, various heavy metals can cause a number of degenerative diseases when they exceed certain standards [4].

The exposure of human to heavy metals may occur through various routes, but the threat of toxicity depends on intensity, frequency, and contact period to the toxin [5]. Most of the toxicity is from non-essential metals when they get entry into a living body. Their bioaccumulation in the human body can damage their organ and organ systems. Thus, wastewater should be treated before it gets entry into the water supply.

Lead and cadmium have acute toxicity, and along with mercury these form “the big three” toxic metals

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*Corresponding author.

with great hazards [4]. Lead gets entry into the water supply through a number of sources like petroleum refining, sulfonation, condensation, ceramics, lead storage accumulators, alloys, paints, and plastics. When it enters into the atmosphere, it can stay as long as for 10 d. It has no biological function and its bioaccumulation is extremely toxic. Lead passes through the placenta, gets entry into breast milk, and can cause infection in infants after absorption by various body parts. Lead poisoning affects reproductive, cardiovascular, nervous systems, etc. Lead absorption also causes deficiency in calcium, iron, and zinc [6].

Naturally, cadmium is present in the Earth's crust in combined form mostly in lead, copper and zinc ores. Sources of cadmium poisoning are mainly human activities such as smelting, plasticizers, batteries, alloys, electroplating, pigments, and smoke. Cadmium enters into the water supply from metal extraction industries [7]. It also does not have any biological role in the human body and causes a number of disorders such as acute and chronic poisoning, progressive osteoporosis, and severe bone pain and brittleness [6].

Biosorption, the removal of materials (compounds, metal ions, etc.) by inactive, non-living biomass due to high attractive forces present between the two [4], is achieving attention nowadays as an alternative to various conventional techniques for removal of toxic substances form aqueous media. Various advantages include high efficiency, regeneration of sorbent, recovery of metal, eco-friendly nature, etc. [4,8,9]. A large number of workers have reported a variety of materials of biological origin. The used biomasses were derived either from micro and macro-organisms, fungi, algae, or higher plants [10–15]. The biomasses obtained from variety of plants used are listed in Table 1.

Ornamental plants have been grown for esthetic purposes, landscaping, water management, windbreaks, and as shelterbelts in gardens [16]. The materials from various ornamental plants have been studied for their potentials toward the biosorption of metal ions. The cone biomass from *Thuja orientalis* was used for the removal of Cu(II) ions with a capacity of 19.23 mg/g [17]. The removal of As(III) and As(V) ions was reported on the seed powder of shelled Moringa oleifera Lamarck [18]. The waste biomass from rose was used for the biosorption studies of Pb(II) and Co (II) ions under batch conditions [19]. The biosorption of Cr(III) and Cr(VI) ions was studied using the biomass from *Cassia fistula* [20]. Still, there is a need to study the biosorption potential of various available materials having relatively greater biosorption capacities.

Table 1
Properties of the biomass from GJB

Property	Results
Particle size	<170 μm
Acid groups	Total = 10.5 mmol/g Carboxylic and lactonic = 5.5 mmol/g Phenol = 5.0 mmol/g
Basic groups	7.0 mmol/g
pH_{pzc}	6.65
Ash content	89.6%
Moisture content	8.8%
Bulk density	0.191 g/cm^3

Gardenia jasminoides (GJB) is an evergreen shrub used for ornamental purpose. It grows in partial shade and requires slightly acidic soil and has moderate tolerance to drought. The constituents of *Gardenia* fruits are iridoid glycosides such as scandoside methyl ester, gradoside, geniposide, deacetyl asperulosidate geniposidic acid, gardenoside, shanzhiside, 1-O-acetylgeniposide, and genipin-1-β-gentiobioside [21]. It is also used to cure different diseases. These plants produce excessive amounts of waste materials on cutting, after their seasonal cultivation. The biosorption using the biomass from GJB will not only reduce solid waste but also reduce air and water pollutions caused by its decaying products. Since these plants are not used as food materials their entry into the food chain is least probable. No harmful degradation products are observed, so it is environmental-friendly too. To the best of our knowledge, no work regarding the biosorption was reported on GJB.

The purpose of the present work is to explore GJB, an ornamental plant, for biosorption. The plant is ever green and so can be cultivated in any season of the year. Its gardens can be grown to enhance natural beauty in industrial as well as neighboring area. These gardens will be a chief source of plant's cutting material. Thus, the biomass can be made available at any time of the year in the respective industry.

2. Materials and methods

All the chemicals being utilized for the present research were of analytical grade. The solutions as well as their dilutions were carried using distilled water. The stock solutions, having concentrations of 1,000 mg/L, were prepared by dissolving a required amount of nitrates of Pb(II) and Cd(II) in water.

2.1. Biomass collection and preparation

The dried branches of GJB plants were obtained from cuttings lying near the jogging track in the

University of the Punjab, Lahore (altitude + 31˚.29´ 41.06″N and latitude + 74˚18´18.89″E). At first, the collected branches were cut into small pieces for easy handling. To remove any dust or dirt particles, the branched were washed thoroughly. These were then washed using distilled water and dried near windows, so that sunlight did not fall on them directly. The partially dried pieces were completely dried to constant mass by heating them in an electric oven (Memmert) at 105˚C to constant mass. It was then ground to a powder (grinder, Kenwood) in three fractions of <170 μm, 170–250 μm, and >250 μm size. The selected fraction (<170 μm) was again washed so that no visible color appeared in the filtrate and the residue was dried in an electric oven at 105˚C to extant experiencing no change mass. The dried fraction of the powdered GJB biomass was designated as GJB and saved in an airtight labeled bottle for further studies.

2.2. Biomass characterization

The Fourier transformed infrared (FTIR) analysis by standard KBr disk method (Perkin Elmer RX-1) was carried out to find various functional groups in GJB. Weak as well as strong acid and base groups were determined through potentiometric titrations. Other characteristics such as ash contents, moisture contents, bulk density, and pH_{pzc} were also determined. The pH_{pzc} was determined using the method described elsewhere [22].

2.3. Batch biosorption experiments

For the batch biosorption studies, the ionic solutions (Pb(II) and Cd(II), 10–100 mg/L) were allowed to come in contact with GJB at a predefined pH, temperature, and known amount of the biomass in a series of Erlenmeyer flasks (250 mL) for a time range of 10–100 min. The orbital shaker (N.S. Engineering concern) was used for shaking Pb(II) and Cd(II) ion solutions at 120 and 125 rpm, respectively. The pH of the solution was adjusted using HNO_3 (0.1 M) and/or NaOH (0.1 M). The suspensions were taken from the shaker after a specific time and filtered through Whatman filter paper 40. Atomic absorption spectrophotometer (Perkin–Elmer AAnalyst 100) was used for the determination of equilibrium concentration of the metal ions in the filtrate.

The metal ions sorption was quantified as sorption capacity which was calculated as:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{1}$$

where, m (mg) is the mass of GJB, C_0 and C_e are initial and equilibrium concentrations of metal ions at volume V (mL). Root mean square error (RMSE, Eq. (2)) was determined for both Langmuir and Freundlich models to determine the suitability of the equilibrium model. The sum of the squares of the difference between metal removal experimental data (q_{exp}) and model predictions (q_{cal}) was divided by the number of data points (N) for each data-set and the square root of this term was taken. To check any detectable sorption by glassware, blank experiments were also performed for Pb(II) and Cd(II) ion solutions. However, no significant sorption by glassware was seen.

$$\text{RMSE} = \sqrt{\frac{\sum (q_{exp} - q_{cal})^2}{N}} \tag{2}$$

3. Results and discussion

3.1. Characterization

The information about the nature of various functional groups and their interactions with metal ions was obtained from FTIR spectra of metal-loaded and unloaded GJB (Fig. 1). A broad band centered around 3,200 cm^{-1} represented O–H group. The peaks due to N–H functional groups also immersed in this region [23]. Thus, the peaks in the region of 3,500–2,800 cm^{-1} represented N–H and O–H stretching vibrations, simultaneously. The peak in the region of 2,300 and 2,100 cm^{-1} indicated unsaturation caused by C≡C and C≡N, respectively. The peak in the region of 1,760–1,670 cm^{-1} might be due to stretching frequencies of carbonyl group (C=O), aldehyde, or ketone present in the large molecules of the cell wall. The C–H and C–O–C stretching was observed around 1,430 and 1,050 cm^{-1}, respectively. The bands in the region of 780–760 cm^{-1} were due to C–X (halide) and C–H deformations. For metal-loaded biomass (Pb(II) and Cd(II)), small shifts in the positions of the bands were observed in case of O–H, N–H, and C=O groups. The shifts indicated that the metal ions attached to the functional groups containing N− and O− donor atoms. This might indicate the presence of weak van der Waals' type forces between metal ions and the biomass. However, a detailed study is required before establishing this inference. The results indicate the presence of various functional groups potentially responsible for the binding of Pb(II) and Cd(II) ions onto GJB.

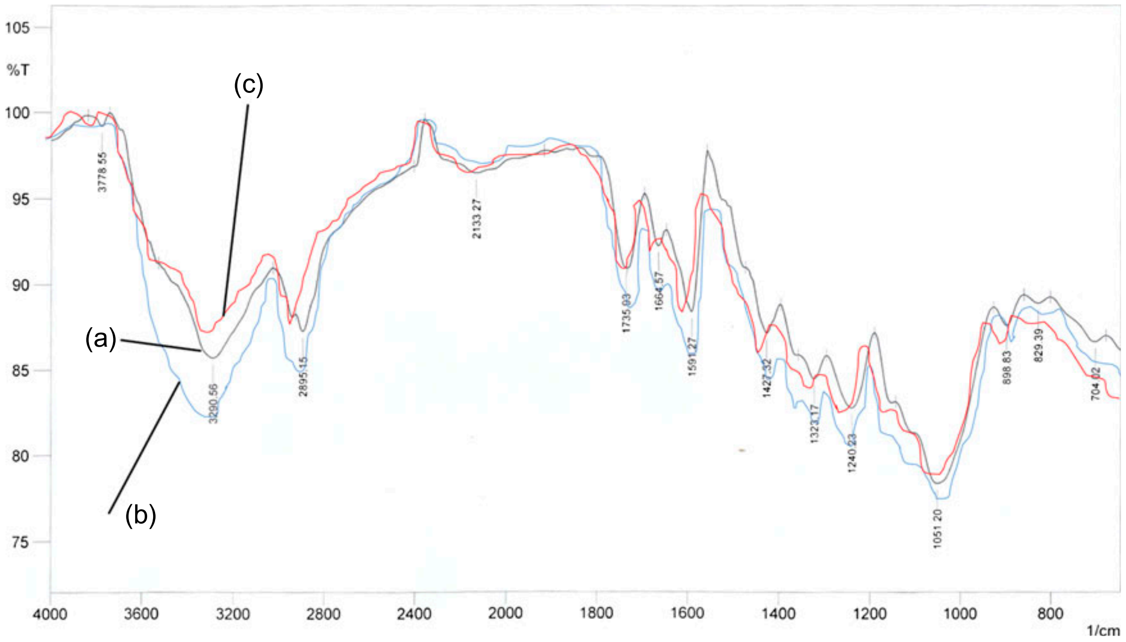

Fig. 1. FTIR spectrum of simple (a), Pb-loaded (b) and Cd-loaded, and (c) biomass from GJB.

The presence of O–H and C=O groups indicated that there might exist acidic (carboxylic as well as phenolic) groups in the biomass. Potentiometric titrations were performed to estimate the concentration of acid and base groups. These titrations have revealed that the concentration of acidic groups was about 10.5 mmol/g, among which 5.5 mmol/g were of carboxylic, and lactonic and phenolic sites were about 5.0 mmol/g. The concentration of total basic sites was calculated to be 7.0 mmol/g. The presence of both acidic and basic sites gave an indication that the actual number of basic and acidic sites could be greater than the observed value. The observed decrease might be due to the mutual interaction between acidic and basic sites. Such an interaction might be explained on the basis of pH of point of zero charge (pH_{pzc}). The pH_{pzc} of GJB was found to be 6.65. A solution pH significantly less than this pH_{pzc} would result in positively charged biomass, resulting in a decreased interaction between the biomass and metal cations. The other characteristics such as ash contents (89.6%), moisture contents (8.8%), and bulk density (0.191 g/cm^3) of GJB were also determined. Table 1 summarizes the characterization of GJB biomass.

3.2. *Biosorption kinetics—effect of time of contact at different initial metal ion concentrations*

The sorption of biomass is influenced greatly by the initial concentration of metal ions in the given solution, time of contact with metal ions, and the accessibility of ions to reach the binding sites without any hindrance. So the biosorption process depends on physical and chemical phenomena. In general trend, the sorption increases with increase in time of contact up to the optimum. The contact time provides information about the liquid–solid interference and help in the scaling process.

It can be seen from Fig. 2 that sorption increased with the increase in the initial concentration of metal ions. This was due to the presence of large number of unoccupied binding sites of GJB. With the increase in the concentration of metal ions, more and more ions reached the binding sites and occupied the available binding sites. Another reason behind this was that as the initial concentration of the metal ion increased, the concentration gradient of metal ions in solution also increased. Thus, more and more metal ions reached the binding sites and bound there. As a result, the sorption was higher for the higher concentration of metal ions.

From Fig. 2(a), it can be seen that GJB showed a very little sorption of Pb(II) ions for low concentration (10 mg/L). Moreover, the equilibrium has established in a very short period of time (early 5 min). This was due to the fact that there was a large number of available active sites, so Pb(II) ions reached the active sites without any hindrance offered by positively charged ions and deposited there. However, as the initial concentration increased, not only the biosorption by GJB

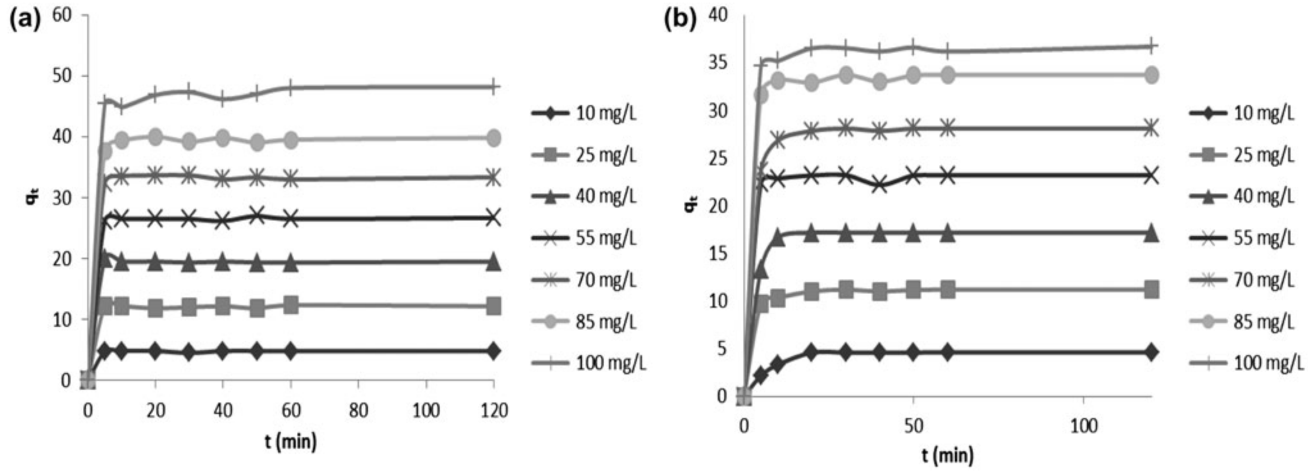

Fig. 2. Effect of the time of contact on the biosorption of (a) Pb(II) ions and (b) Cd(II) ions by GJB.

increased but also a little increment in the equilibrium time of contact was seen with each gradual increase in the initial metal ions concentrations. This was due to the basic reason, i.e. more the metal ions, more the sorption on GJB because of the large number of available binding sites and more time was required to reach equilibrium. This change in the equilibrium time of contact and sorption was continued up to 100 mg/L for Pb(II) ions concentration. It can also be observed that a 10-fold increase in the concentration of Pb(II) ions caused only a fourfold increase in the change in the equilibrium time. For 100 mg/L initial concentration, the graph showed wave-like curves which were due to the fact that there were weak van der Waals attraction between the GJB and metal ions and they show both sorption and desorption phenomena. A very similar behavior was also seen in case of cadmium ions (Fig. 2(b)).

Fig. 2 shows the effect of contact time for Pb(II) and Cd(II) ions binding onto GJB. Since there were large number of binding sites for the sorption of metal ions, the sorption of Pb(II) ions and Cd(II) ions was rapid in the first 20 and 30 min, respectively. As the contact time increased, the metal ions got more and more time to reach the binding sites and to occupy them. Thus, biosorption increases with increase in time of contact. However, the sorption reaches to maximum after this specific time interval due to establishment of equilibrium since the binding sites are almost occupied.

The process reached equilibrium in a short interval of time i.e. 20 min for Pb(II) ions and 30 min for Cd(II) ions, respectively. This time of contact is quite shorter than already reported ones (Table 2). Furthermore, it can be concluded that increase in Pb(II) ions in the solution required a very short increase in the equilibrium time. This fact may help GJB find its application at the industrial level where a short equilibrium time is of prime importance. The biosorption of Cd(II) ions was also good by GJB. The equilibrium time was almost same, even when the concentration of metal ions was increased many times. This shows that GJB can be used for low as well as high concentration to have effective removal of metal ions from aqueous media.

On the basis of the equilibrium time, it can be inferred that GJB has an advantage over a number of already reported biomasses and can be used even at the industrial scale for treatment of contaminated water having Pb(II) and Cd(II) ions [7].

The kinetics for sorption of Pb(II) and Cd(II) by GJB was studied by famous kinetic models, i.e. Elovich, pseudo-first-order (PFO), and pseudo-second-order (PSO) models. The linear forms of Elovich Eq. (3) [24,25], PFO Eq. (4) [26], and PSO Eq. (5) [27] models are

$$q_t = \frac{\ln(a \times b)}{b} + \frac{\ln t}{b} \tag{3}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where a (mg/g min^{-1}) and b (g/mg) are Elovich model constants, k_1 (min^{-1}) and k_2 (mg/g min^{-1}) are pseudo-first-order and PSO rate constants, whereas q_e

Table 2
Various plant-based biosorbents used for the biosorption of metal ions

Plant	Metal ion	Time (min)	Biosorption capacity (mg/g)	Equilibrium model*	Reference
Nordmann cones	Pb(II)	180	29.35	L, F	[32]
	Zn(II)		18.41		
Coconut copra meal	Cd(II)	120	4.99	R–P	[31]
Green coconut shell powder	Cd(II)	120	285.70	L, F	[34]
Barley straw	Cu(II)	90	4.64	L	[33]
	Pb(II)	60	23.20		
Eriobotrya japonica leaves	Cd(II)	60	48.78	L	[35]
Pinus sylvestris	Pb(II)	60	0.829	F	[36]
Moringa oleifera bark	Pb(II)	30	34.60	F	[37]
Rose	Pb(II)	30	156.00	L	[19]
	Co(II)		27.15		
Trifolium resupinatum	Pb(II)	25	10.38	L	[28]
Symphoricarpus albus	Pb(II)	20	44.09	L	[38]
Banana peels	Pb(II)	20	2.18	L	[39]
	Cd(II)		5.71		

*L = Langmuir, F = Freundlich, and R–P = Redlich–Peterson models.

and q_t (mg/g) are the amounts of metal sorbed at equilibrium and at the given the time t, respectively.

The parameters for the Elovich model are provided in Table 3. It was observed from R^2 values that this model was not followed (Figure not shown). The PFO model indicates that the biosorption process is directly proportional to the number of freely available binding sites onto the biomass. The application of PFO for the biosorption process can be found by plotting a graph between $\ln(q_e - q_t)$ and time t. If the plot is a straight line with positive slope and R^2 value greater than 0.98, then PFO is followed by the given data. However, if the values are not in agreement, then the above-mentioned conditions are not followed. The PFO plots for all concentrations (10, 25, 40, 55, 70, 85, and 100) of Pb(II) and Cd(II) ions did not have a positive value of slope and R^2 value greater than 0.98. Moreover, there was a great difference between the calculated and actual amount of equilibrium concentration. The values of all kinetic parameters of PFO for all concentrations are given in Table 3. The results have clearly shown that PFO model is not followed for the biosorption of Pb(II) and Cd(II) ions onto the GJB.

The application of PSO can be observed by plotting a graph between t/q_t vs. t (Fig. 3(a) and (b)). The plot should be a straight line with a positive value of slope and intercept along with R^2 value more than 0.98 for the biosorption process to follow the PSO mechanism. This will also reveal that the biosorption is proportional to number of freely available binding sites. PSO plots resulted in a straight line with R^2 value greater than 0.98 for the biosorption of Pb(II) as well as Cd(II) ions onto GJB at all studied concentrations. Thus, the values of PSO rate constants k_2 and q_e were calculated from the slope and the intercept and given in Table 3. R^2 of PSO plot for 10 mg/L Pb(II) ions was 0.9996 and q_{cal} and q_{exp} were 4.85 and 4.83 mg/g, respectively. The experimental and calculated equilibrium concentrations showed a little difference. The other concentrations also showed very little difference. Similarly, the calculated q_e values for Cd(II) ions for each concentration were also very close to the experimentally determined values. R^2 of PSO plot, for 10 mg/L of Cd (II) ions, was 0.9974 and q_{cal} and q_{exp} were 4.60 and 4.78 mg/g for the sorption of Cd(II) onto GJB. It means that the experimental and calculated equilibrium concentrations showed a little difference.

This showed that PSO kinetics found its application for the biosorption of Pb(II) as well as Cd(II) ions onto GJB. The values of k_2 for the given concentration of each ion are given in table. Based on the theoretical consideration, the sorption of divalent metal ions (M) onto two free binding sites (B) can be expressed as

$$M + 2B \leftrightarrow B_2M$$

$$r = k[M][B]^2$$

The above relation tells that the rate of sorption of metal ions is proportional to the number of freely available binding sites, which corresponds to the term $(q_e - q_t)^2$ in the PSO model. The best fit of the PSO model indicates an application of 1:2 binding stoichiometry, i.e. one is for the divalent metal ion which

Table 3
Kinetics of the biosorption of Pb(II) and Cd(II) ions by GJB

		Pb(II)							Cd(II)						
Model	Parameter	10	25	40	55	70	85	100	10	25	40	55	70	85	100
Elovich model	b	26.81	161.29	−6.66	7.40	6.62	2.10	0.99	1.31	2.07	1.015	4.76	0.81	1.75	1.62
	a	4.66×10^{52}	1.31×10^{847}	-2.01×10^{-59}	6.24×10^{8}	1.98×10^{93}	1.10×10^{34}	4.19×10^{18}	6.04	9.82×10^{7}	7.3×10^{5}	1.84×10^{45}	1.72×10^{8}	3.78×10^{23}	4.42×10^{23}
	R^2	0.0944	0.0013	0.4937	0.2671	0.1202	0.428	0.7471	0.7318	0.7873	0.5627	0.2525	0.6757	0.6767	0.7328
PFO	k_1 (min^{-1})	0.1230	0.0017	NF*	NF*	0.0034	0.0171	0.0279	0.0053	0.0044	0.1979	−0.007	0.0087	0.0033	−0.0061
	$q_{e\ (cal)}$ (mg/g)	0.15	0.27	NF*	NF*	0.55	1.21	2.10	1.70	0.57	2.69	0.24	2.16	0.66	0.34
	$q_{e\ (exp)}$ (mg/g)	4.83	11.83	19.50	26.50	33.67	40.00	46.83	4.60	11.18	17.17	23.20	28.10	33.72	36.51
	R^2	0.6099	0.0162	NF*	NF*	0.0378	0.4737	0.8571	0.4563	0.0128	0.7176	0.0289	0.3849	0.0128	0.0195
PSO	k_2 (g mg^{-1} min^{-1})	0.0460	0.2849	0.7140	0.2230	1.8000	0.0818	0.0240	0.0750	0.1470	0.1160	0.1193	0.0720	0.0800	0.0755
	$q_{e\ (cal)}$ (mg/g)	4.85	12.19	19.46	26.67	33.33	39.84	48.31	4.78	11.26	17.27	23.26	28.25	33.78	36.76
	$q_{e\ (exp)}$ (mg/g)	4.83	11.83	19.50	26.50	33.67	40.00	46.83	4.60	11.18	17.17	23.20	28.10	33.72	36.51
	R^2	0.9996	0.9997	1.000	0.9999	0.9999	0.9999	0.9998	0.9974	0.9996	0.9999	0.9999	0.9999	0.9999	0.9999

*NF = the model was not followed under the studied set of conditions.

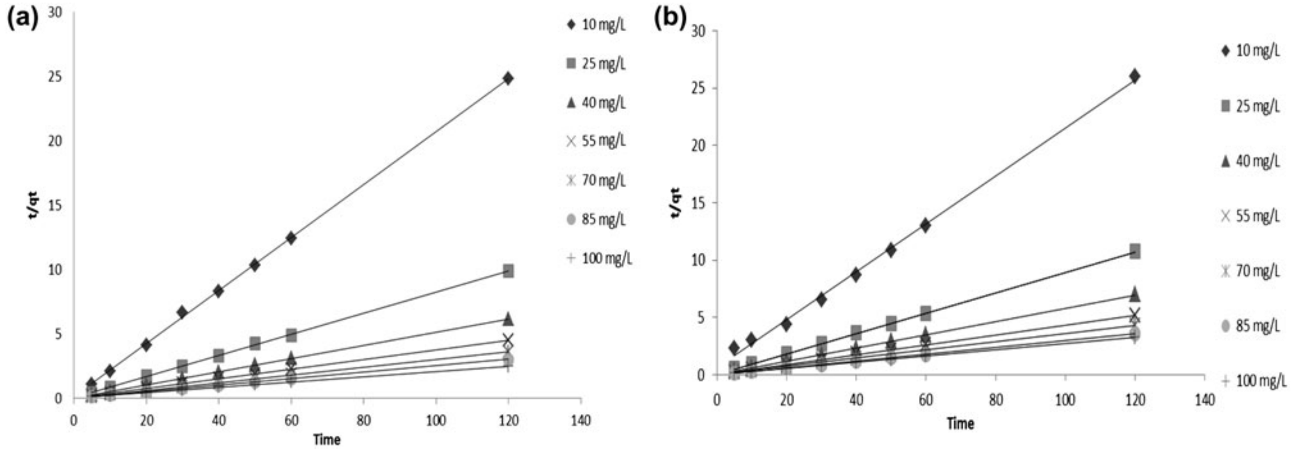

Fig. 3. PSO kinetic plots for (a) Pb(II) ions and (b) Cd(II) ions.

binds to two monovalent available binding sites. The literature survey has also supported that the biosorption of divalent ions mostly follows PSO kinetics [28].

3.3. Equilibrium modeling: effect of varying initial concentrations and adsorption isotherms

Adsorption, along with the other related mechanisms, has been found to play a potential role in the biosorption of metal ions [7]. The adsorption process can be well explained by the equilibrium modeling or adsorption isotherms. These models show a relation between the amounts of sorbed metal ions onto the biomass and the amount of metal ions left behind in the solution after the establishment of equilibrium. The Freundlich and Langmuir models are mostly used for this purpose.

The maximum biosorption capacity of a biomass is represented by the Langmuir model Eq. (6). The basic principle is that the metal ions form a monolayer onto the homogeneous surface of the biomass. In contrast, biosorption intensity of a given biomass can be estimated using the Freundlich model Eq. (7). According to this model, the metal ions form multiple layers over the heterogeneous surface of the sorbent material. The dimensionless parameter, R_L Eq. (8), was also used to show the feasibility of the Langmuir model. The equations are presented as follows

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = K_F \, C_e^{1/n} \tag{7}$$

$$R_L = \frac{1}{1 + K_L C_e} \tag{8}$$

where q_m (mg g^{-1}) represents the maximum metal ions uptake, K_L (L mg^{-1}) and K_F are constants for the respective model, whereas C_e (mg L^{-1}) is the equilibrium solution concentration. Fig. 4(a) and (b) shows non-linear plots for both Langmuir and Freundlich models and the values of constants are given in Table 4.

The Langmuir plot for both the metal ions showed a closer agreement between experimental and model curves. The biosorption capacities for both metal ions are quite high, indicating a greater affinity of the biosorbent for the studied metal ions, greater for Pb (II) than Cd(II). The separation factor, R_L, has a value between 0 and 1 indicating a favorable adsorption. The feasibility of Freundlich model is determined from the $1/n$ value for the biosorption of a particular metal ion onto the given biomass. If the value of $1/n$ is found to be in range 0–1, then the process is favorable [7]. The $1/n$ value for Pb(II) ions was 0.5382, while for Cd(II) ions was 0.6003, so it could be said that the Freundlich model is followed by both kinds of the ions. RMSE is a measure of the degree of difference between experimental and model values. The RMSE value for the Langmuir model is relatively high for both metals, but it is much smaller as compared to that of the Freundlich model. On the basis of comparison of RMSE values, the Langmuir model was found to be a better fit for both the metal ions. The literature survey was also in agreement that the Langmuir model was followed for the biosorption of both Pb(II) and Cd(II) ions onto various kinds of biosorbents (Table 2). Thus, the results showed that these ions

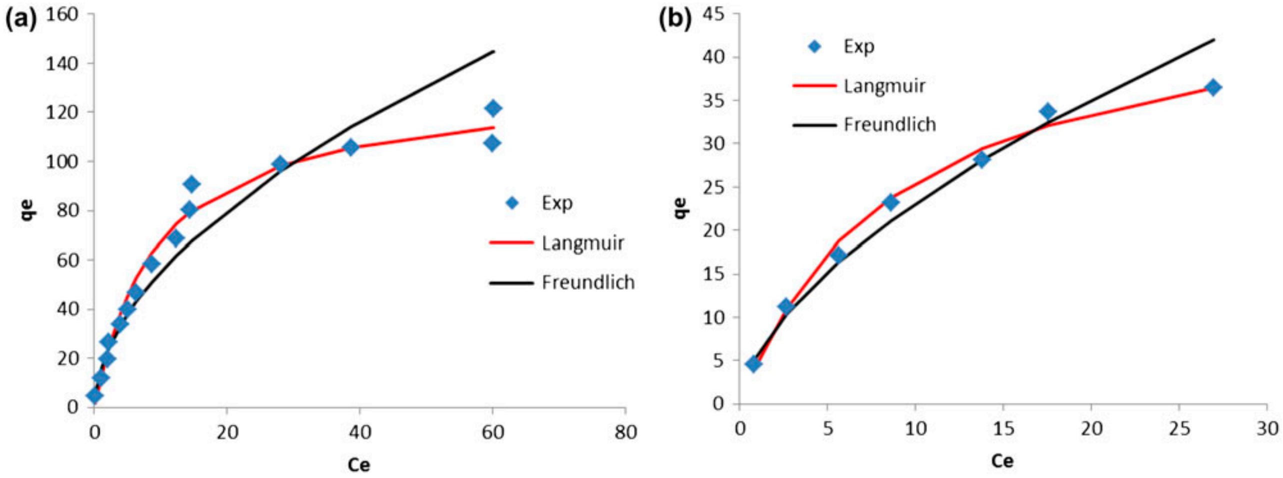

Fig. 4. Non-linear equilibrium modeling for the biosorption of (a) Pb(II) and (b) Cd(II) ions by GJB.

Table 4
Equilibrium parameters for the biosorption of Pb(II) and Cd(II)

Model	Parameters	Pb(II)	Cd(II)
Langmuir	q_m (mg/g)	131.60	48.54
	K_L (L/mg)	0.1060	0.1115
	R_L	0.0304–0.4854	0.0823–0.4728
	RMSE	5.0456	1.045
Freundlich	K_F	15.96	5.82
	$1/n$	0.5382	0.6003
	RMSE	13.829	2.3184

form a monolayer onto GJB surface and q_{max} was calculated as 131.6 and 48.54 mg g^{-1} for Pb(II) and Cd (II) ions, respectively. These values are higher than a number of reported biosorbents (Table 1). The studies also indicated that adsorption had a potential role in the process of biosorption along with other reported mechanisms [7].

3.4. Effect of pH

The pH of the solution is an important factor since it affects the biosorption of metal ions at the solution–solid interface. The chemistry of metal ions in the solution is significantly influenced by the pH. Usually the metal ions are precipitated out in basic pH (pH > 7). In case of lead ions, Pb^{2+} is a dominant ion below pH 6. It precipitates out as $Pb(OH)_2$ above pH 6 [29]. Similarly, cadmium is present as free Cd^{2+} species along the whole acid pH range. Above pH 7.5, it starts to precipitate as $Cd(OH)_2$ [30]. Such a precipitation is not desired for biosorption studies since the metal ions are "removed" and are not available for the binding with the biosorbent. Hence, the precipitation point gives the upper limit of the pH studies. The surface charge on the biosorption is also affected by the pH of the solution. Most of the carboxylic acid groups have ionization constants between 3 and 4. In highly acidic pH, these are protonated and act as positively charged species [7]. GJB was found to have various acid and base functional groups (Table 1 and Fig. 1). The behavior of these functional groups changes with the pH of the solution. As a result of change in the pH, protonation and deprotonation of these functional groups cause a change on the surface charge of GJB. For an effective biosorption of positively charged metal ions, the surface of the biosorbent is required to bear a least positive charge or to bear a negative charge. So, the biosorbent bears relatively less positive charge above pH 3. Moreover, the point of zero charge pH (pH_{pzc} or isoelectric point) of GJB was found to be 6.65. This shows that GJB should have positive charge at a pH below this pH, indicating that a small extent of binding of metal ions is expected at highly acidic pH due to electrostatic repulsion. This is true when the surface complexation and precipitation are considered as the only possible mechanisms for biosorption. However, the role of adsorption and ion-exchange is dominating in the possible mechanisms of biosorption. The smaller extent of biosorption at low pH can also be explained on the basis of the competition between H^+ and metal ions. The concentration of H^+ ions is higher at low pH values; thus H^+ ions have a greater tendency to adhere to the binding sites than the metal ions and this tendency decreases with increase in the pH of the solution.

To investigate the impact of pH onto the sorption of metal ions, the experiments were performed from

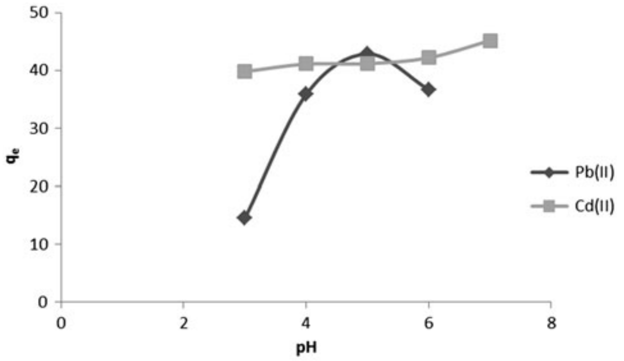

Fig. 5. Effect of the pH on the biosorption of Pb(II) and Cd (II) ions by GJB.

pH 3–7 (3–6 for Pb(II)). From Fig. 5, it can be seen that at low pH, sorption of metal ion was poor due to strong competition between hydrogen and metal ions for the active sites as well as repulsive forces between ions (as expected). However, this competing effect decreased with rise in pH due to decrease in the concentration of H^+ and the metal uptake by the active site of the biomass increased remarkably. Thus, maximum sorption of metal ions was seen at pH 5 for lead and pH 6 for cadmium. The pH values of 5–6 have been reported in the literature for the biosorption of divalent metal cations [7,30–34].

4. Conclusion

The present work explains the capability of the powdered biomass from GJB to remove extremely toxic heavy metals Pb(II) and Cd(II) ions from aqueous medium. Different parameters such as the time of contact, the biosorbent dose, and the initial metal ions concentration were studied. The optimum time was 20 min for Pb(II) and 30 min for Cd(II) ions at pH 5 for Pb(II) ions, while it was 6 for Cd(II) ions. It was found that the biosorption process followed the Langmuir model and the $q_{\max}$ was 131.6 and 48.54 mg/g for Pb(II) ions and Cd(II) ions, respectively, using a non-linear approach. The PSO kinetics was found to best for the biosorption of the ions. The results indicate that *G.jasminoides* can be used as a cost-effective and eco-friendly biosorbent for the removal of Pb(II) and Cd(II) ions from aqueous solutions.

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