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Pb (II) sorption by acidically modified *Cicer arientinum* biomass

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ABSTRACT

In this study, efficacy of native and acidically modified *Cicer arientinum* pod biomass was investigated for Pb (II) removal using metal ion concentration, kinetic, sorbent dose, pH and pretreatment as operational parameters. The metal uptake of biomass increased as a result of pretreatments and maximum sorption capacity (171.28 mg/g) was shown by H_3PO_4 modified biomass. The sorption capacity increased in the order $H_3PO_4 > H_2SO_4 > HCl >$ native, with increase in metal concentration. The equilibrium data was analysed using different sorption models to know sorption mechanism and results of ANOVA showed that Dubinin–Radushkevich model is fitted well to the experimental data. Sorption rate was slow because equilibrium was attained within 7 h and rate was best described by pseudo-first-order, second-order rate equation, Bangham and intraparticle diffusion models. Sorption capacity was maximum at pH 4 and it was observed also that sorption capacity decreased but % removal increased with increase in biosorbent dose.

1. Introduction

The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment [1]. The rate at which effluents are discharged into the environment especially water bodies is increasing as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals. The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment [2,3]. Lead is widely used in many industrial applications such as storage manufacturing battery, printing, pigments, fuels, photographic materials and explosive manufacturing [4]. Lead is highly toxic as its presence in drinking water above the permissible limit (5 ng/mL) causes adverse health effects such as anemia, encephalopathy, hepatitis and nephritic syndrome [5].

Conventionally, the methods employed for the removal of heavy metals from effluents include oxidation and reduction, precipitation, filtration, electrochemical treatment and evaporation [6]. These physiochemical methods have several disadvantages such as unpredictable metal ion removal, high reagent requirements and formation of sludge and its disposal, in addition to high installation and operational costs [7]. Biosorption, a biological method of environment control, can be an alternative to conventional waste-treatment facilities. Several workers have reported on the potential use of agricultural by-products as good substances for the removal of metal ions from aqueous solutions and wastewaters [8]. The ability of some agricultural by-products to adsorb heavy metals from wastewater and aqueous metal solutions has been reported in literature and these include cassava waste [9], sunflower stalk [10], waste tea [11], distillery sludge of sugar-cane industry [12], wheat bran [13] and horseradish tree [14]. Also, research by Park et al. [15] showed that chemical modification of agricultural adsorbents increased the sorption capacity of the adsorbent, thereby increasing the efficiency of the adsorbent.

In this study, pods of *Cicer arientinum* were chosen as a biosorbent for the removal of lead (II) from aqueous solutions because of the composition of *C. arientinum* [16] and its availability. *C. arientinum* belongs to family *Leguminoseae*. Pakistan contributes up to 4.64% of the total *C. arientinum* production in the world. In Pakistan, 933,900 ha area was used for cultivation of *C. arientinum* in 2002 and production was 362,100 tonnes. Now, cultivation of *C. arientinum* has increased in Pakistan. Since removal of heavy metals using *C. arientinum* is already reported [17], biosorbent was chemically modified to observe enhancement or decrease in biosorption capacity of biomass in this study.

2. Material and methods

2.1. Materials

Pods of chickpea (*C. arientinum*) were collected from a field near Chakwal, Pakistan. All pods were washed with distilled water in

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order to remove all particulate material. Then these pods were dried at room temperature and ground using food processor (Moulinex, France). The ground material was divided into four equal parts. Three parts were taken and treated with HCl, H_2SO_4 and H_3PO_4 (Fluka chemicals) in the ratio of 5 g sorbent/100 mL of 1 M reagent, respectively using orbital shaker (Gallenkamp) for 24 h. These acidically modified biomasses were filtered and washed with distilled water up to neutral pH. These washed pretreated biomasses were dried at room temperature and ground using food processor and then sieved (63 and 150 μm) through Octagon siever (OCT-DIGITAL 4527-01) and stored in airtight plastic containers. The fourth untreated biomass part was also sieved and used as native biomass.

Stock Pb (II) solution (1000 mg/L) was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ (Fluka chemical) in some distilled water and making volume up to 1000 mL using distilled water. Pb (II) solutions of different concentrations (50–200 mg/L) were prepared by adequate dilution of the stock solution with distilled water.

2.2. Batch sorption studies

In all experiments, 100 mL of Pb (II) solution (100 mg/L) having pH 4 was mixed with biosorbent (0.05 g) having a definite mesh size at 30 °C and 200 rpm in orbital shaker. To evaluate the effect of initial metal concentration, 100 mL solution having concentration (50–200 mg/L) of Pb (II) was stirred with native and pretreated biosorbents (0.05 g) having mesh size (63 and 150 μm) for 24 h. Further, the effect of contact time (5–480 min), effect of biosorbent dose (0.05, 0.1, 0.2 g) and effect of pH (4, 7 and 9) with 150 μm sieved H_3PO_4 modified biomass were also evaluated. To adjust pH of solution, 0.1N HCl and NaOH were used. At the end of experiments, flasks were removed from shaker and solutions were filtered. Filtrates were stored in precleaned and acid (HNO_3) washed airtight plastic containers and analysed by PerkinElmer AAnalyst atomic absorption spectrophotometer equipped with lead hollow cathode lamp operating at wavelength of 232 nm and slit as 0.2 nm. Blank experiments were also carried out.

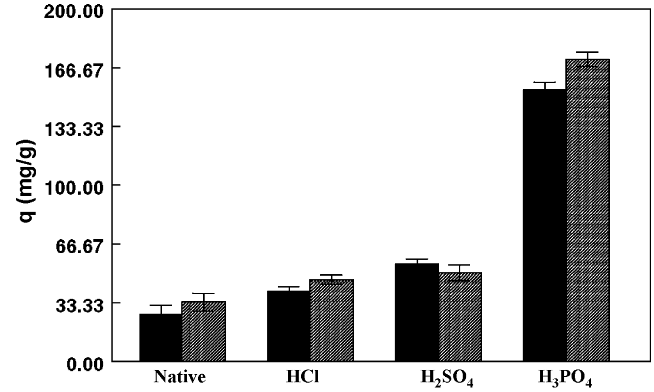

Fig. 2. Effect of pretreatment and particle size on biosorption of Pb^{2+} using 63 μm ■ and 150 μm ▨ sieved native, HCl, H_2SO_4 and H_3PO_4 modified biomasses.

2.3. Calculations

The sorption capacity 'q' (mg/g) was calculated by simple concentration difference method:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

where C_i and C_e (mg/L) are initial and final metal concentrations, V is volume of the solution (L) and M is mass of biosorbent (g). Each experiment was conducted in triplicate and data represents mean of three independent experiments. Two-way analysis of variance (ANOVA) was done to evaluate the concentration data. All calculations were made using Slide Write version 3.0 and Microsoft Office 2000.

3. Results and discussion

3.1. Effect of metal concentration

The amount of metal ion sorbed per unit mass of native and pretreated biosorbents (i.e., sorption capacity) was found to increase

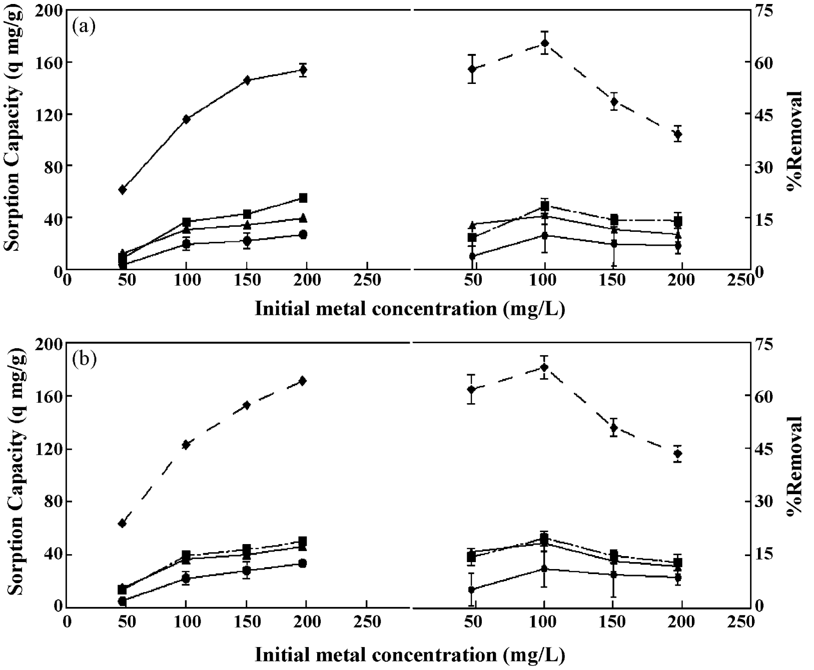

Fig. 1. (a) Effect of initial metal concentration on the biosorption of Pb^{2+} using 63 μm sieved native ●, HCl ▲, H_2SO_4 ■ and H_3PO_4 ♦ modified biomasses. (b) Effect of initial metal concentration on the biosorption of Pb^{2+} using 150 μm sieved native ●, HCl ▲, H_2SO_4 ■ and H_3PO_4 ♦ modified biomasses.

with increase in concentration of metal ion whereas percentage removal was maximum at 100 mg/L for all biomasses and then found to decrease with increase in initial metal ion concentration (Fig. 1a and b). The increase in sorption capacity may be explained by the fact that at low concentrations, the available metal occupies adsorption sites more quickly. However, at higher concentrations, metals diffuse to the biomass surface by intraparticle diffusion. The decrease in percentage removal is explained by the fact that at lower concentrations, almost all the ions were adsorbed very quickly and further increase in initial metal ion concentration led to saturation of biomass surface [18].

3.2. *Effect of pretreatment and biosorbent size*

Comparing the results, one can notice that the pretreatment of biomass by HCl, H_2SO_4 and H_3PO_4 (Fig. 2) increased the sorption capacity (mg/g) of biomass in order H_3PO_4 (171.28) > H_2SO_4 (50.4) > HCl (46.3) > native (33.62) for 150 μm sieved biomass as compared to 63 μm sieved H_3PO_4 (153.8) > H_2SO_4 (55.08) > HCl (39.7) > native (26.9). Generally, acid-treatment has been used for cleaning the cell wall and replacing the natural mix of ionic species bound on the cell wall with protons and other functional groups exposing new active sites for metal removal causing increase in sorption capacity [19–21]. Park et al. [22] also reported an increase in sorption capacity of biomass as a result of acidic pretreatment of Ecklonia biomass. H_3PO_4 treatment showed remarkable increase in sorption capacity of biomass but a slight difference was observed in case of H_2SO_4 and HCl treatments when compared to native biomass. Pretreatment of biomass with acids, apart from removal of mineral matter also resulted in introduction of oxygen surface complexes that change the surface chemistry by increasing the porosity and surface area of original sample. H_3PO_4 pretreated biomass showed more sorption capacity and it was due to solubility of more mineral matter of biomass which resulted more porosity in biomass due to increased cellular mass [12]. When compared results of particle size (63 and 150 μm), 150 μm sieved biomass showed more sorption capacity as compared to 63 μm sieved biomass (Fig. 2). This behavior was also reported by Leusch et al. [23] who showed that larger biomass particles of *Sargassum fluitans* and *Ascophylum nodosum* had higher metal uptake than smaller particles in the case of cadmium, copper, nickel, lead and zinc.

3.3. *Equilibrium studies*

In order to optimize the design of a sorption system for the removal of metals from wastewater, it is important to establish the most appropriate correlation for equilibrium curves. Experimental data acquired at different conditions is fitted to different models of sorption isotherms because equilibrium isotherm models are used to describe the experimental data. The equation parameters and the thermodynamics of these equilibrium models often provide some insight into the sorption mechanisms, surface properties and affinities of the sorbent (Fig. 3a and b). There are many theories relating to adsorption equilibrium.

3.3.1. *Freundlich isotherm model*

The Freundlich isotherm [24] is originally empirical in nature but was later interpreted as sorption to heterogeneous surface or surface supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation. Freundlich model is expressed as

$$\log q_e = \frac{1}{n} \log C_\mathrm{e} + \log k \tag{2}$$

where $1/n$ and k are Freundlich constants. The Freundlich isotherm parameter $1/n$ measures the adsorption intensity of metal ions on biomass and Freundlich constant k is adsorption capacity of biomass. The value of $1/n$ greater than unity indicates that adsorption can take place even at high concentrations but values of $1/n$ in case of native biomass oppose the experimental data. The high $1/n$ value of native biomass in comparison to acidically modified biomass indicated the sorption ability of native biomass but experimental data showed that pretreatment causes enhancement in sorption capacity of biomass. The value of k ($\mathrm{dm^3/g}$) is greater for H_3PO_4 modified biomass as compared to other biomasses in favor of experimental data but order of k ($\mathrm{dm^3/g}$) values is disturbed in case of other biomasses. Values of R^2 in case of H_3PO_4 modified biomass are 0.9773 and 0.9711 for 150 and 63 μm sizes that are equal but greater than R^2 values of native, HCl and H_2SO_4 as indicated from Table 1. Freundlich isotherm model favorably satisfies the experimental data only in case of H_3PO_4 modified biomasses.

3.3.2. *Langmuir isotherm model*

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [25]. Langmuir isotherm can be characterized by a plateau graphically. A saturation point reaches at equilibrium where no further adsorption occurs. Adsorption is assumed to take place at specific homogeneous sites within the adsorbent. Once a sorbate molecule occupies a site, no further adsorption takes place at that site. Linearized form of Langmuir model is:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{X_\mathrm{m} K_\mathrm{L}} + \frac{C_e}{X_\mathrm{m}} \tag{3}$$

where K_L ($\mathrm{dm^3/g}$) is Langmuir constant termed as apparent energy of adsorption and X_m (mg/g) is sorption capacity. When values of R^2 were compared, sorption phenomena did not support the fitness of this model to native, HCl and H_2SO_4 modified biomasses in case of both sizes. However, values of R^2, K_L and X_m (Table 1) for H_3PO_4 modified sorbents indicated that Langmuir theory describes the sorption phenomena for this biomass more favorably.

3.3.3. *Temkin isotherm model*

Temkin isotherm plot [26] was chosen to evaluate adsorption potentials of sorbent for sorbate. The heat of sorption of the molecules in layer decreases linearly with coverage due to sorbate and sorbent interactions [27]. Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic. Temkin isotherm model is shown:

$$q_\mathrm{e} = \frac{RT}{b_\mathrm{T}} \ln K_\mathrm{T} + \frac{RT}{b_\mathrm{T}} \ln C_\mathrm{e} \tag{4}$$

where K_T ($\mathrm{dm^3/g}$) is Temkin adsorption potential and b_T (kJ/mol) is heat of sorption (Table 1). When evaluated with respect to coefficient of determination (R^2), Temkin isotherm model appears to be favorable for fitness to the experimental data. Values of K_T ($\mathrm{dm^3/g}$) for H_3PO_4 modified biomass showed that model favors the experimental data of H_3PO_4 modified biomass of both sizes. Order of b_T values was in accordance with the experimental findings because heat of sorption of the molecules decreases linearly with coverage due to sorbate and sorbent interactions and smaller values of b_T for H_3PO_4 modified biomass concluded this biosorbent as more favorable.

3.3.4. *Dubinin–Radushkevich isotherm model*

The Dubinin–Radushkevich model is used to estimate the charateristic porosity of the biomass and apparent energy of adsorption [28]. The model is represented by

$$\ln\ q_\mathrm{e} = \ln q_\mathrm{D} - 2B_\mathrm{D} RT \ln\left(1 + \frac{1}{C_\mathrm{e}}\right) \tag{5}$$

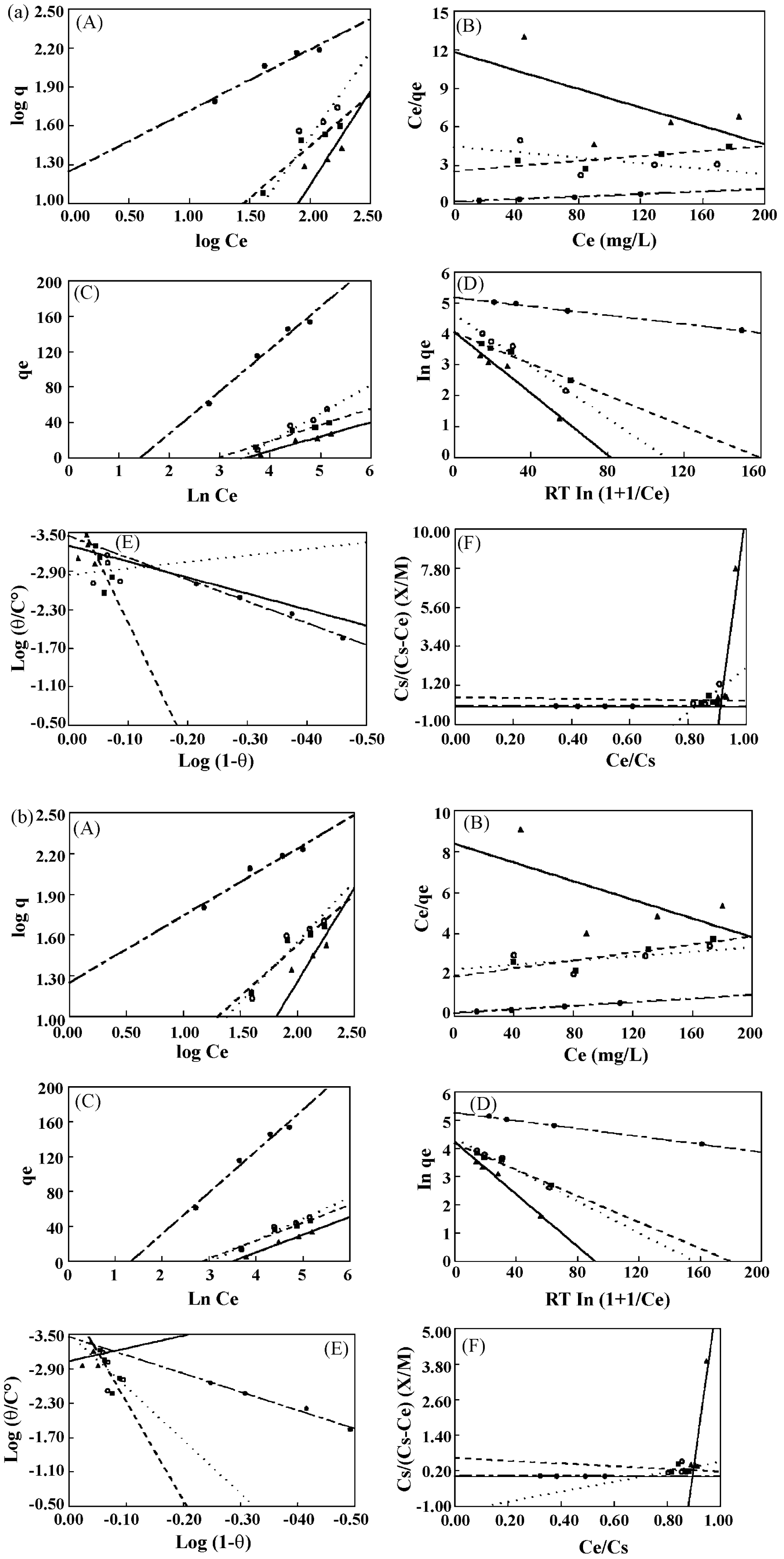

Fig. 3. (a) Equilibrium isotherm analysis of Pb^{2+} biosorption using 63 μm sieved *Cicer arientinum* biomass (control ▲, HCl ■, H_2SO_4 ○ and H_3PO_4 ●) by linear plots of (A) Freundlich (B) Langmuir (C) Temkin (D) Dubinin–Radushkevich (E) Florry–Huggins and (F) BET models. (b) Equilibrium isotherm analysis of Pb^{2+} biosorption using 150 μm sieved *C. arientinum* biomass (control ▲, HCl ■, H_2SO_4 ○ and H_3PO_4 ●) by linear plots of (A) Freundlich (B) Langmuir (C) Temkin (D) Dubinin–Radushkevich (E) Florry–Huggins and (F) BET models.

Table 1
Equilibrium isotherm model parameters for the biosorption of Pb (II) using native and acidically modified *Cicer arientinum* pod biomass.

Equilibrium models	Parameters	63 μm sieved biomass				150 μm sieved biomass			
		Native	HCl	H_2SO_4	H_3PO_4	Native	HCl	H_2SO_4	H_3PO_4
Freundlich	$1/n$	1.45	0.802	1.307	0.472	1.382	0.7524	0.8903	0.4956
	k (dm^3/g)	0.0179	0.6897	0.078	17.69	0.031	1.052	0.588	17.81
	R^2	0.9343	0.9515	0.9461	0.9711	0.955	0.9473	0.9390	0.9773
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28
Langmuir	K_L (dm^3/g)	3.039×10^{-3}	3.753×10^{-3}	2.423×10^{-3}	3.01×10^{-2}	2.7×10^{-3}	5×10^{-3}	2.3×10^{-3}	2.8×10^{-2}
	X_m (mg/g)	27.789	103.69	92.16	200.36	44.01	102.93	191.31	228.52
	R^2	0.5894	0.7774	0.5211	0.9962	0.5937	0.8446	0.5238	0.9981
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28
Temkin	b_T (kJ/mol)	155.75	137.16	78.798	52.745	123.96	122.59	101.92	53.05
	K_T (dm^3/g)	0.0299	0.0516	0.0326	0.2411	0.0299	0.0579	0.0482	0.263
	R^2	0.9749	0.9771	0.9816	0.9882	0.9931	0.9721	0.9699	0.9887
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28
Dubinin–Radushkevich	B_D(mol^2/kJ^2)	0.2493	0.01273	0.02104	0.0359	0.0232	0.0116	0.0139	0.0351
	q_D (mg/g)	58.52	58.89	106.52	179.97	66.523	68.96	79.96	196.42
	R^2	0.9808	0.9896	0.9850	0.9992	0.9917	0.9877	0.9845	0.9993
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28
Florry–Huggins	n	2.492	19.55	1.02	3.397	2.235	17.25	9.29	3.201
	K_{FH}	5×10^{-4}	8.4×10^{-5}	1.44×10^{-3}	3.5×10^{-4}	9.2×10^{-4}	8.4×10^{-5}	2.9×10^{-4}	3.4×10^{-4}
	R^2	0.1413	0.6924	0.0877	0.9936	0.1289	0.7654	0.4742	0.9889
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28
BET	A	1.105	1.553	1.3026	31.929	1.134	0.868	2.256	32.102
	X_m (mg/g)	0.0079	1.2498	0.07262	1.028	0.0152	1.842	0.372	1.034
	R^2	0.8612	0.0225	0.8458	0.6279	0.8978	0.1047	0.2742	0.7179
	q_{exp} (mg/g)	26.9	39.7	55.08	153.8	33.62	46.3	50.4	171.28

where q_D is Dubinin–Radushkevich isotherm constant related to the degree of sorbate sorption by sorbent surface and B_D is related to the free energy of sorption per mole of sorbate as it migrates to the surface of the biomass from infinite distance in the solution. The porosity parameter values 'B_D' for the biomass towards the metal ion were less than unity indicating that sorption of Pb (II) by native and pretreated biomass was significant (Table 1). q_D values obtained from isotherm data were in accordance with the experimental data of all sorbents. R^2 values obtained from data also supported the fitness of model to all sorbents. Overall, this model explains the sorption phenomena for all biomasses.

3.3.5. *Florry–Huggins isotherm model*

The Florry–Huggins isotherm model [18] accounts the degree of surface coverage characteristic of the sorbate on the sorbent. The isotherm is as follows:

$$\log\frac{\theta}{C_o} = \log K_{FH} + n\log(1-\theta) \tag{6}$$

where $\theta = (1 - C_e/C_0)$ is degree of surface coverage, K_{FH} is equilibrium constant, n is metal ions occupying active sites of biomass, C_0 is initial metal concentration and C_e is equilibrium metal concentration.

A greater value of 'n' means that greater number of metal ions are occupying the binding sites. Values of n (Table 1) obtained showed that results are not in good agreement with experimental q values. A greater value of 'n' in case of HCl modified biomass revealed that HCl modified biomass is more efficient than other biomasses for metal removal. Values of K_{FH} showed that H_2SO_4 modified biomass is more favorable among 63 μm sieved biomasses and native biomass is more favorable among 150 μm sieved biomasses because larger value of K_{FH} indicates efficiency of biomass. These findings suggested that Florry–Huggins isotherm plot is not favorable to depict the sorption. However, values of correlation coefficients as 0.9936 in case of 63 μm sieved and 0.9889 in case of 150 μm sieved H_3PO_4 modified biomasses revealed a linear relationship between Florry–Huggins isotherm model and H_3PO_4 modified biomass as compared to other biomasses.

3.3.6. *BET isotherm model*

The BET model assumes that a number of layers of adsorbate molecules are formed at the surface of sorbent and the Langmuir equation applies to each layer [29]. A further assumption of the BET model is that a given layer need not complete formation prior to initiation of subsequent layers; the equilibrium condition will therefore involve several types of surfaces in the sense of number of layers of molecules on each surface. For adsorption from solution with the additional assumption that layers beyond the first have equal energies of adsorption, the BET equation takes the simplified form as

$$\frac{C_S}{(C_S - C_e)(X/M)} = \frac{1}{AX_m} + \frac{(A-1)}{AX_m}\left\{\frac{C_e}{C_S}\right\} \tag{7}$$

where (X/M) is the amount of solute adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the solute in bulk solution (mg/L), C_S is the saturation concentration of the solute in bulk solution (mg/L), A is a constant indicative of the energy of interaction between the solute and the adsorbent surface and X_m is a constant indicative of the amount of solute adsorbed forming a complete monolayer (mg/g). Values of R^2 indicated BET model not appropriate to describe the sorption mechanism (Table 1) for both sizes of native and pretreated biomasses. Also, there is much difference between values of X_m and q_{exp}.

3.3.7. *Correlation coefficient*

The correlation coefficients 'R^2' determined from linearization of the six two-parameter isotherms (Table 1) suggest that Temkin and Dubinin–Radushkevich isotherms are most appropriate to explain the sorption phenomena in case of all biomasses whereas Freundlich and Florry–Huggins isotherms describe sorption phenomena in case of H_3PO_4 modified biomass also. To solve this complication, statistical analysis (two-way ANOVA) at $\alpha = 0.05$ were

Table 2
Two-way analysis of variance (ANOVA) without replication at $\alpha = 0.05$ to evaluate the relationship between isotherm models and biomass.

	Count	Sum	Average	Variance
a				
Freundlich	8	7.6216	0.9527	0.000221346
Langmuir	8	5.8443	0.7305	0.04037448
Temkin	8	7.8456	0.9807	7.31457×10^{-5}
Dubinin–Radushkevich	8	7.9178	0.9897	4.55364×10^{-5}
Florry–Huggins	8	4.2724	0.534	0.145411671
BET	8	4.352	0.544	0.127413246
Blank (63 μm)	6	4.4819	0.7469	0.109286806
HCl (63 μm)	6	4.4105	0.7351	0.13631491
H_2SO_4 (63 μm)	6	4.3673	0.7279	0.128919606
H_3PO_4 (63 μm)	6	5.5762	0.9294	0.021910899
Blank (150 μm)	6	4.5602	0.7600	0.118195447
HCl (150 μm)	6	4.6218	0.7703	0.113576572
H_2SO_4 (150 μm)	6	4.1656	0.6943	0.094809551
H_3PO_4 (150 μm)	6	5.6702	0.9450	0.012444539

Source of variance	Degree of freedom	Sum of squares	Mean sum of squares	F_{cal}	F_{tab}
b					
Biomass	7	0.375713135	0.053673305	1.032711	2.28523517
Isotherm	5	1.858228799	0.37164576	7.150716	2.48514322
Error	35	1.819062839	0.051973224		
Total	47	4.053004773			

done to know about model fitted mostly to experimental data. This method describes the relationship between the isotherm models in describing the sorption systems and between the biomasses for metal ion removal. The summary of the statistical analysis is presented in Table 2a and b. By considering Table 2a, it is clear that Dubinin–Radushkevich isotherm model provides a better fit for the sorption systems because of larger values of sum, average and smaller values of variance of correlation coefficients. Also, it is clear in case of H_3PO_4 modified biomass that sum and average of correlation coefficients for this biomass are large but variance is small (Table 2a). So, H_3PO_4 modified biomass showed remarkable increase in sorption capacity. However, the results of ANOVA (Table 2b) indicate that there is no significant difference among the biomasses for sorption. This indicates that all biomasses can remove metal ions from aqueous solutions. Experimental results also showed that Dubinin–Radushkevich isotherm model is more favorably suitable to explain the sorption phenomena.

3.4. Kinetic study

The kinetic profiles of Pb (II) biosorption by *C. arientinum* biomass are shown in Fig. 4. The biosorption of Pb (II) onto *C. arientinum* biomass was very slow with 6.269% removal within first 20 min. Equilibrium was attained within 7 h. It is well known fact that rapid initial sorption is due to extracellular binding and slow sorption results from intracellular binding [30–32]. In this study, slow sorption may be due to intracellular binding. Saeed et al. [33] studied removal and recovery of lead (II) from single and multi-metal (Cd, Cu, Ni, Zn) solutions by black gram husk and reported that sorption rate was very rapid and equilibrium was attained within 30 min. In this study, pretreatment of biomass by H_3PO_4 leads to slow sorption. Although pretreatment caused changes in active sites of biomass that led to slow sorption but pretreatment enhanced sorption capacity of biomass. Shreedhara and Ryan [34] investigated mercury, cadmium, copper, lead and uranium adsorption on cellulose–dithiocarbamate resins and reported that the adsorption rate was very slow. Actually, there are several parameters which affect biosorption rate. These parameters include stirring rate of aqueous phase, the amount of sorbent, the structural properties of biosorbent, the presence of co-ions and the properties of ion under study. Therefore, it is possible that biosorbents vary in their removal rates of metal ions.

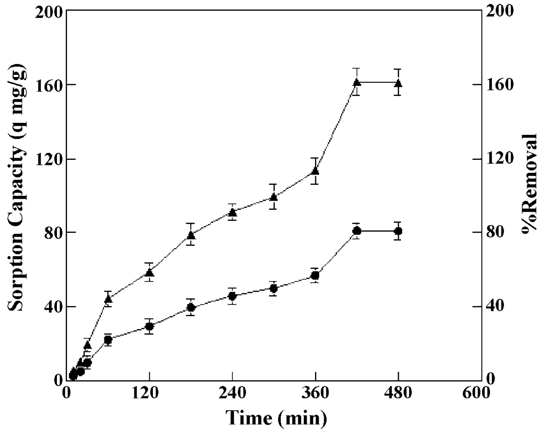

Fig. 4. Effect of time interval on the biosorption of Pb^{2+} (sorption capacity q, ▲ and % removal, ●) by H_3PO_4 modified biomass.

3.5. Kinetic modeling

Kinetics of metal sorption governs the rate that determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent. Sorption kinetics can be controlled by several independent processes that could act in parallel or in series such as external mass transfer (film diffusion), bulk diffusion, intraparticle diffusion [35] and chemisorption (chemical reaction). Film transport is diffusion of heavy metals through boundary around biosorbent [36] whereas bulk diffusion is transport of metal ions in solution [37]. Chemisorpion is chemical reaction between active sites of biomass and heavy metal ions [36] and intraparticle diffusion is diffusion of metals from surface to internal sites [38]. Kinetic equations have been developed to explain the transport of metals onto various adsorbents (Fig. 5). These equations include the pseudo-first-order equation [39], the pseudo-second-order equation [40], the elovich equation [38,41], intraparticle diffusion model [42], saturation (mixed order) model [43], second-order rate equation model [43] and bangham model [44]. The pseudo-first-order is given by

$$\log(q_e - q) = \log\, q_e - \frac{k_{1,\mathrm{ads}} t}{2.303} \qquad (8)$$

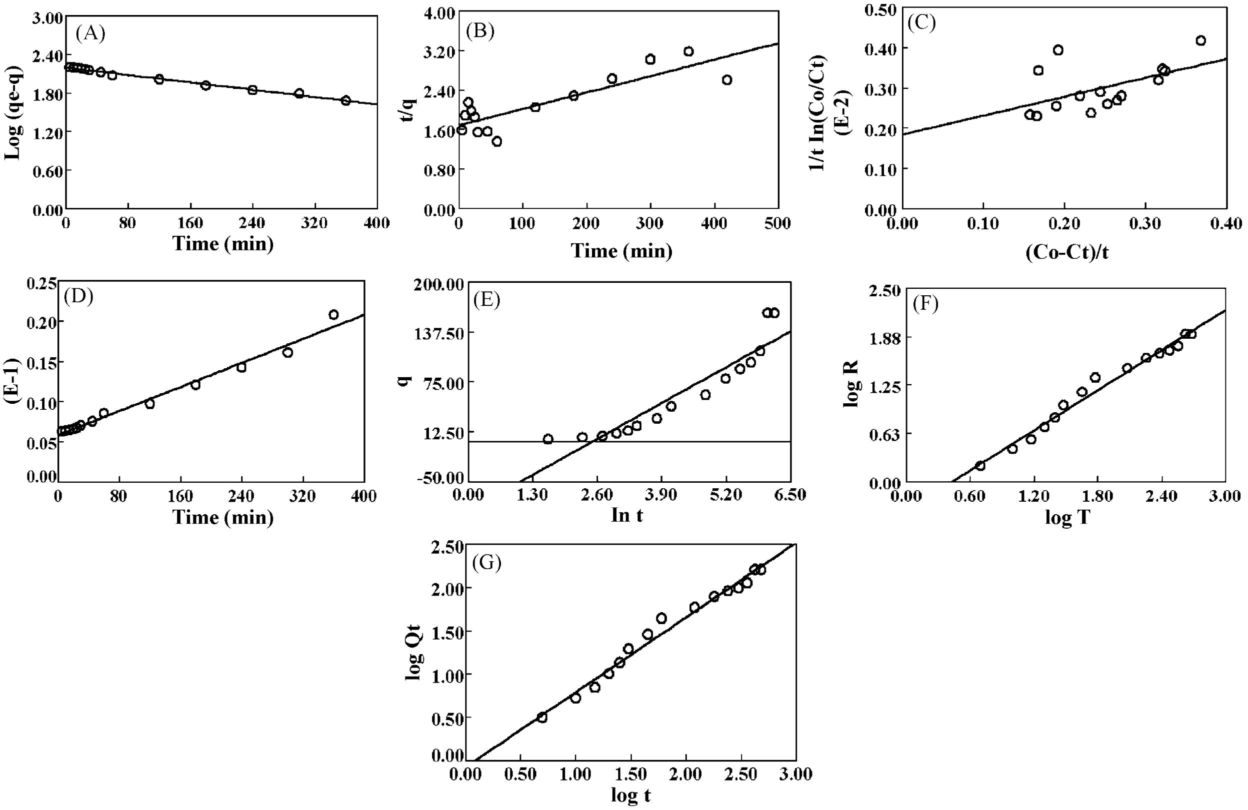

Fig. 5. Kinetic study of Pb^{2+} biosorption by linear plots of (A) pseudo-first-order (B) pseudo-second-order (C) saturation (D) second-order rate equation (E) Elovich (F) intraparticle diffusion and (G) Bangham models using H_3PO_4 modified biomass.

where q_e (mg/g) and q (mg/g) are the adsorption capacities at equilibrium and at time t, respectively, $k_{1,\mathrm{ads}}$ is the rate constant of pseudo-first-order adsorption (min^{-1}). $k_{1,\mathrm{ads}}$ and q_e can be determined from slope and intercept, respectively.

The pseudo-second-order reaction kinetic is expressed as

$$\frac{t}{q} = \frac{1}{k_{2,\mathrm{ads}} q_e^2} + \frac{t}{q_t} \tag{9}$$

where $k_{2,\mathrm{ads}}$ is the rate constant of pseudo-second-order adsorption (g/(mg min)) and q_e is the adsorption capacity at equilibrium (mg/g).

The saturation (mixed order) model is given as

$$\frac{1}{t}\ln\frac{C_0}{C_t} = -\frac{k_0}{K} - \frac{1}{K}\left(\frac{C_0 - C_t}{t}\right) \tag{10}$$

where C_0 and C_t are the concentrations of metal ion (mg/L) at $t = 0$ and at any time, respectively. k_0 (L/(g min)) and K (L/mg) are saturation rate constants of adsorption.

Second-order rate equation is expressed as

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k^0 t \tag{11}$$

where q_e and q_t are the amounts of metal ion sorbed at equilibrium and at any time (mg/g), respectively whereas k^0 is second-order rate constant of adsorption (g/(mg min)).

Bangham model is given as

$$\log\, Q_t = \log K_r + \left(\frac{1}{m}\right)\log t \tag{12}$$

where K_r (mg/(g min)) and $1/m$ are the sorption rate constants. A larger value of K_r depicts the suitability of biosorbent for metal removal and $1/m$ tells that kinetic was applicable to sorption phenomena up to this extent.

Elovich model is described as

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{13}$$

where α is initial adsorption rate (mg/(g min)), β is the desorption constant (g/mg).

The intraparticle diffusion model proposed by Webber and Morris [42] is expressed as

$$\log\, R = \log K_{\mathrm{id}} + a(\log t) \tag{14}$$

where R is % removal, t is contact time, a is gradient of linear plot and it depicts the adsorption mechanism, K_{id} is intraparticle diffusion rate constant (min^{-1}) and can be written as rate factor which describes about percent heavy metal adsorbed per unit time. Comparison of various kinetic model parameters is tabulated in Table 3. The Lagergren pseudo-first-order rate constant ($k_{1,\mathrm{ads}}$) and q_e determined from model along with correlation coefficient indicated that q_e is very close to q_{exp} and correlation coefficient is also greater than 0.98. It suggests that adsorption was a first-order reaction. Pseudo-second-order rate constant ($k_{2,\mathrm{ads}}$) and q_e values determined from pseudo-second-order model suggested that sorption rate cannot be explained by pseudo-second-order reaction. q_e differs substantially from those measured experimentally and correlation coefficient is also less than measured in case of pseudo-first-order model. Value of $k_{2,\mathrm{ads}}$ is less than $k_{1,\mathrm{ads}}$ suggesting that pseudo-first-order reaction can explain sorption rate. The second-order rate equation described the biosorption kinetic of Pb (II) with high correlation coefficient ($R^2 = 0.9913$) and q_e was also close to q_{exp} whereas saturation and elovich models were unable to explain the sorption rate because of correlation coefficient ($R^2 < 0.98$). In elovich model, α is related to rate of chemisorption (initial adsorption rate) and β is related to surface coverage (desorption constant). Elovich model describes about heterogeneous sorption and a small value of β tells

Table 3
Kinetic model parameters for the biosorption of Pb (II) using H_3PO_4 modified *C. arientinum* pod biomass.

Kinetic models	Kinetic parameter values			
Pseudo-first-order model	$k_{1,ads}$ (min^{-1}), 3.298×10^{-3}	q_e (mg/g), 156.91	R^2, 0.9948	
Pseudo-second-order model	$k_{2,ads}$ (g/(mg min)), 6.569×10^{-6}	q_e (mg/g), 300.66	R^2, 0.8507	
Saturation model	K (L/mg), 212.31	k_0 (L/(g min)), 0.3911	R^2, 0.5275	
Second-order rate equation model	k^0 (g/(mg min)), 4×10^{-5}	q_e (mg/g), 171.09	R^2, 0.9913	q_{exp} (mg/g), 161.42
Bangham's model	K_r (mg/(g min)), 0.8401	m, 1.156	R^2, 0.9905	
Elovich model	α (mg/(g min)), 2.836	β, 0.0289	R^2, 0.9324	
Intraparticle model	a, 0.8652	K_{id} (min^{-1}), 0.4212	R^2, 0.9905	

that model is unable to explain heterogeneous surface of biomass. A slow sorption rate and small value of constant α tells that no chemisorption reaction occurred. Hence this model cannot provide an accurate fit to experimental data. Bangham assumption tells that biosorption of Pb (II) followed the $(1/m)$th order sorption rate and constant K_r was 0.8401 (mg/(g min)). Although, value of K_r is small but value of R^2 tells that mechanism told by Bangham was also involved during description of sorption rate. Value of a gives an idea about the thickness of boundary layer, i.e., the larger the intercept (a) value, the greater will be the boundary layer effect [45]. K_{id} is rate factor i.e., percent heavy metal adsorbed per unit time and its value tells that percent heavy metal adsorbed was 0.4212 per unit time. The linearity of this plot ($R^2 = 0.9905$) describes the involvement of intraparticle diffusion during this study up to some extent. Since several independent processes can describe kinetics, therefore applicability of more than one independent sorption rate mechanisms is not a problem.

3.6. Effect of pH

It is well known that sorption of heavy metal ions by solid substrates depends on the pH of the solution. Fig. 6. shows that uptake capacity and % removal of Pb (II) by *C. arientinum* decreased with increase in pH. It is generally known that at low pH values of 1–3, solution is strongly acidic and the surface of the sorbent is surrounded by hydrogen ions, which prevent the metal ions from approaching the binding sites on the sorbent. Due to this reason, it is thought that sorption capacity increases with increase in pH. But it is important that during this study, minimum pH for solution media was 4 and a pH of 4 is not strongly acidic but slightly acidic. At pH value of 4, metal ions can easily compete hydrogen ions and bind active sites of biosorbent. Due to this reason, sorption capacity and % removal was high at pH 4. At pH 7 and 9, sorption capacity and % removal decreased and this decrease can be explained by the fact that at higher pH, number of hydroxyl ions is more and chances of formation of metal hydroxides are also more that result in precipitaion. This precipitaion caused a decrease in sorption capacity and % removal with increase in pH.

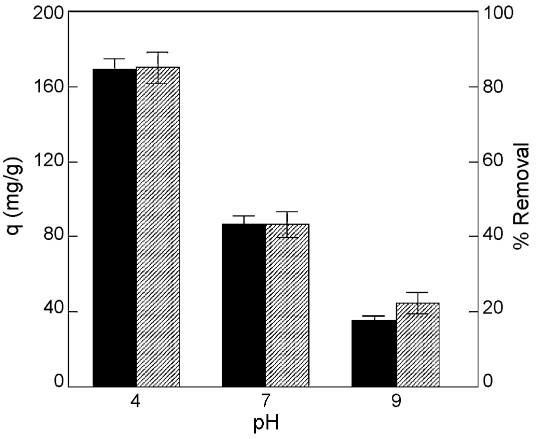

Fig. 6. Effect of pH on the biosorption of Pb^{2+} (q values: ■ % removal: ▨) by H_3PO_4 modified biomass.

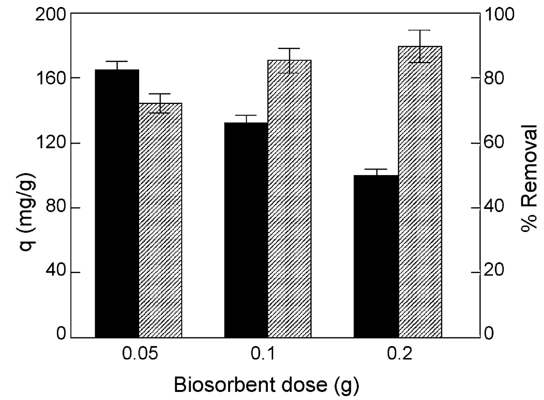

Fig. 7. Effect of biosorbent dose on the biosorption of Pb^{2+} (q values: ■ , % removal: ▨) by H_3PO_4 modified biomass.

3.7. Effect of biosorbent dose

Biosorption is dependent largely on biosorbent dose. Effect of biosorbent dose was studied using H_3PO_4 pretreated *C. arientinum* biomass having 150 μm sieved particle size added to 100 mL of 100 mg/L of Pb^{2+}. A biosorbent dose of 0.05, 0.1 and 0.2 g having mentioned particle size was used to evaluate the effect of biosorbent dose. Fig. 7 shows that with increase in biosorbent dose, sorption capacity decreases but percentage removal increases. A similar behavior was shown by work done by Abu Al-Rab et al. [46]. They observed that during work on biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions, sorption capacity decreases but % removal increases with increase in biosorbent dose. The decrease in metal uptake by increasing sorbent dose may be due to many reasons, such as, electrostatic interactions, interference between binding sites, availability of solute and reduced mixing at high biomass densities [47,48]. It is concluded that because of lower adsorptive capacity of the sorbent, the adsorbent active sites remain unsaturated during the sorption process and due to this, sorption efficiency decreases. Some of these reasons also contribute in limiting the maximum percentage removal and due to this 100% removal was not attained.

4. Conclusion

This study investigated the use of acidically modified *C. arientinum* biomass for the removal of lead (II) from aqueous solutions. Pretreatment enhanced the biosorption capacity of biomass and H_3PO_4 treated biomass showed maximum sorption capacity. The sorption capacity increased in the order $H_3PO_4 > H_2SO_4 > HCl >$ native, with increase in metal concentration and % removal was maximum at 100 mg/L and then decreased. Sorption rate was very slow and equilibrium was attained within 7 h. In case of equilibrium study, Dubinin–Radushkevich isotherm plot was found in better correlation with experimental data. Sorption rate was best explained by pseudo-first-order, second-order rate equation, bangham and intraparticle diffusion models because sorption kinetics can be described by several independent processes that could act in parallel or in series. When evaluated the effect of biosorbent dose, sorption capacity decreased but % removal increased with increase in biosorbent dose. At pH 4, maximum sorption capacity (169.23 mg/g) was attained.

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