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Removal of Cd(II) and Cu(II) from aqueous solution using Bengal gram husk as a biosorbent

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ABSTRACT

In the present work, *Cicer arietinum* husk (Bengal gram husk BGH) has efficiently been utilized for the removal of Cd(II) and Cu(II) from aqueous solutions. Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction and proximate analysis were used to analyse the biosorbent. Batch experiments were conducted to analyse as well as to evaluate the sorption capacity of metal ions. Factors affecting metal ions adsorption, such as contact time, pH, concentration ranges and adsorbent doses were studied. Maximum sorption of Cu(II) was found at pH 5, while for Cd(II), it was achieved at pH 7. From FTIR and NMR results, it has been found that in BGH, –OH group was present in abundance, and participated in metal complex formation in the sorption experiments. The biosorption process was fast enough because equilibrium reached at 120 min, following pseudo-second-order kinetics. The biosorption data fitted well in the Langmuir isotherm model, indicating the monolayer sorption. The maximum biosorption capacity of BGH, using Langmuir adsorption plots has been determined as 8.58 and 9.70 mg g^{-1} for Cd(II) and Cu(II), respectively.

Keywords: Biosorption; Bengal gram husk; Isotherms; Kinetics; Cadmium; Copper

1. Introduction

Nowadays, environmental pollution has become the major threat to the living organism. Although the industrialization has played a significant role in development, but simultaneously released large quantities of chemicals, particularly heavy metals, causing potential harm to many ecosystems [1]. The wastewater released from various industries containing toxic metals like Cd, Pb, Cu, Zn, Ni and Cr is discharged into the water bodies and aquatic environment, thus threatened the biolife. Presence of toxic metal ions in the ecosystem is of the greatest concern because of their bioaccumulation, directly or indirectly, through food chains [2]. The heavy metals accumulation in human bodies leads to damage of many organs, even at very low concentrations. For instance, the excess amount of cadmium intake causes high blood pressure, kidney and liver damage [3], while excess intake of Copper causes stomach and intestinal suffering, liver and kidney damage, anaemia and mental diseases [4,5]. Similarly, presence of excess amount of these metals causes harmful effect on animals, fishes and other aquatic life too. For a given heavy metal, a tolerance limit has been prescribed by various regulating agencies. For example, the United States Environmental Protection Agency has fixed the

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maximum contamination level (or tolerance limit) for various heavy metals in water which is 0.01 and 0.25 mg L^{-1} for Cd and Cu, respectively [6], above which they cause detrimental effect to human health as well as to aquatic life, therefore their removal from ecosystem is extremely important.

Though, a number of techniques, such as chemical precipitation, reverse osmosis, ions exchange, coagulation and flocculation, solvent extraction, membrane separation and adsorption using activated carbon and minerals have been used in the past. However, these techniques are either costlier or less effective below 100 mg L^{-1} concentration of metal ions [7,8]. Biosorption has been emerged as an effective process for removal of toxic metal ions because they are not only cheaper and easily available, but effective, for very dilute solution, even for trace amount of metal ions, too [9]. In the process of biosorption, unique surface chemistry involves, in which biomaterials interact with dissolve species in the liquid, where adsorption, complexation, ion exchange or chemisorption takes place. Heavy metals present in the solution may bind with various organic functional groups present in biomass like ketone, hydroxyl/phenolic, carboxyl, etc., while many physicochemical parameters, like temperature, solution pH, metal ion concentration, adsorbent dose and contact time affect the extent of metal ion uptake.

Among the various sources biological wastes, both dead and living biomass have shown interesting metal binding capacity [10]. However, removal of toxic metal ions using living biomass has limitation because their growth is inhibited in presence of excess amount of toxic metal ions [11]. In view of above, the use of dead biomass, e.g. agricultural by-products is beneficial because they are easily available and cheap; therefore, they can be used at large scale. Moreover, the added advantages of agricultural by-products, over convention biosorbents include their high efficiency, low cost, minimization of sludge and regeneration of biosorbents as well as metals [12,13]. Variety of agricultural wastes and by-products have widely been used for the elimination of toxic metals [14–27]; however, exploration and exploitation of new agricultural by-products have still been developing continuously and endlessly.

Bengal gram (*Cicer arietinum*) is cultivated in almost every part of India. Large amount of Bengal gram husk (BGH) is produced from dhal (pulse)-producing mills, which is consumed by domestic animals in some part of India, while large amount is dumped in the soil as waste material. BGH is composed of crude protein, crude fibre, lignin, tannin, hemicelluloses, cellulose, silica and other inert metal oxides [28–30]. Recently, Reddy et al. successfully used BGH for removal of dyes from aqueous solution [31,32]. Ahalya et al. reported the removal of Cr(VI) from aqueous solution applying the Langmuir and Freundlich isotherm models [33]. Though the above studies done in the past reported metal ions and dyes uptake capacity applying the various isotherms, kinetics and varying the experimental parameters, however, role of biosorbent composition on uptake of different metal ions require further exhaustive study.

Hereunder, in the present investigation, BGH has been used for removal of Cd(II) and Cu(II) from aqueous solutions and role of organic and inorganic constituents of sorbent on metal ions uptake has been explored.

2. Materials and methods

2.1. Preparation of adsorbent

BGH, the seed coat of Bengal gram, was collected from local dhal production mill. The BGH was washed with distilled water four–five times to remove dust and other extra useless adhering particles and dried at room temperature. After few days, it was dried in oven at 80˚C for 1 h. The dried husk was grinded in powder form in an electric grinder and sieved in the mesh size below 155 μm. The sieved powder was used for biosorption experiments.

2.2. Physicochemical characterization of adsorbent

X-ray diffraction (XRD) pattern of the adsorbent was carried out on Panalytical’s X’Pert Pro X-ray diffractometer in 2θ range 10˚–100˚ using Cu Kα radiation in step sizes of 0.02˚ ($d = 1.541$ Å). Fourier transform infrared (FTIR) spectrum of the biosorbent and metal ions-adsorbed biosorbent was recorded using 4100 JASCO, Japan. Nuclear magnetic resonance (NMR) spectrum of the biosorbent was recorded on AV500 instrument.

Proximate analysis (percentage of volatile matter, moisture, fixed carbon and ash content) of the biosorbent BGH was done following standard procedure given in “Vogel’s Text book of Quantitative Chemical Analysis”, 5th edition, Batch Press Ltd., UK and the result is listed in Table 1.

2.3. Reagents

All the chemicals used in this investigation were of analytical reagent grade. Deionized water was used to prepare all solutions. Standard stock solutions of Cd (II) and Cu(II) were prepared by dissolving suitable amounts of $CuCl_2{\cdot}2H_2O$ and $Cd(CH_3COO)_2{\cdot}2H_2O$

Table 1
Proximate analysis data of BGH

S. No.	Component	%
1.	Moisture	4.3
2.	Volatile matter	26.4
3.	Fixed carbon	60.6
4.	Ash content (oxides of various metals (Si, Al, Mn, Fe etc.))	8.7

(purchased from Fisher Scientific) in desired amount of deionizer water to get 1,000 mg L^{-1} Cd(II) and Cu(II) solutions. The stock solutions were diluted by adding desired amount of deionizer water to make the solutions of the required concentration for the experiments.

2.4. Batch adsorption studies

In the present investigation, batch mode operations were performed in order to evaluate the adsorption process. The Batch experiments were done at room temperature (25 ± 1˚C) in 250 mL stoppered conical flask containing 50 mL test solutions. In adsorption pH, contact time as well as for adsorption isotherm experiments, 1 g of adsorbent was mixed with 50 mL of Cd(II) and Cu(II) solutions. pH of the solutions was adjusted by adding suitable amount of 0.1 M HCl and 0.1 M NaOH solutions. After mixing the biosorbent to test solution, the flasks were shaken for a desired contact time in an electrically thermostated reciprocating shaker at 150 rpm. In order to obtain the equilibrium, an aliquot of solution was withdrawn after a regular time interval, centrifuged and analysed for remaining Cd(II) and Cu(II) by Atomic Absorption Spectrophotometer (AA 6300; Shimadzu). The amount of biosorption was calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

The biosorption efficiency, A %, of the metal ion was calculated from:

$$A\ (\%) = \frac{(C_0 - C_e)V}{C_0} \tag{2}$$

Where C_0 and C_e are initial and equilibrium metal ion concentrations (mg L^{-1}), respectively, V is the volume of solution (L) and m is the amount of biosorbent (g). All the adsorption experiments were performed in duplicate, and the mean values were reported.

3. Results and discussion

3.1. FTIR spectroscopy

FTIR spectroscopy is known to be an importance tool for elucidating functional groups present in particular biosorbent. The pattern of sorption of metal ions can be predicted by presence of active organic functional groups and bands present on them [34]. The infrared spectral assignment of BGH was obtained by KBr disc method. The spectral pattern is shown in Fig. 1(a) and the position of different bands and their assignments are given Table 2. The broad and strong peak at 3,409 cm^{-1} is corresponding to O–H stretching vibration of cellulose, hemicellulose and lignin and due to –NH group. The peak observed at 2,923 cm^{-1} is assigned due to C–H stretching vibration of methyl and methoxy groups of cellulose, hemicellulose and lignin. Peak centred at 1,642 cm^{-1} has readily been assigned as C=O stretching, conjugated with –NH deformation mode, thus indicating presence of amide group [33]. The trough at 1,374 cm^{-1} is assigned to –N–H stretching vibration; while peak at 1,152 cm^{-1} is corresponding to –CO and –CN stretching vibrations. The peak between 650 and 850 cm^{-1} correspond to –N–H bending and at 1,243 cm^{-1} corresponds to –C–N

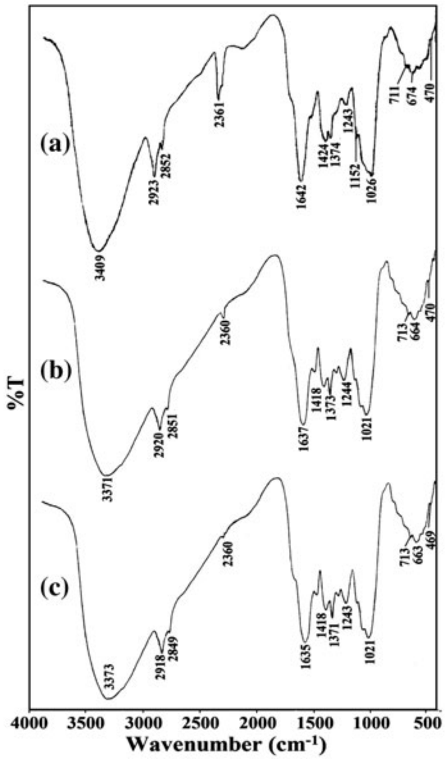

Fig. 1. FTIR spectrum of (a) adsorbent BGH, (b) Cd(II)-adsorbed BGH and (c) Cu(II)-adsorbed BGH.

Table 2
Important FTIR peaks and their assignment in adsorbent BGH, Cd(II)-adsorbed BGH and Cu(II)-adsorbed BGH

		Peak position (cm^{-1})		
S. No.	Modes of vibration	Pure BGH	Cd(II)-adsorbed BGH	Cu(II)-adsorbed BGH
1.	–OH stretch, –NH stretch	3,409	3,371	3,373
2.	–CH stretch strong	2,923	2,920	2,918
3.	–C=O stretch (strong), amide	1,642	1,637	1,635
4.	–N–H stretch (strong)	1,374	1,373	1,371
5.	–C–O, –C–N	1,152	1,152	1,151

linkages, indicating the presence of amide group which forms chelate complex with metal ions. From the FTIR results, it is therefore obvious that the biomass BGH has hydroxyl groups in abundance which may act as proton donor, and may be involved in coordination with metal ions.

In the FTIR spectra of Cd(II)- and Cu(II)-adsorbed BGH (Fig. 1(b) and (c)), the peak corresponding to O–H stretching has been shifted to 3,371 and 3,373 cm^{-1}, respectively. The C=O stretching vibration corresponding to amide has slightly been shifted at 1,637 and 1,635 cm^{-1} in Cd(II) and Cu(II) BGH, respectively. The significant shift of O–H stretching vibrations in metal ions-adsorbed BGH indicates the change of hydroxide group to hydroxide ion during biosorption. FTIR results therefore reveal that the hydroxide group is the predominant contributor in metal ions removal.

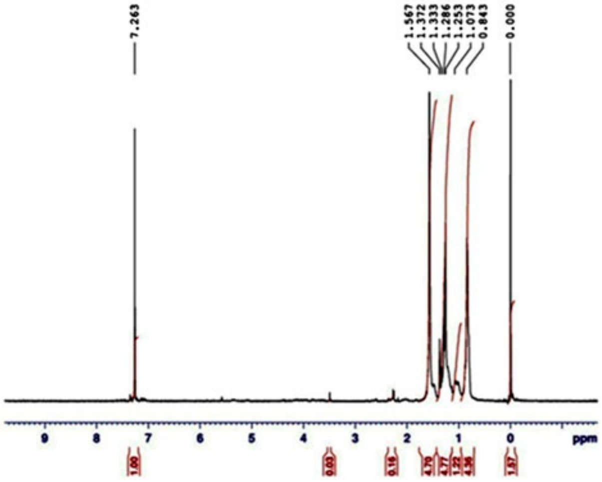

Fig. 2. ^{1}H NMR spectrum of BGH.

3.2. NMR spectroscopy

^{1}H NMR spectrum of biosorbent BGH was recorded by dissolving powdered husk in DMSO-d6 which is shown in Fig. 2. NMR spectrum was recorded in order to find out the presence of the proton and hydroxyl group. The resonance at 1.0–1.57 indicates the presence of hydroxyl group. It increases the adhering forces for the metal ions. The presence of –OH group increases the rate for metal ion adsorption.

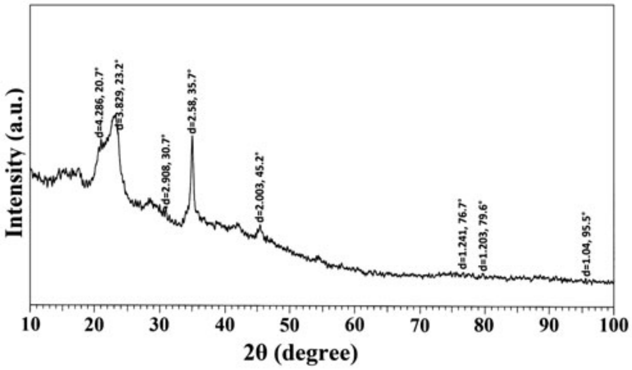

Fig. 3. XRD pattern of BGH.

3.3. X-ray diffraction

XRD pattern of powdered BGH (Fig. 3) was recorded in order to determine phase and crystallinity of biosorbent. Presence of sharp peaks in the XRD pattern indicates that, apart from organic constituents, BGH is also composed of inorganic crystalline materials. The peaks of XRD pattern match well with crystalline silica (tridymite form of silica) [35]. Although tridymite form of silica crystallizes at high temperature (814–1,470°C), however, in the flux of alkali ions, it exists at room temperature too [36]. It is therefore expected that powdered BGH contains sufficient amount of silica, mineralized with other metals (may be in form of oxides).

It is supposed that the organic components of BGH, like cellulose, hemicellulose, lignin, protein, etc. are immobilized in silica matrix, which acts as support, increase the binding sites, control the particle's size and opens the scope for regeneration and reuse of biomass [37].

3.4. Effect of pH

In order to study the effect of pH on the biosorption of Cd(II) and Cu(II) ions, the sorption experiments were conducted at room temperature in the pH range 2–9 by adding 0.1 M HCl and 0.1 M NaOH solutions. pH of the sorbent media has the paramount importance on the sorption capacity, since it determines the surface charge of adsorbent, the degree of ionization and speciation of adsorbate, which ultimately affect the adsorption capacity [38]. Fig. 4 shows the percentage of Cu(II) and Cd(II) adsorption by BGH as a function of pH. Adsorption of Cu(II) is minimum at pH 2, increases with increasing pH, reaches maxima at pH 5 and decreases continuously from pH 5 to 9. In general, in acidic media, the percentage adsorption of Cu(II) is greater than that of Cd(II) ions. At lower pH, the H^+ ions are preferentially adsorbed on the biosorbent surface, since they have higher concentration and higher mobility. Due to preferential adsorption of H^+ ions, biosorbent surface becomes positively charged, thus reducing interaction between biosorbent and positively charged metal ions. On increasing the pH, the concentration of H^+ ions decreases, therefore Cu(II) uptake increases, and maxima attains at pH 5, because of greater concentration of negatively charged ligand available for metal sorption. FTIR results reveal that the biosorbent BGH contains –OH group in abundance, due to presence of cellulose, hemicelluloses, lignin and tannin [28], which is supposed to be the main ligand for M(II)-biosorbent interaction. However, in the acidic medium, at pH 5, probably phenolic –OH of tannin participates in bonding with Cu(II) ions, making Cu(II) chelate complex. It is reported that the BGH contains sufficient amount of tannin [29], having phenolic –OH groups, conjugated with –C=O groups in vicinity, at the aromatic ring, making phenolic –OH more acidic. Therefore at pH around 5, deprotonation of phenolic –OH takes place, which interact with Cu(II) ions to make chelate complex, consequently, Cu(II) uptake increases. In case of Cd(II) ions, the similar trend of metal uptake has been observed (Fig. 4), the lowest adsorption found at pH 2, increases with increase in pH, attain maxima at pH 7, thereafter deceases from pH 7 to 10. The difference in adsorption maxima is probably due to pH-dependent speciation of Cd(II) ions. Cavallaro and McBride [39] demonstrated that Cu(II) is hydrolyzed beyond pH 5 (completely around pH 6) while Cd(II) does not hydrolyze until pH 8. It is expected that Cu(II) species is predominant at pH around 5 and that of Cd(II) it is 7, and therefore maximum uptake of Cu(II) and Cd(II) takes place at pH 5 and 7, respectively. At higher pH, the Cu(II) and Cd(II) ions have been precipitated as hydroxides, decreasing the rate of adsorption and subsequently percentage removal of metal ions decreased.

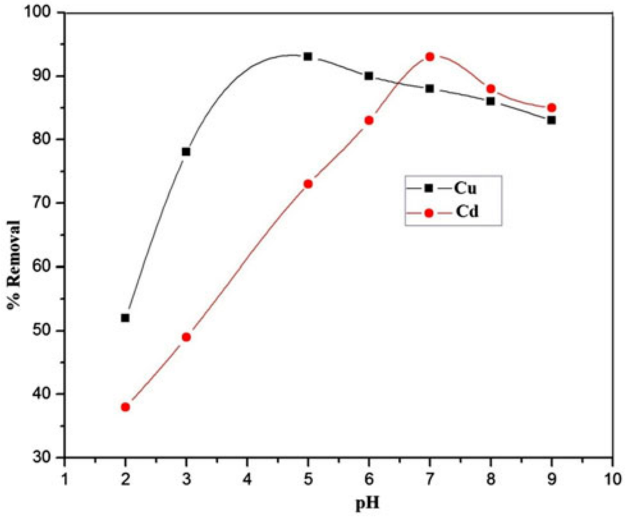

Fig. 4. Effect of pH on adsorption of Cu(II) and Cd(II) onto BGH: 1 g BGH mixed with 50 mL of 100 ppm solutions at room temperature.

3.5. Effect of contact time

In order to evaluate the amount of Cd(II) and Cu(II) uptake with time, a series of experiments were performed taking four Cd(II) and Cu(II) concentrations viz.; 200, 150, 100 and 75 ppm. The pH of solutions was maintained at 7 for Cd(II) and at 5 for Cu(II) sorption. The experiments were performed in the time interval of 10 min up-to 130 min at room temperature. The extent of metal ions adsorption increased rapidly when experiment commenced, while it became slow later till equilibrium attained. The uptake of Cd(II) were 15.4, 13.0, 9.2 and 7.2 mg g^{-1}, respectively, while in case of Cu(II) ions, the uptake was found to be 16.8, 13.6, 9.3 and 7.3 mg g^{-1} from 200, 150, 100 and 75 ppm sorbate solutions (Fig. 5). The equilibrium time for both the ions was 120 min for all four concentrations. From the curves, it is inferred that the equilibrium time was independent of initial metal ions concentration. Further, the

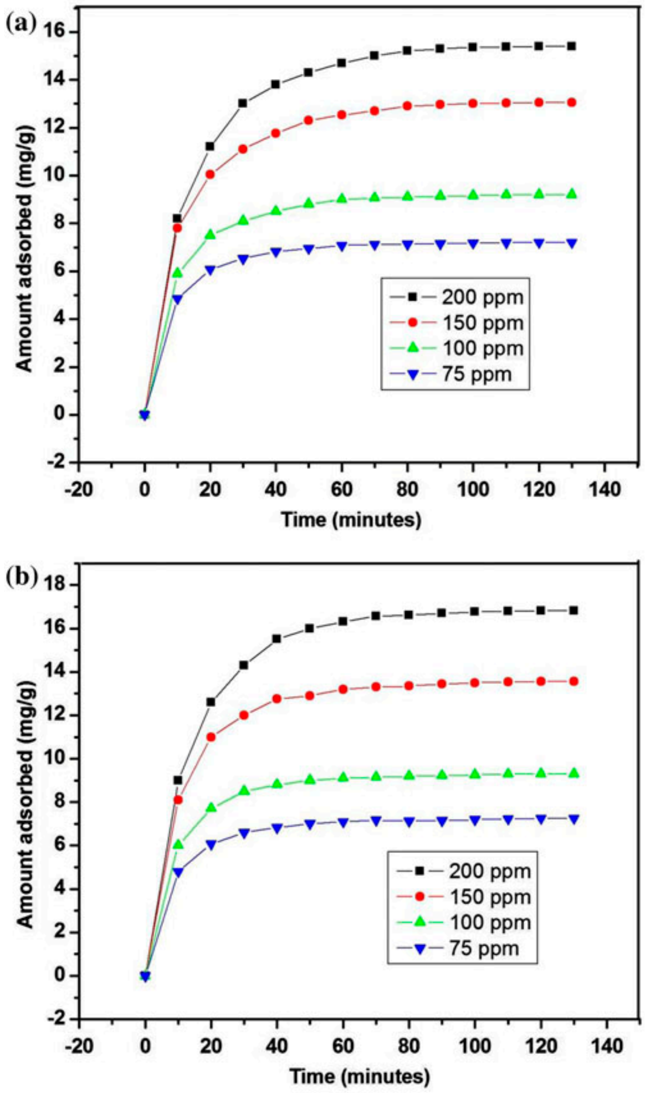

Fig. 5. Effect of contact time and initial metal ions concentration on adsorption for (a) Cd(II) and (b) Cu(II). (Conditions: pH 5 for Cu(II) and 7 for Cd(II); room temperature.)

observance of single smooth continuous curves indicates the formation monolayer of adsorbate at the adsorbent surface [11].

3.6. Adsorption isotherm

In order to understand the sorption mechanism and surface behaviour, Langmuir and Freundlich isotherms models were tested for the observed data. In the Langmuir isotherm, it is assumed that surface of sorbent is composed of finite number of biding sites, homogeneously distributed over the surface. All the sorption sites have equal sorbet affinity and the adsorption at one site does not affect sorption at an adjacent cite [40] by the following equation

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{3}$$

where C_e is the equilibrium concentration (mg L^{-1}) of metal ions in the bulk solution, q_e the amount of metal ions adsorbed per unit weight of sorbent at equilibrium (mg g^{-1}), Q^0 (mg g^{-1}) and b are the Langmuir constants, showing the monolayer sorption capacity and energy of sorption respectively.

The Freundlich isotherm describes the equilibrium at heterogeneous surface and does not assume monolayer formation. The equation in the linear for can be represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where n and K_F are Freundlich isotherm constants, indicating intensity of sorption and relative sorption capacity of sorbent, respectively. The values of n and K_F can be computed from the slope and intercept of the log q_e vs. log C_e plots.

Fig. 6 presents the linear plots between C_e/q_e vs. C_e. Values of Langmuir constants Q^0 and b have been calculated from the slope and intercept of the plots (Table 3). Fig. 7 shows the Freundlich isotherm plots, log q_e vs. log C_e. The correlation coefficient values R^2 was higher for Langmuir isotherm than that of Freundlich isotherm for both the metal ions Cd(II) and Cu(II), indicating Langmuir equation fits well in the present study. The maximum biosorption capacity of BGH for Cd(II) and Cu(II) removal has been calculated using Langmuir adsorption plots, which is found to be 8.58 and 9.70 mg g^{-1}, respectively.

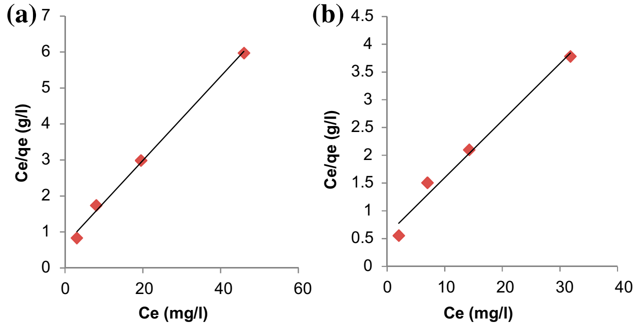

Fig. 6. Langmuir isotherm plots for (a) Cd(II) and (b) Cu(II).

Table 3
Values of Langmuir and Freundlich sorption constants for removal of Cd(II) and Cu(II). (Conditions: pH 5 for Cu(II) and 7 for Cd(II); room temperature.)

	Langmuir constants			Freundlich constants		
Metal ions	Q^0 (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
Cd^{2+}	8.58	0.178	0.9962	2.607	3.45	0.9854
Cu^{2+}	9.70	0.182	0.9812	2.799	3.18	0.9633

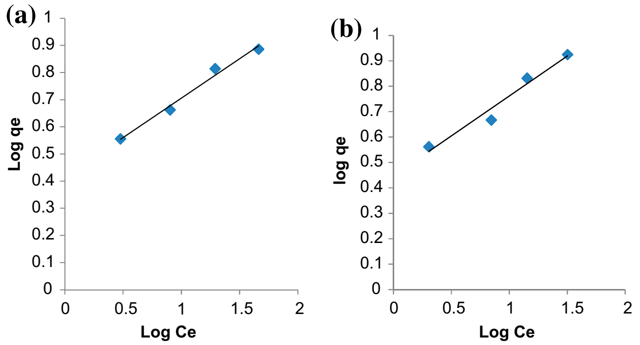

Fig. 7. Freundlich isotherm plots for (a) Cd(II) and (b) Cu(II).

3.7. Biosorption kinetics

To understand the biosorption kinetics in the batch operation, Lagergren pseudo-first-order and pseudo-second-order kinetics models have been applied to the observed data of metal ions. The Lagergren pseudo-first-order kinetics equation [41] can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

where q_e and q_t are amount of metal ions (mg g^{-1}) adsorbed at equilibrium and at time t, respectively, and k_1 is the rate constant of Lagergren pseudo-first-order biosorption (min^{-1}). The q_e and the rate constant k_1 have been calculated from the slope and intercepts of plots between log ($q_e - q_t$) vs. t, as shown in Fig. 8.

The biosorption kinetics data have also been studied by pseudo-second-order equation [42]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

$$h = k_2' q_e^2 \tag{7}$$

where k_2 is the rate constant and h is the initial adsorption rate. The rate constant and q_e values have been determined from the slope and intercept, respectively of t/q_t vs. t plots (Fig. 9). The experimental q_e values, computed q_e values, rate constants and correlation constants (R^2) values for both pseudo-first-order and pseudo-second-order equations are listed in Table 4. Though the correlation coefficient values are very high for both, pseudo-first-order and pseudo–second-order kinetics for Cd(II) and Cu(II) ions at each

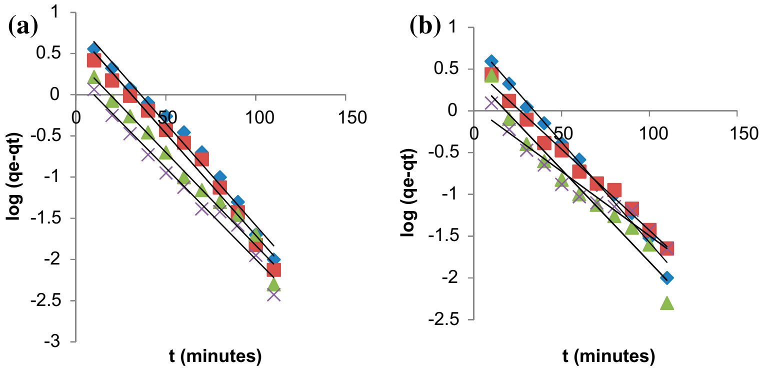

Fig. 8. Pseudo-first-order kinetics plots for (a) Cd(II) and (b) Cu(II).

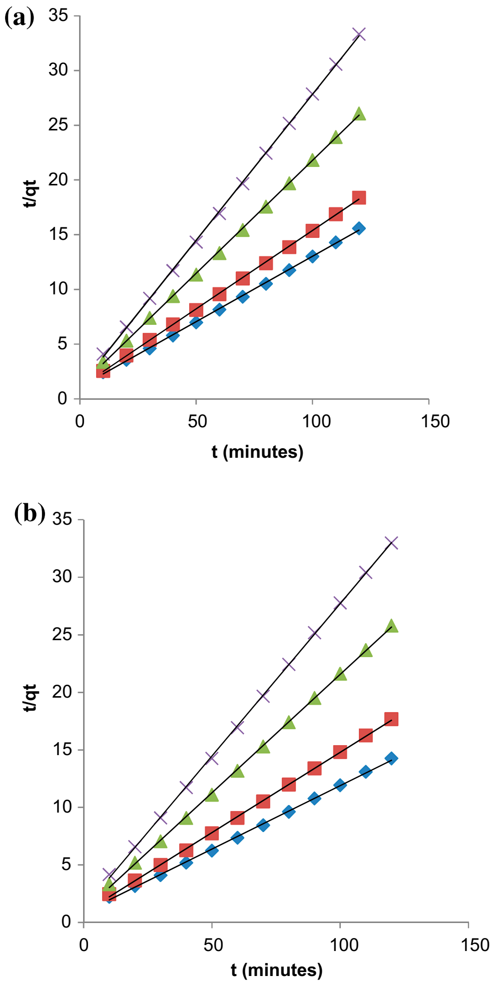

Fig. 9. Pseudo-second-order kinetics plots for (a) Cd(II) and (b) Cu(II).

concentrations, however, they are larger in case of pseudo-second-order kinetics. Moreover, it is expected that the experimental q_e values should be nearer to calculated q_e values [43]. It is obvious from that data (Table 4) that the experimental and calculated q_e values are more nearer in case of pseudo-second-order kinetics than those of pseudo–first-order model. Therefore, it has been concluded that pseudo-second-order kinetics was the suitable pathway to reach the equilibrium for both the metal ions.

3.8. Effect of adsorbent doses

In order to evaluate the effect of adsorbent dose on removal of metal ions, different doses of adsorbent viz. 0.5, 0.75, 1 and 2 g of BGH were mixed in 50 mL solutions of Cd(II) and Cu(II) metal ions. The concentration of each metal ions was 100 ppm, while the pH of Cd(II) and Cu(II) was adjusted at 5 and 7, respectively. As observed in Fig. 10, the percentage removal of Cd(II) ions increases from 55 to 93% on increasing biosorbent amount from 0.5 to 2.0 g. Similar trend is observed in case of Cu(II) ions too. The increase in percentage removal was probably due to increase in the available sorption surface sites. Further, it has been observed that there was no significant increase in removal of metal ions from 1.0 to 2.0 g of biosorbent. For each dose, a platue is reached after 120 min. Moreover, at platue, the percentage removal of metal ions reaches at the same value for both 1.0 and 2.0 g doses; therefore, it is inferred that 1.0 g of biosorbent is suitable amount to reach equilibrium for 100 ppm (50 mL) solutions of both metal ions.

Table 4
Comparison of pseudo-first-order and pseudo-second-order kinetic models for removal of Cd(II) and Cu(II) ions using BGH at different experimental conditions

			Pseudo-first-order			Pseudo-second-order			
Metal ions	Parameters C_0 (mg L^{-1})	q_e (exp.) (mg g^{-1})	q_e (calc.) (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (calc.) (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	R^2
Cd^{2+}	200 ppm	7.70	7.77	0.0571	0.9832	8.37	0.0132	0.9275	0.9994
	150 ppm	6.53	5.83	0.0569	0.9802	6.98	0.0194	0.9446	0.9997
	100 ppm	4.60	2.69	0.0521	0.9815	4.85	0.0370	0.6553	0.9997
	75 ppm	3.60	1.66	0.0507	0.9789	3.75	0.0610	0.8576	0.9998
Cu^{2+}	200 ppm	8.41	6.61	0.0553	0.9898	9.06	0.0141	1.1573	0.999
	150 ppm	6.79	3.23	0.0447	0.9882	7.16	0.0233	1.1976	0.9996
	100 ppm	4.65	2.49	0.0507	0.9502	4.86	0.4304	1.0163	0.9997
	75 ppm	3.65	1.10	0.0355	0.9524	3.78	0.5690	0.5690	0.9998

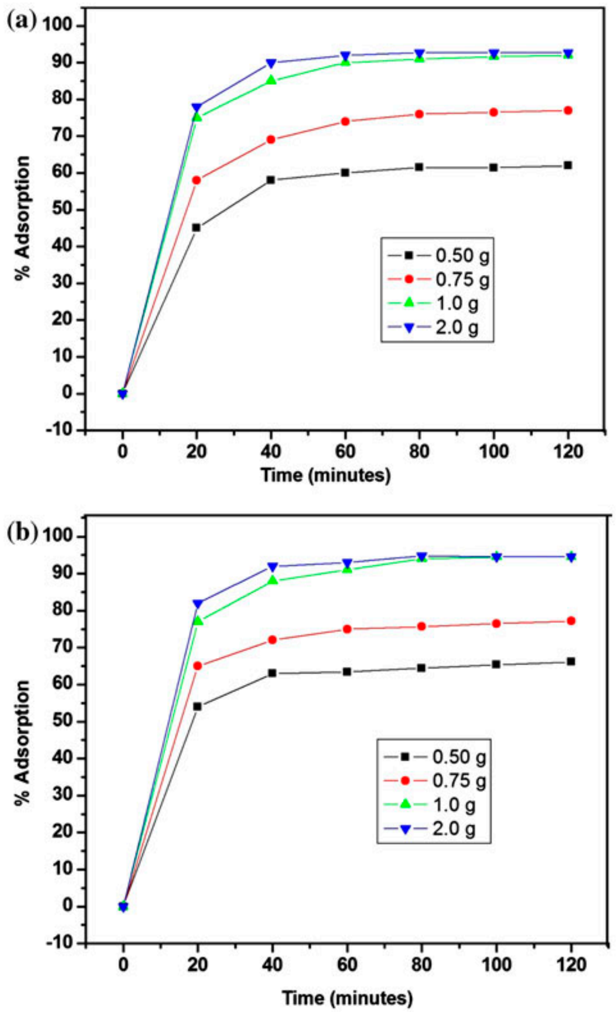

Fig. 10. Effect of adsorbent dose on adsorption of (a) Cd(II) and (b) Cu(II). (Conditions: solutions 50 mL of 100 ppm; pH 5 for Cu(II) and 7 for Cd(II); room temperature.)

4. Conclusion

In summary, the BGH has successfully and efficiently been used for removal of Cd(II and Cu(II) ions from aqueous solutions. XRD analysis revealed that, apart from organic moieties, BGH is also composed of crystalline materials, like tridymite (a crystalline form of silica), which act as support for organic components and thus, increase the binding sites. NMR and FTIR results indicate the presence and participation of hydroxyl group for metal ions uptake via M(II)-BGH complexation. Sorption of Cu(II) increases with increase in pH and reaches maxima at pH 5, since phenolic –OH of tannin is conjugated with –C=O present at adjacent position (suitable for conjugation), increasing the acidity and easing the deprotonation of phenolic H^+, thus facilitating the Cu(II) chelate complex formation. Beyond pH 5, Cu(II) is hydrolyzed, therefore is uptake decreased. In case of Cd(II), similar trend is observed; however, maxima found at pH 7, since Cd(II) does not hydrolyze until pH 7. The biosorption process was fast enough, as the equilibrium reached at 120 min of time, following pseudo-second-order kinetics. The biosorption data fitted more suitably in the Langmuir isotherm model, indicating the monolayer sorption. The maximum biosorption capacity of BGH, using Langmuir adsorption plots has been calculated as 8.58 and 9.70 mg g^{-1} for Cd(II and Cu(II), respectively.

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