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Use of grape vine bark as an effective biosorbent for the removal of heavy metals (copper and lead) from aqueous solutions

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ABSTRACT

Removal of copper and lead from aqueous solutions was carried out by adsorption on unmodified grape vine bark (GVB). Effect of different parameters such as pH, contact time, biosorbent dose and initial metal ion concentration for the removal of metal ions was investigated. Freundlich isotherm was found to best fit the equilibrium data with correlation coefficients (R^2) which was 0.913 for Cu^{2+} and 0.984 for Pb^{2+}. The sorption capacity of GVB obtained was 91 mg/g for Pb^{2+} and 43 mg/g for Cu^{2+}. Kinetic studies showed that adsorption kinetics of copper and lead ions on GVB was best represented by pseudo-second order rate kinetics. Hence, GVB proved a better biosorbent for the removal of copper and lead when compared with many other conventional biosorbents. The analysis of variance of experimental data showed that the sorption capacity is dependent on pH and biosorbent dose.

Keywords: Adsorption isotherms; Biosorption; Equilibrium; Heavy metals; Kinetic studies

1. Introduction

Rapid industrialization in Pakistan and discharge of untreated industrial effluents into receiving waters may give rise to serious water quality issues. These along with routine pollutants (such as total suspended solids, biochemical oxygen demand, etc.), also contain highly toxic elements such as heavy metals. Their high concentration in receiving waters is a serious concern for the public health as the water may be used for drinking purposes at the downstream. Heavy metals are biologically stable and do not degrade easily with time. They travel through the food pyramid by accumulation (environmental build-up), bioconcentration (within living organism) and biomagnifications (through the food chain) [1].

Most of the industries discharge their wastewater to the receiving waters without meeting National Environmental Quality Standards (NEQS) causing surface and groundwater pollution. The research shows that rivers in Pakistan are being polluted due to heavy metal contents thus badly affecting fresh water flora and fauna in river Ravi [2]. The hematological parameters showed ruthless changes in the blood of fish in river Kabul that ultimately affect the human life [3]. Water quality index of river Soan revealed high level of heavy metals than the allowable values for domestic use and aquatic life [4]. In Hyderabad, lead exposure has been assessed in the children residing near industrial area by investigating scalp hair (SH). The results show that the children of exposed area have more SH-Pb than the children of non-exposed area [5].

Heavy metals are not only a problem in Pakistan but also a major global concern. Because of the toxicity related to heavy metal pollution and possible harmful effects on human health, numerous studies have so far been conducted to

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decontaminate wastewaters having lethal metal ions. These efforts proved that adsorption is highly effective method for the removal of heavy metals from wastewaters [6–8]. One of the cost-effective and highly efficient sources for biosorption technology is agriculture wastes. Past studies revealed that a variety of agricultural waste material such as banana peels, walnut hulls, *Cassia fistula* leaves, bark of trees, orange peels, potato peels, peanut hulls, sawdust, mango leaves, wheat bran, dried sunflower leaves, spent tea leaves, kaolinite, multi-walled carbon nanotubes electrodes, etc. [9–13]; effectively remove various pollutants, that is, metal ions either in their natural form or after some physical or chemical modification, through biosorption [14–24]. Similarly, many other studies have also reported the effective adsorption of various heavy metals using green biosorbents, that is, peanut husk and sugarcane bagasse [25], *Vigna radiata* waste biomass [26] and rice husk [27].

Physical and chemical properties of copper and lead have made their use widespread ranging from domestic to industrial level [28]. Copper and lead ions are detected in the wastewater discharge from electrical wiring, air conditioning, plumbing, electroplating, pulp and paper mills, fertilizers, petroleum refineries, steel works, pigments, etc. [29]. The presence of copper in water increases the growth rate of planktons and creates problems for agriculture. Higher levels of copper are associated with damage of cytoplasm and blockage of active sites of proteins in living organisms [30]. On the other hand, lead poisoning is related to heart, kidney, bones, reproductive and nervous system diseases, and disorders [1].

The literature survey reveals that grape vine bark (GVB) has not yet been studied for the removal of Cu^{2+} and Pb^{2+}. Therefore, the objective of this study was to investigate the potential of GVB for the removal of Cu^{2+} and Pb^{2+} from aqueous solutions. According to OVI Statistical Report on World VitiViniculture 2013, the world vineyards covered a surface area of 7,547 million hectare [31]. In Pakistan, grape (*Vitis vinifera*) is one of the major fruit crops grown in high elevated valleys of Balochistan. Total area under cultivation for grapes, in Pakistan, is 13,000 hectares. The main grape producing areas of Pakistan are Quetta, Pishin, Killa Abdullah, Mastung, Kalat, Loralai and Zhob districts.

2. Materials and methods

2.1. Chemicals

All chemicals used were of analytical reagent grade. Salts of copper (copper nitrate ($CuSO_4 \cdot 5H_2O$)) and lead, (lead nitrate, $Pb(NO_3)_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. 0.1 N HCl and 0.1 N NaOH were used for pH adjustments.

2.2. Instrumentation

Sartorius TE214S high precision weighing balance was used for weighing. HACH sens ION + was used for pH measurements. JASCO FT/IR-4100 type A was used for Fourier Transform Transformation Infrared (FTIR) analysis. Atomic Adsorption Spectrophotometer, Perkin Elmer A Analyst 800 was used for measuring the concentrations of metal ions.

2.3. Biosorbent preparation

GVB was used as biosorbent for the removal of copper (Cu^{2+}) and lead (Pb^{2+}) from aqueous solution. It was collected from UET, Lahore, washed repeatedly with tap water to remove dust and soluble impurities and then dried in air for 4 d. The dried biosorbent was then ground and sieved to a uniform size of 24 mesh (710 μm). The sieved GVB was then again washed with deionized water to remove any remaining soluble impurities and dried in sunlight for 48 h. Afterwards, stored in air tight plastic bags for further use.

2.4. Preparation of solutions

The reagents used in the study were of analytical reagent grade. The stock solutions (1,000 mg/L) of Cu^{2+} and Pb^{2+} were prepared by dissolving known quantities of $CuSO_4 \cdot 5H_2O$ and $Pb(NO_3)_2$ salts in deionized water. Required concentrations were prepared by diluting the stock solution.

2.5. Batch adsorption studies

Batch adsorption studies were conducted by taking 100 mL solutions of 50 ppm of Cu^{2+} and Pb^{2+} in separate flasks. Varied amounts of biosorbent dose were agitated with these solutions using orbital shaker in a controlled temperature environment. The solutions remained in contact with biosorbent for fixed intervals of time till the equilibrium was achieved. Afterwards, the solutions were filtered. The filtrates were then analyzed for their metal concentration using atomic adsorption spectrophotometer. The results were analyzed by calculating biosorption uptake capacity, q (mg/g), and removal efficiency using Eqs. (1) and (2) respectively;

$$q = \frac{\left(C_0 - C\right)V}{M} \tag{1}$$

$$\text{Removal effeciency}\left(\%\right) = \frac{\left(C_0 - C\right)100}{C_0} \tag{2}$$

where C = metal ion concentration after biosorption (mg/L); C_0 = initial metal ion concentration (mg/L); M = amount of biosorbent, (g); V = volume of sample solution (L); q = biosorption capacity under sub optimum or optimum conditions (mg/g).

2.6. Chi-square statistics

Chi square statistics (X^2) and sum of squares are very well known statistics to check goodness-of-fit of a regression model. The chi-square test statistic is basically the sum of the squares of the differences between the experimental data obtained by calculating from models with each squared difference divided by the corresponding data obtained by calculating from models. The magnitude of X^2 was used to determine the closeness of the calculated model data to the experimental data; the larger the X^2 value, the higher the discrepancy between the data [32]. The assertion that sometimes correlation coefficient, R^2 does not justify basis for selection of best fit of adsorption model, was investigated by use of

Chi-square (X^2) statistical test [33]. The equivalent mathematical equation is as follows

$$X^2 = \sum_{i=1}^{N} \frac{\left(q_{\exp,i} - q_{m,i}\right)^2}{q_{m,i}} \tag{3}$$

$q_{\exp,I}$ = equilibrium capacity obtained from the experiment (mg/g); $q_{m,i}$ = equilibrium capacity obtained from the model (mg/g); N = sample size or number of experimental data points.

2.7. Characterization of biosorbent

To have the insight of the functional groups responsible for the adsorption of metal ions on the biosorbent, Fourier transform infra-red (FTIR) analysis of GVB was carried out using JASCO FTIR/4100. For analysis, a pallet was prepared using mixture of potassium bromide and adsorbent powder in proportion of 1:25, followed by grinding and compression. FTIR spectrum was observed on the instrument within the range of 4,000–400 cm^{-1}. SEM ("VEGA 3 SEM") was used to identify surface morphology of GVB before and after adsorption process.

3. Results and discussion

3.1. Characterization of biosorbent

Fig. 1 depicts the FTIR spectrum of GVB before and after experimentation. The strongest peak was observed at (point-14) 3,427.85 cm^{-1} which indicated the presence of hydroxyl group (–OH). The other dominant peaks in the spectra were observed at (point-13) 2,938.02 cm^{-1}; (point-12) 1,623.77 cm^{-1}; (point-11) 1,523.49 cm^{-1}; (point-3) 890.952 cm^{-1} and (point-4) 1,032.69 cm^{-1} which indicated C–H stretch, N–H bend, N–O asymmetric stretch, C–H "out-of-plane" aromatics and C–N stretch, respectively. All these functional groups are responsible for the binding of cations.

Fig. 2 depicts the morphology of GVB before and after adsorption process. The uneven surface of adsorbent enhanced the active sites for adsorption process and provided favorable conditions for attracting heavy metals molecules towards active adsorption sites.

3.2. Batch adsorption studies

3.2.1. Effect of solution pH on metal ion removal

pH of the metal ion solutions is one of the prime parameter that influence the removal of metal ions through biosorption. pH variation affects the charge on biosorbent surface, extent of ionization and speciation of adsorbate. pH range of 2.0–5.5 was selected to study the effect of solution pH on metal ions. Beyond pH 5.5, precipitates were observed. Since precipitation is not a part of adsorptive removal, pH range of 2.0–5.5 was fixed for this study. The results of pH effect on adsorption capacity are shown in Fig. 3. It can be seen that the biosorption of metal ion increased with an increase in the pH of the metal ion bearing solutions. It is due to an increase in the total net negative charge on the surface of biosorbent, which amplifies electrostatic attractions in the biosorption process. The pH value for maximum removal of both Cu^{2+} and Pb^{2+} was 4.5.

3.2.2. Effect of contact time on metal ion removal

Time for which the metal ion solution and the biosorbent remain in contact affects the biosorption phenomenon of metal ions. Removal of metal ions was recorded at contact time ranging from 10 to 180 min. The results are presented in Fig. 4. It can be observed that for Cu^{2+} and Pb^{2+}, maximum sorption capacities were achieved at 180 and 60 min, respectively. With further increase in time, adsorption capacities were reduced indicating absence of active adsorption sites for molecules of heavy metals. After optimum adsorption contact time, the sorbent became fully saturated thus no active site was available on its surface for further sorption.

3.2.3. Effect of biosorbent dose on metal ion removal

Removal of metal ions was recorded at biosorbent dose ranging from 0.5 to 2 g, at optimum conditions. With an increase in biosorbent dose, the percentage removal of metal ions increases due to the availability of more active sites for biosorption. The maximum biosorption was observed at 0.5 g/L (Fig. 5). Biosorption capacity decreases with an increase in the dose. It is due to the fact that excess adsorption sites remain unsaturated during the adsorption process when higher dose of biosorbent is used [34]. Further increasing the adsorbent dose caused an increase in the viscosity of solution leading to the difficulty in metal sorption [35].

3.2.4. Effect of initial metal ion concentration on metal ion removal

Rate of biosorption is significantly dependent on the number of ions initially present in the solution which provide the necessary driving force for the adsorption of metal ions. To understand the relation between initial concentration of metal ions and their corresponding removal, experiments were carried out with a concentration range from 10–100 mg/L.

The results are presented in Fig. 6. The sorption capacity of GVB increased with an increase in the metal ion concentration. Similar trend has been observed with many other biosorbents [34]. It is possible that the initial metal ion concentration provides the necessary driving force to overcome the mass transfer resistance of metal ions between the aqueous and the solid phase. The increase in metal ion concentration also enhances interaction between metal ions and adsorbent surface [36].

3.3. Equilibrium studies

Equilibrium studies are used to assess the biosorption potential of a biosorbent. This potential is determined for the equilibrium time which may vary for different biosorbents and may range from few minutes to many hours. Different mathematical models are available to study the equilibrium data of biosorption. In this research, three most commonly used models, that is, Langmuir, Freundlich and Temkin isotherm model were studied. The linear form of Langmuir, Freundlich and Temkin model is given in Eqs. (4)–(6).

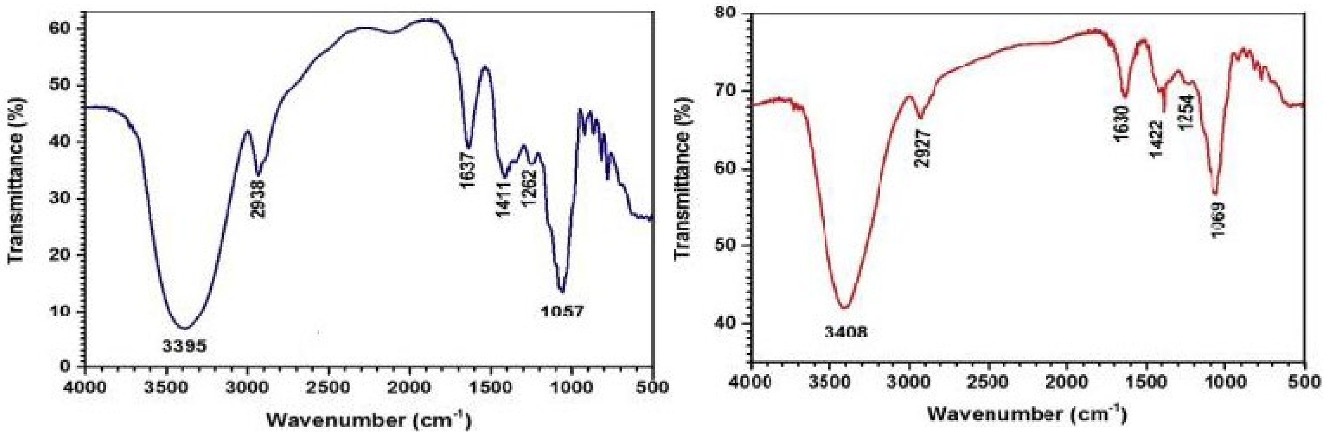

Fig. 1. FTIR spectra of GVB (a) before adsorption and (b) after adsorption.

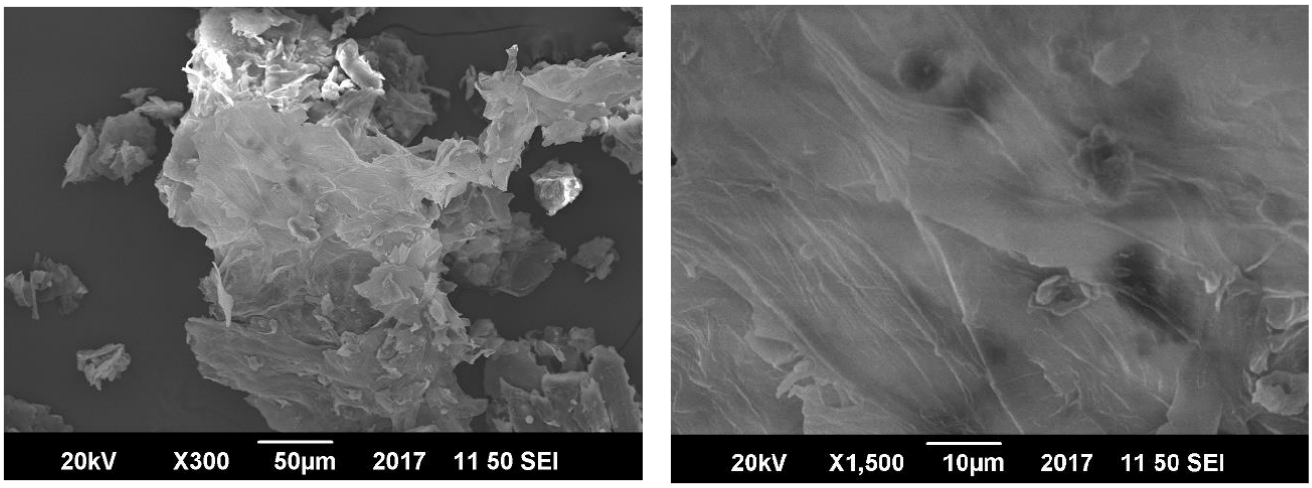

Fig. 2. SEM for GVB; (a) before adsorption and (b) after adsorption.

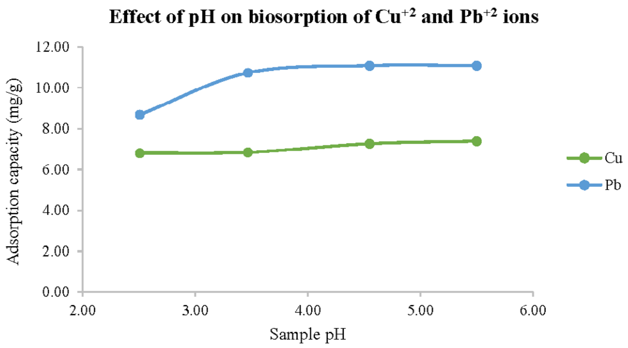

Fig. 3. Effect of pH on biosorption of Cu^{2+} and Pb^{2+} ions.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} b} \tag{4}$$

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \tag{5}$$

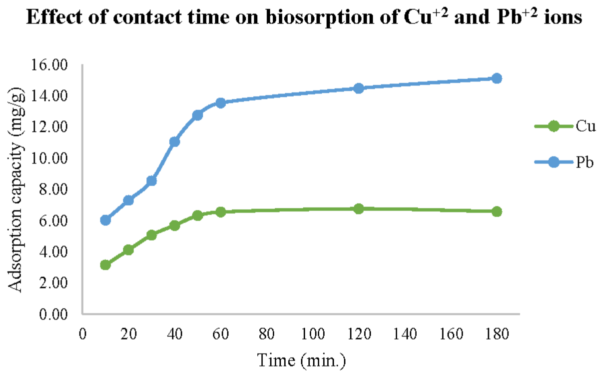

Fig. 4. Effect of contact time on biosorption of Cu^{2+} and Pb^{2+} ions.

$$q_e = \frac{RT}{b_T}\ln A + \frac{RT}{b_T}\ln C_e \tag{6}$$

where $q_{\max}$ = maximum adsorption capacity (mg/g); n = Freundlich constant; R = Universal gas constant,

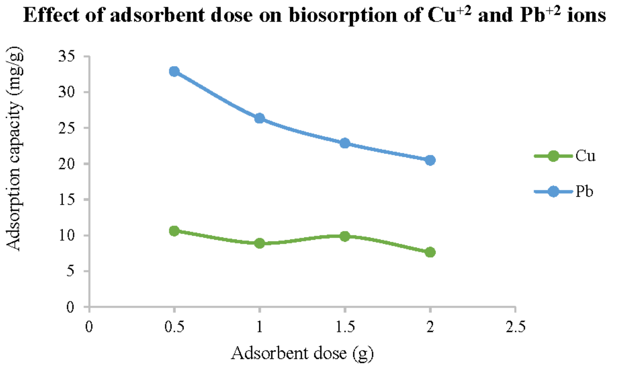

Fig. 5. Effect of biosorbent dose on biosorption of Cu^{2+} and Pb^{2+} ions.

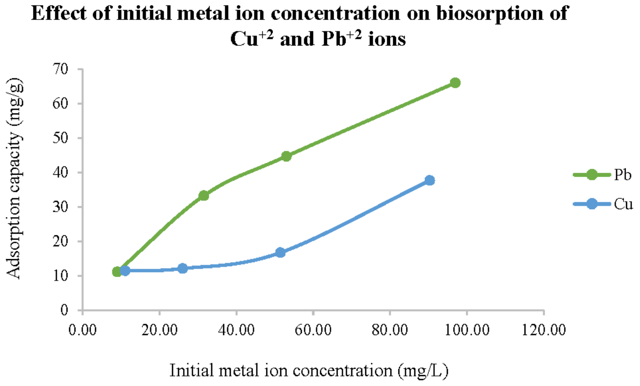

Fig. 6. Effect of initial metal ion concentration on biossorption of Cu^{2+} and Pb^{2+} ions.

8.314 J/mol/K; b = Langmuir constant (L/mg); C_e = equilibrium concentration of sorbate (mg/L); K_f = Freundlich constant, (mg/g) (L.mg) (1/n); q_e = equilibrium adsorption capacity (mg/g); A = Temkin constant (L/g); b_T = Temkin constant.

The calculated isotherm parameters and their corresponding X^2 statistics are shown in Table 1. The results indicate that for both heavy metals, Cu^{2+} and Pb^{2+}, Freundlich isotherm best fits the data for Cu^{2+} and Pb^{2+} with value of equilibrium parameter (R_L) between $0 < R_L < 1$, indicating the isotherm is favorable for both metals. Also a better fit to Freundlich equation was statistically confirmed through the values of correlation coefficient (R^2) which were found to be 0.913 and 0.984 and smaller values of X^2 for both heavy metals, that is, Cu^{2+} and Pb^{2+}, respectively.

3.4. Kinetic studies

Kinetic models are used to study the rate of reactions for equilibrium processes. Contact time, sufficient for desired removal, is the key finding of kinetic studies, which can be further used in the design of full-scale continuous processes [7,29]. In this research, pseudo-first order and pseudo-second order rate equations have been used to study the kinetic data of Cu^{2+} and Pb^{2+} biosorption on GVB. The linearized form of pseudo-first order rate equation and pseudo-second order rate equations is given in Eqs. (7) and (8), respectively.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \quad (7)$$

Table 1
Isothermic and kinetic biosorption studies of Cu^{+2} and Pb^{+2} on GVB

Adsorption models		Parameters	Cu^{+2}	Pb^{+2}
Isotherm Studies	Langmuir	R^2	0.698	0.977
		q_m/mg g^{-1}	43	91
		R_L	0.800	0.747
		X^2	0.645	0.729
	Freundlich	n	2.008	1.664
		K_f/mol g^{-1}	3.027	5.715
		R^2	0.913	0.984
		$1/n$	0.498	0.601
		X^2	0.053	0.021
	Temkin	A/L mg^{-1}	0.304	0.487
		b_T	295	137
		R^2	0.785	0.969
		X^2	0.312	0.458
Kinetic Studies	Pseudo-first-order kinetic model	k_1 (min^{-1})	0.018	0.016
		q_e (mg g^{-1})	10.3753	33.8065
		R^2	0.970	0.901
		$q_{e(exp)}$ (mg g^{-1})	19.78	43.47
	Pseudo-second-order kinetic model	k_2 (min^{-1})	0.003	0.001
		q_e (mg g^{-1})	22.222	55.556
		R^2	0.993	0.978
		$q_{e(exp)}$ (mg g^{-1})	19.78	43.47

$$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_2q_e^2} \quad (8)$$

The calculated values of k_1, k_2, q_e and their corresponding regression coefficient values (R^2) are presented in Table 1 depicting that both metals are best represented by pseudo-second order rate equation with higher coefficient of correlation (R^2) and provide the best agreement between the calculated q_e and experimental q_e. The rate constant of pseudo-second order, k_2, can be used to calculate initial sorption rate (h_i) given in Eq. (8).

$$h_i = k_2q_e^2 \quad (9)$$

The initial sorption rate is used in the design of column studies to set the flow rate. Table 2 presents the initial biosorption rate for Cu^{2+} and Pb^{2+}. It is clear from the results that the Pb^{2+} has more initial biosorption rate on GVB as compared with Cu^{2+}. The high initial biosorption rate for Pb^{2+} depicts that it has more affinity for GVB as compared with Cu^{2+}.

3.5. ANOVA analysis

One-way ANOVA was carried out on the biosorption data of both metals, that is, Cu^{2+} and Pb^{2+}, at an "α" value of 0.05. The null hypothesis used was that "each operating parameter (i.e., pH, contact time, biosorbent dose and initial metal ion concentration) does not affect the biosorption capacity of GVB". The summary of ANOVA results is given below in Table 3. From the table, it can be observed that, for the effect of pH, adsorbent dose and contact time on biosorption capacity of Cu^{2+}, the $F > F_{crit}$, that is, 1,793.331 > 5.987; 20.935 > 5.987 and 4.981 > 4.600), and the $\alpha > p$-value, that is, 0.05 > 1.16×10^{-8}; 0.05 > 0.004 and 0.05 > 0.04.

Thus, the null hypothesis can be rejected and showed that relationship exists between pH, adsorbent dose, contact time and biosorption capacity. For the effect of initial metal ion concentration on biosorption capacity of Cu^{2+}, the $F_{crit} > F$, that is, 5.987 > 0.743, the p-value > α, that is, 0.069 > 0.05. Thus, the null hypothesis cannot be rejected for this factor, and showed that relationship does not exist between initial metal ion concentration and biosorption capacity.

It can also be observed that, for the effect of pH and adsorbent dose on biosorption capacity of Pb^{2+}, the $F > F_{crit}$, that is, 302.117 > 5.987 and 31.027 > 5.987 and the $\alpha > p$-value, that is, 0.05 > 2.32×10^{-6}, 0.05 > 0.001. Thus, the null hypothesis can be rejected and showed that relationship exists between pH, adsorbent dose and biosorption capacity. For the effect of contact time and initial metal ion concentration on bio-sorption capacity of Pb^{2+}, $F_{crit} > F$, that is, 4.600 > 2.0183 and 5.987 > 0.744, and the p-value > α, that is, 0.177 > 0.05 and 0.422 > 0.05. Thus, the null hypothesis cannot be rejected for these factors, and showed that there is no relationship existing between contact time, initial metal ion concentration and biosorption capacity.

4. Conclusion

Adsorption technology offers a very efficient and cost-effective treatment, using waste materials for the removal of heavy metals from water. FTIR analysis identified the presence of C–H stretch, N–H bend, N–O asymmetric stretch and C–N stretch in the material, mainly responsible for adsorption mechanism. Equilibrium isotherm studies revealed that Freundlich isotherm was found to fit the equilibrium data more appropriately with higher correlation coefficients (R^2) than Langmuir and Temkin model for biosorption of both metals on GVB. The maximum biosorption capacity of GVB obtained by Langmuir isotherm was 91 mg/g for Pb^{2+} and 43 mg/g for Cu^{2+}. The adsorption data confirmed the pseudo-second order rate kinetics for the sorption process. It was also found that Pb^{2+} showed more affinity towards GVB than Cu^{2+} ions. The ANOVA analysis was carried out and showed that for both metals, there is strong dependence of pH and biosorbent dose for the removal of metal ions. It can be

Table 2
Initial biosorption rate of Cu^{+2} and Pb^{+2} onto GVB

Metal ion	Initial biosorption rate, h_i (mg/g/min)
Cu^{+2}	1.48
Pb^{+2}	3.09

Table 3
ANOVA results for Cu^{+2} and Pb^{+2}

Metal ions	Parameters	SS	df	MS	F	p-value	F crit
Cu^{+2}	pH vs. biosorption capacity	11,022.7	1	11,022.77	1,793.331	1.16E-08	5.987
	Adsorbent dose vs. biosorption capacity	915.834	1	915.834	20.935	0.004	5.987
	Contact time vs. biosorption capacity	8,366.95	1	8,366.956	4.981	0.042	4.600
	Initial metal ion concentration vs. biosorption capacity	547.336	1	547.336	0.743	0.421	5.987
Pb^{+2}	pH vs. biosorption capacity	15,584.1	1	15,584.1	302.117	2.32E-06	5.987
	Adsorbent dose vs. biosorption capacity	6,105.4	1	6,105.4	31.027	0.001	5.987
	Contact time vs. biosorption capacity	3,484.73	1	3,484.73	2.0183	0.177	4.600
	Initial metal ion concentration vs. biosorption capacity	547.336	1	547.336	0.744	0.422	5.987

concluded that GVB can be used as an alternative adsorbent compared with other costly adsorbents, used for heavy metal removal from wastewater.

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Supplementary information

Comparison of GVB with other biosorbents

A comparison of maximum biosorption capacity of GVB calculated by using Langmuir isotherm, for Cu^{+2} and Pb^{+2}, was made with already conducted studies using other bio-sorbents [37]. Fig. S1 shows a comparison of GVB for Cu^{+2} with other biosorbents. It is evident from the figure that GVB has more biosorption capacity for Cu^{+2} as compared to many other biosorbents. For the biosorption of Pb^{+2}, the comparison of GVB with other biosorbents is shown in Fig. S2 [38,39]. It is evident that GVB has better biosorption capacity for Pb^{+2} when compared with other biosorbents.

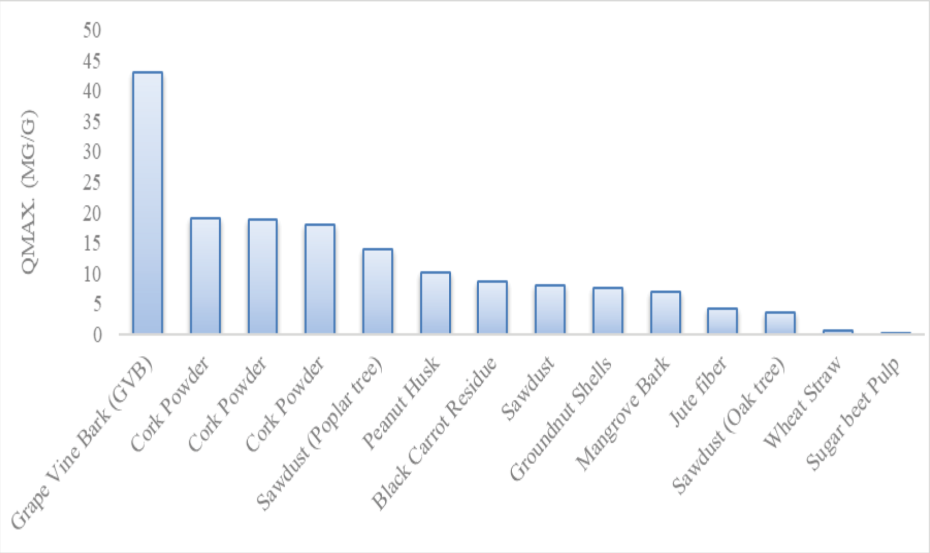

Fig. S1. Comparison of biosorption capacity of GVB with other biosorbents for the removal of Cu^{+2} ions.

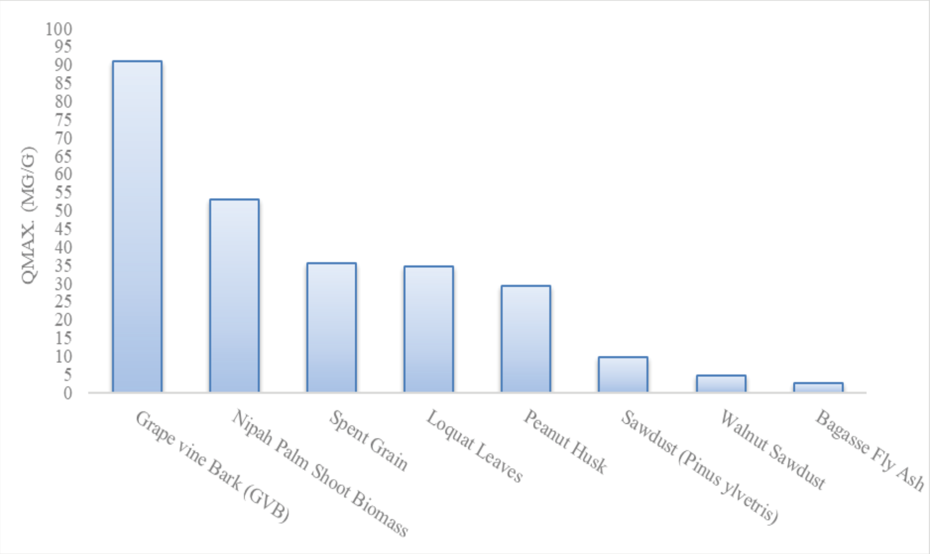

Fig. S2. Comparison of biosorption capacity of GVB with other biosorbents for the removal of Pb^{+2} ions.