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Biosorption capacity of vegetable waste biomass for adsorption of lead and chromium

Rohama Gill[1*], Qurat-ul-Ain Nadeem[1], Raziya Nadeem[2], Rabia Nazir[3], Sadaf Nawaz[1]

[1] *Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi, Pakistan*

[2] *Department of Chemistry and Biochemistry, University Of Agriculture, Faisalabad , Pakistan*

[3] *Applied Chemistry Research Centre, Pakistan Council of Scientific and Industrial Research Laboratories Complex, Lahore, Pakistan*

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Abstract

Adsorption potential of prepared low cost vegetable waste mixture was studied for the removal of Pb (II) and Cr (VI) from their respective aqueous solutions. The optimized biosorbent dose for Pb (II) was 2.5 g and for Cr (VI) was 3.0 g with initial concentration of 50 ppm for both metal ions at temperatures 26°C and 35°C, respectively. The system attained equilibrium when contact time for Pb (II) was 50 minutes and for Cr (VI) it was 30 minutes. Maximum uptake capacity of biomass for Pb (II) (0.465 mg/g) and Cr (VI) (1.089 mg/g) was observed at pH 5 and 2, respectively. FT-IR and ICP studies of neat and metal loaded biomass also revealed the presence of Pb (II) and Cr (VI) onto the biomass. The sorption isotherms followed the Langmuir model for both the metals suggesting a monolayer sorption character with second-order kinetics. The results also demonstrated that for both metals the uptake capacity of prepared biomass used are comparatively higher than most of the work reported earlier.

***Corresponding Author:** Rohama Gill ✉ rohama_gill@hotmail.com

Introduction

Over the last few decades, the discharge of heavy metals into aquatic ecosystems has become a matter of concern especially in South Asian countries. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. The pollutants of concern include lead, chromium, copper, nickel, arsenic, etc. This contamination in the discharge wastewater has rendered colossal damage to the surface water and ground water; therefore concerted efforts are underway for the removal of such contaminants from the aqueous media to improve the water quality (Zafar *et al.*, 2013). Keeping the environmental, ecological and societal health issues in view, it is considered necessary to attempt and provide an easy, feasible, economical and reliable method for the removal of these heavy metals

In the present study Pb (II) and Cr (VI) metals were focused to check the efficacy of mixture of vegetable waste as adsorbent. Lead is considered as a toxic substance because it competes with the action of calcium and adversely affects nervous, renal, cardiovascular and reproductive systems and is also one of the causative agents of stomach, lung and bladder cancer (Patrick, 2006). On the other hand, chromium contaminates various water bodies and soil mainly in the trivalent or hexavalent form. Cr (VI) besides being one the major causes of many health issues and a strong oxidizing agent affects the biological membranes as well, which are impermeable to Cr (III). Cr (VI) may be reduced to Cr (III) after penetrating into mitochondria, nuclei and cytoplasm and readily convert to insoluble chromium hydroxides (Blazquez *et al.*, 2009).

Fervent efforts are underway by researchers and environmentalist to establish appropriate promising methods to remove heavy metals from aqueous media and thus techniques like solvent extraction, ion exchange, chemical precipitation, reverse osmosis and lime coagulation have been considered and reported (Nadeem *et al.*, 2008). However, as it is vital to adopt cost effective and greener pathways for such purposes, the present work is aimed to achieve such goals through adsorption onto a mixture of vegetables which otherwise is a waste. There are several products belonging to food industry and agricultural waste that have been effectively employed for the removal of heavy metals from aqueous media (Demirbas, 2008). As the agricultural by-products are typically made up of fiber comprising functional groups such as aldehydes, ketones, alcohols, carboxylic, phenolic and ether, therefore the presence of such groups can be utilized to form complexes with metal ions (Demirbas, 2008). Biosoprtion is an eco friendly and cost effective excellent tool for the removal of heavy metals from the aqueous solutions. The vegetable waste has the capacity to sequester heavy metal ions and could serve as economical means of treating effluents from tanneries etc, charged with toxic Cr (VI) and Pb (II) ions from the aqueous solutions Hence, the present study was undertaken to investigate the potential of 1:1 mixture of carrot and potato peels as a biosorbent (Gill *et al.*, 2013), for Cr (VI) and Pb (II) and optimize the effects of different experimental conditions such as pH, biosorbent dose, initial metal concentration, contact time and temperature on sorption process.

Materials and methods

Chemicals

All the chemicals and reagents used in this study were of analytical grade, including $Pb(CH_3COO)_2 .3H_2O$ and K_2CrO_4 (Merck), HCl 37 % (Merck) and NaOH (Sigma Aldrich). All chemicals were used without further purification.

Preparation of Biosorbent

Biosorbent was prepared adopting a reported procedure by our group (Gill *et al.*, 2013). Thoroughly washed potatoand carrot peels were oven dried at 60°C for 48 h followed by fine grinding separately in a grinder (Moulinex, France). The ground peels were sieved using a 60 µ mesh size sieve (Seiver Octagon digital Endecott, England). A homogenous mixture of 1:1 ratio was prepared by taking equal amounts of sieved potato peel and carrot peel powders. The prepared mixture was stored in an air tight container placed in a desiccator for further experiments.

Preparation of Pb (II) and Cr (VI) solutions

Stock solutions (1000 mg/L) of respective ion solution were prepared in deionized water (DW) from which working solutions of required concentrations were prepared by adequate dilutions.

Batch biosorption procedure

All the experiments were performed using batch mode in order to receive reliable reproducible results. For each set of experiments conducted for the optimization of conditions required for maximum adsorption, 25 mL of known concentration of Pb (II) and Cr (IV) solution was taken in a conical flask and pH was adjusted using 0.1 M HCl and 0.1 M NaOH. After addition of a known amount of biosorbent, the flask was placed on a rotating shaker (Wiseshake-SHO-2D, Witeg Germany) with constant shaking at 150 rpm for a given time while maintaining a constant temperature. The contents of the flasks were filtered using Whatman No. 40, ashless filter paper, to separate the biomass and then the volume of solution was adjusted back to 25 mL using DW. The amount of metal left in each of the filtrates was then studied via atomic absorption spectroscopy.

Determination of Pb (II) and Cr (VI) contents in the solutions

Flame atomic absorption spectrometer (FAAS-Spectra AA220, Varian Inc. Australia) was used to analyze Pb (II) and Cr (VI) concentration in the solutions before and after the equilibrium. FAAS was equipped with an air–acetylene burner and controlled by an Intel personal computer. The hollow cathode lamp was set at 15 mA and the analytical wavelength was adjusted at 232 nm.

Metal uptake

The Pb (II) and Cr (IV) uptake was calculated by the simple concentration difference method using the following relation (Eq. 1):

$$q_e = \frac{V(C_i - C_e)}{M \times 1000} \qquad \text{(Eq.1)}$$

Where, C_i corresponds to the initial concentrations of metal ion (mg/L) and C_e explains metal concentrations (mg/L) at various time intervals. q_e is adsorption capacity (mg metal/g adsorbent) whereas M is weight of biosorbent (g) and V is the total volume of metal ion solution (L).

% adsorption was calculated by taking the initial (C_i) and final (C_e) concentrations of metal ion at various time intervals, which is given as follows (Eq. 2):

$$\%\ \text{Adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad \text{(Eq. 2)}$$

FTIR and ICP spectroscopic analysis of virgin and spent biomass

FTIR spectrum of the prepared biomass was used to investigate the presence of functional groups present in the virgin biomass compared the vibrational frequencies of the functional groups with those of spent adsorbent. Using a KBr window, the spectra were studied on a Schimadzu, FTIR-8400 spectrometer, Japan, equipped with software-IR Solution, within the range of 4000-400 cm^{-1}.

Inductively coupled plasma (ICP) spectroscopy is a more sensitive, specific and reproducible way to determine heavy metal concentration (Boss and Fredeen, 2010). In the present study, acid digestion was done to prepare sample for ICP-OES. Each sample of spent biosorbent containing Cr (VI), Pb (II) was separately digested by adding 7 mL of H_2SO_4 (96%) and 5 mL of HNO_3 (67%). Double filtration was done using Whattman 40 ashless filter paper and each filtrate was diluted up to 250 mL with DW.

An ICAP 6500 inductively coupled plasma-optical emission spectrometer (ICP-OES) from Thermo Fisher Scientific UK, equipped with ITEVA (version 8) operating software for full control of all instrument functions and data handling, and a high performance solid state CID camera system having a RACID 86 detector containing a 512×512 charge injection devices (CID), was used for measurement of the metals. A high precision peristaltic pump with 12 rollers and 4 channels was employed for the introduction of sample into the plasma.

Results and discussion

Nowadays biosorption has become one of the cost effective technique used for the wastewater treatment, hence this method was adopted to quantify the potential of 1:1 mixture of potato and carrot peels by studying the effects of five parameters, i.e., temperature, initial pH, contact time, initial metal ion concentration and biosorbent dose so as to optimize the parameters required for efficient and effective removal of Pb (II) and Cr (IV). The neat and metal loaded biomass was also subjected to FT-IR and ICP.

Table 1. Values for langmuir and freundlich adsorption isotherm parameters.

Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	Pb (II)	Cr (VI)		Pb (II)	Cr (VI)
K_l	0.2818	0.0432	K_f	6.55	1.157
q_{max}	0.465 mg/g	1.089 mg/g	n	0.436	0.86423
R_L	0.066	0.316	R^2	0.9519	0.9954
R^2	0.9817	1			

FTIR and ICP studies of biosorbent

The FTIR spectra of virgin biosorbent (Fig.1a) was compared to that of Pb (II) loaded and Cr (IV) loaded 1:1 potato-carrot peel mixture (Fig.1b).

The broad peak present in the virgin mixture around 3354.32 cm^{-1} (-OH stretching in alcohols and phenols) shifted to higher frequency (3396.76 cm^{-1}) in Cr (VI) loaded biosorbent while in case of Pb (II) the frequency was slightly reduced to 3346.61 cm^{-1} suggesting that OH group is involved in the binding of Cr (VI) and Pb (II) from aqueous solution. The peak located at 1741.78 cm^{-1} in the virgin mixture, characteristic of carbonyl group (C=O stretching) from aldehydes and ketones shifted to lower frequency of 1737.92 cm^{-1}, this may be attributed carboxyl group involvement in the capturing the Cr (VI) while the peak at 1415.80 cm^{-1} in virgin mixture shifted to higher frequency of 1427.37 cm^{-1} and 1419.66 cm^{-1} when the mixture was loaded with Cr (VI) and Pb (II) respectively indicating shift in that aromatic ring (C=C) stretch. The peaks present in the region of 600-450 cm^{-1} in both spectra can be attributed to C-Metal stretching vibration in spent biosorbent (Silverstein and Webster, 1998).

Analysis of the spent biosorbents was also conducted *via* ICP-OES to validate the uptake of metal ions. ICP results have shown that biosorbent loaded with 50 mg/L of Pb (II) was found to contain 3.395 µg/mL of Pb (II) while in case of Cr (VI), the biosorbent contained 0.845 µg/mL when loaded with 50 mg/L of Cr (VI) thus validating the fact that the prepared biomass has the capacity to adsorb and remove Pb (II) and Cr (VI) metal ions from their respective solutions.

Effect of pH on adsorption

pH of the solution has been recognized as the most vital variable parameter governing metal ion sorption as it determines the adsorbent's surface charge, extent of ionization and adsorbate speciation. Fig. 2, illustrates the effect of pH on the adsorption of Pb (II) and Cr (VI) from the aqueous solutions onto mixture of potato and carrot peels. Good adsorption behavior was observed in 4-6 pH range for Pb (II) with maximum removal of 92.50% at pH 5 while Cr (VI) exhibits maximum removal in pH range 1-3 in aqueous media, pH 2 being the optimal pH for maximum removal of 71.70 % of Cr (VI). Organic biomass contains various functional groups (C=O, -OH, $-NH_2$) that are involved in the binding of Pb (II) and Cr (VI) from the aqueous solution. As all Cr (VI) species (CrO_4^{-2},$Cr_2O_7^{-2}$, $HCrO_4^-$) being negatively charged, a lowering in pH value makes the surface of sorbent to charge positively owing to the protonation of the active groups due to which a sizeable amount of protons can coordinate with the available functional groups on the prepared biomass (Qaiser *et al.*, 2009a). This would create an electrostatic attraction amongst positively charged sorbent and negatively charged sorbate (most commonly in the form of $HCrO_4^-$ at lower pH) thus promoting binding of $HCrO_4^-$ on the biomass surface (Bhatti *et al.*, 2010). The optimal removal of Pb (II) at pH 5 can be due to the fact that as pH rises from 4 the amount of negatively charged sites increases on the surface of biosorbent that facilitate the adsorption of Pb ions due through electrostatic attraction (Almasi *et al.*, 2012). The functional groups present on the sorbent are negatively charged at pH range of 3-7 thereby attracting the cations for binding (Qaiser *et al.*, 2009b). However, at pH 6 and above, Pb (II) ions begin to precipitate out in the form of lead hydroxide (Bulut and Baysal, 2006).

Table 2. Comparison of pseudo first order and pseudo second order kinetic models of Pb (II) and Cr (VI) biosorption.

	Pseudo 1st order Pb (II)	Pseudo 2nd order Pb (II)	Pseudo 1st order Cr (VI)	Pseudo 2nd order Cr (VI)
K	0.036157	0.0032	0.189767	1.74970
q_e(cal)mg/g	16.17	1.19	4.13	0.9811
q_e(exp)mg/g	1.198	1.198	0.963	0.963

Effect of Temperature

It has been observed that for biosorption process, temperature is one of the most important criteria and it affects each site differently and contributes to overall metal uptake and hence their efficient removal (Ajaykumar *et al.*, 2009). Uptake of Pb (II) and Cr (VI) on vegetable waste mixture was investigated in the temperature range of 26°C to 70°C. For Pb (II) ion, it was observed that there is a slight decrease in the percentage removal with the rise in temperature above 26°C, indicating that temperature has very less impact on removal of lead ions. The removal of lead ions at temperature above 26°C tend to decrease due to the weakening of attractive forces between biosorbent and metal ions (Horsfall and Spiff, 2005), while in case of Cr (VI) the increase in adsorption with rise in temperature may be due to the increased active surface sites available on the biosorbent (Qaiser *et al.*, 2009a). The rate of desorption seemed to be more significant than the rate of adsorption, as the temperature increases from 35°C to 70°C which suggests an exothermic nature of Pb (II) and Cr (VI) uptake (Almasi *et al.*, 2012).

At temperature higher than 35°C a change in the nature of the biomass results in the destruction of certain active sites on the biomass surface because of bond ruptures resulting into reduced biosorption capacity (Gill *et al.*, 2013).

Effect of Contact time

As contact time between the adsorbent and the adsorbate has an essential contribution, therefore a number of batch experiments were performed and it was observed that in the first 10 min., the percentage removal is relatively rapid i.e. 74.00% for Cr (VI) and 92.79% for Pb (II). Thereafter, the adsorption increased gradually and reached a maximum of 77.04 % for Cr (VI) in 30 min. and 95.86% for Pb (II) in 50 min. contact time (Fig.4), thus equilibrium is achieved. This is attributed to the fact that the initial removal of Pb (II) and Cr (VI) is faster due to more active sites which favor adsorption (Gupta *et al.*, 2011).

After a certain time lapse, i.e. 50 min. for Pb (II) and 30 min. for Cr (VI) it seemed to be difficult to occupy the available vacant surface sites because of repulsive forces between the adsorbed molecules on the solid surface and in the bulk phase moreover the saturation of active sites can also occur (Venkateswarlu *et al.*, 2007). Hence, prolonged contact time of the adsorbent and the adsorbate up to 130 min. may not yield increase in adsorption.

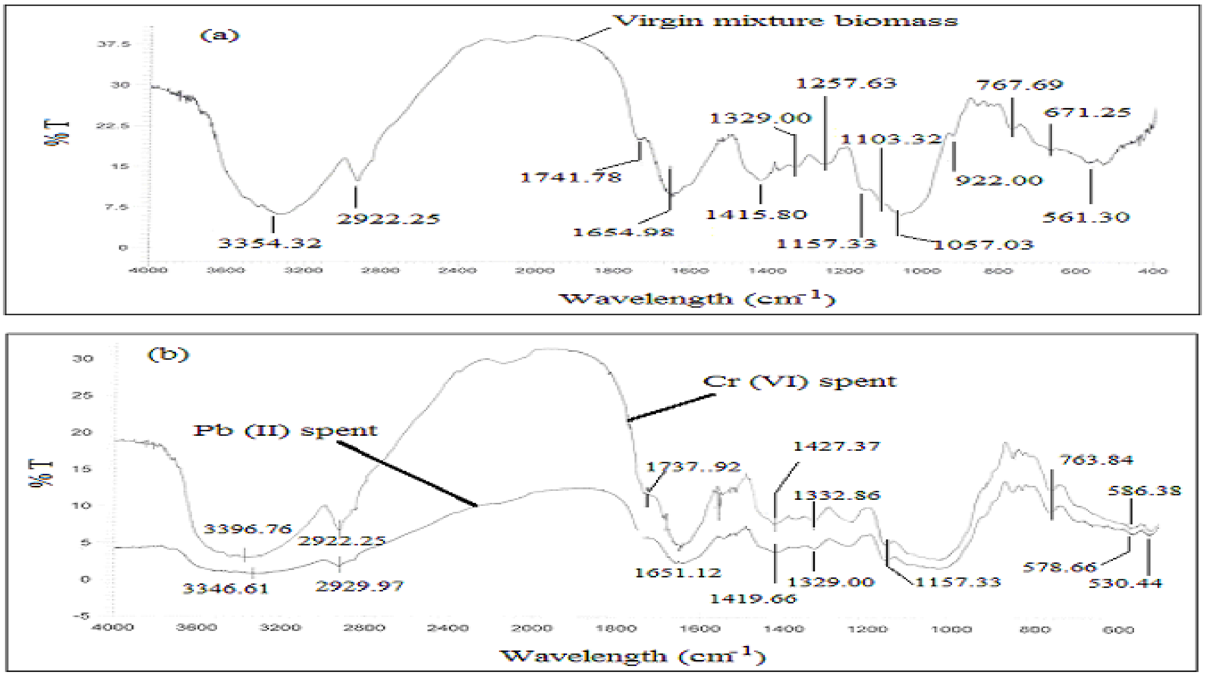

Fig. 1 (a, b). FTIR spectra of virgin mixture biomass (a) and metal loaded biosorbent (b).

Effect of Initial metal ion concentration

Concentration of metal ions affects equilibrium of sorbent/sorbate system. In the present systems, the percentage of Cr (VI) and Pb (II) ions adsorbed onto the prepared biomass improved by increasing gradually the initial concentration of metal to 50 ppm (Fig.5). The reason for such a trend may be that at low concentration of metal ion solution the sorbent surface area is high as compared to the total metal ions available (Sekhar *et al.*, 2004). There are more active sites on the biosorbent surface to be accessible by metal ions and thus the metal ions present can interact with these binding sites with greater chance for metal removal but the equilibrium between the metal ions and the adsorbent's active sites sets up very soon and metal solution does not release more metal ions to adsorb on the biosorbent surface (Gupta *et al.*, 2011; Nadeem *et al.*, 2009).

When the Cr (VI) concentration was further increased from 50 to 130 ppm a trend of decreasing percentage adsorption was observed while increasing the concentration of Pb (II) from 10 to 110 ppm showed less significant increase in adsorption because at higher metal concentrations, there are number of metal ions for the fixed amount of biosorbent (Kumar *et al.*, 2009). Also, at high concentration of metal ions there is a competition between the metal ions to adsorb on the active sites of the adsorbent because less number of active sites is available (constant biosorbent dose of 1.0 g) as compared to the metal ions and more Cr (VI) and Pb (II) ions are left unabsorbed in solution due to the saturation of adsorption sites (Taha *et al.*, 2011).

The agglomeration of adsorbent particles at higher concentrations leads to decrease in adsorption as it tends to decrease the total surface area of the adsorbent particles available for adsorption which ultimately leads to a decrease in adsorption of Pb (II) and Cr (VI) onto the surface of biosorbent (Ajaykumar *et al.*, 2009).

Effect of biosorbent dose

The dose of biosorbent has always been a significant consideration for the biosorption of metal ions from the aqueous medium owing to its effect for the removal of metal per unit mass of biosorbent (Abdulrazaq and Basiru, 2010). The results showed maximum removal of Pb (II) of 98.28% for 2.5 g of prepared biosorbent while 88.89% of Cr (VI) ions were removed effectively onto 3.0 g of prepared biosorbent. The increase in adsorption of lead and chromium ions onto the biosorbent can be attributed to the fact that by increasing the dose of biosorbent, the surface area increases which provides the greater availability of active sites, thereby ensuring efficient removal (Anwer *et al.*, 2009).

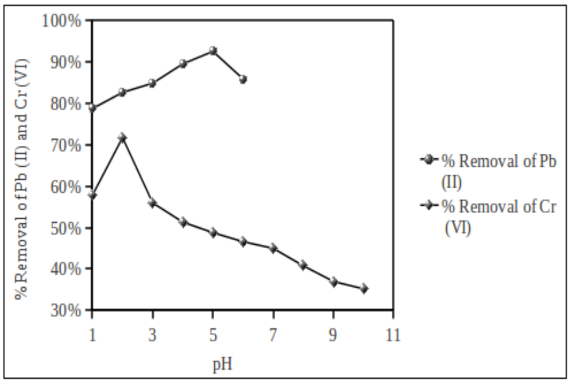

Fig. 2. Effect of solution pH on adsorption of Pb (II) and Cr (VI). [Ambient Temperature = 26±1°C; Contact time =30 min.; Metal ion conc. = 50 ppm; Biosorbent dose =1.0 g; Shaking speed=150 rpm].

Adsorption comparison amongst Potato peel, Carrot peel and potato-carrot waste Mixture

Potato and carrot peels being zero value waste, there potential for biosorption of Pb (II) and Cr (IV) from their respective aqueous solution has been investigated separately following the same protocol as that for their 1:1 mixture.

In Fig.7, a comparison illustrates that mixture shows more promising results. Potato peel waste biomass showed removal of 80.73% and 67.37% for 50 ppm concentration of Pb (II) and Cr (VI) from aqueous solution respectively while it was 83.72% of Pb (II) and 69.05% of Cr (VI), when carrot peel waste used as biosorbent. Maximum percentage adsorption of 96.46% and 77.35 % were shown for mixture from aqueous solution of 50 mg/L of Pb (II) and Cr (VI). This indicates that the prepared biosorbent (mixture) has higher affinity might be due to increased number of available sites for the removal of Pb (II) and Cr (VI) as compared to when they were used separately.

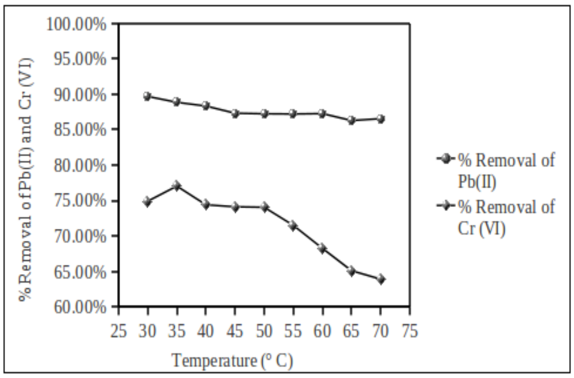

Fig. 3. Effect of temperature on adsorption of Pb (II) and Cr (VI). [pH 5: Pb (II) and pH 2: Cr (VI); Contact time = 30 min.; Metal ion concentration = 50 ppm; Biosorbent dose =1.0 g; Shaking speed=150 rpm].

Analysis of adsorption isotherms

Since, adsorption isotherms also known as equilibrium data, are the essential requirements for designing adsorption systems (Pehlivan *et al.*, 2012) therefore Pb (II) and Cr (VI) biosorption data been correlated with two widely used models i.e. Langmuir and Freundlich.

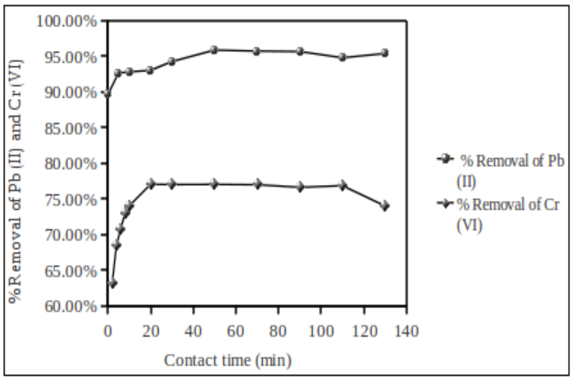

Fig. 4. Effect of contact time on adsorption of Pb (II) and Cr (VI). [pH 5: Pb (II) pH 2: Cr (VI); Temperature = 26± 1°C Pb (II) 35°C: Cr (VI); metal ion concentration= 50 ppm; biosorbent dose =1.0 g; shaking speed=150 rpm].

Langmuir adsorption isotherm

Langmuir equation provides sufficient description on sorption data over a limited range of concentrations (Pehlivan *et al.*, 2012). According to this model, adsorption of solute molecules on the adsorbent surface occurs in the form of a saturated monolayer without any interaction between adsorbed ions. Also, there is no transmigration of adsorbed ions in the plane of the surface (Prasad and Abduallah, 2010) represented in (Eq. 3).

$$\frac{1}{q_e} = \left(\frac{1}{q_{max} k_l}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \qquad \text{(Eq.3)}$$

Where, C_e = concentration of metal in bulk solution at equilibrium after binding (mg/L); q_e = amount of metal adsorbed / g of the adsorbate at equilibrium (mg/g); q_{max} = Langmuir constant related to capacity of adsorption; k_l = Langmuir constant related to adsorption rate.

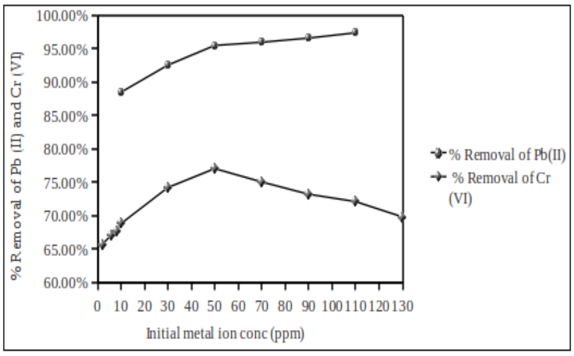

Fig. 5. Effect of metal ion concentration on adsorption of Pb (II) and Cr (VI). [pH 5: Pb (II) pH 2: Cr (VI); Temperature = 26± 1°C Pb (II) 35°C : Cr (VI); Contact Time = 50 min.: Pb(II) 30 min.: Cr (VI); biosorbent dose =1.0 g; shaking speed=150 rpm].

Equilibrium concentration (C_e) and equilibrium capacity (q_e) were calculated for each initial metal concentration. Straight line is fitted by regression by plotting $1/C_e$ against $1/q_e$ (Fig. 8) while slope and intercept of line gives values of q_{max} and k_l. The value of correlation coefficient for both, Pb (II) (R^2 = 0.9817) and Cr (VI) (R^2 =1) indicated a strong positive relationship for the sorption data.

Separation factor "R_L"

"R_L" predicts whether an adsorption system is favorable or unfavorable (Taha *et al.*, 2011) and is expressed as follows (Eq. 4):

$$R_L = \frac{1}{(1+k_L C_o)} \qquad \text{(Eq.4)}$$

Where, K_l = Langmuir Constant; C_o = initial metal ion concentration in mg/L. The parameter R_L indicates the type of biosorption isotherm where R_L can take so many values. Such values are: Favorable: $0 < R_L < 1$, Unfavorable: $R_L > 1$, Linear adsorption: $R_L = 1$, and Irreversible: $R_L = 0$. The value of R_L was found less than unity (Table 1) at initial concentration of 50 mg/L for both the metal ions indicating favorable biosorption.

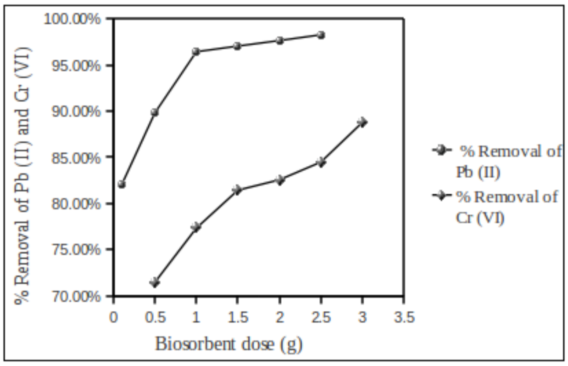

Fig. 6. Effect of biosorbent dose on adsorption of Pb (II) and Cr (VI). [pH 5: Pb (II) pH 2: Cr (VI); Temperature = 26± 1°C: Pb (II) 35°C: Cr (VI); Contact time = 50 min. (Pb II) 30 min.(Cr VI); metal ion concentration= 50 ppm; shaking speed=150 rpm].

Freundlich adsorption isotherm

The Freundlich relationship is an empirical (experimental) equation. Freundlich model proposes that the sorption occurs in the form of a monolayer and active sites are distributed heterogeneously, also there exists an interaction between adsorbed molecules (Qaiser *et al.*, 2009a). It is expressed mathematically as follows (Eq. 5):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

(Eq.5)

Where, q_e = amount of the metal adsorbed per unit weight of the adsorbate at equilibrium (mg/g); C_e =

concentration of metal in bulk solution at equilibrium after binding (mg/L); k_f = Freundlich constant related to adsorbent sorption capacity; n = Freundlich constant related to adsorbent sorption intensity. "n" and "k_f" are Freundlich isotherm constants, calculated from slope and intercept of the linear plot of log q_e versus log C_e (Fig. 9). As explained in Table 1, values of correlation coefficient (R^2) of both models indicated that the Langmuir adsorption isotherm model showed a better fit to the equilibrium data than the Freundlich isotherm model indicating strong binding of Pb (II) and Cr (VI) ions to the surface. Therefore, the present biosorption process of Pb (II) and Cr (VI) can be interpreted as monolayer adsorption.

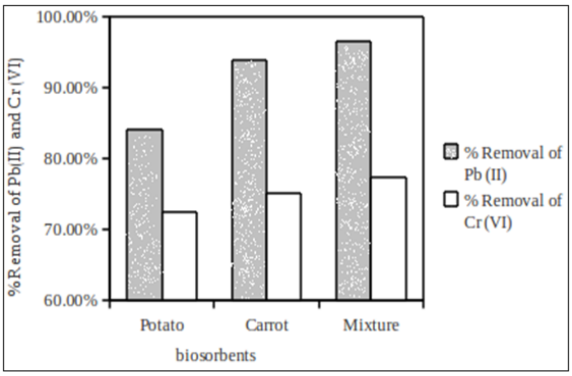

Fig. 7. Adsorption comparison for the removal of Pb (II) and Cr (VI). [pH 5: Pb (II) pH 2:Cr (VI); Temperature = 26± 1°C: Pb (II) ,35°C: Cr (VI); Contact time = 50 min.: Pb (II) 30 min.: Cr (VI); metal ion concentration= 50 ppm; biosorbent dose = 1.0 g; shaking speed=150 rpm].

Kinetic modeling

To study the mechanism and possible rate determining step involved in the process of biosorption, kinetic models have been studied to check the experimental data. The order of adsorbate-adsorbent interactions is further defined by using various kinetic models put forth previously (Venkateswarlu *et al.*, 2007).

Pseudo-first-order kinetic model

Lagergren described the pseudo-first-order kinetic model as follows (Eq. 6):

$$\log(qe - qt) = \log qe - \frac{k_1}{2.303} t \quad \text{(Eq.6)}$$

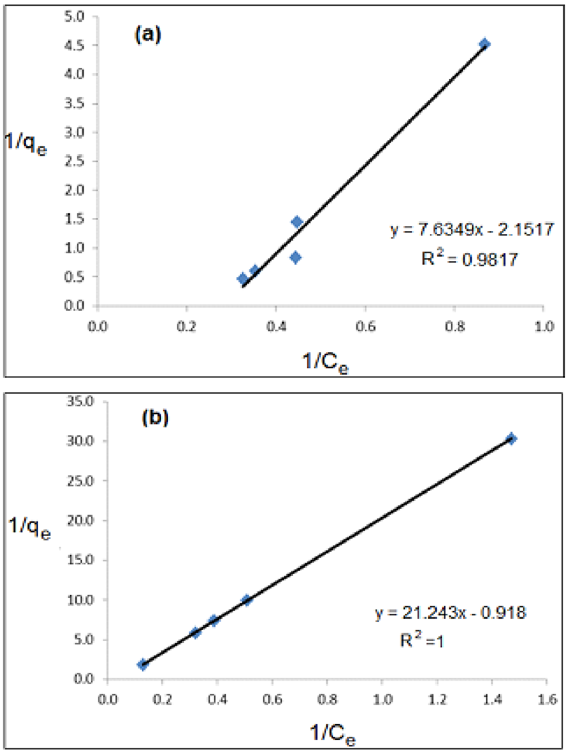

Fig. 8. Langmuir adsorption isotherm for Pb (II) (a) and Cr (VI) (b).

Where, $q_t = (C_o - C_t) V/m_s$ = adsorption capacity at time t; q_e = adsorption capacity at equilibrium (mg/g); C_o = initial metal concentration (mg/L); C_t = Metal concentration (mg/L) at time t (min.); V = Volume of Metal solution (L); m_s = dry weight of the biosorbent (g); k_1 = rate constant of the first-order equation.

A straight line of log (qe - qt) versus t proposes the suitability of this kinetic model; q_e and k_1 can be found from the intercept and slope of the plot, respectively. The experimental q_e must be known for the application of this model. Table 1 shows the pseudo-first-order constants, q_e and k_1 along with the correlation coefficient R^2 for initial concentration of 50 mg/L of Pb (II) and Cr (VI) ions (Fig. 10). As shown in Table 2, the calculated q_e (cal) values of both Pb (II) and Cr (VI) were not in good agreement with their respective experimental qe (exp) values. The results obtained suggested that the pseudo-first-order model is unsuitable for kinetic modeling of the adsorption of Pb (II) and Cr (VI) using present biomass.

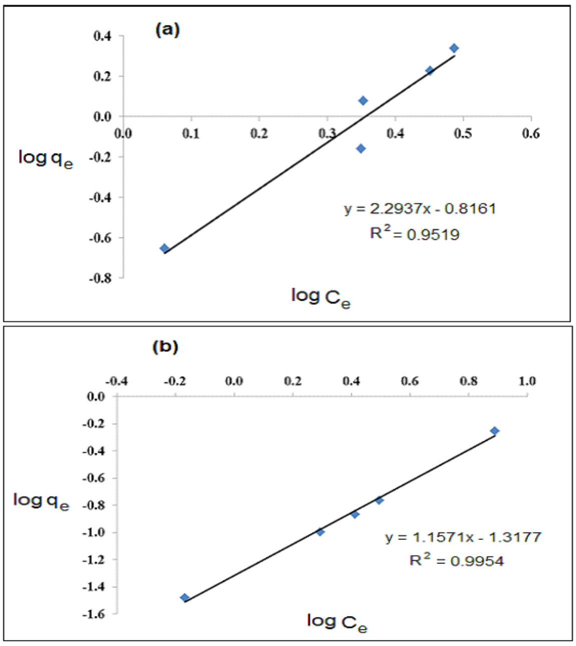

Fig. 9. Freundlich adsorption isotherm for Pb (II) (a) and Cr (VI) (b).

Pseudo-second-order kinetic model

The pseudo-second-order model is expressed as follows (Eq. 7):

$$\log\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{(Eq.7)}$$

Where, q_t = $(C_o\text{-}C_t)\ V/m_s$ = adsorption capacity at time t; q_e = adsorption capacity at equilibrium (mg/g); C_o = initial metal concentration (mg/L); C_t = Metal concentration (mg/ L) at time t (min.); V = Volume of Metal solution (L); m_s = weight of adsorbent (g); k_2 = rate constant of the second-order equation. By comparing the values in Table 2, it is obvious that, the correlation coefficient for the pseudo first-order kinetic model obtained is lower than the pseudo second-order model. For the pseudo second-order kinetic model, a high degree of correlation coefficient was obtained. The results suggest that for both the metals, sorption system follow the pseudo-second order kinetics as the experimental and calculated q_e values are consistent. Also, for the pseudo second order kinetics the plot of log t/q_e versus t shows a linear relationship as represented in Fig. 11. In accordance with the pseudo second order model the rate-limiting step of this sorption system suggest chemisorption that involves sharing or exchange of electrons between the adsorbate and the adsorbent.

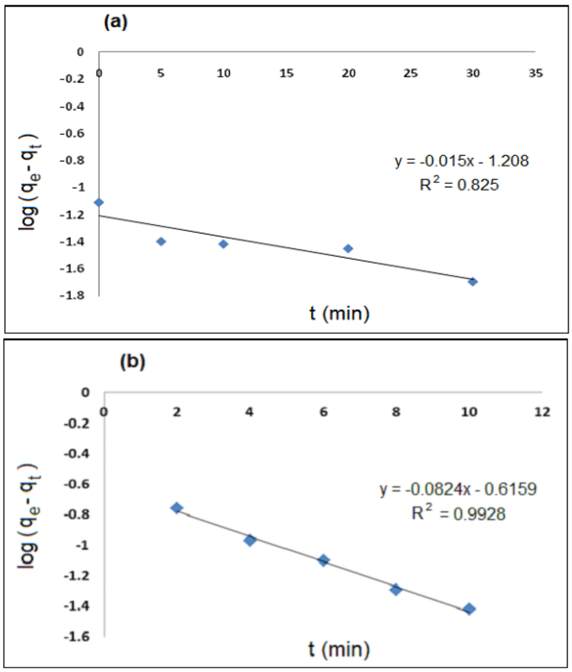

Fig. 10. Pseudo-first-order kinetic model for sorption of Pb (II) (a) and Cr (VI) (b).

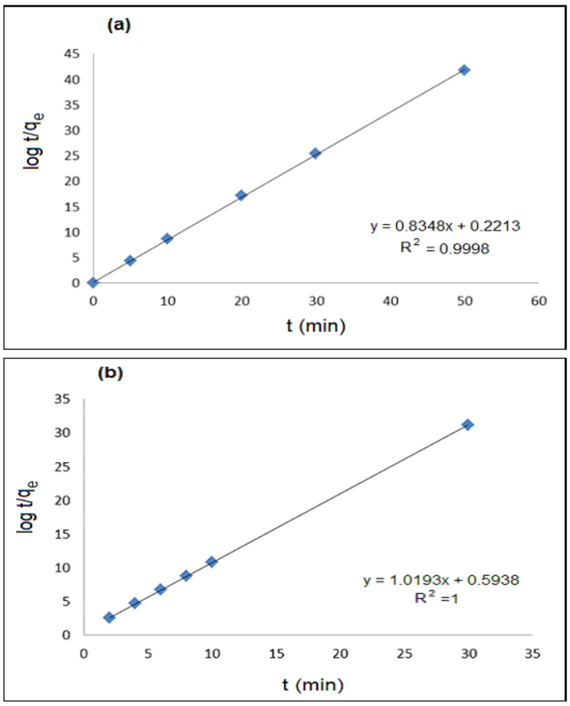

Fig. 11. Pseudo-second-order kinetic model for sorption of Pb (II) (a) and Cr (VI) (b).

Conclusion

It is evident from the present study that inexpensive and locally available materials such as potato carrot peel mixture can be utilized for the elimination of heavy metals which is otherwise adding to the organic waste piles. The removal of Pb (II) and Cr (VI) from aqueous solutions strongly depends on the pH of solution with maximum adsorption obtained at pH 5.0 and 2.0, respectively. Increased temperatures tend to decrease biosorption for both metal ions, suggesting that the adsorption onto the biomass is favorable at low temperature. Furthermore, maximum adsorption with short time span i.e. 50 min. for Pb (II) and 30 min. for Cr (VI) suggests the involvement of surface adsorption phenomenon for removal of both metals. Higher metal concentrations have been found to decrease biosorbent efficiency for the uptake of Pb (II) and Cr (VI) from their respective aqueous solutions. Increasing biosorbent dose tend to increase in % adsorption due to increased available number of adsorption sites. In the present study, Langmuir model (monolayer adsorption) is more suitable than the Freundlich model for the adsorption for both metal ions. Also, the adsorption process for Pb (II) and Cr (VI) follows pseudo-second-order kinetics suggesting that the rate controlling step of this sorption system may be chemisorption.

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