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Removal efficiency of vegetable waste mixture for uptake of Cd (II) and Cu (II) ions

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

Key words: Biosorbent; ICP-OES; Adsorption model; Kinetics studies.

Abstract

The adsorption capacity of prepared vegetable waste mixture to remove Cd (II) and Cu (II) ions from their respective aqueous solutions was investigated in a batch experimental setup. Maximum uptake capacity of biomass for Cd (II) (303.03 mg/g) and Cu (II) (1000 mg/g) was observed at pH 7 and 2, respectively. The optimized biosorbent dosage of 3.0 g was found to remove metal concentration of 110 ppm of Cd (II) and 30 ppm of Cu (II) ions at temperatures 45°C and 50°C, respectively. The system attained equilibrium when contact time for Cd (II) was 30 minutes while for Cu (II) it was 45 minutes. FT-IR and ICP studies of neat and metal loaded biomass also revealed the presence of Cd (II) and Cu (II) onto the biomass. Kinetic studies showed that Cd (II) and Cu (II) adsorption on the prepared biosorbent follows a pseudo-second order reaction, while the system fits well in the Langmuir isotherm model. The present study revealed that the metal uptake capacity of prepared biomass is significantly higher as compared to the work reported earlier.

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

Introduction

Several industrial processes produce aqueous effluents containing toxic metal contaminants, whereas World Health Organization (WHO) the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead, of these Cd (II) and Cu (II) are especially hazardous and highly toxic (El-Sayed *et al.*, 2010). The use of Cd (II) and Cu (II) in industrial sector has increased manifold, and thus escalated the related toxic consequences particularly affecting skin, lung, liver and kidney functions. The major techniques for treatment of Cd (II) and Cu (II) bearing waste streams including precipitation, evaporation, adsorption, ion exchange, membrane processing, solvent extraction (Elshazly and Konsowa, 2003), are either expensive, not environment friendly or usually dependent on the concentration of the waste. Therefore after perpetual efforts, biosorption has been widely perceived as efficient, eco-friendly and cost effective remedy for wastewater treatment in the environmentalist's fraternity. This being either physical adsorption, ion exchange, complexation or precipitation, and pertains to the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Sankaran *et al.*, 2005). The recent trend towards the utilization of waste materials such as agricultural or kitchen waste as biosorbents are cost effective, produce less toxic by-products and can prove to be significant in our region. However, many low-cost biosorbents have been reported such as ground coffee (Azouaou *et al.*, 2010), corncob (Zafar *et al.*, 2013), spent brewery grains (Jaikumar and Ramamurthi, 2009), egg shell (Tsai *et al.*, 2006), potato peel (Taha *et al.*, 2011), tree barks (Abdullah and Prasad, 2009), pomelo peel (Saikaew *et al.*, 2009), olive stone (Blazquez *et al.*, 2005), coconut copra meal (Ho and Ofomaja, 2006), citrus fruit peels (Chatterjee and Schiewer, 2011), spent grain leaves (Low *et al.*, 2000) to name a few.

The food industry produces huge amount of wastes, both solids and liquids, due to the preparation, production, and consumption of food which elevate the disposal issues and are consequently potential pollutants. Potato (*Solanum tuberosum*) processing industry, for instance, is one of the largest food processing industries. Waste generated due to its processing amount is in large percentage of the original potato fresh weight (Singh *et al.*, 2011). Potatoes and carrots are usually peeled during food processing as a consequence a large quantity of peel is generated which poses problem for the food industry for its disposal. Potato and carrot peels contain many active functional groups and hence are effective for the biosorption of heavy metal (Gill *et al.*, 2013). In the present study, optimized conditions were developed for the removal of Cd (II) and Cu (II) ions from the aqueous solution using 1:1 mixture of peels of potato and carrot as sorbent material so as to utilize the vegetable waste from the local potato industry and food market.

Materials and methods

Reagents

All the chemicals and reagents used in the experiments were of analytical grade including $3CdSO_4.8H_2O$ and $CuSO_4{\cdot}5H_2O$ (Merck) while HCl (99%) and NaOH obtained from 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.*, 2014). Thoroughly washed potato and 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 Cd (II) and Cu (II) solutions

Stock solutions (1000 mg/L) of respective ion solution were prepared in deionized water (DW).

Working solutions of Cd (II) and Cu (II) ions of required concentrations were prepared by adequate dilution of the stock solution with DW.

Batch biosorbent experiment

All experiments were carried out using batch mode because of its simplicity and reliability. For each set of experiments conducted for the optimization of conditions necessary for maximum adsorption of Cd(II) and Cu(II) ions, 25 mL of known concentration of Cd (II) and Cu (II) solution was taken and its pH was adjusted using of 0.1 N HCl and 0.1 N NaOH. A defined amount of biosorbent was added and flask was placed on a rotary 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 Whattman No. 40, ash less 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.

Analysis of Cd (II) and Cu (II) ions in solutions

Concentration of Cd (II) and Cu (II) in the solutions before and after treatment was determined by flame atomic absorption spectrometry (FAAS), using the hollow cathode lamp set at 15 mA while the analytical wavelength was adjusted at 232 nm. The data represent the average of three independent experiments for each parameter.

Metal uptake and percent sorption

Cd(II) ions and Cu (II) uptake was calculated by simple concentration difference method. Uptake of both the metals was calculated from the mass balance equation as follows (Eq. 1):

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

Where, q_e (mg of metal adsorbed/g adsorbent) ,V is the volume of the solution (L), Co is the initial concentration (mg/L), Ce is the final concentration in solution (mg/L) and m is mass of the sorbent (g).

Spectroscopic analysis of virgin and spent biomass

FT-IR spectroscopy was used to detect vibration frequency changes in the new, prepared biomass of potato and carrot peels. The FT-IR spectrometer was equipped with software - IR Solution, and the working range was 400–4000 cm^{-1} using a KBr window.

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 Cd (II) was digested by adding 7 mL of H_2SO_4 and 5 mL of HNO_3. 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 array of charge injection devices (CID), was used for measurement of the metals. A high precision peristaltic pump with 12 rollers and 4 channels having adjustable speed (0–125 rpm) was employed for sample introduction into the plasma.

Results and discussion

FTIR and ICP studies of biosorbent

FTIR spectroscopy was applied to identify the functional groups of prepared biosorbent responsible for Cd(II) metal adsorption. As shown in Fig.1, FTIR spectrum of virgin biosorbent was compared to that of Cd (II) loaded biomass. In FTIR spectrum of virgin biomass, broad peaks present at 3354.32 cm^{-1} and 1329 cm^{-1} are due to -OH group of alcohols and phenols, C=C stretching in aromatic ring is shown at 1415 cm^{-1}, peaks at 1654.98 cm^{-1} and 1741.78 cm^{-1} indicate presence of C=O stretching, C-Br stretching appears at 561.30 cm^{-1} while peak present at 2926 cm^{-1} corresponds to -C-H stretching vibration. Rest of the peaks at 2926 cm^{-1}, 2150 cm^{-1}, 1797 cm^{-1}, 1678 cm^{-1} and 1153 cm^{-1} indicate presence of -C-H stretching, -C-C stretching, C=O stretching, C=N stretching and C-O stretching, respectively (Silverstein and Webster, 2009).

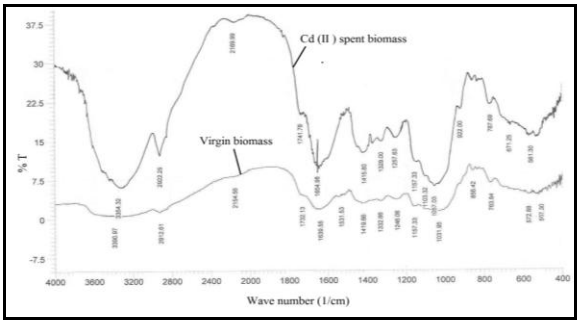

Fig. 1. FTIR spectra of virgin mixture biomass and metal loaded biosorbent.

In case of Cd spent biomass, peaks present in the region of 600-450 cm^{-1} can be attributed to the C-Metal stretching vibration (Schieber and Saldana, 2009). The intensity of peaks in the spectrum of the mixture loaded with Cd (II) was greater than that of the virgin mixture spectrum (Fig. 1). This can be due to adsorption process; metal from solution is being absorbed by the mixture which leads to greater intensity of these peaks in the spectrum of the nickel loaded mixture.

Analysis of the spent biosorbents was also conducted *via* ICP-OES to validate the uptake of metal ions. Biosorbent loaded with 50 mg/L of Cd (II) was found to contain 11.17 µg/mL of Cd (II) while in case of Cu (II), the biosorbent contained 8.5 µg/mL when loaded with 50 mg/L of Cu (II) thus validating the fact that the prepared biosorbent has the capacity to adsorb and remove Cd (II) and Cu (II) ions from their respective aqueous solutions.

Effect of pH

pH has a significant impact on metal uptake since it determines surface charge of the sorbent, solubility of metal ion, concentration of counter ions on functional groups of the biomass and the degree of ionization and speciation of adsorbate. Experiments were conducted at room temperature to study the effect of solution pH on Cd (II) and Cu (II) ions biosorption by contacting with 1.0 g of biosorbent dose and shown in fig. 2. The removal of Cd (II) was about 93.24% at pH 1 and reached its maximum value 97.09% at pH 7. The removal of Cd (II) ions rapidly increases with increasing pH and reaches a maximum at pH 7 (97.09%) and again show decreasing trend of removal at pH 9 (96.33%). So the pH optimized for Cd (II) ions is 7. Low pH values have a greater amount of H$^+$ ions which may compete with Cd (II) ion for adsorption sites, as indicated by the low removal at low pH (Hidalgo-Vazquez *et al.*, 2011). With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption (Hanafiah *et al.*, 2007). At higher values of pH that is at 8, Cd (II) ions precipitate out as $Cd(OH)_2$ (Pino *et al.*, 2006). On the other hand it was observed that there is considerable increase in the adsorption of Cu (II) with increase in pH from 1 to 2. The optimum pH for metal removal was found to be 2 as shown in Fig. 2. This may be ascribed to the competition between the hydrogen and Cu (II) ions on the sorption sites; at low pH due to the high electrostatic forces of attraction the percentage of Cu (II) removal is high. A decrease in adsorption above the pH 2.0 may be due to the activity of anionic species which retard the approach of Cu (II) ions further towards sorbent surface (Gill *et al.*, 2014; Tanska *et al.*, 2007).

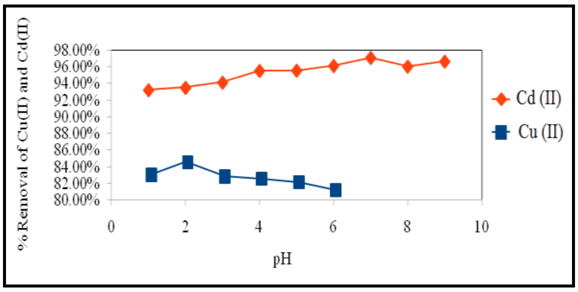

Fig. 2. Effect of solution pH on adsorption of Cd (II) and Cu (II). [Ambient Temperature = 26±1°C; Contact time =30 min.; Metal ion conc. = 50 ppm; Biosorbent dose =1.0 g; Shaking speed=150 rpm].

Effect of temperature

Temperature also has a significant contribution on the rate of biosorption of heavy metals. It affects a number of factors including stability of metal ion species depending on the biosorption sites and the ionization of chemical moieties on the cell wall. The effect of temperature for the adsorption of both metals was studied in the temperature range of 30 °C to 70 °C by keeping pH 2 constant. Each system was then placed in a water bath under controlled temperature. The maximum adsorption for Cd (II) was found to be 97.79% at 45 °C. The uptake of Cd(II) increased with increasing temperature due to the dissolution of the adsorbing species, the changes in the size of the pores and the enhanced rate of intra particle diffusion of adsorbate as diffusion is an endothermic process (Hanafiah *et al.*, 2007). With the increase in temperature further 50 °C to 70 °C decrease in adsorption of Cd (II) ions occur because pores size of material is increased resulting in increased surface area available for sorption, diffusion and penetration of Cd (II) ions within the pores (Rathinam *et al.*, 2010). For the Cu (II) that maximum adsorption occurred at 50 °C as shown in Fig. 3. For Cu (II) the percentage of adsorption increases with increase in temperature which indicates existence of endothermic process i.e. the adsorption reaction absorbs energy in the form of heat from the environment (Schieber and Saldana, 2009). 50°C temperature with percentage adsorption of 78% was optimized for the removal of Cu (II) ions, as at high temperature (60°C and above) denaturing of sorbent can also occur.

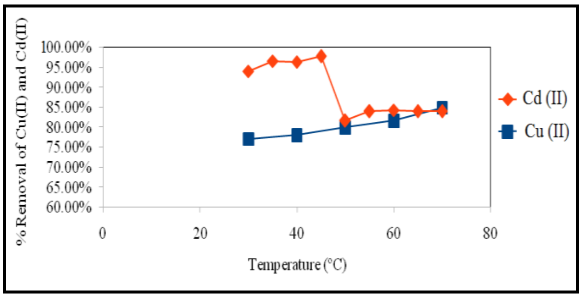

Fig. 3. Effect of temperature on adsorption of Cd (II) and Cu (II). [pH 7: Cd (II) and pH 2: Cu (II); Contact time = 30 min.; Metal ion concentration = 50 ppm; Biosorbent dose =1.0 g; Shaking speed=150 rpm].

Effect of contact time

Contact time between the sorbate and the biosorbent plays a major role in the efficient removal of heavy metals. A series of experiments were done by varying the contact time for Cd (II) and Cu (II) in the range from 0 to 130 min. As apparent in Fig. 4, for Cd (II) biosorption efficiency increases and is quite rapid within the first 30 min. The short contact time of 30 min. is an indicator of surface adsorption of Cd (II) ions (Taha *et al.*, 2011). It is due to the presence of carboxyl and hydroxyl groups of the biosorbent which rapidly attract the metal ions in this short period of time and maximum adsorption was taking place but in the case of Cu (II) it was observed that percentage of Cu (II) metal adsorbed increase with increase in contact time. The optimum contact time for maximum Cu (II) absorption was observed to be 45 min. as after that there is no appreciable increase in the adsorption. The increase in adsorption with time could be attributed to the availability of large number of vacant binding sites during the initial stages, but afterwards the occupation of the remaining vacant sites will be difficult due to the repulsive forces between the Cu (II) ions on the solid and the liquid phases (Abdullah and Prasad, 2009).

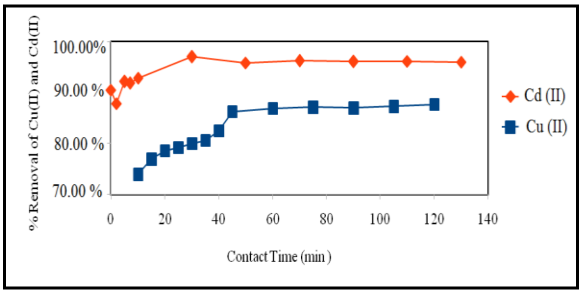

Fig. 4. Effect of contact time on adsorption of Cd (II) and Cu (II). [pH 7: Cd (II) and pH 2: Cu (VI); Temperature = 45°C Cd (II) and 50°C: Cu (II); metal ion concentration= 50 ppm; biosorbent dose =1.0 g; shaking speed=150 rpm].

Effect of metal ion concentration

The metal uptake mechanism is dependent not only on the properties of biosorbent but also on the concentration of metal ions solutions. It provides a driving force to overcome all mass transfer resistances of the metal between solid and aqueous phase (Zahrim *et al.*, 2011). Generally at low concentrations, metals are adsorbed by specific active sites where as at higher concentrations, low adsorption yield is due to the saturation of adsorption sites (El-Sayed *et al.*, 2010). Cd(II) sorption was studied in batch experiments at a range of 10 to 150 ppm while Cu(II) in the range between from 10 to 70 ppm. The maximum percentage removal for Cd (II) was found to be at 97.01% at metal ion concentration of 110 ppm which demonstrates that adsorption of Cd (II) ions increases with increasing concentration of metal ion. This is probably due to higher interaction between metal ions and the biosorbent (Rathinam *et al.*, 2010).The higher adsorption by an increase in the number of metal ions competing for the available binding sites in the adsorbent for complexation of Cd (II) ions at higher concentration levels (Mahvi *et al.*, 2008). It can also be seen from the Fig. 5 that as the concentration of Cu (II) metal is increased from 10 to 30 ppm, % adsorption increases. This might be due to the fact that at low metal ion concentration, the active sites of metal attain equilibrium earlier as compared to that at higher concentration. With the further increase in concentration adsorption decreases this can be attributed to two reasons. Firstly, as the metal ion concentration increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency (Abdullah and Prasad, 2009) and secondly, at higher metal concentrations aggregation of sorbent particles occur which leads to less adsorption (Hussain *et al.*, 2009).

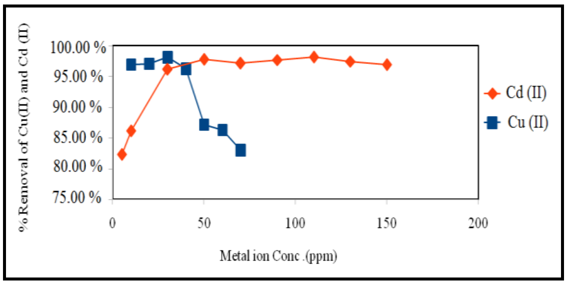

Fig. 5. Effect of metal ion concentration on adsorption of Cd (II) and Cu (II). [pH 7: Cd (II) and pH 2: Cu (II); Temperature = 45°C Cd (II) and 50°C: Cu (II); Contact Time = 30 min. : Cd (II) and 45 min.: Cu (II); biosorbent dose =1.0 g; shaking speed=150 rpm].

Effect of biosorbent dose

The effect of different doses of biomass (1.0 – 3.0 g) on the adsorption of Cd (II) and Cu (II) is summarized in Fig. 6 which showed that the adsorption increases by increase in biosorbent dose. The increase in the adsorption percentage of the metal ion with increase in biosorbent dose is due to the availability of greater number of active sites and consequently more surface area of the adsorbent at higher dose (Arshad *et al.*, 2008). The larger the surface area the large amount of ion adsorbed. This may due to the increase in the number of available sites for the complexation of heavy metals (Zawani *et al.*, 2009)· The maximum percent removal for Cd (II) at 3.0 g was found to be 98.18% and for Cu (II) it was found to be 96.15 %.

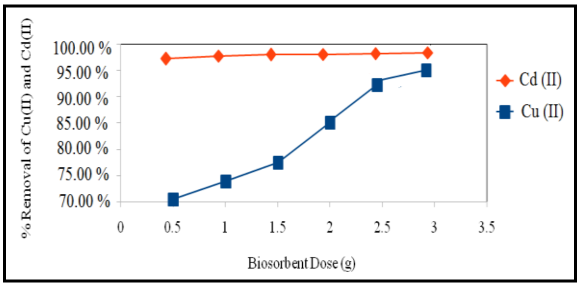

Fig. 6. Effect of biosorbent dose on adsorption of Cd (II) and Cu (II). [pH 7: Cd (II) and pH 2: Cu (II); Temperature = 45°C Cd (II) and 50°C: Cu (II); Contact Time = 30 min. : Cd (II) and 45 min.: Cu (II); metal ion concentration= 110 ppm: Cd (II) and 30 ppm: Cu (II); shaking speed=150 rpm].

Comparison of adsorption potential of Potato peel, Carrot peel and potato-carrot waste mixture

Experiments have been carried out to compare the biosorption potential of potato peel, carrot peel and the prepared mixture biomass for the uptake of Cd (II) and Cu (II) ions. Biosorbent dose of 3.0 g was fixed and the three biosorbents were treated separately with working solutions of Cd (II) and Cu (II).

As shown in Fig.7, mixture shows more promising results. Potato peel waste biomass showed removal of 89.05 % when treated with 110 ppm concentration of

Pb (II) solution and 86.18% when treated with 30 ppm concentration of Cu (II) solution. A further increase in % adsorption (91.34% of Cd (II) and 88.01% of Cu (II) ions) was observed when similar metal ion concentrations were exposed to carrot peel biomass. Maximum percentage adsorption of 98.18% and 96.15% were shown for mixture biomass from aqueous solution of 110 ppm of Pb (II) and 30 ppm of Cu (II), respectively. This indicates that the prepared biosorbent (mixture) has higher affinity might be due to increased number of available sites for the removal of Cd (II) and Cd (II) as compared to when they were used separately.

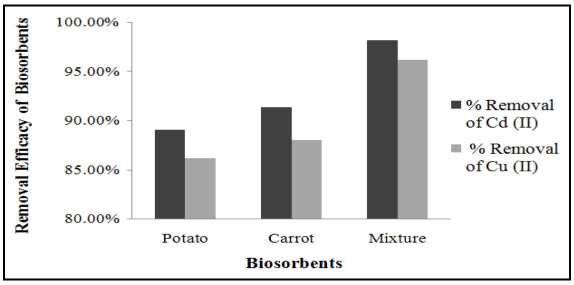

Fig. 7. Adsorption comparison for the removal of Cd (II) and Cu (II). [pH 7: Cd (II) and pH 2: Cu (II); Temperature = 45°C Cd (II) and 50°C: Cu (II); Contact Time = 30 min. : Cd (II) and 45 min.: Cu (II); biosorbent dose = 3.0 g; shaking speed=150 rpm].

Adsorption kinetic studies of Cd (II) and Cu (II) ions

In order to examine the mechanism of biosorption and potential rate controlling steps, kinetic models have been used to test experimental data. To check the dependence of rate of reaction on the concentration of reactants involved, pseudo-first and pseudo-second order models have been applied. The linear equation for the pseudo-first order of kinetic model is (Eq.2);

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad \_\_\_\_\_\_\_\_ \text{(Eq.2)}$$

Here; q_t is adsorption capacity at time t, q_e is adsorption capacity at equilibrium, C_o is initial metal concentration in mg/L, C_t is metal concentration in mg/L at time t, V is volume of metal solution in mL, m_s is weight of adsorbent in g, k_1 is pseudo-first order rate constant. The value of k_1 can be determined by plotting graph of log (q_e-q_t) against time (t). The pseudo first order kinetic models of Cd (II) and Cu (II) have been shown in the Fig. 8 (a) and (b).

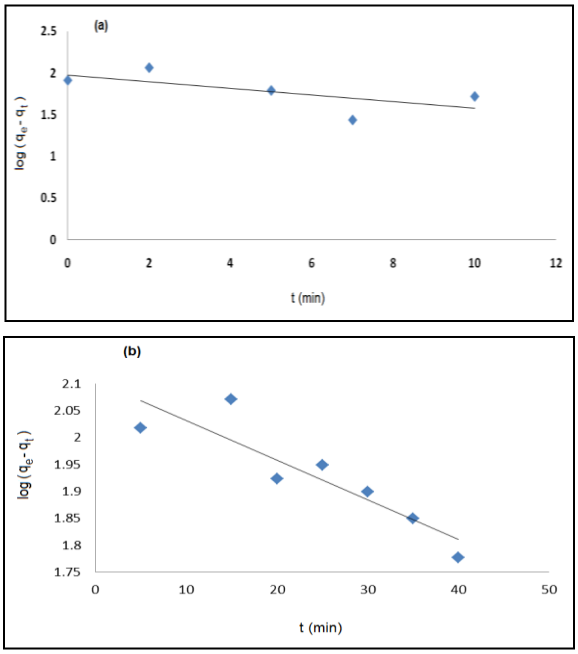

Fig.8. Pseudo-first-order kinetic model for sorption of Cd (II) (a) and Cu (II) (b).

The linearized expression of pseudo-second order reaction is explained as follows (Eq.3):

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad \_\_\_\_\_\_\_\_\_\_\_\_ \text{(Eq.3)}$$

Here; q_t is adsorption capacity at time t, q_e is adsorption capacity at equilibrium, C_o is initial metal concentration in mg/L, C_t is metal concentration in mg/l at time t, V is volume of metal solution in ml, m_s is weight of adsorbent in g and k_2 = pseudo-second order rate constant. The value of k_2 can be determined by plotting a graph of log t/q_e verses time (t) as shown in Fig. 8. The pseudo second order models for both the metals have been shown below.

As shown in Table 1, calculated correlation coefficients are reliable and closer to unity for pseudo-second order kinetics model than the pseudo-first order kinetic model, while the experimental and calculated values of q_e correspond well in case of pseudo-second order and also R^2 value is significant. Hence, the adsorption kinetics of Cd (II) and Cu (II) using potato/carrot adsorbent follows pseudo-second order kinetic model.

Table 1. Comparison of pseudo first order and pseudo second order kinetic models of Cd (II) and Cu (II) biosorption.

	Pseudo first order		**Pseudo second order**	
	Cd(II)	**Cu(II)**	**Cd(II)**	**Cu(II)**
K	0.090969	-0.016	0.02025	0.0009
q_e (cal) mg/g	94.32	127.05	1111.111	1071.81
q_e (exp) mg/g	1213.744	881.75	1213.744	1079.35
R^2	0.4536	0.803	0.9995	0.995

Adsorption isotherms

Equilibrium curves were applied to identify the design of an adsorption system therefore two adsorption isotherms namely; the Langmuir and Freundlich isotherm models were used to describe the obtained equilibrium data (Zawani *et al.*, 2009).

The linear form of Langmuir adsorption isotherm is shown in following Eq.4:

$$\frac{1}{qe} = \left(\frac{1}{q_{max}K_l}\right)\frac{1}{Ce} + \frac{1}{q_{max}} \quad \_\_\_\_\_\_\_\_\_\_\_\_ \text{(Eq.4)}$$

Here, Ce = equilibrium conc. of adsorbate (mg/L), q_e = amount of metal adsorbed/ g of the adsorbent at equilibrium (mg/g), q_{max} = Langmuir constant related to adsorption capacity, K_L = Langmuir constant related to rate of adsorption.

C_e and q_e were calculated for each initial metal concentration. Straight line is fitted by regression when $1/C_e$ is plotted against $1/q_e$ (Fig. 9) while slope and intercept of line gives values of q_{max} and k_l. The value of correlation coefficient for both, Cd (II) (R^2 =0.990) and Cu (II) (R^2 =0.991) indicated a strong positive relationship for the sorption data.

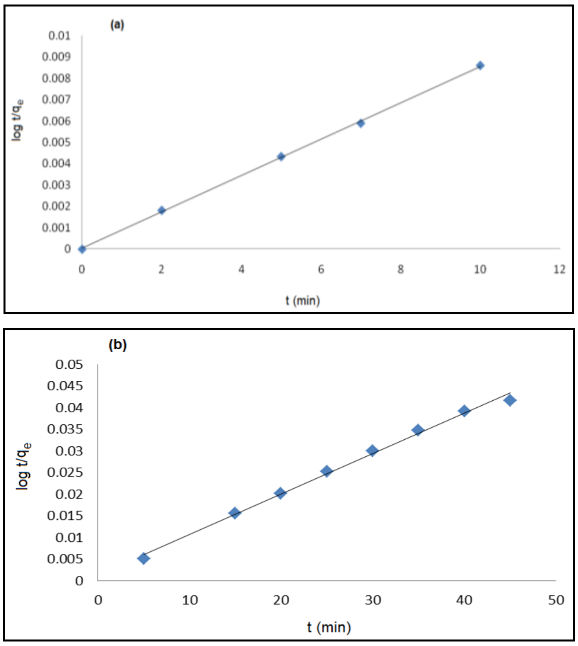

Fig.9. Pseudo-second-order kinetic model for sorption of Cd (II) (a) and Cu (II) (b).

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. 5):

$$R_L = \frac{1}{(1 + k_L C_o)} \quad \_\_\_\_\_\_\_\_\_\_\_\_ \text{(Eq.5)}$$

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 2) at initial concentration of 110 mg/L for Cd (II) ions and 30 mg/L for Cu (II) ions indicating favorable biosorption.

Table 2. Values for langmuir and freundlich adsorption isotherm parameters.

Langmuir adsorption isotherm			**Freundlich adsorption isotherm**		
	Cd (II)	**Cu (II)**		**Cd (II)**	**Cu (II)**
K_l	0.458	0.047619	K_f	333.58	29.31
q_{max}	303.03	1000	n	0.407	0.65
R_L	0.04	0.448	R^2	0.962	0.953
R^2	0.990	0.991			

The linear form of Freundlich adsorption isotherm is explained as follows (Eq.6):

$$\log qe = \log K_f + \frac{1}{n}\log Ce$$ ___________ (Eq.6)

Here, K_f = adsorption capacity and n = adsorption intensity. Larger these values, higher the adsorption capacity and n gives the favorability of the adsorption. The Fig. 11 shows the plot of log Ce and log qe from which n was calculated.

Although both the adsorption isotherms models for Cd (II) and Cu (II) ions held good for the system under study but the value of R^2 calculated from Freundlich isotherm was found to be quite less than the value of R^2 calculated in Langmuir Isotherm (Table 2). Therefore, Langmuir model is more applicable on the adsorption design of both the metals system indicating formation of homogenous biosorbent.

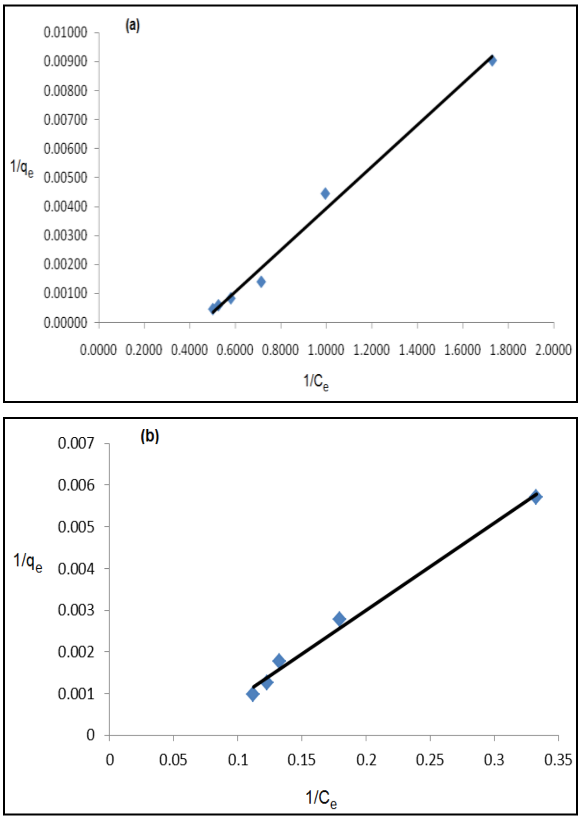

Fig. 10. Langmuir adsorption isotherm for Cd (II) (a) and Cu (II) (b).

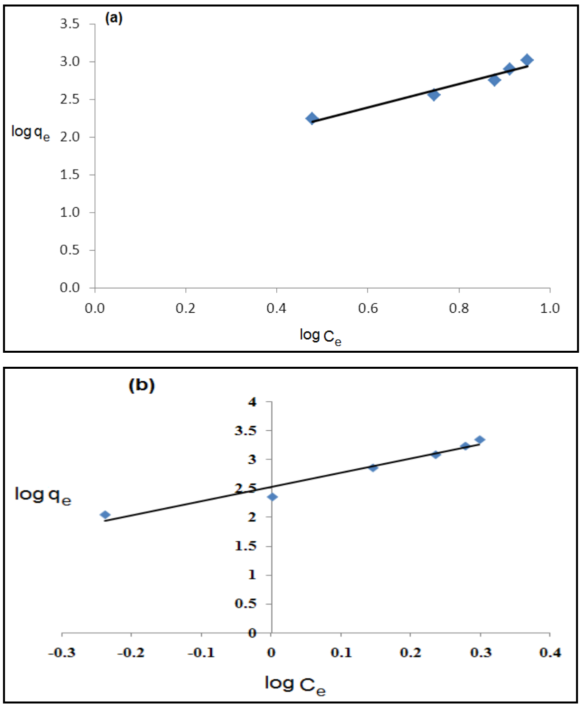

Fig. 11. Freundlich adsorption isotherm for Cd (II) (a) and Cu (II) (b).

Conclusion

The prepared biomass showed maximum uptake capacity of 303.03 mg/g and % adsorption of 98.18% for Cd (II) when optimized conditions (pH 7, 45 °C temperature, contact time 30 min., metal ion concentration 110 ppm and biosorbent dose 3.0 g) were provided to the system. In case of Cu (II), maximum uptake capacity of 1000 mg/g and % adsorption of 96.15 % was achieved with optimized conditions (pH 2, 50°C temperature, contact time 45 min., metal ion concentration 30 ppm and biosorbent dose 3.0 g). FT-IR and ICP studies also confirmed the presence of these metal ions in the spent biosorbent. The rate of reaction follows a pseudo second order model pseudo-second-order kinetics suggesting that the rate controlling step of this sorption system may be chemisorption; whereas the Langmuir model (monolayer adsorption) fits well to the data of both Cd (II) and Cu (II) biosorption.

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