J. Chil. Chem. Soc., 58, Nº 4 (2013)

A DETAILED INVESTIGATION ON ENGINEERING PARAMETERS FOR Cd(II) REMOVAL BY RIPPED CITRUS PARADISI PULP WASTE

TAHIR ISHFAQ[a], SAJIDA NAVEED[b], MOHSIN KAZMI[a,], HAQ NAWAZ BHATTI[b], NADEEM FEROZE[a]*

[a] *Department of Chemical Engineering University of Engineering & Technology Lahore Pakistan*
[b] *Department of Chemistry, University of Agriculture Faisalabad Pakistan*
(Received: March 26, 2013 - Accepted: August 30, 2013)

ABSTRACT

The contemporary investigation presents a fundamental study on the removal of Cd(II) by ripped Citrus Paradisi pulp waste (RCPW). The effects of various engineering parameters such as initial solution pH, biosorbent dose, agitation, contact time, initial concentration, temperature and different eluents were evaluated on the uptake of Cd(II) by RCPW. Optimum uptake of Cd(II) onto RCPW was observed at 6.5 pH, 0.05 g of biosorbent and 100 rpm. Pseudo second order kinetic model best described the process of Cd(II) uptake by RCPW. Results showed that the sequestration of cadmium on RCPW was in monolayer as described by Langmuir's Model. Increase in temperature negatively affected the biosorption capacity of Cd(II) on RCPW indicating exothermic nature of the phenomenon. 0.1N NaOH was found to be the best desorbent among HNO_3, H_2SO_4, HCl and EDTA.

Key Words: Batch study, Biosorption, Desorbent, Engineering parameters, Kinetic & Equilibrium models

1. INTRODUCTION

Rapid metropolitan intensification in the last century has gravely impinged on the fragile balance existing between mankind and nature. Man manufactured voluminous quantities of different compounds to sophisticate his living. Thus, directly or indirectly various toxic chemicals flighted into the aquatic resources. Remediation of heavy metals from the wastewater has been keenly researched for their potential effect on the public. Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Zinc etc. can be detected in both natural and industrial effluents [1-3].

Cadmium has exerted a pull on attention due to its lethal effects on human. Alloy manufacturing, battery, electroplating, mining, pigments, plastics, refining processes, smelting etc. produce cadmium polluted wastes. Cadmium can cause a variety of acute and chronic disorders on ingestion beyond its permissible limits (0.005 mg/L) [2,4]. Bone lesions, cancer, emphysema, hypertension, lung insufficiency, renal disturbances are some of the well documented adverse health effects caused by cadmium exposures. Therefore, it is mandatory to recover cadmium from water as well as wastewater [2,4].

A list of conventional technique can be identified for the removal/ concentration of Cadmium from the aqueous media. It includes reverse osmosis, evaporation, sedimentation, adsorption, coagulation, ion exchange etc [5- 10]. Each of aforementioned technologies is hindered by the economical problem when applied for the remediation of dilute metal solutions. Over the last few decades, biosorption has been recognised as a potential alternative to cope with economical barriers when dealing with lean solutions [11- 15].

Removal of, whether, metals or non metal species by departed biomass has been recognized as biosorption. Literature witnesses the use of diverse types of biomass including bacteria, algae, fungi, agricultural waste and biochemical industries residues [16]. All these biomasses are whether cheaply available in the surrounding or can be generated through simple cultivation process. Low fixed and operating costs, regeneration of biomass, better selectivity, modest residence time, not by product formation and deletion of lethal metals from a wastewater irrespective of its level of toxicity are some salient features of biosorption [17]. The application of dead biomass presents some advantages over other materials viz: (i) the metal elimination process is not limited by metal noxious restrictions, (ii) No requirements of any sort of ingredients for culture and (iii) Ease of metal desorption from biomass and its reuse [1,17].

Citrus fruit are produced abundantly all over the world. Citrus paradise is the botanical name of grape fruit. Grapefruit is an important member of citrus family which has both nutritional and therapeutic characteristics. Diatbatic and high blood pressure patients are being advised to take grape fruit juice. It has been indicated by FAO that in 2002 there was a production of 5 million tons of grapefruit in 74 countries [18,19]. Thus, tremendous amount of pulp waste may generate all over the world. In the current investigation, waste pulp of citrus paradise has been investigated for the removal of Cd(II). The objectives of the current investigation are to determine the effects of pH, biosorbent dose, agitation, initial metal concentration, temperature and eluent on the uptake of Cd(II). Pseudo first and second order models were used for kinetic modelling. Langmuir and Freundlich models were employed to interpret the mechanism of biosorption of Cd(II) onto citrus paradise waste.

2. MATERIALS AND METHODS

2.1 Biosorbent Preparation

In the present study fresh, ripped deep yellow grape fruit were selected to obtain biomass. *Citrus paradisi* (grape fruit) waste biomass used in this work was harvested from "Institute of Horticultural sciences, University of Agriculture, Faisalabad, Pakistan". The lignocellulosic fiber derived from *Citrus paradise* fruit by cold pressing and soaked overnight in distilled water to remove particulate material from its surface. It was first sun dried and then oven dried at 60 °C for 72 hours and used as biomass. One kilogram of biomass was sub sampled for use in the experiments. In order to ensure that homogenous samples are collected, standard sampling techniques were applied. Dried biomass was ground by using food processor (Moulinex, France). The biomass was sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain adsorbent with homogenous known particle size. The fraction with <0.255-0.100 mm was selected for use in the sorption tests. The sieved sorbents were stored in $CaCl_2$ in ambulised form at 4 °C.

2.2 Reagents

All chemicals used in these studies were pro-analysis grade and were purchased from Merck Company (Darmstadt, Germany), and they were of analytical grade including: $Cd(NO_3)_2.4H_2O$ H_2SO_4, HCl, HNO_3, Sodium hydroxide EDTA, Calcium chloride, and Cd(II) atomic absorption spectrometry standard solution (1000 mg/L).

2.3 Batch biosorption studies

Stock Cd (II) solution (1000 mg/ mL) was prepared using DDW. Cadmium solutions of different concentration were prepared by adequate dilution of the stock solution with DDW. In all sets of experiments fixed volume of Cd (II) solutions (100 mL) were thoroughly mixed with biosorbent at 100 rpm and 30 °C. The effect of different experimental parameters such as pH, biosorbent dose, initial metal concentration, shaking speed, temperature and contact time was checked on sorption of Cd (II) by *Citrus paradisi* waste biomass. For adjusting the pH of the medium 0.1 M solutions of NaOH and HCl were used. The conical flasks were covered with aluminium foil and were placed on a rotating shaker with constant shaking. At the end of the experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman No. 40, ash less). Preliminary tests were performed at 30 °C using an initial Cd (II) (initial pH 6.0 and 4.8), and 100 rpm for screening studies. The sorption time was 6 h and the equilibrium on Cd (II) uptake was attained.

2.4 Determination of the Cd (II) contents in the solution

The concentration of Cd (II) in the solution before and after the equilibrium was determined by Flame Atomic Absorption Spectrometry (FAAS), using a Perkin-Elmer A Analyst 300 Atomic Absorption Spectrometer equipped with an air-acetylene burner and controlled by Intel personal computer.

2.5 Metal uptake

The Cd (II) uptake was calculated by the simple concentration difference

 e-mail:engr.smalikazmi@gmail.com

method. The initial concentration C_i (mg/L) and metal concentrations at various time intervals, C_e (mg/L), was determined and the metal uptake q_e (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation as follows:

$$q_e = (C_i - C_e)V/1000w$$

Where V is the volume of the solution in mL and w is the mass of the sorbent in g.

% sorption is given as:

$$\% \text{ Sorption} = (C_i - C_e)/C_i \times 100$$

2.6 Statistical analysis

All data represent the mean of three independent experiments. All results were discussed by using mean ± SD (standard deviation). All statistical analysis done by using Microsoft Excel 2007, version office Xp. The correlation coefficient (R^2) values of the linear form of pseudo-first order and pseudo-second order models also determined using statistical functions of Microsoft Excel, 2007 (version Office XP, Microsoft Corporation, USA)

3. RESULTS AND DISCUSSION

3.1 Effect of pH

Literature shows that initial solution pH has momentous effect on the uptake of a metal from aqueous solution whether the biosorbent is specific or non specific [9]. It has dual effect on a metal biosorption as it not only affects the metal solubility but also ionizes the functional groups present on the biosorbent surface. The interaction of Cd^{++} with RCPW may be represented by the following reversible reaction

$$Cd^{++} + [RCPW] - H_2 \leftrightarrow [RCPW] - Cd + 2H^+$$

Where [RCPW] denotes the concentration of the active sites of the biosorbents. Equation (1) shows that an increase in H+ concentration will shift the equilibrium in the backward direction resulting in lesser uptake of Cd(II) [8]. Thus, to establish an optimum pH a series of experiments were performed in which pH was varied between 3 to 7 and consequent change in uptake of Cd(II) was determined as shown in Fig.1.

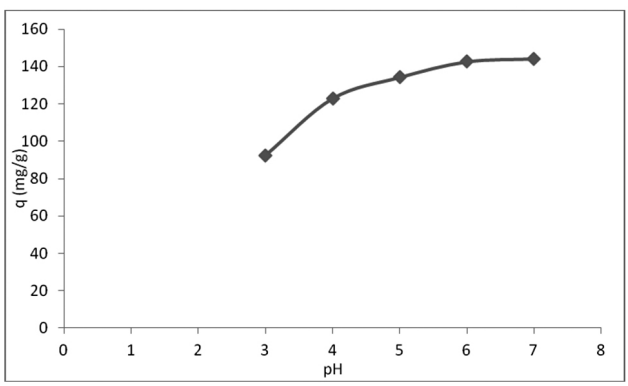


Fig.1. *Effect of pH on uptake of Cd(II) by RCPW (agitation = 100 rpm, T = 30 ºC, Dose = 0.05 g, Time = 6 h. C_o =100 mg/L)*

Similar trends have been observed elsewhere [2]. Fig.1 shows that uptake of Cd(II) increased from 92.2 to 144.2 mg/g as the pH varied from 3 to 7. Thus, the Cd(II) removal by RCPW is highly pH dependent. Increase in uptake of Cd(II) by RCPW was significant between pH 3 to 5 and then approaching a plateau between 5 to 7. The region between pH 3 to 5 is also called adsorption edge [10]. Below pH 3, the surface of RCPW may be blanketed by H^+ making it difficult for Cd^{++} to reach to the binding sites due to electrical repulsion. However, it is important to note that uptake of Cd(II) was not negligible at pH 3 which emphasized the existence of multiple binding mechanisms and hence indicating complex physic-chemical nature of the biosorption phenomenon. The preponderance of H^+ decreases as the pH increases, resulting in electrostatically beneficial atmosphere and hence escalating trend of Cd(II) uptake. To avoid the formation of hydroxo ions of Cd(II), the pH was not increased beyond 7 as these species are not bound to sorption phenomenon and may settle on the biosorbent surface [4]. pH 6.5 was selected as an optimum for the further study.

3.2 Effect of biosorbent dose

Biosorbent dose is an important parameter which is directly linked with the number of available sorption sites in the system. For the given concentration of adsorbate, sufficient number of active sites should be present to carryout sequestration of metal optimally. A sequence of experiments were performed in which amount of RCPW was varied between 0.05g to 0.4 g and its effect on uptake of Cd(II) was examined. Fig. 2 indicates the effect of biosorbent dose on the biosorption of Cd(II). It shows that on increasing dose, the uptake of Cd(II) was reduced. An analogous result was found by Padmavathy et al (2003) [20] while studying the dose of baker's yeast on the biosorption of Ni(II). This trend may be interpreted as, on increase of RCPW dose against fixed concentration of Cd(II) i.e., 100 mg/L, resulted in increase of vacant adsorption sites hence a lower uptake was observed on increasing the biomass dose beyond 0.05 g [8]. Therefore, RCPW was used in 0.05 g in all experiments.

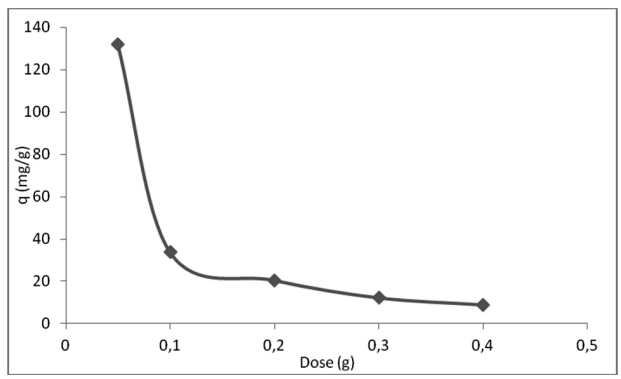


Fig. 2. *Effect of RCPW dose on uptake of Cd(II) (agitation = 100 rpm, T = 30 ºC, pH = 6.5, Time = 6 h. C_o =100 mg/L)*

3.3 Effect of Agitation

Biosorption involves complex mass transfer of solute from the bulk of the solution to the biosorbent surface. Thus, the dispersion of the biomass is a significant parameter which should be carefully monitored. To achieve this objective, effect of rpm of agitation was investigated on the uptake of Cd(II) as depicted in Fig. 3.

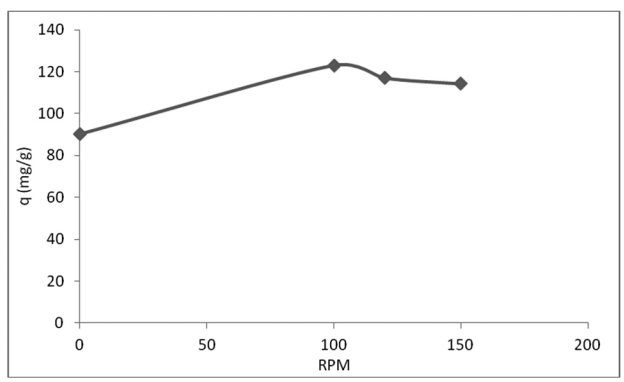


Fig.3. *Effect of agitation on uptake of Cd(II) by RCPW (Dose = 0.05 g, T = 30 ºC, pH = 6.5, Time = 6 h, C_o =100 mg/L)*

It was found that significant amount of Cd(II) was removed even at 0 rpm (90.4 mg/g). The uptake of Cd(II) was improved (123 mg/g) when rpm increased to 100 rpm. This may be interpreted in terms of reduction of convective resistance due to agitation. Further increase in rpm to 150 (114.2 mg/g) did not improve the uptake which may be due to the desorption of Cd(II) from RCPW surface due to weak bonding unable to withstand strong agitation [1-2].

3.4 Effect of Contact Time

Successful practical application of sorption phenomenon demands the determination of rate of metal sorption which is also a precondition for an optimum process and reactor design [8]. To ascertain a suitable contact time between the biomass and Cd(II) synthetic solution, uptake of RCPW was

determined in a series of experiments as a function of time varied from 15 to 1440 minutes. Fig. 4 shows a smooth and continuous curve between uptake of Cd(II) onto RCPW and time suggesting the formation of monolayer [4] on the adsorbent surface.

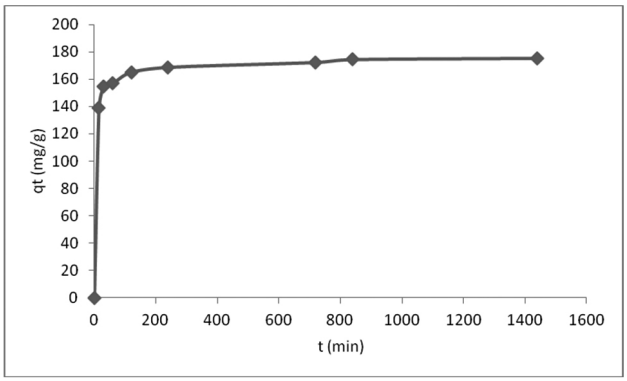


Fig. 4*. Effect of contact time on uptake of Cd(II) by RCPW (Dose = 0.05 g, T = 30 ºC, pH = 6.5, rpm = 100, C_o =100 mg/L)*

The initial segment entails up to first 120 minutes showing rapid adsorption rate chased by a slow Cd(II) uptake step broadened over considerablely long duration until the saturation of the biosorbent was achieved. Prolonging contact time from 120 minutes to 1440 minutes resulted in a small increment of uptake i.e., 165.2 to 175.4 mg/g which indicated the establishment of the equilibrium. 360 minutes (6h.) were taken as equilibrium time. The two step Cd(II) removal process, primary being fast and secondary slower, has also been observed elsewhere [8]. First speedy step may be attributed to the occupation of vacant sites on RCPW resulting in a fast removal of Cd(II). As the biosorption proceeds, the competition to occupy the sites increases and the removal process becomes less efficient [8].

3.4.1 Kinetic Modelling & Mechanism

To explicate the time course of biosorption of metal upon a biomass, several authors have reported the use of multiple kinetic expressions [2]. Table 1 shows the kinetic model used in contemporary study. Pseudo first kinetic model is an abundantly used rate expression.

Table 1. Different Kinetic Models

Kinetic Model	Differential	Integral	Plot	Reference
Pseudo 1st Order	$\frac{dq_t}{dt}=k_1(q_e-q_t)$	$\ln(q_e-q_t)=\ln q_e-k_1t$	$\ln(q_e-q_t)$ vs t	[22]
Pseudo-2nd Order	$\frac{dq_t}{dt}=k_2(q_e-q_t)^2$	$\frac{t}{q_t}=\frac{t}{q_e}+\frac{1}{k_2q_e^2}$	$\frac{t}{q_t}$ vs q_t vs t t	[21]
Weber-Morris	--------	$q_t=kt^{0.5}$		[22]

It is applied for liquid-solid system in equilibrium with each other. It assumes that rate of uptake of specie is directly proportional to vacant adsorption sites. A linear plot between $\ln(q_e - q)$ vs time would indicate the applicability of this rate expression. Fig. 5 shows the use of pseudo first order kinetics for the biosorption of Cd(II) upon RCPW. R^2 for pseudo first order kinetic was 0.7639. Due to poor correlation with the experimental data it was concluded that biosorption of Cd(II) did not follow pseudo first order kinetic.

Literature shows that pseudo second order kinetic satisfies most of the biosorption phenomenon [10,21]. It has been derived based on the assumption that the rate controlling step is chemisorption during biosorption phenomenon. Further, it assumes that the rate of fixation of ion on the biosorbent's active sites is directly proportional to the square of the vacant biosorption sites given in Table 1. The applicability of this model can be checked by plotting t/q_t versus t. Fig. 6 illustrates that the time course of Cd(II) uptake by RCPW followed excellently pseudo second order rate expression with $R^2 = 1.000$. The value of equilibrium uptake q_e estimated based on slope of the graph was 175.84 mg/g which was in close agreement with the experimentally observed (175.4 mg/g). However, there is a draw back of pseudo second model that it does not satisfy the adsorption phenomenon at t = 0.

Particle size, porosity and specific surface area of the biosorbent are few important structural properties which can affect the biosorption of Cd(II) onto RCPW [1]. Therefore, it was important to discuss the intraparticle diffusion. The resistance faced by the Cd(II) ion in the bulk of the solution may be ignored on account of sufficient shaking and dispersion of the biomass. Hence, diffusion of Cd(II) can be studied with respect to three processes viz, diffusion through the liquid film around RCPW, intraparticle diffusion through the biomass and fixation of the Cd(II) on the active sites. Weber and Morris proposed a model given in the Table 1. The relationship between q_t and $\sqrt{t}$ is shown in Fig. 7. It can be seen that plot can be divided into two linear portions indicating the existence of multiple steps in the biosorption of Cd(II) onto RCPW. First linear segment contributed to the diffusion through film and second flat portion indicated the incidence of pore diffusion. Similar results have been shown in multiple papers [1,3-4]. Fig. 7 illustrates that pore diffusion is not the only rate controlling step as the plot did not pass through the origin [1].

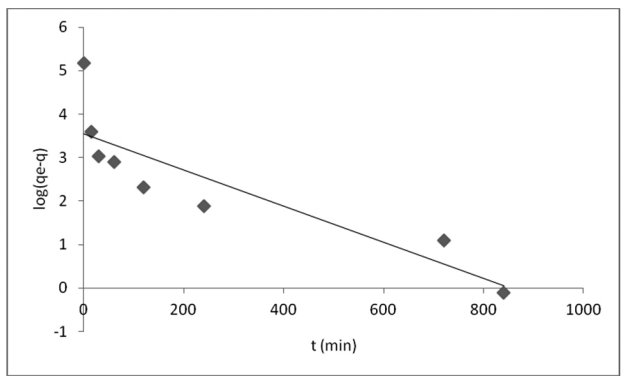


Fig.5 *Fitting of pseudo first order kinetics on the biosorption of Cd(II) by RCPW.*

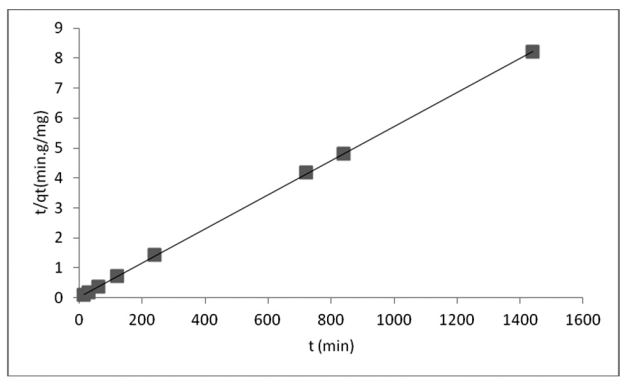


Fig.6 *Fitting of pseudo 2nd order kinetics on the biosorption of Cd(II) by RCPW*

3.5 Effect of Initial Concentration

Performance of RCPW was investigated at different mass transfer driving forces by varying concentration of Cd(II) between 25 to 200 mg/L. Cd(II) uptake by RCPW enhanced from 22.4 mg/g to 307.2 mg/g when the concentration was increased as shown in Fig.8. This can be explained as, greater number of Cd(II) species were adsorbed when its concentration was increased.

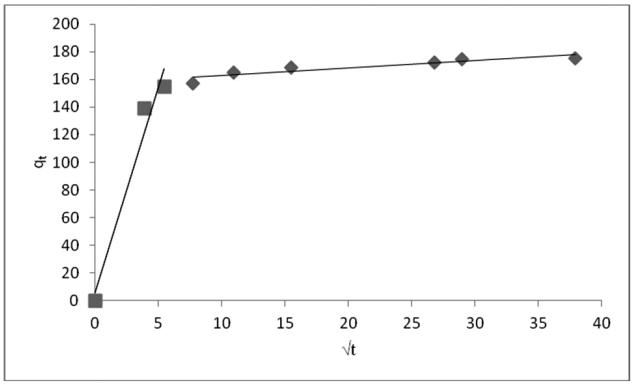


Fig.7. *Fitting of Pore diffusion model on biosorption of Cd(II) by RCPW*

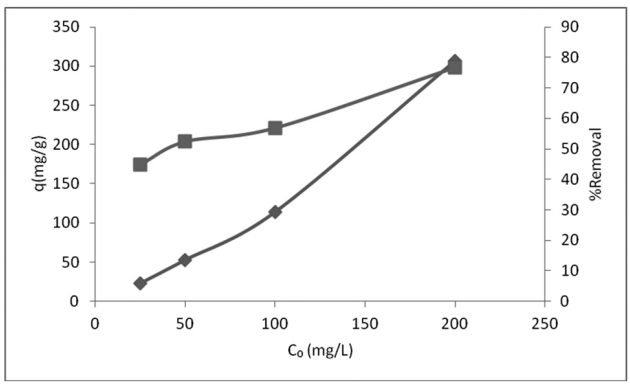
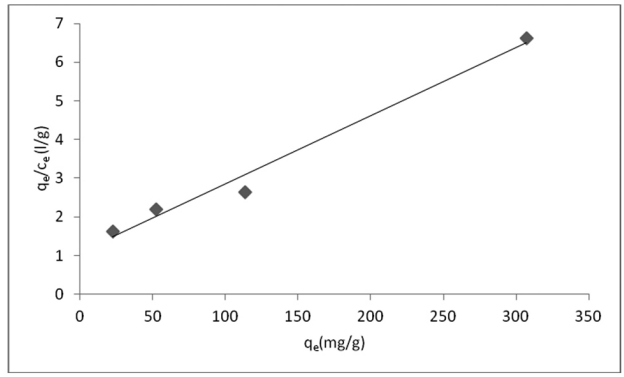


Fig.8. *Effect of initial concentration on the uptake and % Removal (Dose = 0.05 g, T = 30 ºC, pH = 6.5, rpm = 100, Time = 6 h.)*

Also, the percentage removal increased from 44.8 % to 76.8 % when initial concentration was increased from 25 to 200 mg/L. Generally, increase in uptake results in decrease in % removal due to competition among the ions to occupy limited vacant adsorption sites [22]. Thus, the trend indicated in Fig.8 highlighted that numbers of available sites were sufficient and there was no competition among the ions for adsorption.

3.5.1 Equilibrium Modelling

To probe into the nature of adsorption of Cd(II) on RCPW, Langmuir and Freundlich isotherms were studied as given in Table 2.



Langmuir isotherm is a famous and widely used model for the identification of monolayer type adsorption. This isotherm assumes identical binding sites on the biosorbent [22]. Fig. 9 shows the application of Langmuir model on the adsorption of Cd(II) onto RCPW.

Fig. 9. *Fitting of Langmuir's Model for biosorption of Cd(II) by RCPW*

It shows a good fitting for Cd(II) uptake by RCPW as a fairly high value of $R^2 = 0.9822$ was observed. The values of q_{max} and b were estimated from slope and intercept of Fig.9. q_{max} for biosorption of Cd(II) on RCPW was 62.0 mg/g. A comparison of various biosorbents used to remove Cd(II) with present study has been given in the Table 3. It can be seen that RCPW showed fairly high value of uptake as compare to many biosorbents. Also, it was observed that uptake of Cd(II) was higher than the unripped biomass of Citrus paradise [15].

Table 3. Comparison of CPW with other biosorbents for Cd(II) removal

Sr.#	Biosorbent	Biosorbent Capacity (mg/g)	Reference
1	Trametes versicolor	102.3	[9]
2	Escherichia coli (sol gel)	79.9	[3]
3	Mango peel waste	68.92	[8]
4	***Riped Citrus paradisi* waste**	**62.00**	**This study**
5	Unriped *Citrus paradisi* waste	52.63	[15]
6	Pretreated rice husk	20.24	[10]
7	*Saw dust (Pinus sylvestris)*	19.08	[1]
8	baker's yeast	15.63	[13]
9	Grafted rice husk	0.889	[5]
10	*Wheat bran*	0.667	[4]
11	Saw dust	0.291	[5]

Table 2. Adsorption Isotherms

Isotherm	Non-Linear Form	Linearized Form	Parameters	Plot	References
Langmuir	$q_e = \frac{q_{max}(bC_e)}{1 + bC_e}$	$\frac{q_e}{C_e} = bq_{max} - bq_e$	q_{max}, b	$\frac{q_e}{C_e}$ *vs* q_e	[22]
Freundlich	$q_e = K_F C_e^{\left(\frac{1}{n}\right)}$	$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right)\log(C_e)$	K_F, n	$\log(C_e)$ *vs* $\log(q_e)$	[22]

The value of b was 0.0176 L/mg. A salient feature of Langmuir's parameter b is that it helps to determine whether the feasibility of the biosorption process. This parameter is used to calculate separation factor (R_L) calculated by $1/(1+C_o \times b)$ [1]. Fig. 10 shows that the value of R_L was less than 1 in all cases. Thus, it may be concluded that the biosorption of Cd(II) upon RCPW is feasible under the experimental conditions [1]. In addition to Langmuir isotherm, Freundlich model was also applied as shown in Fig. 11. The value of R^2 (0.8982) was much lower than that of Langmuir's. Hence, it may be said that process of Cd(II) removal by RCPW was uniform and resulted in formation of monolayer on the biomass.

3.6 Effect of Temperature

Temperature may influence the biosorption depending upon the nature of the process. Generally, energy dependant mechanisms are affected by the temperature. However, energy independent mechanisms may not affected to a noticeable extent. Such mechanisms are basically physicochemical in nature. In the current investigation, effect of temperature was observed from 30 to 50 °C which resulted in a decrease in uptake from 159.8 mg/g to 106.6 mg/g as shown in Fig.12.

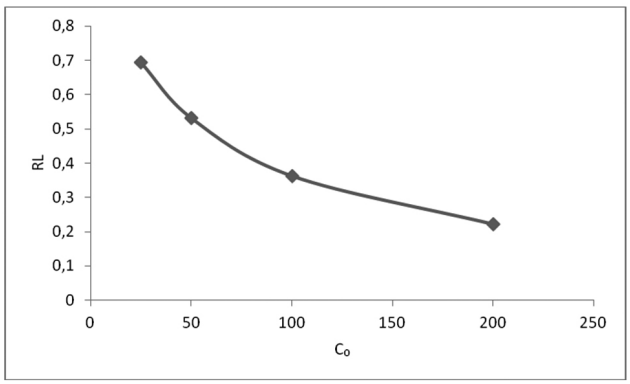


Fig. 10. *Effect of initial Cadmium concentration on separation factor (R_L)*

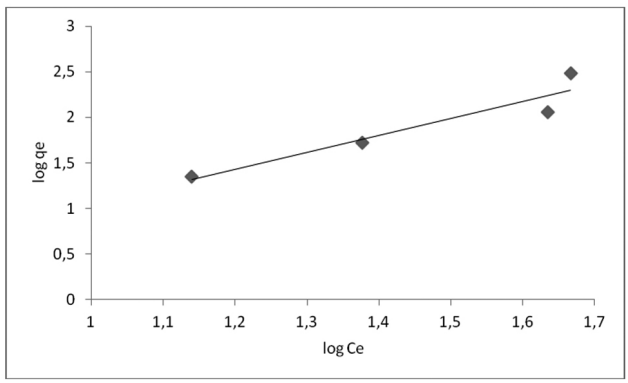


Fig. 11. *Fitting of Freundlich Model on the biosorption of Cd(II) by RCPW*

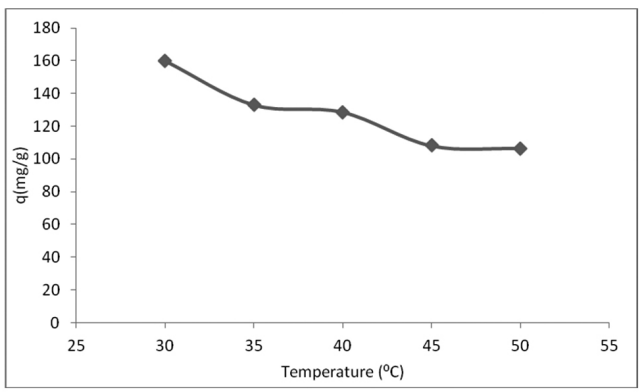


Fig. 12. *Effect of Temperature on uptake of Cd(II) by RCPW (Dose = 0.05 g, Time = 6 h. pH = 6.5, rpm = 100, C_o=100 mg/L)*

This may be interpreted as the enhancement in temperature weaken the bonding of Cd(II) with RCPW as a result lesser uptake observed. Another justification for this behaviour may be the deformation of the binding sites on increase in temperature which resulted in less removal of Cd(II). The trend in Fig.12 also indicated that the biosorption of Cd(II) onto RCPW is exothermic in nature. Similar results have been found elsewhere [2,4,12,14].

3.7 Effect of Desorbent

Recovery of Cd(II) from the loaded biosorbent was also studied. Mainly, acids, bases and complexing agents are employed for the desorption of various metals [9,12, 23-24]. In the current work performance of five eluents was compared for the desorption of Cd(II) from RCPW namely, HCl, H_2SO_4, HNO_3, EDTA and NaOH. All the eluents were 0.1 N in concentration and the results of study is as shown in Fig. 13. All the biosorbents recovered more than 50% Cd(II). The minimum recovery was observed in case of HNO_3 and maximum in case of NaOH.

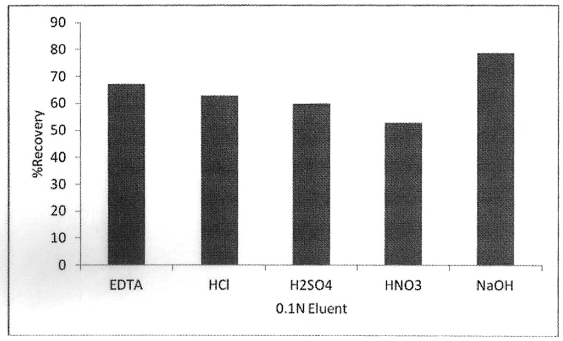


Fig. 13. Effect of nature of eluent on %Recovery of Cd(II) from RCPW(Dose = 0.05 g, Time = 6 h. rpm = 100, T =30 ºC)

Order of eluents in their decreasing %removal was NaOH>EDTA>HCl>H_2SO_4>HNO_3.

4. CONCLUSIONS

Current study shows that RCPW is a promising biosorbent for the sequestration of Cd(II) from dilute solution. As per Langmuir model its capacity was 62.0 mg/g which makes RCPW a good biosorbent when compare with other biomaterials as shown in Table 3. Application of pseudo second order kinetic and pore diffusion model showed that rate of biosorption of Cd(II) onto RCPW was 2nd Order and govern by film diffusion as well as intraparticle diffusion. A comprehensive analysis on the effect of various engineering parameters revealed that biosorption of Cd(II) by RCPW was optimum at 6.5 pH, 0.05 g dose, 100 rpm, 30 ºC. It was possible to recover Cd(II) by the application of different acidic, basic and complexing agents but 0.1M NaOH showed best recovery.

REFERENCES

1. V.C.T. Costodes, H. Fauduet, C. Porte, A. Delacroix, J. Hazard. Mater. B105, 121–142 (2003)
2. C.C.V. Cruz, A.C. A. da Costa, C.A. Henriques , A.S. Luna, Bioresour. Technol.91, 249–257 (2004).
3. J.P. Chen, Y.S. Lin, J. Chin. Inst. Chem. Eng. 38, 235–243 (2007).
4. K.K. Singh, A.K. Singh, S.H. Hasan, Bioresour. Technol. 97, 994–1001(2006).
5. N. Sharma, K. Kaura, S. Kaur, J. Hazard. Mater. 163,1338–1344 (2009).
6. A.T. Sequeira, M.S. Ríos, M.T. Olguín, Hydrom. 97(1-2),46–52 (2009).
7. S. Bunluesin, M. Kruatrachue, P. Pokethitiyook, S. Upatham, G.R. Lanza, J. Biosci. Bioeng.103(6), 509–513 (2007).
8. M. Iqbala, A. Saeeda, S.I. Zafar, J. Hazard. Mater. 164,161–171 (2009).
9. M.Y. Arica, Y. Kacar, O. Genc, Bioresour. Technol.80,121 -129 (2001).
10. U. Kumar, M. Bandyopadhyay, Bioresour. Technol. 97, 104–109 (2006).
11. M.I. Kefala, A.I. Zouboulis, K.A. Matis, Environ. Pollut.104, 283 – 293(1999).
12. Y. Kacar, C. Arpa, S. Tan, A. Denizli, O. Genc, M.Y. Arıca, Process Biochem. 37, 601–610 (2002).
13. Y. Goksungur, S. Uren, U. Guvenc, Bioresour. Technol. 96, 103–109 (2005).
14. K.K. Singh, R. Rastogi, S.H. Hasan, J. Hazard. Mater.A121, 51–58(2005).
15. J. Bayo, G. Esteban, J. Castillo, Environ. Technol.1-12 (2011).
16. B. Volesky, Sorption and Biosorption, By sorbex Inc., Montreal, 35 – 50 (2003).
17. M. Amini, H. Younesi, N. Bahramifar, Colloids and Surface A: Physicochem. Eng. Aspects 337, 67–73(2009).
18. J. M. de la Cerda, A. G. Diez, J.C. R. Ortiz, E. A. G. Zambrano, J. Hort. Forest. 1(3) 052-056 (2009)
19. http://www.pakissan.com
20. V. Padmavathy, P. Vasudevan, S.C. Dhingra, Process Biochem. 38, 1389-1395 (2003).
21. Y.S. Ho, J. Hazard. Mater. B136,681-689 (2006).
22. M. Kazmi, N. Feroze, S. Naveed, S.H. Javed, Korean. J. Chem. Eng. 28(10),2033 – 2040 (2011).
23. A. Hammaini, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, J. Environ. Manag.84, 419–426 (2007).
24. M.M. Areco, M.S. Afonso, Colloids and Surface B: Biointerfaces. 81, 620–628 (2010).