

Full Length Research Paper

# ***Polypogon monspeliensis* waste biomass: A potential biosorbent for Cd (II)**

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***Polypogon monspeliensis* a globally available natural waste material was used for uptake of Cd (II) from aqueous solutions in this study. The results clearly demonstrate the effect of important experimental parameters on the biosorption process in batch experiments. The evaluated pH, biosorbent dose, size and initial metal concentration for Cd (II) uptake by *P. monspeliensis* waste biomass were 6, 0.05 g, 0.10 mm and 100 mg/L respectively. The Cd (II) sorption process by *P. monspeliensis* waste biomass was described well by pseudo second order kinetic model and Langumir sorption isotherm model. Metal equilibrium was reached in 120 min. A further increase in incubation time had no significant effect on the biosorption of the metal. FTIR spectroscopic results pointed out the involvement of hydroxyl and amine groups in the Cd (II) sorption by *P. monspeliensis* waste biomass.**

**Key words:** *Polypogon monspeliensis*, Cd (II), biosorption, kinetics, isotherms.

## **INTRODUCTION**

The entrance of the toxic metals from the industries, either producing or using these metal bearing products, into water bodies is world wide and a well known health hazard (Sudha Bai and Abraham, 2003; Sarwar et al., 2004; Hanif et al., 2005). Cd released through aquatic route, even at ultra trace level, poses serious health risks via their bioaccumulation in living tissue throughout the food chain. Conventional methods such as ion exchange, chemical precipitation, adsorption reverse osmosis, coagulation, membrane filtration, electrochemical process and co-precipitation to remove Cd and other heavy metals fail when the metal levels are extremely low. The other limitations are the high energy requirements, incomplete metal removal and generation of toxic sludge which needs proper disposal in addition to financial constraints (Hanif et al., 2007a). The only solution to all these problems is the biosorption. Biosorption is the uptake of heavy metals by dead biological materials.

Biosorption processes are relatively easy to operate and possess several inherent advantages, including low cost,

operation over a wide range of conditions and the possible reuse of biosorbents (Hanif et al., 2007b; Hanif et al., 2007c).

*Polypogon monspeliensis* (Rabbit's foot grass), a monocot in the family Poaceae, is an annual herb found worldwide. Rabbitfoot grass is an invasive species that has the potential to be a problem weed. This waste biomass was used as potential biosorbent for the removal of Cd (II) from aqueous solutions. The effect of different experimental parameters was evaluated for achieving maximum uptake of Cd (II) using *P. monspeliensis* waste biomass. The equilibrium and kinetic modeling was also fitted to data to determine proper Cd (II) sorption mechanism.

## **MATERIALS AND METHODS**

The *P. monspeliensis* waste biomass was collected from Multan, Pakistan. Deionized water was used to remove debris and other impurities from the surface of the biomass. Subsequently, *P. monspeliensis* waste biomass was sun dried for three days followed by drying in an electric oven for 24 h to obtain moisture free biomass. The obtained biomass was grounded into a fine powder form. *P. monspeliensis* waste biomass was separated into different particle sizes using an ultrasonic sieve, before its storage in the moisture free polyethylene bottles. Experiments were conducted to

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evaluate the effect of pH (2 - 6), dose (0.05 - 0.3 g/100 mL), size (0.10 - 0.35 mm), initial metal concentration (0.5 - 100 mg/L) and contact time (0 – 24 h) on biosorption of Cd (II) by *P. monspeliensis* waste biomass from aqueous solutions. The pH of solution was adjusted using 0.1 M solutions of NaOH and HCl. The agitation to flasks was given on a rotating shaker with constant shaking till the completion of the experiment. After agitating, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman No. 40, ashless). All experiments were carried out at room temperature (25°C). The Cd (II) uptake was calculated by the simple concentration difference method using mass balance equation (equation 1) given below:

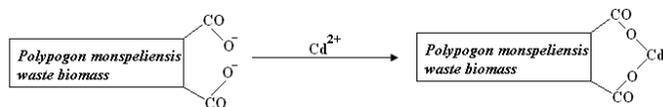
$$q_e = (C_i - C_e) V/1000w \tag{1}$$

Where  $C_i$  is the initial concentration (mg/L),  $C_e$  (mg/L) is the final concentration (mg/L),  $q_e$  is the metal uptake (mg metal adsorbed/g adsorbent),  $V$  is the volume of the solution in mL and  $w$  the mass of the sorbent in g. All data represent the mean of three independent experiments. Statistical analyses were carried out using Microsoft Excel 2004, Version Office Xp.

## RESULTS AND DISCUSSION

### Effect of pH

In the first series of batch experiments, while studying the influence of equilibrium pH on the biosorption of Cd (II), it was found that solution equilibrium pH severely affects the biosorption capacity of *P. monspeliensis* waste biomass (Figure 1). The positively charged Cd ions in solution exhibited electrostatic attraction towards the negatively charged cell surface of *P. monspeliensis* waste biomass. The maximum Cd (II) adsorption was observed at pH 6.0. At pH greater than 6.0, Cd (II) ions precipitated as insoluble hydroxides. So experiments beyond this pH were not carried out. A review of literature on biosorption suggests that the metal uptake is mainly due to presence of carboxyl groups on the cell surface of biomass (Won et al., 2005; Roberts and Caserio, 1977). The carboxyl groups have a negative charge at pHs approximately higher than 5; therefore, will electrostatically bind Cd (II) to *P. monspeliensis* waste biomass. The below reaction (Pavan et al., 2007) clearly explains the pH effect on the biosorption of Cd (II) onto *P. monspeliensis* waste biomass.



At low pH values (acidic range), the carboxyl groups will be in their protonated form and; thus, the overall charge of the biomass will be positive hence, a low metal uptake (Vijayaraghavan and Yun, 2007; Bai and Abraham, 2003; Hu and Reeves, 1997). Hence at higher pH values the uptake capacity of Cd (II) by *P. monspeliensis* waste biomass was greater.

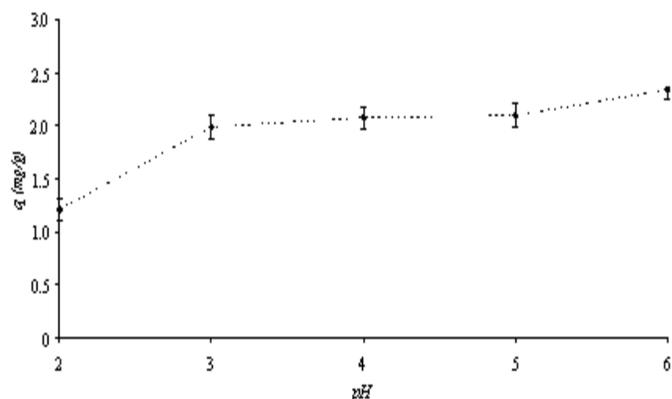


Figure 1. Effect of pH on the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

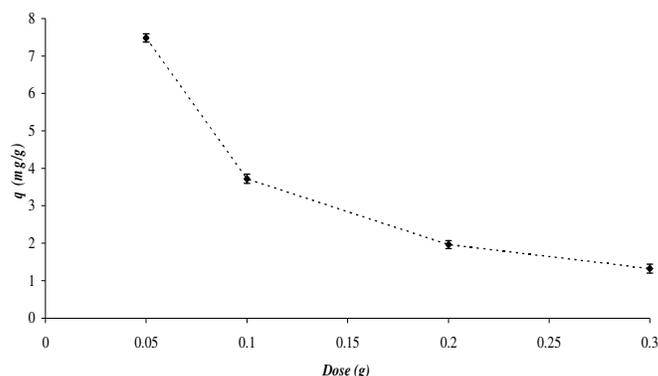


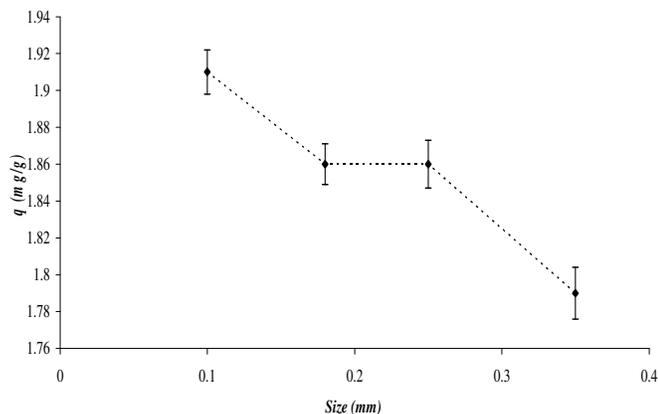
Figure 2. Effect of biosorbent dose on the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

### Effect of biosorbent dose

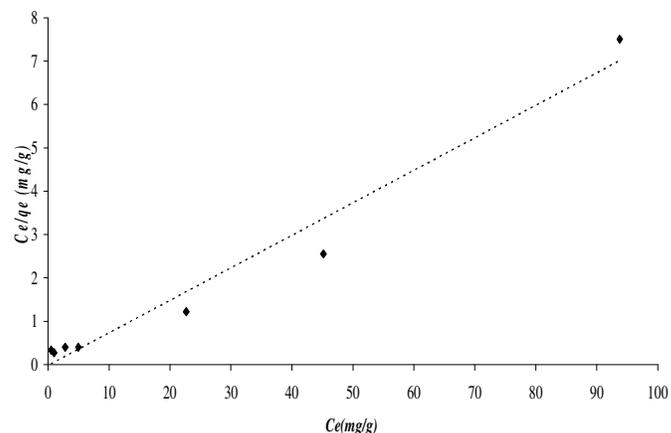
The Cd (II) removal as a function of biomass loading is shown in Figure 2. The uptake of Cd (II) by *P. monspeliensis* waste biomass decreases with increase in the dosage rate as the number of sorbate ions concentration decrease per active site available for sorption on the biomass. The other reason may be that high biomass concentrations result in low metal sorption due to electrostatic interactions between cells, which protect binding sites from metal occupation (Bhatti et al., 2007).

### Effect of particle size of the adsorbent

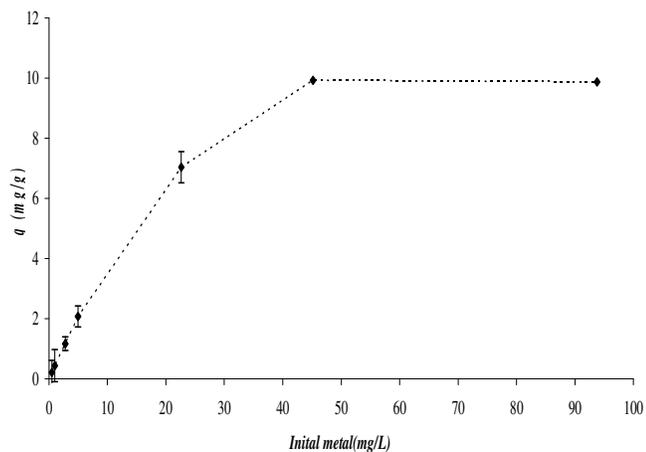
The biosorption of Cd (II) ions onto *P. monspeliensis* waste biomass was investigated for four different particle sizes of 0.1, 0.18, 0.25 and 0.35 mm (Figure 3). The uptake of Cd (II) by *P. monspeliensis* waste biomass increased with decreasing particle size due to larger total surface area of particles at small particle sizes (Zafar et al., 2007).



**Figure 3.** Effect of particle size on the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.



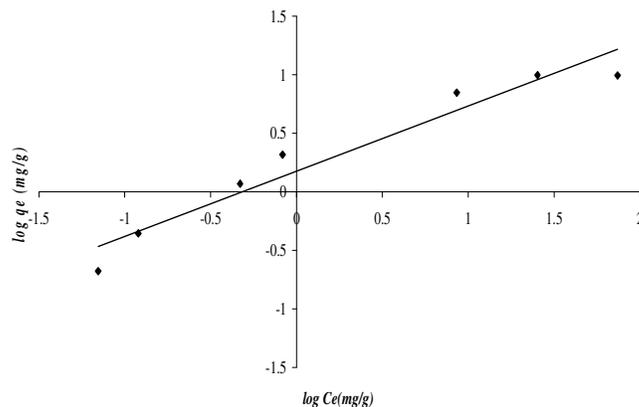
**Figure 5.** Langmuir isotherm plot for the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.



**Figure 4.** Effect of initial concentration on the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

**Effect of initial Cd (II) concentration**

Study was carried out with concentrations ranging from 0.5 to 100 mg/L while other operational parameters were kept constant (Figure 4). There was a continuous increase in the uptake of Cd (II) per gram of biosorbent up to a concentration 50 mg/L, but at further higher concentration uptake is almost constant. It clearly indicates *P. monspeliensis* waste biomass is best for the removal of Cd (II) up to a concentration of 50 mg/L at which conventional methods fail or are very expensive. Langmuir and Freundlich isotherm equations were used to describe the equilibrium state for Cd (II) adsorption experiments (Nasir et al., 2007). The Langmuir isotherms (Figure 5) consider the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface of the cells, having the same affinity for adsorption of a single molecular layer



**Figure 6.** Freundlich isotherm plot for the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

and there is no interaction between adsorbed molecules. Following form of Langmuir isotherm model was used in the present study (equation 2).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{2}$$

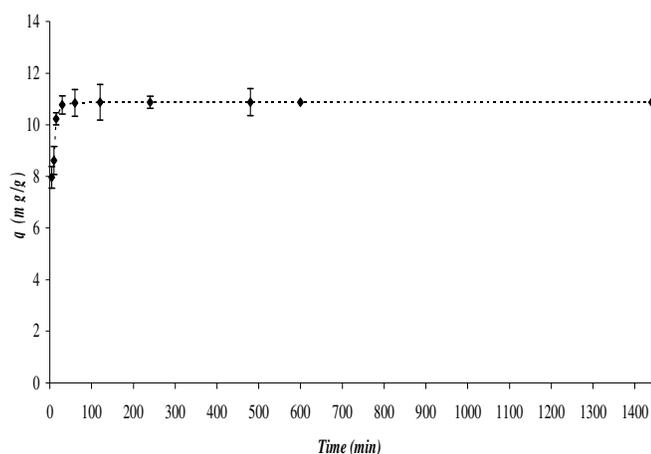
The Freundlich isotherm model (Figure 6) assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The linearized form Freundlich isotherm is given as (equation 3):

$$\log q_e = \frac{1}{n} \log C_e + \log k \tag{3}$$

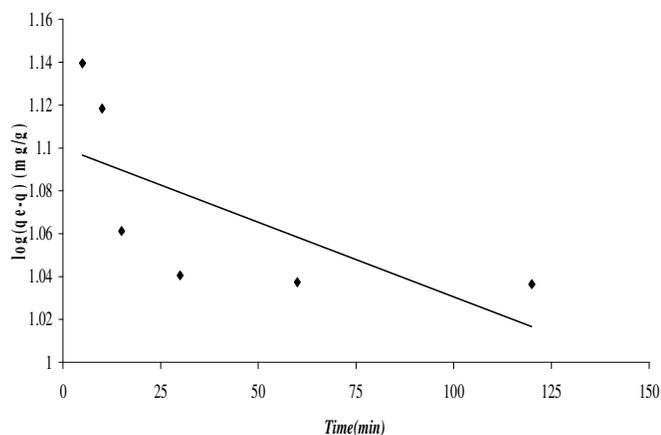
Where  $q_e$  is the metal ion sorbed (mg/g),  $C_e$  the equilibrium concentration of metal ions solution,  $K_L$  is the

**Table 1.** Comparison between Langmuir and Freundlich isotherms models parameters.

Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>		q <sub>max</sub> (mg/g)	q <sub>max</sub> (mg/g)	K (mg/g)	1/n
Cd (II)	13.351	0.075	0.9687	9.870	16.482	1.499	0.557	0.9412

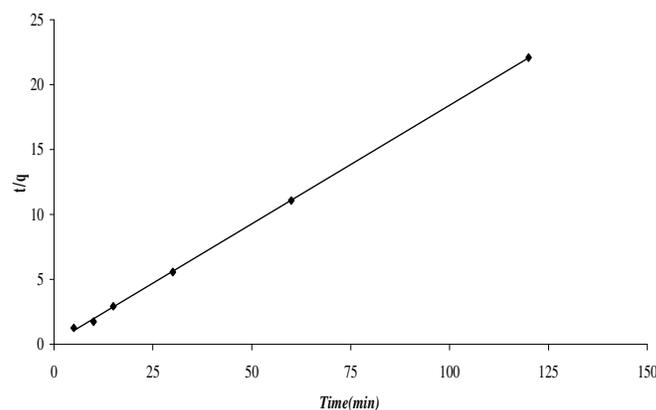


**Figure 7.** Effect of contact time on the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.



**Figure 8.** Lagergren's pseudo-first-order plot for the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

Langmuir adsorption constant and  $k$  is the Freundlich constant. The comparison of Langmuir and Freundlich isotherm models showed that the Langmuir isotherm model fitted well to the adsorption data of Cd (II) (Table 1).



**Figure 9.** Pseudo-first-order plot for the biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.

### Kinetic studies of Cd (II) removal

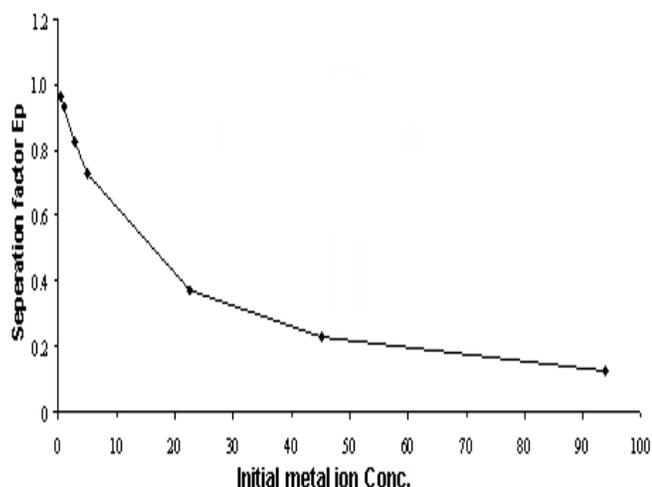
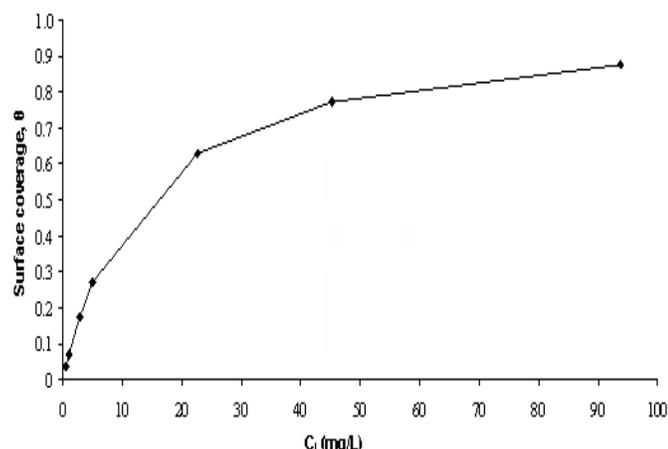
Results showed that the removal of Cd (II) by *P. monspeliensis* was significantly dependent on equilibrium time (Figure 7). A rapid removal of Cd (II) took place in the first 30 min, and the rate became slow thereafter till the equilibrium was reached within 120 min (Nadeem et al., 2007; Nadeem et al., 2008). The biosorption process was likely to be physicochemical transformation as the biomass used in the present study was dead, grounded into fine particles, and might have lost its biological activity. In order to clarify the biosorption kinetics of Cd (II) ions onto *P. monspeliensis* waste biomass, two kinetic models, that is, Lagergren's pseudo-first-order and pseudo-second-order model (Figures 8 and 9) were applied to the experimental data (Javed et al., 2008; Ammara et al., 2008). The linearized form of the pseudo-first-order rate equation by Lagergren is given as (equation 4):

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads} t}{2.303} \tag{4}$$

where  $q_e$  and  $q$  (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and  $t$  (min), respectively, and  $k_{1,ads}$  is the rate constant ( $\text{min}^{-1}$ ). Experimental data

**Table 2.** Comparison between Lagergren's pseudo-first-order and pseudo-first-order models parameters.

Metal	Pseudo first order Kinetic model			Experimental value	Pseudo second order Kinetic model		
	$q_e$ (mg/g)	$K_{1,ads}$ ( $\text{min}^{-1}$ )	$R^2$		$q_e$ (mg/g)	$q_e$ (mg/g)	$K_{2,ads}$ (g/mg min)
Cd (II)	12.592	$3.04 \times 10^{-4}$	0.4541	10.875	5.479	0.244	0.9997

**Figure 10.** The calculated separation factor profile for biosorption of Cd (II) by *Polypogon monspeliensis* waste biomass.**Figure 11.** A plot of surface coverage ( $\theta$ ) against concentration of Cd (II) by *Polypogon monspeliensis* waste biomass.

was fitted to the following form of pseudo-second order kinetic model (equation 5) which states that "chemical sorption being the rate-controlling step":

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{t}{q_t} \quad (5)$$

where  $k_{2,ads}$  (g/mg min) is the rate constant of the second-order equation,  $q_t$  (mg/g) the amount of biosorption time  $t$  (min) and  $q_e$  is the amount of biosorption equilibrium (mg/g). It can be concluded from the estimated  $q$  values and  $R^2$  values that the biosorption of Cd (II) ions onto *P. monspeliensis* waste biomass does not fit to pseudo-first-order kinetic model but fitted well to the pseudo-second-order kinetic model (Table 2).

### Evaluation of theoretical factors

The evaluation of theoretical factors was done following the study of Riaz et al. (2008). Separation factor ( $R_L$ ) values between 0 and 1 represent the favorable isotherm.  $R_L$  was calculated from following equation (equation 6).

$$R_L = 1 / (1 + KLC_i) \quad (6)$$

The fraction of biomass surface covered by the adsorbed metal was calculated from following equation (equation 7).

$$KC_i = \theta / 1 - \theta \quad (7)$$

Where  $KL$  is the constant from Langmuir equation and  $C_i$  is the initial Pb (II) concentration.

The obtained values of  $R_L$  clearly demonstrated that Cd sorption process by *P. monspeliensis* waste biomass was favorable for Cd (II) removal at all concentrations normally found in the aqueous streams (Figure 10). It can be noted from Figure 11 that the higher the metal concentration the greater the fraction of biomass covered which was already accepted. Distribution coefficient ( $D$ ) determines the ratio of metal ion concentration in the adsorbent phase, to the metal ion concentration in aqueous phase.

$D > 0.50$  means more metal in adsorbed phase in comparison to aqueous phase

$D < 0.50$  means less metal in adsorbed phase in comparison to aqueous phase

$D = 0.50$  means the amount of metal in both phases is equivalent

*P. monspeliensis* waste biomass was found to be more effective to adsorb Cd (II) when Cd (II) initial concentration was below 25 mg/L (Table 3).

The Gibbs free energy ( $\Delta G^\circ_{ads}$ ) was calculated from the following equation (equation 8).

**Table 3.** Calculated values of distribution coefficient (D) and Gibbs free energy ( $\Delta G^{\circ}_{\text{ads}}$ ).

Ci (mg/L)	D	$\Delta G^{\circ}_{\text{ads}}$ (KJ/mol)
0.50	0.857143	-29.46239
1.00	0.880000	-29.41798
3.00	0.832740	-29.27802
5.00	0.833333	-29.13922
25.00	0.621466	-28.55538
50.00	0.439256	-28.27814
100.00	0.210493	-28.05659

$$\Delta G^{\circ}_{\text{ads}} = -2.303RT \log \left[ \left\{ \frac{55.4\theta}{C_i(1-\theta)} \right\} \left\{ \theta + \frac{n(1-\theta)^{n-1}}{n^n} \right\} \right] \quad (8)$$

The highly negative values of  $\Delta G^{\circ}_{\text{ads}}$  suggested the spontaneous nature of metal adsorption process at all studied concentrations (Table 3).

#### Fourier transforms infrared (FTIR) studies

The FTIR spectroscopy is a measurement technique for collecting infrared spectra by identifying some characteristic functional groups. The FTIR spectra of *P. monspeliensis* waste biomass before and after Cd (II) sorption. The taken spectra indicated the presence of O-H (H-bonded) displayed by a broad stretching absorption from 3200-3550  $\text{cm}^{-1}$ . Weaker -CH stretch bands are superimposed onto the side of -OH band at 2850 - 3000  $\text{cm}^{-1}$ . The bands observed at about 2870 and 2960  $\text{cm}^{-1}$  could be assigned to the -CH stretch. The peaks located at 1630 - 1680  $\text{cm}^{-1}$  are due to C=C (symmetry reduces intensity) and are characteristics of alkenes. The peaks at 1033-1091  $\text{cm}^{-1}$  are representing C-N bonding in amines. The absorbance of peaks in the metal loaded sample was substantially lower than those in the raw sample. This indicated that bond stretching occurred to a lesser extent due to the exchange of hydrogen ions with Cd (II) and subsequently peak absorbance was attenuated.

#### Conclusions

Following conclusions can be drawn from the batch biosorption studies of Cd (II) ions:

- On the basis of the experimental results, *P. monspeliensis* waste biomass was found to be very effective in Cd (II) removal from aqueous solution especially when Cd (II) concentrations were low and conventional methods cannot be applied due to several reasons.
- Cd (II) uptake by *P. monspeliensis* waste biomass was considerable affected by operational variables.
- The fitting of Langmuir isotherm model to Cd (II) biosorption is apparent from the obtained experimental

results.

iv.) Second order kinetics was found to be more suitable as compared to the first order due to inclusion of both adsorbent and adsorbate species in biosorption of Cd (II) ions onto *P. monspeliensis* waste biomass.

v.) FTIR spectroscopic results pointed out the involvement of hydroxyl and amine groups in the Cd (II) sorption by *P. monspeliensis* waste biomass.

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