



# Adsorption of Pb (II), Cu (II), and Zn (II) Ions onto *Urtica dioica* Leaves (UDL) as a Low Cost Adsorbent: Equilibrium and Thermodynamic Studies

Priyanka Tiwari<sup>1</sup>, Mahesh Chandra Vishwakarma<sup>2</sup>, Sushil Kumar Joshi<sup>3,\*</sup>, Harish Sharma<sup>3</sup>, Narendra Singh Bhandari<sup>3</sup>

<sup>1</sup>Department of Chemistry, Kumaun University, L. S. M. P. G. College, Pithoragarh, Uttarakhand, India

<sup>2</sup>Department of Chemistry, Kumaun University, G. P. G. College, Gopeshwar, Chamoli, Uttarakhand, India

<sup>3</sup>Department of Chemistry, Kumaun University, Soban Singh Jeena Campus, Almora, Uttarakhand, India

## Email address:

priyanka.tiwari1207@gmail.com (P. Tiwari), maheshchandrav3@gmail.com (M. C. Vishwakarma),

sharmaharish887@gmail.com (H. Sharma), dr.s.k.joshi.alm@gmail.com (S. K. Joshi), im\_nsbhandari@yahoo.co.in (N. S. Bhandari)

\*Corresponding author

## To cite this article:

Priyanka Tiwari, Mahesh Chandra Vishwakarma, Sushil Kumar Joshi, Harish Sharma, Narendra Singh Bhandari. Adsorption of Pb (II), Cu (II), and Zn (II) Ions onto *Urtica dioica* Leaves (UDL) as a Low Cost Adsorbent: Equilibrium and Thermodynamic Studies. *Modern Chemistry*. Vol. 5, No. 1, 2017, pp. 11-18. doi: 10.11648/j.mc.20170501.13

**Received:** January 3, 2017; **Accepted:** January 25, 2017; **Published:** March 4, 2017

---

**Abstract:** The biosorption of Cu (II), Zn (II) and Pb (II) ions from aqueous solution onto dried biomass (*Urtica dioica* leaves) is discussed in the present study. The effect of variation of contact time, adsorbent dose, pH, concentration of metal ions and temperature on biosorption of metal ion is studied. Maximum adsorption was recorded for initial metal ion concentration of 10 mg/l, adsorbent dose of 2 gm, at pH 5 with 60 minutes of contact time for Lead and Zinc, 45 minutes of contact time for Copper ion. The equilibrium conditions were well described by Langmuir, Freundlich and Temkin isotherm equations. The Langmuir isotherm model have provided a better fit with the experimental data compared to that of Freundlich and Temkin isotherm models. The values of thermodynamic parameters indicate that the adsorption reactions were spontaneous, feasible and exothermic.

**Keywords:** Biosorption, Heavy Metals, *Urtica dioica* Leaves (UDL), Isotherms, Thermodynamic Parameters

---

## 1. Introduction

The discharge of industrial waste-waters containing heavy metals is increasing due to rapid industrialization. It requires serious consideration because heavy metals at high concentrations are toxic to aquatic eco-system causing harmful effects to living organisms, plants and humans [1]. Heavy metals such as lead, copper, zinc and nickel are among the most common pollutants found in industrial effluents. These metal ions release into environment from many sources including storage battery [2], paints and pigments [3], electronics [4] fertilizers [5, 6] and electroplating [7, 8]. High dose of copper (Cu) concentrations can lead to weakness, lethargy, anorexia and damage to the gastrointestinal tract [9]. Zn is an essential element for human

and its participation in several metabolic processes has been well documented; nevertheless potential gastrointestinal toxicity exists because of an over accumulation of this metal in the human body [10]. The higher concentration of lead causes severe damage to the nervous system and affects the functioning of brain cells [11]. Various regulatory bodies have already set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems [12]. The permissible limits for industrial effluents discharge set by the World Health Organization (WHO) [12] are 5-15mg/l for Zn, 0.05-1.5mg/l for Cu and 0.1 mg/l for Pb.

Among the various methods indicated in literature for the removal of heavy metals from water and waste-water few are chemical precipitation [13], membrane filtration [14], ion exchange [15] and carbon adsorption [16]. However, these methods have their own disadvantages such as secondary

pollution, high cost, high energy input, large quantities of chemical reagents and poor treatment efficiency at low metal concentration [17]. Biosorption has emerged as an alternative and sustainable strategy for cleaning up water [18]. Compare to previously discussed methods, biosorption is relatively update and cost effective method for removal of heavy metals. Many reports have appeared in the development of low cost adsorbent prepared from cheaper and easily available materials. Some of the recent adsorbents used are rice husk [19], cocoa pod husk [20], water fern *Azolla filiculoidis* [21], lignocelluloses substrate extracted from wheat bran [22], activated phosphate [23] and *Moringa oleifera* bark [24] and *Acacia leucocephala* bark [25].

The present work study the possibility of using activated UDL, as an alternative low-cost adsorbent for removal of Pb (II), Cu (II), and Zn (II) ions from synthetic waste water.

## 2. Materials and Methods

### 2.1. Preparation of the Adsorbate

All the reagents used were of A. R. grade. A lead nitrate  $Pb(NO_3)_2$ , zinc sulphate  $ZnSO_4 \cdot 7H_2O$  and copper sulphate  $CuSO_4 \cdot 5H_2O$  stock solution of 1000 mg/l concentration were prepared and the working solution were made by diluting the stock solution using double distilled water. The range in concentration of lead (II), copper (II), and zinc (II) ions prepared from stock solution varied between 10 to 50 mg/l. The pH value of this solution is adjusted to 4 using 0.1 N NaOH and 0.1 N HCl solutions by digital pH meter (Model: Systronic 361).

### 2.2. Adsorbent: Preparation and Collection of Adsorbent

*Urtica dioica* leaves (UDL) were collected from Almora district, Uttarakhand, India. The collected leaves were thoroughly rinsed with double distilled water to remove dust and soluble materials. The biomass was further dried at room temperature and then kept in hot air oven (Popular Traders S.N.-1680) for 24 hrs at 70°C; it was grinded to a fine powder using grinder-mixer then this powdered mass was treated with 0.1 N  $HNO_3$  at room tem for 24 hrs, filtered, washed with double distilled water and dried in hot air oven at 70°C for 2

days and sieved (240 bss) at 63 micron and kept in air tight bottle. The surface functional groups of the activated biomass were identified by Fourier Transform Infrared Spectroscopy.

### 2.3. Adsorption Experiments

The batch sorption experiments were carried out with 250 ml conical flask using 100 ml of working solution with a concentration of 10 mg/l. The experimental conditions applied to examine the effect of adsorbent dose, contact time, pH, temperature and initial metal ion concentration in adsorption of metal ions on adsorbent was shown in Table 1. The UDL was separated from the medium using whatmann filter paper 42 and the concentration of Cu (II), Zn (II) and Pb (II) metal ions in a filtrate was measured using an Atomic Adsorption Spectro-photometer AAS (Optima 4300 DV ICP, Perkin-Elmer, Boston, MA). The percentage removal of lead ions is calculated using the following formula:

$$Removal (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

Where  $C_i$  is initial metal ion concentration (mg/l) and  $C_e$  is the equilibrium metal ion concentration (mg/l).

## 3. Results and Discussion

### 3.1. Characterization of *Urtica dioica* Leaves (UDL)

The FTIR spectrum gives information about the nature of possible interactions between the Functional groups and the metal ions. The various functional groups present in the UDL which bind the metal ions in the biosorption process are shown in Figure 1. In the spectrum, the broad and strong bands at 3200 – 3400  $cm^{-1}$  indicates the presence of hydroxyl (–OH), amine (–NH) and (–COOH) groups of the biomass. The peak around 2928 and 2827  $cm^{-1}$  indicates the C-H stretching vibration of  $CH_2$  and  $CH_3$  respectively. The strong absorption at 1648  $cm^{-1}$  shows the stretching vibration of carboxyl group (–C=O), the band at 1100  $cm^{-1}$  indicate the (C-H) stretching vibration of carboxylic acid and alcohols and a peak at 657  $cm^{-1}$  assigned to phosphate group.

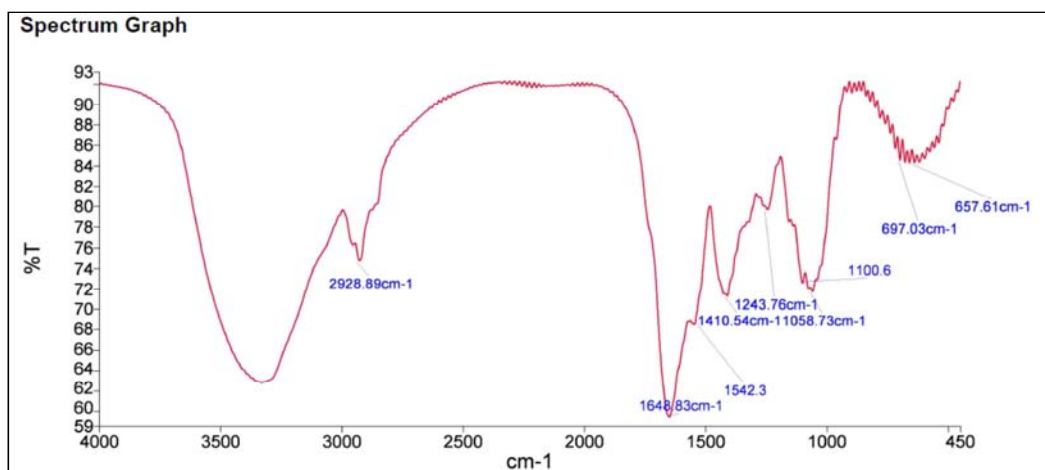


Figure 1. FTIR spectrum of *Urtica dioica* leaves.

### Scanning Electron Microscope (SEM)

SEM analysis is useful for the analysis of the surface morphology of an adsorbent. The SEM images for UDL surface before and after metal ions adsorption are shown in the Figure 2 and 3, respectively. The porous and irregular surface structure of the adsorbent can be clearly observed in the SEM images shown in the Figure 2. As can be seen from Figure 3, there is a clear demarcation in the surface morphology of UDL after treatment.

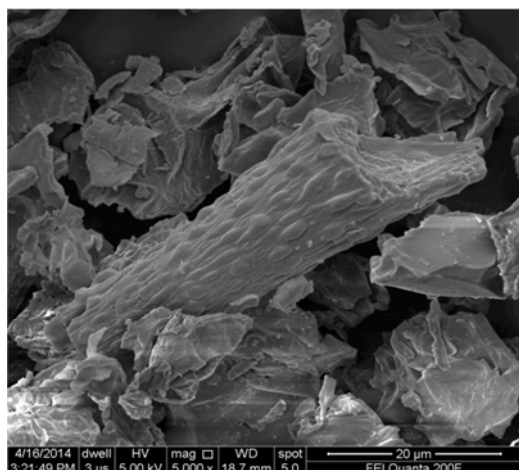


Figure 2. SEM image of UDL before adsorption.

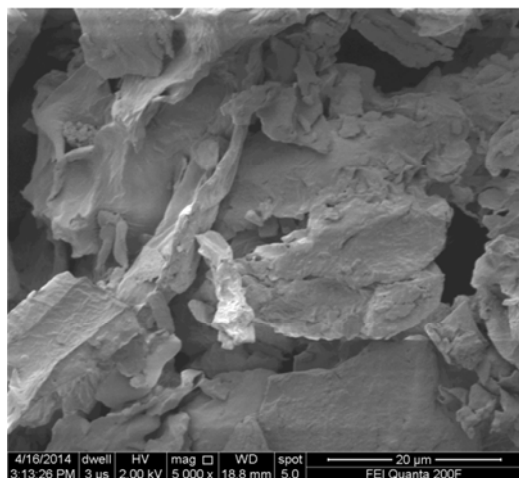


Figure 3. SEM image of UDL after adsorption.

### 3.2. Effect of Contact Time

Figure 4 shows the effect of contact time on the biosorption of Cu (II), Zn (II) and Pb (II) ions on the UDL, and also show that the percentage removal of Cu (II), Zn (II) and Pb (II) ions increase with increase in reaction time. The data obtained from the adsorption of Pb (II), and Zn (II) ions exhibit that a contact time 60 minutes and for Cu (II) the contact time is 45 minutes was sufficient to achieve equilibrium. This clearly reveals that the rate of adsorption is higher at the beginning and it could be related to the availability of a large number of active sites on the adsorbent [26, 27, and 28].

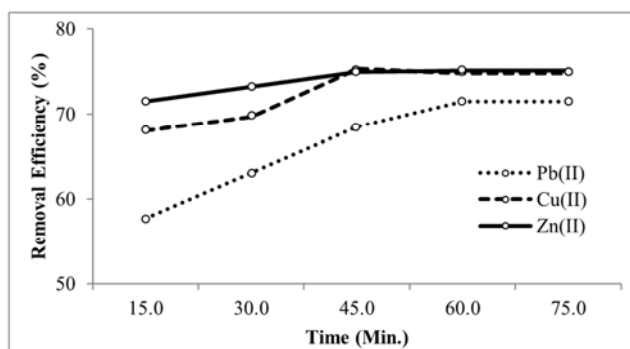


Figure 4. Effect of contact time on lead, copper and zinc adsorption (experimental condition: Initial metal ions concentration 10 mg/l, adsorbent dose 1gm/100 ml, room temperature, 4 pH, agitating speed 170 rpm).

### 3.3. The Effect of Adsorbent Dosage

In this study five different adsorbent dosages were studied by varying the amount of adsorbent 0.5 to 2.5g. It was observed that percentage of metal ion removal increased with increase in adsorbent dose from 0.5 to 2.0 gm for copper, zinc and lead ions. Figure 5 Show that On further increasing the adsorbent dose, the percentage of metal ions removal does not show any remarkable change, the initial increment in removal efficiency with increase in adsorbent dosage is due to the more active sites were available [29, 30]. However, at the same dose the adsorption capacity  $Q_e$  (Figure 6) of Lead (II), Copper (II) and Zinc (II) ions decreased with increased adsorbent dose is due to the increased metal to biosorbent ratio which decreased with increasing the biosorbent dose.

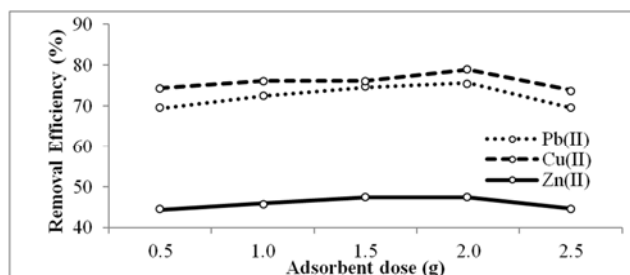


Figure 5. Effect of adsorbent dose on Pb (II), Cu (II) and Zn (II) adsorption (experimental condition: Initial metal ions concentration 10 mg/l, contact time 30 min, room temperature, 4 pH, agitating speed 170 rpm.).

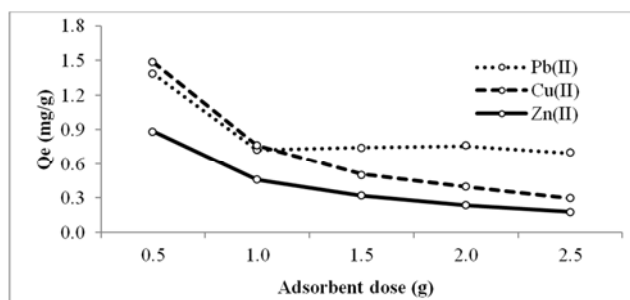
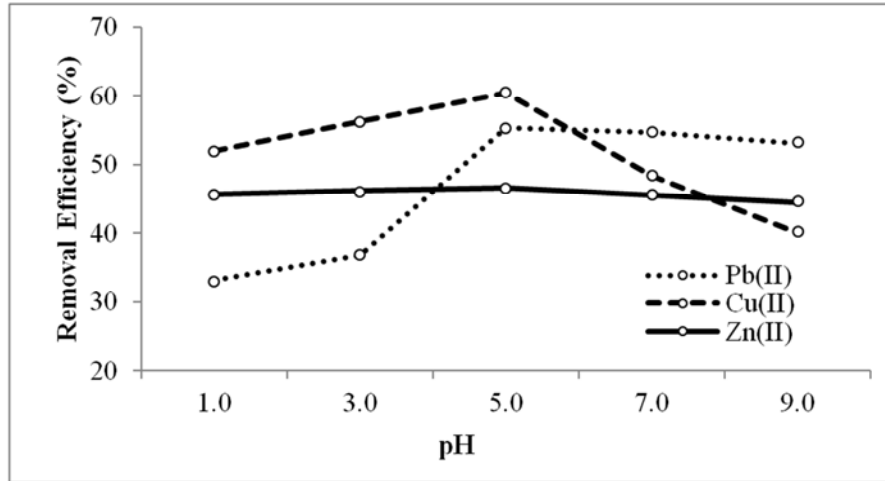


Figure 6. Effect of adsorbent dose on Pb (II), Cu (II) and Zn (II) adsorption capacity (experimental condition: Initial metal ions concentration 10 mg/l, contact time 30 min, room temperature, 4 pH, agitating speed 170 rpm.).

### 3.4. Effect of pH

pH affects the surface charge of the adsorbent, degree of ionisation and specification of adsorbate [31, 32]. Figure 7 shows the effect of solution pH on the adsorption of Pb (II), Cu (II) and Zn (II) on the UDL at 25°C, 10 mg/l of initial metal ion concentration and 1 gm of adsorbent dose. The removal percentage increases with an increase in solution pH from 1 to 5. The minimum biosorption at low pH is due to the fact that high concentration and high mobility of

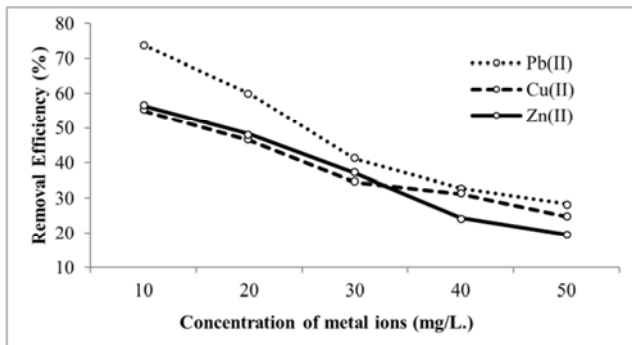
hydrogen ions. The hydrogen ions are preferentially adsorbed rather than the metal ions. At higher pH values, the lower number of hydrogen ion and greater number of ligands with negative charges results in greater metal ions biosorption [33]. The maximum adsorption of metal ions is obtained at pH 5.0 [34], above pH 5, a steady decrease of adsorption of metal ions can be related to the precipitation of metal hydroxide [35, 36].



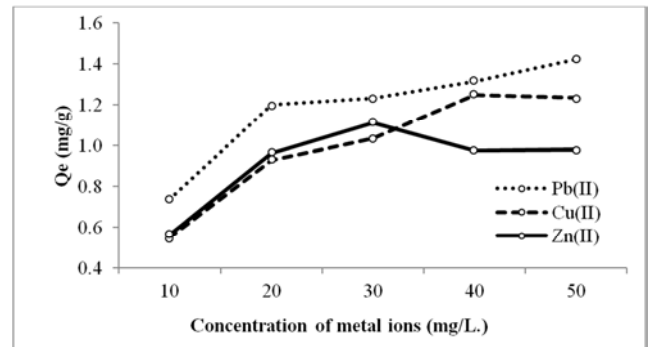
**Figure 7.** Effect of pH on Pb (II), Cu (II) and Zn (II) adsorption (experimental condition: Initial metal ions concentration 10 mg/l, adsorbent dose 1gm/100 ml, 30 min, room temperature, agitating speed 170 rpm.).

### 3.5. Effect of Initial Pb (II), Cu (II) and Zn (II) Ions Concentration

Figure 7 presents the effect of different initial metal ions concentration onto UDL. As shown in Figure 8 the percentage removal of Cu (II), Zn (II) and Pb (II) ions decreases with the increase of metal ion concentration. with 1gm of adsorbent dose (UDL) the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration i.e. saturation of the adsorbent [37]. While the equilibrium uptake  $Q_e$  has been increased with increases initial metal ion concentration from 10 to 50 mg/l. (Figure 9).



**Figure 8.** Effect of initial Pb (II), Cu (II) and Zn (II) ions concentration on adsorption (experimental condition: adsorbent dose 1gm/100 ml, room temp, 30 min. and pH 4).



**Figure 9.** Effect of initial Pb (II), Cu (II) and Zn (II) ions concentration on adsorption capacity (experimental condition: adsorbent dose 1gm/100 ml, room temp, 30 min. and pH 4).

### 3.6. Adsorption Isotherm

The equilibrium relationships between adsorbent and adsorbate are best explained by sorption isotherms [38]. In the present study Langmuir, Freundlich and Temkin models were used to describe the adsorption process of Pb (II), Cu (II) and Zn (II) ions onto UDL.

#### 3.6.1. Langmuir Isotherm

Langmuir isotherm [39] model assumes that biosorption occurs at specific homogeneous sites on the biosorbent and is used successfully in many monolayer biosorption processes. This model can be written as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (2)$$

Where  $C_e$  is the equilibrium concentration of Pb (II), Cu (II) and Zn (II) in mg/l.  $Q_e$  is the amount of metal adsorbed per specific amount of adsorbent (mg/g),  $K_L$  (L/mg) is the Langmuir constant related to the energy of adsorption and  $Q_{max}$  is maximum adsorption capacity (mg/g). Values of Langmuir parameters  $Q_{max}$  and  $K_L$  were calculated from the slope and intercept of linear plot of  $\frac{C_e}{Q_e}$  Vs  $C_e$  shown in Figure 10. The value of evaluated constants is given in Table 1.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor " $R_L$ " which is used to predict the adsorption system is favourable or unfavourable and is given as [40].

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (3)$$

Where  $C_0$  is the initial metal ion concentration in mg/l,  $K_L$  is the Langmuir equilibrium constant. The value of  $R_L$  indicated the type of Langmuir isotherm to be irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ). The value of  $R_L$  was found less than one in all the cases. This confirms that the Langmuir isotherm model is favourable for adsorption of Pb (II), Cu (II), and Zn (II) onto UDL.

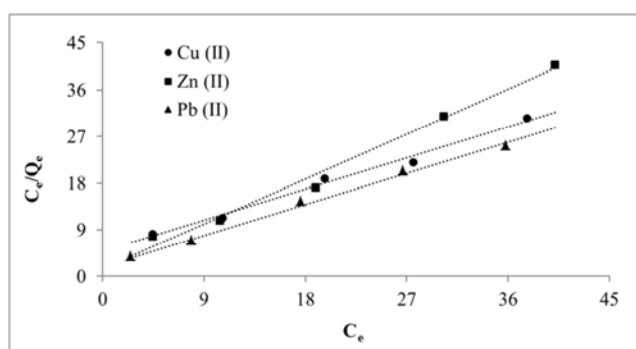


Figure 10. Langmuir Isotherm for biosorption of Pb (II), Cu (II) and Zn (II) ions onto UDL.

### 3.6.2. Freundlich Isotherm

This model proposes heterogeneous distribution of active sites, accompanied by interaction between adsorbed molecules. The linear form of isotherm can be represented as [41]:

$$\log Q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (4)$$

Where  $K_F$  is a constant related to the adsorption capacity and  $n$  is related to the adsorption intensity of the adsorbent.  $K_F$  and  $\frac{1}{n}$  can be determined from the linear plot of  $\log Q_e$  versus  $\log C_e$  (Figure 11). The evaluated constants are given in Table 1.

Table 1. Adsorption isotherm constants for adsorption of Cu (II), Zn (II) and Pb (II) onto UDL plant.

Metals->	Cu(II)	Zn(II)	Pb(II)
Langmuir parameters			
$Q_{max}$ (mg/g)	1.490	1.039	1.493
$K_L$ (L/mg)	0.140	0.674	0.361

Metals->	Cu(II)	Zn(II)	Pb(II)
$R^2$	0.985	0.979	0.994
Freundlich parameters			
$K_f$ (mg/g) ( $L \cdot mg^{-1}$ ) <sup>1/n</sup>	0.663	0.718	0.824
$n$	2.876	4.255	4.34
$R^2$	0.593	0.494	0.847
Temkin parameters			
$B$ (mg/g)	0.33	0.179	0.238
$A$	1.279	10.57	11.16
$R^2$	0.949	0.455	0.887

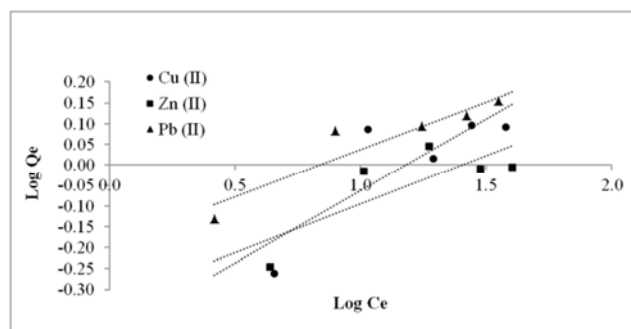


Figure 11. Freundlich Isotherm for biosorption of Pb (II), Cu (II) and Zn (II) ions onto UDL.

### 3.6.3. Temkin Isotherm

The Temkin isotherm model [42] suggests an equal distribution of binding energies over a number of exchange sites on the surface. The linear form of Temkin isotherm model is given below:

$$Q_e = B \ln A + B \ln C_e \quad (5)$$

Where  $C_e$  concentration of the adsorbate at equilibrium mg/L,  $Q_e$  is the amount of metal adsorbed per specific amount of adsorbent (mg/g).  $B = RT/b_T$  where  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature in Kelvin,  $b_T$  is the Temkin isotherm constant,  $A$  is the equilibrium binding constant and  $B$  corresponds to the heat of sorption. The value of  $A$  and  $B$  are given in Table 1.

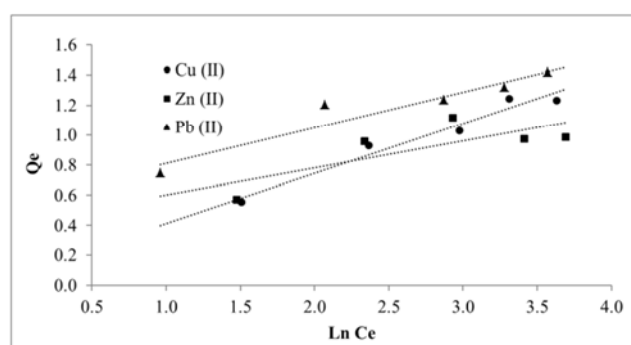


Figure 12. Temkin Isotherm for biosorption of Pb (II), Cu (II) and Zn (II) ions onto UDL.

From Table 1 it is observed that the Langmuir isotherm is a good fit to the experimental equilibrium adsorption data than the Freundlich and Temkin isotherm for Cu (II), Zn (II) and Pb (II) sorption according to the values of  $R^2$ . It was also seen from Table 2 that the Langmuir constant  $Q_{max}$  is 1.490, 1.039 and 1.493 and  $K_L$  is 0.140, 0.674 and 0.361 for Cu (II), Zn (II), Pb (II). The separation factor ( $R_L$ ) values were found

to be less than one and greater than zero indicating the favourable sorption of Cu (II), Zn (II) and Pb (II) ions onto UDL. The Freundlich constant  $K_F$  indicates the sorption capacity of the sorbent and the value of  $K_F$  is 0.663, 0.718 and 0.824 mg/g. It could be observed from the table 2, that the regression coefficient was low for Cu (II) and Zn (II), and show that Freundlich isotherm was not obeyed, however,  $n$  was high an indication that the adsorption on the adsorbate was favourable. Furthermore, the value of ' $n$ ' at equilibrium is 2.876, 4.25, and 4.34 for Cu (II), Zn (II), and Pb(II) ions, the value of ' $n$ ' lies between 1 and 10 indicating favourable adsorption [43]. The Temkin isotherm show favourable adsorption for copper then zinc and lead ions according to regression coefficient.

### 3.6.4. Biosorption Thermodynamics

Thermodynamic parameters such as enthalpy change  $\Delta H^\circ$ , free energy change  $\Delta G^\circ$ , and entropy change  $\Delta S^\circ$  used for thermodynamics behaviour of Cu (II), Zn (II) and Pb (II) onto UDL and can be calculated from the following equations:

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

Where  $\Delta G^\circ$  is standard free energy change,  $R$  is the universal gas constant (8.314 J/mol K),  $T$  is the temperature in Kelvin and  $K_D = \frac{C_{Ae}}{C_e}$  is the distribution coefficient [44] as given in equation (6). Where  $C_e$  is the equilibrium concentration in solution in mg/L, and  $C_{Ae}$  is the equilibrium concentration on the sorbent in mg/L. Free energy change indicates the degree of spontaneity of the adsorption process and the higher (-) ve value a more energetically favourable adsorption [45, 46].

The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  calculated from the slope and intercept of the plot  $\ln K_D$  against  $1/T$  as given in equation (7). The value of  $\Delta G^\circ$  and  $\Delta S^\circ$  are listed in Table 2.

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

**Table 2.** Thermodynamic parameters for adsorption of Cu (II), Pb (II) and Zn (II) onto UDL.

Heavy metals	T(K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ ( $\frac{J}{mol K}$ )
Cu (II)	288	-1.440	-19.88	-58.84
	303	-3.058		
	318	-3.748		
	333	0.973		
	348	1.428		
Zn (II)	288	-2.442	-32.94	-91.10
	303	-4.700		
	318	-5.868		
	333	0.166		
	348	3.528		
Pb (II)	288	-2.786	-30.92	-98.26
	303	-3.508		
	318	-5.838		
	333	0.984		
	348	2.287		

From Table 2 it is clear that the reaction is spontaneous in nature. The negative values of  $\Delta H^\circ$  suggested the exothermic nature of the adsorption and the negative values of  $\Delta G^\circ$  indicated the spontaneous nature of the adsorption process,

$\Delta G^\circ$  values were found to be negative at lower temperature from 288 to 318 K and becomes positive at higher temperature it indicates the adsorption decreased with an increase in temperature and it is also correlated with exothermic nature of reaction. The negative  $\Delta S^\circ$  value suggests a decrease in the randomness at the solid/solution interface during the biosorption process [47].

## 4. Conclusion

The *Urtica dioica* biomass as a low cost adsorbent is used for the removal of copper zinc and lead from the synthetic waste water. The maximum removal was found at pH 5.0. At pH greater than 5 the metal ions get precipitated due to the formation of metal hydroxides. The adsorption decreases with increasing the initial metal ion concentration, adsorption of Pb (II), Cu (II) and Zn (II) ions on UDL increases with increasing the adsorbent dosage, Langmuir, Freundlich, and Temkin adsorption models were used to represent the experimental data and data fitted well to the Langmuir isotherm model. Thermodynamic analysis suggests that the removal of Pb (II), Cu (II) and Zn (II) from synthetic waste water onto UDL is a spontaneous and exothermic in nature.

## References

- [1] Ahluwalia, S. S., Goyal, D. "Microbial and plant derived biomass for removal of heavy metals from wastewater". *Biores. Technol.*, 98, 2243–57, 2007.
- [2] Naiya, T. K., Bhattacharya, A. K., Mandal, S. and Das, S. K., "The sorption of lead (II) ions on rice husk ash", *J. Hazard. Mater.*, 163, 1254–1264, 2009.
- [3] Monken, A., "Water pollution control for paint booths". *Met. Finish*, 98, 464– 471, 2000.
- [4] Veglio, F., Quaresima, R., Fornari, P. and Ubaldini, S., "Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning", *Waste Manage.*, 23, 245–252, 2003.
- [5] Nicholson, F. A., Smith, S. R., Alloway, B. J., Carlton-Smith, C. and Chambers, B. J., "An inventory of heavy metals inputs to agricultural soils in England and Wales", *Sci. Total Environ.*, 311, 205–219, 2003.
- [6] Otero, N., Vitoria, L., Soler, A. and Canals, A. "Fertiliser characterisation: major, trace and rare earth elements", *Appl. Geochem.*, 20, 1473–1488, 2005.
- [7] Castelblanque, J. and Salimbeni, F. "NF and RO membranes for the recovery and reuse of water and concentrated metallic salts from waste water produced in the electroplating process", *Desalination*, 167, 65–73, 2004.
- [8] Alvarez-Ayuso, E., Garcia-Sanchez, A. and Querol, X. "Purification of metal electroplating waste waters using zeolites", *Water Res.*, 37, 4855–4862, 2003.
- [9] Theophanides, T. and Anastassopoulou, J., "Copper and carcinogenesis", *Crit Rev Oncol Hematol*, 42, 57–64, 2002.

- [10] Walsh, C. T., Sandstead, H. H., Prasad, A. S., Newberne, P. M. and Fraker, P. J. "Zinc: Health effects and research priorities for the 1990s, Environ Health Perspect, 102, 5-46, 1994.
- [11] Ho, Y. S., Ng, J. C. Y. and McKay, G., "Removal of lead (II) from effluents by sorption on peat using second-order kinetics", Separ. Sci. Technol., 36, 241-261, 2001.
- [12] Ahmaruzzaman, M., "Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals", Adv Colloid Interface Sci., 166, 36-59, 2011.
- [13] Matlock, M. M., Howerton, B. S. and Atwood, D. A., "Chemical precipitation of heavy metals from acid mine drainage", Water Res., 36, 4757-4764, 2002.
- [14] Blocher, C., Dorda, J., Mavrov, V., Chmiel, H., Lazaridis, N. K. and Matis, K. A "Hybrid flotation membrane filtration process for the removal of heavy metal ions from wastewater", Water Res., 37, 4018-4026, 2003.
- [15] Rengaraj, S., Joo, C. K., Kim, Y. and Yi, J., "Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H", J. Hazard. Mater, 102, 257-275, 2003.
- [16] Kobya, M., Demirbas, E., Senturk, E. and Ince, M. "Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone", Bioresource Technol. 96, 1518-1521, 2005.
- [17] Ding, Y., Jing, D., Gong, H., Zhou, L. and Yang, X., "Biosorption of aquatic cadmium (II) by unmodified rice straw", Bioresource Technol., 114, 20-25, 2012.
- [18] Flores-Garnica, J. G., Morales-Barrera, L., Pineda-Camacho G., Cristiani- Urbina, E., "Biosorption of Ni(II) from aqueous solutions by Litchi chinensis seeds", Bioresource Technol., 136, 635-643, 2013.
- [19] Akhtar, M., Iqbal, S., Kausar, A., Bhangar, M. I., and Shaheen, M. A., "An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk", Colloids Surf. B: Biointerf., 75, 149-155, 2010.
- [20] Odoemelam, S. A., Iroh, C. U. and Igwe, J. C., "Copper (II), Cadmium (II) and Lead (II) adsorption kinetics from aqueous metal solutions using chemically modified and unmodified cocoa pod husk (Theobroma cacao) waste biomass". Res. J. Applied Sci., 6, 44-52, 2011.
- [21] Zhao, M. and Duncan, J. R., "Batch removal of hexavalent chromium by *Azolla filliculoids*", Biotech. Appl. Biochem., 26, 179 - 182, 1997.
- [22] Dupont, L., Bouanda, J., Dumoneau, J. and Applincourt, M., J., "Metal ions binding onto a lignocellulosic substrate extracted from wheat bran: A nica donnan approach" Colloid Int. Sci., 263, 35-41, 2003.
- [23] Moufilh, M., Aklil, A., and Sebti, S., "Removal of lead from aqueous solutions by activated phosphate", J. Hazard. Mater., 119, 183-188, 2005.
- [24] Reddy, D. H. K., Seshiah, K. Reddy, A. V. R. Rao, M. M. and Wang, M. C., "Biosorption of Pb (II) from aqueous solutions by Moringa oleifera bark: equilibrium and kinetic studies", J. Hazard. Mater., 174, 831-838, 2010.
- [25] Munagapati, V. S., Yarramuthi, V., Nadavala, S. K., Alla, S. R. and Abburi, K. "Biosorption of Cu (II), Cd (II) and Pb (II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics". Chem. Eng. J., 157, 357-365, 2010.
- [26] Dupont, L., Bouanda, J., Dumoneau, J. and Applincourt, M. "Biosorption of Cu (II) and Zn (II) onto a lignocellulosic substrate extracted from wheat bran". Environ. Chem. Lett., 2, 165-168, 2005.
- [27] Gardea-Torresdey, J. L., de la Rosa, G. and Peralta-Videa, J. R., "Use of phytofiltration technologies in the removal of heavy metals: A review", Pure Appl. Chem., 76, 801-813, 2004.
- [28] Martini, M. I., Lopez, F. A. and Alguacil, F. J., "Possibility of using by-products of the steelmaking industry for removing lead from aqueous solutions", Revista de Metalurgia, 44, 258-264, 2008.
- [29] Venugopal, V. and Mohanty, K., "Biosorptive uptake of Cr (VI) from aqueous solutions by *Parthenium hysterophorus* weed: Equilibrium, kinetics and thermodynamic studies", Chem. Eng J., 174, 151-158, 2011.
- [30] Veneu, D. M., Torem, M. L. and Pino, G. A. H., Fundamental aspects of copper and zinc removal from aqueous solutions using a *Streptomyces lunalinhaesii* strain. Miner Eng., 48, 44-50, 2013.
- [31] Rawajfih, Z. and Nsour, N., "Thermodynamic analysis of sorption isotherms of chromium (VI) anionic species on reed biomass", J. Chem. Thermodyn., 40, 846-851, 2008.
- [32] Imamoglu, M. and Tekir, O., "Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks", Desalination, 228, 108-113, 2008.
- [33] Feng, N., Guo, X., Liang, S., Zhu, Y. and J. Liu, "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel", J. Hazard Mater, 185, 49-54, 2011.
- [34] Zafar, S., Aqil, F. and Ahmad, Q., "Metal tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil", Bioresource Technol., 98, 2557 - 2561, 2007.
- [35] Rao, R. A. K. and Ikram, S., "Sorption studies of Cu (II) on gooseberry fruit (*Embllica officinalis*) and its removal from electroplating wastewater", Desalination, 277, 390-398, 2011.
- [36] Lodeiro, P. Barriada, J. L., Herrero, R. and Vicente, Sastre de M. E., "The marine macroalga *Cystoseira baccata* as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies", Environ. Pollut., 142, 264-273, 2006.
- [37] Azouaoua, N., Sadaouia, Z., Djaafri, A. and Mokaddema, H., "Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics" Journal of Hazardous Materials, 184, 126-134, 2010.
- [38] Mittal, A., Mittal, J., Malviya, A. Kaur, D. and Gupta, V. K., "Adsorption of hazardous dye crystal violet from wastewater by waste materials", J. Colloid Interface Sci., 343, 463-473, 2010.
- [39] Langmuir, I., "The Adsorption of Gases on plane surfaces of Glass, Mica and Platinum" J. Am. Chem. Soc., 40, 1361-1403, 1918.

- [40] Ho, Y. S., Huang, C. T. and Huang, H. W., "Equilibrium sorption isotherm for metal ions on tree fern", *Process Biochem.*, 37, 1421–1430, 2002.
- [41] Freundlich, H. M. F., "Over the adsorption in solution", *J. Phys. Chem.*, 57, 385- 471, 1906.
- [42] Kausar, A., Nawaz, H. and Mackinnon, G., "Equilibrium, kinetic and thermodynamic studies on the removal of U (VI) by low cost agricultural waste", *Colloids Surfaces B Biointerfaces* 111, 124-133, 2013.
- [43] Slejko, F. L., "Adsorption technology. A step-by-step approach to process evaluation and application", *Chemical Industries Series*, New York/Basel: Marcel Dekker, Inc. Vol. 19, ISBN 08247-7285-7, 1985.
- [44] Aravindhan, R., Rao, J. R. and Nair, B. U., "Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*", *J. Hazard. Mater.*, 142, 68–76, 2007.
- [45] Dakiky, M., Khamis, M., Manasra, A. and Mereb, M. "Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents", *Advance Environ. Res.*, 6, 533–540, 2002.
- [46] Aksu, Z., "Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*", *Process Biochem.*, 38, 89–99, 2002.
- [47] Sarı A. and Tuzen M., "Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass" *Journal of Hazardous Materials*, 164, 1004–1011, 2009.