A comparative analysis on Pb(II) removal from wastewater using peels of Citrus limetta and leaves of Brassica campestris by biosorption method

Gupta Vikal*, Dev Kapil and Rathore Sawai Singh
Department of Chemistry, J.N.V. University, Jodhpur-342001, Rajasthan, INDIA
*vikal_chem@yahoo.co.in

Abstract
The presence of heavy metals such as copper, chromium, lead, cadmium, arsenic in wastewater is one of the serious environmental problems of our country. These metal ions are nonbiodegradable, hence they have to be removed by human efforts. The recent study has been carried out to compare removal of Pb^{+2} *from wastewater using Citrus limeeta peel powder [CLPP] and Brassica campestris leaves powder [BCLP] as bioadsorbents.*

In present study, activated CLPP and BCLP were used as sorbent for removal of Pb^{+2} *from aqueous medium. Adsorption studies were performed by batch experiments as a function of process parameters such as contact time, adsorbent dosage, pH. The biosorption data was modeled using the Langmuir and Freundlich adsorption isotherm.*

Keywords: Citrus limeeta, Brassica campestris, Pb^{+2} ion, Adsorption isotherm.

Introduction
Many areas of our country face water shortage problem by which farmers are using wastewater to irrigate their crops and vegetable. Instead of ground water, wastewater also provides organic material and essential element which are required for growth of plant. But this may contain heavy metal ions such as Pb^{+2}, Cu^{+2}, Cr^{+3}, As^{+3}, Cd^{+2} etc. which are poisonous for animals and human. This poisonous heavy metal ion is transformed through food chain to the next generation.[1] More over metal ion contaminated drinking water and wastewater become a major environmental and ecosystem problem which leads to serious health hazards during these days.[2]

Industries such as paints, battery, electroplating etc. contain Pb^{+2} ion in their wastewater and release their waste water into water bodies. We know that Pb^{+2} is toxic for aquatic animal at very low concentration and it is fatal to the health in high concentration. When Pb^{+2} is consumed by human, it affects central nervous system, kidney, lungs, premature birth in pregnant women and it is also carcinogenic.[3,4]

There are various method for removing Pb^{+2} ion including ion exchange method, chemical precipitation, membrane technologies, activated carbon etc.[5-7] But these method have some disadvantages such as high costs, low efficiency and disposal of waste generated by these method.[8] To overcome these disadvantages, natural materials are used as bioadsorbents for Pb^{+2} removal. These material are easily available in large quantity which are agricultural waste product. They are environmental friendly also.[9] Several low cost and easily available biosorbents and agricultural wastes have been employed for removal of toxic heavy metal ions.

Biosorption is a physiochemical process in which adsorption of metal ion take place by bioadsorbents. It is highly cost effective and versatile technique for removal of heavy metal ion form industrial waste water. Bioadsorbent used in this technique is biodegradable, low cost by product with several functional groups which act as binding site for metal ion.[10]

The main aim of this research is to compare adsorption efficiency of CLPP and BCLP for the removal of Pb^{+2} ion from wastewater with help of various sorption parameters such as pH, metal ion concentration, adsorbent dosage, particle size and contact time. Citrus limeeta is locally named as mousambi or sweet lime and Brassica campestries is locally named as mustard. It grows in tropical as well as sub- tropical climate of Rajasthan. At the same time, this can be considered a way of recycling such environmentally harmful materials. The nature of sorption in terms of isotherm modals, rate kinetics and thermodynamics aspects has also been studied.

Material and Methods
A. Preparation of biosorbent: Citrus limetta peel and Brassica campestris leaves sample were randomally collected from the field located at Jodhpur district. The collected sample were washed in running tap water to remove dust and other particle. The washed samples were dried in sun light for 4 days. After 4 days, these samples were dried in hot oven for 2 hours at 50 ^{0}C. These sample were crushed separately in a mechanical grinder and sieved at mesh sieves (150 µm) to obtain Citrus limeeta peel powder [CLPP] and Brassica campestris leaves powder (BCLP) separately. Further CLPP and BCLP were activated by treating with 0.05M nitric acid (HNO_3) solution for 4 hr and also keeping it in air oven for 15 hours at 55^{o}C.

B. Preparation of Pb(II) solution: The stock solution of Pb^{+2} containing 1000 mg/L was prepared by dissolving 1.598 g of $Pb(NO_3)_2$ in 1L double distilled water. This solution was diluted as required to obtain standard solution containing 25-125 mg/L of Pb^{+2}. Before mixing the biosorbent, the pH of each test solution was adjusted to require value with H_2SO_4 and NaOH solutions.

C. Batch biosorption studies: Biosorption experiments were carried out by batch experiment method as function of metal ion concentration (25, 50, 75, 100, 125 and 150) mgL^{-1}, pH (1 to 6), adsorbent dosage (2 to 14) g, contact time (20, 40, 60, 80, 100,110 and 120) min and particle size (150 µm). One parameter had been changed at a particular time and all other parameters were maintained constant according to table 1. After completion of every set of experiment, finally metal bearing solution was allowed to settle and then the residual metal ion solutions were filtered using Whatmann no. 42 filter paper. 20 mL of each sample was stored for residual Pb^{+2} analysis.

After the completion of experiment, the concentration of residual ion Pb^{+2} was directly measured by atomic adsorption spectroscopy[11].

Eq. (1) was used to determine the percentage adsorption of metal (in %) by adsorbents.

$$\% \text{ Removal of Cr (VI)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is initial metal ion concentration and C_e is the concentration of metal ion after adsorption.

D. Adsorption isotherm: According to Langmuir theory, the saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_{\max}\ bC_e}{1 + bC_e} \quad (2)$$

The equation (2) can be rearranged by following linear form:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e \quad (3)$$

where C_e is the equilibrium concentration, q_e is the amount of metal ion adsorbed, q_{max} is q_e for a complete monolayer (mgL^{-1}) and b is sorption equilibrium constant ($L\ mg^{-1}$). A graph of Ce versus C_e/q_e should indicate a straight line of slope $1/q_{max}$ and an intercept of $1/bq_{max}$.

Fruendlich had found that if the concentration of solute in solvent at equilibrium Ce (mgL^{-1}) was raised to the power of m, the amount of solute adsorbed being q_e, then C_e/q_e was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation in the form of logarithm of both sides.

$$\log q_e = \log K_f + m \log C_e \quad (4)$$

An adsorption isotherm is characterized by certain constant, the value of which expresses the surface properties and affinity of the sorbent and can also be used to compare bio-chemosorptive capacity of biomass for different metal ions. Out of several isotherm equations, two have been applied for this study i.e. the Fruendlich and Langmuir isotherms.

Results and Discussion

The effects of different parameters (contact time, pH, adsorbent dosage etc.) on the removal of Pb^{+2} ion by biosorption onto CLPP, BCLP were investigated. The metal ion removal studies are shown in the table 1 and 2 which indicated that removal of Pb^{+2} ion was strongly affected by different operating conditions.

Effect of concentration of Pb(II) ion: The biosorption of Pb(II) ion on CLPP and BCLP was carried out separately with concentration range of 25-150 mg/L and maintaining other conditions as constant i.e. adsorbent dosage 10 gL^{-1}, contact time 80 min and pH 4.

It is found that percentage adsorption decreases with increase in concentration of metal ion (Fig. 1). The concentration of metal ion (adsorbate) plays an important role with the fix amount of adsorbent. Such behavior can be because of the unchanging number of available active site on the adsorbent, here the amount of adsorbent is constant. Therefore Pb(II) ions are left unabsorbed in solution due to the saturation of binding sites on the available adsorbents.

The percentage removal efficiency of Pb^{+2} in CLPP decreases from 97.4% to 63.8% with increase in concentration 25 to 150mg/L. Similarly, with BCLP it decreases from 89.9% to 51.0%.

Higher removal efficiency at lower concentration is due to more interaction of metal ion with sorption site. Higher efficiency of CLPP as compared to BCLP may be due to voids and cracks on adsorbents surface in CLPP suitable for adsorption of Pb^{+2}.[11]

Table 1
Experimental conditions

Experimental conditions	*M*s (g L^{-1})	pH	*P*s (µm)	*T* (min)	C_o (mg L^{-1})
Effect of biosorbent dosage *M*s (g L^{-1})	2–14	4	150	80	25
Effect of pH	10	1–6	150	80	25
Effect of contact time *T* (min)	10	4	150	20–120	25
Effect of concentration of Pb^{+2} ion C_o (mg L^{-1})	10	4	150	80	25–150

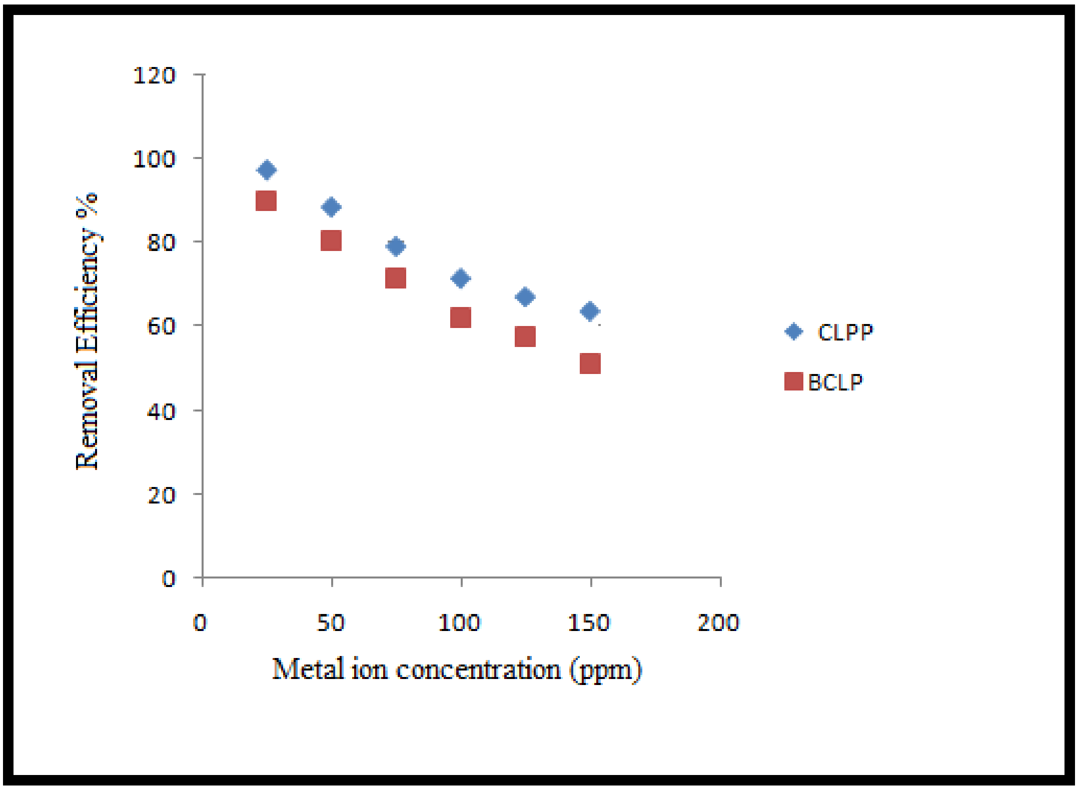

Fig. 1: Effect of Metal ion concentration on biosorption of Pb(II) ions by CLPP and BCLP

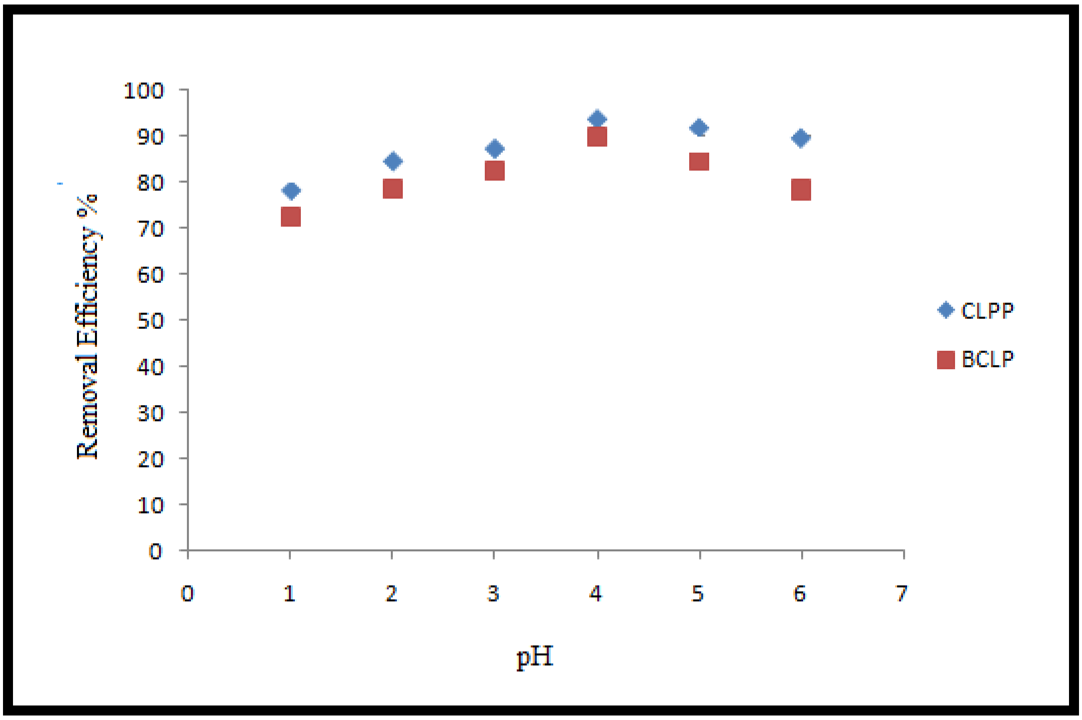

Fig. 2: Effect of pH on biosorption of Pb(II) ions by CLPP and BCLP

Effect of pH: Biosorption of Pb^{+2} ion from both CLPP and BCLP, was examined separately with the change in pH from 1 to 6 and other parameters were maintained constant i.e. adsorption dosage 10gL^{-1}; the concentration of Pb^{+2} 25 mg L^{-1} and contact time 80 minutes. Biosorption of Pb^{+2} was found to be dependent upon the pH of the solution. The optimum pH for the biosorption Pb^{+2} was found to be 4 which was acidic.

At low pH (below 3) interaction between metal ion and hydrogen ion is high as well as there is excessive protonation of the active site (at the surface of adsorbant) which reduces the adsorption of Pb^{+2} ion on the active site. At moderate pH (3 to 5), H^{+} ion is released from protonated active site and provides more active site for the adsorption of Pb^{+2} ion, so adsorption is higher at moderate pH. At higher pH (above 5) the precipitate of Pb^{+2} ion is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. This condition is often not desirable .[12]

Effect of contact time: Biosorption of Pb^{+2} ion was examined with change in the contact time 20 to 120 minute; other parameters were kept constant i.e. pH 4, the metal ion concentration of Pb^{+2} 25mg L^{-1}, adsorbent dosage 10gL^{-1} and particle size of biomasses 150 μm.

Contact time between adsorbent and adsorbate species play an important role in the process of removal of metal pollutant from wastewater by biosorption at particular pH and temperature.[13,14]

As shown in fig. 3, removal efficiency increases with increase in contact time because more time is available for contact of metal ion with biosorbents. But after 80 minute, the contact time does not prove to be effective because effective time is already taken.[15]

Effect of biosorbent dosage: The effect of biosorbent dosage on the biosorption of Pb^{+2} ion was determined with the range of 2gm – 14mg/L while other parameters remained constant. It is found that percentage removal of Pb^{+2} ion increases with increase in biomass dosage from 65.3% to 96.1% in CLPP and from 59.4% to 84% in BCLP. Increase in removal efficiency is due to fact that number of biosorption sites increases by increasing the biosorbent dosage.[16]

The subsequent constant in the removal efficiency can be explained by aggregation or over lapping of the adsorption site which is supported by literature[17,18].

Isotherm models of the Biosorption: The isotherm models are mathematical models describing the distribution of Pb^{+2} ion between two phases that are in contact. The extent of the attraction of both biosorbents (BCLP and CLPP) for the Pb^{+2} metal ion is responsible to determine their distribution between solid and liquid phases. Langmuir and Freundlich isotherms were used in explaining the experimental data in this study. Langmuir and Freundlich isotherm model parameters estimated from fitting of experimental point of Pb^{+2} adsorption were reported in table 2.

Conclusion

Based on the present study, it could be concluded that some low cost plant such as Citrus limetta peel powder (CLPP) and Brassica campestris leaves powder (BCLP) materials can be used efficiently in the removal of heavy metal ions like Pb^{+2} from industrial wastewater. This biosorption process is easy to carry out for effluent treatment. It is found that CLPP is more effective than BCLP as a biosorbent in removal of Pb^{+2}.

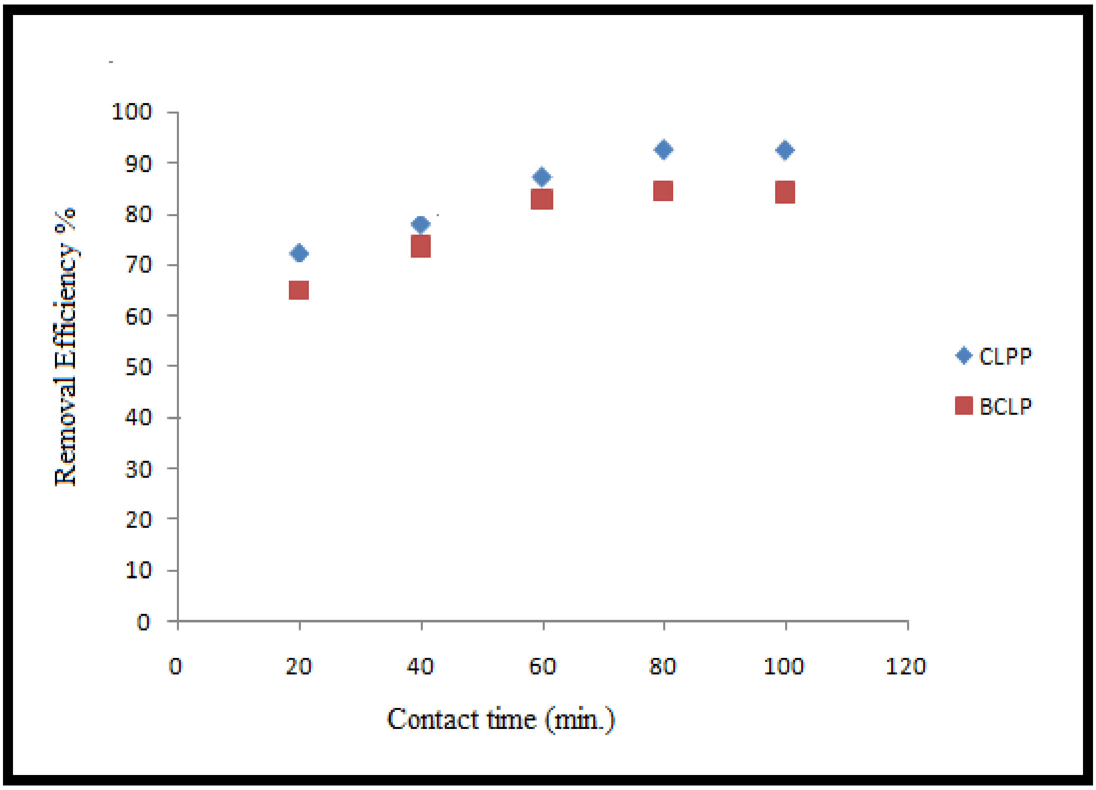

Fig. 3: Effect of contact time on biosorption of Pb(II) ions by CLPP and BCLP

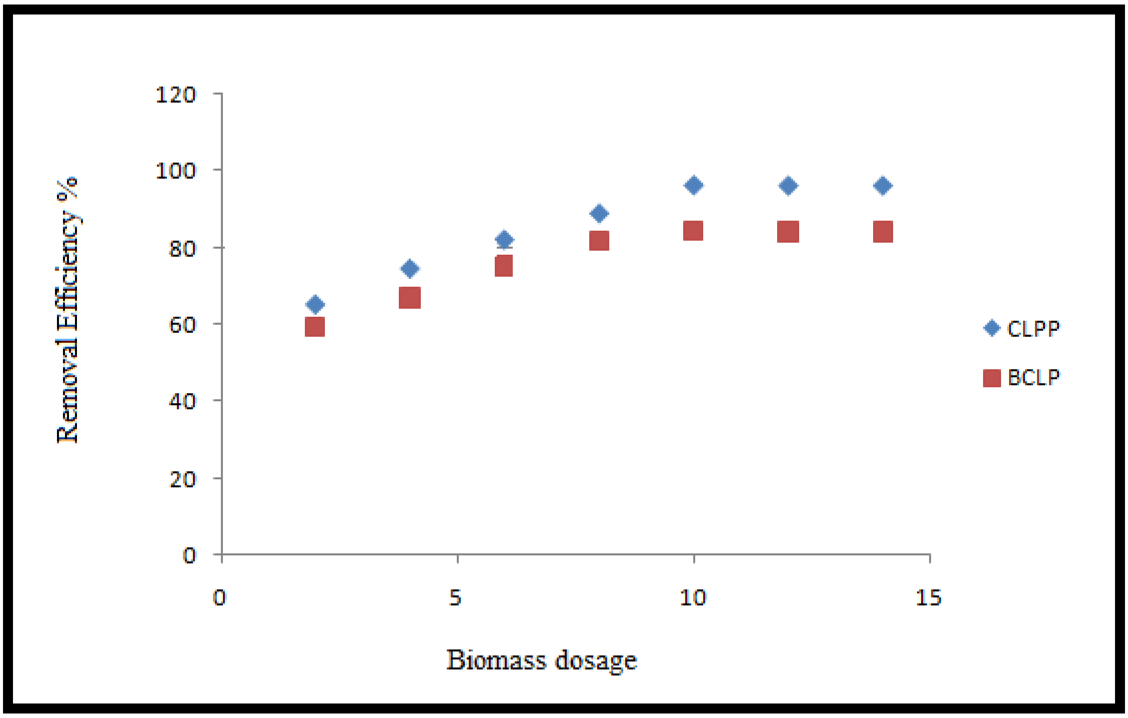

Fig. 4: Effect of biomass dosage of CLPP and BCLP on biosorption of Pb(II).

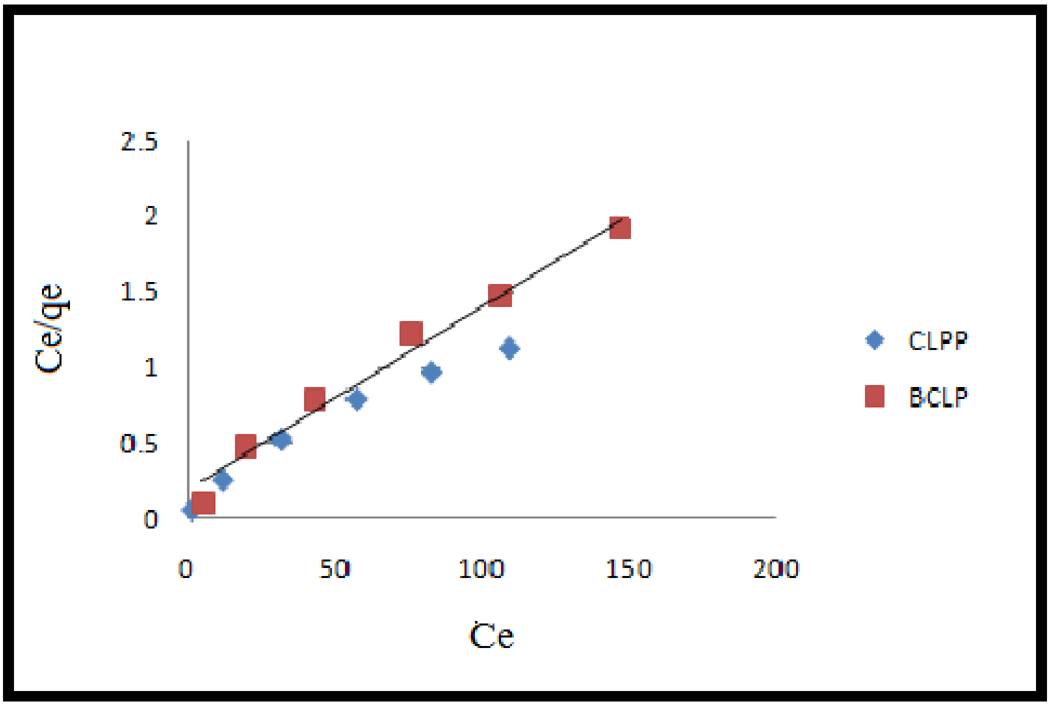

Fig. 5: Langmuir adsorption isotherm for CLPP and BCLP.

Table 2
Langmuir and Fruendlich isotherms model parameters

	Langmuir isotherm				Freundlich isotherm		
	R^2	q_{max} mg g^{-1}	b, L mg^{-1}		R^2	K_f, mg g^{-1}	m
CLPP	0.965	11.11	0.028		0.992	21.47	0.304
BCLP	0.980	8.33	0.062		0.992	12.56	0.370

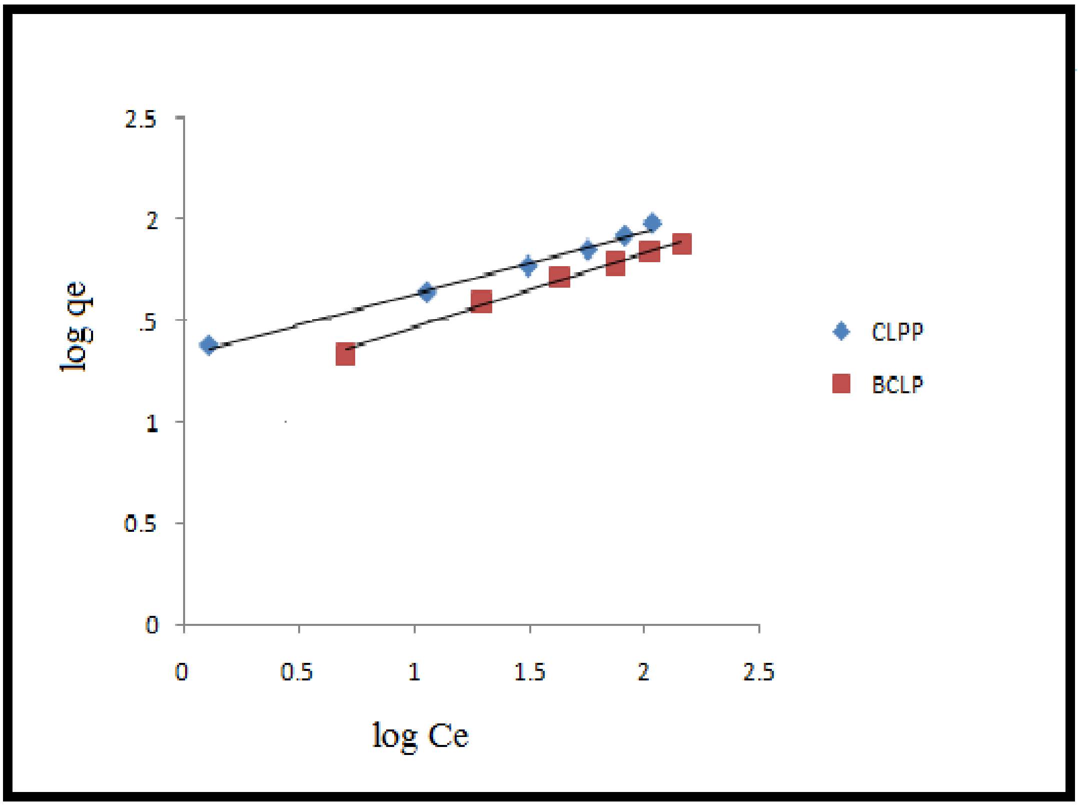

Fig. 6: Freundlich adsorption isotherm for CLPP and BCLP.

The maximum biosorption was found 97.4% for CLPP and 89.9% for BCLP at pH=4. The experimental adsorption data have been found to be best fitted with Langmuir and Freundlich adsorption isotherms thus indicating the applicability of monolayer coverage of Pb(II) on surface of adsorbent.

References

1. Afkhami A., Madrakin T. and Karimi Z., Effect of the impregnation of carbon with ethylenediamintetraaceticacid on its adsorption capacity for the adsorption of several metals ion, *J. Hazard Mater*., **150**, 408-412 **(2008)**

2. Akpor O.B. and Muchie M., Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications, *International J. Physical Science*, **5**, 1807-1817 **(2010)**

3. Al-Subu M.M., Salim R., Abu-Shqair I. and Swaileh K.M., Removal of dissolved copper from polluted water using plant leaves: i, Effects of acidity and plant species, *Rev. Int. Contam. Ambient*., **17**, 91-96 **(2001)**

4. Devaprasath P.M., Solomon J.S. and Thomas B.V., Removal of Chromium (VI) from Aqueous Solution using Natural Plant Mater, *J. Appl. Sci. Environ. Sanitation*, **2**, 77-83 **(2007)**

5. Fatima T., Nadeem R., Masood A., Saeed R. and Ashraf M., Sorption of lead by chemically modified rice bran, *Int. J. Environ. Sci. Technol*, **10**, 1255-1264 **(2013)**

6. Lingamdinne L.P., Roh H., Choi Y., Koduru J.R., Yang J. and Chang Y., Influencing factors on sorption of TNT and RDX using rice husk *biochar*, *J. Ind. Eng. Chem*., **32,** 178-186 **(2015)**

7. Malik R., Ramteke D.S. and Wate R.A., Physico-chemical and surface characterization of adsorbent prepared from groundnut shell by $ZnCl_2$ activation and its ability to adsorb colour, *Indian J. Chem. Technol*., **13**, 319-328 **(2006)**

8. Mihajlovic M.T., Lazarevic S.S., Jankovic-Castvan I.M., Kovac J., Jokic B.M., Janackovic D.T. and Petrovic R.D., Kinetics, thermodynamics andstructural investigations on the removal of Pb^{+2}, Cd^{+2} and Zn^{+2}, from multicomponent solutions onto natural and Fe(III)-modified zeolites, *Clean Technol. Environ. Policy*, **14**, 407-419 **(2015)**

9. Mousavi H.Z., Hosseynifar A., Jahed V. and Dehgani S.A.M., Removal of lead from aqueous solution using waste tire rubber ash as an adsorbent, *Braz. J. Chem. Eng*., **27**, 79-87 **(2010)**

10. Moyo M. and Chikazaza L., Bioremediation of lead(II) from polluted wastewaters employing sulphuric acid treated maize tassel biomass, *Am. J. Anal. Chem*., **4**, 689-695 **(2013)**

11. Murtaza G., Ghafoor A., Qadir M., Owens G. and Aziz M.A., Disposal and use of sewage on agriculture lands in Pakistan, A review, *Pedosphere*, **20**, 23-34 **(2010)**

12. Navarro R.R., Sumi K. and Matsumura M., Improved metal affinity of chelating adsorbents through graft polymerization, *Water Res*., **33(9)**, 2037–2044 **(1999)**

13. Olorundare O.F., Krause R.W.M., Okonkwo J.O. and Mamba B.B., Potential application of activated carbon from maize tassel for the removal of heavy metals in water, *Phys. Chem. Earth*, doi: 10.1016/j.pce **(2012)**

14. Shafaghat A., Salami F., Valiei M., Salehzadeh J. and Shafaghat M., Removal of heavy metals (Pb^{+2}, Cu^{+2}, Cr^{+3}) from

aqueous solutions using five plant materials, *African Journal of Biotechnology*, **11(4)**, 852-855 **(2012)**

15. Wang J. and Chen C., Biosorbents for heavy metals removal and their future, *Biotechnol. Adv.*, **27**, 195-226 **(2009)**

16. Wan Ngah W.S. and Hanafiah Abas M.A.K.M., Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, *Bioresource Technology*, **99**, 3935–3948 **(2008)**

17. W.H.O. Lead poisoning and health, Available online: http//www.Who.int/mediacentre/facesheet/FS379/en **(2014)**

18. Wu Y., Zhang S., Guo X. and Huang H., Adsorption of Cr(III) On lignin, *Bioresour. Technol.*, **99**, 7709-7715 **(2008)**.

(Received 03rd December 2020, accepted 07th January 2021)