Competitive adsorption of metals on cabbage waste from multi-metal solutions

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Abstract

This study assessed the adsorption capacity of the agro-waste 'cabbage' as a biosorbent in single, binary, ternary and quaternary sorption systems with Cu(II), Pb(II), Zn(II) and Cd(II) ions. Dried and ground powder of cabbage waste (CW) was used for the sorption of metals ions. Carboxylic, hydroxyl, and amine groups in cabbage waste were found to be the key functional groups for metal sorption. The adsorption isotherms obtained could be well fitted to both the mono- and multi-metal models. In the competitive adsorption systems, cabbage waste adsorbed larger amount of Pb(II) than the other three metals. However, the presence of the competing ions suppressed the sorption of the target metal ions. Except the case of binary system of Cd(II)-Zn(II) and Cd(II)-Cu(II), there was a linear inverse dependency between the sorption capacities and number of different types of competitive metal ions.

Keywords: Cabbage waste, competitive adsorption, biosorption, multi-metals, isotherm model, antagonism mechanismµ

1. Introduction

Untreated and uncontrolled discharge of heavy metal containing wastewaters into the natural environment could be toxic to humans, animals, plants, and to urban ecosystems (Ahmad et al., 2010; Pamukoglu and Kargi, 2006). Cu(II), Pb(II), Cd(II) and Zn(II) are used in various remove heavy metals from wastewater with high solute loadings and even at dilute concentrations (<100 mg/L) (Popuri et al., 2009). Among the adsorbents, activated carbon is commonly used as a commercial adsorbent for removing heavy metals from wastewater. However, this is still an expensive material, requiring costly regeneration. This has prompted the search for an inexpensive yet effective alternative adsorbent.

Removal of heavy metals by biosorption is a relatively new and an emerging technology in the explain the binding characteristics of metallic cations during biosorption (Karthikeyan et al., 2007).

First time by this investigation, cabbage-biosorbent is used to determine the biosorption

2.2.2 Metals solutions and measurement

A stock solution of Pb(II), Cd(II), Cu(II) and Zn(II) were obtained by dissolving the exact quantity of $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ in Milli-Q water. The test solutions containing single ions were prepared by diluting 1000 mg/L of stock solutions of metal ions to the desired concentrations. The ranges of concentrations of both metal ions prepared from stock solutions varied between 1 mg/L to 500 mg/L.

For the investigation with binary metal solutions, the desired combinations of Cu(II)-Pb(II), Pb(II)-Cd(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions were obtained by diluting 1000 mg/L of stock solutions of metal ions and mixed them in the test medium. Before mixing the biosorbent, the pH of each test solution was adjusted to the required value with 0.1 N H_2SO_4/NaOH. Similarly, the ternary solutions of Pb(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Cd(II), Cu(II)-Pb(II)-Zn(II) and Cu(II)-Cd(II)-Zn(II) were quaternary solution of Cu(II)-Pb(II)-Cd(II)-Zn(II) was prepared with required dilutions from the stock solutions.

The concentrations of heavy metal ions in solution were determined by Atomic Adsorption Spectroscopy (AAS) (Contra®AA 300, Analytikjena, Germany) after samples were filtered with Whatman™ GF/C-47mm ϕ circle filters (GE Healthcare, Buckinghamshire, UK).

2.3 Adsorption experiments

2.3.1 Effect of pH

shaken at 120 rpm for 120 min at room temperature (20 °C). These experiments were conducted in three replicates.

2.3.2 Adsorption isotherm

Adsorption isotherm experiments were studied at eight concentrations ranging from 1 to 500

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_{e.i} = \frac{q_{m.i} K_{L.i}\left(C_{e.i}\right)}{1 + \sum_{j=1}^{N} K_{L.j} (C_{e.j})} \quad (2)$$

$$q_{e.Pb} = \frac{q_{m.Pb} K_{L.Pb} C_{e.Pb}}{1 + K_{L.Pb} C_{e.Pb}} \quad (3)$$

For Cd(II): $$q_{e.Cd} = \frac{q_{m.Cd} K_{L.Cd} C_{e.Cd}}{1 + K_{L.Cd} C_{e.Cd}} \quad (4)$$

For Cu(II): $$q_{e.Cu} = \frac{q_{m.Cu} K_{L.Cu} C_{e.Cu}}{1 + K_{L.Cu} C_{e.Cu}} \quad (5)$$

And for Zn(II): $$q_{e.Zn} = \frac{q_{m.Zn} K_{L.Zn} C_{e.Zn}}{1 + K_{L.Zn} C_{e.Zn}} \quad (6)$$

(ii) Binary metal adsorption system

$$q_{e.Pb} = \frac{q_{m.Pb} K_{L.Pb} (C_{Pb})}{1 + K_{L.Pb} C_{e.Pb} + K_{L.Cd} C_{e.Cd}} \quad (7)$$

For Cd (II): $$q_{e.Cd} = \frac{q_{m.Cd} K_{L.Cd} (C_{Cd})}{1 + K_{L.Pb} C_{e.Pb} + K_{L.Cd} C_{e.Cd}} \quad (8)$$

Similarly, the equation (2) can be transformed for the binary solution of Cu(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) adsorption systems.

(iii) Ternary metal adsorption system

$$q_{e.Cu} = \frac{q_{m.Cu}K_{L.Cu}\left(C_{Cu}\right)}{1 + K_{L.Cu}C_{e.Cu} + K_{L.Pb}C_{e.Pb} + K_{L.Cd}C_{e.Cd}} \quad (9)$$

for Pb(II): $$q_{e.Pb} = \frac{q_{m.Pb}K_{L.Pb}\left(C_{Pb}\right)}{1 + K_{L.Cu}C_{e.Cu} + K_{L.Pb}C_{e.Pb} + K_{L.Cd}C_{e.Cd}} \quad (10)$$

and for Cd(II): $$q_{e.Cd} = \frac{q_{m.Cd}K_{L.Cd}\left(C_{Cd}\right)}{1 + K_{L.Cu}C_{e.Cu} + K_{L.Pb}C_{e.Pb} + K_{L.Cd}C_{e.Cd}} \quad (11)$$

Similarly, the equation (2) can be rewritten for Pb(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Zn(II) and Cu(II)-Cd(II)-Zn(II) adsorption systems.

(iv) Quaternary metal adsorption system

$$q_{e.Cu} = \frac{q_{m.Cu}K_{L.Cu}\left(C_{Cu}\right)}{1 + K_{L.Cu}C_{e.Cu} + K_{L.Pb}C_{e.Pb} + K_{L.Cd}C_{e.Cd} + K_{L.Zn}C_{e.Zn}} \quad (12)$$

For Pb(II): $$q_{e.Pb} = \frac{q_{m.Pb}K_{L.Pb}\left(C_{Pb}\right)}{1 + K_{L.Cu}C_{e.Cu} + K_{L.Pb}C_{e.Pb} + K_{L.Cd}C_{e.Cd} + K_{L.Zn}C_{e.Zn}} \quad (13)$$

For Cd(II): $$q_{e.Cd} = \frac{q_{m.Cd} K_{L.Cd} (C_{Cd})}{1 + K_{L.Cu} C_{e.Cu} + K_{L.Pb} C_{e.Pb} + K_{L.Cd} C_{e.Cd} + K_{L.Zn} C_{e.Zn}} \quad (14)$$

And for Zn(II): $$q_{e.Zn} = \frac{q_{m.Zn} K_{L.Zn} (C_{Zn})}{1 + K_{L.Cu} C_{e.Cu} + K_{L.Pb} C_{e.Pb} + K_{L.Cd} C_{e.Cd} + K_{L.Zn} C_{e.Zn}} \quad (15)$$

2.4 Data analysis and validation

The isotherm data were modelled with a modelling technique of Excel Spreadsheet and MATLAB. Data fitting was assessed by the magnitude of R^2, RMSE and χ^2 (Hossain et al., 2012) error functions. The percent reduction in adsorption capacities in the competitive systems (binary, ternary and quaternary) were calculated by the following expression:

$$\%\,\text{reduced} = \frac{(\text{q}_\text{m}\ \text{from single metal system} - \text{q}_\text{m}\ \text{from multi-metal system})}{\text{q}_\text{m}\ \text{from single metal system}} \times 100$$

3. Results and discussion

3.1 Characterization of biosorbent with FTIR and SEM

The surface structures of biosorbents produced from cabbage waste was analysed by an SEM. Generally, the micro-graphs revealed that it contained asymmetrical particles. In lower magnification (1KX), the heterogeneous structures were noticed. It was observed that the surface of the particles was built with uneven, asymmetric steps and pores. It is believed that irregular shapes of particles have more internal binding or uptakes places and eventually adsorb more metals (Ricordel et al., 2001). The BET surface area of cabbage-biosorbent was 1.027 m²/g, which is lower than conventional biosorbents available in literature (Hossain et al., 2013).

A biosorbent may consist of complex organic and inorganic materials such as proteins, lipids, carbohydrate polymers and sometimes metals. Chemisorptions and ions exchange mostly depends on the available functional groups in a particular biosorbent and eventually metal adsorption depend on it. Carbon-oxygen and carbon bonds are the attracting and stimulating bonds of metals adsorption (Ricordel et al., 2001). From FTIR spectra of the biosorbent, the following major functional groups were noticed: O-H stretch-free hydroxyl for alcohols/phenols (3624.54 cm^{-1}), O-H stretch for carboxylic acids (between 3300-2500 cm^{-1}), C-N stretch for aliphatic amines (1024.25 cm^{-1}), C-O stretch for alcohols/carboxylic acids/esters/ethers (between 1320-1000 cm^{-1}), =C-H bend for alkanes (between 1000-650 cm^{-1}) and C-H "OOH" for aromatics (817.85 cm^{-1}). Among the functional groups, hydroxyl, amines and carboxyl groups could bind heavy metal ions with adsorbent (Kongsuwan et al., 2009; Sheng et al., 2004).

3.2 Effect of pH

al., 2012). It was observed that the Cu(II), Cd(II), Zn(II) and Pb(II) metals precipitates as a form of $Cu(OH)_2$, $Cd(OH)_2$, $Zn(OH)_2$ and $Pb(OH)_2$ beyond a pH of 7. Hence, to avoid metal precipitation the remaining experiments were conducted between 6.0 and 6.5 pH.

Fig. 1

3.3 Adsorption isotherm

3.3.1 Single metal adsorption

Langmuir model is applicable for monolayer adsorption onto a surface containing a finite number of identical sites (Aksu, 2005). This model was used to describe experimental data from adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions onto cabbage. The sorption data were fitted to the non-linear form of Langmuir isotherm model (Eq. 1) and parameters are evaluated

In this study, apart from Cd(II), diverse relationship between the adsorption capacity and the ionic radius (Cu=73, Zn = 74, Cd = 95 and Pb = 77.5 nm) (Kusvuran et al., 2012) was observed. Higher ionic radii of heavy metals generally led to higher maximum adsorption capacities. For example, because the ionic radius of Pb(II) is larger than that of Cu(II), the maximum adsorption capacities of cabbage were higher in case of Pb(II) than Cu(II) (Table 1). Table 1 also reveals a higher maximum adsorption capacity for Cd(II) as its ionic radius is

16.660 mg/g for Pb(II), Cu(II), Pb(II), Pb(II), Cd(II) and Cu(II) ions in binary sorption of Pb(II)-Cd(II), Cu(II)-Zn(II), Cu(II)-Pb(II), Pb(II)-Zn(II), Cd(II)-Zn(II) and Cd(II)-Cu(II) systems, respectively. The results indicate that the adsorption capacity for Pb(II) was higher than that of Cd(II), Cu(II) and Zn(II) as Pb(II) could bind with more varieties of functional groups (Kongsuwan et al., 2009). The maximum adsorption capacities of Cd(II), Zn(II), Cu(II) and Pb(II) obtained from binary metals sorption were less than those obtained from the single metal system (Table 1).

3.3.3 Adsorption behaviour in ternary solutions

Wastewaters may contain more than one metal ion and therefore, the examination of multiple metal interactions simultaneously is very important for accurate representation of adsorption data (Hammaini et al., 2003). The competitive adsorption among the Cu(II), Pb(II), Cd(II) and Zn(II) in the ternary systems of Cd(II)-Pb(II)-Cu(II), Cd(II)-Pb(II)-Zn(II), Cu(II)-Cd(II)-Zn(II) and Cu(II)-Pb(II)-Zn(II) were conducted in batch systems between 1 to 200 mg/L of initial concentration. It was experimented for 3 hours at 120 rpm and room temperature. The adsorption parameters of ternary systems is tabulated in Table 3. The experimental data were well fitted with the ternary adsorption model (Eq. 9-11) as evident by the R2 values exceeding 0.99. (Tables 1, 2 and 3). The adsorption capacities of cabbage were found to be 12.264, 8.785 and 40.963 mg/g for Cd(II)-Cu(II)-Pb(II) system, 7.587, 1.828 and 50.216 mg/g for Cd(II)-Zn(II)-Pb(II) system, 4.965, 7.584 and 5.844 mg/g for Cd(II)-Cu(II)-Zn(II) system, and 8.194, 6.380 and 22.803 mg/g for Cu(II)-Zn(II)-Pb(II) system of ternary-metal interactions, respectively (Table 3). The findings could be explained by the fact that the ionic charge, ionic radius, and electrochemical potential affect adsorption capacity of biosorbent in the multi-metal ion sorption system (Yakup Arıca et al., 2004) while adsorption capacity decreases in the multi-metal adsorption system with respect to single metal adsorption capacity (Padilla-Ortega et al., 2013).

Table 3

3.3.4 Adsorption behaviour in quaternary solutions

The calculated parameters from the quaternion Langmuir isotherms are summarised in Table 4. This isotherm model successfully fitted the competitive adsorption of Cu(II)-Pb(II)-Cd(II)-Zn(II) onto the biosorbent prepared from cabbage.

Table 4

The experimental adsorption capacities of Cu(II), Pb(II), Cd(II) and Zn(II) from the four metals system [Cu(II)-Pb(II)-Cd(II)-Zn(II)] were compared to the molar uptake values of Cu(II), Pb(II), Cd(II) and Zn(II) predicted with the quaternary Langmuir isotherm (Eqs. 12-15). The Langmuir isotherm accurately estimated the adsorption capacities for all fours metal uptake as evident by the superimposing predicted lines and the experimental plots. However, it overestimated the molar uptake of Zn(II) and showed the similar adsorption capacity (10.170 mg/g)with single metal systems (Table 1). The other three uptakes for metals Cu(II), Pb(II) and Cd(II) are underestimated as the magnitude of the adsorption capacities (2.415mg/g, 15.085mg/g and 8.697mg/g) are lower than the single metals system.

The values of the parameter K_L of the Langmuir isotherm provides indication of the affinity of the biosorbent for the systems with two, three or four metal ions in the test solution: greater the value of these parameters, lesser is the affinity for a metal ion. The values of K_{L-Cu}, K_{L-Pb}, K_{L-Zn}, and K_{L-Cd} are higher in the case of the binary, ternary and quaternary system than the value of K_L derived for the single metal system using the Langmuir sorption isotherm for single-metal (Tables 1, 2, 3 and 5). This means that the affinity of cabbage biosorbent for metal ions was reduced in multi-metals metal system.

3.3.5 Competitive adsorption in multi-metal systems

It is evident from available literature (Christophi and Axe, 2000; Leyva-Ramos et al., 2001) that the multi-metal Langmuir model provides a reasonable fit to the multi-metals adsorption data as long as the q_m values for each metal calculated from single-metal Langmuir isotherm are similar to each other. However, the prediction for q_m values from all binary, ternary and quaternion system are lower than single metals system (Kumar et al., 2008), evidencing competitive sorption of the metals. In this regard, the 3D surface plots of Cu(II)-Zn(II), Pb(II)-Cd(II), Cd(II)-Zn(II), Cu(II)-Cd(II) and Pb(II)-Cu(II) are prepared for the binary systems (Figures 2 and 3). The area plot for ternary system [Cd(II)-Pb(II)-Cu(II), Cd(II)-Pb(II)-Zn(II), Cu(II)-Cd(II)-Zn(II) and Cu(II)-Pb(II)-Zn(II)] is shown in Figure 4 and the spider diagram for the quaternary system [Cd(II)-Pb(II)-Cu(II)-Zn(II)] is given in Figure 5.

Fig. 2

Fig. 2(A) shows the effect of the presence of Zn(II) on the capacity of the cabbage for adsorbing Cu(II). The competitive surface of Cu(II) adsorption indicates that the presence of Zn(II) reduced drastically the uptake of Cu(II) adsorbed on the cabbage. A moderate reduction of the uptake of Cu(II) can be noted as compared to the single metal systems (from 10.315 to 7.140 mg/g). On the other hand, the effect of the presence of Cu(II) on the capacity for adsorbing Zn(II) is shown in Fig.2(B). The effect is stronger and reduced to half of the uptake of Zn(II) (from 8.970 to 4.760 mg/g) though the surface of adsorption is perfectly slanting evenly (Padilla-Ortega et al., 2013). In the Pb(II)-Cd(II) system the effects of Pb(II) and Cd(II) ions on the uptake of Cd(II) and Pb(II) on to the cabbage are plotted in Fig.2(C) and Fig.2(D), respectively. The Pb(II) uptake was reduced to 43.907 mg/g in binary system from 60.568 mg/g in single metals. Similarly, the reduction of the adsorption capacity for Cd(II) is changed significantly (from 20.565 to 18.582 mg/g). These metals significantly interfered in the adsorption of each other, as evidenced by the uneven surface of adsorption in 3D graphs (Fig.2).

Similarly, the partial aggression on the adsorption of Cd(II) and Zn(II) in Cd(II)-Zn(II), Cu(II) and Cd(II) in Cu(II)-Cd(II), and; Pb(II) and Cu(II) in Pb(II)-Cu(II) binary system are plotted in 3D graph of Fig.3. As can be seen in Fig.3, strong interference existed between the metals but the dominance of Pb(II) and Cd(II) uptake did not change by their counter pairs of metals (Apiratikul and Pavasant, 2006). High affinity of cabbage toward the Pb(II) and Cd(II) ions are internal causes (functional groups) for the significant adsorption of those metals. For instance, in Cd(II)-Zn(II) system Cd(II) uptake (18.030 mg/g), and in Pb(II)-Cu(II) system Pb(II) (60.311 mg/g) uptake were more than their pairs of Zn(II) and Cu(II) (Tables 1 and 2). Fig.3 (A, C, and E) shows that the adsorption surfaces are more even than counter metals. However, a significant change was found in Cu(II)-Cd(II) system where Cu(II) uptake increased (from 10.315 mg/g in single metal system to 20.660 mg/g in binary system) in the presence of Cd(II) ions. It is also noticeable that Zn(II) adsorption slightly increased in binary system (11.053 mg/g) with the presence of Cd(II) ions. It might be due to the fact that the presences of Cd(II) ions enhance the uptake of Cu(II) and Zn(II) with considering of minor change of its own uptake (Papageorgiou et al., 2009).

Fig. 3

The results of the competitive adsorption of ternary system of Cu(II)-Cd(II)-Zn(II), Cu(II)-Pb(II)-Zn(II), Cu(II)-Pb(II)-Cd(II) and Cd(II)-Pb(II)-Zn(II) onto cabbage are demonstrated in the surface plot of Fig.4 (a, b, c and d). It is revealed that the Pb(II) ions presented a higher affinity for the binding sites of the cabbage than the Cu(II), Cd(II) and Zn(II) ions. In other words, the cabbage was much more selective towards Pb(II) than to other three metals in the competitive adsorption. The Pb(II) ions presented strong resisatnce against (i) the adsorption of Cu(II) and Cd(II) ions in Cu(II)-Pb(II)-Cd(II), against of Cd(II) and Zn(II) ions in Cd(II)-Pb(II)-Zn(II) system; (ii) against of Cu(II) and Zn(II) in Cu(II)-Pb(II)-Zn(II) system whereas the Cu(II) and Cd(II) ions, Cd(II) and Zn(II) ions; and (iii) Cu(II) and Zn(II) ions exhibited light resistance against the adsorption of Pb(II) (Apiratikul and Pavasant, 2006; Padilla-Ortega et al., 2013). This behaviour could not be predicted from the single metal adsorption system. It is also found from Fig. 4 (b, c and d) that Pb(II) ions took higher physical surface area than capacity for Cd(II) ions,; however, it dropped to 16%, 18.50% and 26.4% for binary, 44.56%, 65.71% and 77.56% for ternary and 60.7% for quaternary systems. It is apparent that the highest declined in adsorption capacities were observed for Pb(II) and Cd(II) ions in all adsorption systems. Conversely, an inconsistent trend (decrease and increase) was observed in case of the adsorption of the Cu(II) and Zn(II) ions. The Cu(II) and Zn(II) ions adsorption capacities increased to 29% and 1.5% for Cd(II)-Cu(II) and Cd(II)-Zn(II) binary systems. However, it dropped for binary, ternary and quaternary systems with other coexisting metals. Thus, it may be stated that Cd(II) ions acted as a stimulant for the adsorption of Cu(II) and Zn(II) ions. In other words, inhibition or enhancement of adsorption depends on the coexisting metal(s) (Laus and de Fávere, 2011).

7. Demirbas, A. 2008. Heavy metal adsorption onto agro-based waste materials: A review. *Journal of Hazardous Materials*, **157**(2-3), 220-229.

8. Hammaini, A., González, F., Ballester, A., Blázquez, M.L., Muñoz, J.A. 2003. Simultaneous uptake of metals by activated sludge. *Minerals Engineering*, **16**(8), 723-729.

9. Han, R., Zou, L., Zhao, X., Xu, Y., Xu, F., Li, Y., Wang, Y. 2009. Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. *Chemical Engineering Journal*, **149**(1), 123-131.

10. Hossain, M.A., Ngo, H.H., Guo, W.S., Nguyen, T.V., Vigneswaran, S. 2013. Performance of cabbage and cauliflower wastes for heavy metals removal. *Desalination and Water Treatment*, 1-17.

11. Hossain, M.A., Ngo, H.H., Guo, W.S., Setiadi, T. 2012. Adsorption and desorption of copper(II) ions onto garden grass. *Bioresource Technology*, **121**(0), 386-395.

12. Hu, Z., Yang, X., Gao, A., WEI, X. 2007. Remediation of mycorrhiza on Cd contaminated soil. *Journal-china university of mining and technology-chinese edition-*, **36**(2), 237.

13. Karthikeyan, S., Balasubramanian, R., Iyer, C. 2007. Evaluation of the marine algae *Ulva fasciata* and *Sargassum sp.* for the biosorption of Cu (II) from aqueous solutions. *Bioresource Technology*, 98(2), 452-455.

14. Kongsuwan, A., Patnukao, P., Pavasant, P. 2009. Binary component sorption of Cu(II) and Pb(II) with activated carbon from Eucalyptus camaldulensis Dehn bark. *Journal of Industrial and Engineering Chemistry*, **15**(4), 465-470.

15. Kumar, D., Singh, A., Gaur, J.P. 2008. Mono-component versus binary isotherm models for Cu(II) and Pb(II) sorption from binary metal solution by the green alga Pithophora oedogonia. *Bioresource Technology*, **99**(17), 8280-8287.

16. Kurniawan, T.A., Chan, G., Lo, W., Babel, S. 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment*, **366**(2), 409-426.

17. Kusvuran, E., Yildirim, D., Samil, A., Gulnaz, O. 2012b. A Study: Removal of Cu(II), Cd(II), and Pb(II) Ions from Real Industrial Water and Contaminated Water Using Activated Sludge Biomass. *CLEAN – Soil, Air, Water*, **40**(11), 1273-1283.

18. Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, **40**(9), 1361-1403.

19. Laus, R., de Fávere, V.T. 2011. Competitive adsorption of Cu(II) and Cd(II) ions by chitosan crosslinked with epichlorohydrin–triphosphate. *Bioresource Technology*, **102**(19), 8769-8776.

20. Leyva-Ramos, R., Bernal-Jacome, L.A., Guerrero-Coronado, R.M., Fuentes-Rubio, L. 2001. Competitive adsorption of Cd(ii) and Zn(ii) from aqueous solution onto activated carbon. *Separation Science and Technology*, **36**(16), 3673-3687.

21. Nghiem, L.D., P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall., S.D. Kolev. "Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs)". *Journal of Membrane Science*, 2006. **281**(1-2), 7-41.

22. Padilla-Ortega, E., Leyva-Ramos, R., Flores-Cano, J.V. 2013. Binary adsorption of heavy metals from aqueous solution onto natural clays. *Chemical Engineering Journal*, **225**(0), 535-546.

23. Pamukoglu, M.Y., Kargi, F. 2006. Batch kinetics and isotherms for biosorption of copper (II) ions onto pre-treated powdered waste sludge (PWS). *Journal of Hazardous Materials*, **138**(3), 479-484.

24. Papageorgiou, S., Katsaros, F., Kouvelos, E., Kanellopoulos, N. 2009. Prediction of binary adsorption isotherms of Cu^{2+}, Cd^{2+} and Pb^{2+} on calcium alginate beads from single adsorption data. *Journal of Hazardous Materials*, **162**(2), 1347-1354.

25. Popuri, S.R., Vijaya, Y., Boddu, V.M., Abburi, K. 2009. Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresource Technology*, **100**(1), 194-199.

List of Caption and Tables

Table 1
The Langmuir monolayer adsorption constant for the adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions on cabbage biosorbent at room temperature, 5g/L adsorbent dose, 2 hours, 120 rpm and pH:6.0-6.5.

Table 2
Calculated parameters from Langmuir model for binary adsorption of Pb(II)-Cd(II), Cu(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions on cabbage waste.

Table 3
Ternary adsorption parameters calculated from Langmuir model for Pb(II), Cd(II), Cu(II) and Zn(II) adsorption

Table 4
Isotherm parameters of Langmuir model of fournary metals [Cd(II)-Cu(II)-Zn(II)-Pb(II)] adsorption

Table 1
The Langmuir monolayer adsorption constant for the adsorption of Cu(II), Pb(II), Zn(II) and Cd(II) ions on cabbage biosorbent at room temperature, 5 g/L adsorbent dose, 2 hours, 120 rpm and pH:6.0-6.5.

Langmuir isotherm model	**Equilibrium parameters**	**Cu(II) adsorption**	**Pb(II) adsorption**	**Zn(II) adsorption**	**Cd(II) adsorption**
$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_{m.Exp}$ (mg/g)	12.955±0.45	61.267±0.85	10.890±0.72	22.123±0.67
	$q_{m.Mod}$(mg/g)	10.315±0.32	60.568±0.38	8.970±0.56	20.568±0.23
	K_L (L/g)	0.022	0.021	0.019	0.021
	R^2	0.991	0.996	0.997	0.996
	RMSE	0.383	8.219	0.189	8.219
		0.081	2.555	0.357	2.554
	R_L	0.21-0.92	0.27-0.98	0.18-0.95	0.28-0.99

Table 2
Calculated parameters from Langmuir model for binary adsorption of Pb(II)-Cd(II), Cu(II)-Pb(II), Cd(II)-Zn(II), Cd(II)-Cu(II), Cu(II)-Zn(II) and Pb(II)-Zn(II) ions on cabbage waste.

Pb(II)-Cd(II)	**Cu(II)-Zn(II)**	**Cu(II)-Pb(II)**

Pb(II)-Zn(II)	Cd(II)-Zn(II)	Cd(II)-Cu(II)
For Pb(II):	For Cd(II):	For Cd(II):
q_{m-Pb} = 42.942±0.88 mg/g	q_{m-Cd} =18.030±0.78 mg/g	q_{m-Cd} = 16.280±0.95 mg/g
K_{L-Pb} = 0.036±0.006 L/g	K_{L-Cd} = 0.060±0.005 L/g	K_{L-Cd} = 0.041±0.002 L/g
K_{L-Zn} = -0.050±0.035 L/g	K_{L-Zn} = -0.044±0.0019 L/g	K_{L-Cu} = -0.0306±0.001 L/g
R^2 = 0.997	R^2 = 0.999	R^2 = 0.999
For Zn(II):	For Zn(II):	For Cu(II):
q_{m-Zn} = 9.460±0.92 mg/g	q_{m-Zn} =11.053±0.34mg/g	qm-Cu = 16.660±0.81 mg/g
K_{L-Pb} = 0.036±0.012 L/g	K_{L-Cd} = 0.060±0.004 L/g	KL-Cd = 0.041±0.003 L/g
K_{L-Zn} = -0.050±0.005 L/g	K_{L-Zn} = -0.044±0.001 L/g	KL-Cu = -0.0306±0.001 L/g
R^2 = 0.997	R^2 = 0.998	R2 = 0.999

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Table 3
Ternary adsorption parameters calculated from Langmuir model for Pb(II), Cd(II), Cu(II) and Zn(II) adsorption

Cd(II)-Pb(II)-Cu(II)	Cd(II)-Pb(II)-Zn(II)	Cu(II)-Cd(II)-Zn(II)	Cu(II)-Pb(II)-Zn(II)

Table 4
Isotherm parameters of Langmuir model of quaternion metal [Cd(II)-Cu(II)-Zn(II)-Pb(II)] adsorption system

For Cd(II)	For Cu(II)	For Zn(II)	For Pb(II)
$q_{m\text{-}Cd}$ = 8.697±1.53 mg/g	$q_{m\text{-}Cu}$ = 2.415±0.82 mg/g	$q_{m\text{-}Zn}$ = 10.170±1.77 mg/g	$q_{m\text{-}Pb}$ = 15.085±0.78mg/g
$K_{L\text{-}Cu}$= 0.0034±0.001L/g	$K_{L\text{-}Cu}$ =-0.039±0.004 L/g	$K_{L\text{-}Cu}$ = -0.063±0.007 L/g	$K_{L\text{-}Cu}$ = -0.052±0.007 L/g
$K_{L\text{-}Cd}$ = 0.050±0.006 L/g	$K_{L\text{-}Cd}$ = 0.038±0.007 L/g	$K_{L\text{-}Cd}$ = 0.004±0.001 L/g	$K_{L\text{-}Cd}$ = 0.055±0.002 L/g
$K_{L\text{-}Zn}$ = -0.014±0.006L/g	$K_{L\text{-}Zn}$ = -0.022±0.0003L/g	$K_{L\text{-}Zn}$ = 0.029±0.005 L/g	$K_{L\text{-}Zn}$ = -0.034±0.004 L/g
$K_{L\text{-}Pb}$ = -0.015±0.008L/g	$K_{L\text{-}Pb}$ = 0.029±0.0016 L/g	$K_{L\text{-}Pb}$ = 0.038±0.007 L/g	$K_{L\text{-}Pb}$ = 0.038±0.001 L/g
R^2 = 0.999	R^2 = 0.998	R^2 = 0.999	R^2 = 0.998

List of Captions and Figures

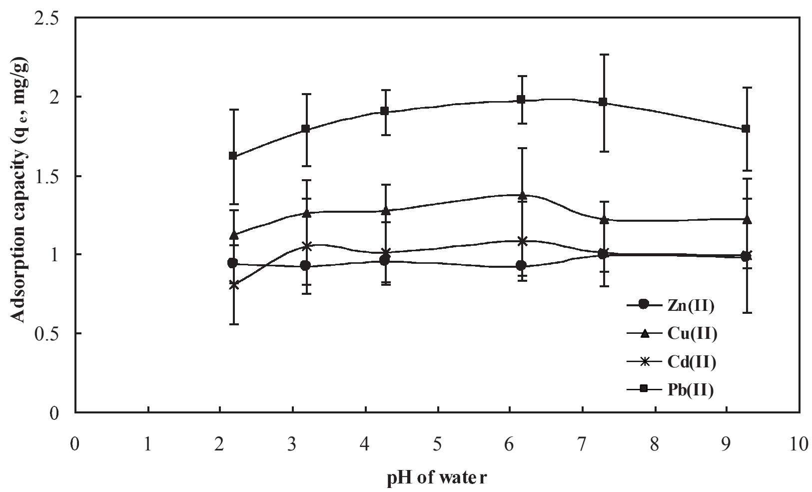

Fig.1. Effect of pH on Cd(II), Cu(II), Zn(II) and Pb(II) adsorptions (C_o = 10 mg/L; adsorbent dose = 5g/L). Error bars show the standard deviation of three replicate experiments

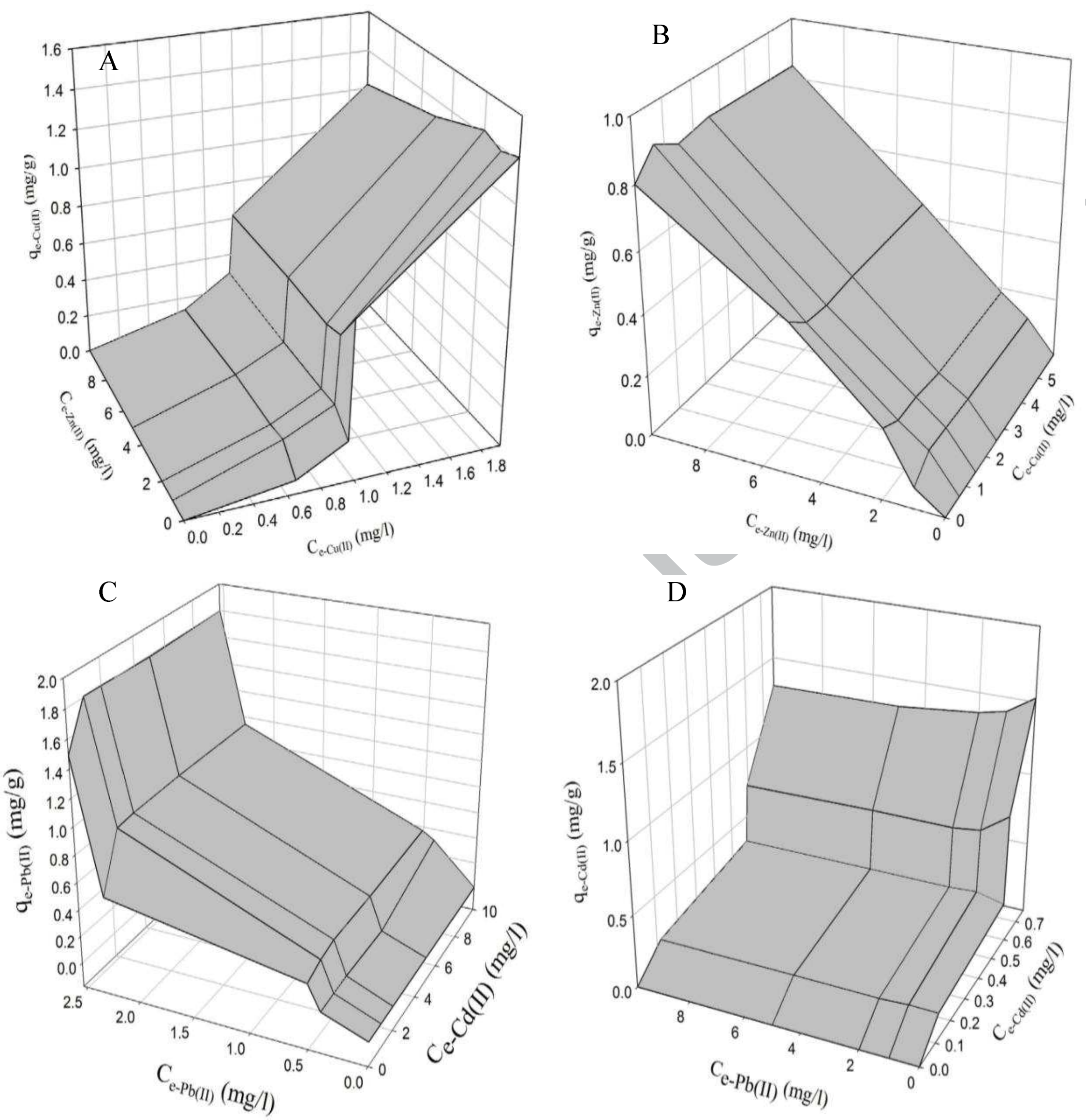

Fig.2. Antagonism among the metals for Cu(II)-Zn(II) (A&B) and Pb(II)-Cd(II) (C&D) binary system

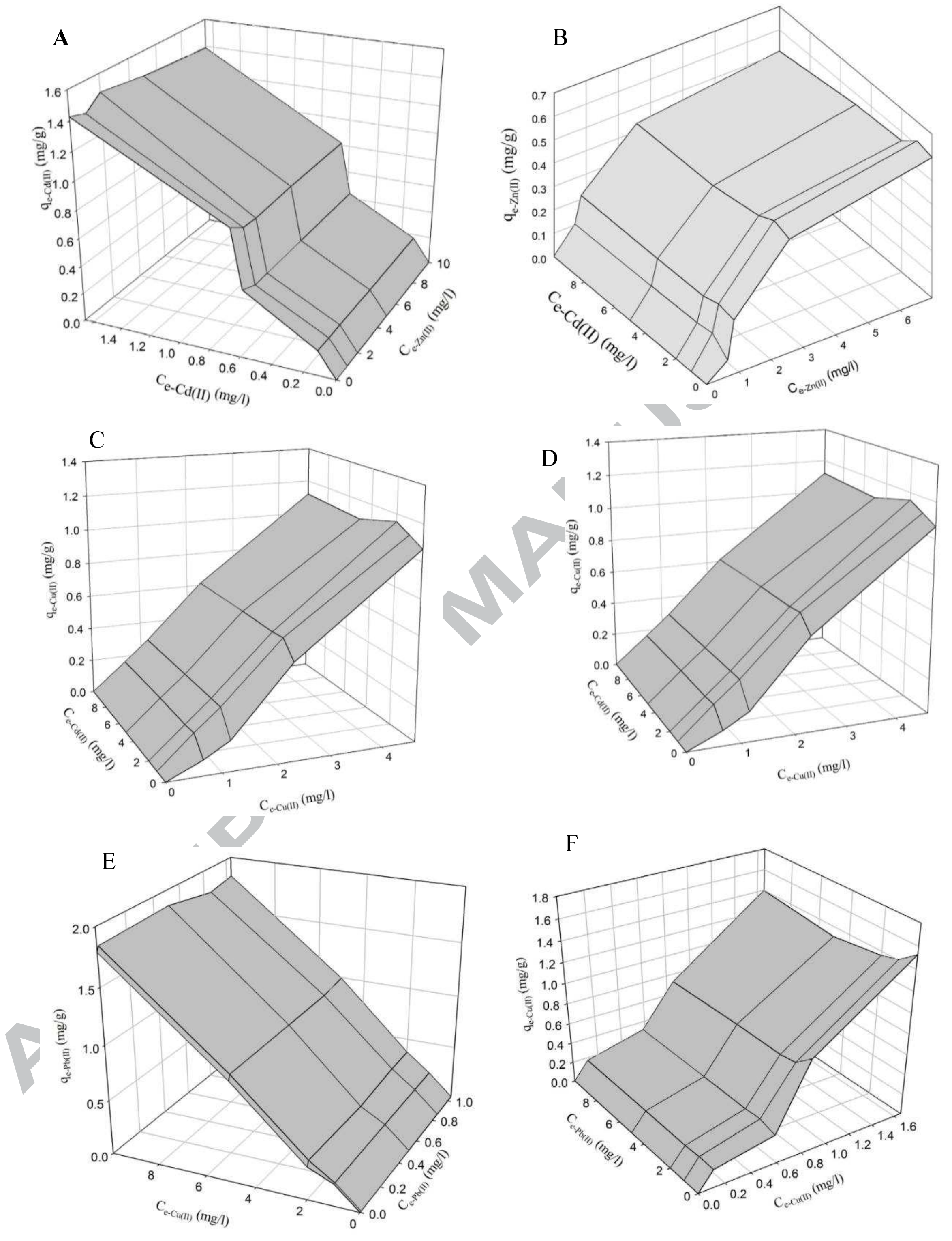

Fig.3. Antagonism among the metals for Cd(II)-Zn(II) (A&B), Cu(II)-Cd(II) (C&D) and Pb(II)-Cu(II) (E&F) binary system

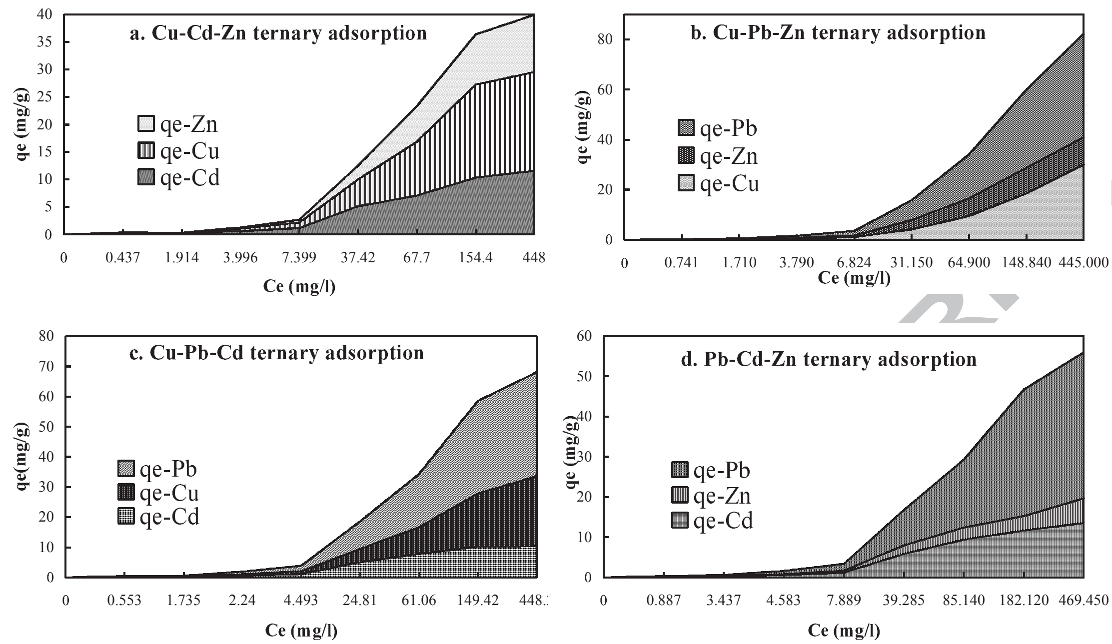

Fig.4. Occupied physical surface area of metals in terms of capacity for ternary metals adsorption system onto cabbage

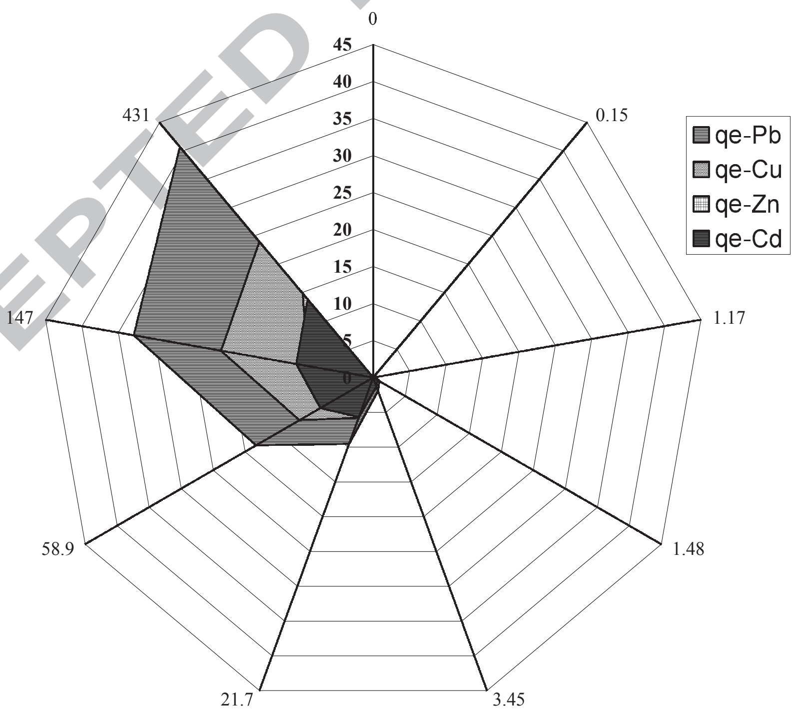

Fig.5. Engaged area in terms of capacity of metals in spider diagram for quaternary metals adsorption onto cabbage

Highlights

- Modified Langmuir model described well the multi-metal adsorption system.
- Adsorbent from cabbage waste is effective for Pb(II) and Cd(II) adsorption.
- High interference among the metals was observed in a multi-metal system.
- Adsorption capacity was suppressed by the presence of other metal ions.
- The highest reduced in adsorption capacities were found for Pb(II), Zn(II) and Cd(II).