


# Comparative and competitive adsorption of Cu(II), Cd(II) and Pb(II) onto *Sepia pharaonis* endoskeleton biomass from aqueous solutions

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## Keywords

adsorption; biomass; cadmium (II); copper (II); heavy metals; lead (II); *Sepia pharaonis* endoskeleton.

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## ABSTRACT

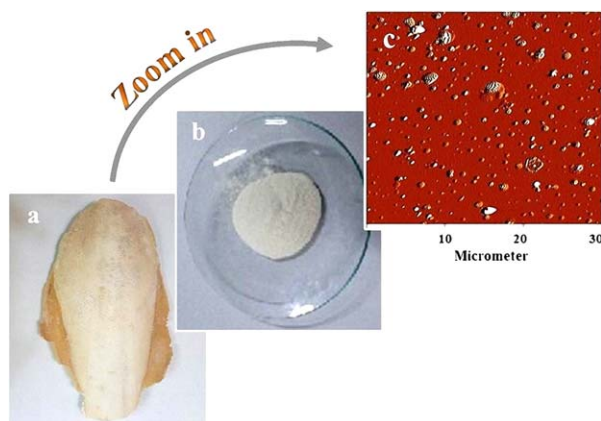
In this research, the possibility of simultaneous removal of lead, cadmium and copper divalent ions from water samples through the use of *Sepia pharaonis* endoskeleton powder (SPEB) as bio-material, was investigated. The bio-sorbent was characterised by Fourier transform infrared spectrum (FT-IR), atomic force microscopy (AFM) and X-ray fluorescence (XRF). The different factors affecting the bio-sorption process were studied. Langmuir and Freundlich isotherm models were applied to analyse the experimental data. The kinetic studies showed that the pseudo-second order model kinetics were compatible with the investigated systems. It was found that under optimal conditions, this bio-sorbent was efficient in the uptake of these heavy metal ions from both mono and multi-metal solutions, and high removal percentages were achieved. This study verified the potential ability of SPEB as an efficient natural adsorbent for removal of Pb(II), Cd(II) and Cu(II) ions from river, tap and mineral water samples.

## Introduction

From environmental and economic points of view, the removal and recovery of heavy-metal ions from water and industrial wastewater have been a significant concern in most industrial activities (Uddin 2017; Wen *et al.* 2017). Many methods such as coagulation and precipitation (Tang *et al.* 2016), membrane filtration (Bennani and M'hiri 2015), ion exchange (Dąbrowski *et al.* 2004), adsorption (Jiang *et al.* 2013; Mukherjee *et al.* 2016; Islam *et al.* 2017) and bio-sorption (Hodgson *et al.* 2016; Phetphaisit *et al.* 2016) have been developed to remove these contaminants from polluted water and wastewater streams. Among these different methods, adsorption and bio-adsorption techniques have attracted more attention due to the simplicity, effectiveness and ease of handling the adsorbent (Liu *et al.* 2013; Zhu *et al.* 2013; Hossain *et al.* 2014; Visa and Chelaru 2014; Wang *et al.* 2014; Yuan *et al.* 2016; Sahraei & Ghaemy 2017). Over the past few years, much attention has been paid to utilise various bio-materials such as agricultural and biological waste materials as adsorbent for heavy metals due to the increasing demand for new, cost effective and environment

friendly processes for the removal and recovery of these metals from industrial effluents (Dhir 2014; Feizi & Jalali 2015). Many research have been carried out using bio-adsorbents such as Leaves of *Arundo donax* reed (Ammari 2014), bio-sorbent made from a combination of tea wastes, maple leaves and mandarin peels (Abdolali *et al.* 2016), jute fibre (Du *et al.* 2016), modified *Saccharomyces pastorianus* biomass (Kordialik-Bogacka & Diowksz 2014), rice husk (Sobhanardakani *et al.* 2013), sawdust (Wahab *et al.* 2010), peanut shell (Witek-Krowiak *et al.* 2011), sugarcane bagasse (Khoramzadeh *et al.* 2013) and banana peels for heavy metal removal (Liu *et al.* 2012).

Cuttlefish belongs to a main class of marine shellfish called Cephalopods. The most common species of cuttlefish in the Persian Gulf is *Sepia pharaonis* (SP) (Shushizadeh *et al.* 2015; Mostoufi 2016). Cuttlefish has an endoskeleton called cuttlebone. *Sepia pharaonis* endoskeleton is illustrated in Fig. 1(a). Cuttlebone is the waste left after the processing of cuttlefish as seafood and also exists naturally in beaches where cuttlefish lives. According to the literature, little published data is available for the adsorption capability of this bio-mass (Li *et al.* 2010; Ben Nasr *et al.* 2011).



**Fig. 1.** (a) *Sepia pharaonis* endoskeleton, (b) the pulverised particles and (c) the AFM photograph of SPEB. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

The main goal of this study was to assess the comparative and competitive adsorption behaviour (adsorption extent in optimum conditions, isotherm and kinetic mechanism) of three model divalent heavy metals [Pb(II), Cd(II) and Cu(II) ions] in mono and multi-metal forms on *Sepia pharaonis* endoskeleton biomass (SPEB) as a green and highly efficient natural adsorbent, without any chemical treatment or activation.

## Materials and methods

### Reagents and apparatus

Stock solutions of Pb(II), Cd(II) and Cu(II) ions (1000 mg/L) were purchased from Merck (Germany). SP endoskeleton was collected from Nakhiloo Island near the North coast of Persian Gulf in Bushehr Province, Iran. Analytical grade reagents such as hydrochloric acid and sodium hydroxide and deionised water were used in this study. Absorption measurements were carried out using an Analytik Jena, model AAS 5 FL atomic absorption spectroscope (Germany). The FT-IR spectrum was recorded with a Bruker spectrometer (model Tensor 27, Germany). AFM image was obtained by Nanowizard II, Germany. Elemental analysis was done by using an Oxford model ED2000 X-ray fluorescence (XRF) instrument (England). A Costhec CHNSO analyser model ECS 4010 (Italy) was used to determine the carbon, hydrogen and nitrogen contents of SPEB. The Brunauer–Emmett–Teller (BET) specific surface area of SPEB particles was obtained on the nitrogen adsorption and desorption isotherms by a NanoSORD-93 instrument (Iran).

### Preparation of adsorbent

Before use, the cuttlefish endoskeleton was brushed to remove any adhered materials. After that, it was rinsed with

deionised water, dried at 60°C for 12 h and allowed to cool. Then, it was crushed and sieved through size 100 mesh (Fig. 1b). These pulverised particles were stored in desiccators.

### Batch adsorption tests

The uptake experiments were performed by mixing appropriate amounts of SPEB (0.01–1.00 g) with 50 mL of heavy metals solutions. The initial pH of solution was adjusted to differing values in the range of 3–10, by HCl and NaOH solutions. After stirring for 2–120 min at room temperature and 250 rpm, the solid phase was removed from the solution by using a suitable filter paper. All experiments were performed in triplet. The percentage of ion removed ( $R\%$ ) was calculated by using the following equation:

$$R\% = 100 \times (C_0 - C_e) / C_0 \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and the equilibrium concentrations of the ions in solutions (mg/L), respectively. The metal loading capacity of SPEB at equilibrium ( $q_e$ , mg/g) was determined as:

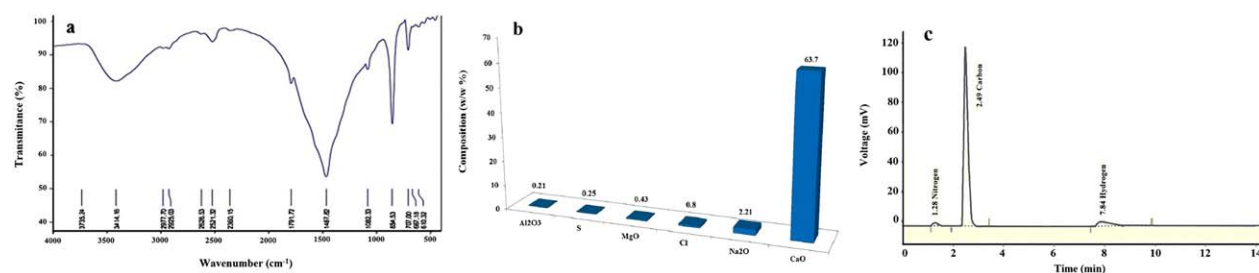
$$q_e = (C_0 - C_e) \times V / W \quad (2)$$

where  $V$  is the volume of solution (L) and  $W$  is the amount of adsorbent (g). The concentration of metal ion in solution after the removal procedure was analysed by using flame atomic absorption spectroscopy (FAAS).

## Results and discussion

### Characterisation of SPEB

The AFM micrograph for the SPEB is illustrated in Fig. 1(c). As shown in this figure, SPEB particles have spherical shape with diameter of  $<1 \mu\text{m}$ . The FT-IR Spectra of the SPEB is shown in Fig. 2(a). The major band at  $1467 \text{ cm}^{-1}$  is related to C–O bands in carbonate. The sharp band at  $854 \text{ cm}^{-1}$  is caused by the Ca–O bond. These major and sharp bands show that  $\text{CaCO}_3$  is the main constituent of this compound. Moreover, the broad absorption band of –OH and –NH at  $3414 \text{ cm}^{-1}$ , reference bands of chitin at  $2977$  and  $2925 \text{ cm}^{-1}$  may correspond to the chitinous constituent of SPEB (Li *et al.* 2010; Yilmaz 2012). The results obtained from the XRF analysis (Fig. 2b) showed that CaO percentage in the SPEB composition was about 64% (w/w). In addition, as seen in Fig. 2(c), the CHN analyser could determine the carbon (13.80%), hydrogen (0.46%) and nitrogen (0.70%) elemental concentrations (w/w) may attribute to chitin material in SPEB (Shushizadeh *et al.* 2015). Also, according to the BET results, the average surface area of SPEB particles was  $7.2 \text{ m}^2/\text{g}$ .

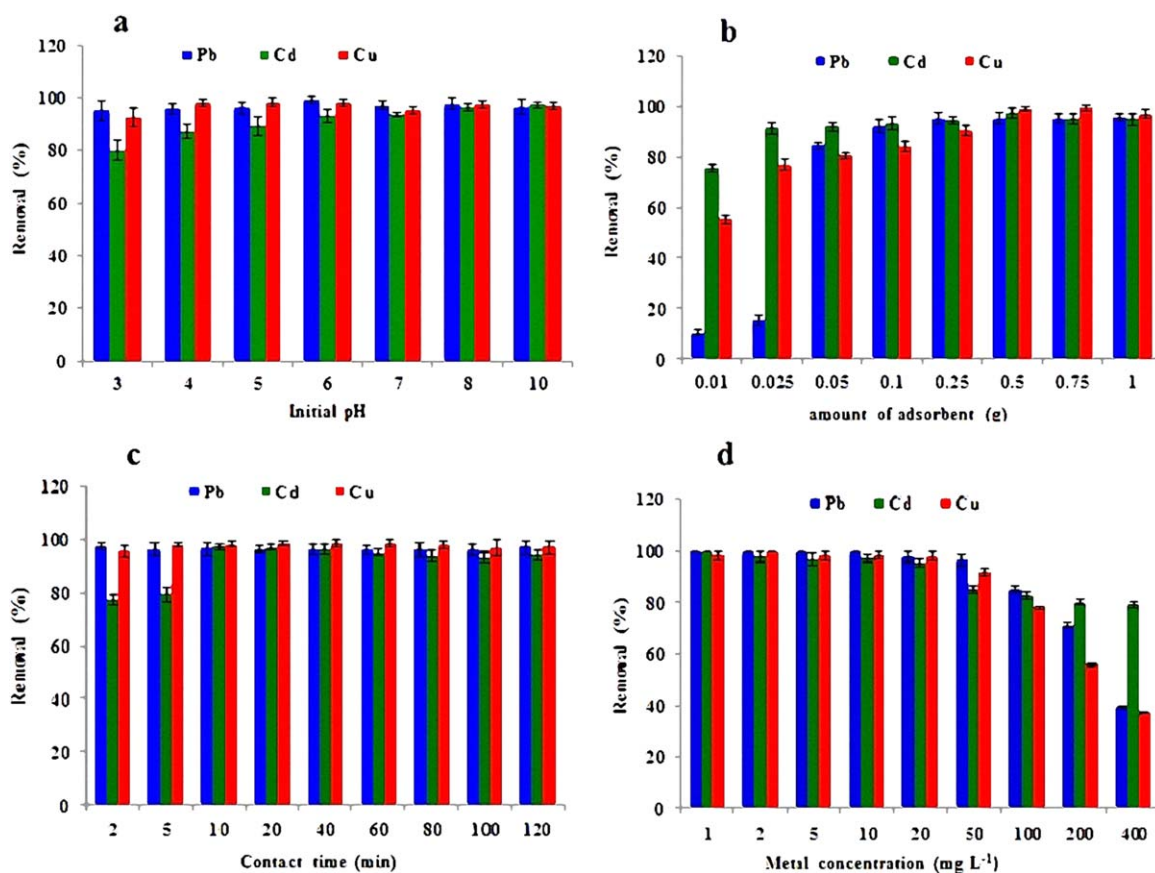


**Fig. 2.** (a) FT-IR spectra of SPEB, (b) the XRF results of SPEB composition and (c) the chromatogram obtained from CHN analyser. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

### Effect of initial pH

Dependence of metal removal on pH is due to both the metal chemistry, the ionisation state of the functional groups, and ion exchanger ability of the adsorbent (Afkhami *et al.* 2010). In order to evaluate the effect of this parameter, the experiments were performed in initial pH range of 3–10. According to the results (Fig. 3a), the removal of the cations was not severely influenced by the solution pH and all the tested metal ions were quantitatively adsorbed onto SPEB at pH 7 (96–99%). As stated before, Calcium carbonate as the main

constituent of SPEB causes a predictable increase in pH when the bio-sorbent is agitated with the sample solution. By adjusting the initial pH of the examined cation solutions in the range of 3–10, the final pH values were 8.6–9.3 after agitation with SPEB. Therefore, one can assume that the thin layer of calcium carbonate molecules on the SPEB's surface start to dissolve and produce Ca(II) and HCO<sub>3</sub><sup>-</sup> ions, which is due to the ionisation constants of carbonic acid ( $pK_{a1} = 3.6$  and  $pK_{a2} = 10.3$ ). Later, the tested metal ions can be adsorbed onto SPEB by ion-exchange mechanism (Li *et al.*



**Fig. 3.** Effect of (a) pH, (b) amount of SPEB, (c) contact time and (d) the metal-ion concentration on the uptake of the metal ions by SPEB (Conditions: 0.5 g SPEB, 50 mL of 20 mg/L of each metal ion, contact time of 10 min and pH 7). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

2010). Calcium ion can be easily exchanged and substituted by examined ions because of the capability of these ions to form stronger insoluble carbonate salts than calcium ion [ $pK_{sp}$ :  $PbCO_3$  (13.13),  $CdCO_3$  (11.3),  $CuCO_3$  (9.6) and  $CaCO_3$  (8.32)] (Xu *et al.* 2013). Furthermore, micro-precipitation and metal hydroxide condensation onto the bio-sorbent can be participated as another mechanism for the chemisorption of examined cations. However, the removal of metal ions from sample solution via surface complex formation and electrostatic adsorption mechanisms that can be attributed to the functional groups (hydroxyl groups and amide groups which can be changed to amine groups in alkaline medium) of chitinous material of SPEB might be of lesser importance (Varma *et al.* 2004).

### Effect of the amount of SPEB

The amount of SPEB for the maximum adsorption of mentioned metal ions in 50 mL solution (containing 20 mg/L of cations) at initial pH 7 was tested over a range of 0.01–1.00 g of the adsorbent. As illustrated in Fig. 3(b), a maximum removal percentage (96–99%) was achieved when the amount of SPEB was 0.50 g. The effective chemisorption via above aforementioned mechanisms as well as availability of so much adsorption sites on the adsorbent even in low dosages are two reasons for complete removal of the examined cations in these concentrations. Greater amounts of SPEB did not cause an increase in the removal percentage of metal ions.

### Effect of contact time and kinetic studies

The principal characteristic determining sorption efficiency is the kinetics of bio-sorption, representing the rate of adsorption of the sorbate controlled by the time in the solid–liquid interface (Sassi *et al.* 2010). The influence of contact time on sorption process was assessed by mixing the 20 mg/L solution of metal ions with 0.5 g SPEB at initial pH 7 at different time intervals ranging from 2 min to 2 h. The illustrated results in Fig. 3(c) revealed that the adsorption rates for all examined cations were high and Pb(II), Cu(II) and Cd(II) ions reached equilibrium in 2, 5 and 10 min, respectively. Such rapid adsorptions rates reveal a strong attraction between metal ions and SPEB via chemical binding or electrostatic attraction. Moreover, as mentioned above, these

results might be due to the electronegativity order of Pb(II) (2.33), Cu(II) (1.95) and Cd(II) (1.69). As previously discussed, the most probable mechanism in metal ion adsorption on SPEB, is suspected to be the ion-exchange between Ca(II) and tested metal ions. Thus, the existence of competition between examined metal ions and Ca(II) is reasonable. There is higher rate of exchange when the metal ion is more electronegative (Futalan *et al.* 2011; Park *et al.* 2016). Three kinetic mechanisms, pseudo first-order, pseudo second-order and intra-particle diffusion, were employed to define the kinetic model and rate constants for surface adsorption of mentioned metals on SPEB. These kinetic models are expressed by the following equations, respectively:

$$1/q_t = k_1/q_e t + 1/q_e \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

$$q_t = k_p t^{0.5} \quad (5)$$

where  $q_e$  and  $q_t$  (mg/g) present the sorption capacities in equilibrium and time  $t$  (min), respectively, and  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$ :  $\text{g}/(\text{mg min})$  and  $k_p$ :  $\text{mg}/(\text{g min}^{0.5})$  are the pseudo-first-order, pseudo-second order and intra-particle diffusion rate constants. A plot of  $1/q_t$  versus  $t$  should give a linear relationship;  $k_1$  and  $q_e$  can be calculated from the slope and intercept of the plot [Eq. (3)]. If the pseudo-second order kinetic is applicable, the plot of  $t/q_t$  against  $t$  should give a linear relationship;  $k_2$  and  $q_e$  can be calculated from the slope and intercept of this plot [Eq. (4)]. A good linearity of the plot of  $q_t$  versus  $t^{0.5}$  can show that intra-particle diffusion model might play a significant role in the adsorption kinetic [Eq. (5)]. The best fit model was selected based on the correlation coefficient;  $R^2$  values (Monier & Abdel-Latif 2012; Jiang *et al.* 2013). The results obtained from kinetic study on the removal process are summarised in Table 1. These results indicated that the pseudo second-order model gives better description for the bio-sorption of lead, cadmium and copper onto the SPEB (Supporting Information Figs S1–S3).

### Effect of heavy metals concentrations and adsorption isotherms study

The investigation of equilibrium adsorption isotherms can reveal the interaction between the adsorbate and sorbent. The equilibrium adsorption isotherms of the metal ions was

**Table 1** Kinetic parameters for Pb(II), Cd(II) and Cu(II) adsorption onto SPEB

Metals	Pseudo first-order-model		Pseudo second-order-model		Intra-particle model	
	$K_1$ (mg/g) <sup>a</sup>	$R^2$	$K_2$ (g/mg/min) <sup>b</sup>	$R^2$	$K_p$ (mg/g/ min <sup>0.5</sup> ) <sup>c</sup>	$R^2$
Pb(II)	0.0153	0.5574	6.62	1	0.0009	0.0050
Cd(II)	0.5081	0.8515	1.18	0.9999	0.0316	0.6092
Cu(II)	0.0075	0.8499	3.62	0.9998	0.0025	0.1579

a, b and c are the rate constants of three kinetic models.



**Table 2** Adsorption isotherms parameters for Pb(II), Cd(II) and Cu(II) adsorption onto SPEB

Isotherm model	Parameter	Lead(II)	Cadmium(II)	Copper(II)
Langmuir	$q_{\max}$ (cal) (mg/g) <sup>a</sup>	14.92	38.46	14.92
	$q_{\max}$ (exp) (mg/g)	14.67	32.05	14.71
	$K_L$ <sup>b</sup>	2.32	0.03	10.00
	$R^2$	0.9990	0.6481	0.9923
	$R_L$ <sup>c</sup>	0.02	0.87	0.04
Freundlich	$K_F$ <sup>d</sup>	3.68	1.34	2.49
	$n$ <sup>e</sup>	3.04	1.49	2.92
	$R^2$	0.7575	0.9933	0.9738

<sup>a</sup>The maximum adsorption capacity of SPEB.<sup>b</sup>The Langmuir constant.<sup>c</sup>The separation factor ( $0 < R_L < 1$  is suitable).<sup>d</sup>The Freundlich constant.<sup>e</sup>The intensity of adsorption ( $1 < n < 3$ ).

investigated with the initial concentrations of cations being varying from 1 to 400 mg/L under optimum conditions for each metal ion as described above. As shown in Fig. 3(d), all the tested ions were removed quantitatively by SPEB up to 20 mg/L. To describe equilibrium adsorption data in this study, the widely used Langmuir and Freundlich isotherm models were employed (Kołodźńska 2012; Monier & Abdel-Latif 2012; Park *et al.* 2016).

The Langmuir isotherm assumes that all adsorption sites on adsorbent are homogeneous and energetically identical, and a monolayer of adsorbate is formed on the surface of adsorbent. However, the Freundlich isotherm describes the metal adsorption in a heterogeneous system and is not restricted to the monolayer formation (Rahbar *et al.* 2014). The linear graphs of the Langmuir and Freundlich isotherms were plotted for each ion and the parameters of adsorption isotherms are shown in Table 2 (Supporting Information Figs S4 and S5). The results revealed that the Langmuir equation best fitted the equilibrium data of Pb(II) and Cu(II) ions and the calculated maximum adsorption capacities ( $q_{\max}$ ) were nearly consistent to their experimental  $q_{\max}$ . Suitable correlation coefficients ( $\geq 0.992$ ) for Pb(II) and Cu(II) ions showed the applicability of the Langmuir model for these ions.

The  $K_F$  and  $n$  values ( $1 < n < 3$ ) given in Table 2 as well as suitable correlation coefficient (0.9933) indicated the ability of SPEB to retain Cd(II) ion on multilayers at high concentrations and therefore, the adsorption process of this ion can be explained by the Freundlich model. As shown in Fig. 3(d), the removal percentage of Cd(II) ion from 400 mg/L solution of this cation was 79%, whereas Pb(II) and Cu(II) ions could be removed 40 and 37%, respectively. Also, according to the results shown in Table 2, for mono-metal sample solutions, the large value of experimental  $q_{\max}$  for Cd(II) ions in comparison to the other tested ions, suggests the multilayer adsorption mechanism of this cation onto SPEB. Based on

these results, it can be concluded that the retention sequence of Pb(II) > Cu(II) > Cd(II) is valid in low and moderate concentrations of metal ions (up to nearly 50 mg/L) and also in monolayer coverage of SPEB surface. However, in high concentrations, Cd(II) ions show better adsorption efficiencies than other tested ions due to its possible multi-layer adsorption.

### Simultaneous removal and selectivity sequences

About 0.50 g of adsorbent was suspended in 50 mL of mixture each containing Pb(II), Cd(II) and Cu(II) with a range of concentration of 2–50 mg/L at pH 7 and contact time of 10 min. The results showed that SPEB was capable of simultaneously removing the target metal ions in model solutions (Table 3 and Supporting Information Fig. S6). Based on the results, no strong competitions were seen between the metal cations in low concentration (2 mg/L) and almost complete removal for tested cations were achieved because of availability of so much adsorption sites on SPEB. However, in higher concentrations ( $\geq 20$  mg/L), Pb(II) ion presented the highest removal efficiency showing it was the most retained cation by SPEB and competition between ions affected adsorption process. Distribution coefficient ( $K_d$ ) is referent to potential mobility of heavy metals which is extensively used to compare the intensity of adsorption of heavy metal ions on a particular adsorbent and is calculated by the following equation (Park *et al.* 2016):

$$K_d = C_{EA}/C_{ES}$$

where  $C_{EA}$  (mg/kg) is the equilibrium concentration of adsorbed metal and  $C_{ES}$  (mg/L) is the equilibrium concentration of metal ion in solution. This index has been used to compare the retention ability of particular sorbent toward various heavy metal cations for both mono-metal and multi-metal adsorption processes. In concentrations below 50 mg/L, the removal efficiency for mono-metal solutions were high (99–96%) and the examined cations were almost thoroughly adsorbed onto SPEB. Therefore, the  $K_d$  values at 50 mg/L of each cation was employed to obtain the comparable distribution coefficients for both mono-metal and multi-metal

**Table 3** Simultaneous removal of Pb(II), Cd(II) and Cu(II) from model solutions

Ion concentration (mg/L)	Removal (%)		
	Lead(II)	Cadmium(II)	Copper(II)
2	99.6 ± 1.2	99.2 ± 1.3	100.0 ± 1.1
20	98.3 ± 1.7	76.5 ± 1.2	94.1 ± 2.2
50	90.8 ± 1.3	71.4 ± 1.9	87.7 ± 1.8

 $\bar{x} \pm s$  ( $n = 3$ ).

**Table 4** Simultaneous removal of Pb, Cd and Cu ions from real water samples

Sample	Added metal ions (mg/L)	Removal (%)		
		Lead (II)	Cadmium (II)	Copper (II)
Karoun River water	0	–	–	–
	2	99.3 ± 1.5	81.5 ± 1.3	100.3 ± 1.7
	10	97.9 ± 1.6	82.3 ± 2.5	99.4 ± 1.9
Tap water	0	–	–	–
	2	100.2 ± 1.2	81.7 ± 1.6	100.1 ± 1.3
	10	99.2 ± 1.7	80.1 ± 1.8	98.8 ± 2.4
Bottled mineral water	0	–	–	–
	2	98.1 ± 2.4	94.8 ± 1.7	100.0 ± 1.2
	10	99.2 ± 1.8	91.2 ± 1.2	100.5 ± 1.6

 $\bar{x} \pm s$  ( $n = 3$ ).

experiments. The order of  $K_d$  values (L/kg) for the mono-metal heavy metal solutions was as follows: Pb(II) (3233) > Cu(II) (1150) > Cd(II) (613). The highest  $K_d$  value for Pb(II) showed that it was better retained than Cu(II) followed by Cd(II). In higher concentrations,  $K_d$  values were rapidly decreased for Pb(II) and Cu(II) whereas this value for Cd(II) was relatively remained high. This phenomenon can be explained in the context of adsorption isotherms and was discussed previously. For the multi-metal solutions these coefficients were in the order of: Pb(II) (986) > Cu(II) (713) > Cd(II) (249). As seen, the same selectivity sequence as mono-metal adsorption was seen for multi-metal experiments. The preference of SPEB for Pb(II) compared to the other cations in the multi-metal adsorption process can be interpreted in the context of its characteristics and the resultant affinity for sorption sites. This selectivity sequence of heavy metal adsorption for SPEB can be explained by order of electronegativity, first hydrolysis constant [ $pK_1$ : Pb(II) (7.71), Cu(II) (7.9) and Cd(II) (10.1)] and hydrated radius [Pb(II) (4.01 Å), Cu(II) (4.19 Å) and Cd(II) (4.26 Å)] for tested cations (Bryantsev *et al.* 2009; Arshadi *et al.* 2014; Park *et al.* 2016). On the other hand, this preference order of adsorbent can be attributed to differences in  $pK_{sp}$  values between the tested cations for the formation of insoluble carbonate salts. Although, according to this theory, after Pb(II) with highest  $pK_{sp}$  value, preferential retention of Cd(II) against Cu(II) is expected, Cu(II) showed better retention on SPEB than Cd(II) in both mono-metal and multi-metal adsorption. This observed phenomenon suggests that the aforementioned factors (electronegativity, hydrolysis constant and hydrated radius) are predominant factors that predict preferential retention of heavy metal cations on various adsorbents. The results obtained from competitive adsorption of heavy metal ion in this study are in agreement with previously observations regarding the tested cations' retentions follow the order of Pb(II) > Cu(II) > Cd(II) (Uchimiya *et al.* 2010; Xue *et al.* 2012).

### Application to real samples

Due to the accurate estimation of multi-metal adsorption behaviour of the tested cations using SPEB natural environments, the proposed separation method was applied to the removal of lead, copper and cadmium ions in various water samples: (1) River Karoun (Ahvaz, Iran), (2) tap water (Ahvaz, Iran) and (3) bottled mineral water. The real waters spiked with 2.0 and 10.0 mg/L of each of the target metals were employed to further evaluate the effects of real matrices on the removal efficiency of heavy metals under optimised conditions. The results are presented in Table 4. The removal percentages of the target heavy metals were calculated, and the results showed that their removal was not severely affected by the presence of excess amounts of Ca(II), Mg(II) and other common ions in real waters.

### Conclusion

- (1) The present study proves the capability and effectiveness of SPEB adsorbent for removing heavy metals from various water samples.
- (2) This adsorbent possesses some advantages such as high metal adsorption, low cost, safety and environment compatibility.
- (3) In addition, it is notable that the adsorption process is fast in comparison to some other reports and reaches equilibrium at 2, 5 and 10 min for Pb(II), Cu(II) and Cd(II), respectively (Singh *et al.* 2006; Sassi *et al.* 2010; Liu *et al.* 2013; Ammari 2014).
- (4) It was found that sorption isotherms were better described by the Freundlich model for Cd(II) ion and by the Langmuir model for Pb(II) and Cu(II) ions.
- (5) Metal adsorption by SPEB showed an increase in the sequence of Pb(II) > Cu(II) > Cd(II) in moderate concentrations (20 mg/L < metal concentration < 200 mg/mL), in both multimetal or monometal solutions.

(6) The high metal uptake of SPEB can be likely related to various mechanisms such as ion-exchange [between Ca(II) and metal ion in solution], complexation via groups in the chitinous constituent having coordination power and micro-precipitation as metal-hydroxide in higher pHs.

(7) The adsorption results using SPEB open an important area for future applications of this adsorbent for removing heavy metals from waste waters.

(8) Moreover, these findings might be beneficial for therapeutic utilisation in the cases of acute exposure to these poisons.

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## References

- Abdolali, A., Ngo, H.H., Guo, W., Lu, S., Chen, S.-S., Nguyen, N.C., Zhang, X., Wang, J. and Wu, Y. (2016) A Breakthrough Biosorbent in Removing Heavy Metals: Equilibrium, Kinetic, Thermodynamic and Mechanism Analyses in a Lab-Scale Study. *Sci. Total Environ.*, **542**, 603–611.
- Afkhami, A., Saber-Tehrani, M. and Bagheri, H. (2010) Simultaneous Removal of Heavy-Metal Ions in Wastewater Samples Using Nano-alumina Modified with 2,4-Dinitrophenylhydrazine. *J. Hazard. Mater.*, **181**, 836–844.
- Ammari, T.G. (2014) Utilization of a Natural Ecosystem Bio-waste; Leaves of *Arundo donax* Reed, as a Raw Material of Low-Cost Eco-biosorbent for Cadmium Removal from Aqueous Phase. *Ecol. Eng.*, **71**, 466–473.
- Arshadi, M., Amiri, M.J. and Mousavi, S. (2014) Kinetic, Equilibrium and Thermodynamic Investigations of Ni(II), Cd(II), Cu(II) and Co(II) Adsorption on Barley Straw Ash. *Water Resour. Ind.*, **6**, 1–17.
- Ben Nasr, A., Walha, K., Charcosset, C. and Ben Amar, R. (2011) Removal of Fluoride Ions Using Cuttlefish Bones. *J. Fluorine Chem.*, **132**, 57–62.
- Bennani, C.F. and M'hiri, O. (2015) Comparative Study of the Removal of Heavy Metals by Two Nanofiltration Membranes. *Desalin. Water Treat.*, **53**, 1024–1030.
- Bryantsev, V.S., Diallo, M.S. and Goddard, W.S. (2009) Computational Study of Copper(II) Complexation and Hydrolysis in Aqueous Solutions Using Mixed Cluster/Continuum Models. *J. Phys. Chem. A*, **113**, 9559–9567.
- Dąbrowski, A., Hubicki, Z., Podkościelny, P. and Robens, E. (2004) Selective Removal of the Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method. *Chemosphere*, **56**, 91–106.
- Dhir, B. (2014) Potential of Biological Materials for Removing Heavy Metals from Wastewater. *Environ. Sci. Pollut. Res.*, **21**, 1614–1627.
- Du, Z., Zheng, T., Wang, P., Hao, L. and Wang, Y. (2016) Fast Microwave-Assisted Preparation of a Low-Cost and Recyclable Carboxyl Modified Lignocellulose-Biomass Jute Fiber for Enhanced Heavy Metal Removal from Water. *Bioresour. Technol.*, **201**, 41–49.
- Feizi, M. and Jalali, M. (2015) Removal of Heavy Metals from Aqueous Solutions Using Sunflower, Potato, Canola and Walnut Shell Residues. *J. Taiwan Inst. Chem. Eng.*, **54**, 125–136.
- Futalan, C.M., Kan, C.-C., Dalida, M.L., Hsien, K.-J., Pascua, C. and Wan, M.-W. (2011) Comparative and Competitive Adsorption of Copper, Lead, and Nickel Using Chitosan Immobilized on Bentonite. *Carbohydr. Polym.*, **83**, 528–536.
- Hodgson, E., Lewys-James, A., Rao Ravella, S., Thomas-Jones, S., Perkins, W. and Gallagher, J. (2016) Optimisation of Slow-Pyrolysis Process Conditions to Maximise Char Yield and Heavy Metal Adsorption of Biochar Produced from Different Feedstocks. *Bioresour. Technol.*, **214**, 574–581.
- Hossain, M.A., Ngo, H.H., Guo, W.S., Nguyen, T.V. and Vigneswaran, S. (2014) Performance of Cabbage and Cauliflower Wastes for Heavy Metals Removal. *Desalin. Water Treat.*, **52**, 844–860.
- Islam, M.S., Choi, W.S., Nam, B., Yoon, C. and Lee, H.-J. (2017) Needle-like Iron Oxide@CaCO<sub>3</sub> Adsorbents for Ultrafast Removal of Anionic and Cationic Heavy Metal Ions. *Chem. Eng. J.*, **307**, 208–219.
- Jiang, H., Chen, P., Luo, S., Tu, X., Cao, Q. and Shu, M. (2013) Synthesis of Novel Nanocomposite Fe<sub>3</sub>O<sub>4</sub>/ZrO<sub>2</sub>/Chitosan and Its Application for Removal of Nitrate and Phosphate. *Appl. Surf. Sci.*, **284**, 942–949.
- Khoramzadeh, E., Nasernejad, B. and Halladj, R. (2013) Mercury Biosorption from Aqueous Solutions by Sugarcane Bagasse. *J. Taiwan Inst. Chem. Eng.*, **44**, 266–269.
- Kolodyńska, D. (2012) Adsorption Characteristics of Chitosan Modified by Chelating Agents of a New Generation. *Chem. Eng. J.*, **179**, 33–43.
- Kordialik-Bogacka, E. and Diowksz, A. (2014) Metal Uptake Capacity of Modified *Saccharomyces pastorianus* Biomass from Different Types of Solution. *Environ. Sci. Pollut. Res.*, **21**, 2223–2229.
- Li, Y.-Z., Pan, H., Xu, J., Fan, X.-W., Song, X.-C., Zhang, Q., Xu, J. and Liu, Y. (2010) Characterization of Metal Removal by os Sepiae of *Sepiella maindroni* Rochebrune from Aqueous Solutions. *J. Hazard. Mater.*, **179**, 266–275.
- Liu, C., Ngo, H.H., Guo, W. and Tung, K.L. (2012) Optimal Conditions for Preparation of Banana Peels, Sugarcane Bagasse and Watermelon Rind in Removing Copper from Water. *Bioresour. Technol.*, **119**, 349–354.
- Liu, L., Wu, J., Li, X. and Ling, Y. (2013) Synthesis of poly(dimethyldiallylammonium chloride-co-acrylamide)-graft-triethylenetetramine-dithiocarbamate and its removal performance and mechanism of action towards heavy metal ions. *Sep. Purif. Technol.*, **103**, 92–100.

- Monier, M. and Abdel-Latif, D.A. (2012) Preparation of Cross-Linked Magnetic Chitosan-Phenylthiourea Resin for Adsorption of Hg(II), Cd(II) and Zn(II) Ions from Aqueous Solutions. *J. Hazard. Mater.*, **209–210**, 240–249.
- Mostoufi, A. (2016) New Applications of Cuttlebone (CB) as a Natural Marine Compound. *Jundishapur J. Nat. Pharm. Prod.*, **11**, e41762.
- Mukherjee, R., Bhunia, P. and De, S. (2016) Impact of Graphene Oxide on Removal of Heavy Metals Using Mixed Matrix Membrane. *Chem. Eng. J.*, **292**, 284–297.
- Park, J.-H., Ok, Y.S., Kim, S.-H., Cho, J.-S., Heo, J.-S., Delaune, R.D. and Seo, D.-C. (2016) Competitive Adsorption of Heavy Metals onto Sesame Straw Biochar in Aqueous Solutions. *Chemosphere*, **142**, 77–83.
- Phetphaisit, C.W., Yuanyang, S. and Chaithasith, W.C. (2016) Polyacrylamido-2-methyl-1-Propane Sulfonic Acid-Grafted-Natural Rubber as Bio-adsorbent for Heavy Metal Removal from Aqueous Standard Solution and Industrial Wastewater. *J. Hazard. Mater.*, **301**, 163–171.
- Rahbar, N., Jahangiri, A., Boumi, S. and Khodayar, M.J. (2014) Mercury Removal From Aqueous Solutions With Chitosan-Coated Magnetite Nanoparticles Optimized Using the Box-Behnken Design. *Jundishapur. J Nat. Pharm. Prod.*, **9**, e15913.
- Sahraei, R. and Ghaemy, M. (2017) Synthesis of Modified Gum Tragacanth/Graphene Oxide Composite Hydrogel for Heavy Metal Ions Removal and Preparation of Silver Nanocomposite for Antibacterial Activity. *Carbohydr. Polym.*, **157**, 823–833.
- Sassi, M., Bestani, B., Said, A.H., Benderdouche, N. and Guibal, E. (2010) Removal of Heavy Metal Ions from Aqueous Solutions by a Local Dairy Sludge as a Biosorbent. *Desalination*, **262**, 243–250.
- Shushizadeh, M.R., Moghimi Pour, E., Zare, A. and Lashkari, Z. (2015) Persian Gulf  $\beta$ -Chitin Extraction from *Sepia pharaonis* sp. Cuttlebone and Preparation of Its Derivatives. *Bioact. Carbohydr. Diet. Fib.*, **6**, 133–142.
- Singh, K.K., Singh, A.K. and Hasan, S.H. (2006) Low Cost Bio-Sorbent Wheat Bran for the Removal of Cadmium from Wastewater: Kinetic and Equilibrium Studies. *Bioresour. Technol.*, **97**, 994–1001.
- Sobhanardakani, S., Parvizmosaedi, H. and Olyaei, E. (2013) Heavy Metals Removal from Wastewaters Using Organic Solid Waste-Rice Husk. *Environ. Sci. Pollut. Res.*, **20**, 5265–5271.
- Tang, X., Zheng, H., Teng, H., Sun, Y., Guo, J., Xie, W., Yang, Q. and Chen, W. (2016) Chemical Coagulation Process for the Removal of Heavy Metals from Water: A Review. *Desalin. Water Treat.*, **57**, 1733–1748.
- Uchimiya, M., Lima, I.M., Thomas Klasson, K., Chang, S., Wartelle, L.H. and Rodgers, J.E. (2010) Immobilization of Heavy Metal Ions (CuII, CdII, NiII, and PbII) by Broiler Litter-Derived Biochars in Water and Soil. *J. Agric. Food Chem.*, **58**, 5538–5544.
- Uddin, M.K. (2017) A Review on the Adsorption of Heavy Metals by Clay Minerals, with Special Focus on the Past Decade. *Chem. Eng. J.*, **308**, 438–462.
- Varma, A.J., Deshpande, S.V. and Kennedy, J.F. (2004) Metal Complexation by Chitosan and Its Derivatives: A Review. *Carbohydr. Polym.*, **55**, 77–93.
- Visa, M. and Chelaru, A.-M. (2014) Hydrothermally Modified Fly Ash for Heavy Metals and Dyes Removal in Advanced Wastewater Treatment. *Appl. Surf. Sci.*, **303**, 14–22.
- Wahab, M.A., Jellali, S. and Jedidi, N. (2010) Ammonium Biosorption onto Sawdust: FTIR Analysis, Kinetics and Adsorption Isotherms Modeling. *Bioresour. Technol.*, **101**, 5070–5075.
- Wang, J., Luo, C., Qi, G., Pan, K. and Cao, B. (2014) Mechanism Study of Selective Heavy Metal Ion Removal with Polypyrrole Functionalized Polyacrylonitrile Nanofiber Mats. *Appl. Surf. Sci.*, **316**, 245–250.
- Wen, Z., Zhang, Y., Guo, S. and Chen, R. (2017) Facile Template-Free Fabrication of Iron Manganese Bimetal Oxides Nanospheres with Excellent Capability for Heavy Metals Removal. *J. Colloid Interf. Sci.*, **486**, 211–218.
- Witek-Krowiak, A., Szafran, R.G. and Modelski, S. (2011) Biosorption of Heavy Metals from Aqueous Solutions onto Peanut Shell as a Low-Cost Biosorbent. *Desalination*, **265**, 126–134.
- Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H. and Gao, B. (2013) Removal of Cu, Zn, and Cd from Aqueous Solutions by the Dairy Manure-Derived Biochar. *Environ. Sci. Pollut. Res. Int.*, **20**, 358–368.
- Xue, Y., Gao, B., Yao, Y., Inyang, M., Zhang, M., Zimmerman, A.R. and Ro, K.S. (2012) Hydrogen Peroxide Modification Enhances the Ability of Biochar (Hydrochar) Produced from Hydrothermal Carbonization of Peanut Hull to Remove Aqueous Heavy Metals: Batch and Column Tests. *Chem. Eng. J.*, **200–202**, 673–680.
- Yilmaz, G. (2012) Structural Characterization of Glass–Ceramics Made from Fly Ash Containing SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–CaO and Analysis by FT-IR–XRD–SEM Methods. *J. Mol. Struct.*, **1019**, 37–42.
- Yuan, J.-J., Dong, W.-Y., Sun, F.-Y., Zhao, K. and Li, P. (2016) Enhanced Heavy Metal Removal by Wetland Vegetations and Its Significance for Vegetation-Activated Sludge Process Configuration. *Desalin. Water Treat.*, **57**, 25153–25160.
- Zhu, Z., Gao, C., Wu, Y., Sun, L., Huang, X., Ran, W. and Shen, Q. (2013) Removal of Heavy Metals from Aqueous Solution by Lipopeptides and Lipopeptides Modified Na-Montmorillonite. *Bioresour. Technol.*, **147**, 378–386.

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