Self-purification of marine environments for heavy metals: a study on removal of lead(II) and copper(II) by cuttlebone

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ABSTRACT

The aim of this study was to determine adsorption properties of cuttlebone, cuttlefish bone as dead biomass, for lead(II) and copper(II) from aqueous solutions. Adsorption kinetic, isotherm and effect of pH (in the range of 2.0–7.0) were investigated in a single component batch system at room temperature (25 ± 1 °C). The heavy metal adsorption by cuttlebone was relatively rapid and reached to equilibrium in 120 min in all the cases. The pseudo-second order rate equation described the adsorption kinetic of both the ions. The adsorption capacities of Pb^{2+} and Cu^{2+} were constantly increased by pH and the optimum condition of pH was determined to be 7.0. The Freundlich model was better fitted than other models with the isotherm data indicating sorption of the metal ions in a heterogeneous surface. According to the Langmuir model, the maximum adsorption capacities (q_m) of cuttlebone for Pb^{2+} and Cu^{2+} were determined to be 45.9 and 39.9 mg/g, respectively. The results indicated cuttlebone as a promising adsorbent for Pb^{2+} and Cu^{2+} that presents a high capacity of self-purification in marine environments as well as can be used for removal of the metal ions from water and wastewater.

Key words | adsorption, cuttlebone, heavy metals, isotherm, kinetic

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INTRODUCTION

Environmental pollution tends to be a serious problem which possesses human health risks and harmful effects to abiotic and biotic factors. Heavy metals as one of the main pollutant groups of marine and freshwater environments have become a public health and environment concern because of their toxic effects, accumulation through the food chain and non-biodegradable and indelible nature (Nabizadeh *et al.* 2005b; Naddafi *et al.* 2007; Naddafi & Saeedi 2009; Abtahi *et al.* 2015; El-Sayed *et al.* 2016).

Among the heavy metals, special favour has been given to lead (Pb^{2+}) and copper (Cu^{2+}). Pb^{2+} can be found in effluents from lead mining, battery manufacturing and recycling

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plants, electronic assembly plants, etc. and it can damage the nervous system, gastrointestinal track, kidney and reproductive system particularly in children. Although Cu^{2+} is known to be an essential trace element in humans, excess intake of the ion can cause adverse gastrointestinal responses and liver toxicity. Based on the health effects, WHO has set the guideline values for lead and copper in drinking water to be 2 and 0.01 mg/L, respectively (Naddafi & Saeedi 2009; WHO 2011; Yu *et al.* 2013; Mungondori *et al.* 2016).

In the past decades, various technologies such as ion-exchange, precipitation, reverse osmosis, coprecipitation, electrochemical treatment and adsorption have been widely used for the removal of heavy metals form aqueous solutions (Nabizadeh *et al.* 2005a; Boldaji *et al.* 2009; Fu & Wang 2011; Chen *et al.* 2013). Among these methods, adsorption is one of the most recommended physicochemical treatment processes due to its some merits like high efficiency, simple operation, fast response, cheapness and environmental favorable. Up to now, various materials like algae, bacteria, zeolite, clay minerals, polymeric materials, iron oxide nanomaterials, activated carbons, etc. have been used as adsorbents. Research on removal of heavy metals by dead biomass of organisms is useful from two perspectives: estimating self-purification capacity of natural environments and obtaining a feasible method to remove heavy metals from water and wastewater (Mi *et al.* 2012; Xu *et al.* 2012; Shams *et al.* 2013; Dobaradaran *et al.* 2014, 2015; Fang *et al.* 2014; Zazouli *et al.* 2014; Langeroodi & Safaei 2016).

Cuttlebone or cuttlefish bone is an internal shell found in all members of the family cuttlefish. There are huge quantity of cuttlebone in marine environments and beaches. Cuttlebone can be collected form beaches as an inexpensive and easily available material. To the best of our knowledge, this material has not been used before for adsorption of heavy metals. The objective of this study was to estimate self-purification capacity of marine environments for Pb^{2+} and Cu^{2+} by cuttlebone as well as to determine feasibility of cuttlebone application for removal of heavy metals form water and wastewater. Kinetic and isotherm experiments were performed and the effect of pH on adsorption of Pb^{2+} and Cu^{2+} by cuttlebone was studied in a single component batch system.

MATERIAL AND METHODS

Adsorbent preparation

The cuttlebone was collected along the Persian Gulf in the Bushehr seaport coastal area (Figure 1). The biosorbent was transferred to laboratory and thoroughly washed two times by tap water and then by de-ionized water in order to remove clay, sand, and other impurities. The washed cuttlebone was subsequently dried in an oven (Memmert, Germany) at 105 °C for 24 h and finally ground and sieved to select particles between 0.3 and 0.7 mm.

Characterization of adsorbent

The surface functional groups of cuttlebone were recorded by Fourier transform infrared spectroscopy (FTIR) spectrometer (Model Spectrum RXI, Perkin Elmer FTIR) over the wave number range from 4,000 to 400 cm^{-1}.

Solution preparation

All the chemicals used in the experiments were made of analytical reagent grade. Pb^{2+} and Cu^{2+} synthetic solutions were composed by dissolving the appropriate amounts of lead nitrate ($Pb(NO_3)_2$) and copper nitrate pentahydrate

Figure 1 | Images of cuttlefish (a) and cuttlebone (b).

($Cu(NO_3)_2.5H_2O$) in de-ionized water. Initial pH of solutions was measured using a pH meter (Model 827, Metrohm) and modified to favorite values by using 0.1–1.0 M HCl and/or 0.1–1.0 M NaOH.

Adsorption experiments

All the adsorption experiments were conducted in a single component batch reactor on a rotary shaker in 120 rpm at room temperature (25 ± 1 °C). Initial pH of solution was adjusted to 5.0 in kinetic and isotherm experiments. Kinetic experiments were carried out in three initial concentrations of metal ion to be 10, 20 and 50 mg/L. The experiments were continued for 4 h and samples were taken from the experiment vessels at predesignated time intervals (3, 10, 20, 40, 60, 120, 180 and 240 min) for analysis. Adsorption isotherm was studied in equilibrium contact time obtained from kinetic tests to be 2 h and initial ion concentration of 50 mg/L. Isotherm experiments were conducted by variation of adsorbent dose in the extent of 0.1 to 1.0 g/L and constant initial ion concentration of 50 mg/L. Due to interference of the metal ions precipitation in pH values higher than 7.0, effect of pH on equilibrium capacity of heavy metal adsorption by cuttlebone was studied in initial pH range of 2.0 to 7.0.

Analytical methods

The metal ions were measured using an atomic absorption spectrophotometer (AA200, Perkin Elmer) according to the instruction of Standard Methods (APHA AWWA and WEF 2005). To control analytical quality, blank solutions of Pb^{2+} and Cu^{2+} were examined between samples and reagent solutions were analyzed sporadically.

Calculation

The adsorption capacity was calculated using Equation (1):

$$q = \frac{(C_i - C)V}{m} \tag{1}$$

where C_i and C (mg/L) are initial and final concentrations of metal ion, respectively, q (mg/g) is the adsorption capacity, V (L) is the solution volume and m (g) is the adsorbent dosage.

The adsorption kinetic was analyzed by the pseudo-first-order, pseudo-second-order, Elovich and Intraparticle diffusion models presented below as Equations (2)–(5), respectively (Abtahi *et al.* 2013; Dehghani *et al.* 2015; Naddafi *et al.* 2016):

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \tag{2}$$

$$\frac{1}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q_t = \beta \ln(\alpha) + \beta \ln(t) \tag{4}$$

$$q_t = k_{id} t^{0.5} + a \tag{5}$$

where q_e and q_t (mg/g) are adsorption capacities at equilibrium and any time, respectively, k_1 (1/min) is the pseudo-first-order rate constant, t (min) is the contact time, k_2 (g/mg min) is the pseudo-second-order rate constant, α (mg/g min) and β (g/mg) are the rate constants of the Elovich model, where k_{id} (mg/g min$^{0.5}$) is the rate constant of intraparticle diffusion and a (mg/g) is a measure of the boundary layer thickness. If the plot of q_t versus $t^{0.5}$ forms a straight line that passes through the origin, the intraparticle diffusion will be the rate limiting step. Otherwise, the rate of the adsorption process is controlled by the other sorption steps.

To characterize the adsorption isotherms of Pb^{2+} and Cu^{2+} by cuttlebone, four common isotherm models including Freundlich, Langmuir, Redlich–Peterson and Temkin models were used that their linear forms are presented below as Equations (6)–(9), respectively (Naddafi & Saeedi 2009; Yu *et al.* 2013; Dehghani *et al.* 2015):

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \tag{6}$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{7}$$

$$\ln\left(\frac{K_{RP}C_e}{q_e} - 1\right) = \ln(a_{RP}) + \gamma \ln(C_e) \tag{8}$$

$$q_e = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(C_e) \tag{9}$$

where K_F and n are the Freundlich model constants indicating adsorption capacity and intensity, respectively, C_e (mg/L) is the equilibrium concentration; q_m (mg/g) is the maximum adsorption capacity; b (L/mg) is the Langmuir constant as a function of the adsorption energy, K_{RP} (L/g), a_{RP} ((L/mg)$^{\gamma}$)

and γ (dimensionless) are the Redlich–Peterson constants, R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute temperature, b_T (J/mol) is the Temkin constant of adsorption heat and A_T (L/g) is the Temkin binding constant.

RESULTS AND DISCUSSION

Characterization of adsorbent

The FTIR spectra of cuttlebone before and after adsorption of Pb^{2+} and Cu^{2+} are shown in Figure 2. Based on Figure 2, a broad and strong absorption band observed at 3,426.13 cm^{-1} corresponds to the hydroxyl stretching. The presence of band at wave numbers 2,924.14 cm^{-1} is due to alkyl groups. The strong band at 2,520.55 cm^{-1} is the characteristic of NH. The absorption bands at 1,474.23 cm^{-1} represent the pyranose ring bending. The prominent bands at 1,082.51, 854.25 and 712.98 cm^{-1} can be attributed to stretching vibrations of CO, CH and CH_2, respectively. There were significant changes on FTIR spectra of cuttlebone following adsorption of Pb^{2+} and Cu^{2+}. Furthermore, new absorption bands were observed at wave numbers 2,522.53 and 2,523.15 cm^{-1} after interaction with Pb^{2+} and Cu^{2+}, respectively. These bands are relevant to NH bending vibration of amine group.

Kinetic study

Kinetic profiles of Pb^{2+} and Cu^{2+} adsorption by cuttlebone and fitness of the data to the pseudo-second-order kinetic model are presented in Figure 3 and Table 1. As can be seen in Figure 3, the adsorption of Pb^{2+} and Cu^{2+} was relatively fast, so that the process proceeded over 95% in 60 min and reached to equilibrium in 120 min in all the cases. This rapid kinetic counts as an advantage for the process, because it will reduce required contact time and reactor volume and will increase cost efficiency (Azizian 2004; Nabizadeh et al. 2005b).

According to Figure 3 and Table 1, the pseudo-second-order rate model best described the kinetic data ($R^2 > 0.99$). The experimental data were also well fitted to the Elovich equation ($R^2 > 0.90$). The consistency of kinetic of Pb^{2+} and Cu^{2+} adsorption by cuttlebone with the pseudo-second-order model indicated that the adsorption limiting step might be surface complexation reactions at surface adsorption sites (Behnamfard & Salarirad 2009; Zhao et al. 2011; Asgari et al. 2012). The pseudo-second-order rate constants of Pb^{2+} and Cu^{2+} adsorption by cuttlebone were in the range of 0.004–0.023 g/mg min which was promising in comparison with those of other adsorbents (Abtahi et al. 2013; Dehghani et al. 2015). Also, kinetic data of Pb^{2+} and Cu^{2+} adsorption by cuttlebone were observed to be very similar in terms of profile shape, equilibrium time, equilibrium capacity, the best fitted model and kinetic constants.

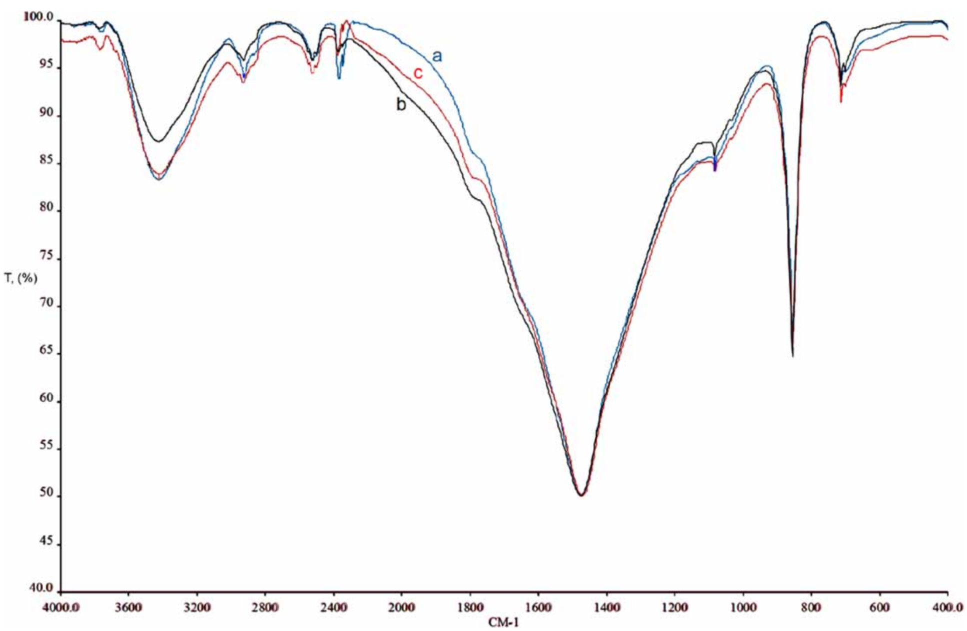

Figure 2 | FTIR spectra of cuttlebone before (a) and after adsorption of Pb^{2+} (b) and Cu^{2+} (c).

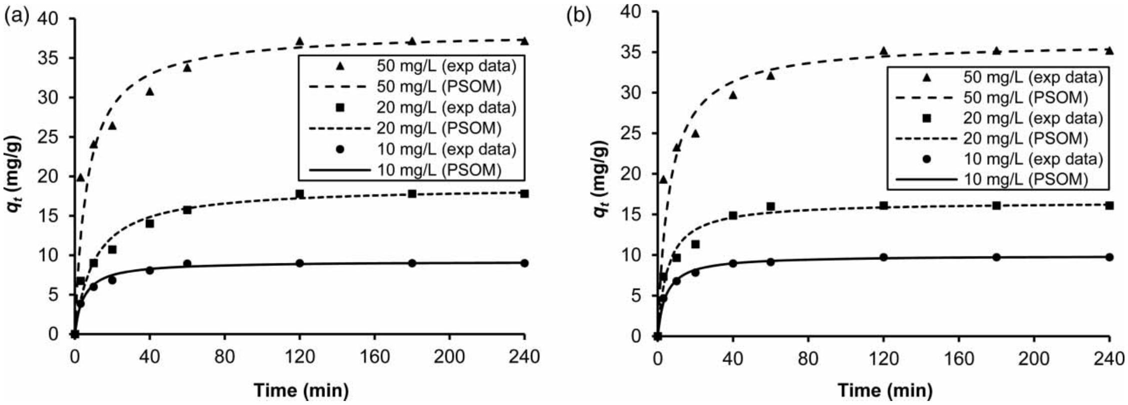

Figure 3 | Kinetic profiles of Pb^{2+} and Cu^{2+} adsorption by cuttlebone and their consistency with the pseudo-second-order rate equation as the best fitted model: (a) Pb^{2+} and (b) Cu^{2+} (exp data: experimental data; PSOM: pseudo-second-order model; adsorbent dose: 0.1 g/L; initial pH value: 5.0).

Table 1 | Kinetic parameters of Pb^{2+} and Cu^{2+} adsorption by cuttlebone

		Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intraparticle diffusion model		
Metal ion	**C_0 (mg/L)**	**q_e**	**k_1**	**R^2**	**q_e**	**k_2**	**R^2**	**α**	**β**	**R^2**	**k_{id}**	**a**	**R^2**
Pb^{2+}	50	9.0	0.034	0.827	9.2	0.023	1.000	13.8	1.2	0.916	0.48	3.4	0.675
	20	17.9	0.024	0.876	18.7	0.005	0.999	3.0	2.8	0.966	1.04	4.9	0.821
	10	37.2	0.031	0.875	38.3	0.004	0.999	28.2	4.4	0.973	1.90	14.0	0.712
Cu^{2+}	50	9.8	0.021	0.836	9.9	0.023	1.000	32.3	1.2	0.929	0.49	3.9	0.648
	20	16.2	0.022	0.745	16.6	0.011	0.999	10.8	2.2	0.907	0.87	5.8	0.696
	10	35.3	0.026	0.872	36.3	0.004	0.999	36.4	4.0	0.969	1.78	13.6	0.699

Isotherm study

Figure 4 shows the isotherm profiles of Pb^{2+} and Cu^{2+} adsorption by cuttlebone and their fitness with the isotherm models. Isotherm parameters of Pb^{2+} and Cu^{2+} adsorption onto cuttlebone are given in Table 2. As observed in Figure 4 and Table 2, the isotherm data of both the metal ions were fitted with the Freundlich model better than the other models ($R^2 > 0.97$) indicating surface adsorption sites of cuttlebone were heterogeneous. The Redlich–Peterson model

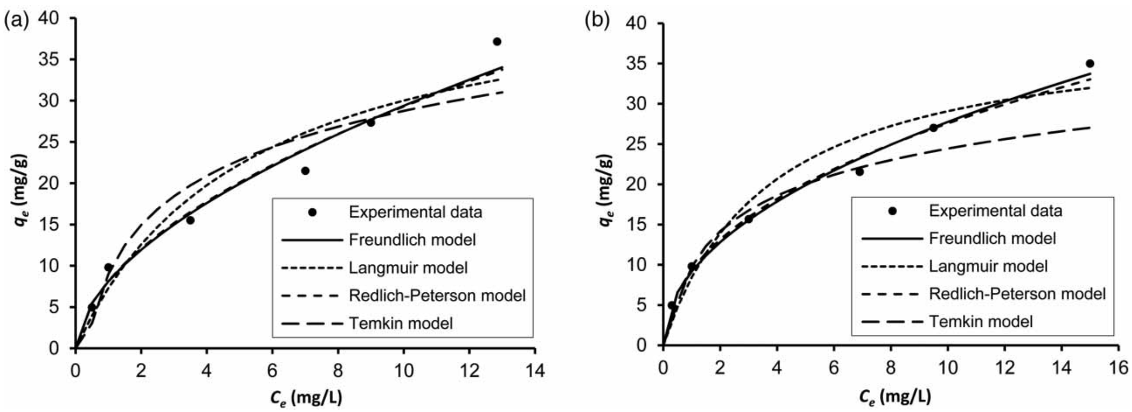

Figure 4 | Isotherm profiles of Pb^{2+} and Cu^{2+} adsorption by cuttlebone and their fitness with the isotherm models: (a) Pb^{2+} and (b) Cu^{2+} (initial metal concentration: 50 mg/L; initial pH value: 5.0).

Table 2 | Isotherm parameters of Pb^{2+} and Cu^{2+} adsorption by cuttlebone

Isotherm models	Parameters	Pb^{2+}	Cu^{2+}
Freundlich	n	1.79	2.08
	K_f	8.11	9.17
	R^2	0.973	0.996
Langmuir	q_m	45.9	39.9
	b	0.189	0.268
	R^2	0.859	0.931
Redlich–Peterson	K_{RP}	75.2	78.1
	a_{RP}	8.19	7.32
	γ	0.478	0.572
	R^2	0.957	0.995
Temkin	A_T	2.85	4.59
	b_T	289	388
	R^2	0.887	0.919

also described the isotherm data with high correlation coefficients ($R^2 > 0.95$). The Langmuir constant of q_m as the maximum adsorption capacity is the most common parameter to compare adsorbents for the same adsorbate. The values of the parameter q_m for adsorption of Pb^{2+} and Cu^{2+} were determined to be 45.9 and 39.9 mg/L, respectively. These values were relatively high in comparison with the values obtained in the other studies for the same metal ions, therefore cuttlebone could be classified as an efficient adsorbent for Pb^{2+} and Cu^{2+} (Shen *et al.* 2009; Fu & Wang 2011; Murugesan *et al.* 2011). For example, Pellera *et al.* (2012) determined the parameter q_m for adsorption of Cu^{2+} by rice husks, dried olive pomace, orange waste and compost to be 6.3, 7.1, 10.3 and 10.1 mg/g, respectively. In another study by Kamari *et al.* (2014) the maximum adsorption capacities (q_m) of Pb^{2+} and Cu^{2+} by coconut dregs residue were obtained to be 9.7 and 2.8 mg/g, respectively.

Based on the results, in addition to feasibility of using cuttlebone in water and wastewater treatment plants for removal of Pb^{2+} and Cu^{2+}, the dead naturally abundant biomass offers a large capacity of self-purification in marine environments for the heavy metals. This self-purification capacity has a special importance in the marine environments exposed to heavy metal discharges (Bronfman 1992; Wang *et al.* 2002; Cukrov *et al.* 2008). The Persian Gulf is a good example of the marine environments receiving a large quantity of heavy metals through man-made resources including oil and gas industries and transportation, therefore the self-purification capacity would play an important role in reduction of probability of heavy metal pollution in the environment. It is recommended that the self-purification capacity be considered in harvesting cuttlebone for human uses.

Effect of pH

The degree of ionization of metal ions in aqueous solutions and the charge of adsorbent surface are greatly influenced by solution pH (Heidari *et al.* 2013). Figure 5 shows the effect of pH on the adsorption of Pb^{2+} and Cu^{2+} by cuttlebone. The adsorption studies were performed within the pH range of 2.0 to 7.0, because the metal ions formed insoluble hydroxide precipitates simultaneously at pH value greater than 7.0; therefore removal of the metal ions at pH value greater than 7.0 was not solely by adsorption onto cuttlebone, but due to hydroxide precipitation as well. According to Figure 5, it is apparent that the amounts of Pb^{2+} and Cu^{2+} adsorption by cuttlebone increased with increasing the solution pH, so that the highest adsorption capacities of Pb^{2+} and Cu^{2+} were observed in pH value of 7.0 to be 18.7 and 19.8 mg/g, respectively. This trend can be explained by the fact that the high concentration of H^+ in low pH leads to competition and repulsion between H^+ and metal ions for active sites on the surface of adsorbent (Reddy *et al.* 2010). By increasing the solution pH, H^+ was less available and therefore more metal ions could be bound to adsorption sites.

Similar results have been reported in the removal of Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution using natural kaolinite clay (Jiang *et al.* 2010). In another study, Laus *et al.* (2010) examined Cu^{2+}, Cd^{2+} and Pb^{2+} removal using chitosan cross-linked with epichlorohydrin-triphosphate in the pH range of 2 to 11. In this study, the maximum adsorption was observed at neutral pH values. Huang & Liu (2013) also studied effect of pH on removal of Pb^{2+} by biosurfactant-producing bacteria and observed that the adsorption capacity of Pb^{2+} continuously increased

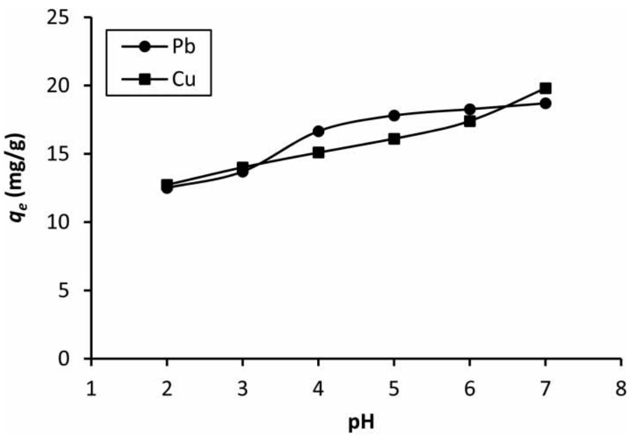

Figure 5 | Effect of pH on equilibrium capacities of Pb^{2+} and Cu^{2+} adsorption by cuttlebone (adsorbent dose: 0.1 g/L; initial metal concentration: 20 mg/L).

with pH from 2 to 7. In contrast, the maximum uptakes of Cu^{2+} and Pb^{2+} by exopolysaccharide were observed at pH values 5.0 and 5.5, respectively (Shuhong *et al.* 2014). Sadia Waseem *et al.* (Waseem *et al.* 2014) found that pH had no significant effect on Pb^{2+} removal by *Acacia nilotica*. The neutral optimum pH obtained in this study can be an advantage of using cuttlebone as adsorbent because of lower requirement of pH adjustment and cost saving.

CONCLUSION

This study focused on adsorption of Pb^{2+} and Cu^{2+} onto cuttlebone biomass from aqueous solution. Similar behavior and results were observed for adsorption of both Pb^{2+} and Cu^{2+} by cuttlebone in the same operating condition. The adsorption process was relatively fast and reached to equilibrium in 120 min and the kinetic data were described by the pseudo-second-order model. The isotherm data of Pb^{2+} and Cu^{2+} followed the Freundlich model and were also found to be in good fitness with the Redlich–Peterson model. According to the Langmuir model, the maximum adsorption capacities (q_m) of cuttlebone for Pb^{2+} and Cu^{2+} were determined to be 45.9 and 39.9 mg/g, respectively. Taking into consideration present results, it can be stated that cuttlebone is an efficient adsorbent for Pb^{2+} and Cu^{2+} that offers a promising capacity of self-purification in marine environments as well as can be a feasible option for treatment of water and wastewater containing Pb^{2+} and Cu^{2+}.

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