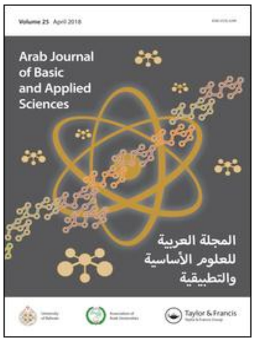

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ORIGINAL ARTICLE

Lala clam (*Orbicularia orbiculata*) shell as an eco-friendly adsorbent for Cd(II), Cu(II) and Pb(II) ions

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ABSTRACT

In this study, the effectiveness of lala clam (*Orbicularia orbiculata*) shell, a fishery waste, as an adsorbent for removal of Cd(II), Cu(II) and Pb(II) ions from contaminated water was evaluated by characterization and adsorption studies. The characterization study was performed using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) Spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy techniques. The effects of solution pH (pH 1.0 to 6.0), adsorbent dosage (0.125 to 0.750 g) and initial adsorbate concentration (10 to 200 mg/L) on adsorption capacity of lala clam shell were studied. The capability of lala clam shell to remove metal ions from aqueous solution was assessed in both single- and mix-metal systems. The adsorption equilibrium data were fitted to Freundlich and Langmuir isotherm models. At an optimum solution pH of 6.0 and initial metal ion concentration of 200 mg/L, the maximum adsorption capacity (Q_{max}) values of Cd(II), Cu(II) and Pb(II) ions were determined as 66.66, 64.94 and 100.00 mg/g, respectively. The removal performance of lala clam shell (63.80 to 93.79%) for metal ions from battery manufacturing wastewater was comparable to that of three commercial activated carbons derived from olive tree wood (73.01 to 94.83%), coconut shell (68.10 to 95.17%) and bamboo (69.33 to 94.48%), which are commonly used for water treatment in Libya, Malaysia and Indonesia, respectively. The results obtained from this study suggest that lala clam shell exhibits a great potential to be used as an effective alternative to expensive adsorbents for water treatment.

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KEYWORDS
Adsorption; equilibrium isotherm; lala clam shell; metal ions

1. Introduction

Wastewater regulations are established to minimize human and environmental exposure to hazardous chemicals. The type and concentration of heavy metals that may be present in the wastewater have been of great concern (Davarnejad, Moraveji, & Havaie, 2018). For instance, high level of copper in water environment particularly in drinking water may cause Wilson's disease, which leads to accumulation of copper in tissues such as the liver and brain, thus leading to liver disease as well as psychiatric and neurological symptoms to human (Stock, Reuner, Gohll, & Beste, 2016). In addition, it has been reported that lead exposure was accounted for about 853,000 deaths in 2013 due to long-term effects on health, with the highest number of cases in low and middle-income countries (Zhou et al., 2016). Many industrial processes involve heavy metals as important components for electrical appliances. Mining, batteries and plating manufacturing are the main sources of metal ions in industrial wastewater, which must be treated prior to discharge (Alharbi, Basheer, Khattab, & Ali, 2018). In 2014, approximately 2531.67 million tonnes of wastewater were discharged by the mining industry in China (Li, Lei, Ge, & Wu, 2017).

Various methods such as chemical precipitation, coagulation-flocculation, ion exchange and adsorption have been employed for sequestering heavy metals from aqueous solutions (Li et al., 2017). In developing countries, some aspects such as simple operation and low operational cost must be taken into consideration when a method is chosen to treat water (Aziz, Abdelmajid, Rachid, & Mohammadine, 2018; Saravanan et al., 2016). Adsorption is one of the most efficient methods to remove heavy metals from aqueous solutions. Undoubtedly, activated carbon is widely used as an adsorbent due to its large surface area and high adsorption capacity (Razi, Al-Gheethi, Al-Qaini, & Yousef, 2018; Păcurariu, Paşka, Ianoş, & Muntean, 2016). However, its application in wastewater treatment is restricted because of its

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high-cost production and regeneration (Davarnejad et al., 2018; Kausar et al., 2018). Therefore, activated carbon is not regarded as an economical adsorbent, especially in developing countries (Razi et al., 2018). Consequently, low-cost and eco-friendly adsorbents such as rice husk (Raikar, Correa, & Ghorpade, 2015), sugarcane bagasse (Kong, Ren, Wang, & Chen, 2014), coconut husk (Agbozu & Emoruwa, 2014), banana peel (Li et al., 2016) and several other agricultural wastes (Bandela, Babrekar, Jogdand, & Kaushik, 2016) have been preferred to treat metal laden contaminated water.

In the present study, a natural waste material obtained from fishery industry, namely short neck clam (*O. orbiculata*) shell or locally known as lala clam was evaluated as an alternative adsorbent for remediation of contaminated water. Lala clam shell is abundantly available in Malaysia and Indonesia with no economical value. To the best of our knowledge, it has not been used for purification of water contaminated by heavy metals. Lala clam shell contains calcium carbonate (95%), which may be beneficial to act as an adsorption site for metal ions. Hence, the ultimate aim of this study was to investigate the efficacy of lala clam shell as an adsorbent for the removal of Cd(II), Cu(II) and Pb(II) ions from aqueous solutions. A comprehensive and systematic adsorption experiments were carried out in both single- and mix-metal systems, which involved several experimental parameters such as solution pH, adsorbent dosage and initial adsorbate concentration.

2. Materials and methods

2.1. Preparation of adsorbent

Lala clam shells were supplied by a seafood processing factory in Pangkor Island, Perak, Malaysia. The shells were washed with tap water and then rinsed thoroughly with deionised water to clean thoroughly. The cleaned shells were dried in an oven at 70 °C for 24 h and then they were crushed and sieved to 150–250 µm size by using an American Society for Testing and Materials (ASTM) standard sieve. The ground materials were stored in self-sealing bags for use in the adsorption and characterization studies. Lala clam shell powder has a white brownish colour.

2.2. Preparation of adsorbate

The stock solutions of 1000 mg/L of Cd(II), Cu(II) and Pb(II) ions were prepared by dissolving the appropriate amount of metal salts, namely $Cd(NO_3)_2{\cdot}4H_2O$ (Scharlau), $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich) and $Pb(NO_3)_2$ (Fisher Scientific) in deionised water, separately. These solutions were then diluted to the appropriate concentrations. All chemicals were of analytical grade and used without further purification. Deionised water was used in all experiments in this study.

2.3. Characterization studies

Surface analyser, FESEM, EDX Spectrometer and FTIR Spectrometer were used to characterize lala clam shell before and after the interaction with Cd(II), Cu(II) and Pb(II) ions. The surface area and average pore diameter analyses were performed using a Quantachrome Autosorb 1 Surface Analyser. The surface area of lala clam shell was determined according to Brunauer-Emmett–Teller (BET) multipoint technique (Brunauer, Emmett, & Teller, 1938; Taufiq-Yap, Lee, & Lau, 2012), whereas the pore diameter measurement was based on Barrett, Joyner and Halenda (BJH) method (Barrett, Joyner, & Halenda, 1951; Rouquerol, Rouquerol, Sing, Llewellyn, & Maurin, 2014). The surface morphology and elemental composition of the adsorbent before and after the adsorption of metal ions were observed and examined using a Hitachi SU 8020 UHR FESEM equipped with an EDX Spectrometer. FTIR spectra were recorded conducted in the range of 4000 to 400 cm^{-1} over 32 cumulative scans using a Thermo Nicolet 6700 FTIR Spectrometer. This spectral analysis has been taken as fundamental in order to identify functional groups present on the surface of lala clam shell and to elucidate possible adsorption mechanism(s) prevailing between the adsorbent and the metal ions.

2.4. Adsorption experiments

Batch adsorption experiments for Cd(II), Cu(II) and Pb(II) ions were carried out by adding approximately 0.1 g of lala clam shell into each 50 mL of metal ion solution in 250 mL Erlenmeyer flasks. A Protech Orbital Shaker (model 720) was used to agitate the solutions for 1 h at 100 rpm. After equilibration, the solutions were filtered through a piece of filter paper (Filtre Fioroni 601, 110 mm). The metal ion concentration in the supernatant was determined using a Perkin-Elmer AAnalyst 400 Atomic Absorption Spectrometer (AAS).

For single-metal system, the influence of solution pH, adsorbent dosage and initial metal concentration on metal ion adsorption was studied. The effect of solution pH was studied in the pH range of 1.0–6.0. The initial pH of 50 mL of 100 mg/L metal ion solutions was adjusted by adding a few drops of diluted 0.05 mol/L HCl or 0.05 mol/L NaOH solutions. A Thermo Scientific Orion 2-Star pH meter was used to measure the pH of the solutions. The effect of adsorbent dosage on removal percentage was assessed using four various doses of adsorbent, namely 0.125, 0.250, 0.500 and 0.750 g. Isotherm studies were performed by shaking 0.1 g of lala clam shell in 50 mL of metal ion solution with an initial metal concentration ranging from 10 mg/L to 200 mg/L. The experiment was carried out at the optimum pH.

Competitive adsorption study was carried out in the mix-metal system. About 0.5 g of lala clam shell was added to 50 mL solution containing 10, 100 or 200 mg/L of each metal ion. All experiments were run in triplicates. The adsorption capacity at equilibrium (q_e) was calculated using Eq. (1):

$$q_e = \frac{(Co - Ce)V}{W} \tag{1}$$

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), C_o is the initial metal ion concentration (mg/L), C_e is the equilibrium metal ion concentration (mg/L), W is the weight of the adsorbent (g) and V is the volume of the metal ion solution (L).

2.5. Desorption study

For desorption studies, 0.1 g of lala clam shell was loaded with 100 mg/L of each of metal ion at the optimum solution pH. Metal ion loaded adsorbent was filtered using Whatman filter paper, followed by determination of metal concentration in the supernatant using AAS. The amount of metal ions absorbed (m_a) onto adsorbent was calculated using Eq. (1). Adsorbent was air-dried at room temperature for overnight. Dried spent adsorbent was then agitated in 50 mL of EDTA or HCl solution (0.50, 0.10 and 0.05 mol/L) to desorb any remaining metal ions. Metal ion concentration in EDTA and HCl was then quantified, and the amount of any metal ions that remained (m_d) on the adsorbent was computed according to Eq. (2). The desorption percentage (DP) was estimated from Eq. (2):

$$DP(\%) = \frac{m_d}{m_a} \times 100 \tag{2}$$

where, m_d and m_a (mg) are the weights amount of desorbed and adsorbed metal ions.

2.6. Industrial wastewater treatment: comparative study

The feasibility of lala clam shell to adsorb metal ions in contaminated water was assessed using industrial wastewater. The industrial wastewater was sampled from a battery manufacturing factory in Shah Alam, Selangor, Malaysia. The amber glass bottles containing wastewater samples were kept in a cold contained kept at 4 to 6 °C and carefully brought to the laboratory. The suspended solid in the industrial wastewater was removed by filtering through a filter paper. The concentration of metal ions in the wastewater sample was then measured using AAS. In addition to lala clam shell, the adsorption capacity of three commercial activated carbons derived from olive tree wood, coconut shell and bamboo was also determined and compared. The adsorption study was performed under optimum experimental conditions and each adsorbent was applied to wastewater sample at the ratio of 1:50 (weight (g):volume (mL)).

3. Results and discussion

3.1. Characterization studies

3.1.1. Surface area, pore volume and pore diameter analyses

The effectiveness of lala clam shell for adsorption of metal ions is greatly influenced by its physical and chemical properties (Caglar, Afsin, Tabak, & Eren, 2009). Therefore, the surface area, pore volume and pore diameter of lala clam shell were determined to elucidate the interaction mechanism of adsorbent with metal ions. The surface area, pore volume and pore diameter of lala clam shell were measured as 2.09 m^2/g, 0.16 cm^3/g and 0.15 nm, respectively. The surface area of lala clam shell is relatively comparable to the values of several other shells reported previously by Wei et al. (2018) for *Mytilus edulis* mussel shell (1.120 m^2/g), Tsai (2013) for *Crassostrea gigas* Pacific oyster shell (4.05 m^2/g) and de Paiva, Fraga, Sales, Carvalho, and Sobrinho (2018) for *Anomalocardia brasiliana* clam shell (4.44 m^2/g).

According to the IUPAC, the porosity of substances can be grouped into three different classes of diameter groups (d), namely micropores ($d < 2$ nm), mesopores ($2 < d < 50$ nm) and macropores ($d > 50$ nm). Based on this classification, the pore diameter of the lala clam shell can be classified as micropores.

3.1.2. FESEM analysis

The FESEM images of lala clam shell taken before and after the adsorption of Cd(II), Cu(II) and Pb(II) at 10,000× magnification are shown in Figure 1. The lala clam shell had an uneven structure with non-uniform size distribution on the surface (Figure 1(a)). The surface morphologies of lala clam shell after interaction with metal ions are depicted in Figure 1(b–d). Interaction with Cd(II) resulted in a square-shape surface texture (Figure 1b), while lump-like deposits were observed on the surface of the adsorbent after Cu(II) adsorption (Figure 1(c)). Interaction with Pb(II) led to the formation of rod-like deposits on the surface of lala clam shell (Figure 1(d)). From FESEM analysis, it is apparent that the

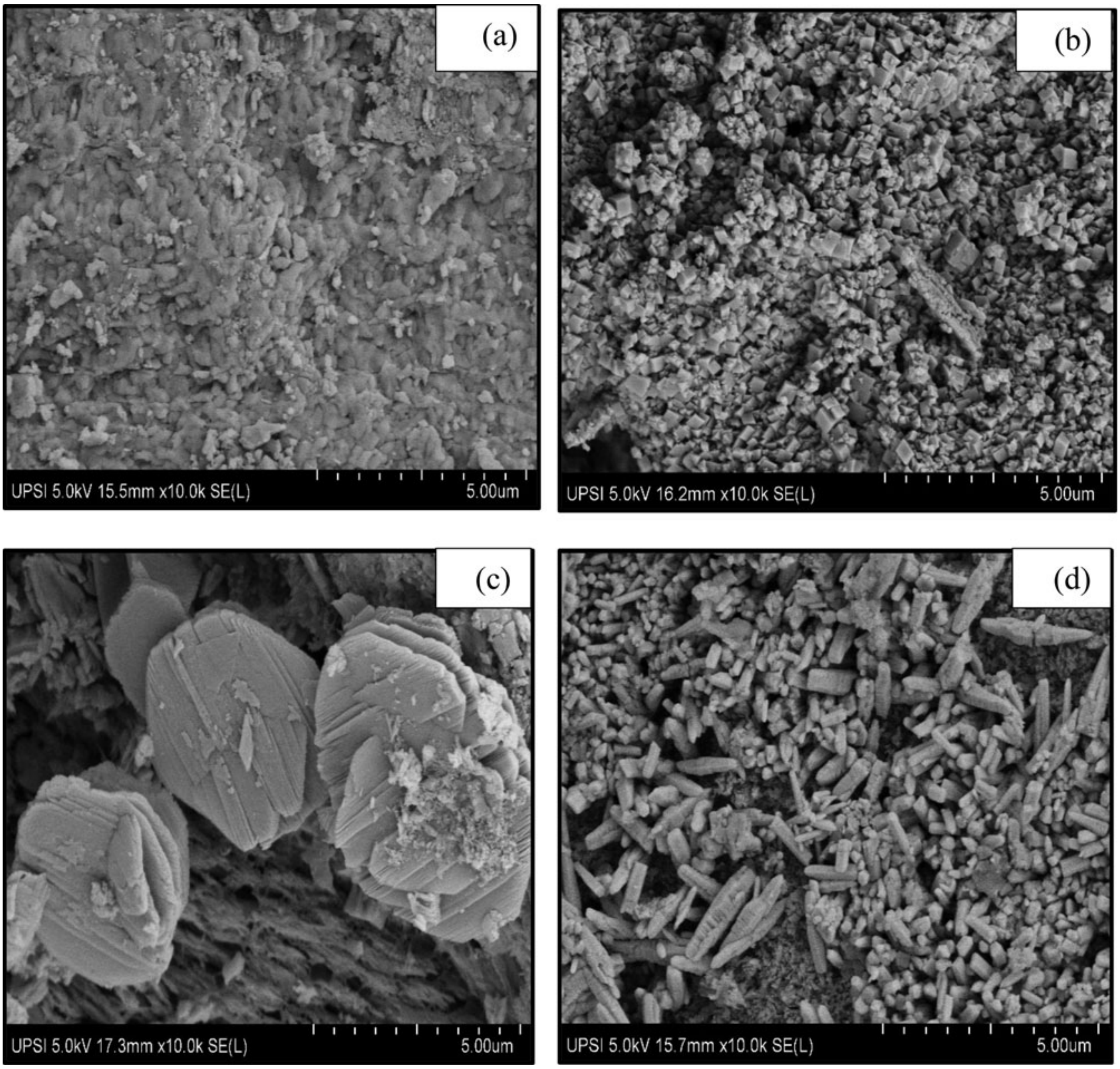


Figure 1. FESEM images of lala clam shell before metal ion adsorption (a) and after adsorption of (b) Cd(II), (c) Cu(II) and (d) Pb(II) ions (10,000× magnification).

adsorption of metal ions modified the surface morphology of lala clam shell. In addition, the interaction gives rise to the formation of deposits on the adsorbent surface.

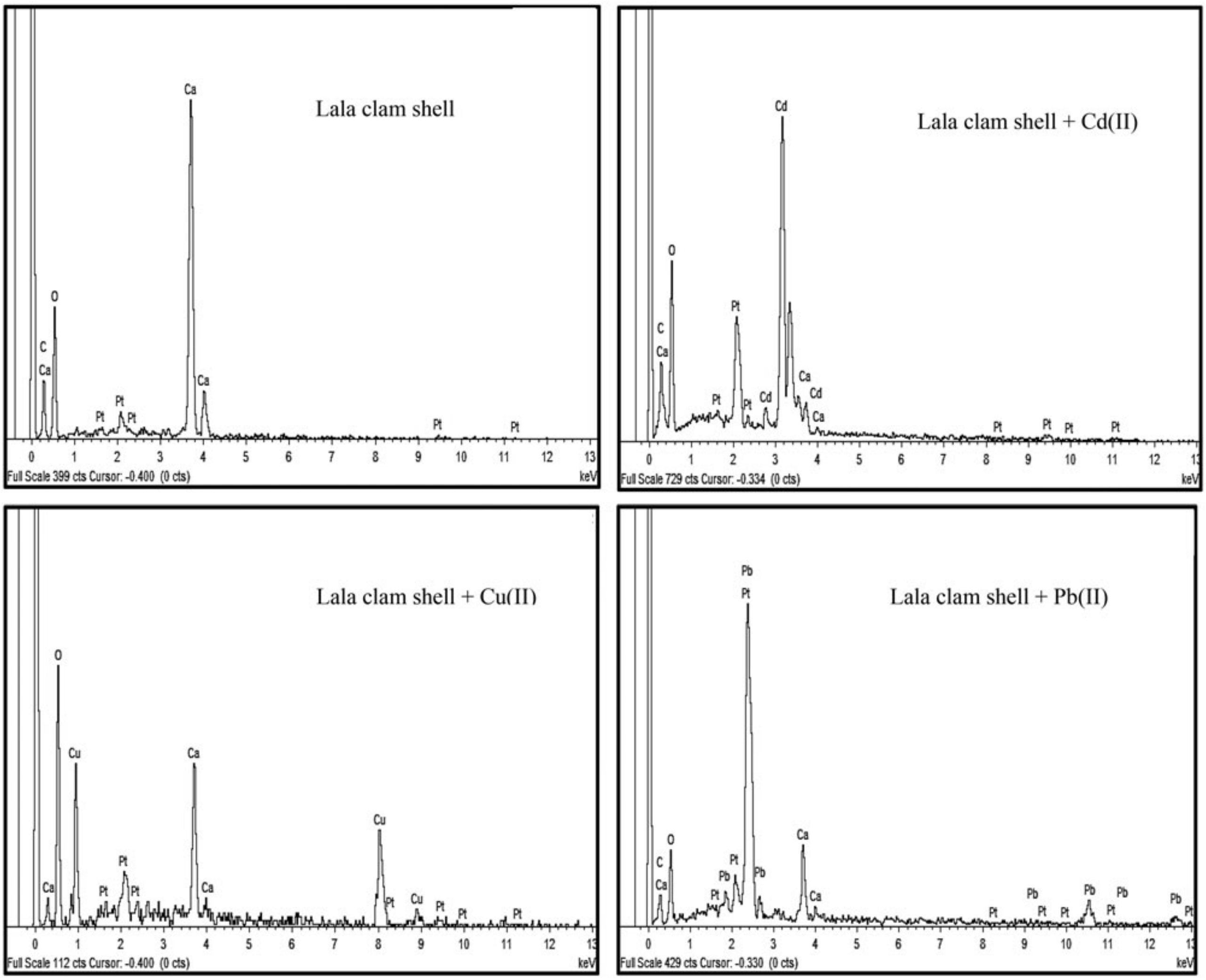
3.1.3. EDX analysis

The EDX spectra of lala clam shell before and after interaction with metal ions are shown in Figure 2. Calcium and oxygen were the major constituents in lala clam shell. The features of calcium and oxygen can be observed at energy lines of 3.68 and 0.27 keV, respectively. In this study, lala clam shell was coated using platinum to avoid electron charging that might interfere SEM analysis. Accordingly, the features of platinum were detected on the EDX spectra at the energy lines of 2.00, 9.45 and 10.60 keV.

Following interaction of lala clam shell with metal ions, the features of Cd, Cu and Pb were observed in each EDX spectrum of the adsorbent. As shown in Figure 2, the Cd(II) features were observed at the energy lines of 3.20 and 3.91 keV. Exposure of lala clam shell to Cu(II) resulted in the appearance of Cu features at 0.93 and 8.04 keV. Meanwhile, the characteristic peaks for Pb(II) were observed at 2.34 and 10.58 keV after Pb(II) adsorption. Overall, the results from EDX analysis suggest that the lala clam shell was capable of binding the metal ions.

3.1.4. FTIR analysis

Figure 3 presents the FTIR spectra of the lala clam shell, before and after the adsorption of metal ions. As shown in (Figure 3(a)), the two prominent bands observed at 1448 cm^{-1} and 854 cm^{-1} represent the


Lala clam shell

Lala clam shell + Cd(II)

Lala clam shell + Cu(II)

Lala clam shell + Pb(II)

Figure 2. EDX spectra of lala clam shell before and after metal ion adsorption.

carbonate (CO_3^{2-}) group (de Paiva et al., 2018). The band appearing at 1781 cm^{-1} is the characteristic of carbonyl (C = O) vibration (Jones & Jackson, 1993). There were significant changes on the FTIR spectrum of lala clam shell following the interaction with Cd(II), Cu(II) and Pb(II) ions (Figures 3(b–d)). As depicted in Figure 3(b), the absorption bands of carbonate group shifted from 1448 cm^{-1} to 1380 cm^{-1} and from 854 to 857 cm^{-1} after the treatment with Cd(II). Following the adsorption of Cu(II), the peak at 1448 cm^{-1} split into two peaks at 1419 and 1342 cm^{-1}. Subsequent to interaction with Cu(II) new bands appeared at 3535 and 2358 cm^{-1} (Figure 3(c)), which can be assigned to hydroxyl and alkyl groups (Mohrig, Hammond, & Schatz, 2006).

The vibration band of carbonate at 1448 cm^{-1} shifts to 1451 cm^{-1} on adsorption of Pb(II) (Figure 3(d)). It is important to note that the band of carbonate group becomes stronger after the interaction with metal ions and this effect is most prominent for Cd(II) adsorption. Presumably, the shift in the peak position, the change in the peak intensity and the appearance of new vibrational features could be related to the interaction of positively charged metal ions with negatively charged adsorption site of lala clam shell through electrostatic attraction.

3.2. Adsorption studies

3.2.1. Single-metal system

3.2.1.1. Effect of solution pH. The removal of metal ions from aqueous solutions by adsorption process is highly dependent on the pH of the solution, which influences the surface charge of the adsorbent, degree of ionization and the type of the adsorbate species (Aziz et al., 2018). Figure 4 shows the effect of solution pH on the amount of metal ion adsorbed by lala clam shell. In this study, the range of solution pH was set from 1.0 to 6.0. It may be concluded based on the results and observations from preliminary studies that, metal ions form insoluble hydroxide precipitates at solution pH values higher than 6.0.

From Figure 4, it is obvious that the amount of Cd(II), Cu(II) and Pb(II) adsorbed onto adsorbent increased with the increase of pH from 1.0 to 6.0. This trend can be related to high concentration of H^+ ions in acidic medium. At low pH values, the

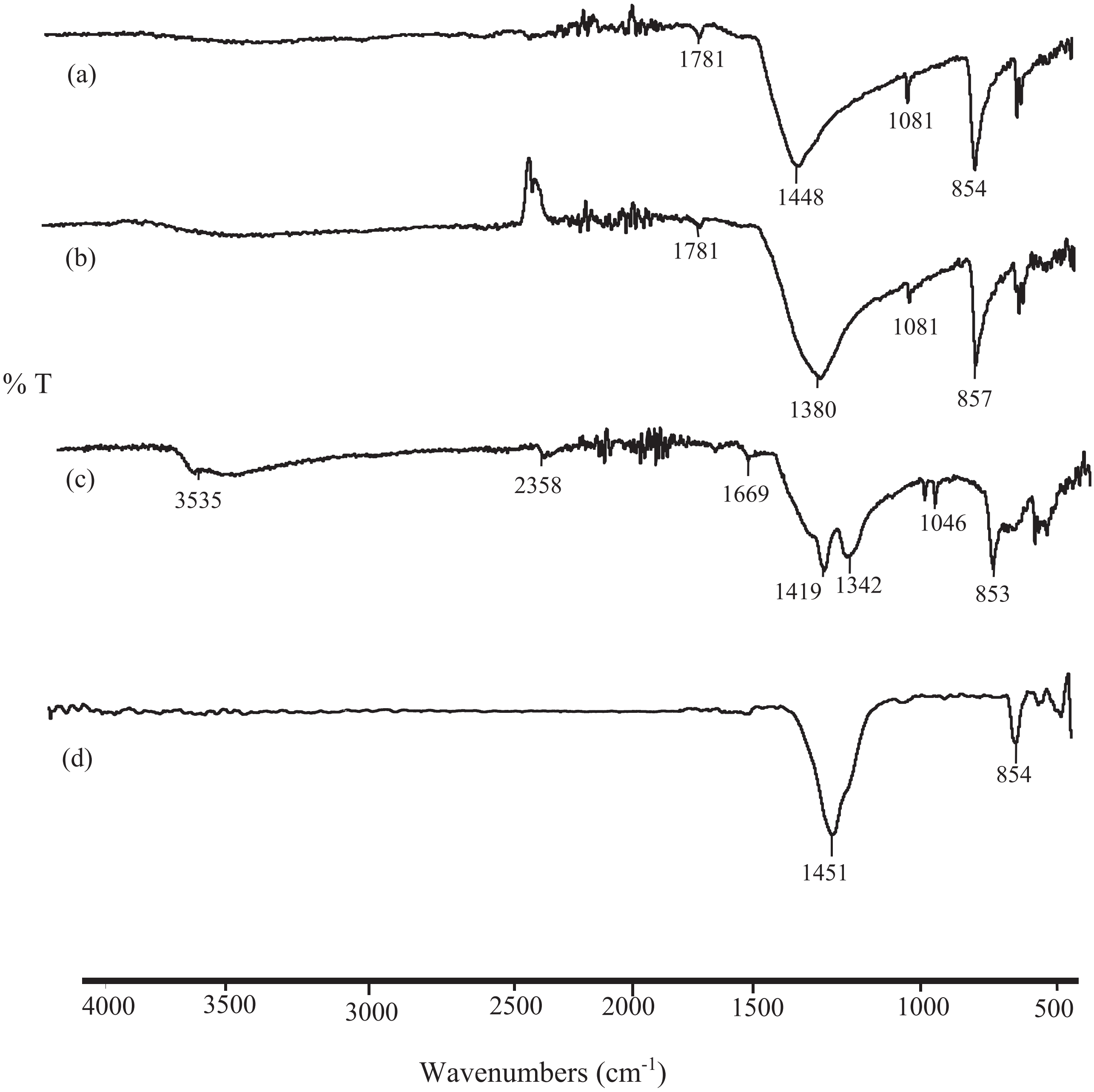


Figure 3. The FTIR spectra of lala clam shell before metal ion adsorption (a) and after the adsorption of (b) Cd(II), (c) Cu(II) and (d) Pb(II) ions.

excessive H^+ ions will likely to compete with metal ions for adsorption sites of adsorbent (Anna, Kleopas, Constantine, Anestis, & Maria, 2015; He, Chen, Tang, & Hu, 2016). On the other hand, when the solution pH was increased further, H^+ ions were no longer dominant (less available). This scenario leads to interaction between metal ions and adsorption sites.

The pH of zero point of charge (pH_{zpc}) can be used to describe the adsorption behaviour of contaminants onto adsorbent from aqueous solutions under the influence of the solution pH (Bakka et al., 2018). In this study, the pH_{zpc} of lala clam shell was determined as 3.5 using pH drift method described by Foo and Hameed (2012). Theoretically, the surface of adsorbent becomes positively charged at pH values below pH_{zpc}, and it is negatively charged at pH values above pH_{zpc} (Bakka et al., 2018; Foo & Hameed, 2012). As depicted in Figure 4, the maximum adsorption of metal ions onto lala clam shell was obtained at pH 6.0, which was higher than the pH_{zpc} value. This phenomenon could be related to high electrostatic attraction between the positively charged Cd(II), Cu(II) and Pb(II) ions and negatively charged sites of lala clam shell.

The role of ion exchange mechanism during the adsorption of metal ions adsorption onto lala clam shell was confirmed by measuring the pH values of solution, before and after the adsorption process. This mechanism was derived based on the relationship between pH and H^+ ions ($pH = -\log [H^+]$). Generally, if ion exchange mechanism involved in

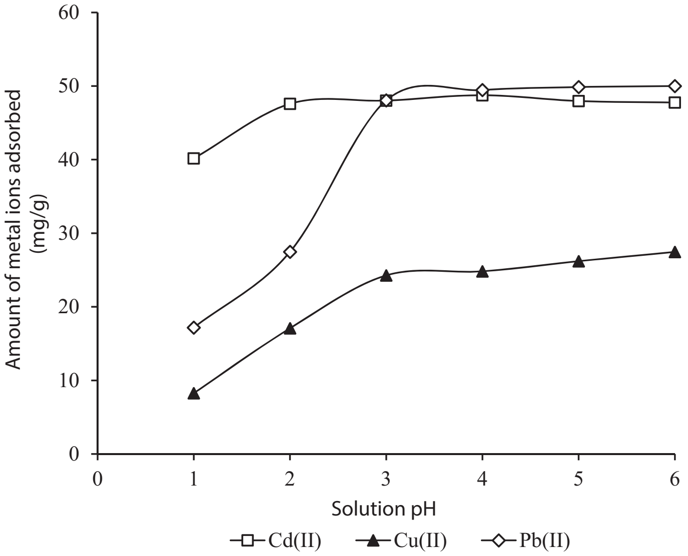


Figure 4. Effect of solution pH on adsorption of Cd(II), Cu(II) and Pb(II) ions onto lala clam shell.

the adsorption process, significant differences will be observed in the pH values of the solution. In this study, the difference in pH values (ΔpH) was found to be less than 0.5, indicating the ion exchange was not the main binding route of metal ions by lala clam shell.

From Figure 4, it is clear that the most affected metal ion by solution pH is Pb(II), which is followed by Cd(II) and Cu(II). The amounts of Pb(II), Cd(II) and Cu(II) ions adsorbed at optimum solution pH 6.0 were found as 50.0, 47.8 and 27.5 mg/g, respectively. A similar optimum solution pH value was reported by Hizal et al. (2013) for removal of Cd(II), Cu(II) and Pb(II) ions from wastewater by red mud. In accordance to these results, the Q_{max} capacity of sugarcane bagasse for successfully removal of Cd(II), Cu(II) and Pb(II) ions was reported at pH 6.0 (Kong et al., 2014).

3.2.1.2. Effect of adsorbent dosage. The adsorbent dosage significantly affect the capacity of the adsorbent for a given concentration of metal ion solution (Anna et al., 2015; Aziz et al., 2018). It is of fundamental importance to determine the adsorption capacity of the adsorbents prior to design and improve the adsorption system in real applications (Bakka et al., 2018).

Figure 5 shows the adsorption amount (mg/g) and removal percentage (%) of metal ions by lala clam shell. It is apparent that the amount of metal ion adsorbed decreased with an increase in adsorbent dosage. When the adsorbent dosage was increased from 0.125 to 0.750 g, the amount of Cd(II), Cu(II) and Pb(II) ions adsorbed by lala clam shell decreased significantly from 38.75 to 6.58 mg/g, 27.20 to 6.26 mg/g and 38.94 to 6.65 mg/g, respectively. A lower adsorbent dosage which presumed a larger overall total surface of lala clam shell was exposed and thus, higher amounts of metal ions per gram of lala clam shell were removed.

In contrast to adsorption capacity, the removal percentage increased when the amount of lala clam shell was increased from 0.125 to 0.750 g. This trend might be due to the availability of more adsorption sites. The removal percentage of Cd(II), Cu(II) and Pb(II) by lala clam shell was increased from 96.88 to 98.76%, 68.00 to 94.03% and 97.36 to 99.88%, respectively. It can be seen that Pb(II) was the best adsorbed ion by lala clam shell. A similar trend was reported by Anna et al. (2015) for the adsorption of Cd(II), Cu(II) and Pb(II) ions onto natural bentonite. Agbozu and Emoruwa (2014) reported that the amounts of Cd(II), Cu(II), Cr(VI), Fe(III) and Pb(II) ions removed increased with the decrease of the adsorption capacity when the amount of coconut husk used was increased. When a high amount of lala clam shell is used, the surface became masked due to the aggregation of particles on the adsorbent. Consequently, there occurs a reduction in the number of contacts between the active sites (the carbonate groups) and metal ions.

3.2.1.3. Effect of initial metal concentration. The trends observed on the effect of initial concentration on adsorption of metal ions by lala clam shell are shown in Figure 6. It is obvious that the amount of metal ions adsorbed by lala clam shell increased when the initial metal ion concentration was increased from 10 mg/L to 200 mg/L. From the initial concentration of 10 to 200 mg/L, the adsorption capacity of Cd(II), Cu(II) and Pb(II) ions increased from 4.93 to 97.44 mg/g, 4.54 to 85.34 mg/g and 4.85 to 99.25 mg/g, respectively.

High adsorption capacity at high initial metal concentration can be related to two main factors: (i) the

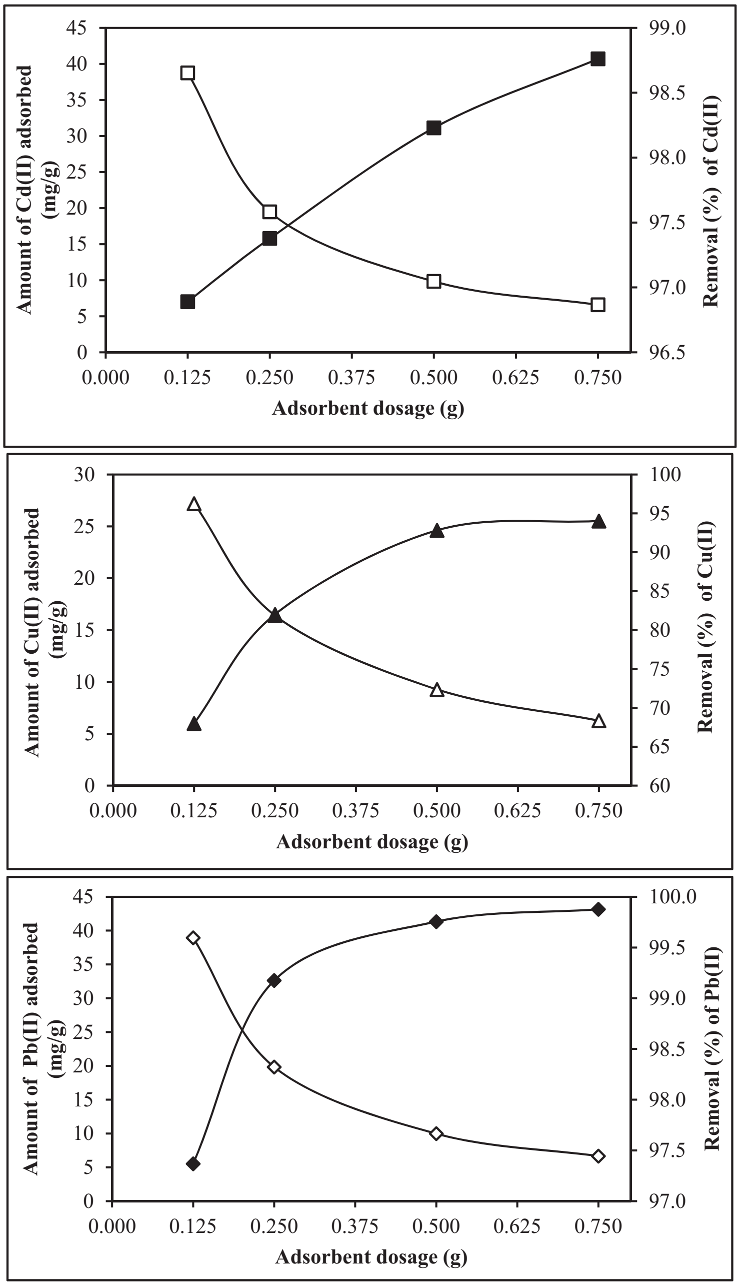


Figure 5. Effect of adsorbent dosage on adsorption of Cd(II), Cu(II) and Pb(II) ions.

increase in the number of collisions between the metal ions and the adsorption sites of lala clam shell and (ii) high diffusion rate of the metal ions into lala clam shell (Li et al., 2016; Anna et al., 2015). The adsorption capacity of metal ions onto lala clam shell followed the order of Pb(II) > Cd(II) > Cu(II) which is similar to the results obtained for the adsorption of metal ions retained by red marine alga *Kappaphycus alvarezii* (Praveen & Vijayaraghavan, 2015).

It may be concluded from the present data that Pb(II) ion exhibited much stronger affinity towards lala clam shell than Cd(II) and Cu(II) ions. This means that different cations can have different affinities for the binding sites on the same adsorbent. This behaviour can be explained by the differences in ionic radius and atomic weight of metal ions studied. Pb(II) has a larger ionic radius (0.119 nm) than Cd(II) (0.097 nm) and Cu(II) (0.071 nm). Pb(II) ion also has a much higher atomic weight (207.2 g/mol) than Cd(II) ion (112.411 g/mol) and Cu(II) ion (63.546 g/mol), indicating that the electrons of Pb(II) are easier to polarise and are less slightly retained by the nucleus (Ali et al., 2016; Wu, Wang, Zhang, Cai, & Yin, 2015).

3.2.1.4. Adsorption isotherms. Adsorption isotherm models have been widely used in adsorption studies to describe the interaction and distribution of metal ions on the adsorbent surface (Păcurariu et al., 2016; Bakka et al., 2018). Freundlich and Langmuir adsorption isotherms were applied to analyse the equilibrium data. Freundlich isotherm model contains empirical equations that are used to describe multilayer adsorption and assumes that sites with different adsorption

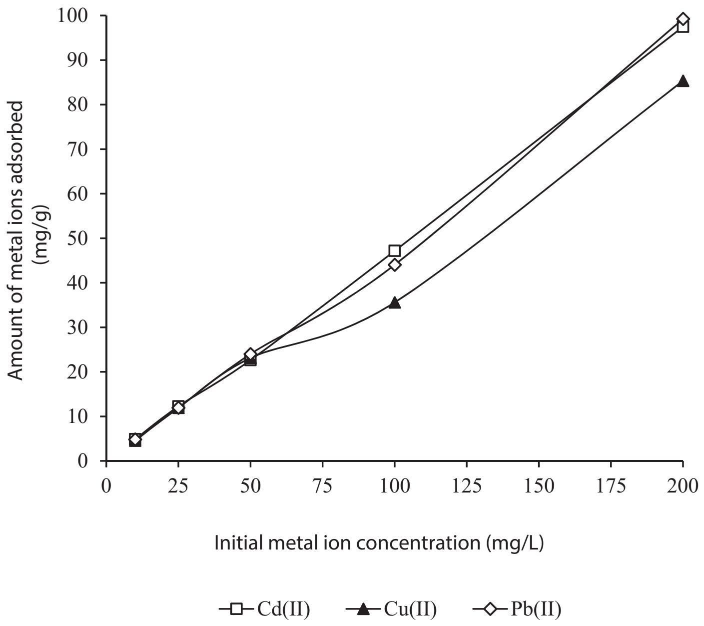


Figure 6. Effect of initial metal ion concentration on adsorption of Cd(II), Cu(II) and Pb(II) ions onto lala clam shell.

energies are involved (Freundlich, 1906; Păcurariu et al., 2016). The linear form of the Freundlich equation can be expressed as Eq. (3) (Freundlich, 1906).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where C_e is the equilibrium concentration of metal ion (mg/L), q_e is the amount of metal ion adsorbed per unit weight of adsorbent at equilibrium (mg/g), K_F (mg/g) and n are the Freundlich constants related to adsorption capacity and strength, respectively. The K_F and n values can be obtained from the plot of log q_e against log C_e.

The Langmuir isotherm model deals with monolayer adsorption on the adsorbent surface where all sites are equivalent (Langmuir, 1916; Aziz et al., 2018). The Langmuir adsorption model can be given by Eq. (4) (Langmuir, 1916):

$$\frac{Ce}{qe} = \frac{Ce}{Q} + \frac{1}{Qb} \tag{4}$$

where Q is the monolayer capacity (mg/g) and b is the Langmuir constant related to the affinity of binding sites (mL/mg) as well as a measure of the energy of adsorption. The Q and b values can be determined from the linear plot of C_e/q_e against C_e.

The Freundlich and Langmuir constants determined are given in Table 1. The adsorption data of Pb(II) onto lala clam shell fit well the Langmuir isotherm model ($R^2 = 0.9994$). The adsorption data of Cd(II) and Cu(II) fit the Freundlich model rather than the Langmuir model with R^2 values of 0.9982 and 0.9973, respectively. A different correlation of metal ions with isotherm model at different surfaces was also reported in the literature by some researchers. For example, Ali et al. (2016) stated that the equilibrium data for Cd(II) ion adsorbed by *Chlorella vulgaris* were correlated well with the Freundlich model, whereas the adsorption of Cu(II) and Pb(II) ions on the same surface followed well the Langmuir behaviour.

Table 1. Freundlich and Langmuir isotherm constants and correlation coefficients.

	Freundlich			Langmuir		
Metal ion	K_F (mg/g)	$1/n$	R^2	Q_{max} (mg/g)	b (L/mg)	R^2
Cd(II)	19.42	0.60	0.9982	66.66	0.46	0.8980
Cu(II)	7.98	0.59	0.9973	64.94	0.13	0.7895
Pb(II)	17.44	0.56	0.8664	100.00	0.26	0.9994

The $1/n$ values calculated using the Freundlich model were between 0 and 1 (Table 1) which suggest the adsorption of Cd(II), Cu(II) and Pb(II) ions by lala clam shell is favoured. On the other hand, the behaviour of metal ions adsorption by lala clam shell can be further analysed by using a separation factor (R_L) derived from the Langmuir model which is given in Eq. (5) (Hall, Eagleton, Acrivos, & Vermeulen, 1966):

$$R_L = \frac{1}{1 + bCo} \tag{5}$$

where C_o is the initial adsorbate concentration (mg/L). The value of R_L indicates whether the nature of the adsorption process is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Hall et al., 1966). The R_L values for the adsorption of Cd(II), Cu(II) and Pb(II) ions by lala clam shell were determined as in the range of $0 < R_L < 1$ implying that the adsorption of these ions onto lala clam shell was favourable.

The maximum adsorption capacity (Q_{max}) values found using the Langmuir equation for Cd(II), Cu(II) and Pb(II) were 66.66, 64.94 and 100.00 mg/g,

Table 2. Comparison of maximum adsorption capacities of Cd(II), Cu(II) and Pb(II) ions onto various low-cost adsorbents.

	Q_{max} (mg/g)			
Adsorbent	Cd(II)	Cu(II)	Pb(II)	References
Lala clam shell	66.66	64.94	100.00	This study
Natural Ca-bentonite	31.25	32.25	85.47	Anna et al. (2015)
Zeolite synthesized from fly ash	52.12	56.06	65.75	He et al. (2016)
Mirabilis jalapa leaves	38.46	–	38.46	Begum, Tharakeswar, Kalyan, and Naidu (2015)
Red mud	29.00	16.00	103.00	Hizal et al. (2013)
Terminalia ivorensis seed waste	12.58	–	52.91	Babalola et al. (2017)
Hizikia fusiformis	14.42	–	26.47	Shin and Kim (2014)
Dead cells of *Chlorella vulgaris*	45.04	57.14	62.50	Ali et al. (2016)
Dead anaerobic biomass	29.99	–	54.92	Sulayman, Ebrahim, and Mohammed-Ridha (2013)
Hazelnut shell powder	–	21.14	32.74	Lu, Jiang, Jia, Ai, and Wu (2017)
Biochar from *Prosopis africana shell*	29.90	–	38.30	Elaigwu, Rocher, Kyriakou, and Greenway (2014)

Table 3. Amount of ions adsorbed onto Lala clam shells in single- and mix-system determined from Langmuir isotherm model.

Adsorption system	Metal ion	Initial metal ion concentration (mg/L)	Amount of metal ion adsorbed (mg/g)
Single-metal system	Pb(II)	10	4.83
		100	44.50
		200	99.25
	Cd(II)	10	4.82
		100	47.19
		200	97.48
	Cu(II)	10	4.54
		100	35.59
		200	85.34
Mix-metal system	Pb(II)	10	3.54
		100	40.95
		200	90.06
	Cd(II)	10	3.18
		100	41.00
		200	89.27
	Cu(II)	10	2.47
		100	24.85
		200	73.48

Table 4. Comparison of amount of ions adsorbed onto Lala clam shells and commercial activated carbon in mix-metal system determined from Langmuir isotherm model.

Adsorbent	Metal ion	Initial metal ion concentration (mg/L)	Amount of metal ion adsorbed (mg/g)
Lala clam shell	Pb(II)	10	4.09
		100	41.52
		200	90.03
	Cd(II)	10	3.18
		100	48.03
		200	97.83
	Cu(II)	10	2.47
		100	34.85
		200	84.48
Commercial activated carbon derived from olive tree wood	Pb(II)	10	4.54
		100	43.45
		200	8.48
	Cd(II)	10	1.98
		100	43.78
		200	93.76
	Cu(II)	10	2.62
		100	41.28
		200	91.20

respectively (Table 2). The Q_{max} order of Pb(II) $>$ Cd(II) $>$ Cu(II) on lala clam shell is similar to that reported by Hizal et al. (2013) for the adsorption of metal ions by red mud and coal fly ash. The same Q_{max} order for poly (arylene ether sulfone) was observed by Wu et al. (2015).

The Q_{max} values of lala clam shell and selected low-cost adsorbents used for the removal of Cd(II), Cu(II) and Pb(II). Although these Q_{max} values were obtained under different optimum experimental conditions, they may have been of importance in comparison the performance and capacity of different low-cost adsorbents. The Q_{max} values obtained for Cd(II) and Pb(II) on lala clam shell are about five and two times higher than the values determined on *Terminalia ivorensis* seed waste (Table 2). The differences in Q_{max} value of various adsorbents could be attributed to the different physico-chemical properties of the adsorbents as well as the adsorbates.

3.2.2. Mix-metal system

A real industrial wastewater contains a number of several types of contaminants. Therefore, competitive adsorption study at laboratory scale is necessary in order to provide insight into designation of an effective wastewater treatment system for industrial sector (Oladipo & Gazi, 2015). For mix-metal system, Cd(II), Cu(II) and Pb(II) ions are mixed at different initial concentrations, namely 10, 100 and 200 mg/L. Adsorption experiments were carried out under the experimental conditions optimized earlier (Sections 3.2.1.1–3.2.1.3) and the dosage of lala clam shell was set as 0.5 g. The amounts of metal ions adsorbed by lala clam shell in single- and mix-metal systems determined from Langmuir isotherm model are given in Table 3.

The amount of metal ions adsorbed by lala clam shell in the mix-metal system was lower than those adsorbed in the single-metal system (Table 3). A marked reduction was obtained for Cu(II) ion. At the initial Cu(II) concentration of 200 mg/L, the amount of Cu(II) bound onto lala clam shell was found to be 85.34 and 73.48 mg/g for single- and mix-metal systems, respectively. In the presence of two or more metal ions in the solution, competition between metal ions for the same active adsorption sites occurs. This effect reduces the amount of metal ions adsorbed by the adsorption significantly.

Table 5. Percentages of adsorption and desorption Pb(II), Cd(II) and Cu(II) ions from lala clam shell.

		HCl		EDTA	
Metal ions	Concentration (mol/L)	Adsorption (%)	Desorption (%)	Adsorption (%)	Desorption (%)
Cu(II)	0.05	89.02	46.54	89.38	51.13
	0.10	92.65	54.69	89.15	66.91
	0.50	88.71	60.76	89.23	71.87
Cd(II)	0.05	69.18	42.83	71.26	54.70
	0.10	70.10	51.67	70.05	59.47
	0.50	69.53	56.88	71.20	67.88
Pb(II)	0.05	56.88	41.35	56.72	45.96
	0.10	57.10	47.09	56.94	51.46
	0.50	55.89	50.80	57.07	59.70

Table 6. Removal of Cd(II), Cu(II) and Pb(II) ions from battery manufacturing wastewater.

Adsorbent	Metal ion	Final metal ion concentration (mg/L)	Removal (%)
Lala clam shell	Pb(II)	0.88	81.93
	Cd(II)	0.59	63.80
	Cu(II)	0.18	93.79
Olive tree wood derived activated carbon	Pb(II)	0.52	89.32
	Cd(II)	0.44	73.01
	Cu(II)	0.15	94.83
Coconut shell derived activated carbon	Pb(II)	0.40	91.79
	Cd(II)	0.52	68.10
	Cu(II)	0.14	95.17
Bamboo derived activated carbon	Pb(II)	0.48	90.14
	Cd(II)	0.50	69.33
	Cu(II)	0.16	94.48

The ability of lala clam shell to remove metal ions from the mix-metal system was compared with that of a commercial activated carbon derived from olive tree wood (Table 4). It is clearly seen that based on Langmuir isotherm model the amount of Cd(II) ion adsorbed by lala clam shell was higher than by the activated carbon. For instance, at the initial Cd(II) concentrations of 100 and 200 mg/L, the amount of Cd(II) adsorbed by lala clam shell was 48.03 and 97.83 mg/g, meanwhile 43.78 and 93.76 mg/g of Cd(II) was adsorbed by activated carbon, respectively. In the case of Cu(II) and Pb(II) ions, the best adsorption in mix-metal system was obtained by using olive tree wood derived activated carbon. At an initial Cu(II) concentration of 200 mg/L, the amount od Cu(II) adsorbed by lala clam shell and commercial activated carbon was 84.48 and 91.20 mg/g, respectively. It may be concluded based on the results obtained from the present study that lala clam shell has a good potential to be used as an efficient adsorbent to remove heavy metals in wastewater.

3.2.3. Desorption study

In this study, the findings obtained from desorption study are crucial in order to elucidate and confirm the possible mechanism(s) involved for adsorption of metal ions onto lala clam shell. The findings are also importance in order to assess the regeneration potential of lala clam shell. Desorption process was evaluated by using HCl and EDTA as desorption agents. It was conducted after the adsorption studies and the data obtained from this experiment are presented in Table 5.

It is observed that the percentage of desorption increased with an increase in the agent desorption concentration (from 0.05 mol/L to 0.50 mol/L). For instance, the desorption percentage of Pb(II) using 0.05, 0.10 and 0.50 mol/L of HCl was 41.35, 47.09 and 50.80%, respectively. It is found that EDTA was more efficient than HCl to desorp three metal ions studied. In the case of Cd(II), the desorption percentage by using 0.05, 0.10 and 0.50 mol/L of HCl was 42.83, 51.67 and 56.88%, respectively. Meanwhile, 54.70, 59.47 and 67.88% of Cd(II) was desorbed following regeneration using 0.05, 0.10 and 0.50 mol/L of EDTA. It is known that EDTA is a strong hexadentate chelating agent. Therefore, it is capable to capture and to form complexes with Cd(II), Cu(II) and Pb(II) ions.

Of metal ions studied, Pb(II) was the least desorbed by both HCl and EDTA. From Table 5, the desorption percentage of metals ions from adsorbent using HCl and EDTA was in the order of Cu(II) $>$ Cd(II) $>$ Pb(II). In the preceding section (Section 3.2.1.4), the Q_{max} for metal ions adsorption onto lala clam shell was in the order of Pb(II) $>$ Cd(II) $>$ Cu(II). It is clear that Pb(II), the ion most adsorbed by adsorbent became the least desorbed by desorption agents. This suggests that the interaction between negatively charged carbonate group of lala clam shell and positively charged Pb(II) ion was relatively stronger and more stable than Cd(II) and Cu(II) ions. Results also indicate the possibility of adsorbent regeneration at the rate of more than 40%.

3.2.4. Industrial wastewater treatment: comparative study

The applicability of lala clam shell to treat metal contaminated water was further evaluated using a battery manufacturing wastewater. The wastewater contained 4.87, 2.90 and 1.63 mg/L of Pb(II), Cu(II) and Cd(II) ions, respectively. The metal ion adsorbing capacity of lala clam shell was compared with that of three commercial activated carbons. The activated carbons derived from olive tree wood, coconut shell and bamboo are commonly used for water treatment in Libya, Malaysia and Indonesia, respectively. The removal percentages of metal ions from battery manufacturing wastewater using the adsorbents mentioned above are given in Table 6. It is obvious from these data that lala clam shell which was able to sequester Cu(II), Pb(II) and Cd(II) ions by 93.79, 81.93 and 63.80%, respectively, exhibited a slightly lower performance to remove metal ions from wastewater as compared to commercial activated carbons.

It is worth noticing that lala clam shell, and activated carbon samples derived from olive tree wood, coconut shell and bamboo reduced Cu(II) concentration in the wastewater from 2.90 mg/L to 0.18 mg/L, 0.15 mg/L, 0.14 mg/L and 0.16 mg/L, respectively. This value fulfills in particular the maximum limit introduced for the battery manufacturing wastewater under the Malaysian Environmental Quality Act 1974 which is 0.20 mg/L for Cu in industrial wastewater to be discharged into inland surface water (Department of Environment Malaysia (DOE), 1974).

Although lala clam shell has the smallest specific surface area of 2.09 m^2/g as compared to olive tree wood activated carbon (1176 m^2/g), coconut shell activated carbon (1244 m^2/g) and bamboo activated carbon (1460 m^2/g), its adsorption capacity was comparable to that of commercial activated carbons. It is clear that the performance of an adsorbent is not solely dependent on one single aspect.

4. Conclusions

The results of the present study highlight the feasibility of lala clam shell as an eco-friendly adsorbent for Cd(II), Cu(II) and Pb(II) ions. The interaction of metal ions with lala clam shells was studied using several analytical instruments. Major findings suggest that the carbonate (CO_3^{2-}) group served as an important adsorption site of lala clam shell, which was able to bind metal ions during the interaction. The removal percentage of metal ion from battery manufacturing wastewater was in the order of Cu(II) (93.79 to 95.17%) > Pb(II) (81.93 to 91.79%) > Cd(II) (63.80 to 73.01%). HCl and EDTA were able to regenerate lala clam shell at the rate of more than 40%, suggesting a great potential for reusability. The utilization of clam shell wastes as adsorbents for water treatment is not limited to Libya, Malaysia and Indonesia, instead it is applicable to any country where similar wastes are available. Fishery waste-based materials are abundantly available worldwide. The application of fishery waste-based materials which are abundant around the globe for remediation of contaminated water will not only reduce the operational treatment cost particularly in developing countries, but it will make help a greener environment as well.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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