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Performance of cabbage and cauliflower wastes for heavy metals removal

M.A. Hossain, H.H. Ngo*, W.S. Guo, T.V. Nguyen, S. Vigneswaran

School of Civil and Environmental Engineering, Centre for Technology in Water and Wastewater,
University of Technology Sydney, Broadway, Sydney, NSW 2007, Australia
Tel. +61 2 9514 2745/1693; Fax: +61 2 9514 2633; email: h.ngo@uts.edu.au

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ABSTRACT

From this study, the cabbage and cauliflower, a well-known agro-waste were used as biosorbents for removing toxic lead(II) and cadmium(II) from water. A batch of experiments for both biosorbents indicated that the lead(II) and cadmium(II) sorption depended on pH (5.0–6.5), doses of biosorbents (3–8 g/L) and contact time (15–45 min). The adsorption processes were fast, and equilibrium time was reached at 45 and 15 min for lead(II) and 45 and 30 min for cadmium(II) adsorption onto cabbage and cauliflower biosorbents, respectively. Both biosorbents showed higher preferences for lead(II) than cadmium(II) towards adsorption from a binary solution. Langmuir model was the best-predicted model, but three-parameter models (Redlich-Peterson, Koble Corrigan, Khan and SIPS) were shown good fitness with equilibrium data, and the adsorption coefficients indicate favourable adsorption. The maximum monolayer capacities for lead(II) were 60.57 and 47.63 mg/g onto cabbage and cauliflower biosorbents, respectively, which is higher than cadmium(II) adsorption (20.57 and 21.32 mg/g). Adsorption kinetic was multi-order and steps as it is followed the pseudo-second order and Avrami model. As a low-cost adsorbent, cabbage and cauliflower biosorbents could be preferable for the removal of heavy metals from water and wastewaters.

Keywords: Cabbage wastes; Cauliflower wastes; Adsorption; Lead(II) and cadmium(II) removals

1. Introduction

Presently, heavy metal pollution is one of the most severe environmental issues and has become a matter of environmental concern among the environmental researchers [1,2]. Lead, copper, cadmium, zinc, nickel, etc. are the most common heavy metals found in industrial wastewater [3]. The key sources of adding those heavy metals to the water and wastewater are the effluents of mining, tannery, jewellery, chemical, metallurgical, electrical, and electronics industries in the industrial nations, and also arts and crafts industries in developing countries [4]. These metals

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*Corresponding author.

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ions and its derivatives are non-biodegradable, and some are remained long time in toxic forms in the environment and creates toxicity to living organisms [5]. Among the heavy metals, lead and cadmium are very toxic and fall under the US-EPA prescribed group of carcinogen. It could damage the nervous, reproductive, and skeletal systems and the kidney of human and could even cause cancers [6]. It has also negative effect on the life of marine's fauna and flora [7]. Remediation of adverse effects on living beings and decontamination of lead and cadmium from water and wastewater have demanded intensive research for finding a sustainable solution. Even though conventional methods are used for the removal of lead and cadmium, such as chemical ion exchange, precipitation, filtration, electrolysis, extraction, evaporation, reverse osmosis and adsorption [8–10], but those methods are restricted by applied techniques or financial factors [8]. Adsorption removal of metals is also an emerging technology in the recent times which is used different biosorbents. The conventional biosorbents are not economically suitable enough for the removal of heavy metals from water and wastewater. Generally, activated carbon is used for the removal of metals, which poses high metal adsorption capacity but expensive and difficult to recover after uses. Therefore, a growing research interest has been developed in search of low-cost alternatives to these biosorbents.

Biosorption of heavy metals from aqueous solution is a potential technology for the treatment of water and wastewater [11]. Biosorbents produced from suitable bio-materials could be used for the effective removal and recovery of heavy metals from water and wastewater. The key benefits of the biosorption methods are its effectiveness in dropping the metals concentration to considerable low levels from water and its easy availability and low costs. Biosorbents are particularly appropriate for the treatment of water and wastewater containing dissolve metal ions and contains low concentration. Apart from the profound benefits, the restrictions of the technology are included that mass-scale production of effective biosorbent materials has not been recognised and restricted to the practical lab applications. In addition to this, it could add organic load to the water and create anoxic condition in water. Recently, agricultural waste materials and biomass for the removal of metal ions have been explored [12,13]. By-products or wastes from large-scale agro-production are attracting interest from researchers for using to remove heavy metals from water and wastewater [14,15]. A wide variety of agricultural waste materials such as modified palm oil empty fruit branch [16], meranti sawdust [7], bagasse fly ash [12], rubber tree leaf powder [17], *Saraca indica* leaf powder [18], tree fern [19], ligin from woods [20], corncobs [21], moss peat [22] and activated carbon prepared from apricot stone [23] and coconut shell [24], etc. are developed and used for lead removal from water as low-cost alternatives to expensive biosorbents.

Cabbage and cauliflower (*brassica oleracea*) are the commonly used vegetables all over the world. From farms to dining tables, travelling this path huge amount of agro, market and kitchen wastes are produced by these two vegetables. On an average, 30–50% of wastes produce from cabbages and cauliflowers as stems and leaves while process for selling in farm and in markets and for the process of cooking in kitchen [25,26]. Twenty million tonnes of food wastes produce each year in Australia, and 10% of food waste is recycled and the other 90% is sent to landfill [27]. Cabbage and cauliflower wastes contain more water and therefore readily decompose and create unpleasant environmental consequences [28]. This research aims to produce biosorbents from cabbage and cauliflower wastes and used for lead(II) and cadmium(II) removal from water through a detailed experimental study on characterisation of the biosorbents, evaluation and comparison of the lead(II) and cadmium(II) uptake capacities.

2. Materials and methods

2.1. Materials

2.1.1. Biosorbents preparation

The cabbage and cauliflower wastes were collected from local fruits and vegetable market (Campsie Vegetables Worlds, Campsie, NSW, Australia). Collected wastes were chopped into small pieces (<5 mm) and washed three times with tap and distilled water for removing dirt. The washed wastes were dried in air and transferred to oven for drying at 102˚C for 24 h. The oven-dried wastes were grounded into powder with coffee grinder and kept in air-tight bottle and used for experiments.

2.1.2. Stock solutions

The stock solutions (1,000 mg/L) of lead(II) and cadmium(II) were prepared by dissolving 2.744 and 1.5985 g of the $Cd(NO_3)_2$ and $Pb(NO_3)_2$, in 1 L milli-Q water, respectively. The working solutions were prepared with diluting the above stock solution and used throughout the experiment.

2.2. Methods

2.2.1. Characterisation of biosorbents

BET surface areas of cabbage and cauliflower wastes were measured by Micrometric Gemini 2360, UK. Surface morphologies of cabbage and cauliflower wastes were studied by JEOL (JSM-35CF, UK) scanning electron microscope (SEM). Fourier transform infrared (SHIMADZU FTIR 8400S, Kyoto, Japan) analysis was carried out on cabbage and cauliflower wastes to determine the surface functional groups, and the spectra were recorded.

2.2.2. Effect of pH

Hundred millilitres of water with pre-set lead(II) and cadmium(II) concentrations (10 mg/L) and adjusted pH (pH from 2.0 to 10.0) were transferred into a 150-mL Erlenmeyer flask. The cabbage and cauliflower wastes' powder (0.5 g) was added to the water and shaking at 120 rpm. After 3 h, the water was filtered, and metals concentration in the water was determined by atomic adsorption spectroscopy (AAS) (Contra®AA 300, Analytikjena, Germany).

2.2.3. Effect of contact time and kinetics

Kinetic experiments were performed in order to determine the contact time required to attain the equilibrium of biosorption. One litre of water with 50 mg/L initial lead(II) and cadmium(II) concentrations were prepared in two 1-L beakers and mixed with 5 g/L of cabbage and cauliflower wastes, separately. The biosorption process was carried out in a stirrer at 120 rpm and room temperature. Samples were taken and filtered for the analysis of lead(II) and cadmium(II) concentration at predefined time intervals. The process was continued till three hours. The lead(II) and cadmium(II) concentration retained in the biosorbent phase ($q_{t,}$ mg/g) was calculated by the following expression:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t are the initial and concentrations of the lead(II) or cadmium(II) at t time in the water (mg/L), V is the water volume (l), and m is the mass of used biosorbent (g).

2.2.4. Effect of doses

Effect of doses (g) of cabbage and cauliflower wastes on lead(II) and cadmium(II) adsorption were conducted at an initial lead(II) and cadmium(II) of 10 mg/L at room temperature, while the doses was varied from 0.1, 0.25, 0.5, 1, 2, 5, 7.5 and 10 g/L.

2.2.5. Competitive uptake of metal ions

To ascertain whether there was any competition between the lead(II) and cadmium(II) ions for uptake by a particular biosorbent (cabbage or cauliflower wastes), adsorption on dual metal ion(II) was used as the metal ions and used for both biosorbents. These experiments were conducted according to the standard adsorption methodology described earlier. The abilities of the biosorbents to adsorb one metal (Pb or Cd) were compared with the adsorption of other metal (Cd or Pb) where two metals were present in the same solution. The concentrations of each metal ion in the solutions collected after filtration and were determined by AAS.

2.2.6. Desorption experiments

To explore the prospect of repeated use of the cabbage and cauliflower wastes, desorption experiments were performed. After biosorption experiments, the lead(II) and cadmium(II)-loaded biosorbents were washed and transferred to 100 mL of 8 types of eluents namely tape water, milli-Q water, distilled water, 0.1 N H_2SO_4, 0.1 N HCl, 0.1 N HNO_3, 0.1 N NaOH and 0.1 N CH_3COOH. The 100 mL samples were agitated at 120 rpm at room temperature for 3 h. Samples were then filtered with Whatman™ GF/C-47 mm ϕ circle (GE Healthcare, Buckinghamshire, UK) filter paper, and the concentrations of metal ions desorbed in the filtrate were determined. The filtered biosorbent was washed repeatedly with Milli-Q water to remove any residual desorbing solution and added into metal containing water for the next adsorption cycle. The regeneration efficiency was calculated as follows:

$$\text{Metal desorbed efficiency (\%)} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100$$

2.2.7. Equilibrium experiments

The equilibrium of biosorption experiments was carried out in the batch mode at room temperature. Water of 100 mL with lead(II) or cadmium (II) (1–500 mg/L) ions was transferred into 150 mL Erlenmeyer flask; and 0.5 g powder of cabbage or cauliflower wastes was added and put in shaker at 120 rpm. After 3 h, the water was filtered, and lead(II) or cadmium(II) concentration in the filtrate was determined. Adsorption capacities (q_e) were calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e, is the equilibrium adsorption capacity (mg/g); C_o and C_e, the initial and equilibrium lead/cadmium concentrations in the water (mg/L), respectively; V, volume of used solution (L); and m, the mass of used biosorbent (g).

2.3. Data analysis and models fitness

The equilibrium data are used to fit with Langmuir, Freundlich, SIPS, Redlich-Peterson, Koble Corrigan and Khan Isotherm models. All model's parameters were evaluated and optimised by non-linear regression using by MATLAB® (R2010b). The evaluation of fitness of the model equations with experimental data requires an error function with optimisation [29]. The fitness was signified by the coefficient of determination (R^2), non-linear error functions: the residual root mean square error (RMSE) and the chi-square test (χ^2). The standard equations are as follows:

$$R^2 = \frac{1 - \sum_{n=1}^{n} (q_{e.n} - q_{m.n})^2}{\sum_{n=1}^{n} (q_{e.n} - \overline{q_{e.n}})^2} \tag{3}$$

$$\text{RMSE} = \sqrt{\frac{1}{n-1}\sum_{n=1}^{n} (q_{e.n} - q_{m.n})^2} \tag{4}$$

$$\chi^2 = \sum_{n=1}^{n} \frac{(q_{e.n} - \mathrm{q}_{m.n})^2}{q_{e.n}} \tag{5}$$

where q_e is the equilibrium sorption capacity, q_m is the prediction from the isotherm model for corresponding to C_e and n is the number of observations. The small values of RMSE and χ^2 indicate the better model fitting and the similarity of model with the experimental data, respectively [30].

The kinetics data were used to fit with the pseudo-first-order, pseudo-second-order, Elovich and Avrami models. The parameters are optimised by non-linear analyses. Along with the coefficient of determination (R^2), the degree of fitness of kinetics models are judged by two non-linear errors: the normalised standard deviation (NSD) and average relative error (ARE). The equations are defined as follows :

$$\text{NSD} = 100 \times \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left[\frac{q_{t.e} - q_{t.m}}{q_{t.e}}\right]_i^2} \tag{6}$$

$$\text{ARE} = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{q_{t.e} - q_{t.m}}{q_{t.e}}\right]_i \tag{7}$$

where $q_{t.e}$ and $q_{t.m}$ (mg/g) are experimental (e) and model (m) predicted amount of metal (Pb or Cd) adsorbed onto cabbage or cauliflower wastes at time t and N is the number of observations made. The smaller values of NSD and ARE would indicate the better fitness of the model.

3. Results and discussion

3.1. Characterisation of biosorbent

The surface structures of biosorbents produced from cabbage and cauliflower wastes were analysed by SEM and shown in Fig. 1. Generally, the micro-graphs (Fig. 1) revealed that both biosorbents contained irregular shaped particles. In lower magnification, the heterogeneous structures are noticed from both Fig. 1(a) and (c). From higher magnification (10 k), surface of the particles (both biosorbents) is seemed to be constructed with uneven, asymmetric steps and pores (Fig. 1(b) and (d)). In comparison, cabbage biosorbent seemed to be contained more irregular shaped particle than cauliflower biosorbent. As the irregular shapes of particles holds more internal biding or uptakes places, it might help for more adsorption of lead (II) or cadmium(II) than others. The BET surface area of cabbage biosorbent was 1.0265 m² /g which is higher than cauliflower biosorbent (0.891 m² /g). The specific surface areas for both biosorbents are lower than the biosorbents and activated carbons produced from agro-wastes (Table 3).

Functional groups are the influential parameters for any biosorbents in context of chemisorption of metals. Bond likes carbon-oxygen and carbon bonds might attract and stimulate the metals adsorption [31]. FTIR spectra for cabbage and cauliflower biosorbents were determined for recognising the functional groups that could be responsible for metals adsorption, and the spectra are shown in Fig. 2. Astonishingly similar functional groups are found from both adsorbents that are also similar to the other biomaterials [32]. The major found functional groups were O–H stretch-free hydroxyl for alcohols/phenols (3,624.54 cm^{-1}), O–H

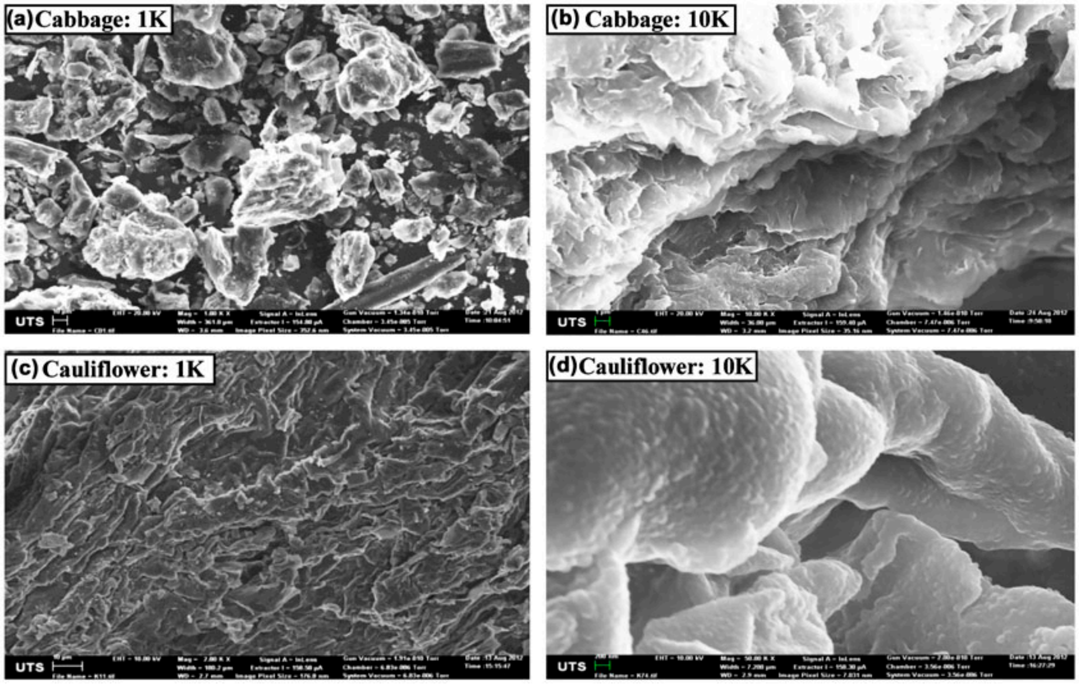

Fig. 1. Micro-graphs of cabbage and cauliflower wastes taken by SEM (1X, 10X).

stretch for carboxylic acids (between 3,300 and 2,500 cm^{-1}), C–N stretch for aliphatic amines (1,024.25 cm^{-1}), C–O stretch for alcohols/carboxylic acids/esters/ethers (between 1,320 and 1,000 cm^{-1}), =C–H bend for alkanes (between 1,000 and 650 cm^{-1}) and C–H "OOP" for aromatics (817.85 cm^{-1}). Among the functional groups, hydroxyl and carboxyl groups could bind heavy metal ions with adsorbent [33].

3.2. Effects of experimental conditions

3.2.1. pH

The pH of the aqueous solution is an important factor that affects the adsorption of the metal at the adsorbent water interfaces. It also affects the surface charge of biosorbents, ionisation and speciation of metals [34]. To determine the pH effect on adsorption capacity of materials, solutions were prepared at different pH levels (2–10 pH) before adding cabbage and cauliflower biosorbents. The effect of pH on metals Pb(II) and Cd(II)) adsorption was determined in batch experiments, and the results are presented in Fig. 3(a)–(d). The adsorption values were increased with increasing pH values for both metals. The percents removal of Cd(II) increases from 40.55 to 54.32% for cabbage biosorbent (Fig. 3(c)) and increases from 31.94 to 81.31% for cauliflower biosorbent (Fig. 3(d)) with an increase in pH of solution from 2 to 7.5. Also, the adsorption removal of Pb(II) were increased from 80.79 to 98.85% for cabbage biosorbent (Fig. 3(a)) and 93.34 to 96.06% for cauliflower biosorbent (Fig. 3(b)). At lower pH, the amount of adsorptions was low as the binding sites of the adsorbent was more protonated and competitive adsorption occurred between H^+ protons and free metal ions towards the binding sites [35]. Therefore, H^+ ions react with anionic functional groups on the surface of the adsorbent and result in occupancy of the number of binding sites favourable for the adsorption of metal ions. For avoiding precipitation of metals, high pH values were not preferable [34]. Wide range of pH variation in context of removal is found in cauliflower than cabbage biosorbents. The optimum pH was chosen as 6–7.5 for this experiment for both metals.

3.2.2. Contact time

The effect of contact time on adsorption capacity was studied using a constant concentration of metal ions (50 mg/L) solution at room temperature. The adsorption of Pb(II) and Cd(II) by cabbage and cauliflower biosorbents were studied by taking 0.5 g adsorbents with 1 L of metal solutions in beaker. The water was agitated by rotary shafts, and samples were taken at different time intervals. The results are given in Fig. 4. In the first stage (until 10 min), biosorption

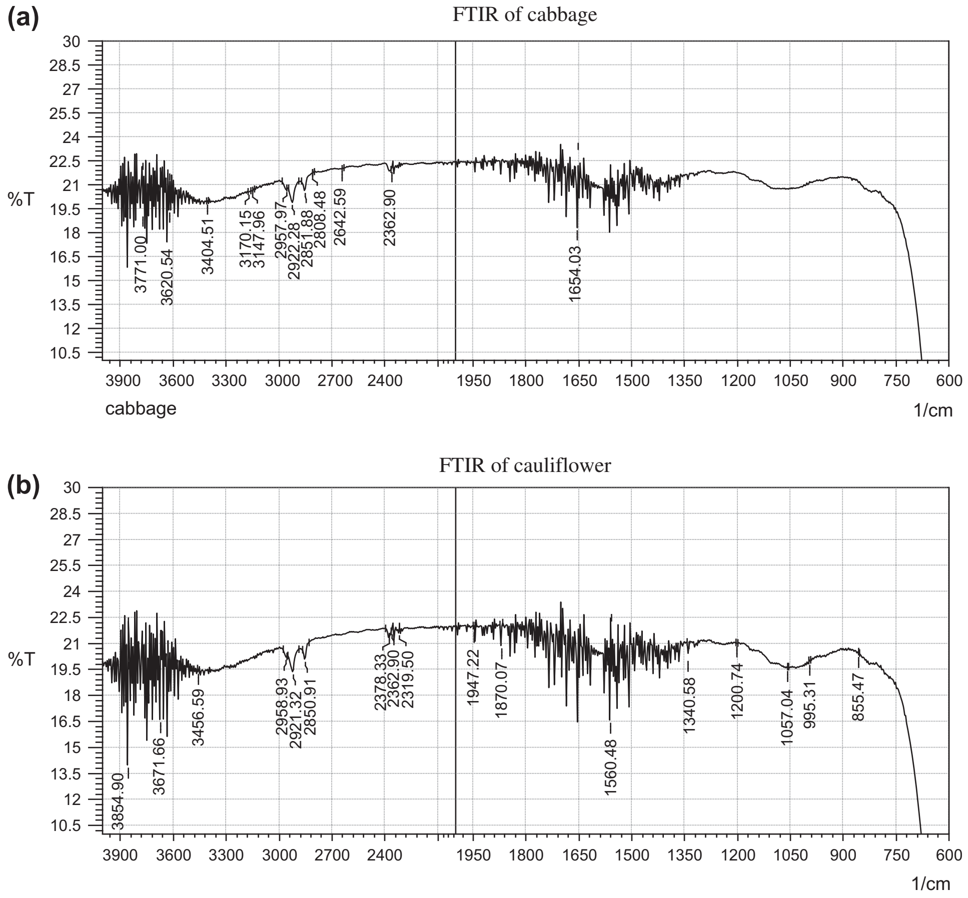

Fig. 2. FTIR spectra of cabbage and cauliflower wastes.

process was rapid, and during this period, a large amount of lead(II) and cadmium(II) were removed from water (Fig. 4). The second stage was much slower than previous and reached in equilibrium after 45, 15, 45, and 30 min for lead(II) and cadmium(II) adsorption on cabbage and cauliflower biosorbents, respectively. The cadmium adsorption reached in equilibrium faster than the lead adsorption on both adsorbents. This rapid kinetics has an important practical potentiality in developing of metal biosorption system with cabbage and cauliflower wastes.

3.2.3. Doses

The dose (adsorbent amount) is also vital parameter to obtain optimum adsorption of metal ion. The adsorption of metals was studied in the relation to the amount of adsorbent. The results of the dependence of Pb(II) and Cd(II) adsorption on the amount of cabbage and cauliflower biosorbents are shown in Fig. 5. For this purpose, the concentration of metals and stirring time were fixed at 10 mg/L and 120 min, respectively, while the amount of cabbage and cauliflower biosorbent were varied from 0.1 to 10 g/L. The percentage adsorption values were increased (99.78 and 97.62%) with increasing amount of adsorbents up to 5 and 3 g/L doses for Pb(II) onto cabbage and cauliflower biosorbents. It was increased up to 6 and 8 g/L doses for Cd(II) onto both adsorbents. These results were anticipated because for fixed metal ions, increasing doses provides greater surface area and binding sites [36]. It is readily understood that the number of available sorption sites increases by increasing adsorbent amount. Though a wide variation of doses posed higher removal for both biosorbent, optimum adsorbent was chosen as 0.5 g for both metals to make simple of the experiments.

3.3. Competitive uptake of Pb and Cd in a binary metal solution

The percents removals of Pb(II) and Cd(II) in a binary metal solution are shown in Fig. 6. In the competitive adsorption, Pb(II) ion is dominated for

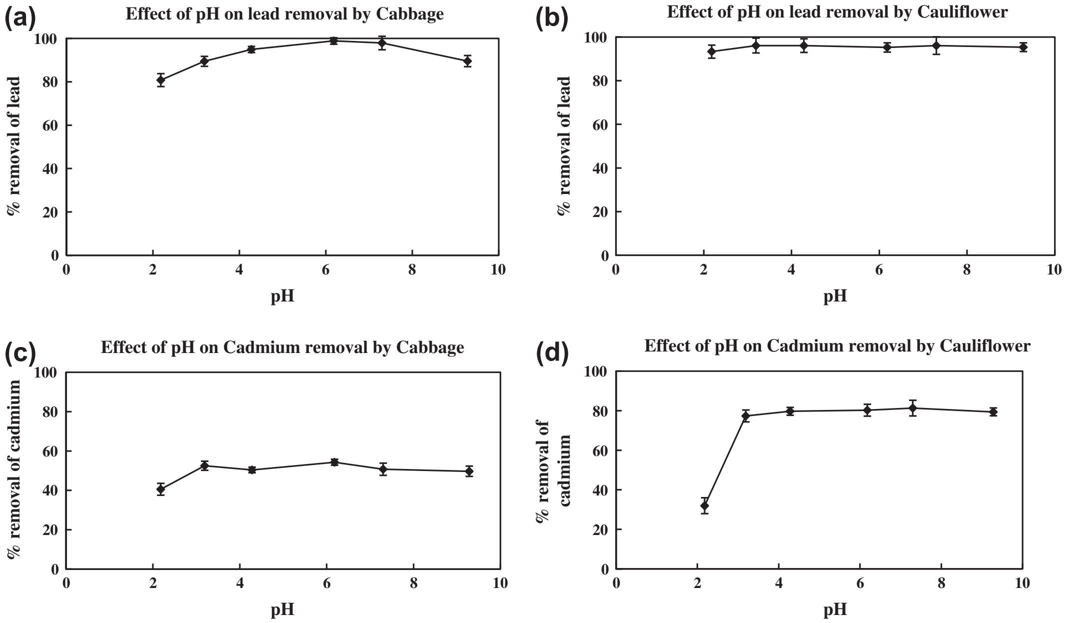

Fig. 3. Effects of changes of pH on the removals of lead(II) and cadmium(II) from water by the biosorbents produced from cabbage and cauliflower wastes.

binding with the both cabbage and cauliflower biosorbent. There were no significant changes found for Pb(II) removals by cabbage biosorbent in the both cadmium (Fig. 6(a)) and lead-constant (Fig. 6(b)) systems. Among the two metals, Pb(II) adsorptions were almost remained un-interrupted in both system, because Pb(II) removals were 94.92 and 91.72%, respectively. It is revealed from this competitive adsorption that Pb(II) has got enhanced preferences by cabbage biosorbent. Similar trend were observed from Pb(II) and Cd(II) ions adsorption onto cauliflower biosorbent (Fig. 6(c) and (d). Pb(II) ions also got high preferences by cauliflower biosorbent for cadmium (Fig. 6(c) and lead-constant (Fig. 6(d)) systems, because Pb(II) removals were 96.34 and 96.26%, respectively. The binding capacity of individual ion is different from single adsorption system though the adsorption depends on a number of factors such as ionic potential, ionic radius, chemical properties and hydrolysis [37].

3.4. Desorption studies

The regeneration of biosorbents is a crucial step to reuse and recapture of valuable metals. It is also involved for reducing the operating cost for any type of water treatment system. Regeneration experiments were conducted with eight eluents. The batch results of adsorption with eight eluents are shown in Fig. 7. Among the eluent, 0.1 N H_2SO_4 eluent showed higher efficiency for lead(II) and cadmium(II) from both cabbage adsorption and cauliflower-desorption. Marginal higher lead(II) recoveries (86.67 and 85.67%) were found from cabbage and cauliflower biosorbents than cadmium(II) recoveries (82.34 and 79.74%). Adsorbed Pb(II) or Cd(II) onto biosorbent might be replaced by H^+ released from acidic aqueous systems [38].

3.5. Biosorption kinetics of Pb(II) and Cd(II)

The kinetics parameters are calculated from the adsorption data of lead (II) and cadmium (II) onto the surfaces of cabbage and cauliflower biosorbents with elapsed time. These parameters represent the characteristics of biomaterials and indicate the nature of chemical/physical adsorption and cation-exchange processes [39]. Four kinetics models namely pseudo-first-order, pseudo-second-order, Elovich and Avrami models,were used to describe the kinetics of Pb(II) and Cd(II) adsorption onto both biosorbents. The models' parameters were optimised by non-linear analyses by Excel spread sheet with 'solver' add-in; and errors were also calculated and compared. The experimental as well as predicted parameters from four models are shown in Fig. 8 and Table 1. On the whole, the kinetics data were well fitted with the used models (R^2: 0.967–0.999) for both lead(II) and cadmium(II) adsorption onto both biosorbents.

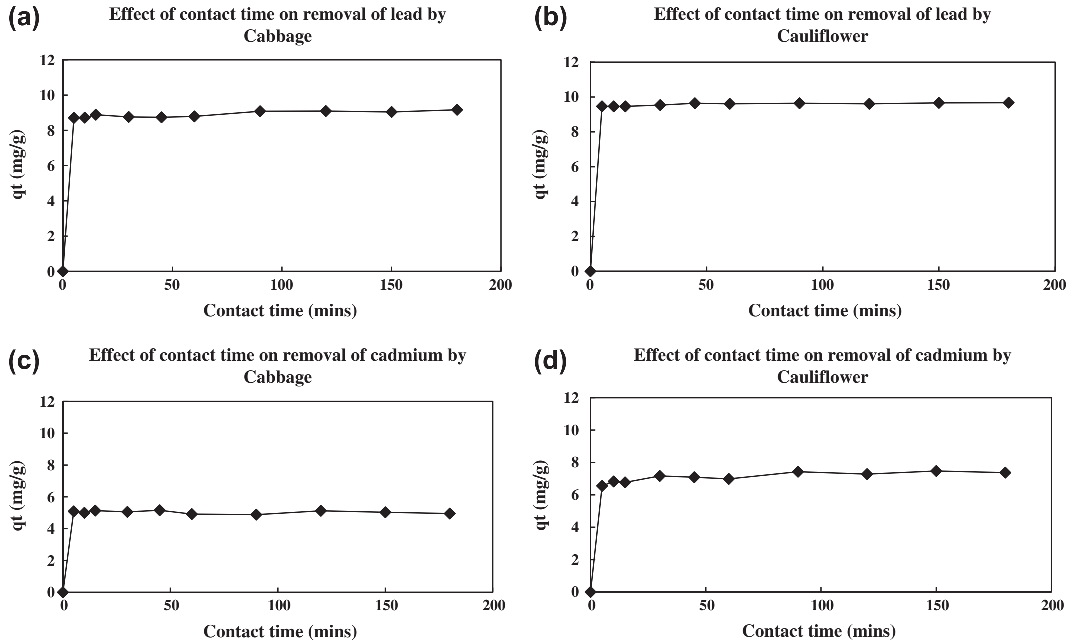

Fig. 4. Effects of contact times on the removals of lead(II) and cadmium(II) from water by the biosorbents produced from cabbage and cauliflower wastes.

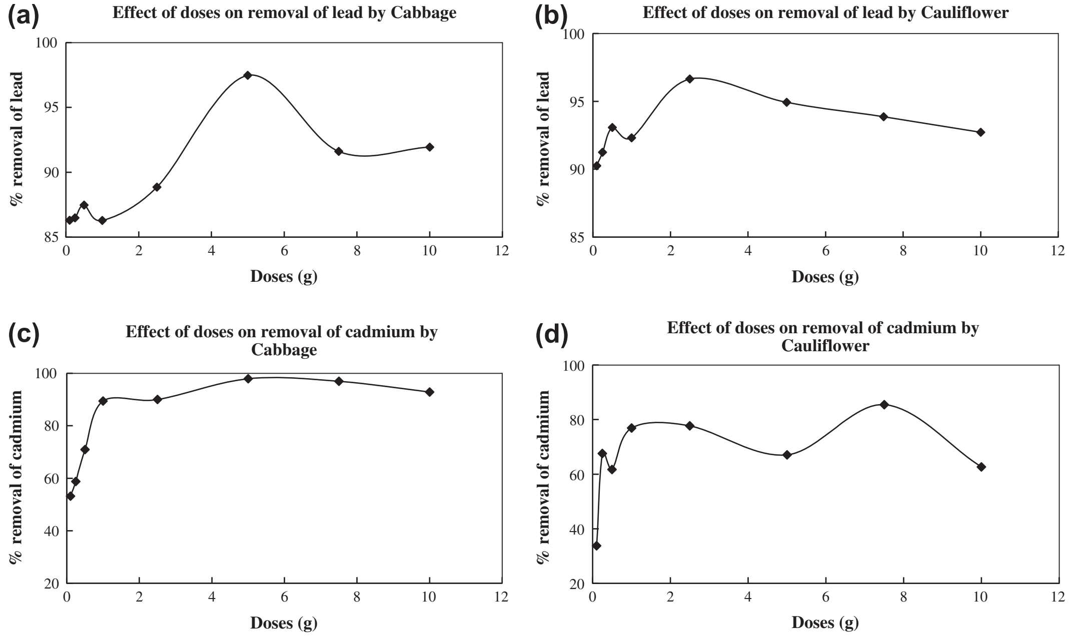

Fig. 5. Effects of different doses on the removals of lead(II) and cadmium(II) from water by the biosorbents produced from cabbage and cauliflower wastes.

3.5.1. Order kinetics

The pseudo-first-order kinetics expression is known as Lagergren equation [40] that is derived from solid adsorption capacity and the non-linear form is generally expressed as follows:

$$q_{\mathrm{t}} = q_{\mathrm{e}} - q_{\mathrm{e}} e^{(-k_1 t)} \tag{8}$$

where k_1, constant of pseudo-first-order adsorption (min^{-1}); q_e, adsorption capacity at equilibrium (mg/g) and q_t, the adsorption capacity (mg/g) at time t(min).

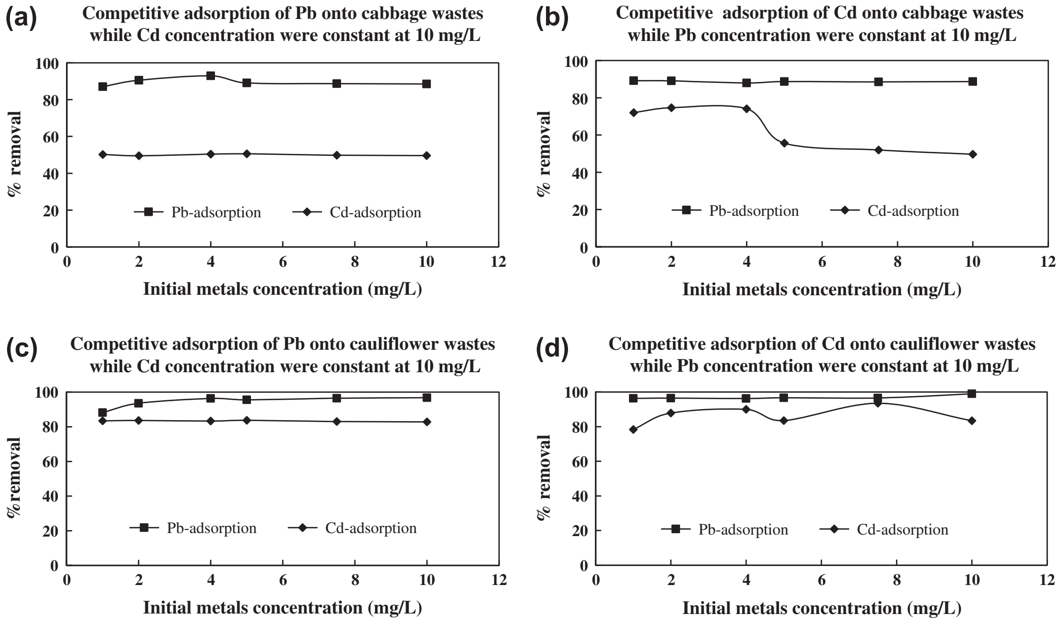

Fig. 6. Competitive adsorption of lead(II) and cadmium(II) from binary solution by cabbage and cauliflower biosorbent.

The second-order mechanism of metals adsorption is expressed by pseudo-second-order kinetic and the non-linear form of the equation is as follows [41]:

$$q_t = \frac{k_2 q_e^2 t}{(1 + q_e k_2 t)} \tag{9}$$

where k_2, rate constant of pseudo-second-order adsorption (g/(mg min)) and q_e, adsorption capacity at equilibrium (mg/g). The initial adsorption rate of metal was calculated by the following equation [41]:

$$h = k_2 q_e^2 \tag{10}$$

Among the two order kinetics the experimental data (both lead and cadmium adsorption) showed better fitness with pseudo-second-order model than the pseudo-first-order model for both cabbage and cauliflower biosorbents, which implies that Pb(II) and Cd(II) adsorption is a rate-controlling multi-step and might be chemisorption [42]. Higher R^2 (0.994–1.00) values from experimental data and prediction (Table 1) of pseudo-second-order model also reinforced the proposition and argument. Experimental and predicted values of equilibrium adsorption capacities (q_e) showed better consistencies with the pseudo-second-order model than the pseudo-first-order model for both biosorbent and metals. The Pb (II) adsorption capacities are found 8.983 and 9.628 mg/g from prediction of pseudo-second-order model, while it are 8.738 and 9.457 mg/g for experimental data, for cabbage and cauliflower biosorbents, respectively. On the other hand, prediction for Cd(II) are 5.077 and 7.311 mg/g while 5.152 and 7.164 mg/g for experimental data for cabbage and cauliflower biosorbents, respectively. Significantly low NSD (1.599 and 0.554 for lead and 2.537 and 2.148 for cadmium) and small ARE (0.025 and 0.003 for lead and 0.043 and 0.040 for cadmium) values were also obtained from pseudo-second order for cabbageand cauliflower biosorbents, which further advocate the chemisorption process was the rate-controlling step [42].

3.5.2. Multi-step kinetics

The Elovich equation is derived from the based on a general second-order reaction mechanism for heterogeneous adsorption processes [43]. It assumes that the active sites of the biosorbent are heterogeneous [44] and therefore exhibit different activation energies for chemisorption [45]. The Elovich model is presented by the following equation [46]:

$$q_t = \beta \times \ln(\alpha\beta t) \tag{11}$$

where α is the initial adsorption rate (mg/g/min) and β is desorption constant (g/mg). Teng and Hsieh [43] proposed that constant α is related to the rate of chemisorption, and β is related to the surface coverage. This model provides the best fit with the experimental data as the R^2 values lies in-between 0.967 and 1.00 (Table 1) for both biosorbents and

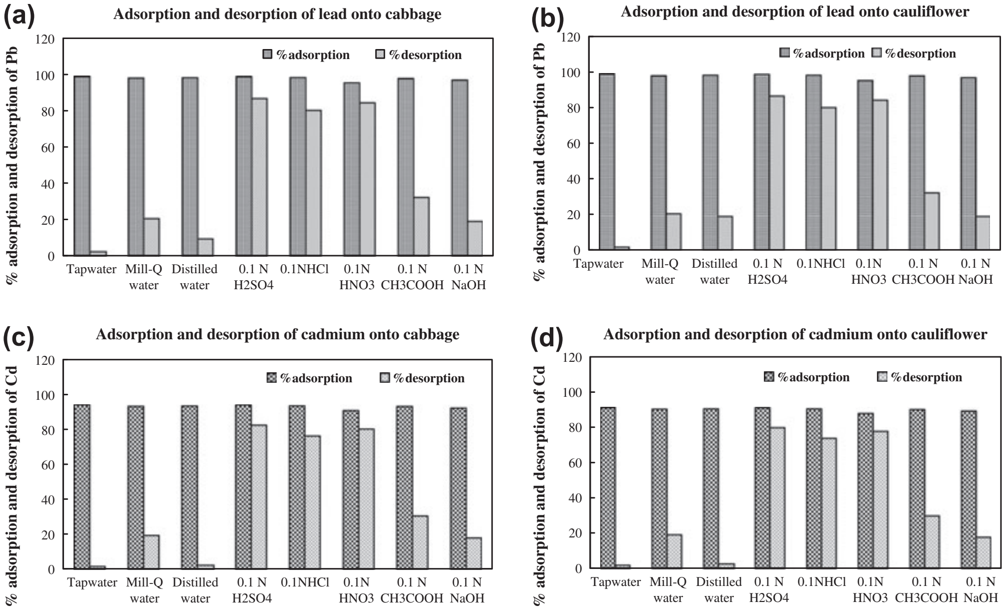

Fig. 7. Adsorption and desorption of lead(II) and cadmium(II) onto cabbage and cauliflower biosorbent.

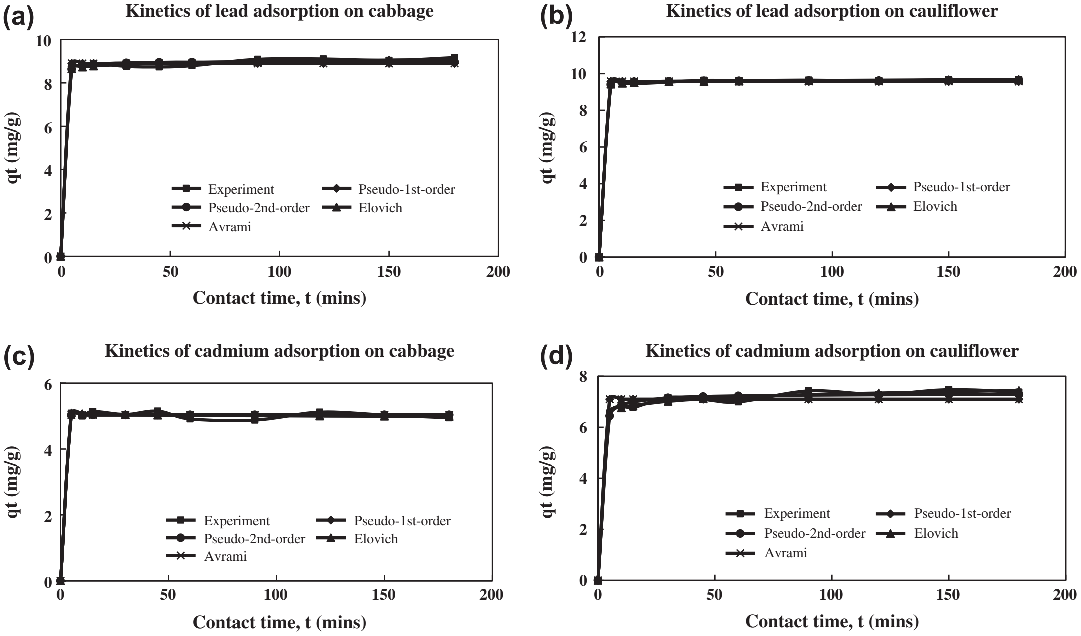

Fig. 8. Kinetics modelling of adsorption of lead(II) and cadmium(II) onto cabbage and cauliflower wastes doses (C_o: 50 mg/L; d: 0.5 g; t: 3 h: pH: 5–6.5; rpm: 120; T: room temp).

metals. The successful applications of the Elovich equation to describe the kinetics implies that Pb(II) and Cd(II) adsorption was on heterogeneous surfaces [44,45] of both cabbage and cauliflower biosorbents. In fact, the SEM and FTIR analysis of the cabbage and cauliflower wastes also showed the presence of heterogeneous surfaces with different functional groups. A higher value of α (8.455 and 9.320 for lead(II) onto cabbage biosorbent; and 5.137 and 6.211 for cadmium (II) onto cauliflower biosorbent) and low values of β (0.118 and 0.068 for lead(II) onto cabbage biosorbent; and 0.028 and 0.237 for cadmium(II) onto cauliflower biosorbent) also certified that the adsorption mechanism was chemisorptions [47].

Table 1
Kinetics modelling of lead(II) and cadmium(II) adsorption onto cabbage and cauliflower wastes

Kinetic models	Parameters	Lead(II) adsorption		Cadmium(II) adsorption	
		Cabbage	Cauliflower	Cabbage	Cauliflower
Experimental	q_e (mg/g)	8.738	9.457	5.152	7.164
	Equili. time, t (min)	45	15	45	30
1. Pseudo-first-order	q_e (mg/g)	8.921	9.587	5.035	7.171
$q_t = q_e - q_e e^{(-k_1 t)}$	k_1 (l/h)	0.741	0.859	1.000	0.471
	R^2	0.997	0.999	0.996	0.990
	NSD	1.856	0.821	1.983	3.285
	ARE	0.034	0.007	0.036	0.096
2. Pseudo-second-order	q_e (g/mg min)	8.983	9.628	5.077	7.311
$q_t = \frac{k_2 q_e^2 t}{(1+q_e k_2 t)}$	k_2 (1/h)	0.997	0.851	1.000	0.202
	R^2	43.824	1.00	0.994	0.996
	$h = k_2 q_e^2$(mg/g min)	1.599	78.884	25.779	10.799
	NSD	0.025	0.554	2.537	2.148
	ARE		0.003	0.043	0.040
3. Elovich	α	8.455	9.320	5.137	6.211
$q_t = \beta \ \ln(\alpha\beta t)$	β	0.118	0.068	0.028	0.237
	R^2	0.991	1.000	0.967	0.975
	NSD	1.201	0.333	1.797	1.527
	ARE	0.014	0.001	0.032	0.024
4. Avrami	q_e (mg/g)	8.899	9.573	5.031	7.096
$q_t = q_e(1 - e^{(-K_{AV} t)^{n_{AV}}})$	K_{AV} (/min)	1.00	3.000	1.000	6.000
	n_{AV}	25.076	10.00	25.076	20.076
	R^2	0.996	0.999	0.996	0.982
	NSD	2.002	0.925	1.928	4.427
	ARE	0.041	0.009	0.036	0.192

The adsorption could also be evaluated using the Avrami exponential function [48] and the equation is follows:

$$q_t = q_e(1 - e^{(-K_{AV} t)^{n_{AV}}}) \qquad (12)$$

where K_{AV} is the Avrami kinetic rate constant (min^{-1}), and n_{AV} is the Avrami exponent (dimensionless), which is related to the interaction of mechanism changes. The Avrami kinetic equation was used to describe the adsorption kinetics of lead(II) and cadmium(II) adsorption onto cabbage and cauliflower biosorbents. The fractionary number (n_{AV}) predicted from adsorption processes were greater than unity ($n_{AV} > 1$) for both metals and biosorbents, which indicates that the reaction order were greater than first order [48]. It could be assumed that Pb(II) and Cd(II) adsorption might followed several order during the processes. The values of equilibrium adsorption capacity (q_e) for both Pb(II) and Cd(II) adsorption processes (8.899 and 9.573 mg/g for lead onto cabbage and 5.031 and 7.096 mg/g for cadmium onto cauliflower biosorbent) were similar to the prediction of pseudo-second-order model (Table 1) and close to experimental values (Table 1). These finding postulated the possible changes occurred on adsorption mechanism during the adsorption processes [49]. Therefore, the adsorption mechanism of Pb(II) and Cd (II) onto cabbage-biosorbent and cauliflower-biosorbent wastes followed multiple kinetic orders [48].

3.6. *Adsorption equilibrium of lead(II) and cadmium (II)*

An equilibrium isotherm denotes the relationship between the amounts of adsorbate (metals) removed from water per unit of mass of biosorbent and equivalent metals concentration in water, at constant temperature and at equilibrium state. Six isotherm models namely two two-parameter: Langmuir and Freundlich models and four three-parameter: SIPS, Redlich-Peterson, Koble-Corrigan and Khan Models were judged with the predictions and equilibrium data obtained from experiments for Pb(II) and Cd(II) adsorption onto cabbage and cauliflower biosorbents. Non-linear regression does the analysis of data on the basis of original form of isotherms' equation and eventually avoids errors. Therefore, non-linear regression (MATLAB-based program) was used to estimate and optimise the parameters. The predicted and experimental parameters are shown in Table 2 and presented in Fig. 9.

3.6.1. Langmuir isotherm

The assumptions of Langmuir isotherm are chemisorptions of metals at a fixed number of well-defined sites, one ion in each site, energetically equivalent sites, and no interaction between the ions [50]: The Langmuir equation is formulated as [51]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{13}$$

where C_e (mg/L) and q_e (mg/g) are the equilibrium concentrations in the liquid and solid phase, respectively. q_m is a Langmuir constant that expresses the maximum metal uptake (mg/g) and K_L is also a Langmuir constant related to the energy of adsorption and affinity of the biosorbent. The isotherm was found to be well fitted with experimental data for lead(II) and cadmium(II) adsorption onto cabbage and cauliflower biosorbent as it is resulted a good coefficient of determination values (R^2: 0.994–0.996) and small RMSE and χ^2 values. The value of R^2 is higher than the values of Freundlich isotherm and similar to three-parameter models. In all cases (lead(II) and cadmium(II) adsorption onto both biosorbents), the Langmuir equation maintained a better fitness with the experimental data (Fig. 9 and Table 2). The monolayer saturation capacity (q_m) of Pb(II) was found to 60.568 and 47.628 mg/g on cabbage biosorbent while it was 20.568 and 21.317 mg/g on cauliflower biosorbent for Cd(II), respectively. The q_m values are higher for lead(II) adsorption onto the both biosorbent than cadmium(II), which indicates the higher affinity of biosorbent towards lead. These values are similar to the experimental values (Table 2) and comparable with the adsorption capacities of some other biosorbent (Table 3). The negative values of ΔG (Gibbs free energy) for Langmuir isotherm confirmed the process feasibility and the spontaneous nature of the adsorption. The values of K_L are less than unity ($K_L < 1$) for both metals and biosorbents; and indicate the higher affinity [52].

The essential characteristics of Langmuir isotherm can be articulated in terms of a dimensionless constant separation factor, R_L, which is defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{14}$$

The value of R_L indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values were found to vary within a range, 0.021–0.99 and 0.01–0.96 for lead(II) adsorption; and 0.21–0.99 and 0.22–0.99 for cadmium(II) adsorption onto cabbage and cauliflower biosorbents, respectively, for the initial Pb(II) and Cd(II) concentration of 1–500 mg/L. They are in the range of 0–1 and indicate the favourability of Pb(II) and Cd(II) adsorption onto both biosorbent [53] (Table 2).

3.6.2. Freundlich isotherm

The Freundlich isotherm is an exponential equation which assumes that the concentration of adsorbates (metals) on the biosorbent surface increases with the adsorbates concentration. Hypothetically, using this expression, an infinite amount of adsorption can occur [54]. The equation is widely used in heterogeneous systems:

$$q_e = K_F C_e^{1/n} \tag{15}$$

where K_F (l/g) and n are Freundlich constants characteristic of the system, indicating the adsorption capacity and adsorption intensity, respectively. The fitness of data with Freundlich model are low compare to used five models as the R^2 values lies between 0.964 and 0.987 (Table 2) for both Pb(II) and Cd(II) adsorption onto cabbage biosorbent and cauliflower biosorbent, respectively. Lead(II) adsorption onto cabbage t and cauliflower biosorbents were favourable as the magnitude lies between 1 and 3 [55], but the cadmium (II) adsorption was unfavourable as the n values lies greater than 3.

3.6.3. Sips isotherm

This model is derived from combining the Langmuir and Freundlich isotherm and expected to better description of heterogeneous surfaces. At low sorbates (metals) concentrations, it effectively reduces to a Freundlich isotherm, while at high sorbates concentrations, it predicts monolayer characteristics of

Table 2
The prediction of isotherm parameters for the adsorption of lead(II) and cadmium(II) onto cabbage and cauliflower wastes

Isotherm models	Parameters	Lead(II)		Cadmium(II)	
		Cabbage	Cauliflower	Cabbage	Cauliflower
Experimental	q_m(mg/g)	61.267	48.325	22.123	20.879
1. Langmuir	q_m	60.568	47.628	20.568	21.317
$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	K_L	0.021	0.281	0.021	0.020
	R_L	0.21–0.99	0.01–0.96	0.21–0.99	0.22–0.99
	R^2	0.996	0.994	0.996	0.994
	$\Delta^\circ G$	−9.426	−3.089	−9.426	−9.514
	χ^2	2.555	1.122	2.554	1.831
	RMSE	8.219	1.898	8.219	9.853
2. Freundlich	K_F	26.277	21.981	26.277	28.446
$q_e = K_F C_e^{1/n}$	n	1.942	4.999	1.942	2.120
	R^2	0.966	0.987	0.966	0.964
	χ^2	126.962	40.736	126.962	91.078
	RMSE	24.904	8.427	24.904	23.391
3. SIPS	K_s	36.932	19.628	6.931	3.005
$q_e = \frac{K_s C_e^{\beta_s}}{1+\alpha_s C_e^{\beta_s}}$	α_S	0.017	0.311	0.017	0.009
	β_S	1.101	0.898	1.100	1.321
	R^2	0.997	0.995	0.997	0.996
	χ^2	1.485	1.941	1.485	0.039
	RSME	0.996	0.141	0.996	2.318
4. Redlich-Peterson	K_{RP}	8.363	19.487	8.363	6.234
$q_e = \frac{K_{RP} C_e}{1+\alpha_{RP} C_e^{\beta}}$	α_{RP}	0.012	0.343	0.012	0.003
	β	1.085	0.982	1.085	1.294
	R^2	0.997	0.995	0.997	0.997
	χ^2	2.268	1.367	2.268	1.222
	RSME	1.593	0.294	1.593	1.089
5. Koble-Corrigan	A_{KC}	6.908	20.828	6.908	2.932
$q_e = \frac{A_{KC} C_e^p}{1+B_{KC} C_e^p}$	B_{KC}	0.017	0.328	0.017	0.009
	p	1.101	0.861	1.101	1.328
	R^2	0.997	0.996	0.997	0.996
	χ^2	1.474	0.468	1.474	0.029
	RSME	1.012	0.191	1.012	2.359
6. Khan	q_m	69.897	52.271	29.897	38.410
$q_e = \frac{q_m b_k C_e}{(1+b_k C_e)^{a_k}}$	b_k	0.014	0.281	0.014	0.020
	a_k	1.207	1.000	1.207	1.00
	R^2	0.996	0.994	0.996	0.994
	χ^2	2.366	1.122	2.366	1.831
	RSME	1.374	0.382	1.378	0.001

adsorption like Langmuir isotherm. The Sips model takes the following form [56]:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + \alpha_s C_e^{\beta_s}} \tag{16}$$

where q_m is monolayer adsorption capacity (mg/g), β_s is exponent, and α_s is Sips constant related to energy of adsorption. According to the model prediction, the monolayer adsorption capacity values were 36.932 and 19.628 mg/g for lead(II), and 6.932 and 3.003 mg/g for cadmium(II) adsorption onto cabbage and cauliflower

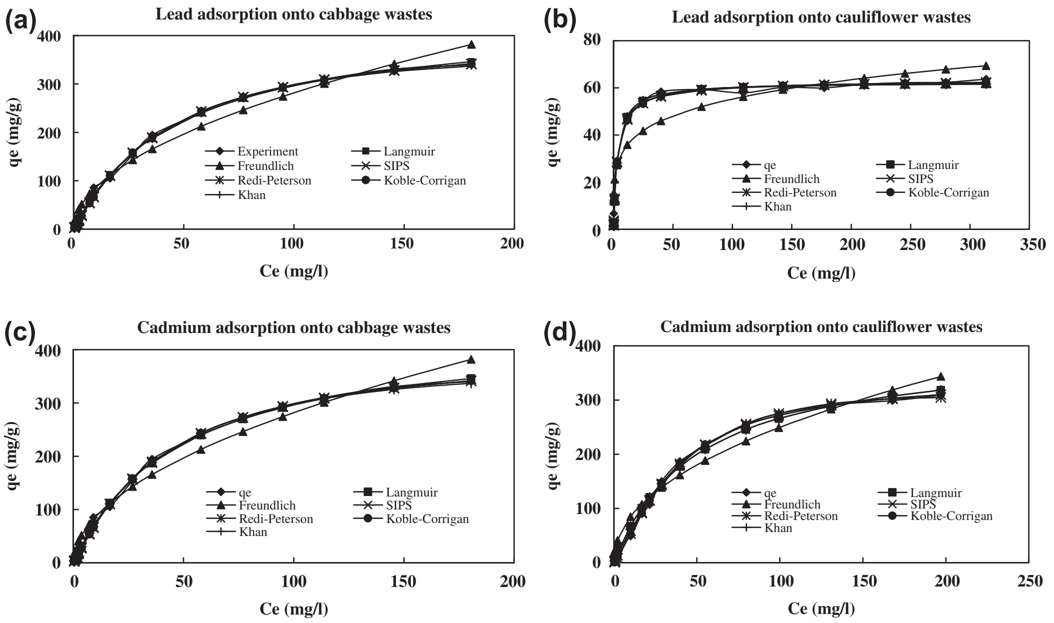

Fig. 9. Isotherm modelling of adsorption of lead(II) and cadmium(II) onto cabbage and cauliflower wastes (C_o: 1–500 mg/L; d: 0.5 g; t: 6 h: pH: 5.0–6.5 non adjusted; rpm: 120; T: 20°C).

biosorbents, respectively (Table 2), which is lower than experimental values and Langmuir prediction (Table 2). The exponent $\beta_s(\cong 1/n)$ values was closer to unity for both biosorbents. It means that Pb(II) and Cd(II) adsorption onto the both biosorbents were similar of Langmuir form rather than that of Freundlich.

3.6.4. Redlich-Peterson isotherm

Redlich and Peterson [57] proposed an empirical equation to represent equilibrium data:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta}} \quad \text{where } \beta \leq 1 \tag{17}$$

where K_{PR} (l/g), α_{PR} (l/mg) and β are Redlich-Peterson isotherm constants that lies between 0 and 1. This equation reduces to a linear isotherm in the case of low surface coverage and to a Langmuir isotherm when $\beta = 1$. Redlich-Peterson isotherm constants for the adsorption of Pb(II) and Cd(II) onto cabbage and cauliflower wastes are shown in Table 2. The isotherm constants, K_{PR} were calculated to be 8.363 and 19.487 for Pb(II) and 8.363 and 6.234 (l/g) for Cd(II) adsorption onto cabbage and cauliflower biosorbents, respectively. The model constant, α_{PR} was calculated to be 0.012 and 0.343 (L/mg) for lead(II) and 0.012 and 0.003 (L/mg) for cadmium(II) adsorption onto cabbage and cauliflower biosorbents, respectively.

3.6.5. Koble-Corrigan isotherm

Koble-Corrigan model is another one of the three-parameter empirical model for representing the equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm type models and is given by:

$$q_e = \frac{A_{KC} C_e^p}{1 + B_{KC} C_e^p} \tag{18}$$

where A_{KC}, B_{KC} and p are the Koble-Corrigan parameters [58]. Examination of the data shows that the Koble–Corrigan isotherm is an appropriate description of the data for Pb(II) and Cd(II) ion adsorption onto cabbage and cauliflower biosorbents. The values of constant p are near unity (Table 2) for both Pb(II) and Cd(II) adsorption onto cabbage biosorbent and cauliflower biosorbent, and it indicates the isotherm is approaching to the Langmuir form.

3.6.6. Khan isotherm

Khan et al. [59] have suggested a generalised isotherm for pure solutions. Khan isotherm is given as:

$$q_e = \frac{q_m b_k C_e}{(1 + b_k C_e)^{a_k}} \tag{19}$$

Table 3
Comparison of performance of lead(II) and cadmium(II) adsorption by cabbage and cauliflower wastes with other bioadsorbent produces from agricultural wastes

Names	Pb q_m (mg/g)	Cd q_m (mg/g)	Temp.(℃)	pH	RPM	Initial Conc. (mg/L)	BET surface area (m^2/g)	Reference
Cabbage wastes	60.57	20.57	Room temp	5–6.5	120	1–500	1.0265	This study
Cauliflower wastes	47.63	21.32	Room temp	5–6.5	120	1–500	0.8905	This study
Spent grain	35.5	17.3	28 ± 2	5.6	150	50–450	NA	[60]
Pinus pinaster bark	3.3	8	–	–	–	10–150	NA	[61]
Rice hulls	11.4	21.4	20	–	100–150	10–100	NA	[62]
Peels of banana	2.18	5.17	250	3–5	100	30–80	22.59	[52]
Pine wood char	4.13	0.34	25	3–5	100	5–100	2.73	[63]
Oak wood char	2.62	0.37	25	3–5	100	5–100	2.04	[63]
Pine bark char	3.00	0.34	25	3–5	100	5–100	1.88	[63]
Oak bark char	13.10	5.40	25	3–5	100	5–100	25.4	[63]
Carbon F-400	30.11	8.00	25	3–5	100	5–100	984	[63]
Sphagnum moss peat	40	5.8	–	–	–	50–750	NA	[64]
Bengal gram husk	49.97	39.99	25 ± 2	5.0	150	10–800	NA	[65]
Mango peel	99.05	68.92	25 ± 2	2–7	100	10–600	NA	[66]

where q_m and b_K is the Khan model constant and a_K is the Khan model exponent. For the results given in Table 2, q_m values were observed to be 69.897 and 52.271 mg/g for lead(II) and 29.897 and 38.410 mg/g for cadmium(II) adsorption on cabbage and cauliflower biosorbents, respectively. These values are similar to the prediction of Langmuir isotherm and experimental values (Table 2). The values of b_K and a_K were near unity which implies the fitness of the model for both metals adsorption onto the both biosorbents.

3.7. Comparison to other biosorbents

The acceptability of biosorbent depends on the metal adsorption capacity, specific surface area, user friendliness, availability and environment friendly applications. The q_m values of the cabbage and cauliflower biosorbents shown in Table 3 are compared with the lead(II) and cadmium(II) adsorption capacities for other adsorbents reported in literature. Generally, the lead(II) and cadmium(II) removal capacities were higher than that of other biosorbent produced from agro-wastes showed in Table 3, though it has low BET surface area. It could be assumed that adsorption process includes the chemisorption, physio-sorption and bio-sorption. Relating to activated carbon (Carbon F-400), cadmium (II) uptakes are higher for cabbage and cauliflower biosorbents, but lead(II) uptake are comparable for both biosorbents (Table 3). It could be concluded that both biosorbents are capable enough to uptake lead(II) and cadmium(II) ions from water.

4. Conclusions

- The Pb(II) and Cd(II) ions removal from aqueous solutions depends on the pH of water (6–7.5), doses of biosorbent (0.1–10 g/L) and contact time (15–45 min).
- Both cabbage and cauliflower biosorbents have better capability and efficiency for the removal of lead (II) than cadmium(II) ions from aqueous medium.
- The adsorption processes were fast and equilibrium time and higher preferences towards lead(II) than cadmium(II) adsorption from a binary solution.
- Langmuir model was the best-predicted model but three-parameter models (Redlich-Peterson, Koble-Corrigan, Khan and SIPS) were shown better fitness with equilibrium data than two-parameter models

and the adsorption coefficients indicate favourable adsorption.

- The maximum monolayer capacities were higher for lead(II) onto cabbage and cauliflower biosorbent and it were 60.568 and 47.628 mg/g respectively.
- Adsorption kinetic followed the pseudo-second order and multi step Avrami model.

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