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A polymer – zeolite composite for mixed metal removal from aqueous solution

Merve Yıldız Yiğit, Esra Sultan Baran and Çiğdem Kıvılcımdan Moral

ABSTRACT

Heavy metals become inevitable pollutants that are toxic to life. Lots of treatment methods are available; adsorption is a cheap option. Metals are mostly found as mixtures in wastewaters. Taking this into account, a natural composite adsorbent aims to remove multiple heavy metals (Pb^{2+}, Cu^{2+}, Cd^{2+}). Alginate was combined with clinoptilolite to form alginate – clinoptilolite (A–C) beads. First, factors influencing the removal efficiency of metals were investigated. Then, continuous column experiments were performed to evaluate the real application potential of the adsorbent. A–C beads preferably adsorbed Pb^{2+}. Batch experiments showed metal uptake reached equilibrium after 24 hours and kinetics were compatible with the first-order. Also, pH values near neutral levels were observed to increase heavy metal removal. On the other hand, adsorption equilibrium was well described by the Langmuir model for Cu^{2+} and Cd^{2+} and by the Freundlich model for Pb^{2+}. The highest heavy metal uptake was calculated as 2,145 mg /g A–C beads for Pb^{2+}. Continuous column operations were suggested to apply low flow rates (<2 mL/min) and heavy metal concentration (<10 mg/L) for effectiveness. A–C beads can be a good candidate for mixed heavy metal removal composed of environmentally friendly and low-cost materials.

Key words | alginate, cadmium, clinoptilolite, copper, heavy metals, lead

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HIGHLIGHTS

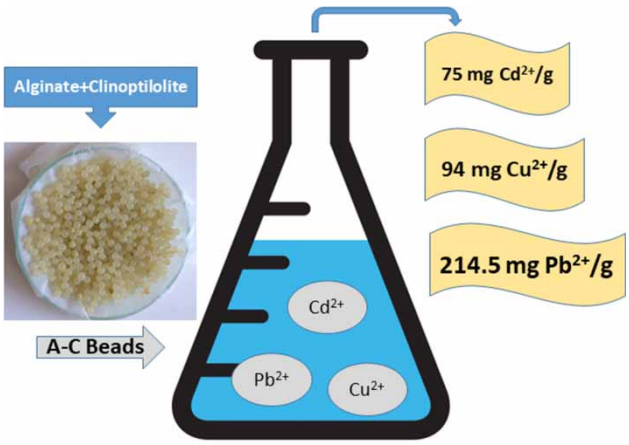
- Alginate – Clinoptilolite beads were used for removal of metals.
- Metals uptake was rapid for 8 hours then reached equilibrium after 24 hours.
- The highest metal uptakes were observed as 214.5 mg Pb^{2+}, 94 mg Cu^{2+}, 75 mg Cd^{2+} per g adsorbent.
- 98% of Pb^{2+} removal was achieved at 2 mL/min of flow rates and 10 mg/L of initial metal concentration.
- The adsorbent could be reused up to three times after regeneration by nitric acid.

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doi: 10.2166/wst.2021.057

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GRAPHICAL ABSTRACT



INTRODUCTION

The environment has been damaged seriously by a variety of pollutants. Heavy metal discharges from industrial wastewaters, acid mine drainages, and agricultural activities without proper treatment affect the whole components of the ecosystem. A lot of heavy metals are concerns due to persistency, hazardous effects, and accumulation in the food chain. As a result, their treatment is necessary. Some methods are available; for example, chemical precipitation, membrane separation, ion exchange, electrodialysis, and adsorption (Wang & Chen 2009). Among these methods, adsorption is getting attention because it is highly efficient, easy to handle, and cost-effective. However, there are still limitations on the practical application of adsorption. For this reason, researchers continue seeking novel adsorbents.

Alginate is an eco-friendly and inexpensive alternative known for its high affinity towards heavy metals. This is a biopolymer composed of mannuronic and guluronic acids. Because alginates make an 'egg box' structure of guluronic acid segments together with divalent cations, particularly with calcium ions, they are mainly applied in bead form for wastewater treatment. In recent years, alginate beads have been combined with some promising materials such as activated carbon (Park *et al.* 2007) living/dead materials (Loutseti *et al.* 2009), industrial by-products/wastes (Shim *et al.* 2014), and nanoparticles (Vu *et al.* 2017) to have more effective and low-cost adsorbents for removal of various metals such as Al^{3+}, As^{3+}, As^{5+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{+2}, and Zn^{2+}.

Clinoptilolite is a natural zeolite and similarly to alginate, it can take heavy metals by mainly ion exchange. For this reason, clinoptilolite and other zeolites have been used for heavy metal removal such as Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, Pb^{2+}, Fe^{3+} (Zanin *et al.* 2017; Emami Moghaddam *et al.* 2020; Sáez *et al.* 2020). In this study, clinoptilolite is selected to improve the heavy metal adsorption capacity of alginate beads because there are abundant resources in Turkey of about 20 million tons. Zeolites are also investigated for this purpose, but the studies are limited and mainly applied to remove only one metal at a time using batch reactors, although wastewaters, particularly from industrial origins, contain a mixture of them (Dang *et al.* 2014). As a consequence, alginate was combined with clinoptilolite to form alginate–clinoptilolite (A–C) beads and investigated for the removal of heavy metal mixtures (Pb^{2+}, Cu^{2+}, and Cd^{2+}). For this purpose, characterizations of A–C beads were performed first. Then, one set of batch experiments was conducted. Kinetics of heavy metal uptake, the effect of clinoptilolite size, A/C ratio, pH, and initial metal concentration were evaluated together with equilibrium models during experiments. Last, an adsorption column was operated continuously to determine the application potential of the adsorbent. Effect of flow rate, initial heavy metal concentration, and the amount of A–C beads (height of adsorption column) was examined.

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MATERIALS AND METHODS

Materials

Alginate (Sigma 71238), $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ were obtained as analytical grade and used without further purification. Clinoptilolite was obtained from Manisa-Gördes, Turkey. Synthetic wastewater was prepared by listed metal salts at 1,000 mg/L concentration as a stock solution. Then these solutions were diluted to have predetermined concentrations. All of the solutions were prepared with deionized water (<18MΩcm).

A–C bead formation and characterization

Clinoptilolite, first, was ground and sieved into different sizes. Then 10 g clinoptilolite was added into 500 mL NaCl (1 M) solution and shaken for 24 hours at 30 °C and 200 rpm. After that, it was filtered and dried at 105 °C for 24 hours. The reason for this pretreatment of clinoptilolite is to remove certain cations from the structure of the zeolite and exchange them with more easily removable sodium. This may help to improve the homoionic state and the ion exchange capacity of clinoptilolite.

A–C beads were formed by adding a predetermined amount (depending on A/C ratios of 1/2, 1/1, and 2/1) of clinoptilolite into a 2% alginate solution. Then this mixture was added drop-wise into $CaCl_2$ (50 mM) solution to form a bead structure under constant stirring at 50 rpm. These beads were incubated overnight within this solution to harden. After that, they were filtered and washed with deionized water to remove excess ions. Finally, A–C beads were dried at 35 °C until constant weight.

For the characterization of A–C beads, the ImageJ program was used to determine size distribution and average size. Furthermore, Scanning Electron Microscopy (SEM), Brunauer – Emmett – Teller (BET), and Energy Dispersive X-ray (EDX) analyses were performed to show the surface properties of the beads. SEM analysis was performed by gold and carbon coating. For clinoptilolite, the BET analysis procedure began with heating in a drying oven at 150 °C for 1 hour and then at 250 °C for 3 hours under N_2 atm. For alginate and A–C beads, the procedure was performed as heating in a drying oven at 90 °C for 1 hour and then at 100 °C for 6 hours under N_2 atm.

Sorption experiments

Experiments were performed in both batch and continuous modes. For batch heavy metal adsorption experiments, 50 mL of synthetic wastewaters at different heavy metal concentrations was poured into a flask (250 mL). Then 100 mg of A–C beads were added and agitated at 150 rpm and 30 °C. If it is not stated otherwise, clinoptilolite size, A/C ratio, heavy metal concentration, and pH were set as <100 μm, 1 g/1 g, 100 mg/L, and 4, respectively.

To determine adsorption kinetics, samples were collected for 48 hours at predetermined time intervals. Three different clinoptilolite sizes (<100 μm, 100–300 μm and 300–500 μm), A/C ratios (1/2, 1/1, and 2/1), pH values (3, 4, and 5) were investigated for possible effects on adsorption efficiencies of the heavy metal mixture until equilibrium. Finally, heavy metal concentrations were changed from 25 mg/L to 1,250 mg/L depending on the metals.

For continuous adsorption experiments, a glass column (40 cm × 2 cm), filled with A–C beads and supported by glass wool, was used. The aqueous metal solution was fed downflow by a peristaltic pump. Default set values for the amount of the adsorbent, heavy metal concentration for each metal, flow rate, and pH were 10 g, 10 mg/L, 5 mL/min, 5, respectively. For these experiments, two different amounts of adsorbent (10 and 20 g), three heavy metal levels (10, 25, and 50 mg/L), and flow rates (2, 5, and 75 mL/min, which correspond to 0382, 0.955, and 1.433 m/h, respectively) were examined to evaluate possible effects on heavy metal uptake by A–C beads.

To determine the reusability of A–C beads, EDTA, HNO_3, and H_2SO_4 were used. For this purpose, metal loaded adsorbents were shaken in these solutions (0.5 M) for 24 hours at 150 rpm. After washing to remove excessive agents, they were subjected to a series of metal uptake studies at optimum conditions obtained by batch experiments.

All samples were filtered and the supernatant was acidified and stored below 4 °C before residual metal analysis by ICP–OES. Experiments were conducted in triplicate to confirm reproducibility and the average results reported.

Data evaluation

The percentage of heavy metal adsorption (Equation (1)) and adsorption capacity (mg cation/g alginate) (Equation (2)) at equilibrium are calculated by using the equation below in batch experiments:

$$\text{Removal rate } (\%) = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

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

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where C_0 and C_e (mg/L) are metal concentrations at time zero and equilibrium, respectively. m is the mass of adsorbent (g) and V is the volume of solution (L).

For kinetics of adsorption, the nonlinear equations for pseudo 1st order (Equation (3)) and 2nd order (Equation (4)) adsorption reactions are used as follows:

$$q_t = q_e \times (1 - e^{-k_1 \times t}) \tag{3}$$

$$q_t = (q_e^2 \times k_2 \times t)/(1 + k_2 \times q_e \times t) \tag{4}$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t (h). k_1 (1/h) and k_2 (g/mg.h) are the rate constants of reactions.

For equilibrium modeling, the nonlinear forms of the Langmuir (Equation (5)) and Freundlich (Equation (6)) equations are used as below:

$$q_e = (Q^0_{max} \times k_L \times C_e)/(1 + k_L \times C_e) \tag{5}$$

$$q_e = k_F \times C_e^n \tag{6}$$

where Q^0_{max} (mg/g) is the maximum adsorption capacity, k_L (L/mg) is a constant related to sorption energy. k_F ((mg/g)/(mg/L)^n) and n are constant related to sorption capacity and intensity, respectively. Also, the dimensionless constant separation factor R_L (Equation (7)) is as follows:

$$R_L = 1/(1 + k_L \times C_0) \tag{7}$$

For evaluation of the experimental data obtained from continuous heavy metal uptake, breakthrough curves were drawn between C/C_0 and time. C/C_0 is equal to 0.1 and 1 defined as breakpoint and saturation of the adsorption, respectively. Maximum column capacity (q_{top}) and amount of pollutants fed to the column (m_{top}) are determined as follows:

$$q_{top} = Q \int_{t=0}^{t=top} (C_0 - C) dt \tag{8}$$

$$m_{top} = C_0 \times Q \times t_{top} \tag{9}$$

where t_{top} is total flow time (min), Q is the flow rate, C is the metal concentration at time t. Then, equilibrium adsorption capacity can be calculated:

$$q_e = q_{top}/m \tag{10}$$

$$\text{Removal rate (\%)} = (q_{top}/m_{top}) \times 100 \tag{11}$$

RESULTS AND DISCUSSION

A–C beads were applied for the removal of a heavy metal mixture containing lead, copper, and cadmium. Except for copper, lead and cadmium are not essential to the human body and all can have toxic effects at certain concentrations for both human health and nature. However, they can be found together with other heavy metals particularly in industrial wastewaters such as metal plating, fertilizer production. Discharges of these metals are limited by environmental regulations.

First, the performance of the beads was compared with alginate and clinoptilolite used alone. The results (data not shown) revealed that composite beads were more efficient with the highest adsorption capacity for lead as 45 mg Pb^{2+}/g A–C beads (corresponds to 92% of reduction) which were calculated as 38 mg Pb^{2+}/g alginate and 25 mg Pb^{2+}/g clinoptilolite. In this study, the heavy metal uptake capacity of alginate could be improved by combining the polymer with clinoptilolite. A–C beads are more effective for decreasing heavy metals concentration compared to alginate and clinoptilolite because both alginate and clinoptilolite can capture heavy metals by particularly adsorption and ion exchange. Therefore, A–C beads were used for further experiments.

Characterization of A–C beads

First, some properties of A–C beads such as size distribution and surface characteristics were determined. ImageJ program was applied to calculate the average size of the beads and Figure S1 shows the results. A–C beads were mostly uniform in size. The average value was calculated as 1.48 mm. Similarly, the average diameter of dried beads was determined within the range of 1.26–2.42 mm in another study (El-Sherbiny *et al.* 2013). Also, SEM, BET, and EDX analysis were performed for alginate and A–C beads before experiments and after adsorption. BET analysis results are summarized in Table S1. Alginate surface area was quite small and actually, clinoptilolite surface area was better (32.72 m^2/g). When these two were combined, the clean bead surface area was increased from 1.688 m^2/g (alginate beads) to 4.921 m^2/g for

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A–C beads. Therefore, clinoptilolite improves the available surface area for adsorption, which can be seen from SEM images of composite beads with rugged surfaces. SEM analysis of alginate beads showed that they had very smooth, uniform, and homogeneous surfaces (Figure 1). When alginate was combined with clinoptilolite, an increase in roughness could be observed on the bead surface. This led to an increase in surface area as indicated in BET analysis. The image of alginate and A–C beads were similar to the one previously reported (Kwon *et al.* 2016). Some cracks were identified in SEM images of the beads after adsorption. This might be attributed to changes of bead structure by substitution of calcium ion with the metals. Because adsorption led to the occupation of pollutants mainly on the surface of the adsorbent, the surface area of A–C beads was decreased to 4.307 m^2/g after heavy metal uptake. Surface changes were further followed by EDX analysis (Figure S2). Alginate beads had only oxygen, carbon, and calcium in their structure. However, with the addition of clinoptilolite, aluminum and silisium were found to prove successful impregnation within the alginate matrix. They are common constituents in zeolite structure. After adsorption experiments, some lead and cadmium peaks were also shown, confirming adsorption phenomena.

Kinetics of heavy metal uptake by A–C beads

To estimate the equilibrium time for maximum heavy metals uptake onto A–C beads, kinetic studies were conducted during 48 hours by time depended sampling because the mass transfer is a significant factor for heavy metal removal. Proper agitation (at 150 rpm) was supplied in the experiments that bulk transport of the metal in solution and film transport through water boundary layer should be negligible. Thus, kinetics is only determined by intraparticle diffusion. The results are shown in Figure 2. Adsorption of Pb^{2+} was extremely fast compared to other heavy metals. Even after 30 minutes of the experiment, an initial rapid Pb^{2+} uptake by A–C beads resulted in 94 and 83% removal rates for non-competitive (Figure 2(a)) and competitive (Figure 2(b)) adsorption. On the other hand, Cu^{2+} and Cd^{2+} adsorptions were observed to be comparably slow. The adsorption patterns were similar for these two metals in that the rate of adsorption decreased after 2 hours. Also, the equilibrium time for all metals was found the same as 24 hours, which is a bit longer exposure time. First, active sites having high binding affinity seem to be occupied and external mass transfer resistance can be handled leading to the higher driving force. Then lower affinity binding sites lead to a slow equilibrium. Similar equilibrium durations were also observed by previous studies (Shang & Yu 2015; Kwon *et al.* 2016). Furthermore, a wide range of adsorption equilibrium times were reported in the literature depending on experimental conditions, target metals, and adsorbent characteristics. The highest removal efficiency was calculated as 97.3% for Pb^{2+} at 24 hours. Aluminosilicate and carboxylic groups are the active sites responsible for metal uptake of clinoptilolite and alginate, respectively. They are similar in terms of

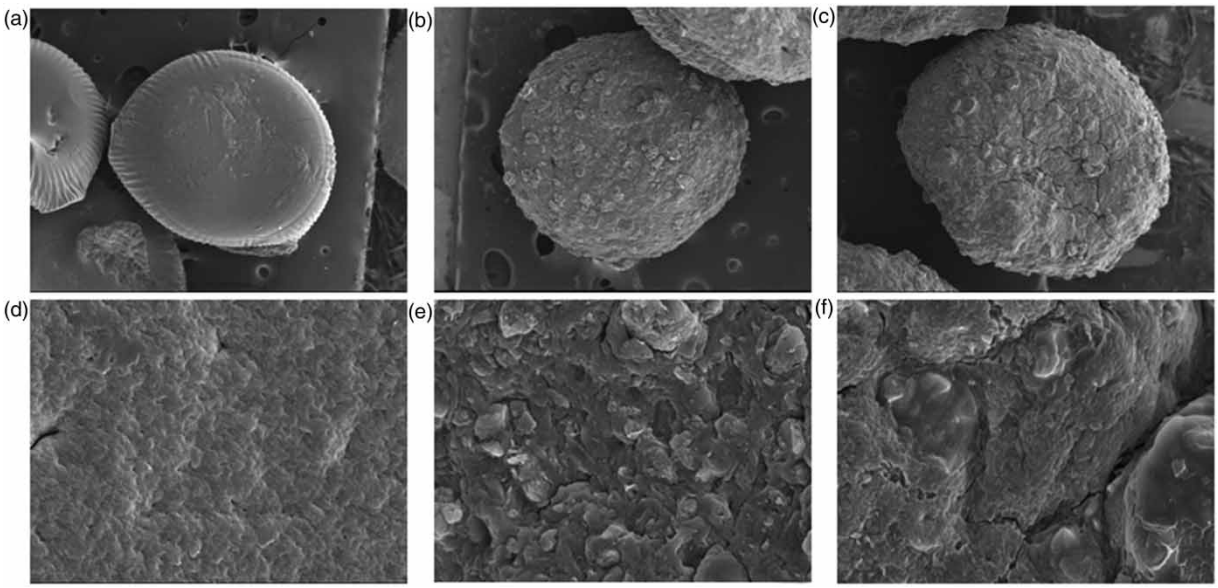


Figure 1 | SEM analysis of Alginate beads (a, d), A–C beads (b, e) before and (c, f) after adsorption.

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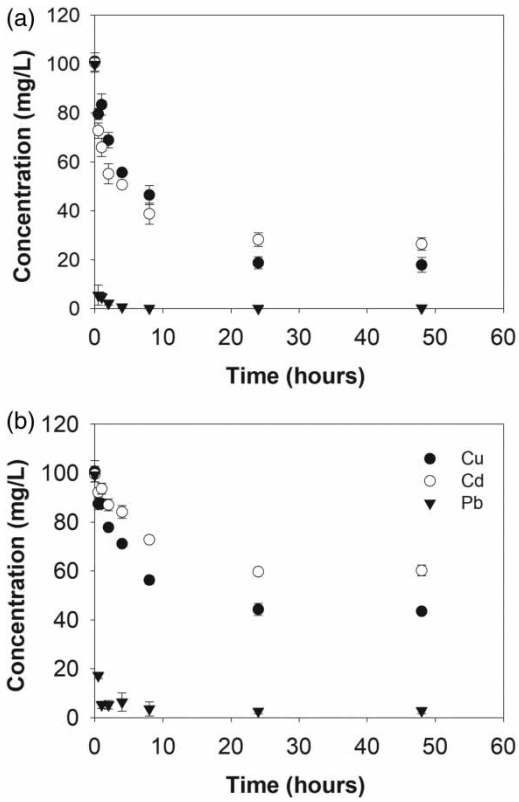


Figure 2 | Kinetics of non-competitive (a) and competitive (b) mixed metal adsorption by A–C beads in the batch reactor.

affinity and nature. Although the decrease of Pb^{2+} was fast and the final concentration after the incubation period was considerably lower compared to the other metals, it might not be the most preferred ion by A–C beads. Because ion exchange is one of the mechanisms leading metal uptake by both clinoptilolite and alginate, comparing adsorption capacities in the unit of mole seems better. The highest adsorption capacity was obtained as 0.441 mmol/g A–C beads for Cu^{2+} ion. The order of preference was followed by Pb^{2+} (0.232 mmol/g A–C beads) and finally with Cd^{2+} (0.178 mmol/g A–C beads). The maximum reduction levels were achieved as 56 and 40.1% for competitive adsorption of Cu^{2+} and Cd^{2+}, respectively. Although competition between metals did not have a drastic effect on Pb^{2+} ion removal, these values were quite better in the case of Cu^{2+} and Cd^{2+}. The highest treatment levels were calculated as 82.3 and 73.7%, respectively. For competitive adsorption, the maximum heavy metal uptake was calculated as 48 mg Pb^{2+}/g A–C beads at the end of the adsorption experiment. Besides, the values were found as 28 mg Cu^{2+}/g A–C beads and 20 mg Cd^{2+}/g A–C beads.

The data obtained from kinetic studies of competitive adsorption were modeled by common equations such as pseudo-first and second-order models using nonlinear forms. Rate constants k_1, k_2, and q_e values are calculated and the results are summarized in Table 1. By comparing correlation coefficients (R^2) of pseudo 1st and 2nd order, the data for Cu^{2+} seemed to be compatible with the pseudo 2nd-order model whereas that for Pb^{2+} and Cd^{2+} were compatible with the 1st order model. On the other hand, there was a good agreement between experimental and 1st order model q_e values. In other words, 1st order model was superior for predicting adsorption capacities. The order of rate constants for adsorption of the metals was similar to Figure 1 because the highest k_1 value was calculated as 3.981 1/h for Pb^{2+} ion. The results of the current study are found to be compatible with the literature that, particularly when the nonlinear forms of the models are applied, pseudo 1st order model dominantly expressed the adsorption kinetics (Tran *et al.* 2017).

Effect of adsorbent composition: clinoptilolite size and A/C ratio

Adsorption is a surface phenomenon that area of the adsorbent may play a crucial role in adsorption efficiency. For this reason, clinoptilolite sizes in A–C beads were changed in the range of 100–500 μm. Then, the effect of various clinoptilolite sizes on competitive adsorption of mixed heavy metals was investigated and the results are illustrated in Figure S3a. As it is seen from the graph, there were no drastic changes for removal efficiencies of Cu^{2+}, Cd^{2+}, and Pb^{2+}

Table 1 | Modelling of adsorption kinetics by pseudo 1st and pseudo 2nd order

		1st order			2nd order		
Metals	**q_e, exp (mg/g)**	**k_1 (1/h)**	**q_e, calc (mg/g)**	**R^2**	**k_2 (mg/g.h)**	**q_e, calc (mg/g)**	**R^2**
Cu^{2+}	28.21	0.222	28.06	0.961	0.009	31.30	0.977
Cd^{2+}	19.96	0.147	19.99	0.971	0.007	23.21	0.969
Pb^{2+}	48.25	3.981	47.55	0.930	0.276	48.36	0.832

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at different clinoptilolite sizes in the tested range. In other words, heavy metal uptake ratios were almost the same. For example, the final Pb^{2+} concentrations after treatment varied in the range of 4.31–8.14 mg/L. Similar maximum adsorption capacities were achieved for all sizes. The maximum q_e values were calculated as 47 mg Pb^{2+}, 31 mg Cu^{2+}, and 21 mg Cd^{2+} per g A–C beads. Thus, reduction in clinoptilolite size did not improve heavy metal removal within the clinoptilolite sizes of 100–500 μm. The general idea is adsorption efficiency would be improved when the surface area of the adsorbents is increased by grinding. However, for some cases, grinding only increases the outer surface area. If the inner surface area of the adsorbent is mainly responsible for the adsorption of pollutants, reduction in adsorbent size would not have an important effect on adsorption. Likewise, clinoptilolite size does not improve the adsorption efficiency of the mixed heavy metal solution.

The next parameter affecting the adsorption of the heavy metal mixture was the alginate to clinoptilolite ratio. The range was changed between 1/2 and 2/1. Results are shown in Figure S3b. As a reference point, first, the A/C ratio of 1/1 (mass ratio) was examined, and then both alginate and clinoptilolite mass were increased twice. When the amount of clinoptilolite was increased (at 1/2 ratio), Cu^{2+} and Cd^{2+} removals were influenced negatively. Particularly the results were drastic for Cd^{2+} ion with a 24% decrease in the removal efficiency probably being the least preferred ion for A–C beads. When the amount of alginate was increased (at 2/1 ratio), there were no crucial additives to removal efficiencies. For example, Pb^{2+} could be adsorbed by A–C beads at almost the same level. In other words, somehow similar results were obtained, although Cd^{2+} has still been removed better at A/C ratio of 1/1 as 38%. Also, an increase in alginate level deteriorated the shape of the beads which might not be suitable for practical application such as column operations. Another study used magnetite graphene oxide (mGO) in alginate beads for the removal of Cr^{6+} and As^{5+}. The alginate and mGO were similarly mixed from 1/0.5 to 1/2 ratios. The adsorbed amount of the metals was increased with increasing mGO ratio in beads contrary to our results (Vu *et al.* 2017). The adsorption phenomena of heavy metal mixture look to be governed by alginate rather than clinoptilolite. However, having a high amount of alginate in bead structure with clinoptilolite may lead to diffusion limitations for heavy metals. Thus, the use of A/C ratio at 1/1 seems to be optimum for mixed heavy metal with the highest number as 45 mg Pb^{2+}/g adsorbent.

Effect of pH

pH is one of the key parameters in adsorption because ionization of active sites (i.e. carboxyl, amine groups) on adsorbents is mostly affected by pH. Also, it is a critical parameter for the surface charge, speciation, and solubility of metals and competition with hydrogen on functional groups of adsorbents. Alginate is composed of mannuronic and guluronic acids, which have carboxyl groups for possible ion exchange with metals. These groups have pH_{pzc} values around pH 3.5 (Haug *et al.* 1974). At $pH > pH_{pzc}$, all of the carboxyl groups are ionized to have negative charges, which promote electrostatic interaction between heavy metals and A–C beads. Because of this, the starting point for the investigation of the pH effect was selected as pH 3. Furthermore, among the heavy metals involved in this study, Cu^{2+} begins to precipitate as copper hydroxide at around pH 5.5. Therefore, the highest pH was selected as 5 to exclude the effect of precipitation over sorption and the results are presented in Figure 3. Furthermore, it should be stated that pH_{pzc} of composite adsorbents might be different from their components. pH_{pzc} values were

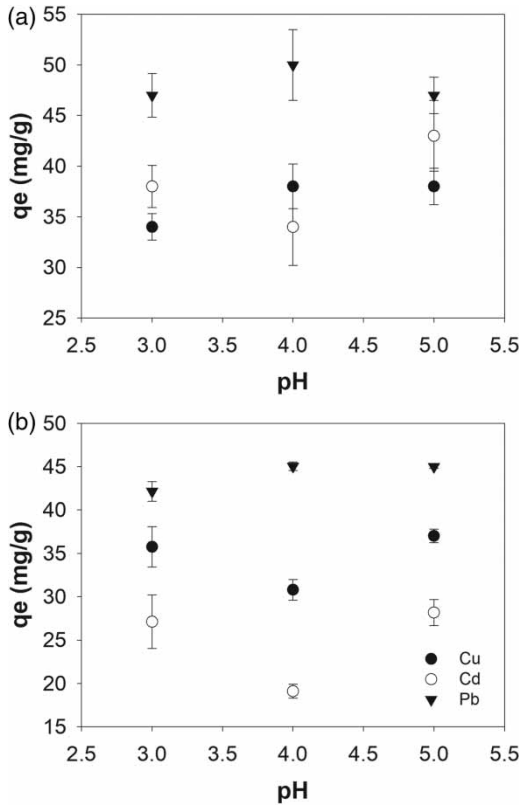


Figure 3 | Effect of pH on non-competitive (a) and competitive (b) heavy metals adsorption in batch reactors.

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found as 4.6 and 5.1 for clinoptilolite and A–C beads. As one can see from the figure, competition between metals seemed to affect particularly Cd^{2+} ion removals. For example, the highest adsorption capacities were 43 and 28 mg/g for non-competitive (Figure 3(a)) and competitive (Figure 3(b)) adsorption of Cd^{2+} ion. On the other hand, the trend of heavy metal removal was similar at certain pH values. For competitive adsorption at pH 3 and 5, similar heavy metal decreases were obtained except for Pb^{2+} removal, which is 6% lower in the case of pH 3. Also, these pH values were found to be better in both Cu^{2+} and Cd^{2+} ion removals compared to pH 4. Having almost the same heavy metal uptake capacities at pH 3 is surprising, due to the electrostatic repulsion forces between metal ions and positively charged surface groups of the adsorbent. A competition between H^+ and metal ions for adsorption sites is also possible under acidic conditions. Also, adsorption differences might be related to other factors such as ionic radii, ion coordination number in solution, or thermodynamic properties (Zanin *et al.* 2017). The specific binding reactions on the surface of composite adsorbent may be more effective than electrostatic attraction in the current study (Lee *et al.* 2015). On the other hand, the maximum heavy metal uptakes for competitive and non-competitive adsorption experiments were observed at pH 5, probably because the pH_{pzc} of the composite adsorbent is equal to 5.1. At pH values near or higher than the pH_{pzc} level of the adsorbent, active sites are deprotonated and become available to metal uptake. As an example, Cd^{2+} removal efficiency was increased from 38 to 55% when the pH was increased from 4 to 5 for competitive adsorption. For these reasons, pH 5 was selected for further experiments. In the literature, results of heavy metal uptake studies had some variations depending on the metal concerned and adsorbent type. For example, copper removal was continuously increased when pH was increased from 2 to 6.5 by zirconium oxide-immobilized alginate beads (Kwon *et al.* 2016), while it was fairly constant at pH 4–6 by alginate hydrogel beads (An *et al.* 2015).

For alginate-based adsorbents, the heavy metal removal mainly depends on carboxyl groups on the polymer and to a lesser extends hydroxyl groups. Furthermore, mannuronic and guluronic acid groups have different availability in adsorption. The conformation differences between acid groups particularly affected low-affinity metals such as Cd^{2+} because Pb^{2+} could be easily attached to guluronic and mannuronic acid blocks (Papageorgiou *et al.* 2006). Also, another theory called the 'hard-soft-acid-base theory' claims that hard acids prefer to bind with hard bases and soft acids with soft bases. Pb^{2+} and Cu^{2+} are known as intermediate acids while Cd^{2+} is a soft acid. Therefore, hard base carboxyl groups prefer to uptake Pb^{2+} and Cu^{2+} rather than Cd^{2+} (Pearson 1963).

Effect of initial metal concentration and adsorption equilibrium models

Heavy metals concentrations in wastewaters coming from different sources change a lot. Also, adsorption efficiencies are influenced by heavy metal levels. Initial concentration is an important parameter for adsorption because pollutant concentration is a driving force for the diffusion of pollutants through the pores of adsorbents. To elucidate the relations between adsorbed and final heavy metal concentration at equilibrium and to find the saturation sorption capacity, the initial heavy metal concentration was changed from 25 to 1,250 mg/L. For all heavy metals, concentrations were increased until there was no change in aqueous metal concentration at equilibrium. Results are illustrated in Figure 4. A sharp rise of isotherm can be seen at low initial heavy metal concentrations then it reaches a plateau when heavy metal concentration increases. Adsorption capacities of the heavy metals were increased by increasing metal concentration because higher metal concentrations probably supplied driving forces to overcome mass transfer resistance between sorbent and liquid interfaces. Also, a unit mass of beads was trying to be filled by higher numbers of metal ions. On the other hand, this caused the inefficient treatment of heavy metals required to be considered for adsorption. For example, when copper ion concentration was increased from 25 mg/L to 400 mg/L, percent removals decreased from 80 to 47. This may be explained as when the concentration of metal is increased, there are high amounts

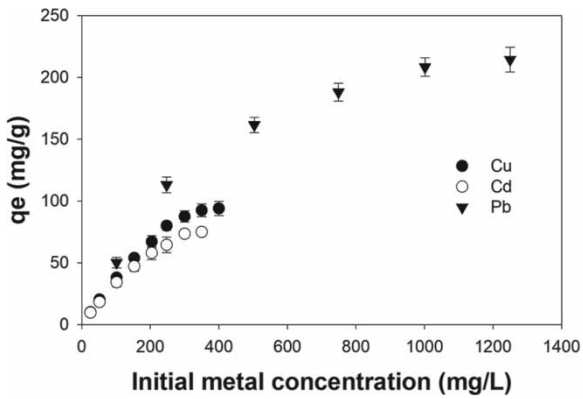


Figure 4 | Effect of different initial metal concentration on adsorption of metals (a) Cu^{2+} (b) Cd^{2+} (c) Pb^{2+}.

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of pollutants for the same amount of active sites on the adsorbent. This causes competition which eventually decreases removal efficiency. At low metal levels, there are enough active sites and metal uptake is not depending on initial concentration (Bhattacharyya & Gupta 2007). Compatible with the other findings, Pb^{2+} had the highest experimental adsorption capacity, which was 214.5 mg Pb^{2+}/g A–C beads. Cu^{2+} followed by Pb^{2+} with an adsorption capacity of 94 mg Cu^{2+}/g A–C beads and then Cd^{2+} with an adsorption capacity of 75 mg Cd^{2+}/g A–C beads. This may be due to active binding sites being preferred by large radii metals. They can form more stable structures with the coordination of oxygen atoms (Shang & Yu 2015).

Common adsorption equilibrium models, namely Freundlich and Langmuir, were adopted in the nonlinear form to analyze the data. According to the Langmuir model, adsorption is homogeneous monolayer coverage while Freundlich is an empirical model that claims heterogeneous surfaces with different binding energies and multilayer adsorption. Freundlich constant k_F, n, and Langmuir constant k_L, Q^0_{max} are calculated and summarized in Table 2. Both model results were satisfactory with high correlation coefficients (R^2). On the other hand, Langmuir model results were fit better for adsorption of Cu^{2+} and Cd^{2+} whereas the Freundlich model results were simulated better for adsorption of Pb^{2+}. This suggests that the mechanism of adsorption is different for the metals. Freundlich's constant n values varied between 0.199 and 0.491. The highest number was calculated for the Cd^{2+} ion. Favorable adsorption was valid for all heavy metals tested. For k_F values, Cu^{2+} and Cd^{2+} had similar lower levels; however, for Pb^{2+}, the value was 57.55. This indicates higher separation efficiency of Pb^{2+} compared to the other metal ions. On the other hand, the Langmuir model gives an idea about maximum adsorption capacities of the adsorbents, namely Q^0_{max}. The maximum adsorption capacity is influenced by the amount and accessibility of active sites on beads and the affinity of the metals towards these functional groups.

Table 2 | Evaluation of adsorption equilibrium: Freundlich and Langmuir models

	Langmuir			Freundlich		
Metals	**Q^0_{max} (mg/g)**	**k_L (L/mg)**	**R^2**	**n**	**k_F (mg/g)/(mg/L)^n**	**R^2**
Cu^{2+}	121.2	0.019	0.998	0.443	9.687	0.958
Cd^{2+}	101.3	0.015	0.997	0.491	5.998	0.974
Pb^{2+}	202.3	0.063	0.878	0.199	57.55	0.993

These values were calculated as 202.3, 121.2, and 101.3 mg metal adsorbed per g A–C beads for Pb^{2+}, Cu^{2+}, and Cd^{2+}, respectively. q values from experiments were found to be compatible with model data. On the other hand, the Langmuir constant, K_d, is related to the bonding energy of sorbed material. This means a high K_d value shows high bonding strength (Lee *et al.* 2015).

The Langmuir model defines homogenous adsorption with negligible interaction between adsorbed molecules (Langmuir 1918; Ghaemi *et al.* 2013). For comparison with the literature, maximum adsorption capacities for the related metals by different adsorbent materials are summarized in Table 3. In general, A–C beads have higher heavy metal uptake capacities compared to relevant literature, although it is not easy to compare the results directly because experimental conditions are changing in these studies. Another parameter showing the characteristics of the Langmuir isotherm is the separation factor R_L. When the value is higher than 1, this indicates unfavorable adsorption. If the value is between 0 and 1, the adsorption process is favorable. The calculated R_L values for all metals were in the range of 0 and 1, which showed favorable heavy metal uptake (Table S2).

Table 3 | Comparison of Langmuir adsorption capacities of different adsorbent materials

	q_{max} (mg/g)			
Adsorbent	**Cu^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**References**
Zirconium oxide immobilized AB	69.9	–	–	Kwon *et al.* (2016)
Phosphate-embedded AB	–	82.64	263.16	Wang *et al.* (2016)
Corn cob silica AB	4.24	4.07	–	Shim *et al.* (2014)
Meso-iron-oxyhydroxide AB	9.9	14.1	60.1	Chung *et al.* (2014)
Polianiline nanofiber AB	67.95	–	251.45	Jiang *et al.* (2012)
Tricholoma lobayense	91.7	22.1	370.4	Cao *et al.* (2010)
Micro algal/bacterial filter	18.36	31.33	–	Loutseti *et al.* (2009)
Montmorillonite	32.3	33.2	34	Bhattacharyya & Gupta (2007)
Aluminosilicates/zeolite composite	140	–	77.8	Kouznetsova *et al.* (2020)
Zeolite 13X-algal-alginate beads	85.88	–	–	Emami Moghaddam *et al.* (2020)
Alginate-clinoptilolite beads	121.2	101.3	202.3	This study

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Use of A–C beads in continuous heavy metal removal

A–C beads were also applied for multiple metal removals in a continuously operated adsorption column. The breakpoint for heavy metal uptake is assumed as 10% of initial metal concentrations. Furthermore, when the effluent metal concentration is equal to the initial concentration, the operation is terminated due to saturation of adsorption sites. Some parameters affect heavy metal removal in adsorption columns, such as flow rate, heavy metal concentration, and bed depth (amount of adsorbent loaded to the column). Firstly, the effect of flow rate was determined within the range of 2 and 7.5 mL/min at 10 mg/L of initial heavy metal concentrations. Results are presented in Figure 5. Data were found to be compatible with the batch system because A–C beads were more efficient for the removal of Pb^{2+} in the continuous system (Figure 5(a)). In addition, for all flow rates, no saturation was observed for Pb^{2+} whereas A–C beads could not capture both Cu^{2+} and Cd^{2+} after a certain duration of time, depending on the flow rates applied. At 2 ml/min of flow rate, a breakpoint of Pb^{2+} adsorption was not observed. After treatment of about 110 L synthetic wastewater, the effluent Pb^{2+} concentration was as low as 0.45 mg/L although higher flow rates increased effluent Pb^{2+} levels. On the other hand, the trend of heavy metal concentration in the effluent during column operations was quite similar for Cu^{2+} and Cd^{2+}. When the flow rate was increased from 2 to 5 mL/min, heavy metal removals were negatively affected. For example, breakpoints of the adsorbent for Cu^{2+} were observed after 23 and 10 litres of wastewater treated at 2 and 5 mL/min flow rates, respectively (Figure 5(b)). The only difference between Cu^{2+} and Cd^{2+} was Cu^{2+} uptake was more favorable, resulting in an earlier adsorption breakpoint for Cd^{2+} (Figure 5(c)). These findings are compatible with the literature where buffalo weed biochar–alginate beads were used for Cd^{2+} removal at three different flow rates (changing from 0.25 to 1 ml/min) (Roh *et al.* 2015). Faster breakthroughs were attained at higher flow rates. This might be explained by lower detention time under this condition. In the current study, with further increase in flow rate, at 7.5 mL/min, changes in effluent concentrations for Cu^{2+} and Cd^{2+} were not drastic although the differences were more clear in the case of Pb^{2+} levels.

Adsorptions at different flow rates were evaluated in terms of the amount of the metal loaded to the system and adsorbed by A–C beads (Table S3). Also, heavy metal removal rates as percent and per unit mass of the adsorbent were calculated. According to the table, the heavy metal

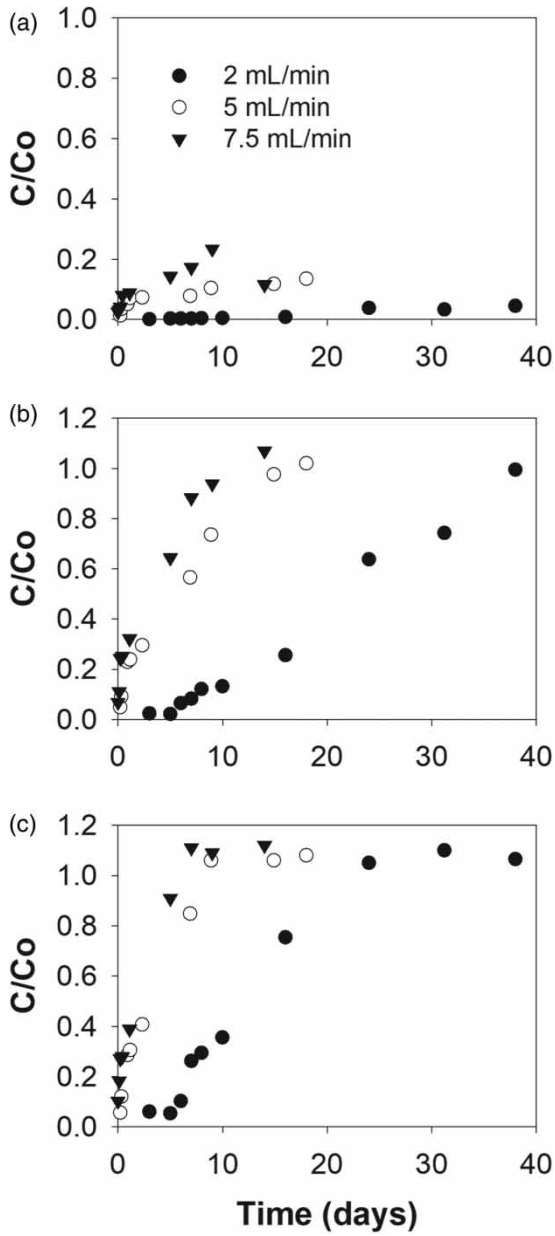


Figure 5 | Effect of flow rate on (a) Pb^{2+}, (b) Cu^{2+}, (c) Cd^{2+} removal in adsorption columns.

load was increased by about 30% when the flow rate was increased from 2 to 7.5 mL/min. This improved Pb^{2+} uptake; 1,283 mg of the metal was removed from the solution at 7.5 mL/min, which was the highest level obtained in these experiments. On the other hand, the adsorbed amount of Cd^{2+} at the end of column operation was reduced to 242.7 mg at the same flow rate. A similar trend was also observed for Cu^{2+}. Furthermore, removal rates of the metals and maximum adsorption values were affected by

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changing flow rates. For all metals, removal efficiencies were decreased by increasing flow rates. The best removal efficiencies were 98, 57, and 32% for Pb^{2+}, Cu^{2+}, and Cd^{2+}, respectively. It was claimed removal efficiency of Pb^{2+} was affected by increasing flow rate at 50 mg/L of initial metal level (Li *et al.* 2013). The system could treat 8,880 mL of metal-containing solution at 2 mL/min of flow rate compared to 6,000 mL at 4 mL/min of flow rate. All these can be explained by the required contact time for effective removal of the metal by the adsorbent. The longer the residence time due to a lower flow rate, the greater the opportunities to be held by active sites or to diffuse into the interior surface of the adsorbent. Similar results were also obtained by other researchers (Hedström & Amofah 2008; Shawky 2011). Also, the highest q_e value was achieved for Pb^{2+} ion at 7.5 mL/min as 128.3 mg Pb/g A–C beads whereas the values were calculated as 62.9 mg Cu^{2+}/g A–C beads and 35.4 mg Cd^{2+}/g A–C beads at 2 mL/min.

The effectiveness of multiple metal adsorption was tested at different initial metal concentrations, namely 10, 25, and 50 mg/L, at 5 mL/min (Figure 6). Since the uptake rate of A–C beads appeared to be highest for Pb^{2+}, effluent Pb^{2+} concentration was considerably low and the C/Co ratio fluctuated around 0.1 (Figure 6(a)). That is, no saturation was observed during 18 days of experiment, even when the initial Pb^{2+} concentration was increased five times. For breakpoints of Pb^{2+}, the amount of treated metal solution was reduced from 64 L to 21 litres when the metal levels were increased from 10 to 25 mg/L. Similar results were found in another study (Li *et al.* 2013). According to the results, important reductions in service time of columns composed of magnetic sodium alginate gel beads were observed by increasing Pb^{2+} concentration from 50 to 200 mg/L. On the other hand, similar to the results obtained at different flow rates, Cu^{2+} (Figure 6(b)) and particularly Cd uptakes (Figure 6(c)) of A–C beads were not good enough to supply efficient treatment. Especially the removal potential of the beads was decreased at higher initial metal concentrations, both 25 and 50 mg/L were beyond the effective removal levels when a multiple heavy metal solution is concerned. An increase in initial heavy metal concentration also affected the saturation times of the metals. For instance, at 10 mg/L, the column was saturated for Cu^{2+} after 18 days, which was reduced to 2 days at 50 mg/L. Therefore, for both Cu^{2+} and Cd^{2+}, metal concentrations lower than 10 mg/L seemed to be favorable in a mixed heavy metal solution for efficient metal treatment.

The data evaluation from adsorption of mixed metals throughout the column at different initial metal concentrations is summarized in Table S4. As expected, the amount of total metal uploaded to the column was increased and 2,475 mg of metal was applied at 50 mg/L of initial concentration level. Results showed that Pb^{2+} uptake by A–C beads was stimulated by increasing the ion concentration from 10 to 50 mg/L. For example, total Pb^{2+} adsorption was increased up to 2,385 mg which was the highest level obtained among metals. This value corresponds to a 96% removal rate. Similarly, the amount of Pb^{2+} adsorbed per g A–C beads was also increased from

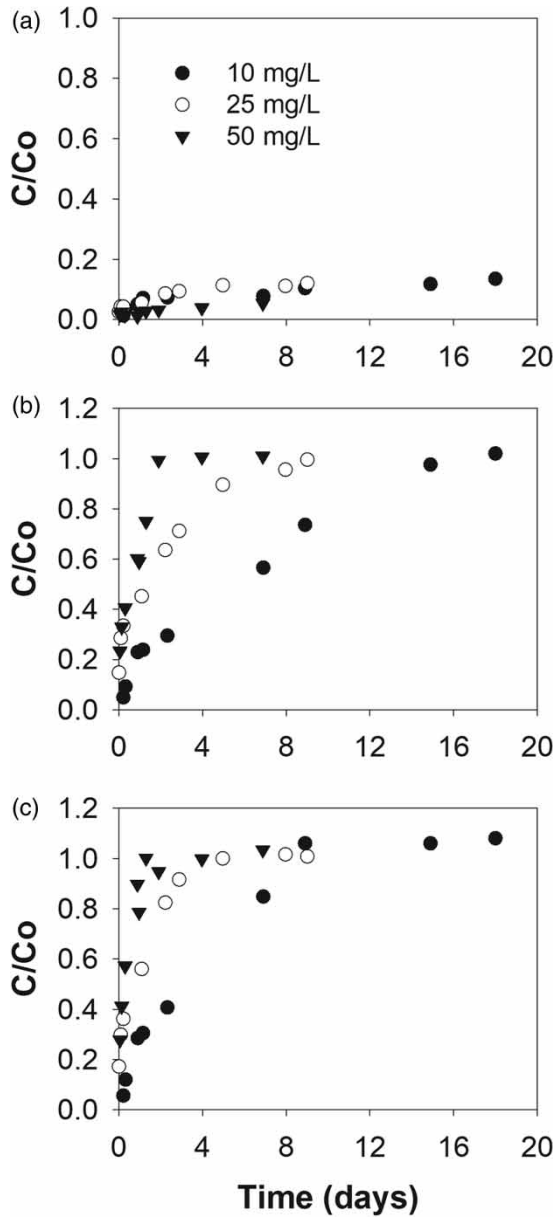


Figure 6 | Effect of initial metal concentration on (a) Pb^{2+}, (b) Cu^{2+}, (c) Cd^{2+} adsorption in adsorption columns.

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117.3 mg/g at 10 mg/L to 238 mg/g at 50 mg/L. Meanwhile, Cu^{2+} and Cd^{2+} adsorption by A–C beads were affected negatively by increasing the metal concentration. Cu^{2+} removal percentages could be listed as 34, 23, and 10 at 10, 25, and 50 mg/L, respectively. Furthermore, Cd^{2+} uptake could be as low as 16.3 mg/g, which was the lowest level among other metals. In general, these results are compatible with the literature. In the study of Roh *et al.* (2015), increasing Cd^{2+} level from 10 to 20 mg/L decreased the adsorption efficiency of the ion. A similar trend was also obtained by Shawky (2011). They suggested 100 mg/L of Pb^{2+} as the highest concentration could be completely treated and the effectiveness of the metal recovery was lowered beyond this concentration. A possible explanation for these results is that high initial heavy metal levels were subjected to a limited number of active sites on the adsorbents. This resulted in more metals left in the solution. Furthermore, competition would be likewise important in our study because Pb^{2+} ion removal rate was improved whereas both Cu^{2+} and Cd^{2+} adsorption were decreased.

Although Pb^{2+} ion removal was considerably high, Cu^{2+} and Cd^{2+} uptakes were not satisfactory in previous trials. For this reason, the effect of bed depth (amount of adsorbent) was also investigated. A–C beads were doubled (increased to 20 g) and as expected the bed height of the column was increased from about 9.5 to 19 cm. Results are illustrated in Figure 7. According to the results, an increase in adsorbent amount might be promising for effective multiple heavy metal removal since both Cu^{2+} (Figure 7(b)) and Cd^{2+} (Figure 7(c)) uptakes were improved. Similarly, Pb^{2+} ion removal was much better and final Pb^{2+} ion concentrations were as low as 0.4 mg/L (which was the maximum level) (Figure 7(a)). That is, no breakpoint was observed for Pb^{2+} ion. On the other hand, breakpoints for Cu^{2+} and Cd^{2+} were significantly delayed at 20 g of A–C beads. For example, for the Cu^{2+} ion, the value was reached after 7.5 and 70 hours at 10 and 20 g of A–C beads, respectively. The possible reasons for these findings are a higher number of adsorption sites available for treatment and time supplying opportunities to access deeper pores in the adsorbents. Furthermore, the saturation of the column was delayed until the end of experiments for Cu^{2+} and Cd^{2+}, and no saturation was observed for Pb^{2+}. Saturation concentrations for Cd^{2+} and Cu^{2+} were measured after 172 litres of heavy metal solution were treated through the column. Similar trends were observed in the study of Jung *et al.* (2016). Powdered drinking water treatment residue was entrapped in alginate and applied to remove fluoride from industrial wastewater. Effect of fixed-bed height was examined in the

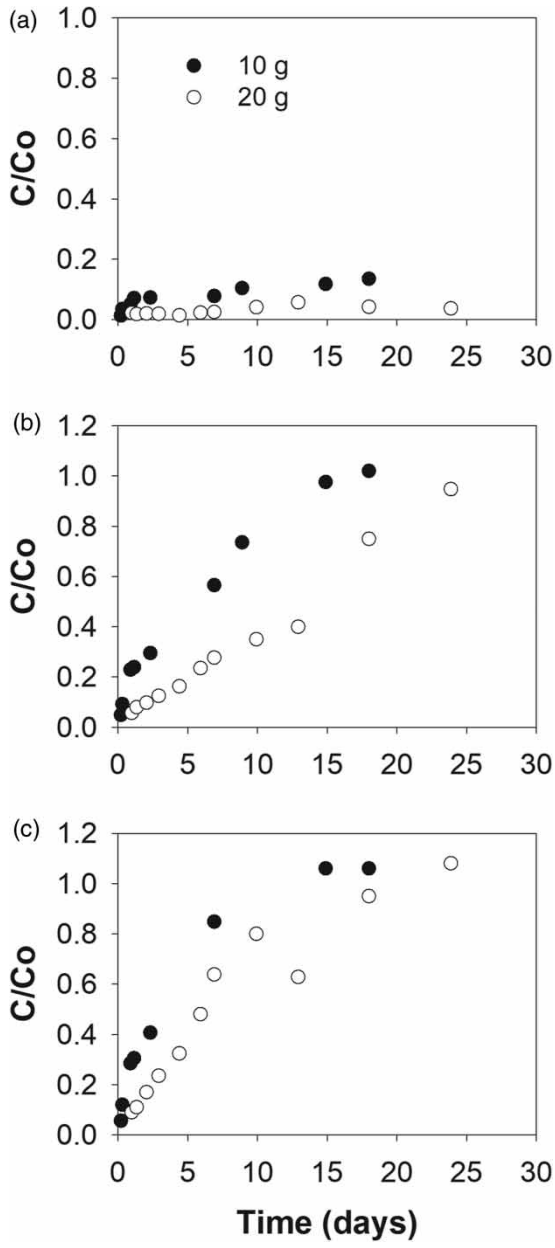


Figure 7 | Effect of bed depth on (a) Pb^{2+}, (b) Cu^{2+}, (c) Cd^{2+} removal in adsorption columns.

range of 20 and 60 cm. A very sharp breakthrough was observed at 20 cm height, while breakthrough capacity was considerably increased at 60 cm height.

Evaluation of adsorption data obtained at different bed depths is summarized in Table S5. By adding higher amounts of A–C beads the resulting deeper fixed bed supplied better heavy metal uptake. This was clear, particularly for Cd^{2+} ions. While the amount of Pb^{2+} ions removed from the aqueous phase increased from 1,173 to

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1,658 mg, this value was improved more than double for Cd^{2+}, from 256.3 to 570.2 mg. Furthermore, heavy metal removal efficiencies were increased especially for Cu^{2+} ions. The values were 34 and 54% at 10 and 20 g of A–C beads, respectively. On the other hand, the q_{eq} level for Pb^{2+} ions was decreased from 117.3 to 82.9 mg/g. Meanwhile, almost the same metal uptake ratios for Cu^{2+} and Cd^{2+} ions were obtained at both adsorbent depths. Although the adsorption pattern was similar to a previous study (Jung *et al.* 2016), maximum adsorption capacities were significantly improved from 0.87 to 19.36 mg fluoride/ g adsorbent by increasing fixed-bed height from 20 to 60 cm.

For economy of adsorption, the reusability of an adsorbent is one of the key issues in practice. To elucidate whether A–C beads could be regenerated or not, a series of experiments were performed by using EDTA, HNO_3, and H_2SO_4 as desorbing agents. Since the calcium ion was used as the crosslinking ion, EDTA seemed to break the bonds within the bead structure, which resulted in shape deterioration of the beads. Thus, A–C beads may not be suitable for further use when EDTA is applied. In addition, H_2SO_4 was not effective particularly for the release of Pb^{2+} ions (Figure S4). The reason might be the precipitation of low-soluble $CaSO_4$, which makes the adsorbent unstable. On the other hand, HNO_3 was found to be the most successful agent among them. As presented in the figure, the reuse potential of A–C beads was maintained three times especially for Pb^{2+} and Cu^{2+} ions. However, the fourth use of the beads might not be favorable because heavy metal uptake potentials decreased more than 15% for all metals tested. After certain trials of heavy metal recycling using the acid, the availability of the functional sites seemed to be reduced. The recovery efficiency of metals after adsorption changed according to the regeneration agent, adsorbent, and metal type. However, most of the metals can be desorbed and repeated use of the adsorbents appeared to be possible to reduce the adsorption cost (Cai *et al.* 2016).

CONCLUSION

A–C beads were formed and applied for mixed heavy metal removal using batch and continuous reactors in the current study. They were found to be efficient particularly for lead removal up to 214.5 mg/g A–C beads and to a lesser extent for copper and cadmium uptake. Continuous operation of an adsorption column resulted in 98% of Pb^{2+} removal at 2 mL/min of flow rates and 10 mg/L of initial metal concentration. Furthermore, the adsorbent could be successfully reused up to three times after regeneration by nitric acid solution. As a result, the system seemed to be useful as a polishing step for low heavy metal concentrations to achieve discharge standards.

ACKNOWLEDGEMENT

This work was supported by The Scientific Research Projects Coordination Unit of Akdeniz University. Project Number: FYL-2016-2001, FYL-2017-2948.

DISCLOSURE STATEMENT

No competing financial interests exist.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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First received 30 October 2020; accepted in revised form 29 January 2021. Available online 10 February 2021

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