

# Preparation of granular activated carbons from composite of powder activated carbon and modified $\beta$ -zeolite and application to heavy metals removal

S. M. R. Seyedein Ghannad and M. N. Lotfollahi

## ABSTRACT

Heavy metals are continuously contaminating the surface and subsurface water. The adsorption process is an attractive alternative for removing the heavy metals because of its low cost, simple operation, high efficiency, and flexible design. In this study, influences of  $\beta$ -zeolite and Cu-modified  $\beta$ -zeolite on preparation of granular activated carbons (GACs) from a composite of powder activated carbon (PAC), methylcellulose as organic binder, bentonite as inorganic binder, and water were investigated. A number of granular samples were prepared by controlling the weight percentage of binder materials, PAC and zeolites as a reinforcing adsorbent. Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction techniques were employed to characterize zeolite, modified zeolite and produced GAC. The produced GACs were used as the adsorbent for removal of  $\text{Zn}^{+2}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solutions. The results indicated that the adsorption of metals ions depended on the pH (5.5) and contact time (30 min). Maximum adsorption of 97.6% for  $\text{Pb}^{2+}$ , 95.9% for  $\text{Cd}^{2+}$  and 91.1% for  $\text{Zn}^{+2}$  occurred with a new kind of GAC made of Cu-modified  $\beta$ -zeolite. The  $\text{Zn}^{+2}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions sorption kinetics data were well described by a pseudo-second order model for all sorbents. The Langmuir and Freundlich isotherm models were applied to analyze the experimental equilibrium data.

**Key words** | binders, composite, Cu-modified beta-zeolite, granular activated carbon, heavy metals removal, kinetic models

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## INTRODUCTION

Zeolites, as microporous aluminosilicates with crystalline structures, are extensively used as selective adsorbents in the environmental aspects or for catalysts in various chemical processes. Zeolites, such as  $\beta$  zeolite (a 12-ring aperture (3D) high-silica zeolite), have been broadly employed for diverse purposes encompassing separation and adsorption processes (Kunkeler *et al.* 1998; Motlagh-Bahadory-Esfahani & Faghihian 2014).

Activated carbons (with high porosity and large surface area) are applied in a variety of forms including granular activated carbon (GAC) and powder activated carbon (PAC). Typical applications of PAC are use in sugar decolorization, food processing and pharmaceuticals. GAC is frequently used in continuous processes of gas and liquid phase applications. GAC has a number of advantages over PAC including lower pressure drop, regeneration and reusability, high hardness and low attrition (Oh *et al.* 2009; Al-Rahbi & Williams 2016).

In the recent decades, different methods have been proposed to produce the shaped activated carbons (Garcia-Garcia *et al.* 1997; Lim *et al.* 2010). In order to improve the properties of the shaped activated carbons, using binders are a conventional method. In several studies, a range of binders were used including ammonium phenolic resin, lignosulphonate (ALSA), araldite resin, PVA, sodium salt and humic acid (Shi *et al.* 2003; Smith *et al.* 2012), clays and organic binder (Carvalho *et al.* 2006; Lim *et al.* 2010; Saeidi & Lotfollahi 2015). In addition to the effects of the binders (organic and inorganic) in shaping the GAC, previous researches examined the effects of particle size distribution of PAC on the properties of their products. They concluded that controlling the particle size distribution of PAC improved the products quality (Saeidi & Lotfollahi 2014, 2015a, 2015b, 2016).

Recently, the study of zeolites/activated carbon composite is considered as a new material which has properties of

both zeolites and carbon. The zeolites/activated carbon composites were extensively used in scientific and experimental studies as a result of the adsorptive features of zeolite and activated carbon and their extensive uses in the wastewater industries and gas purification. Composite materials produced from activated carbon and zeolite materials contain hydrophobic and hydrophilic properties. For that reason, this new composite is appropriate for sorption of both organic materials and metallic ions from aqueous and gaseous phases (Babic *et al.* 2011; Foo & Hameed 2011; Ma *et al.* 2012). Zhu *et al.* (2016) produced a set of spherical samples by activated carbon, ZSM-5, and phenolic resin as binder. Their results demonstrated that the produced samples (with high surface area) showed well removal effects for benzene, suitable iodine number and an acceptable bactericidal effect.

Heavy metals (such as cadmium (Cd), zinc (Zn), and lead (Pb) ions) in wastewater streams have attracted the attention of the environmental researchers due to their toxicity and threat to human beings. Therefore, removal of heavy metals from wastewater is one of the most significant environmental and economic topics (Amer *et al.* 2017; Bahabadi *et al.* 2017). Between the several methods for removing the heavy metals from the wastewater streams, the adsorption process is an attractive alternative because of its low cost, simple operation, high efficiency, and flexible design.

In the present study, a mixture of methylcellulose (MC),  $\beta$ -zeolite, Cu-modified  $\beta$ -zeolite, bentonite and PAC was used for producing GAC as a new composite. The effects of the binders,  $\beta$ -zeolite and Cu-modified  $\beta$ -zeolite compositions on the mechanical strength and the adsorption properties of the produced samples were examined. The sorption of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions from aqueous solutions using modified GAC was also investigated under different experimental conditions. The kinetic models were used in this study to analyze the adsorption rate data. The Langmuir and Freundlich isotherm models were applied to analyze the experimental equilibrium data.

## MATERIALS AND METHODS

### Materials

Bentonite (specific surface area of  $16\text{ m}^2/\text{g}$ ) and methyl cellulose (400 cps) as binders were provided from Shah industrial mining company (Iran) and BDH (UK), respectively. PAC with iodine number of 1,270 mg/g (ASTM standard D4607-94) was purchased from Jacobi commercial

company (Sweden). Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), potassium iodide (KI), iodine (I), starch, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Merck Company (Germany).  $\beta$ -Zeolite was purchased from Zeolyst International Company (USA). The chemicals used for the study were analytical grades of Lead nitrate ( $\text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ), cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) all purchased from Sigma-Aldrich. These chemicals were used to prepare the metal solutions by dissolving them in double distilled water.

### Modification of $\beta$ -zeolite

Preparation of Cu-modified  $\beta$ -zeolite was carried out by an ion-exchange method (Azizi & Ehsani-Tilami 2013). In this method, 0.1 g  $\beta$ -zeolite was mixed with 10 mL aqueous solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) (1 M) at  $\text{pH} = 4$  in a 50 mL reaction flask. Cu ion-exchanged  $\beta$ -zeolite was prepared at 298 K for 4 h. The bright blue solid phase was filtered, washed with distilled water. Then the solid was dried at 343 K for 24 h and calcinated at 823 K for 4 h.

### Characterization of Cu modified $\beta$ -zeolite

$\beta$ -zeolite and the modified samples were characterized by a series of complementary analytical techniques. In this work, for preparing the Cu-modified  $\beta$ -zeolite, 0.1 g  $\beta$ -zeolite was mixed with 10 mL aqueous solution of copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) (1 M). Powder X-ray diffraction (XRD) was obtained using a GBC MMA X-ray diffractometer (Cu  $K\alpha$  as radiation resource) in the scope of scanning angle ( $2\theta$ )  $5^\circ$ – $50^\circ$  with scanning rate of  $5^\circ/\text{min}$ . Fourier transform infrared spectroscopy was performed (Nicolet 400 D Impact spectrum single FT-IR device) at the scanning scope of  $4,000$ – $400\text{ cm}^{-1}$  with the resolution of  $4\text{ cm}^{-1}$ .

### Preparation of GAC

In order to form the zeolite + PAC + binders composite, different proportions of PAC, MC as organic binder,  $\beta$ -zeolite or Cu-modified  $\beta$ -zeolite, bentonite as inorganic binder and water was mixed. The mixing was performed in a laboratory mixer with 300 rpm for 20 min in a water bath at  $80^\circ\text{C}$  (The temperature was regulated by a thermostatic bath with the precision of  $\pm 0.2^\circ\text{C}$ ). The mixture's plasticity related to the ratio of binders in the mixture (Saeidi & Lotfollahi 2015). The components were weighed on an analytical balance (A&D Company, GF-600, Japan) with

an accuracy of 0.001 g. The produced mixture was injected into a cylindrical mold (1 cm diameter and 1 cm long). Then, the produced GACs were dried at 100 °C for 48 h. It should be noted that the uniform mixing using high-speed mixer improves the adsorption capacities of the produced samples (Saeidi & Lotfollahi 2015).

The FT-IR spectra of GAC is presented in Figure 1. The peak at 3,453.6 cm<sup>-1</sup> can be attributed to the O–H stretching of the hydroxyl groups and intermolecular hydrogen bonds. The characteristic bands at 2,700–2,900 cm<sup>-1</sup> were considered as the C–H stretching due to presence the CH and CH<sub>2</sub> groups of the cellulose structure. The peak at 2,352.5 cm<sup>-1</sup> was related to the C–H stretching of methyl groups. The characteristic bands at region 1,000–1,250 cm<sup>-1</sup> were related to the Si–O–C structure (peaks at 1,188.4 cm<sup>-1</sup> and 1,066.7 cm<sup>-1</sup>). In addition to, the existence of Si–C bonding was confirmed by the peak at 764.4 cm<sup>-1</sup>. Another, peaks were attributed to the  $\beta$ -zeolite and AC structure. These changes in the peaks and the creation of various functional groups indicated that the new adsorbent (GAC) has been produced.

### Evaluation of the produced GAC

The produced GACs were evaluated by investigating their adsorption capacity, including iodine number and removal of heavy metals from aqueous solutions. For this purpose, the produced GACs were used for adsorption of Zn<sup>+2</sup>, Cd<sup>+2</sup> and Pb<sup>+2</sup> ions as heavy metals from aqueous solution based on the new composites ( $\beta$ -zeolite or Cu-modified

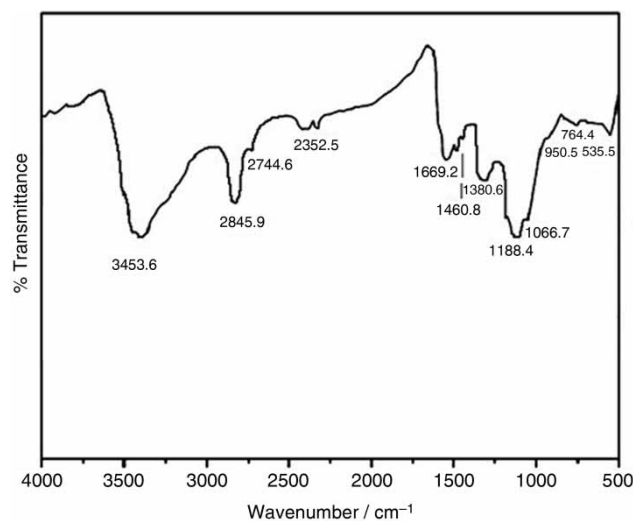


Figure 1 | FT-IR spectra of GAC.

$\beta$ -zeolite). Atomic absorption spectrometer (AAS) with the Zn<sup>+2</sup>, Cd<sup>+2</sup> and Pb<sup>+2</sup> hollow cathode lamps and air acetylene flames were applied for specifying the ions concentrations in the solutions. The adsorption capacity ( $q$ ) and removal efficiency ( $R$ ) were determined by Equations (1) and (2):

$$q = \frac{(C_i - C_f)V}{m} \quad (1)$$

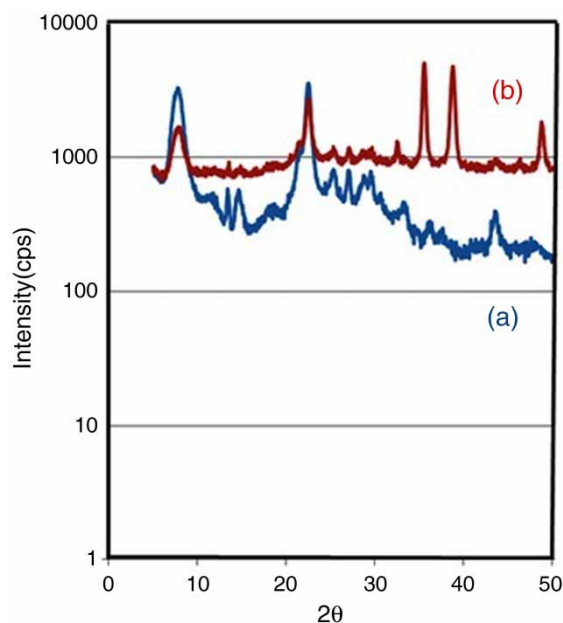
$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where  $C_i$  and  $C_f$  are the initial and final concentration (mg/l) of heavy metal ions, respectively.  $m$  and  $V$  are the mass of adsorbent (g) and the volume of solution (l), respectively. The pH of solution was controlled at a desired value by adding the dilute solution of ammonia or hydrochloric acid. A Jenway 3510 model pH meter was applied for pH measurement. The effects of contact time (20–40 min) and pH (3.0–7.0) on the adsorption of Zn<sup>+2</sup>, Cd<sup>+2</sup> and Pb<sup>+2</sup> ions were investigated. Another important factor for investigating the adsorption capacity of the produced samples is the iodine number of samples. The iodine number is determined as the value of iodine adsorbed per gram of AC at an equilibrium concentration that is measured according to the method established by the American Society for Testing and Materials (ASTM D4607-94 (ASTM 2006)). This factor is used as a rapid and easy indicator of the GACs porosity (Saeidi & Lotfollahi 2016). Another important property of the produced GAC is measuring of the compression strength. It was measured as the sample was destroyed by supplying a force on the sample using a U.T.M. device (H25KS, Hounsfield) at a velocity of 10 mm/min.

## RESULTS AND DISCUSSION

### Physical and chemical properties of Cu modified $\beta$ -zeolite

Figure 2 demonstrates the XRD spectra of the  $\beta$ -zeolite and the Cu modified  $\beta$ -zeolite studied in this work. The location of diffraction lines which remained unchanged demonstrated that the structure of  $\beta$ -zeolite remained intact after introducing the Cu cations. The XRD patterns of Cu modified  $\beta$ -zeolite as a CuO phase, which can be defined with the main diffraction peaks at  $2\theta = 32.42^\circ$ ,  $35.54^\circ$ ,  $38.75^\circ$ ,



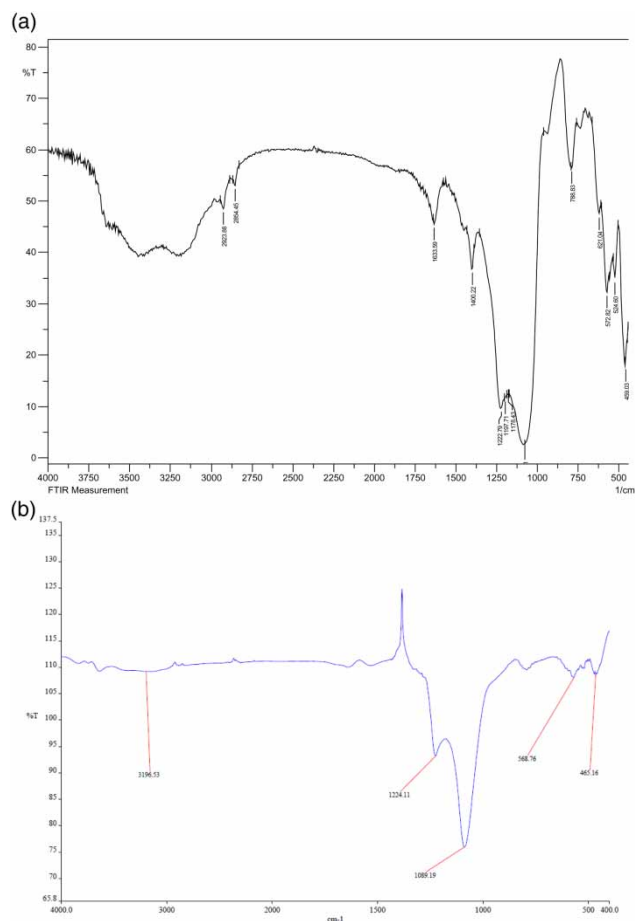
**Figure 2** | XRD patterns of (a)  $\beta$ -zeolite and (b) Cu-modified  $\beta$ -zeolite.

48.74°, indicated that the oxidation of  $\text{Cu}^{2+}$  could be occurred during the thermal treatment.

The FT-IR spectra of  $\beta$ -zeolite and Cu modified  $\beta$ -zeolite are presented in Figure 3. The characteristic bands at 1,070–1,090  $\text{cm}^{-1}$  observed in both spectra were considered as the Si–O stretching of Si–O–Si structure. The bands within the ranges 1,000–1,300  $\text{cm}^{-1}$  and 400–700  $\text{cm}^{-1}$  were attributed to the  $\beta$ -zeolite structure (Figure 3). Based on the comparison of Figure 3(a) and 3(b), it can be concluded that the intensity of diffraction lines decreased as the Cu cation was introduced. Comparing two spectra for  $\beta$ -zeolite and Cu-modified  $\beta$ -zeolite (Figure 3(a) and 3(b)) indicated that the bands of Cu-modified  $\beta$ -zeolite decreased sharply at 1,089  $\text{cm}^{-1}$  and 1,224  $\text{cm}^{-1}$ . They are powerful evidences for the presence of copper. The same trend was observed in the other bands. In order to obtain more information about the existence of Cu in the  $\beta$ -zeolite (Figure 3(b)), the bands at range of 465.16 and 568.76  $\text{cm}^{-1}$  are related to  $\text{Cu}^{2+}$  interacting with oxygen in the  $\beta$ -zeolite structure. The results indicated that Cu has affected all functional groups in the  $\beta$ -zeolite.

### Determination of binder content

In this work, PAC, MC,  $\beta$ -zeolite, Cu modified  $\beta$ -zeolite and bentonite were used to produce the GAC. The surface area of produced samples depends on the value of organic binder (MC) (Saeidi & Lotfollahi 2016). Increasing the



**Figure 3** | FT-IR spectra of (a)  $\beta$ -zeolite and (b) Cu-modified  $\beta$ -zeolite.

content of MC (wt%) leads to decreasing surface area of produced samples. Therefore, the minimum amount of MC should be determined to reach good shape and high mechanical strength accompanied with suitable surface area. For this reason, the amount of MC was increased in order to reach an appropriate amount. Increasing the MC content to 5 wt% led to production of samples with good qualities both in appearance and mechanical strength. The samples with less than this value (1, 2, 3, 4 wt%) did not have good shape and mechanical strength. The MC content was increased to 6, 7 and 8 wt% in order to study its effects on the properties of the produced GAC samples. Increasing MC content from 5 to 8 wt% in the constant inorganic binder led to a decrease in the surface areas of the produced samples. However, the mechanical strength of the samples increased and the iodine number of the samples decreased with increasing MC content in the produced samples. The results of the mechanical strength show an improvement in the mechanical strength

**Table 1** | Iodine number and mechanical strength of the produced GAC at different contents of MC,  $\beta$ -zeolite and bentonite

Number of test	Bentonite (wt)%	MC content (wt)%	$\beta$ -zeolite (wt)%	Iodine number (mg/g)	Mechanical strength (N)
1	10	5	0	1,210.8	222.78
2	9.5	5	0.5	1,226.1	219.85
3	9	5	1	1,230.4	218.15
4	8.5	5	1.5	1,233.8	211.98
5	8	5	2	1,241.2	210.17
6	7.5	5	2.5	1,248.2	207.07
7	7	5	3	1,253.6	202.10
8	6.5	5	3.5	1,259.1	191.37
9	9	6	1	1,228.8	220.64
10	9	7	1	1,227.6	221.95
11	9	8	1	1,227.2	224.28

of the samples with the increase in the bentonite content (Table 1).

### Effects of $\beta$ -zeolite and Cu modified $\beta$ -zeolite on the properties of GAC

As can be seen in Table 1, by increasing the  $\beta$ -zeolite content in the initial mixture from 0 to 3.5 wt%, the iodine number of the samples increased from 1,210.8 to 1,259.1 mg/g and the mechanical strength of the samples reduced from 222.78 to 191.37 N. In order to improve properties of the produced GAC,  $\beta$ -zeolite was modified by copper and the properties of modified samples were compared with the properties of the original  $\beta$ -zeolite. Using Cu for modification of  $\beta$ -zeolite led to higher adsorption (iodine number) compared to other metals due to an increased number of active sites after modification (Wen *et al.* 2016; Bahabadi *et al.* 2017). The results indicated that by using the Cu modified  $\beta$ -zeolite content, the iodine number of samples increased (Table 2). For example, the iodine number of samples containing 5 wt% MC, 1 wt%  $\beta$ -zeolite, and 9 wt% bentonite in the composite, which was 1,230.4, increased to 1,251.3 mg/g when Cu- $\beta$ -zeolite was used in the composite. The mechanical strength of samples was slightly increased from 218.15 to 218.79 N.

### Adsorption experiments

Sorption experiments have been conducted to find the optimum pH and contact time as very important parameters in the adsorption process. The produced GACs, with different amounts of Cu modified  $\beta$ -zeolite or  $\beta$ -zeolite, MC, and

**Table 2** | Iodine number and mechanical strength of the produced GAC with different contents of MC and Cu modified  $\beta$ -zeolite and bentonite

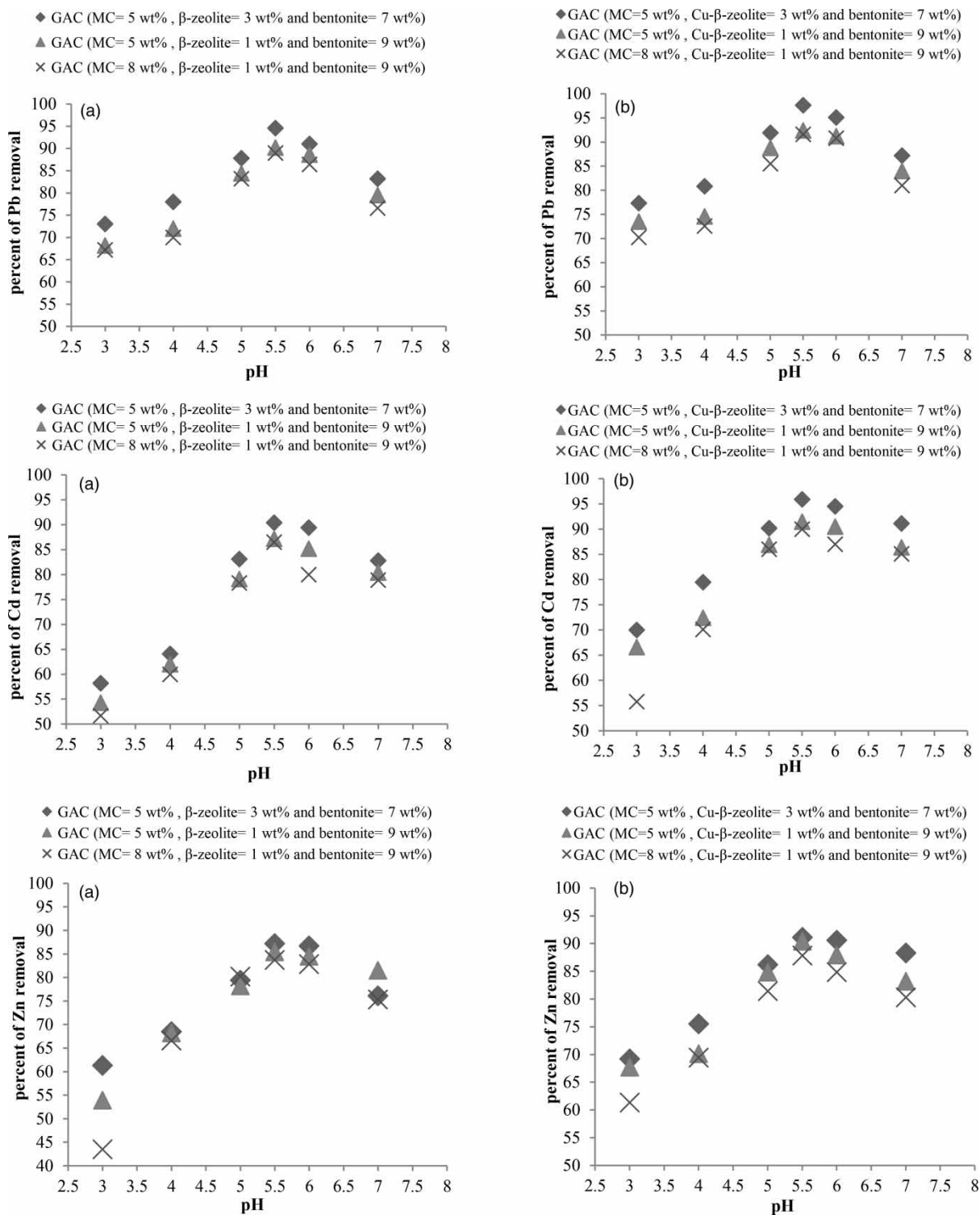
Number of test	Bentonite (wt)%	MC content (wt)%	Cu modified $\beta$ -zeolite (wt)%	Iodine number (mg/g)	Mechanical strength (N)
1	10	5	0	1,210.8	222.78
2	9.5	5	0.5	1,247.7	220.03
3	9	5	1	1,251.3	218.79
4	8.5	5	1.5	1,256.5	212.34
5	8	5	2	1,259.5	212.19
6	7.5	5	2.5	1,266.9	209.25
7	7	5	3	1,270.4	202.66
8	6.5	5	3.5	1,272.7	192.72
9	9	6	1	1,250.4	221.40
10	9	7	1	1,247.1	223.08
11	9	8	1	1,245.3	224.83

bentonite (wt%), were used for removing  $Zn^{+2}$ ,  $Cd^{+2}$  and  $Pb^{2+}$  ions from aqueous solutions. Zinc, lead and cadmium poisoning are important health issues in every country (Ghasemian-Lemraski & Sharafinia 2016). Ion solutions were prepared by dissolving a suitable amount of  $Cd(NO_3)_2 \cdot 4H_2O$ ,  $Pb(NO_3)_2 \cdot H_2O$  and  $Zn(NO_3)_2 \cdot 6H_2O$  in 1,000 ml of distilled water. A series of 100 ml conical flasks was used in this study. The method involved filling each flask with 100 ml of Zn, Cd and Pb ion solutions with a concentration of 50 ppm and adding 0.75 g of the sorbent to the solution. The flasks were shaken at room temperature by a mechanical shaker. At the end of the test, the sorbent was filtered out and washed using deionized water. The concentration of Zn, Cd and Pb ions in the solution was obtained by AAS.

### Effect of pH on sorption

The pH of a solution is one of the most important operational parameters in the removal of heavy metal ions from solution with the adsorption process. The effect of initial pH on the sorption of Zn, Cd and Pb from solutions was investigated for all of the produced sorbents at room temperature. In these experiments, 0.75 g of the sorbents was added to 100 mL of a 50 ppm solution at different pHs in the range of 3–7 (shown in Figure 4). As can be observed in Figure 3, increasing the pH led to an increase in the sorption of Zn, Cd and Pb, which reached a maximum value at pH 5.5 and then decreased. It can be seen from Figure 3 that pH values less than 5 are not suggested for the adsorption process. The low adsorption capacity at low





**Figure 4** | Effect of pH on the removal of lead, cadmium and zinc by samples containing various amounts of (a) MC,  $\beta$ -zeolite and bentonite and (b) MC, Cu modified  $\beta$ -zeolite and bentonite.

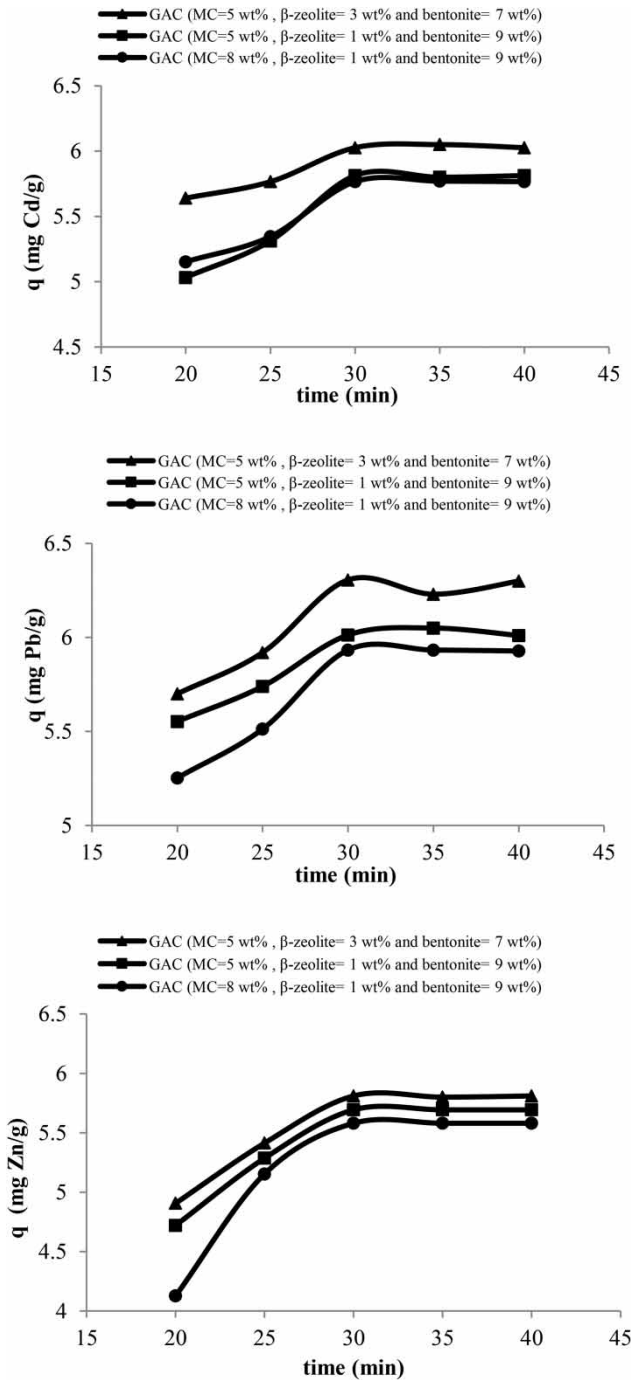
pH can be justified because of destruction in the structure of zeolites (Apiratikul & Pavasant 2008; Malamis & Katsou 2013). Therefore, the structure of zeolite may collapse in

the presence of acids (Rao *et al.* 2006) especially at a low pH. The amount of damage to the structure of zeolite depends on the pH of the solution.

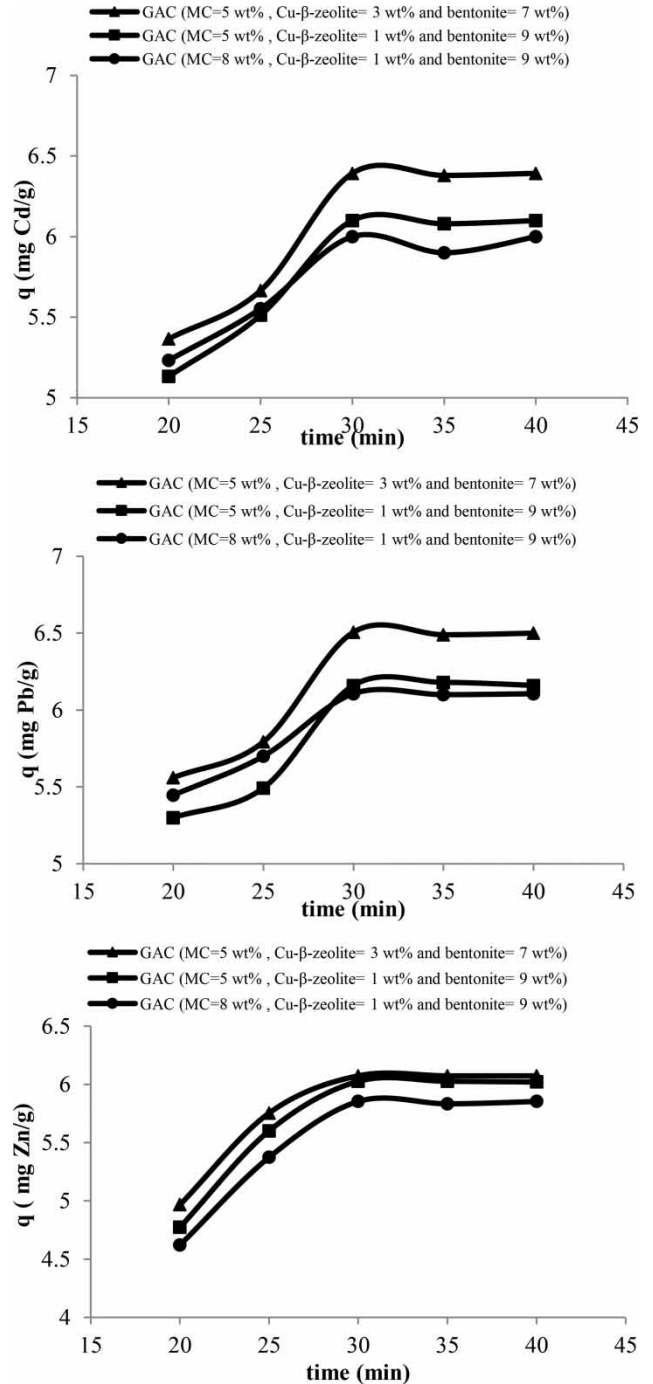
### Effect of contact time

The adsorption of metal ions on the produced GAC with different values of MC content, bentonite and  $\beta$ -zeolite or Cu modified  $\beta$ -zeolite (wt%) were conducted as a function of contact time. The experiments were carried

out in a metal ion concentration of 50 ppm, pH 5.5 (maximum value) and 0.75 gram of the sorbents at room temperature. It was observed that the amount of Zn, Cd and Pb sorption increased with an increase in the contact time. As shown in Figures 5 and 6, efficiency of removal first followed an increase and then a



**Figure 5** | Sorption capacity ( $q$ ) versus contact time by Cd, Pb and Zn ions for samples containing various amounts of MC,  $\beta$ -zeolite, and bentonite.



**Figure 6** | Sorption capacity ( $q$ ) versus contact time by Cd, Pb and Zn ions for samples containing various amounts of MC, Cu modified  $\beta$ -zeolite, and bentonite.

stationary state was observed. It was concluded that 30 min was adequate for sorption to attain equilibrium. The order of maximum sorption capacity for GAC (MC = 5 wt%, Cu modified  $\beta$ -zeolite = 3 wt% and bentonite = 7 wt%) at contact time of 30 min, in a unit of  $\text{mg}\cdot\text{g}^{-1}$  was:  $\text{Pb}^{2+}$  (6.506) >  $\text{Cd}^{2+}$  (6.393) >  $\text{Zn}^{2+}$  (6.073). The maximum capacity was obtained after 30 min of sorption and at pH 5.5 by GAC (MC = 5 wt%, Cu modified  $\beta$ -zeolite = 3 wt% and bentonite = 7 wt%) as the most effective adsorbent, and the efficiencies of removal were 97.6%, 95.9% and 91.1% for lead, cadmium and zinc, respectively (Table 3).

## Adsorption kinetics

Two kinetic models were utilized in this study to analyze the adsorption rate data. First, the pseudo-first order kinetic model was considered to describe the sorption kinetics of Zn, Cd and Pb ions by various adsorbents.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where  $q_t$  and  $q_e$  ( $\text{mg}$  of adsorbed metal/ $\text{g}$  of the sorbent) are the sorption capacities at time  $t$  ( $\text{min}$ ) and at equilibrium, respectively and  $k_1$  ( $\text{min}^{-1}$ ) is the sorption first order rate

**Table 3** | Percent of Pb, Cd and Zn removal by different adsorbents at pH 5.5 and contact time 30 min

Sorbents	Removal (Pb %)	Removal (Cd %)	Removal (Zn %)
GAC (MC = 5, $\beta$ -zeolite = 1, bentonite = 9) wt%	90.2	87.2	85.4
GAC (MC = 5, $\beta$ -zeolite = 3, bentonite = 7) wt%	94.6	90.4	87.2
GAC (MC = 8, $\beta$ -zeolite = 1, bentonite = 9) wt%	89	86.5	83.7
GAC (MC = 5, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	92.4	91.5	90.4
GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt%	97.6	95.9	91.1
GAC (MC = 8, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	91.6	90	87.8

**Table 4** | Kinetic parameters of pseudo-first order and pseudo-second order models for  $\text{Cd}^{+2}$  sorption by sorbents

Sorbents	Pseudo-first order		Pseudo-second order		
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$q_e$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$
GAC (MC = 5, $\beta$ -zeolite = 3, bentonite = 7) wt%	0.2218	0.9527	0.0510	6.5189	0.9982
GAC (MC = 5, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.2861	0.9461	0.0190	6.9979	0.9917
GAC (MC = 8, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.2197	0.9509	0.0270	6.6357	0.9942
GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt%	0.3071	0.9326	0.0117	8.1566	0.9946
GAC (MC = 5, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.2699	0.9546	0.0135	7.6394	0.9973
GAC (MC = 8, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.3019	0.9528	0.0222	7.0224	0.9916

**Table 5** | Kinetic parameters of pseudo-first order and pseudo-second order models for  $\text{Pb}^{+2}$  sorption by sorbents

Sorbents	Pseudo-first order		Pseudo-second order		
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$q_e$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$
GAC (MC = 5, $\beta$ -zeolite = 3, bentonite = 7) wt%	0.2169	0.9027	0.0311	7.0621	0.9955
GAC (MC = 5, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.2306	0.8673	0.0452	6.5487	0.9975
GAC (MC = 8, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.2473	0.9685	0.0249	6.8681	0.9933
GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt%	0.2870	0.9282	0.0133	8.0900	0.9950
GAC (MC = 5, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.3145	0.9221	0.0145	7.6308	0.9928
GAC (MC = 8, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.1933	0.9712	0.0264	7.0028	0.9943



**Table 6** | Kinetic parameters of pseudo-first order and pseudo-second order models for Zn<sup>+2</sup> sorption by sorbents

Sorbents	Pseudo-first order		Pseudo-second order		
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$q_e$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$
GAC (MC = 5, $\beta$ -zeolite = 3, bentonite = 7) wt%	0.3101	0.9743	0.0163	7.1275	0.9948
GAC (MC = 5, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.4292	0.9594	0.0147	7.1430	0.9923
GAC (MC = 8, $\beta$ -zeolite = 1, bentonite = 9) wt%	0.1307	0.9161	0.0141	7.0670	0.9954
GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt%	0.1331	0.9178	0.0206	7.7560	0.9987
GAC (MC = 5, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.1578	0.9705	0.0192	7.2310	0.9903
GAC (MC = 8, Cu- $\beta$ -zeolite = 1, bentonite = 9) wt%	0.4015	0.9674	0.0170	7.0771	0.9991

constant could be obtained from the slope of plotting  $\ln(q_e - q_t)$  versus  $t$ . Another most widely used kinetic model is the pseudo-second order model (Vassileva *et al.* 2013):

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (4)$$

where  $q_t$  and  $q_e$  are the sorption capacities at time  $t$  (min) and at equilibrium, respectively.  $q_e$  and  $k_2$  ( $\text{g}/(\text{mg}\cdot\text{min})$ ) could be calculated from the intercept and slope of linear plotting ( $t/q_t$ ) vs.  $t$ .

The sorption kinetic parameters are in Tables 4–6. The sorption capacities of Zn, Cd and Pb ions by GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt% as the best sorbent versus time are plotted in Figure 7. As can be seen in Figure 7 and Tables 4–6, the pseudo-second order model could be used to describe the sorption kinetic behavior of Zn, Cd and Pb on sorbents more satisfactorily than the first-order kinetics model based on its higher regression coefficient ( $R^2 > 0.99$ ) value.

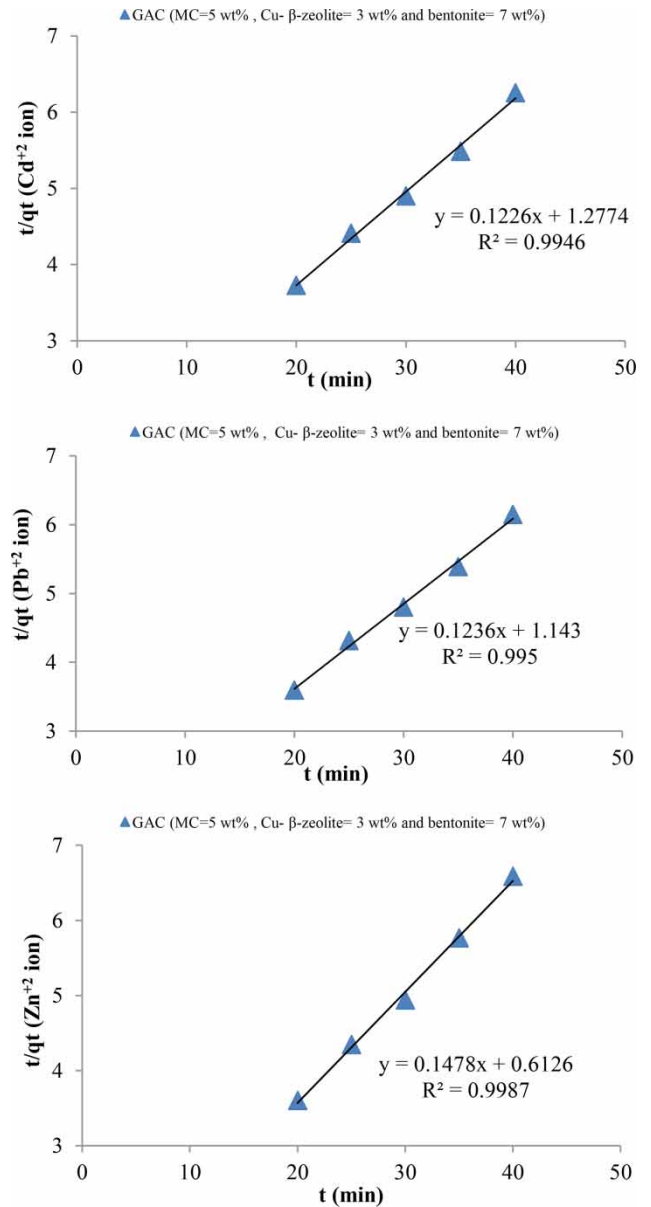
### Adsorption isotherms

In this work, the Langmuir and Freundlich isotherm models (Vassileva *et al.* 2013) were applied to analyze the experimental equilibrium data. The Langmuir and Freundlich isotherm models are presented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m} \quad (5)$$

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

where  $q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the Langmuir constant related to the maximum monolayer sorption capacity,  $C_e$  ( $\text{mg}/\text{L}$ ) is the



**Figure 7** | Time profile and pseudo-second order kinetic model for sorption of Cd<sup>+2</sup>, Pb<sup>+2</sup> and Zn<sup>+2</sup> ions by GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt% as the best sorbent.

**Table 7** | Isotherm constants for GAC (MC = 5, Cu- $\beta$ -zeolite = 3, bentonite = 7) wt% as best sorbent

Isotherms	Heavy metal ions	Constants		
		$k_l$ ( $l \cdot mg^{-1}$ )	$q_m$ ( $mg \cdot g^{-1}$ )	$R^2$
Langmuir equation	Cd	0.5127	15.1017	0.9918
	Pb	0.7915	15.4231	0.9943
	Zn	0.7670	15.3712	0.9936
		$1/n$	$k_f$ ( $l \cdot mg^{-1}$ )	$R^2$
Freundlich equation	Cd	0.1752	29.2708	0.9354
	Pb	0.1707	27.1200	0.9417
	Zn	0.1815	30.8929	0.9089

equilibrium concentration,  $k_l$  ( $l \cdot mg^{-1}$ ) is the Langmuir constant related to the energy of adsorption,  $k_f$  ( $l \cdot mg^{-1}$ ) and  $n$  are the Freundlich constants related to the sorption capacity. The sorption data were fitted to Langmuir and Freundlich isotherm models. The calculated isotherm parameters and the regression coefficients ( $R^2$ ) are in Table 7. Comparison of the ( $R^2$ ) values shows that the Langmuir model fitted quite well with the experimental data, with a high correlation coefficient ( $R^2 > 99\%$ ).

## CONCLUSIONS

The aim of this study was preparation of GACs with different proportions of PAC, MC as an organic binder,  $\beta$ -zeolite or Cu-modified  $\beta$ -zeolite as a reinforcing adsorption and bentonite as an inorganic binder. The produced GACs were tested for evaluating their mechanical strength, adsorption capacity (iodine number) and their capability for removing zinc, cadmium and lead ions from aqueous solutions. The produced GAC was prepared with the minimum amount of MC (5%wt) and bentonite (6.5–10 wt%) to obtain samples with suitable shape. To increase the adsorption capacity of the produced GAC,  $\beta$ -zeolite and Cu modified  $\beta$ -zeolite were used. The results showed that by using  $\beta$ -zeolite modified with copper, the adsorption capacity of samples was increased while their mechanical strength remained stable. The GAC samples produced by Cu-modified  $\beta$ -zeolite was found to be a very good adsorbent for separating metal ions from solutions. The results indicated that the optimum pH for removal of metal ions was 5.5 and contact time at 30 min was adequate to reach equilibrium sorption. The maximum capacity of sorption by GAC (MC = 5 wt%, Cu modified  $\beta$ -zeolite = 3 wt% and bentonite = 7 wt%) as the most effective adsorbent was 97.6%, 95.9% and 91.1% for Pb, Cd and Zn, respectively. This adsorbent had acceptable

mechanical strength. The kinetic experimental data were described with the sorption kinetic models (pseudo-second and pseudo-first order kinetic models). The sorption kinetic data were well coordinated with the pseudo-second order kinetic model.

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First received 18 October 2017; accepted in revised form 10 January 2018. Available online 29 January 2018