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Alkali solid-state conversion of kaolin and zeolite to effective adsorbents for removal of lead from aqueous solution

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ABSTRACT

The adsorption of lead [Pb(II)] ions onto adsorbents prepared by alkali solid-state conversion of kaolin and natural zeolite mixture was investigated. The adsorption isotherms were obtained and the Langmuir parameters were calculated in order to make a comparison between the adsorption capacities of synthesized adsorbents and those of their constituents. The synthesized adsorbents exhibit much higher adsorption capacity than kaolin and zeolite. Therefore, the low-cost adsorbent based on kaolin and Jordanian zeolite has important features since it has an extraordinary adsorption capacity towards Pb(II) ions (157 mg Pb(II)/g at pH 6.0 and 0.1 M ionic strength). Furthermore, the results implied the advantage of using zeolite as filler in kaolin-based geopolymers and the advantage of using kaolin as a binder for zeolite in their use as industrial adsorbents in water purification. The adsorption capacity of the synthesized adsorbents, unexpectedly, increases with pH decrease and ionic strength increase. The XRD pattern of the synthesized adsorbent prepared from Jordanian kaolin (JK) and zeolite indicates that it is amorphous.

Keywords: Adsorption; Lead; Kaolin; Jordanian zeolitic tuff; Alkali solid-state conversion

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1. Introduction

Kaolin possesses two kinds of charges. The first is the permanent negative charge which is produced from isomorphic replacement of Si^{4+} with Al^{3+} in the silica tetrahedral sheet or of trivalent metal ions (such as Al^{3+}) by divalent ions such as Fe^{2+} and Mg^{2+} in the alumina octahedral sheet. The second is the pH dependent charge on the edge surfaces resulting from surface hydroxyl groups [1–3]. Many workers reported that the adsorption of metal ions takes place at surface hydroxyl groups at the edge of sheets rather than in the layers [4,5].

On the other hand, zeolite has different sites available for adsorption of heavy metal ions. Zeolite has a cage-like structure suitable for ion exchange. The adsorption of metal ions onto zeolite particles is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, crystal edges and other imperfections on the surface [6].

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It has been observed [7] that through alkali-activated polymerization reactions, or so called mineral polymerization techniques, the minerals such as clay could be hardened and transformed into useful construction materials. These synthesized geopolymers, which may be described as mineral polymers or inorganic polymers are produced at low temperature by using minimal energy input. In this process, the aluminosilicate kaolinite reacts with alkali at low temperature and polycondenses into hydroxysodalite, which is a stable and hard material [8]. As a result, geopolymers have been gaining the attention of the world as they are becoming potential revolutionary materials [8]. These geopolymers can be synthesized by low-cost alkali solid-state conversion of kaolin [9].

Several methods have evolved over the years on the removal of heavy metal ions present in industrial wastewaters and soils. These are chemical precipitations, conventional coagulation, reverse osmosis, ion exchange and adsorption on activated carbon. Out of these methods, adsorption appears to be the most widely used for the removal of heavy metals. Substances like activated carbon and synthetic zeolites have assumed a wide application in this regard, but their high cost limits their utilization. The possibility of using cheaper adsorbents like kaolin clay suffers from the problem that adsorption of metal ions onto kaolin is much less than that of zeolite [1,2,4]. Since both Jordanian zeolite (ZT) and Jordanian kaolin (JK) are available at low-cost, we suggest here a new possibility for developing a new cheaper adsorbent based on JK and ZT mixture. The alkali solid-state conversion of a mixture of kaolin and zeolite is important from two different points of view: the first is that zeolite can be used in kaolin-based geopolymers for the purpose of water purification. The second is that kaolin can be used as a binder for zeolite which makes it possible for zeolite to be shaped into bodies such as granules, spheres and extrudates with high mechanical strength before application as industrial adsorbents in water purification [10,11].

Little work was found in the literature on the adsorption behaviour of geopolymers. Li et al. studied the adsorption of methylene blue dye onto geopolymeric adsorbent based on fly ash as a source of aluminosilicates. The synthesized geopolymer was found to have much higher adsorption capacity towards methylene blue than fly ash itself [12]. Wang et al. reported an amorphous aluminosilicate geopolymer resulted from alkali solid-state conversion of fly ash. The synthesized geopolymer was also found to have higher adsorption capacity towards Cu(II) ion than the fly ash itself [13].

The present work studied the adsorption of Pb(II) ions onto adsorbents prepared by alkali solid-state conversion of a mixture of kaolin and ZT. The adsorption properties of the starting materials, i.e. zeolitic tuff (ZT) and kaolin will be studied also for the purpose of comparison.

2. Experimental

2.1. Materials

2.1.1. Jordanian kaolin (JK)

JK was obtained from El-Hiswa deposit, which is located in the south of Jordan about 45 km to the east of Al-Quweira town. Preparation of the JK samples involved crushing (using Jaw crusher) of oven dried clay (at 105 °C) with a grain size less than 425 μm. Then the samples were mixed in 50 L plastic drum for several times to make samples more homogenous.

2.1.2. Reference kaolin (RK)

RK from Ukraine (purchased by Jordan international modern trade Co.) with a purity of 95% was used as a reference for JK (with a purity of 60%).

2.1.3. Jordanian ZT

Jordanian ZT was from North to East Jordan deposits (Aritayn area) located around 50 km to the east from Amman, which belongs to phillipsite type of zeolites [14–18].

2.2. Alkali treatment of a mixture of kaolin and zeolite

A mixture of kaolin (Jordanian or reference) and ZT was converted into a paste by adding 35% NaOH solution followed by moulding and curing by placing them in an oven at a temperature of about 80 °C for about 24 h in a ventilated oven. After this curing, the specimens were removed and allowed to cool down at room temperature. Two adsorbents were prepared: one from RK and ZT (M-RZ) and the second from JK and ZT (M-JZ).

About 50 g sample of each adsorbent, i.e. M-RZ and M-JZ, were crushed using Retsch RM 100-crusher. The crushed samples as well as the ZT and the clay materials (JK and RK) were sieved (Fema-SAIZGITTER) at different meshes. The portion with a particle size of 250–500 μm was washed seven times with distilled water (100 mL each) then dried in the oven overnight at 105 °C and kept in a desiccator over anhydrous $CaCl_2$.

2.3. Adsorption studies

Several standard solutions (10–280 ppm) of lead nitrate (98%, PRS Panreac) in 0.1 M $NaClO_4$ (98%, Eurostar Scientific Ltd.) at two pH-values, i.e. 4 and 6, were prepared (pH adjustment using $NaOH/HClO_4$). The absorbance of standard solutions were measured using atomic absorption spectrometer (Varian, AA-250 plus) in order to draw the calibration curve.

In different sets of 100 mL reagent bottles, a 0.05 g of synthesized adsorbent sample (M-RZ and M-JZ) as well as the ZT and clay materials (JK and RK) were placed. To each set of samples, 50.0 mL of standard Pb(II) solutions were independently added. A 10.0 mL portions from each reagent bottle were withdrawn after 24 h of shaking in a shaker water bath (Clifton-11268), then filtered by microfilters (0.45 μm Nylon) and centrifuged (ANNITA.III 6500 rpm, 10 min). The metal concentrations were determined using the atomic absorption spectrometer. The batch adsorption experiments were repeated for M-RZ and M-JZ without supporting electrolyte ($NaClO_4$) to study the effect of changing ionic strength.

3. Results and discussion

The adsorption isotherms of Pb(II) ion onto synthesized adsorbents (M-RZ and M-JZ) were investigated. In order to compare the adsorption properties of the synthesized adsorbents with the minerals from which they are made, the adsorption isotherms of Pb(II) on RK, JK and Jordanian ZT were also investigated.

The Langmuir parameters Q_m and K were determined by nonlinear regression of the Langmuir equation:

$$Q = Q_m KC/(1 + KC)$$

where Q is the amount of Pb(II) adsorbed (mg Pb(II)/g adsorbent), Q_m is the adsorption capacity (mg Pb(II)/g adsorbent), K is the affinity constant (L/mg Pb(II)) and C is the equilibrium concentration of Pb(II) (mmol/L). The resultant plots of nonlinear fitting of the adsorption isotherms of Pb(II) on RK, JK, ZT, M-RZ and M-JZ specimens at ionic strength = 0.1 M $NaClO_4$ and pH 4.0 and 6.0 are shown in Figs. 1 and 2. The resultant Langmuir parameters determined from these nonlinear regression are given in Table 1.

3.1. Adsorption of Pb(II) onto the materials from which synthesized adsorbents are made (RK, JK and ZT)

As shown in Fig. 1 and Table 1, ZT exhibits higher adsorption capacity (Q_m) than kaolin clays (RK and JK). This is in agreement with many studies reported in the literature [1,2,4,19,20], which showed that the adsorption capacity of metal ions onto natural zeolite is higher than that of natural kaolin. This may be due to that the adsorption of Pb(II) onto zeolite occurs via cation exchange. The cation exchange capacities of phillipsite and chabazite (major constituents of ZT) are 3.39 and 3.86 mmol/g, respectively [21], which are much higher than that of kaolin (0.03–0.15 mmol/g) [22].

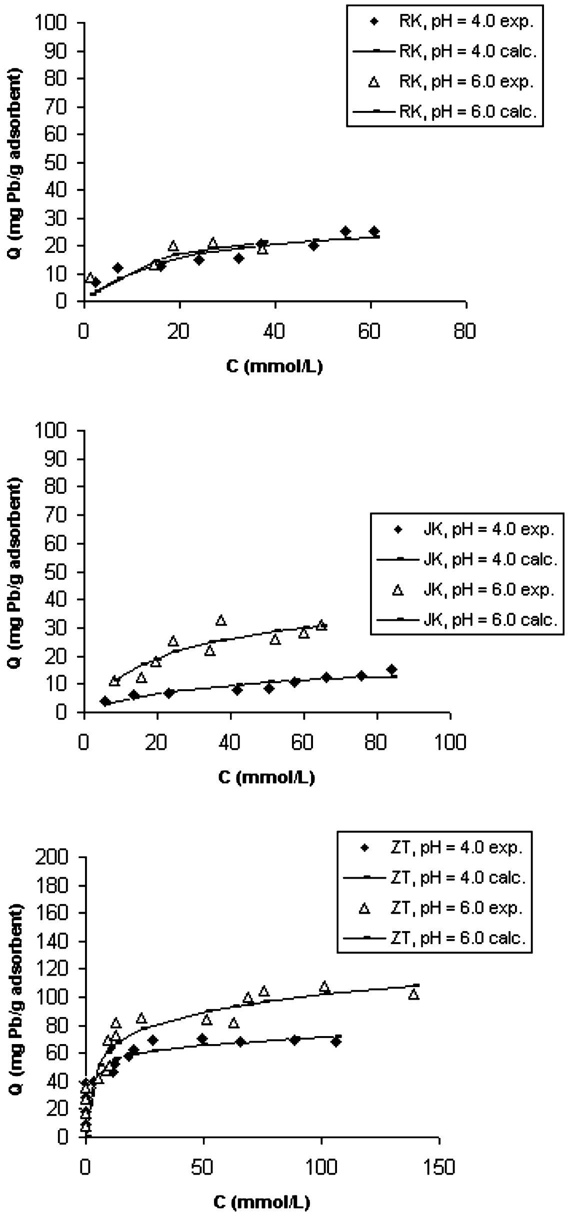

Fig. 1. Adsorption isotherms of Pb(II) onto RK, JK and ZT at pH 4.0 and 6.0 (0.1 M background electrolyte).

As expected, increasing pH favors the adsorption of Pb(II) ions onto RK, JK and ZT (Fig. 1 and Table 1)

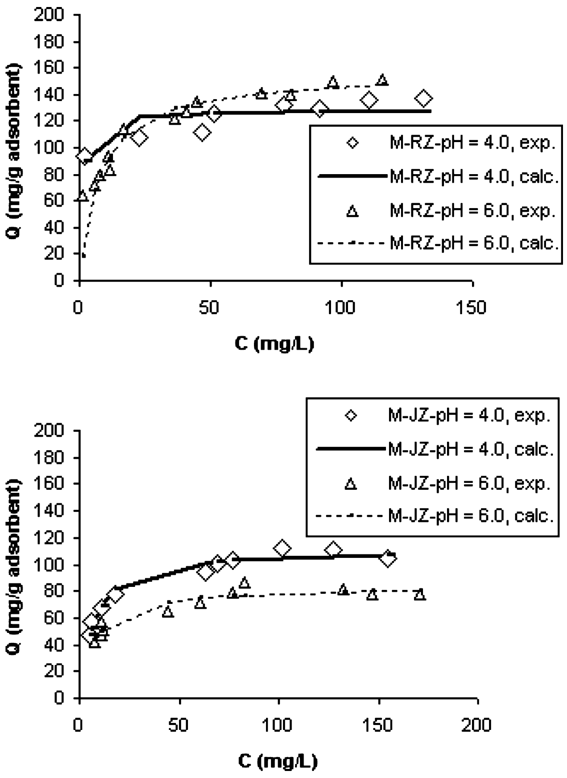

Fig. 2. Adsorption isotherms of Pb(II) onto synthesized adsorbents M-RZ and M-JZ at pH 4.0 and 6.0 (0.1 M background electrolyte).

because of less competition between H^+ and metal ions for adsorption sites [22]. Furthermore, the adsorption of Pb(II) ions onto kaolin was reported to be due to cation exchange at the permanently negatively charged sites at pH < 5 and by complexation with surface hydroxyl groups at the crystal edges at pH > 5 [23]. Thus, pH dependent sites of surface hydroxyl groups at the crystal edges of kaolin may be involved in the adsorption process.

3.2. *Adsorption of Pb(II) onto synthesized adsorbent based on RK and ZT (M-RZ)*

The synthesized adsorbent based on RK and ZT (M-RZ) was found to have much higher adsorption capacity towards Pb(II) ions than RK and ZT (Fig. 2 and Table 1). This may indicate that alkali treatment generates new adsorption sites for Pb(II) ions.

Similar to that in the case of RK, JK, ZT, the adsorption of Pb(II) ions onto M-RZ increases with pH (Fig. 2 and Table 1).

The adsorption capacity (Q_m) for M-RZ at pH 6 and 0.1 M ionic strength (157 mg Pb(II)/g adsorbent, Table 1) was found to be nearly 70% of the highest reported value in literature, which was found for adsorption of Pb(II) onto microporous titanosilicate ETS-10 [24]. This is an interesting achievement because the materials employed in preparation of M-RZ (ZT, Ukrainian kaolin and NaOH) are much less expensive than those employed in ETS-10 (SiO_2, $NaSiO_4$, TiF_4, NaOH and KOH).

3.3. *Adsorption of Pb(II) onto synthesized synthesized adsorbents based on JK and ZT (M-JZ)*

Synthesized adsorbents based on JK and ZT (M-JZ) showed lower adsorption capacity than their corresponding synthesized adsorbents based on RK (M-RZ) (Fig. 2 and Table 1). This may be due to that JK contains less amount of kaolin (60%) than RK (95%). However, the adsorption capacity of M-JZ is higher than its constituents (JK and ZT).

Table 1
Langmuir adsorption parameters for the adsorption of Pb(II) ion onto ZT, JK, RK, M-RZ and M-JZ at 0.1 M $NaClO_4$ background electrolyte[a]

	pH 4.0			pH 6.0		
Specimen	Q_m (mg Pb/g adsorbent)	K (L/mg)	Sum of square residuals	Q_m (mg Pb/g adsorbent)	K (L/mg)	Sum of square residuals
RK	29.7	0.056	63	34.4	0.060	68
JK	21.0	0.020	19	41.3	0.044	109
ZT	72.6	0.253	127	108	0.131	991
M-RZ	128	1.20	655	157	0.128	294
	(108)	(2.19)	943	(138)	(0.046)	258
M-JZ	112	0.146	168	83.8	0.135	242
	(79.9)	(0.249)	1194	(73.5)	(1.31)	683

[a] Values in brackets are for adsorption without background electrolyte.

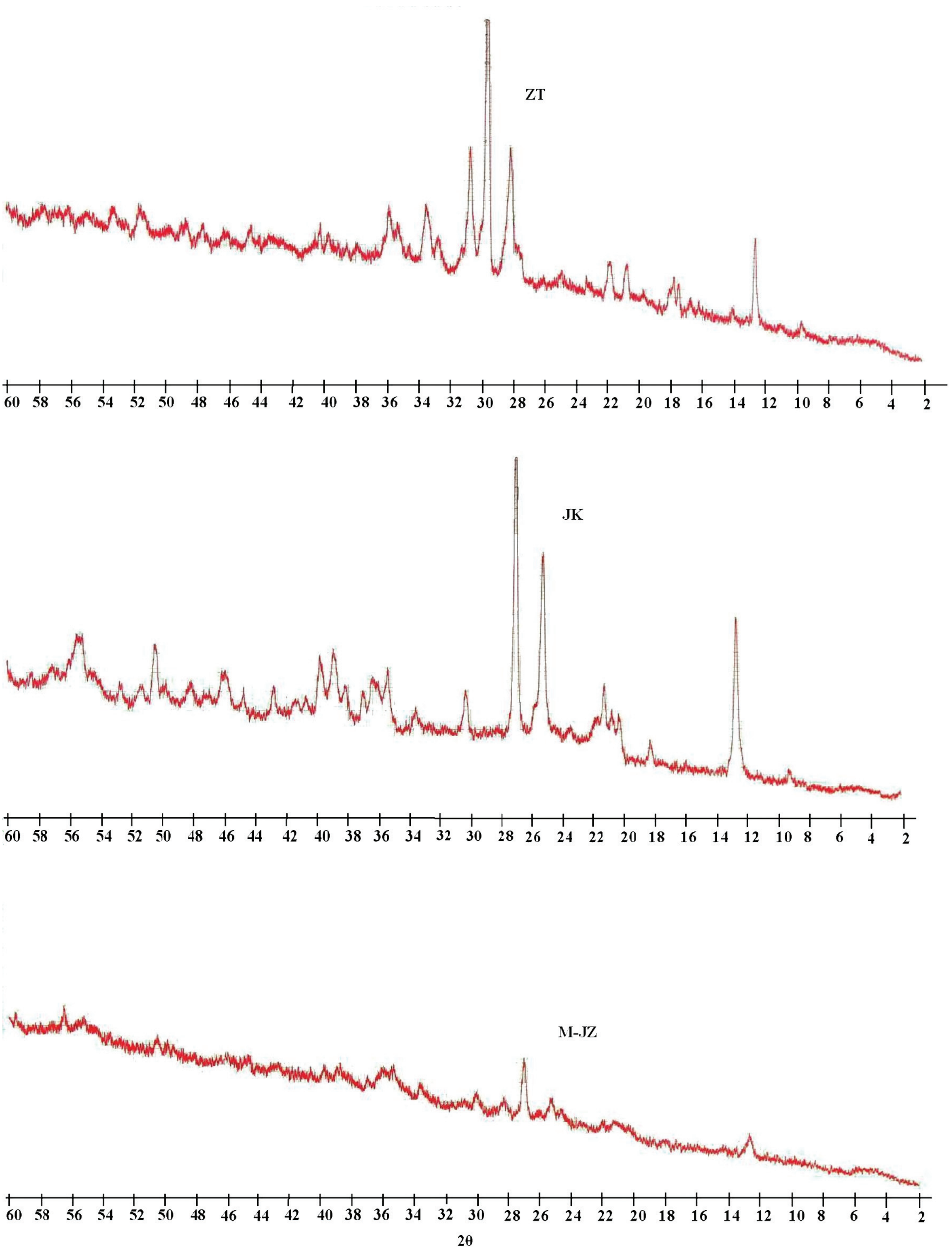

Fig. 3. XRD pattern of the synthesized adsorbent M-JZ and its starting materials; ZT and JK.

As shown in Fig. 3, the XRD pattern of the synthesized adsorbent M-JZ is much more amorphous than that of starting materials; viz., ZT and JK. This may indicate that alkali treatment destructs the crystallinity of the starting materials.In contrast to the behaviour observed in the case of RK-based adsorbent (M-RZ), the adsorption of Pb(II) onto JK-based adsorbent (M-JZ) was found to decrease with increase of pH

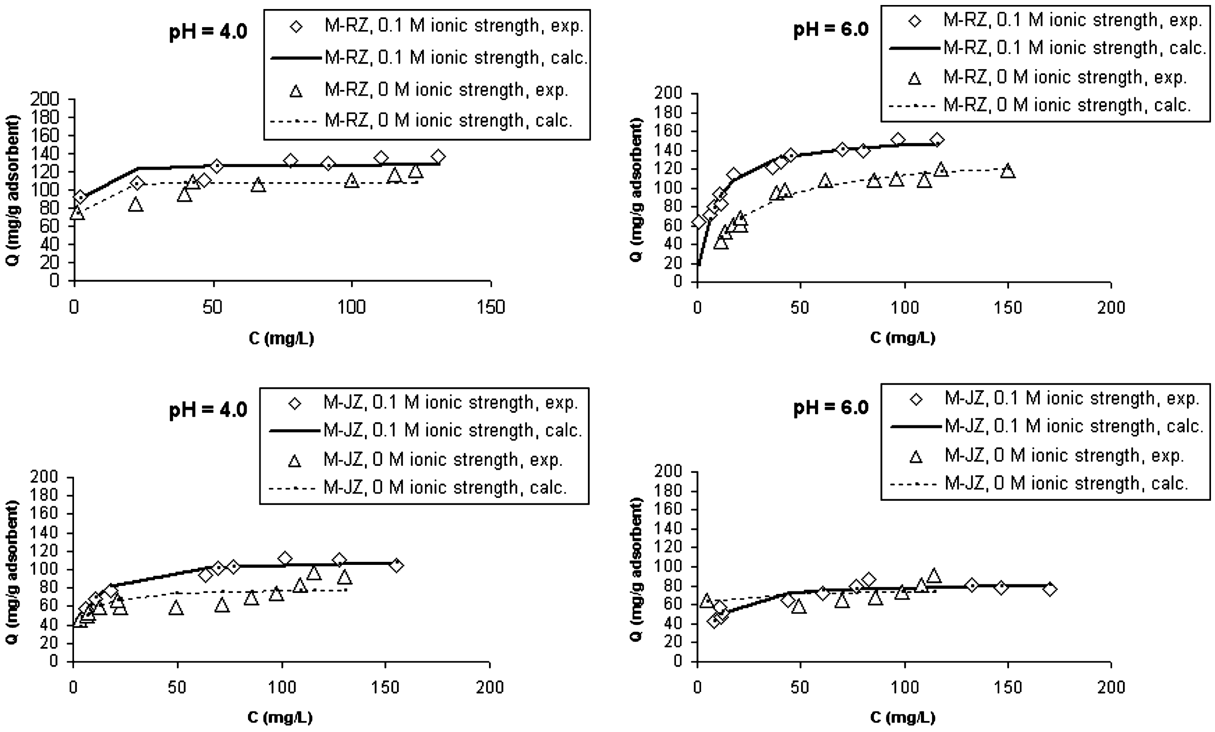

Fig. 4. The effect of ionic strength on the adsorption isotherms of M-RZ and M-JZ at pH 4.0 and 6.0.

(Fig. 2 and Table 1). This may be due to that alkali treatment converts adsorption sites into the basic Na^+ form.

3.4. Effect of ionic strength on the adsorption of Pb(II) onto synthesized adsorbents (M-RZ and M-JZ)

It was reported in the literature [22] that increasing the concentration of Na^+ background electrolytes decreases Pb(II) ions adsorption onto kaolin due to increasing the competition between Na^+ and Pb(II) ions. However, in the case of synthesized adsorbents M-RZ and M-JZ, the adsorption of Pb(II) ions was found to increase with increase of ionic strength (Fig. 4 and Table 1). Since the synthesized adsorbents were prepared in NaOH medium, we expect all the cation exchange sites generated by alkali treatment to be in the Na^+ form. Thus the effect of competition between Na^+ and Pb(II) ions is excluded. Instead, the high concentration of Na^+ electrolyte may open the aggregates of synthesized adsorbent leading to higher surface area and thus higher adsorption.

4. Conclusion

The alkali solid-state conversion of a mixture of kaolin and zeolite leads to increase of adsorption relative to zeolite and kaolin. These low-cost adsorbents have important features since they have extraordinary adsorption capacities towards Pb(II) ions, which increases with increasing ionic strength.

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