Removal of lead by using Raschig rings manufactured with mixture of cement kiln dust, zeolite and bentonite

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ABSTRACT

The present investigation is a follow-up of study on manufacturing Raschig ring for removal of lead from aqueous solution. The mixtures were formulated using cement kiln dust, zeolite, and bentonite, normally used as natural adsorbents in the industrial scale, according to mixture design algorithm and response surface method. The pastes were prepared by addition of 28.0 wt.% de-ionized water, containing 0.1 wt.% carboxymethyl cellulose, with mixed powders. The adsorbents were fabricated by extrusion of the pastes in Raschig ring form and calcination at 500 °C after drying in oven. The effects of starting materials on the mechanical behavior of rings were studied from view point of mixture design algorithm to optimize the adsorbent composition. This method demonstrated to yield valuable information on the effects of used materials on mechanical characteristics. The study concluded that the strength, reliability and sorption capacity of ring can be simultaneously optimized by the addition of 47.5 wt.% cement kiln dust, 32.5 wt.% zeolite, and 20.0 wt.% bentonite. In the next part of work, the sorption kinetics was investigated. The kinetic study indicated that the modified model can successfully correlate the sorption data. The equilibrium result showed the possibility of lead immobilization by fabricated rings.

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1. Introduction

The industrialization of countries causes the deterioration of water and soil by heavy metal ions such as lead, cadmium, mercury etc. In fact, the presence of heavy metals in water results in adverse effects on health and environmental toxicity. Natural water and industrial wastewater may be contaminated with several heavy metal ions arising from mining wastes and industrial discharges such as chemical, metallurgical, electrical and electronic units. In order to solve the heavy metal pollution in the water and wastewater, it is important to use the applicable removal techniques. From an environmental protection point of view, heavy metal ions should be removed at the production sources to avoid the pollution of natural water and accumulation in the agriculture products and foods. Regard to this aim, many advance methods such as filtration, coagulation, flotation, solvent extraction, membrane separation, electrochemical technique, biological process, and reverse osmosis can be used for the removal of toxic heavy metals from wastewater [1]. All these procedures have significant disadvantages, for instance incomplete removal and high energy requirements.

Adsorption, precipitation, cementation, sedimentation, and ion exchange methods are preferred because of high efficiency and low cost as well as availability of different adsorbents compared to advance techniques [2]. Several materials have been used as new adsorbents such as activated carbons [3], polymers [4], biomass [5,6], waste mud [7], silica [8], zeolite [9], and clays [10]. Recently, the sorption properties of various low cost industrial by-products or natural materials have been investigated intensively for immobilization of heavy metal ions from wastewater. It is important to note that the metal sorption capacity of low cost adsorbents depends on the material characteristics, surface modification and the initial concentration. In overall, the technical applicability and cost effectiveness are two key factors in the selection of suitable adsorbent for treating inorganic effluents.

In the manufacturing Portland cement, a part of materials are transported by the exhaust hot gas that contains raw and partially calcined materials namely cement kiln dust, CKD [11]. Recently, CKD has been reported as a potentially important adsorbent due to the high amounts of alkali oxides [12]. It was indicated that CKD can effectively remove heavy metal ions from wastewater by the hydroxide precipitation [13,14]. However, CKD produced by cement factories is considered as waste by manufacturers and frequently remains unutilized. CKD containing high CaO content and low loss on ignition, LOI, prefers for most applications. Several processing factors influence the chemical and physical properties

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of CKD. The chemical and mineralogical compositions of dusts produced by different plants can vary remarkably, because manufactures use different raw materials, fuels, and dust collection facility. This material contains from 8 to 61 wt.% total CaO, and from zero to 37% free lime. The free lime makes it attractive for use as a neutralization or precipitation agent [15]. It was found that CKD particles are smaller than that for the commercial quicklime. The main factor affecting the reactivity of CKD depends on free lime content. Therefore, it can be used as a material in neutralizing acidic wastewater.

Natural zeolites can remove contaminants from water and wastewater such as inorganic ions. As a result, it can be used in water treatment. Zeolite is naturally aluminosilicate mineral consisting of a framework of tetrahedral molecules, linked with shared oxygen atoms. Zeolite has a large surface area and high cation exchange capacity, providing an exchange complex to remove different ions [16]. Due to these properties, zeolite is preferred to use as an adsorbent in wastewater treatment systems [17]. The previous research demonstrated that zeolite is less expensive material than activated carbon for removing heavy metals from wastewater [18]. In practice, the mix use of zeolite and other less-costly inorganic materials such as Portland cement and clays have been formulated for specific treatments and to reduce material cost [19]. Sorption of lead, copper, cadmium, and nickel onto clinoptilolite has an ion-exchange nature. The process begins with fast sorption on the zeolite microcrystal surfaces [20].

Granular bentonite is a suitable material for the uptake of lead, cadmium and mercury from aqueous solutions [21]. The sorption capacity depends on pH, increasing with increment of pH. The commercial Iranian zeolite and bentonite showed high sorption behavior for removing of lead from aqueous solutions. Because of high surface area and cation exchange capacity, zeolite removes more lead than bentonite in the same chemical condition [22]. The sorption capacity of zeolite containing clinoptilolite varies from 64 to 81 mg g^{-1} [22–24]. The sorption capacity of bentonite was reported between 21 and 75 mg g^{-1} [22,25].

Nowadays, packed beds are developed in chemical and wastewater treatments such as sorption, distillation, and cooling towers. The particular shape of these beds is Raschig rings that were normally shaped by the extrusion technique and introduced as a method to achieve a relatively high strength and reliability because of uniform distribution of pores in microstructure of ring [26]. In the manufacturing of packed beds, mixtures of inorganic binders such as kaolin or bentonite are used to improve the physical and mechanical properties of green, dry, and calcined specimens [27]. A deep knowledge about the interactions between the used materials can provide an optimization between the composition and mechanical properties of final product.

Though CKD, zeolite and bentonite can remove metal ions, but the use of these materials as adsorbents are limited in the industrial scale. In contact with water, bentonite swells and forms a very stable colloidal suspension, causing very difficult separation of solid and liquid phases. In order to avoid the above problems, the powders are extruded in different forms such as Raschig ring to facilitate the use of adsorbents in the treatment of wastewater. The extruded adsorbents are separated easily after the sorption of heavy metal ions from aqueous solutions in batch or continuous operations. The success of shaped adsorbents in removing heavy metals provides a new way to use these materials, economically. The aim of this paper is to assess the ability of extruded materials containing CKD, zeolite, and bentonite to remove lead from aqueous solutions. The effect of composition on lead sorption was investigated in first step. Furthermore, detailed studies on optimization of different parameters for manufacturing reliable adsorbent are presented to simultaneously improve the sorption capacity, compressive strength and the reliability by the statistical results. Finally, a modified equation was

Table 1
The chemical analysis of the used material.

Oxides	Cement kiln dust	Zeolite	Bentonite
SiO$_2$	6.64	70.67	68.33
Al$_2$O$_3$	1.81	11.78	16.8
Fe$_2$O$_3$	1.44	0.95	1.63
TiO$_2$	0.1	0.19	0.22
CaO	23.73	1.73	1.79
MgO	0.91	1.14	2.41
K$_2$O	23.34	1.8	0.52
Na$_2$O	0.99	2.74	2.47
SO$_3$	17.03	0.06	0.27
L.O.I[a]	21.15	8.39	5.1

[a] Loss on ignition.

used to model the kinetics of lead sorption on optimum extruded composition.

2. Materials and methods

2.1. Materials and characterizations

The CKD used in this investigation was from Iranian Sufiyan Cement Company situated in North West of Iran. Natural zeolite (Miyaneh Company, Iran) and bentonite (Iran Barite Company, Iran) were used as starting materials for preparation of adsorbent compositions. The selected materials were ground to obtain the fine powders and then passed through a 230-mesh, 63 μm, standard sieve. The chemical compositions of used powders determined by XRF technique (Model S4 Explorer 7KP103, Brucker, Karlsruhe, Germany) are listed in Table 1. The mineralogical analyses of the materials were determined by X-ray diffraction (Model D8-Advance, Brucker, Karlsruhe, Germany). The FTIR spectra were obtained by a Fourier transform infrared spectrometer (Model Unicam Mattson 1000, Philips, Almelo, Netherlands). The specific surface area of powders was obtained from low-temperature nitrogen adsorption isotherms, using a Quantachrome instrument (Model ChemBET3000, FL, USA). Finally, thermogravimetric tests (Model SII, Perkin Elmer, California, USA) were performed on the used materials and the samples were heated from room temperature to 600 °C at a heating rate of 5 °C min^{-1}.

2.2. Preparation procedure of compositions

The mixture design algorithm and the response surface analysis, which were considered in this investigation for mixing of powders, are based on statistical and mathematical techniques for determining optimum composition. The synergetic effect of two or three components on material characteristics such as strength and sorption capacity can be easily identified by mixture design method [28,29]. In this experiment approach, the total amount of materials is held constant and measured properties such as sorption capacity and strength can be evaluated as a function of component fractions. The best composition can be determined by using the composition–property in a triaxial diagram. A polynomial equation, which describes the property, can be correlated as a function of material fractions. In a system with n components, there are $n − 1$ independent compositions, x_i. The polynomial function, F, can be expressed by following equation:

$$F = \sum_{i=1} \beta_i x_i + \sum \sum_{i<j} \beta_{ij} x_i x_j + \sum \sum_{i<j} \beta_{ij} x_i x_j (x_i - x_j)$$
$$+ \sum \sum_{i<j} \sum_{j<k} \beta_{ijk} x_i^2 x_j x_k + \cdots \qquad (1)$$

where β is the constant of equation. This equation should be evaluated over $M > n$ number of points (in this study, M was considered

Fig. 1. The proportions of materials in selected compositions according to the mixture design method.

equal to 10). The compositions were prepared according to the scheme illustrated in Fig. 1. The maximum amounts of CKD, zeolite, and bentonite were considered 55.0, 40.0 and 35.0 wt.%, respectively. Also, the amounts of starting materials in compositions are reported in this figure.

2.3. Extrusion and characterization of adsorbents

First, 0.1 wt.% of carboxymethyl cellulose was dissolved in 28 wt.% de-ionized water, based on dry weight of powders, and then mixed with selected compositions. The prepared pastes were left for 48 h to obtain materials with homogenous moisture. Before forming process, the pastes were de-aired using a laboratory pug mill and then shaped by a single screw extruder, prototype, to produce green Raschig rings. The extruded rings were dried at 100 °C to remove the physical water absorbed by the selected materials. The extrusion behavior was evaluated by determining bulk density and total porosity of dry specimens. The bulk density was calculated from the weight and the geometrical dimensions of rings as reported in Table 2. The true density of powders determined using a helium pycnometer. The total porosity was calculated using the following equation:

$$\varepsilon_t = 1 - \frac{\rho_b}{\rho_t} \qquad (2)$$

where ρ_b and ρ_t are bulk and true densities, respectively. ε_t is porosity of ring.

After drying, the test specimens were calcined from room temperature to 500 °C at a rate of 5 °C.min^{-1} and were maintained for 2 h at this temperature in a laboratory electrical furnace (Model EX. 1500-6L, Exciton, Tehran, Iran). The dimensions of calcined specimens are reported in Table 3. Bulk density and porosity were measured according to the Archimedes immersion technique. The total porosity was calculated by Eq. (2).

The diametrical compressive strengths of dry and calcined rings were measured using an electronic universal tester (DY-26, Adamel Lhomargy, Roissy en Brie, France). The diametrical measurements were carried out using two steel plates that a test ring was located between the plates. The specimens were compressed by moving the upper plate with a loading speed of 1 mm min^{-1}. In order to evaluate the reliability of final products, the statistical Weibull

theory was used. The Weibull equation for brittle materials such as inorganic adsorbents is presented as a follows [26]:

$$P_i = 1 - \exp\left[-\left(\frac{\sigma_i}{\sigma_0}\right)^m\right] \qquad (3)$$

where P_i is the probability of failure at a stress of σ_i, σ_0 is characteristic strength and m is Weibull modulus indicating the scatter of strength data. The probability of failure were calculated by $P_i = i/N + 1$ that was reported as a suitable function for computing this parameter [30]. In the present equation i is ranking number and N is the total number of specimens used in the mechanical tests for each run. At least twenty rings were used for evaluation each composition.

The fracture surfaces of specimens were observed using a scanning electron microscope equipped with an energy dispersion X-ray attachment, EDX, (Model EOL 4401, Oxford, England). For this purpose, the samples were coated by gold in vacuum system.

2.4. Determination of sorption capacity of rings

In order to study the sorption properties, the de-ionized water and nitrate salt, 99.9 wt.% as received, were used to prepare the lead solution with concentration of 960 mg L^{-1}. An experimental setup was designed to evaluate the ability of adsorbents in removal of lead in dynamic system as illustrated in Fig. 2. The lead solution, 300 mL, was circulated easily by a laboratory pump. The experiments were performed at different residence times ranging 1–8 h. The pH of the solutions was monitored to evaluate the sorption mechanism. Finally the aqueous samples were taken to measure the concentration of lead by atomic absorption (Varian, Model Spectra AA 220, California, USA) for determining the sorption capacity. It was observed that the appearance of solutions remained transparent after sorption under the experimental conditions.

3. Results and discussion

3.1. Physico-chemical characteristics of used materials

The mineral phases in CKD, zeolite, and bentonite are shown in Fig. 3. In the CKD considered in this study, CaO actually exists in calcite. The major mineral phases presented in CKD were calcite, arcanite, and sylvite. Also, quartz and mica were found in little amounts. The peaks of clinoptilolite were observed in zeolite. In

Table 2
The geometrical dimensions of dry specimens.

Composition	Length (cm)	Internal diameter (cm)	External diameter (cm)	Bulk density (g cm^{-3})	Porosity (%)
C1	1.50 ± 0.01	0.61 ± 0.01	1.48 ± 0.01	1.54 ± 0.02	36.9 ± 0.8
C2	1.50 ± 0.01	0.60 ± 0.02	1.50 ± 0.01	1.41 ± 0.03	39.2 ± 0.8
C3	1.49 ± 0.02	0.60 ± 0.02	1.46 ± 0.01	1.53 ± 0.03	35.2 ± 0.8
C4	1.50 ± 0.01	0.62 ± 0.01	1.48 ± 0.01	1.52 ± 0.03	36.0 ± 0.7
C5	1.49 ± 0.02	0.62 ± 0.01	1.48 ± 0.01	1.53 ± 0.02	37.9 ± 0.6
C6	1.50 ± 0.01	0.61 ± 0.01	1.48 ± 0.01	1.46 ± 0.02	38.4 ± 0.7
C7	1.50 ± 0.01	0.60 ± 0.02	1.47 ± 0.01	1.51 ± 0.03	36.9 ± 0.9
C8	1.49 ± 0.02	0.60 ± 0.01	1.47 ± 0.01	1.49 ± 0.03	36.8 ± 0.7
C9	1.49 ± 0.02	0.62 ± 0.01	1.49 ± 0.01	1.47 ± 0.02	35.6 ± 0.4
C10	1.48 ± 0.02	0.62 ± 0.01	1.48 ± 0.01	1.51 ± 0.03	36.7 ± 0.7
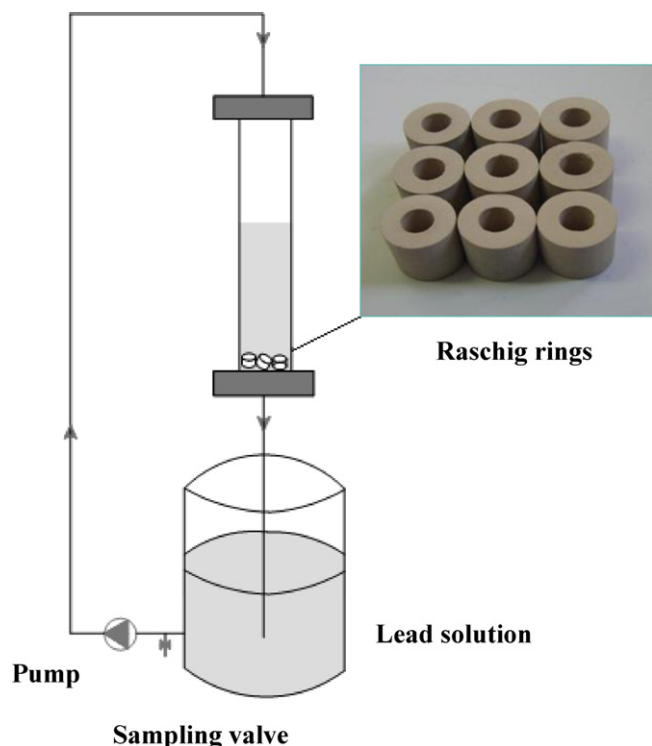
Fig. 2. The experimental setup for evaluation of sorption capacity in dynamic system.

Fig. 3. The XRD patterns of starting materials.

addition, little amounts of albite and quartz were also presented in zeolite. The XRD pattern of bentonite was dominated by the montmorillonite peaks. Also, illite and quartz were identified in bentonite.

The strong peaks for carbonate were found also by Fourier transform infrared spectroscopy, Fig. 4. The major form of calcium in CKD is calcium carbonate with little calcium oxide. The FTIR spectrum displayed in Fig. 4 confirms the fundamental vibrations of CO_3^{2-} group at wave number of 870 and 1400 cm^{-1}. The presence

of Ca–O group characterized at wave number of 1110 cm^{-1} may be due to free CaO. However, the vibration related to K–O is observed at wave number of 620 cm^{-1}. The frequency band at wave number of 715 cm^{-1} is related to vibration of Si–O groups.

The presence of OH groups in zeolite could be detected from FTIR spectrum in the region around 3300–3600 cm^{-1} and OH deformation of water was detected at wave number of 1600–1700 cm^{-1}. The transmission in wave number of 1100 cm^{-1} was described Si–O banding vibration related to silica tetrahedral groups. The transmission at 600 and 800 cm^{-1} was related to Si–O–Al group.

The pronounced wide absorption band in the 3200–3700 cm^{-1} is characterized by OH groups in bentonite. The band at 1650 cm^{-1} also corresponds to OH deformation of water. The peak in wave numbers of 700 and 1030 cm^{-1} is assigned to Si–O vibration in the clay layers. The bands at 600 and 800 cm^{-1} are related to Si–O–Al vibration.
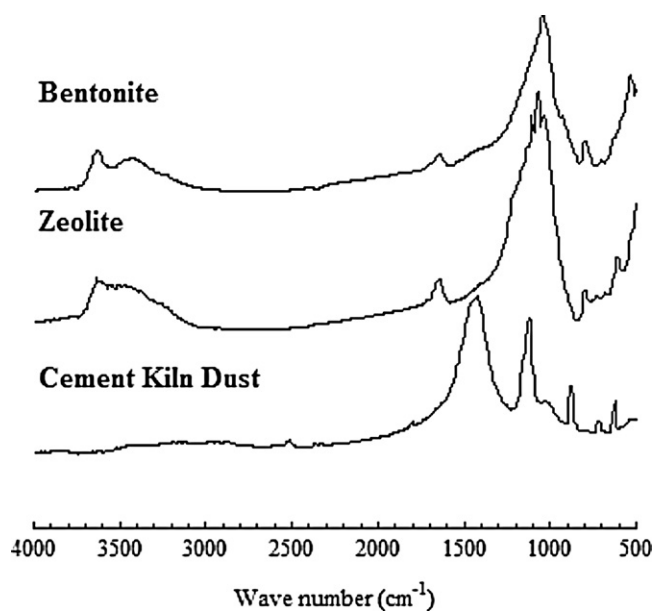
Table 3
The geometrical dimensions of calcined specimens.

Composition	Length (cm)	Internal diameter (cm)	External diameter (cm)	Bulk density (g cm^{-3})	Porosity (%)
C1	1.50 ± 0.01	0.61 ± 0.01	1.49 ± 0.01	1.37 ± 0.02	45.8 ± 0.8
C2	1.50 ± 0.02	0.61 ± 0.02	1.51 ± 0.01	1.31 ± 0.02	45.2 ± 0.7
C3	1.50 ± 0.02	0.61 ± 0.02	1.47 ± 0.01	1.40 ± 0.02	42.3 ± 0.8
C4	1.50 ± 0.01	0.63 ± 0.01	1.49 ± 0.01	1.37 ± 0.02	45.6 ± 0.9
C5	1.49 ± 0.02	0.61 ± 0.01	1.48 ± 0.01	1.33 ± 0.03	45.6 ± 0.8
C6	1.50 ± 0.02	0.61 ± 0.02	1.48 ± 0.01	1.33 ± 0.01	47.2 ± 0.5
C7	1.50 ± 0.02	0.61 ± 0.02	1.48 ± 0.02	1.35 ± 0.03	46.4 ± 0.9
C8	1.49 ± 0.02	0.60 ± 0.01	1.47 ± 0.01	1.35 ± 0.03	45.6 ± 0.8
C9	1.48 ± 0.02	0.62 ± 0.01	1.48 ± 0.01	1.37 ± 0.03	41.5 ± 0.7
C10	1.49 ± 0.02	0.62 ± 0.01	1.48 ± 0.01	1.39 ± 0.03	40.3 ± 0.9

Fig. 4. The FTIR spectra of used materials.

Fig. 6. The response surface analysis for dry strength as a function of composition.

The specific surface areas of CKD, zeolite, and bentonite as measured by the nitrogen BET technique, are 2.1, 22.8 and 20.4 $m^2 g^{-1}$, respectively. The obtained results show that the highest specific surface area is related to zeolite. Though, the specific surface area of zeolite is higher than bentonite, but this difference is about 2.4 $m^2 g^{-1}$. The measured values indicate a very low surface area for CKD.

The thermogravimetric curves of powders are presented in Fig. 5. These variations correspond to the dehydration of powders and loss of physically adsorbed water molecules. With increasing temperature from 350 to 500 °C the efficient changes are not observed which confirms the thermal stability of materials in studied range of temperature. The weight loss between 50 and 100 °C might be due to the loss of water from the bentonite pores. The weight loss of 11 wt.% is corresponded to dehydration of zeolite appeared between 50 and 350 °C. It is obvious that the dehydration of zeolite is difficult than that for bentonite due to small pores in structure of clinoptilolite.

3.2. Evaluation of physico-mechanical characteristics of extruded Raschig rings

The characteristics of dry rings prepared by different amounts of starting materials are reported in Table 2. By considering the amounts of materials in the adsorbent compositions, it is possible to determine the desired composition to achieve maximum bulk density. The bulk density of rings increases as a function of bentonite amount and the maximum value is achieved in the presence of 35.0 wt.% bentonite. The high value of bulk density is responsible for maximum compaction during extrusion. The corresponding response surface plot for dry strength variation is illustrated in Fig. 6. The mechanical strength of dry rings is improved as the amounts of bentonite or CKD increases in composition. From this point of view, bentonite and CKD are more efficient materials compared to zeolite. The following equation represents the correlation between the dry strength, σ_D, CKD, zeolite, and bentonite fractions denoted by x_1, x_2 and x_3, respectively.

$$\sigma_D = 168x_1 - 967x_2 + 727x_3 + 1606x_1x_2 - 1737x_1x_3 + 506x_2x_3$$
$$- 325x_1x_2x_3 - 2607x_1x_2(x_1 - x_2) + 1800x_1x_3(x_1 - x_3) \quad (4)$$

The coefficient of bentonite fraction is higher than the coefficients of CKD and zeolite. On the contrary, the coefficient related to the combination of CKD and zeolite is positive. It means that the mixture of these powders could produce a suitable coherence between the particles. CKD causes the strong coherence and produces relatively low porosity compared to composition containing maximum content of zeolite. It can be concluded that the mixing of zeolite with CKD and bentonite is important to achieve a maximum dry strength.

The changes in physical properties of calcined adsorbents such as bulk density and porosity are reported in Table 3. The bulk density of ring gradually increased with addition of CKD. The density of sample prepared by 50.0 wt.% CKD, 27.5 wt.% zeolite, and 22.5 wt.% bentonite is considerably higher than that for the other rings. However, the composition containing 45.0 wt.% CKD, 30.0 wt.% zeolite, and 25.0 wt.% bentonite indicates maximum porosity.

The combination of materials significantly affects the strength of rings. Fig. 7 shows the relation between the strength and fraction of materials. It is seen that the mixture of CKD, zeolite and bentonite shows synergistic interactions with the surface of particles. The strength increases to reach a maximum value if 47.5 wt.% CKD, 32.5 wt.% zeolite, and 20.0 wt.% bentonite are used in composition.
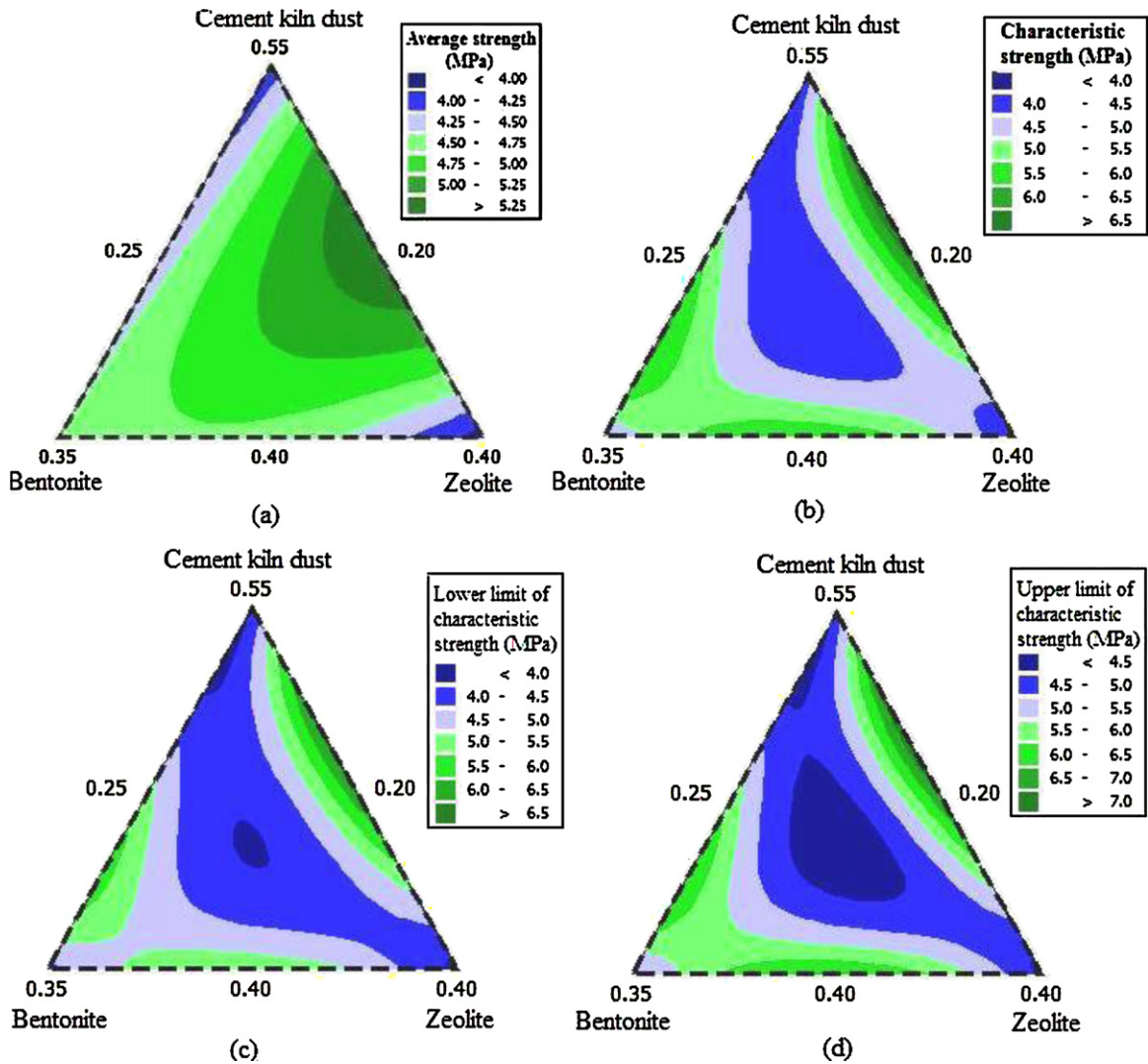

Fig. 5. The TG curves of starting materials.

Fig. 7. The response surface analysis for strength of calcined rings (a) average strength, (b) characteristic strength, (c) lower and (d) upper limits of characteristic strength.

According to the following equation CKD and zeolite permit to fabricate the rings with suitable average strength, σ_{av}. In other word, mixing of CKD and zeolite is more efficient with the worst performance due to an effective increment in strength.

$$\sigma_{av} = -548x_1 - 655x_2 - 2425x_3 + 6403x_1x_2 + 2788x_1x_3$$
$$+ 7655x_2x_3 - 17543x_1x_2x_3 - 2463x_1x_2(x_1 - x_2) + 1475x_1x_3$$
$$(x_1 - x_3) \tag{5}$$

It should be noted that the strength of rings fabricated by maximum content of CKD or zeolite is lower than that for rings prepared by mixing of them. Though, the dry strength increases directly with content of these materials, but the use of 55.0 wt.% CKD in composition decreases strength after calcination. Hence, the substitution a part of CKD by zeolite leads to improve the strength.

Weibull theory can be considered for understanding the role of used materials on the reliability of rings. In order to calculate the Weibull's parameters, the system of equations obtained by maximizing the logarithm likelihood function for N number of the failed rings is given by the following equations [31]:

$$\frac{\sum_{i=1}^{N}(\sigma_i)^m \ln(\sigma_i)}{\sum_{i=1}^{N}(\sigma_i)^m} - \frac{1}{N}\sum_{i=1}^{N}\ln(\sigma_i) - \frac{1}{m} = 0 \tag{6}$$

and

$$\sigma_0 = \left[\frac{\sum_{i=1}^{N}(\sigma_i)^m}{N}\right]^{\frac{1}{m}} \tag{7}$$

According to ASTM C-1239 standard, the confidence bounds can be constructed for estimated Weibull modulus and characteristic strength [31]. The 90% confidence bound on characteristic strength is obtained from the 5 and 95 percentile distributions as shown in Fig. 7. The response surface plot of Weibull modulus accompanied with lower and upper limits for fabricated rings are presented in Fig. 8. As shown in the surface plots, the reliability is affected by the mixing ratio of CKD, zeolite, and bentonite. It is evident from the following equation that Weibull modulus was strongly affected by mixing ratio of materials:

$$m = 2004x_1 + 1347x_2 + 2761x_3 - 7310x_1x_2 - 10561x_1x_3$$
$$- 15940x_2x_3 + 45295x_1x_2x_3 - 2838x_1x_2(x_1 - x_2) - 3805x_1x_3$$
$$(x_1 - x_3) \tag{8}$$

The coefficient of bentonite fraction is higher than the coefficients of CKD and zeolite. On the contrary, the coefficient related to the combination of two materials is negative. It means that the
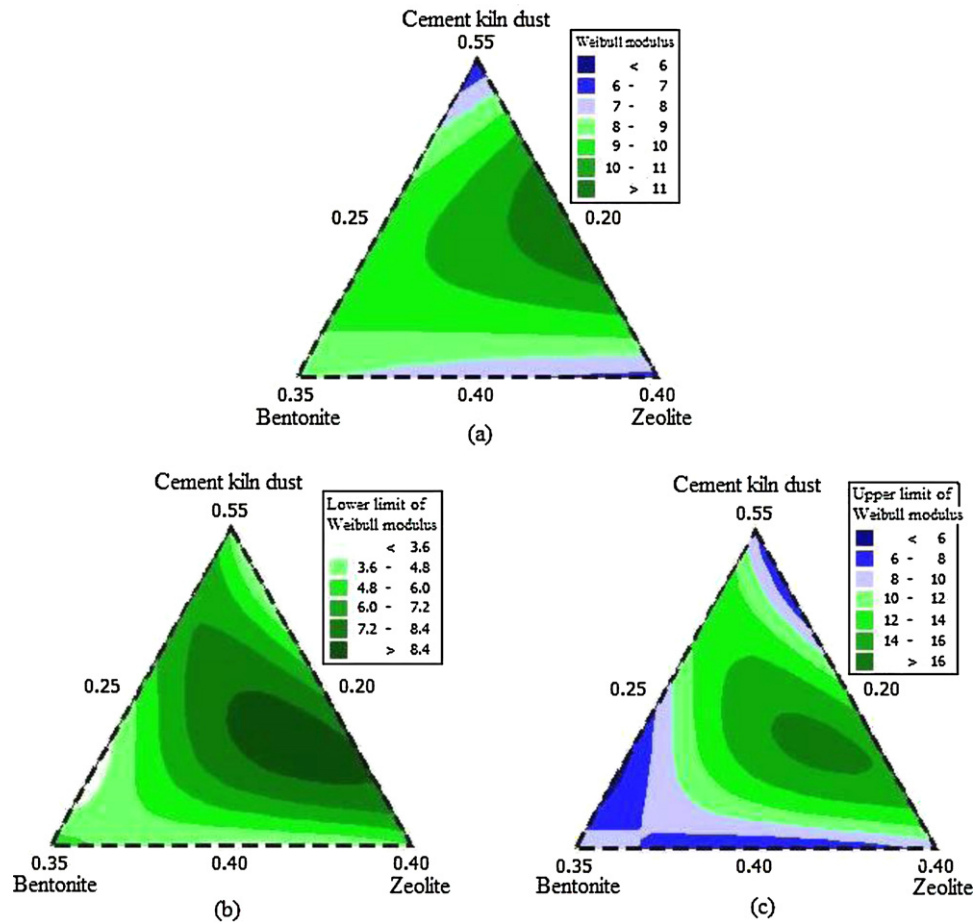
Fig. 8. The response surface analysis for (a) Weibull modulus of calcined rings, (b) lower and (c) upper limits of Weibull modulus.

binary combination of materials could not produce a suitable reliability. The maximum Weibull modulus is obtainable with addition of 47.5 wt.% CKD, 37.5 wt.% zeolite, and minimum content of bentonite, 20.0 wt.%. The increase in amount of CKD leads to improve the reliability, but it is impossible to improve Weibull modulus with more use of CKD or bentonite. If 40.0 wt.% CKD is added to composition, the minimum Weibull modulus is obtained. It is evident that the addition of 40.0 wt.% CKD does not enhance reliability, while it substantially increases the strength after calcination.

SEM photographs of fracture surface of adsorbents are presented in Fig. 9. The remained defect is observable in the ring prepared with 55.0 wt.% CKD. The defect with large dimension that is heterogeneously distributed in the structure of adsorbent is responsible for the low values of strength and Weibull modulus. If 7.5 wt.% CKD is partially replaced by zeolite, the both of defect number and dimensions decrease considerably. This change in the number of defects significantly promotes the strength and Weibull modulus. SEM photograph of ring containing 45.0 wt.% CKD, 30.0 wt.% zeolite, and 25.0 wt.% bentonite indicates an improvement in distribution of defects and pores. Hence, the improvement in Weibull modulus is due to reduction in defect size during extrusion. It should be noted that the reliability of rings can been considerably promoted due to the homogenous distribution of defects. The adsorbent prepared with maximum amount of zeolite, 40.0 wt.%, shows the defect with large dimension which appeared in a uniform texture. Hence, it is impossible to eliminate the inherent defects in the structure of ring by addition of 40.0 wt.% zeolite into the adsorbent composition. The pore size of studied rings is different in all cases. A significant difference between the morphology of pores was found in the

adsorbents. Therefore, the small size of pores in dense microstructure and the uniform distribution in the matrix lead to increment in strength and Weibull modulus.

3.3. Evaluation of removal efficiency of extruded Raschig rings

For the easy comparison, the removal efficiency of lead by rings during 4 h is plotted in Fig. 10. The primary difference in the removal of lead was observed when the maximum content of CKD was used in composition. With increment in CKD content, the removal efficiency of lead was increased. The response surface plot shows that the removal efficiency nonlinearly grows with content of zeolite and reaches maximum value if 40.0 wt.% zeolite is added to composition. On the contrary, the amount of CKD can not be increased up to 55.0 wt.% due to significant change in strength and Weibull modulus. For this reason, the CKD content can not be increased more than 47.5 wt.%. The following equation correlates the removal efficiency, R, of lead as a function of material fractions:

$$R = -1387x_1 + 9837x_2 - 3893x_3 - 16123x_1x_2 + 9757x_1x_3$$
$$- 5213x_2x_3 + 3341x_1x_2x_3 - 12593x_1x_2(x_1 - x_2) + 27763x_1x_3$$
$$(x_1 - x_3) \tag{9}$$

This equation indicates that the removal efficiency is more sensitive to change in amount of zeolite. Also, CKD amount can be increased up to 47.5 wt.% without introducing significant change in strength and Weibull modulus. Fig. 10 also represents that removal efficiency significantly decreases as the amount of bentonite rises in
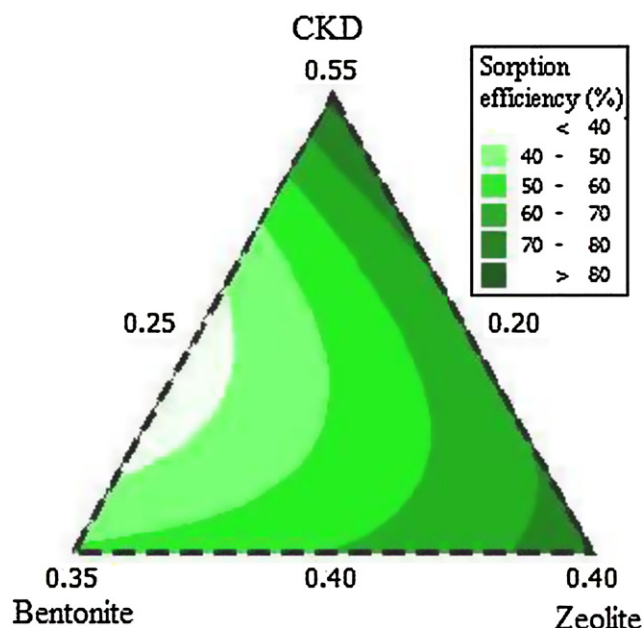
Fig. 9. The SEM micrograph of calcined rings.

composition. It falls down to 35% if 47.5 wt.% CKD, 25.0 wt.% zeolite, and 27.5 wt.% bentonite are added to composition.

3.4. Optimization of adsorbent composition

The experimental values of strength and Weibull modulus strongly depend on the interaction of particles. At least a dry strength of 3.3 MPa is needed for the industrial production of adsorbent in the shape of Raschig ring. Fig. 11 displays the overlap of dry and calcined strengths with Weibull modulus and removal efficiency. It is obvious that the strength of 5.0 MPa and Weibull modulus of 9.5 are simultaneously obtainable with acceptable removal efficiency, 60%, by mixing 47.5 wt.% CKD, 32.5 wt.% zeolite, and 20.0 wt.% bentonite. The sorption of lead on surface of ring prepared with mentioned amounts of starting materials was identified by EDX examinations as presented in Fig. 12. The data of Table 4 show that lead was heterogeneously distributed on surface of ring.

Table 4
The elemental analyses of selected points in Fig. 12 carried out by EDX technique.

Element (wt.%)	Number point			
	1	2	3	4
Ca	0.86	1.55	0.01	1.83
K	27.5	5.25	0.52	18.7
Na	6.55	0.83	0	3.12
Pb	55.62	88.48	93.86	67.02
S	6.55	2.85	5.06	7.51
Si	2.91	1.03	0.54	1.82

3.5. Modified kinetic model

The optimum composition is heterogeneous mixture of several minerals therefore, different retention processes such as precipitation, cation exchange and surface adsorption may contribute simultaneously regarding to removal of lead. The sorption capacity–time variation is plotted in Fig. 13. These curves represent

Fig. 10. The response surface analysis for sorption capacity of rings during 4 h.
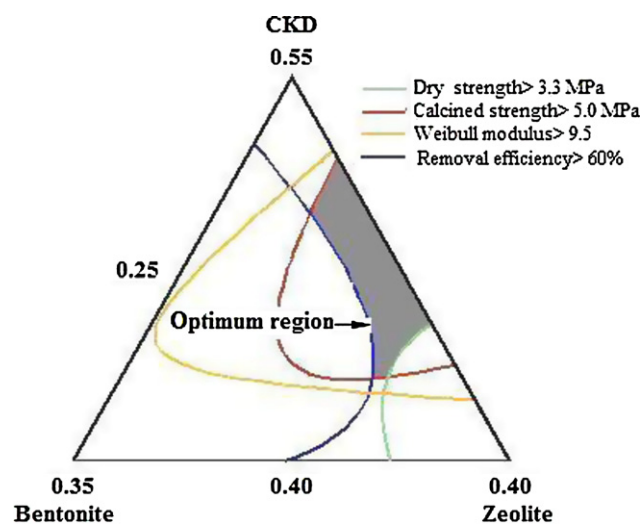
Fig. 11. The overlap of dry and calcined strengths with Weibull modulus and removal percentage.
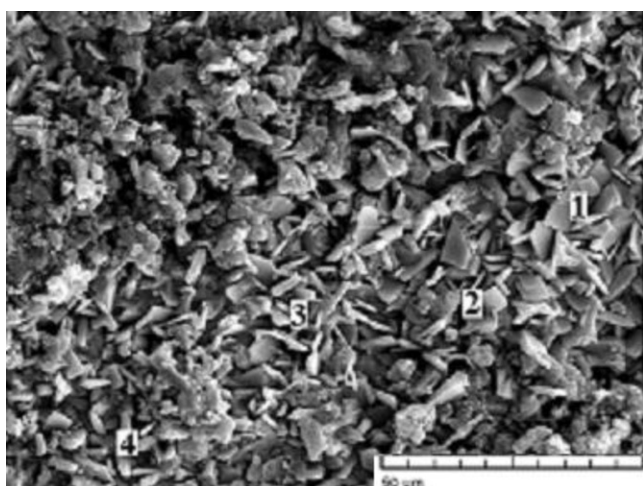
Fig. 12. The selected points on ring prepared with optimum composition for EDX analysis.
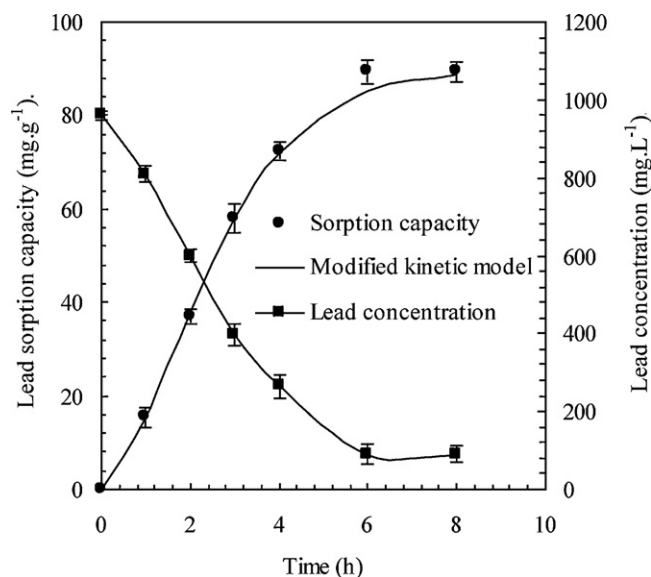

Fig. 13. The sorption capacity–time data for ring prepared with optimum composition.

the changes in sorption capacity of prepared ring and concentration of lead as a function of residence time. The variation of pH is well known as a key important factor that can affect the sorption mechanism by zeolite and clay minerals. In order to establish the effect of pH on the sorption of lead by selected ring, the process was studied by pH monitoring. The pH of solution over the studied range of residence time varies between 5 and 9. The process begins with fast adsorption on the zeolite and clay minerals. With increasing pH from 5 to 7, it can be deduced that the minerals surfaces become negatively charged, favoring Pb^{2+} sorption. A sharp increase from 15.5 to 57.8 $mg\,g^{-1}$ in the sorption capacity occurred in the pH range of 5–7. A part of used adsorbent composition is clay minerals which naturally act as good adsorbents. In addition to the precipitation reaction, other retention mechanisms are cationic exchange and surface adsorption by bentonite. Beyond pH 7, Pb^{2+} ions were precipitated as $Pb(OH)_2$ into the pores [20,22]. The mechanism of lead sorption from the solution by CKD can be explained by the heavy metal hydrolysis and sorption of $Pb(OH)_2$ on the surface of fine particles according to the following reactions:

$$K_2O + H_2O \rightarrow 2K(OH) \tag{10}$$

$$Pb^{2+} + 2K(OH) \rightarrow Pb(OH)_2 \downarrow +2K^+ \tag{11}$$
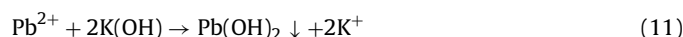
When sorption was carried out during 6 h, the lead concentration and sorption capacity reach constant values and equilibrium condition is achieved. From the nature of curves a rapid sorption stage was established before the equilibrium. Several kinetic models are available to study the mechanism of the sorption kinetics. The pseudo-first-order and pseudo-second-order kinetic models did not correlated sorption-time data presented in this study. Therefore, the following modified equation is used to study the kinetics of sorption process:

$$q = q_e(1 - \exp(-at^b)) \tag{12}$$

where q is the sorption capacity of ring and t is residence time. Also, a and b are the constant parameters. To obtain the kinetic parameters, the maximum amount of sorption capacity corresponding to equilibrium condition, q_e, was used. This complex mathematical model depicts the structural changes taking place in the matrix of adsorbent during the sorption of lead and also accounts the exponential behavior of curve. Model parameter, a, is related to the kinetic rate constant and depends on lead concentration. b is
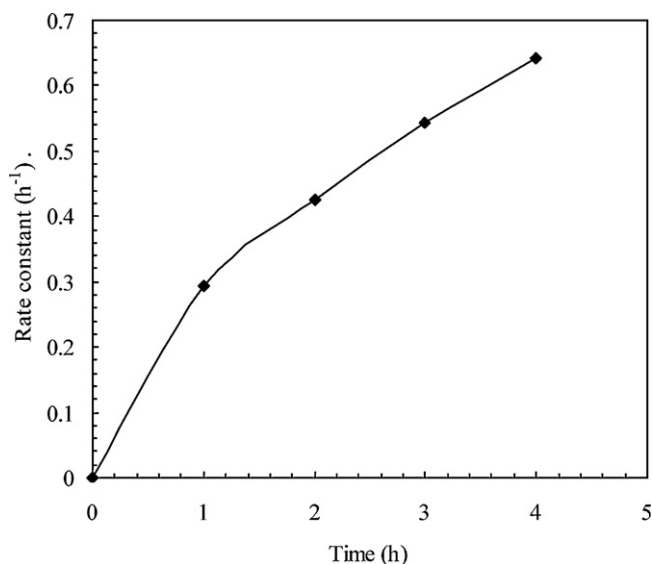
Fig. 14. The variation of rate constant as a function of residence time for ring prepared with optimum composition.

related to physical changes occurring in the adsorbent matrix. This parameter is very important since its value determines the sorption mechanism. Thus for $b = 1$, the sorption follows pseudo-first-order kinetics. For $b > 1$ an exponential behavior is guaranteed. A linear plot of $\ln[-\ln(1 - q/q_e)]$ versus $\ln t$ gives slope b and intercept a. The values of a and b were found equal to 0.187 and 1.562, respectively. Very good agreement can be observed between the experimental data and calculated values as illustrated in Fig. 13, which substantiates the validity of modified kinetic model, $r^2 = 0.999$. By use of the constant parameters, the rate constant is obtainable. In the sorption process, the rate varies continuously with time due to continuous structural change in adsorbent matrix. By comparing the above equation with the pseudo-first-order kinetic model, the expression for the rate constant, $k(q)$, can be obtained as a follows:

$$k(q) = ba^{\frac{1}{b}}\left[-\ln\left(1 - \frac{q}{q_e}\right)\right]^{\frac{b-1}{b}} \tag{13}$$

$k(q)$ can be calculated at each ratio of sorption capacity. It is observed from Fig. 14 that the value of rate constant depends on sorption capacity. This phenomenon indicates that the mechanism of structural changes in ring matrix is function of lead concentration. Therefore, the sorption rate increases with increment in residence time.

4. Conclusions

The mixture design algorithm was used to better understand the effect of the cement kiln dust, zeolite, and bentonite on the sorption of lead and strength as well as the reliability of adsorbent shaped as a Raschig ring in a quantitative way. According to the experimental results, reliable rings can not be manufactured by using one of the mentioned materials only, because the defects with large dimensions remain in the structure of adsorbent. Both of mechanical characteristics and sorption properties are optimized if 47.5 wt.% cement kiln dust, 32.5 wt.% zeolite, and 20.0 wt.% bentonite are added to adsorbent composition. Also, the sorption kinetics of selected composition was studied by a modified kinetic model. The kinetic parameters demonstrated that the model can successfully correlate the sorption data. The above findings clearly indicated that the selected composition can potentially be a cost effective adsorbent for treatment of wastewater which contains lead ions. The obtained results can be useful in industrial practice because, the natural zeolite and bentonite are traditionally applied in treatment of wastewater containing heavy metal ions.

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