Removal of lead from solution by combination of natural zeolite–kaolin–bentonite as a new low-cost adsorbent

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ABSTRACT

Recently several kinds of low-cost adsorbents were developed for the extreme environmental and waste treatment processes. The adsorption capacity and physico-mechanical properties of adsorbent are basically affected by mixing ratio of the used materials. These requirements cause to apply the technique of experiment to optimize mentioned properties. In the present investigation commercial zeolite, bentonite and kaolin were used in experimental design algorithm due to their abilities in removal of heavy metal ions. Different amounts of used powders were mixed according to mixture design algorithm and shaped by extrusion technique in the form of Raschig ring. The test rings were calcined at 600 and 700 °C after drying in laboratory oven and characterized by determining porosity, diametrical compressive strength and adsorption capacity. In order to manufacture applicable adsorbent, the response surface analysis method was used to optimize mixing ratio of materials. The investigation was concluded that the strength and adsorption capacity can be simultaneously optimized by the addition of 66.67, 29.17 and 4.16 wt.% zeolite, bentonite and kaolin respectively. In the next part of work, the kinetics and adsorption isotherm of lead on selected composition was mathematically investigated. The Langmuir isotherm and pseudo second order kinetic model showed the acceptable accuracy in prediction of adsorption data. The possibility of lead immobilization by fabricated rings can be useful in industrial practice.

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1. Introduction

Industrial wastes containing heavy metal ions and their applications in agriculture means have contributed to a continuous accumulation of the heavy metals in soil, ground and surface waters. The presence of low concentration of heavy metals in the food is well known to have harmful effects on human heath in elemental forms as well as in combined with other materials. The mobility of these ions in soil strongly depends upon the extent of their adsorption with solid minerals. The interaction between heavy metals and adsorbents is controlled by technical factors such as surface area, surface charge, pH and concentration of ions [1].

Lead immobilization through cation exchange and adsorption is considered as a common mechanism to decrease the metal in contaminated solution. Minimizing the mobility of lead from labile to non-labile phase via physically or chemically transformations provides a technique that has the potential to remove lead from solutions [2]. For this point of view, two important factors should be considered (i) the system must be effective under a variety of chemical conditions and (ii) immobilized lead should be stable and remain non-leacheable under varying environmental conditions.

The lead mobility largely depends upon adsorption and desorption with different materials. The idea of treating lead contaminated solutions with natural zeolite has recently shown good promise and has been proposed as an alternative to active carbon [3]. Zeolite minerals such as clinoptilolite and chabazite have been investigated as a potential agent to treat heavy metal contaminated waste water especially in the case of Pb and Zn. Trgo et al. [4] studied the ion exchange of zinc and lead ions on natural clinoptilolite. A higher selectivity of natural clinoptilolite was observed for lead adsorption. The effectiveness of natural clinoptilolite for immobilizing heavy metals from aqueous solutions was also studied by Inglezakis et al. [5]. Equilibrium and kinetic data for Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} exchange on clinoptilolite were presented by the authors. Equilibrium was favorable for Pb^{2+} and selectivity series deduced from equilibrium isotherms was reported as $Pb^{2+} > Cr^{3+} > Fe^{3+} > Cu^{2+}$. The immobilization of lead in contaminated solution using clinoptilolite was investigated by Gunay et al. [6]. It was found that clinoptilolite is an effective adsorbent for the removal of lead from aqueous solution and the adsorption increases with increment in initial lead concentration. The authors concluded that clinoptilolite can be used, as a low-cost adsorbent for the removal of lead and it may be an alternative to more costly materials such as synthetic resins.

The possibilities of using a typical natural zeolitic tuff containing 50% clinoptilolite for adsorption of Zn, Cu, and Pb ions from wastewater have been studied by Peric et al. [7]. The maximum exchange

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capacities for Cu and Pb are double than that for Zn. The immobilization of heavy metal ions from aqueous solutions on natural zeolitic tuff is a complex process consisting mainly ion exchange and adsorption. In the presented investigation by Smiciklas et al. [8], the adsorption of Co^{2+}, Sr^{2+} and Cs^+ on the natural clinoptilolite was studied. The experimental results showed that the adsorption capacity of the natural clinoptilolite decreases by the competition among the metal ions in solution. Natural clinoptilolite is used by Stylianou et al. [9] for the removal of lead, copper and zinc from aqueous solutions in a fixed bed. The results indicated that the fixed bed is efficient for removal of lead than that for copper and zinc.

Three different stages are observed by Sprynskyy et al. [10] in the ion-exchange adsorption of lead, copper, cadmium, and nickel onto clinoptilolite. The process begins with fast adsorption on the zeolite and then the inversion stage has a short-time prevalence of the desorption process connected with the diffusion flow from the clinoptilolite. The third stage is the moderate adsorption on zeolite.

The ability of clinoptilolite and bentonite to remove lead from aqueous solutions has been compared by Inglezakis et al. [11]. Bentonite was found to be more effective for the removal of lead than clinoptilolite. Clinoptilolite dust is found to be more efficient than granular clinoptilolite. According to results reported by Hamidpour et al. [12], the commercial Iranian zeolite and bentonite showed high adsorption 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. Percent removal of Pb on both adsorbents increases with the increment of contact time, pH of suspension and amount of adsorbents.

Clays have been found to remove heavy metal ions from wastewaters. Environmental factors like pH affect the adsorption capacity of clays. The edge hydroxyl groups are particularly active for various types of interactions. Clays and modified clays have been found particularly useful for adsorption of heavy metals. It was shown that clays can remove As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn in their ionic forms from aqueous medium [13]. The results of study carried out by Jiang et al. [14] demonstrated that modified kaolin can enhance the Pb removal and it could be a potential adsorbent to remove Pb from real wastewater. The amount of Pb adsorbed by modified kaolin was higher than that for unmodified kaolin. Natural kaolinite clay was used by Omar and Al-Itawi [15] as a low cost adsorbent for the removal of toxic lead ions from wastewater and industrial solutions. The obtained results indicated that a very fast and efficient removal of lead ions can be achieved using kaolinite clay as an adsorbent. This study concluded that a faster removal of lead ions can be achieved by increasing the temperature up to 45 °C and increasing the pH in the acidic medium to 4.9.

Suitable plasticizers are necessary to shape zeolite adsorbents because zeolite is a non-plastic material with a high water adsorption capacity. If the zeolite or clays are applied as powders, the use of filtration is necessary for separation of adsorbents. Therefore, it is better to form it as plates, granules, Raschig ring etc. Bentonite and kaolin have been found to be suitable materials providing plasticizing properties during the extrusion of zeolite. The use of plastic materials will enhance the particle interactions in the paste and cause the compaction of final product. The more use of a plasticizer in the paste should be avoided because it can cause defects through liquid migration or expansion of the adsorbent during extrusion. On the other hand bentonite and kaolin can remove lead from solution therefore it was suggested to use in combination with zeolite [16].

The different values were reported for adsorption capacity of natural zeolite and clays in literature and it depends on chemical and mineralogical composition of raw material. The adsorption capacity of zeolite containing clinoptilolite varies from 64 to 81 mg/g [4,6,12,13]. The adsorption capacity of bentonite was

Table 1
The chemical analysis and specific surface area of the used materials.

Oxides	Zeolite	Bentonite	Kaolin
SiO_2	70.67	68.33	58.00 ± 1.00
Al_2O_3	11.78	16.8	28.00 ± 1.00
Fe_2O_3	0.95	1.63	0.35
TiO_2	0.19	0.22	0.25
CaO	1.73	1.79	0.5
MgO	1.14	2.41	0.15
K_2O	1.8	0.52	4.5
Na_2O	2.74	2.47	0.2
SO_3	0.06	0.27	0
L.O.I.[a]	8.39	5.1	6
Specific surface area (m^2/g)	22.8	20.4	3.6

[a] Loss on ignition.

reported between 21 and 75 mg/g [12,13]. It was also mentioned about 5 mg/g for kaolinite [13].

To our knowledge, most studies on heavy metal adsorption and related mechanisms have been focused on individual natural and synthetic adsorbents and a few studies has been performed regard to combination with other adsorbents. Therefore in the present study, the combination of zeolite, bentonite and kaolin was considered in removal of lead from the contaminated solution. In order to manufacture the applicable adsorbent, it is necessary to optimize composition for reaching suitable compressive strength and adsorption capacity simultaneously. The aim of the present work was to increase the knowledge on the adsorption mechanism of lead on optimum extruded composition. This was done through a comparison of adsorption and strength data. Finally, a detailed study of the adsorption process was performed by kinetic models and adsorption isotherms.

2. Materials and methods

2.1. Methods of powder characterizations

The zeolite, bentonite and kaolin used in this study were commercially produced materials. The selected materials were ground to obtain the fine powders and passed through a 200-mesh, 75 μm, standard sieve. The chemical analyses of used materials were determined by XRF technique (Model S4 Explorer 7KP103, Brucker, Karlsruhe, Germany) as reported in Table 1. The mineralogical phases were identified with an X-ray diffractometer (XRD; Model D8-Advance, Brucker, Karlsruhe, Germany) using Cu Kα radiation at 35 kV and 20 mA. The diffraction was digitally recorded in the range of 3–50°. The FTIR spectra were also obtained by Fourier transform infrared spectrometer (Model Unicam Mattson 1000, Philips). All FTIR spectra were recorded in the wave number of 400–4000 cm^{-1}. The specific surface areas of materials were measured by low-temperature nitrogen adsorption isotherms, using a Quantachrome (Model ChemBET3000, USA) instrument.

2.2. Preparation of adsorbents as Raschig ring form

The mixture design method and the response surface analysis, which were selected in this study for preparation of compositions, is based on statistical and mathematical methods for optimizing composition with improved properties. The synergetic effect of two or three components on material characteristics such as strength and adsorption capacity can be easily identified by mixture design method. In this experiment approach, the total amount of materials is considered to be constant and a measured property of mixed composition was evaluated as a function of component fractions. Therefore, the main purpose of this method is to determine the optimum composition in which the suitable property is achieved. The best composition can be determined by using