

ADSORPTION OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTIONS BY MODIFIED OIL SHALE ASH

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Abstract. Oil shale ash, which is a by-product from oil shale processing, was converted into an adsorbent by alkali hydrothermal activation using sodium hydroxide. The alkali-treated ash was studied for its capacity to remove lead and cadmium ions from aqueous solutions. The results of the study showed that the adsorption of lead and cadmium ions by the modified oil shale ash depended on adsorbent concentration, ash particle size, contact time and pH of solution. When the initial concentration of an aqueous solution was 10mg/L and that of the adsorbent 5g/L, 91% of lead and cadmium ions was removed from the solution. The adsorption isotherm data of the alkali-treated oil shale ash were fitted to the Langmuir isotherm model with R^2 of 0.9995 and 0.9963 at 20 °C. The scanning electron microscopic (SEM) analysis showed that after modification the porosity of the ash increased and, as a result, complex spatial networks were formed, which provided sufficient space for the adsorption of lead and cadmium ions. The energy dispersive spectrometric (EDS) analysis confirmed the adsorption of lead and cadmium ions in the modified oil shale ash sample, while in the control sample these elements were absent. Its excellent adsorption capacity and efficiency makes the alkali-treated oil shale ash a good candidate for heavy metals removal from wastewater.

Keywords: modified oil shale ash, adsorption, lead, cadmium.

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1. Introduction

With the global shortage of petroleum and the continuing rise in oil prices, oil shale has become an alternative source of energy and has hence been attracting a lot of attention in recent years [1, 2]. Oil shale is primarily used for shale oil production and electricity generation by retorting and burning, respectively, during which almost 60–80% of raw oil shale is converted to a by-product, oil shale ash [3]. Oil shale ash is commonly discarded as solid waste, which occupies a huge area of land and causes serious environmental problems [4, 5]. Therefore, an environmentally safer method of utilizing oil shale ash is highly desirable.

Today oil shale ash is used in the building materials industry to produce some concrete types, and also in agriculture, but these applications are of low efficiency. Therefore, many researchers worldwide are working on the synthesis of new kinds of adsorbents [6] and filter materials [7], as well as on the extraction of Al_2O_3 [8] and preparation of novel inorganic polymer coagulants [9] using oil shale ash, which eventually should add value to the ash. However, most of the work is currently limited to lab-scale experiments or has not yet given economically feasible results. This undoubtedly cannot meet the needs of the fast-developing electricity generation sector for the disposal of oil shale ash. Due to its advantages such as low cost and high adsorption efficiency, but also in view of the fact that its large amounts generated need disposing of or utilizing, oil shale ash has also been investigated for its capacity to remove heavy metals from wastewater. The results of researches are promising. For example, Panday used thermal power plant ash to remove copper from aqueous solutions [10]. Bayat reported that two different kinds of fly ash adsorbed nickel, copper and zinc from aqueous solutions [11]. As the country's base of heavy industry (e.g., metal smelting, mining), northeastern China is notorious for its heavy metals contamination, with lead and cadmium being the most common pollutants in the region [12]. Lead and cadmium containing wastewater is discharged directly into the river water or even used to irrigate rice fields [2], which poses a serious threat to human health and the eco-system in general. In light of this, there is a high need for a comprehensive utilization of oil shale ash and development of an economically feasible method for cadmium and lead removal from wastewater.

The aim of this study was to investigate the feasibility and optimum conditions of removal of lead and cadmium ions from aqueous solutions by using the alkali-hydrothermal oil shale ash, a solid waste from Huadian power station, Jilin province, China. The effect of different operating conditions, such as adsorbent concentration, ash particle size, contact time and pH of solutions, on the adsorption of lead and cadmium by this oil shale ash was systematically studied. The research provided basic operational data to be made use of in the practical removal of lead and cadmium from aqueous solutions by oil shale ash in the heavily industrialized northeastern China.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

Oil shale ash samples were collected at Huadian power station, Jilin province, China. $\text{Pb}(\text{NO}_3)_2$, CdSO_4 , NaOH and HNO_3 were purchased from the North of Beijing Fine Chemicals Co., China, and were of analytical reagent grade.

2.1.2. Preparation and characterization of oil shale ash adsorbent

Oil shale ash samples were crushed to ash particle sizes of 200 Mesh (0.074 mm), 32 Mesh (0.495 mm) and 16 Mesh (0.991 mm). The screened samples were burned in a KSY-16C muffle furnace (Yifeng Co., China) at 950 °C for 8 h to remove all hydrocarbons incorporated. The remaining ash was ground and stored. The oil shale ash (50 g) was mixed with a 32 g/L sodium hydroxide solution. After the reaction was completed, the slurry was placed in an oven and kept at 160 °C for 24 h. The activated product was collected, washed with distilled water, filtered, dried at 105 °C and stored in a closed container for analysis [6].

The main elemental constituents of oil shale ash were oxygen, sodium, aluminum, silicon and calcium. Of their compounds, SiO_2 was the most abundant (55.92%), followed by CaO (16.77%), Al_2O_3 (15.49%) and Na_2O (10.01%). The chemical composition of raw ash samples was determined using a JSM-5310 EDS (UK).

2.2. Adsorption experiments

The stock solutions of Pb and Cd (as metal ions, 1g/L) were prepared by adding the exact amounts of $\text{Pb}(\text{NO}_3)_2$ and CdSO_4 to distilled water. The modified oil shale ash (particle size 200 Mesh, 0.074 mm; 1.0 g) was added to 200 ml aqueous solutions containing lead and cadmium at various concentrations (10, 20, 30, 40, 60, 80 and 120 mg/l) in 250 ml flasks. The flasks were agitated in an isothermal shaker (20 ± 1 °C) for 15 min. The treatments were carried out in triplicate and the deionized water was used as control. After the equilibrium was reached, the samples were filtered by a 0.22 μm filter (Millipore Corp., USA) and the concentrations of Pb and Cd were measured by inductively coupled plasma-mass spectrometry (ICP-MS).

2.3. ICP-MS operating parameters

The ICP-MS operating parameters were as follows: high frequency transmission power 1200 W; sampling depth 6.4 mm; auxiliary air flow 1.0 L/min; cooling air flow 16.0 L/min; atomization gas flow 1.02 L/min; ascension 1.1 mL/min; atomization temperature 5 °C; analysis time of one sample 3 min.

3. Results and discussion

3.1. SEM analysis

Fig. 1 depicts the SEM images (3300X magnification) of raw (a) and modified (b) oil shale ash samples. As seen from the Figure, the two ash samples significantly differ in morphology. After the oil shale ash sample was modified, the formation of a large number of pores in it was observed, while no pores were found in the raw ash sample. The development of pores was responsible for the increase of the cation exchange capacity (CEC).

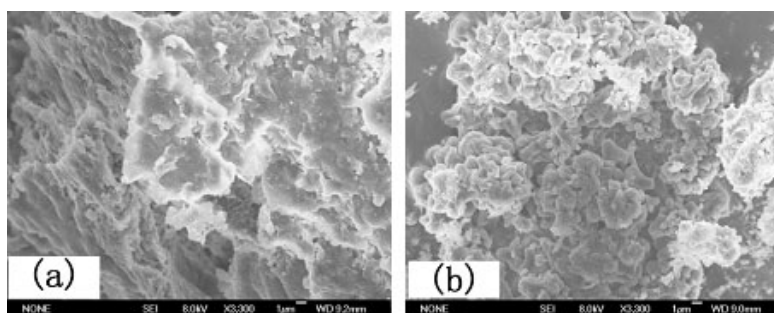


Fig. 1. Scanning electron micrographs of raw and modified oil shale ash samples.

3.2. Effect of oil shale ash particle size on adsorption

Oil shale ash samples with different particle sizes were studied for the effect of particle size on adsorption. The results are shown in Fig. 2. It can be noticed that the ash sample of the smallest particle size (200 Mesh, 0.074 mm) exhibited the highest capacity to adsorb both lead and cadmium ions. This behavior can be attributed to the relationship between the effective specific surface area of the adsorbent particles and their size. The effective specific surface area decreases with increasing particle size. As a consequence, the saturation adsorption per unit mass of the adsorbent will decrease [13, 14]. In the experiments, the modified oil shale ash sample of a particle size of 200 Mesh (0.074 mm) was employed.

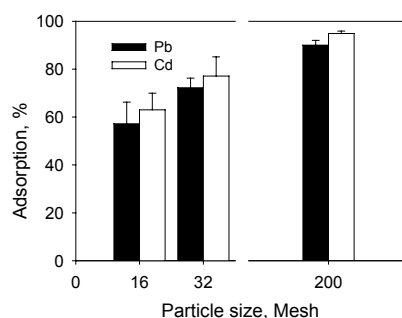


Fig. 2. Effect of ash particle size on the adsorption of lead and cadmium by modified oil shale ash.

3.3. Effect of the pH of solutions on adsorption

The effect of the pH of aqueous solution on lead and cadmium adsorption was studied by performing equilibrium sorption tests at different initial pH values of solutions. The results demonstrated that the adsorption of lead and cadmium was similar, i.e. it increased with increasing pH (Fig. 3). The removal of lead by the modified oil shale ash increased from 61.67 to 94.17% as pH increased from 3.0 to 7.0. However, as pH continued to rise from 7.0 to 11.0, the removal of lead decreased from 94.17 to 83.12%. The removal of cadmium by the modified oil shale ash increased from 69.27 to 97.21% as pH increased from 3.0 to 7.0. The removal of cadmium decreased to 85.89% as pH continued to increase to 11.0. Hence, the pH value 7.0 was shown to be the most optimal for lead and cadmium adsorption.

The lead and cadmium removal decreased gradually following the rise of pH from 7.0 to 11.0. This may be due to the precipitation of $\text{Pb}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ on the surface of the modified oil shale ash sample. The deposited $\text{Pb}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ blocked the pores in the ash, which led to a decrease of its adsorption capacity. For example, cadmium is a close-shell cation when its d^{10} orbital valance is full, which favors a coulomb-type reaction on the zeolite surface as opposed to an inner-sphere surface reaction [15]. In solution, cadmium ions exist in different forms such as Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2$, $[\text{Cd}(\text{OH})_3]^-$ and $[\text{Cd}(\text{OH})_4]^{2-}$, depending on the pH of the buffer solution. The higher pH of the buffer solution can make the cadmium ion hydrolyze to form $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_4^-$. Therefore, the adsorption of lead and cadmium ions was found to increase with increasing pH of the buffer solution [5]. Lead and cadmium removal increased gradually with increasing pH from 3.0 to 7.0. This may be due to the competitive adsorption of metal and hydrogen ions. When pH is lower than 7.0, H^+ will adsorb stongly onto the surface of the oil shale ash sample, which will inhibit the adsorption of lead and cadmium. Lead and cadmium will precipitate as Pb^{2+} and Cd^{2+} and the charge on the surface of the modified oil shale ash sample is positive, which is affected by the pH of the buffer solution. While hydrogen ions

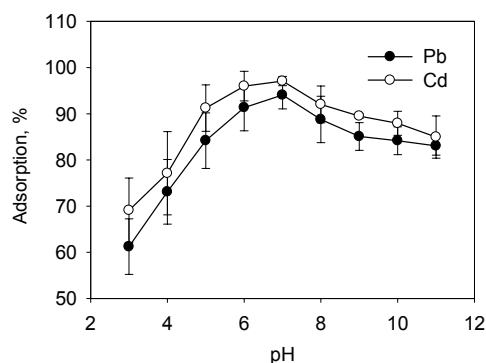


Fig. 3. Effect of the pH of solution on the adsorption of lead and cadmium by modified oil shale ash.

adsorbed quite strongly, the adsorption of the other ions was influenced by the pH of the aqueous solution. Hence, the competition between metal and hydrogen ions in aqueous solutions occurred. Hydrogen ions may change the direction of the reversible ion exchange equilibrium back to the starting materials.

3.4. Optimal adsorbent concentration

The lead and cadmium adsorption by the modified oil shale ash of different concentrations is illustrated in Fig. 4. It is evident that this ash has a significant adsorption capacity. Cadmium (91%) and lead (87%) were adsorbed by only 1 g/L of the modified ash when the initial concentration of Cd and Pb was 20mg/L each, the corresponding adsorption capacities being 18.2 mg cadmium/g oil shale ash and 17.4 mg lead/g oil shale ash. The adsorption capacity of the ash no longer increased after its concentration reached 2g/L.

The increase of adsorption of lead and cadmium ions with increasing adsorbent concentration was due to the availability of a larger surface area of the adsorbent for adsorption.

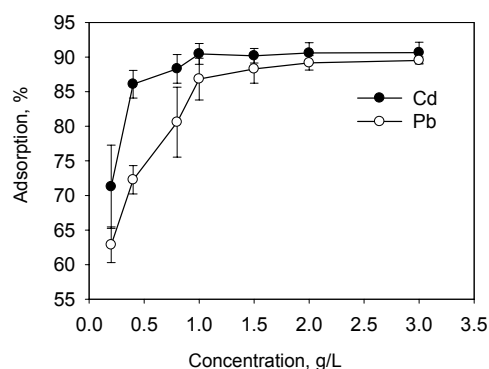


Fig. 4. Optimal adsorbent concentrations for the adsorption of lead and cadmium by modified oil shale ash.

3.5. Effect of contact time on adsorption

To determine the adsorption saturation time, lead and cadmium adsorption by the modified oil shale ash was performed at different contact times (Fig. 5). As the contact time increased, the time of lead and cadmium ions removal increased from 1 to 15 min, after which the adsorption reached maximum. The removal of lead and cadmium ions was the most intensive during the first 15 min, remaining thereafter unchanged and attaining the equilibrium. The time needed to reach the equilibrium was determined by the type of adsorbent and the availability of adsorption sites. Initially, all adsorption sites were vacant and the solute concentration gradient was high, but after 15 min the uptake rate by the adsorbent decreased following the

decrease in adsorption sites. Hence, the contact time upon the lead and cadmium ions removal by the modified oil shale ash was determined to be 15 min.

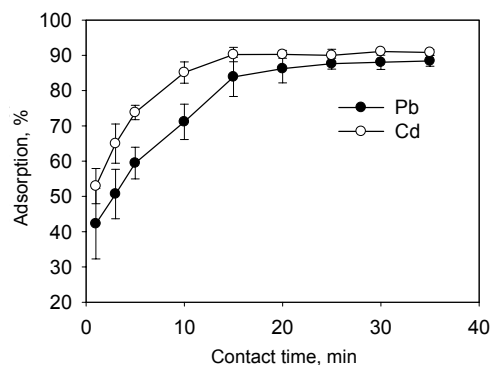


Fig. 5. Effect of contact time on the adsorption of lead and cadmium by modified oil shale ash.

3.6. Energy dispersive spectrometry (EDS)

EDS was used to determine the elemental constituents of the material before and after the lead and cadmium adsorption. The modified oil shale ash sample (particle size 200 Mesh, 0.074 mm) was added to 100 ml aqueous solutions of lead and cadmium in 250 ml flasks at pH 7.0. The flasks were agitated in an isothermal shaker (20 ± 1 ° C) for 15 min. The modified oil shale ash was separated from the solution and dried in the air. The samples were analyzed using EDS.

It can be observed from Fig. 6 that lead (Fig. 6b) and cadmium (Fig. 6c) were adsorbed by the modified oil shale ash, but these elements are not present in the control sample (Fig. 6a), which corroborated the effective adsorption of Pb and Cd by this material.

3.7. Adsorption of lead and cadmium under optimum conditions

Under the optimum conditions, the removal of lead and cadmium from aqueous solutions reached 91% (Fig. 7). So, the modified oil shale ash as a new kind of adsorbent could be effective for the treatment of heavy metals rich wastewater.

3.8. Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches the equilibrium. In this study, the Langmuir isotherm model was employed to fit the isotherm data.

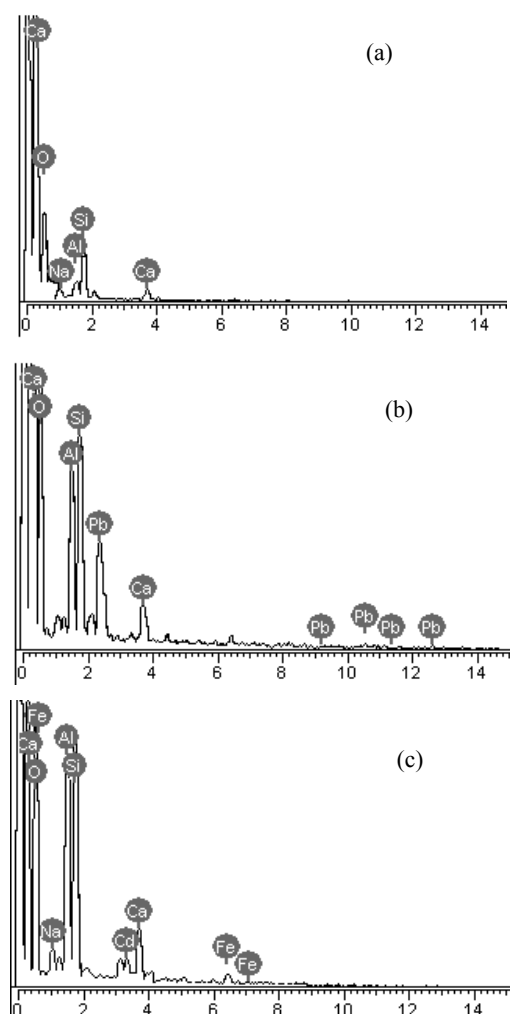


Fig. 6. EDS diagrams of the modified oil shale ash; (a) control sample, (b) after contact with lead, (c) after contact with cadmium.

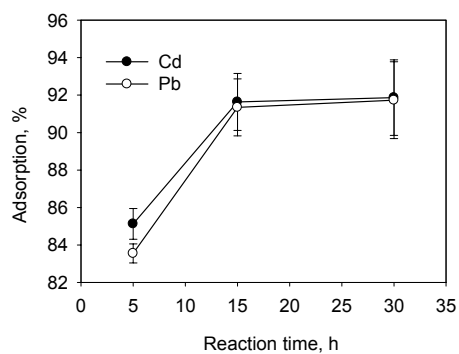


Fig. 7. The adsorption capacity of the modified oil shale ash under the optimum conditions.

A Langmuir mathematical equation is described as follows:

$$Q_e = \frac{bC_eQ}{1+bC_e}$$

where Q_e is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), Q is the maximum metal uptake under the given conditions (mg/g), b is the constant related to the affinity between the adsorbent and the adsorbate. Figure 8 shows a plot of Langmuir isotherms for the adsorption of lead and cadmium ions.

Table 1. Langmuir isotherm constants for modified oil shale ash

Heavy metal ion	Langmuir isotherm constants		
	Q, mg/g	b	R ²
Pb ²	9.407	4.016	0.9995
Cd ²	12.05	4.416	0.9963

Table 1 presents the constants and regression coefficients for the Langmuir model. R² is the correlation coefficient which is used as a parameter of isotherms. R² of 0.9995 and 0.9963, respectively, demonstrate that the isotherm data was best fitted using the Langmuir model. The maximum adsorptions of lead and cadmium were 9.407 mg/g and 12.05 mg/g, respectively.

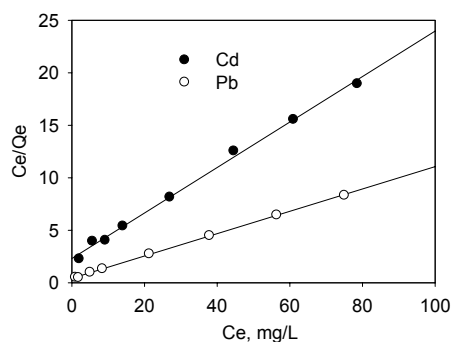


Fig. 8. Langmuir adsorption isotherms for lead and cadmium ions

4. Conclusions

The modified oil shale ash sample was prepared from the solid waste, which was collected at Huadian power station, Jilin province of China, using a sodium hydroxide solution at a temperature of 160 ° C. The ash was cha-

racterized by SEM and had an enlarged surface area and porosity. The optimum conditions of lead and cadmium adsorption by the modified oil shale ash were as follows: pH 7.0, adsorbent concentration 5.0 g/L, ash particle size 200 Mesh (0.074 mm), temperature 20 ° C, contact time 15 min. Under these conditions, the modified ash exhibited an excellent capacity for adsorbing lead and cadmium ions, the values being 9.407 mg lead/g ash and 12.05 mg cadmium/g ash. The Langmuir isotherm well fitted the adsorption by the alkali-treated oil shale ash, with R^2 being 0.9995 and 0.9963 for lead and cadmium, respectively. So, the results of experiments demonstrate that the alkali-treated oil shale ash is a superb adsorbing medium for lead and cadmium. This treatment technique not only enables the reduction of the amount of oil shale ash waste to be disposed of by a power plant, but also provides a cost-effective material for removal of heavy metals from wastewater.

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