

# Copper and zinc sorption by treated oil shale ash

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## Abstract

Jordanian oil shale ash was used as an adsorbent for the removal of copper and zinc from aqueous solution. This ash was treated with either hydrochloric, nitric, sulfuric or phosphoric acids followed by washing and/or neutralization with sodium hydroxide in order to enhance its adsorption capacity. The sample that was treated with nitric acid showed the highest cation exchange capacity (CEC) of 146 meq/100 g, while the one that was treated with sulfuric acid showed a value of 32 meq/100 g. Different adsorption isotherm data for both copper and zinc were obtained using the nitric acid-treated sample at different pH values. Freundlich and BET models were used to fit the experimental data, which showed that BET best-fitted these data. The separation factor for these isotherms shows unfavorable adsorption type at lower pH value.

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*Keywords:* Oil shale; Ash; Adsorption; Copper and zinc removal

## 1. Introduction

The discharge of large quantities of heavy metals into water resources has an adverse impact on the environment. Unlike organic pollutants, heavy metals do not degrade into less harmful substances and can accumulate in soil and water reservoirs, which leads to harmful effects on living species if they enter into the food chain. Copper and zinc, for example, are highly toxic as they are carcinogens and mutagens in nature [1,2]. Moreover, high intakes of these metals can cause liver, kidney and pancreas damage [3]. The maximum allowable limit for both metals in discharged water was set by the Environmental Protection Agency (EPA) to be 1.3 and 5 mg/L, respectively [4]. To attain these values different remediation techniques for treatment of wastewater can be applied [5–7]. Adsorption is considered an effective technique that was extensively used in the last few years [8,9]. Several adsorbents can be applied for removal of heavy metals from wastewater [10]. The choice of these adsorbents depends on their adsorption capacity, availability and cost. Ash is considered a cheap and a good adsorbent material toward metal ions because it contains reasonable amount of silica and alumina [11]. Several studies showed that ash from different sources could be used as an adsorbent material for

removal of either gases or heavy metals. Gray et al. [12] studied the capturing of CO<sub>2</sub> from gas streams by the utilization of amine-enriched fly ash from carbon. Panday et al. [13] examined the suitability of thermal power plant ash for removal of copper from aqueous solutions. They found that the adsorption capacity is greatly affected by concentration, pH and temperature of solution. Gupta and Ali [14] utilized fly ash from sugar industry waste for adsorption of copper and zinc from wastewater. The adsorption efficiency toward both copper and zinc by this ash was 90 and 95%, respectively. Bayat [15] compared the adsorption properties for two different fly ash samples for uptake of nickel, copper and zinc. This study showed that the increase in lime content in ash sample would increase the effectiveness of this ash for removal of the studied metal from aqueous solutions. A similar finding was obtained by Ricou et al. for removal of copper, zinc and lead from aqueous solution [16]. They concluded that solution pH, sorbent/adsorbent mass ratio, fly ash/lime ratio and fly ash origin were dominant factors for adsorption. Pan et al. [17] reused sewage sludge as adsorbent for copper removal from wastewater. The removal efficiency for this material was greater than 98%. Chu and Hashim [18] used the oil palm ash for adsorption of copper and nickel from aqueous solution. In the above studies, the fly ash was used directly as is and no further treatment was made in order to enhance its sorption capacity.

This work aims at utilizing the ash that is produced from burning the Jordanian oil shale as an adsorbent for removal

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of copper and zinc ions from aqueous solutions. Different oxidizing and reducing agents will treat this ash in order to enhance its surface coverage toward the target metals.

## 2. Experimental methods

### 2.1. Materials

Oil shale was brought from El-Lajjoun deposits, Jordan. This material was crushed and sieved to a particle sizes less than 2 mm then stored in closed bottles. All chemical were analytical grade reagents supplied by Scharlau Chemical Company. The glassware was Pyrex washed with diluted nitric acid, soap, and deionized water to minimize surface adsorption of copper and zinc ions.

### 2.2. Methods

#### 2.2.1. Treatment of oil shale ash

Ten samples of oil shale with 500 g each were combusted in Muffle furnace at 950 °C to remove water and organic matters. Then these samples were allowed to cool down in an open atmospheric condition for 24 h. Treatment method involved mixed the ash samples with four different oxidizing agents, mainly HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, for 24 h with vigorous agitation in 2 L beaker. The concentration of each acid was fixed at 5 M. The volume of the solution was also fixed at 1 L for comparison purposes. After oxidation, each of these samples was washed several times by deionized water until the solution pH was 6, then filtered and dried at 105 °C. These dried samples then divided into two equal weights; one part was stored for analysis while the other was further treated with 5 M NaOH solution.

#### 2.2.2. Cation exchange capacity test

Cation exchange capacity (CEC) was determined using the method of sodium acetate solution. 4 g of each treated ash sample was mixed with 1.0 M sodium acetate solution. Then, the sample was rinsed three times with isopropyl alcohol to remove any excess sodium ions exist freely in solution, followed by the addition of ammonium acetate solution (1.0 N) to regenerate the adsorbed sodium ion from the surface of these ashes. The amount of sodium was collected and analyzed using SOLAAR S4 Atomic Absorption Spectrophotometer.

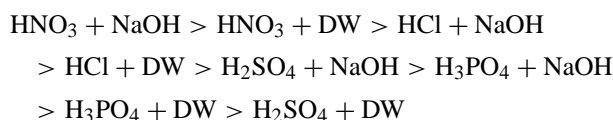
#### 2.2.3. Adsorption isotherm

Equilibrium experiments for each of copper and zinc were conducted in two sets of 250 mL Erlenmeyer flasks by mixing different concentrations of metal of interest with 0.1 g of the treated ash and allowed to equilibrate in an isothermal shaker (22 ± 1 °C) for 24 h. After equilibration, the solution was separated from the solid by filtration. The final concentration of the copper and zinc solution was then measured using SOLAAR S4 Atomic Absorption Spectrophotometer.

Similar procedure was used for blank samples where the treated ash samples were mixed with only deionized water.

## 3. Results and discussion

Chemical analysis of oil shale ash is presented in Table 1. The main constituent of this ash is lime with a percentage of 43.4, followed by silica (26.6%) and alumina (7.2%). Moreover, phosphorus pentoxide and ferric oxide show reasonable values of 5.9 and 2.9%, respectively. Diffractograms of this ash (Fig. 1) showed that it has mainly gypsum, quartz, lime, ferrous oxide and calcium-aluminates. Treatment of ash samples was performed by soaking with different acids followed by either washing with deionized water or neutralizing with sodium hydroxide solution. The treated ash samples were tested for their capacity toward cationic species. Fig. 2 illustrated the values of these CECs for each treated sample. There is a gradual decrease in the CEC values of the ash samples treated by the acids in the order of:



where DW stands for ‘distilled water’. It is appeared that the ash treated by nitric acid gained the highest CEC value (146 meq/100 g) while the one treated by sulfuric acid showed the lowest value of 32 meq/100 g. This could be due to the opening of more macro and micropores inside the ash particles. Nitric acid reacts with lime and gypsum that exist within the skeleton structure of the ash to produce a soluble calcium nitrate. During the washing of calcium nitrate, the solid is left with an open structure of aluminum, silicon and iron oxides. Soaking this treated sample with sodium hydroxide after successive washing enhanced its active surface and enriched it with negative functional groups and consequently increased the CEC [19,20]. Shim et al. [21] showed that activation with nitric acid and sodium hydroxide would increase the lactone groups. El-Henddawy [22] showed that treatment of activated carbon with nitric acid promotes hydrophilicity of the carbon surface and hence increases its CEC value. Lillo-Rodenas et al. [23] indicated that activation with sodium hydroxide can increase the surface area of the activated carbon and provides more micropores.

Table 1  
The analysis of the El-Lajjun oil shale ash

Component	Proportions (wt.%)
SiO <sub>2</sub>	26.6
Al <sub>2</sub> O <sub>3</sub>	7.2
Fe <sub>2</sub> O <sub>3</sub>	2.9
CaO	43.4
MgO	0.8
Na <sub>2</sub> O	0.3
SO <sub>3</sub>	9.1
P <sub>2</sub> O <sub>5</sub>	5.9

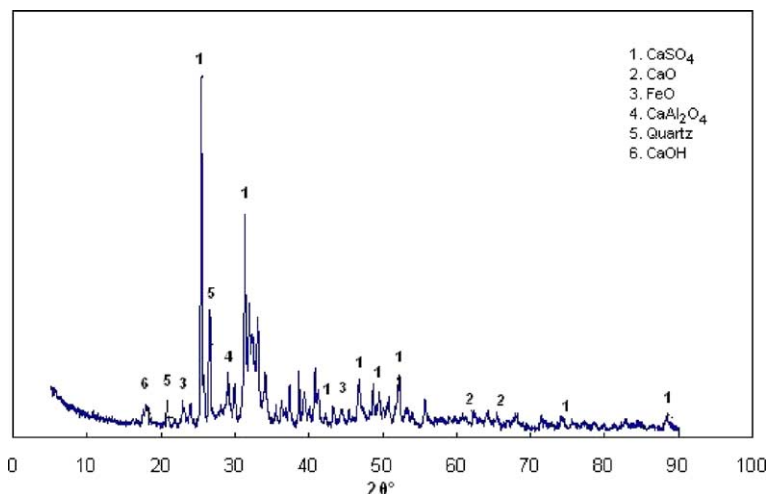


Fig. 1. XRD of the ash sample from EL-Lajjun oil shale.

Activation of the ash with either hydrochloric or phosphoric acid shows similar findings but with less CEC values.

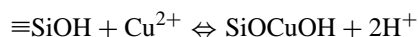
On the other hand, when the ash samples were treated by sulfuric acid, the free lime reacts with the sulfates to produce calcium sulfate. This increases the percentage of gypsum in this sample and may consequently block the available micropores in the original ash. Accordingly, samples treated with nitric acid were chosen for further investigations.

The adsorption of copper and zinc was studied at various pH values of 4, 6 and 12. These pH values were selected in order to test the ability of the treated ash to uptake these metals of interest in acidic solution (pH 4), actual solutions from down streams (pH 6–7) and in basic solutions (pH 12). Different initial concentrations of each of these metals were prepared and mixed with the treated ash samples. For both metals the extent of sorption capacity was increased when the ash was treated with the nitric acid followed by soaking with sodium hydroxide. This behavior was more apparent for adsorption of zinc rather than for copper (Figs. 3–6). The amount of zinc ions left in the solution that is mixed initially with HNO<sub>3</sub>/NaOH treated ash is much lower than that for the same solution but treated with only HNO<sub>3</sub> (Figs. 5

and 6). On the same zinc uptake obtained by both treated ash samples, 50 mg/g for example, the one that followed by washing with water result in 95 mg/L zinc ions in solution, while for the ash that further treated with sodium hydroxide leave only 7 mg/L when the solution pH was 6. Furthermore, when the solution acidity increases to pH 4, the situation becomes worse which leaves 113 and 10 mg/L, respectively. This gives evidence that soaking with sodium hydroxide enriched the surface with more oxygen and consequently provided the surface with more negative charges. On the other hand, adsorption of copper by both treated nitric acid samples did not show a great difference in the amount of copper ions left in solution. When the amount of uptake was 100 mg Cu<sup>2+</sup>/g ash, the solution concentrations were 260 mg/L for the one that was washed with water only and 220 mg/L for the sample that was further treated with sodium hydroxide at pH 4. This is due to the adsorption of copper ions onto the surface of ash as hydroxocomplexes that are inclined to the formation of polynuclear diamagnetic clusters [24] as



and



The first reaction provides a positive charge surface, which yield a repulsion force between part of the adsorbed surface and the copper ions that exist freely in the solution. The second reaction takes place between the surface and the free Cu<sup>2+</sup> in solution leading to formation complex surface of SiOCuOH. It is cleared that an extra proton produced in the solution at the hydrolysis of the adsorbed copper. This proton was released from water molecules in the coordination sphere of the hydrated Cu<sup>2+</sup> ions. The possibility of the formation of such complexes is confirmed by Vlasova and coworkers [25,26]. Consequently, this surface adsorbs about 30–40% of copper ions and leaving the rest in the solution. The copper and zinc ions exist in solution based on the pH as

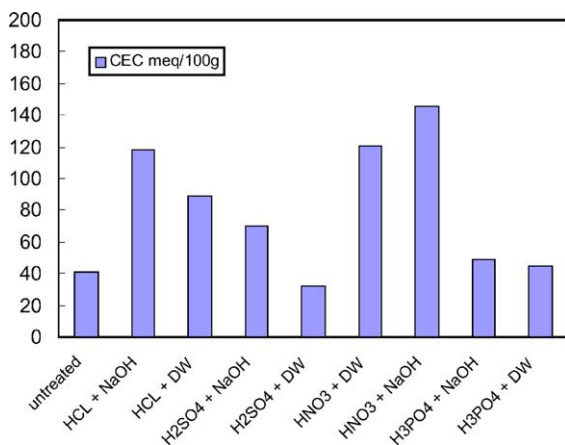


Fig. 2. Cation exchange capacities for the treated ash samples.

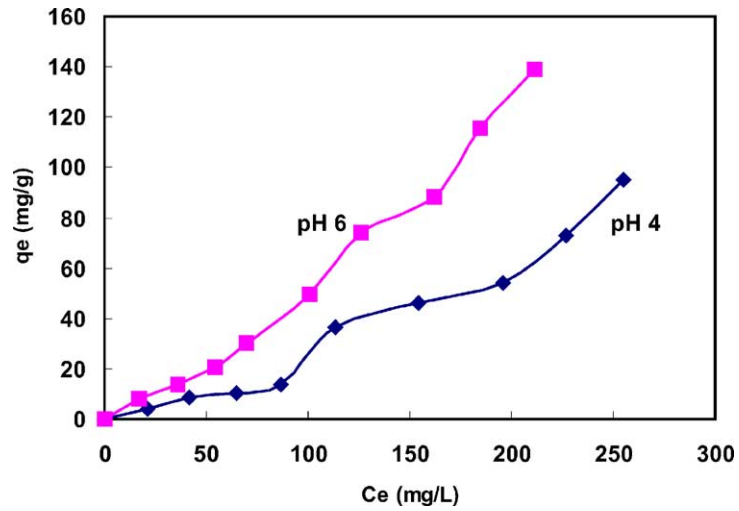


Fig. 3. Adsorption isotherm for copper onto ash sample treated with nitric acid.

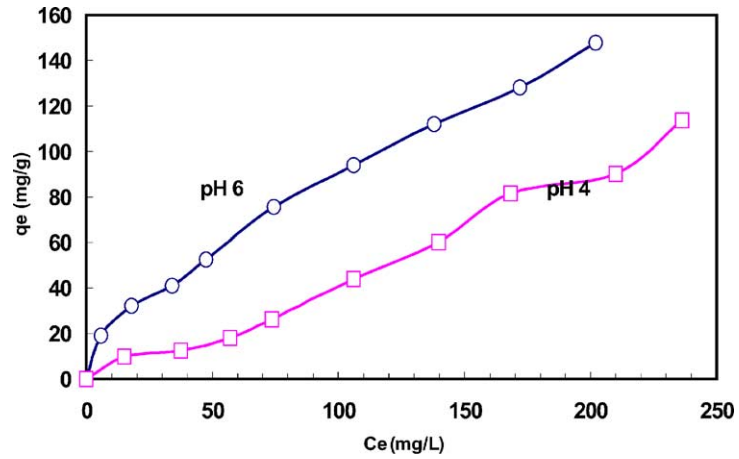


Fig. 4. Adsorption isotherm for copper onto ash sample treated with nitric acid and sodium hydroxide.

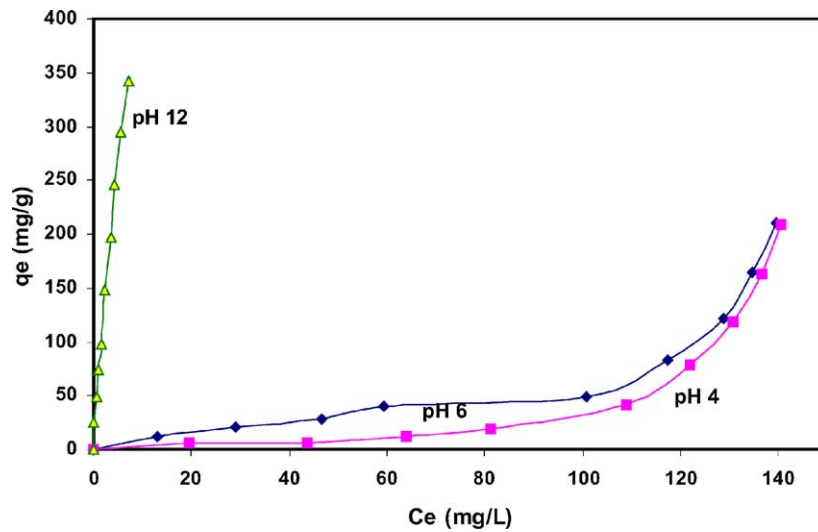


Fig. 5. Adsorption isotherm for zinc onto ash sample treated with nitric acid.

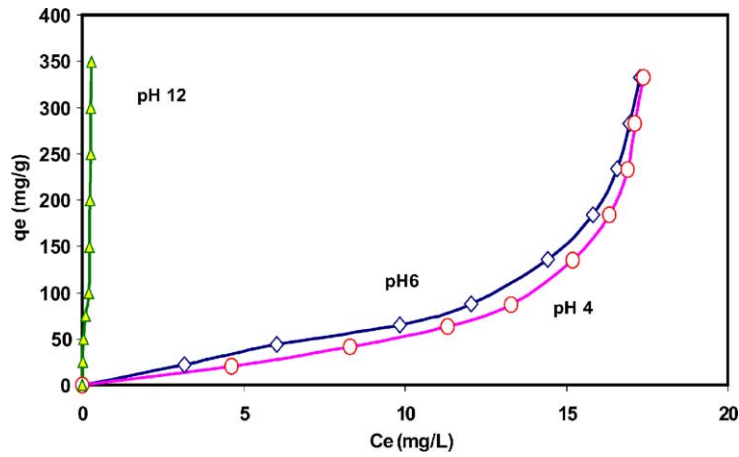
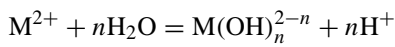


Fig. 6. Adsorption isotherm for zinc onto ash sample treated with nitric acid and sodium hydroxide.

$\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Zn}^{2+}$ ,  $\text{Zn}(\text{OH})^+$ ,  $[\text{Zn}(\text{OH})_4]^{2-}$ . In the case of copper, adsorption is supposed to be occurring by the electrostatic interaction with only surface silica sites [26]. At low pH repulsion force between metal ions in solution is occurred, which forces these ions to migrate into the macro and micropores. At higher pH value greater than 7 copper precipitates as  $\text{Cu}(\text{OH})_2$ . On the other hand, zinc adsorption shows different trend especially at higher pH. As the pH increases from 6 to 12, zinc ions undergoes complexes such as  $[\text{Zn}(\text{OH})_4]^{2-}$  where zinc can hydrolysis according to the general expression for divalent metals as [27]:



This complex can interact with the negative functional groups on the ash surface forming more strongly bound ‘inner sphere’ complexes (such as  $\text{Si-O-Zn}$ ) or rather loosely bound ‘outer sphere’ complexes via hydrogen bridges ( $\text{Si-O}\cdots\text{H-O-Zn}$ ,  $\text{Si-O}\cdots\text{HOH Zn}$ ) [28,29].

The effect of isotherm shape was studied based on favorable or unfavorable type. The isotherm trend for copper and

zinc was fitted according to the dimensionless separation factor,  $f$ , as

$$f = \frac{C_e(q_s - q_e)}{q_e(C_s - C_e)}$$

where  $C_e$  and  $q_e$  are the equilibrium concentration of the metal ion in solution and solid, respectively. While  $C_s$  and  $q_s$  are the corresponding saturated values for both solution and solid. When the value of the separation factor is equal to 1, the isotherm is considered linear. Above this value the isotherm is considered unfavorable, while below it the degree of favorable increases till this value becomes zero as for the case of irreversible isotherm. Treatment of the ash with nitric acid produced surface that adsorb copper and zinc of favorable at higher pH values. This may due to the existence of multilayer of adsorption as appeared for zinc at pH 12.

The isotherm data for both copper and zinc where plotted as  $q_e/q_s$  versus  $C_e/C_s$  which show unfavorable type at lower pH values (Figs. 7–10). Treatment with only nitric acid showed a favorable adsorption isotherm for copper

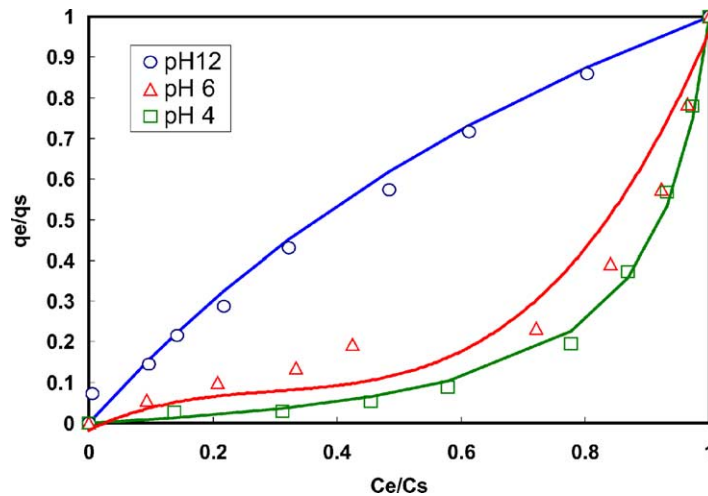


Fig. 7. Dimensionless concentration isotherm for zinc treated with nitric acid.

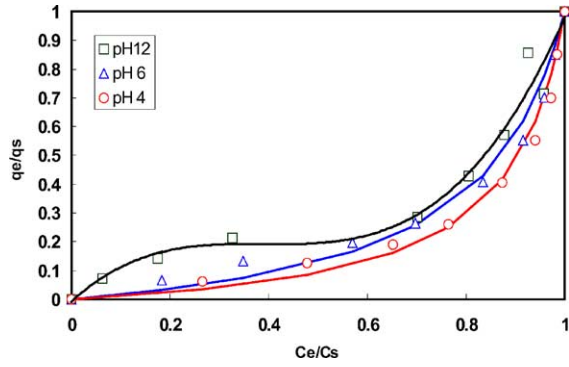


Fig. 8. Dimensionless concentration isotherm for zinc treated with nitric acid and sodium hydroxide.

at pH greater than 6. The isotherms of copper on the ash treated further with sodium hydroxide shows unfavorable type even at pH 6. Zinc isotherm shows only favorable type for the ash sample that treated with nitric acid and sodium hydroxide solution at pH 12. This could be attributed to the

formation of multilayer of adsorption of zinc at this pH value. To assure this assumption, two isotherm models were used to fit the experimental data for adsorption of both ions by HNO<sub>3</sub>/NaOH treated ash. Brunauer–Emmett–Teller (BET) model was used to fit the data that follow multilayer of adsorption according to the following equation:

$$q_e = \frac{a_0 a_1 C_e}{(1 - a_2 C_e)[1 + (a_1 - a_2)C_e]} \quad (1)$$

where  $C_e$  is the concentration of metal ions in solution (mg/L),  $q_e$  the amount of metal ion uptake per gram of ash (mg/g), and  $a_0$ ,  $a_1$  and  $a_2$  are constants.

Also Freundlich model was used to fit the experimental data for the case when adsorption is considered to take place on an energetically heterogeneous surface as

$$q_e = a_0 C e^{a_1}$$

The obtained constants and the regression coefficients for these models were illustrated in Table 2. It is cleared that

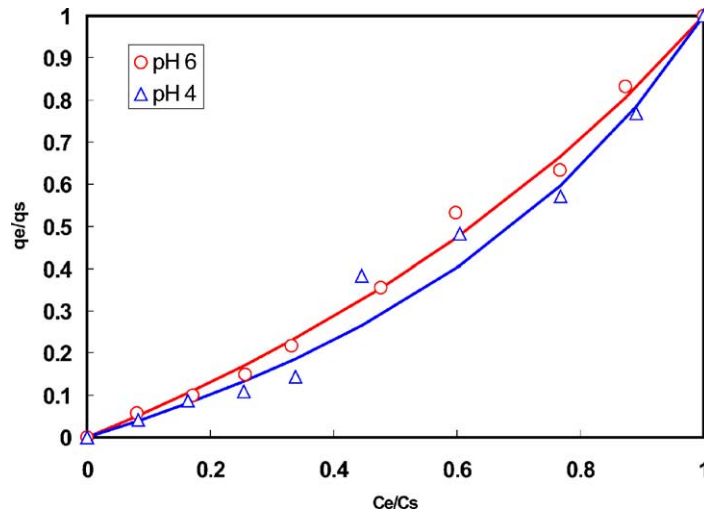


Fig. 9. Dimensionless concentration isotherm for copper treated with nitric acid.

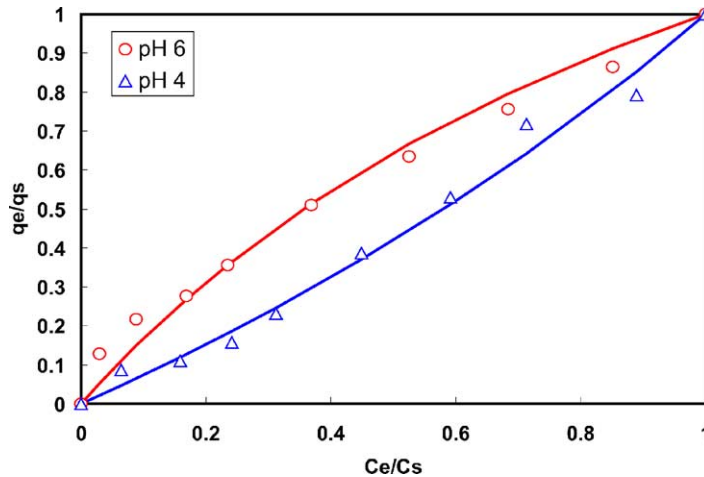


Fig. 10. Dimensionless concentration isotherm for copper treated with nitric acid and sodium hydroxide.

Table 2  
Freundlich and BET constants for copper and zinc isotherms at pH 6

Adsorbate/adsorbent system	Freundlich constants			BET constants			
	$a_0$	$a_1$	$R^2$	$a_0$	$a_1$	$a_2$	$R^2$
Cu/(ash treated with HNO <sub>3</sub> )	0.098	1.352	0.994	817.748	$4.790 \times 10^{-4}$	0.001	0.994
Cu/(ash treated with HNO <sub>3</sub> and NaOH)	4.237	0.665	0.994	96.583	0.021	0.002	0.996
Zn/(ash treated with HNO <sub>3</sub> )	$1.549 \times 10^{-3}$	2.349	0.892	20.416	0.143	0.006	0.995
Zn/(ash treated with HNO <sub>3</sub> and NaOH)	0.198	2.540	0.927	36.099	0.357	0.052	0.999

all the isotherm data were best-fitted using BET model with regression coefficient of 0.996 and 0.999 obtained for both copper and zinc ions, respectively, using HNO<sub>3</sub>/NaOH ash treated samples.

#### 4. Conclusions

Oil shale ash can be used as adsorbent for the removal of metal ions from solution after treatment with nitric acid and sodium hydroxide solution. Treatment with nitric acid changed the chemical composition of the ash and helped in opening more micropores while sodium hydroxide enriched this surface with hydroxyl groups. Batch adsorption isotherms for copper and zinc showed an increase in the removal capacity for both metals at high pH values.

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#### References

- [1] R. Shawabkeh, D. Rockstraw, R. Bhada, Carbon 40 (2002) 781.
- [2] J. Moore, S. Ramamoorthy, Heavy Metals in Natural Waters: Applied Monitoring and Impact Assessment, Springer, New York, 1984.
- [3] Agency for Toxic Substances and Disease Registry (ATSDR). <http://www.atsdr.cdc.gov>.
- [4] Environmental Protection Agency (EPA). <http://www.epa.gov>.
- [5] C. Mulligan, R. Yong, B. Gibbs, Eng. Geol. 60 (2001) 193.
- [6] C. Mulligan, R. Yong, B. Gibbs, J. Hazard. Mater. 85 (2001) 145.
- [7] A. Chmielewski, T. Urbaski, W. Migda, Hydrometallurgy 45 (1997) 333.
- [8] S. Yiaocumi, C. Tien, Kinetics of Metal Ion Adsorption from Aqueous Solutions: Models, Algorithms and Application, Kluwer Academic Publishers, New York, 1995.
- [9] N.C. de Souza, J.R. Silva, C.A. Rodrigues, L. da F. Costa, J.A. Giacometti, O.N. Oliveira Jr., Thin Solid Films 428 (2003) 232.
- [10] A. Margot, T. Llosa, D. Tanaka, V. Flores, T. Nagase, T.M. Suzuki, React. Funct. Polym. 53 (2002) 91.
- [11] D. Van Velzen, H. Langenkamp, K. Schaber, J. Hofele, Chem. Eng. Process. 35 (1996) 295.
- [12] M. Gray, Y. Soong, K. Champagne, J. Baltrus, R. Stevens Jr., P. Toochinda, S. Chuang, Sep. Purif. Technol. 35 (2004) 31.
- [13] K. Panday, G. Prasad, V. Singh, Water Res. 19 (1985) 869.
- [14] V. Gupta, I. Ali, Sep. Purif. Technol. 18 (2000) 131.
- [15] B. Bayat, J. Hazard. Mater. 95 (2002) 251.
- [16] P. Ricou, I. Lécuyer, P. Le Cloirec, Water Sci. Technol. 39 (1999) 239.
- [17] S. Pan, C. Lin, D. Tseng, Resour. Conserv. Recycl. 39 (2003) 79.
- [18] K. Chu, M. Hashim, J. Ind. Eng. Chem. 9 (2003) 163.
- [19] C. Woolard, J. Strong, C. Erasmus, Appl. Geochem. 17 (2002) 1159.
- [20] A. Singer, V. Bergaut, Fuel Energy Abstr. 36 (1995) 421.
- [21] J. Shim, S. Park, S. Ryu, Carbon 39 (2001) 1635.
- [22] A. El-Hendawy, Carbon 41 (2003) 713.
- [23] M. Lillo-Rodenas, D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, Carbon 39 (2001) 751.
- [24] N. Vlasova, Colloids Surf. A: Physicochem. Eng. Aspects 163 (2000) 125.
- [25] A. Kokorin, N. Vlasova, A. Pridantsev, N. Davidenko, Bull. Russ. Acad. Ser. Chem. 10 (1997) 1765.
- [26] K. Xia, R. Taylor, W. Bleam, P. Helmke, J. Colloid Interf. Sci. 199 (1998) 77.
- [27] J. Ayala, F. Blanco, P. García, P. Rodriguez, J. Sancho, Fuel 77 (1998) 1147.
- [28] H. Ochs, D. Bublak, U. Wild, M. Muhler, B. Kolbesen, Appl. Surf. Sci. 133 (1998) 73.
- [29] Y. Mori, K. Uemura, K. Shimano, T. Sakon, J. Electrochem. Soc. 142 (1995) 3104.