



The study of Oilfield produced Water treatment using Zeolite based Geopolymer from Oil shale ash

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Abstract

In this work, we will try to investigate the effectiveness of zeolite derived from oil shale ash as an adsorbent to remove of heavy metal ions from an oilfield wastewater. Different parameters effect like contact time, pH, adsorbent dosage, initial concentration and adsorption isotherms will be examined. XRD and SEM methods are used to identify characterization of synthesized adsorbent. The pseudo first/second order were employed to evaluate the process kinetics. The results show that Batch kinetic data are in good agreement with the pseudo second order model. The adsorption data for Cr(III), Pb(II), Zn(II), Cd (II) and Ni(II) have been well fitted by Freundlich isotherm model. The adsorption efficiency of zeolite at optimum condition for Cr(III), Pb(II), Zn(II), Cd (II) and Ni(II) were equal to 93.4, 86.1, 89.9, 93.6 and 83.3%, respectively.

Keywords: Oil shale, oilfield, wastewater, adsorption, Zeolite.

Introduction

Rapid economic growth has caused a significant increment in the exploration/extraction/utilization rate of oil to meet the modern industrial processes. Like to many other industrial activities, the crude oil exploration process unavoidably produces solid, liquid and gaseous pollutants which have effects on the environment. One of these threats to environments is oil polluted water which includes heavy metal contamination. The existence of heavy metal ions in the oil fields water have been reported in numerous studies.

Oil contaminant is considered the main responsible to heavy metals existence in oily polluted water. The degradation of hydrocarbons in water increases the level of organic compounds and reacts with heavy metals which produce organ metallic complexes. In addition, local water characteristics could be changed by oil spillage and drilling process in crude oil extraction. As a result, extraction processes of crude oil will very likely alter heavy metals migration and distribution in the water. Higher environmental risks will be resulted by heavy metal and oil contaminations accumulation which is inevitable results of increasing duration of oil-extraction processes. With respect to mentioned facts, clarifying the heavy metals speciation, migration and distribution in oil polluted water seems to be very necessary and urgently needed. Consequently prior to discharge to the environment, it is required to treat and remove metallic contamination from oilfield wastewater. In spite of its importance, researches in this field have not received sufficient considerations.

Conventional treatment processes like electrochemical removal, ion exchange, and chemical precipitation can be used to treat

heavy metal from oil field discharged wastes¹⁻³. Producing of toxic sludge, requiring higher amount of energy and incomplete removal are the major disadvantages of these processes. Because of no toxicity, ash is environmentally friendly. What is more, in view of that fact it is obtained from wastes these materials are low-cost⁴. For these reasons the use of these adsorbents for heavy metal ions removal from waters and waste waters is an excellent solution to the environmental problems – cleaning waters and waste waters as well as exploiting waste products⁵⁻⁶. It is known that the adsorption process conditions such as contact time, temperature, pH, and adsorbent dosage are essential. The source and operation of ashes production make its chemical composition and properties vary and are different from one sample to another sample. However, alumina and silica components are the major parts of fly ashes which make them a good candidate for the synthesis of zeolites. This study shows the results of the investigations on the above listed parameters for adsorption of Cd(II), Zn(II), Pb(II), Cr(III) and Ni(II) on Zeolite derived from oil shale ash.

Material and Methods

zeolite-X has been synthesized in two-step process. 6 g of fly ash were mixed with 7.2 g of NaOH and then heated at 550 C for 1 hr. The mixture then cooled at room temperature. To control the molar ratio of SiO₂/Al₂O₃, NaAlO₂ was added to the mixture and then it mixed with water. After stirring for 16 hour at ambient temperature, the mixture was heated to 150 C for 24 hr in an oven to complete hydrothermal synthesis. The mixture then was cooled at room temperature and washed with deionized water. Then it was filtered and washed again with deionized water and then dried at 100 C for 16 hr.

The X-ray diffraction (XRD) patterns of ZFA and RFA were obtained using X-ray diffract meter (GBC made, Australia). The operational conditions is 28.5 mA and 35 kV, employing Cu K α radioactive source. The scanning electron micrograph (SEM) was applied to obtain the surface morphology of ZFA and RFA. The range of 10° to 60° was considered to scan the sample and crystalline compounds were identified by using JCPDS files.

Raw wastewater was collected from an oilfield wastewater and stored in a box before the experiments.

Results and Discussion

XRD patterns of zeolite was presented in figure-1. The major crystalline phases in the ash are quartz, clay minerals and so on. After alkaline fusion, the glass phase on the surface of ash

particles transforms from quartz into more reactive species. The XRD pattern of the final product indicates the appearance of diffraction peaks of zeolite crystal, which could be easily indexed as zeolite.

The morphology changes of ash and zeolite are shown in figure 2a and 2b. The image of zolite shows that it is totally different from the original ash. The hydroxy compounds form zeolite surface entirely and gets into porous network structure, and at the same time, the granule size also increases sharply. Particle size is a significant factor to influence the removal efficiency. The particle size of the synthesized zeolite was determined by dynamic light scatter (DLS) measurement. The synthesized zeolite has a particle size distribution range from 0.9 μ m to 3.9 μ m with an average diameter of 1.65 μ m.

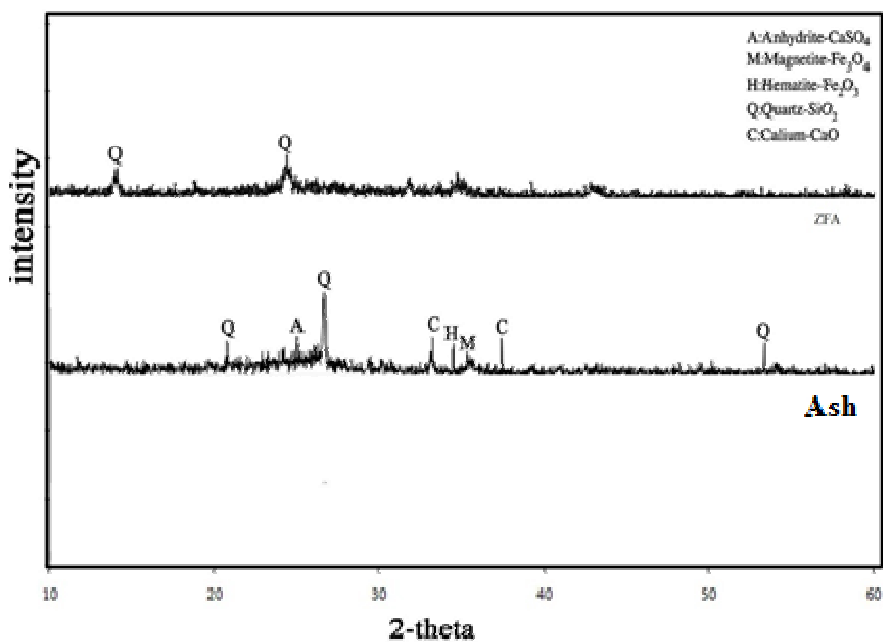


Figure-1
X-ray diffraction patterns of Ash and Zeolite

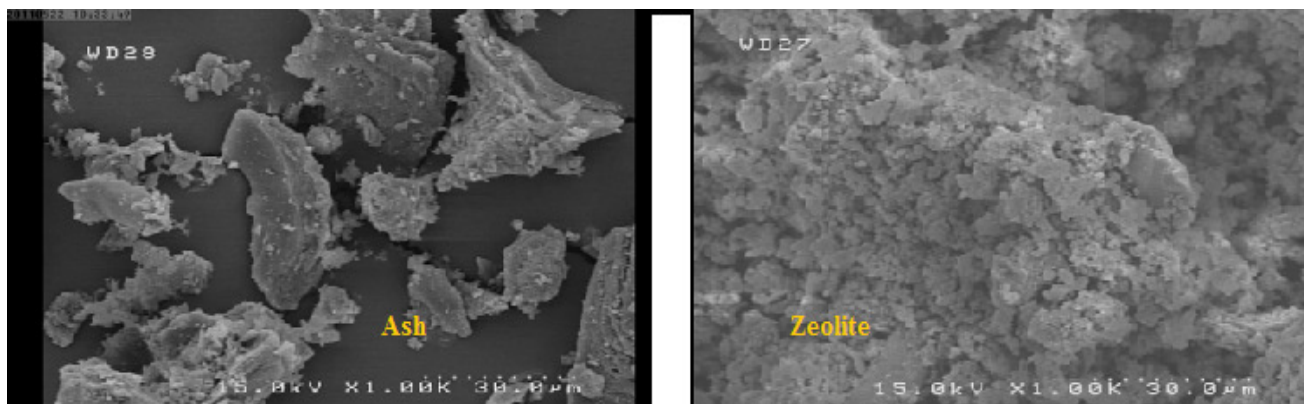


Figure-2
SEM images of Ash and Zeolite

pH has important influence on pollutant molecules, zeolite surface charge, and also on the mechanism and the rate of hydroxyl radical generation. Figure-3 shows the effect of pH on removal efficiency. As the figure shows, increasing pH value results in improving process efficiency. When pH is below, the surface charge of the adsorbent is positive. However, at pH less than pH ZPC, the predominant metal species are positively charged, therefore, uptake of metals in the pH range of 2–6 is a H^+ -Metal⁺ exchange process. Decreasing metal ions removal at lower pH is clearly because of the H^+ ions higher concentration presence in the mixture of reaction which compete for the adsorption sites with the metal ions. Quite reversible situation is observed in the case of metal ions, which occurs as a negatively charged oxoan ions. On the other hand, pH appears to control

the desorption of metals from the surface of the ash surfaces. It was proved that desorption increases as the pH increases.

The effect of adsorbent dosage is the next parameter which must be considered for removal process (figure-4). It can be showed that percentage of ions adsorption improved almost linearly with adsorbent dose increment. It is caused by the availability of more active adsorption sites and increase in the adsorption surface area. It was found that the maximum adsorption for all investigated heavy metal ions was achieved with 0.3 g of adsorbent (data not presented). The adsorption percentage (S%) was the highest for Cu(II) (81.5–89.5%) and decreased in the order: Zn(II) (7.9–39.8%), As(V) (0.42–38.19%), Cr(III,VI) (4.0–35.0%) and Cr(VI) (3.1–11.3%).

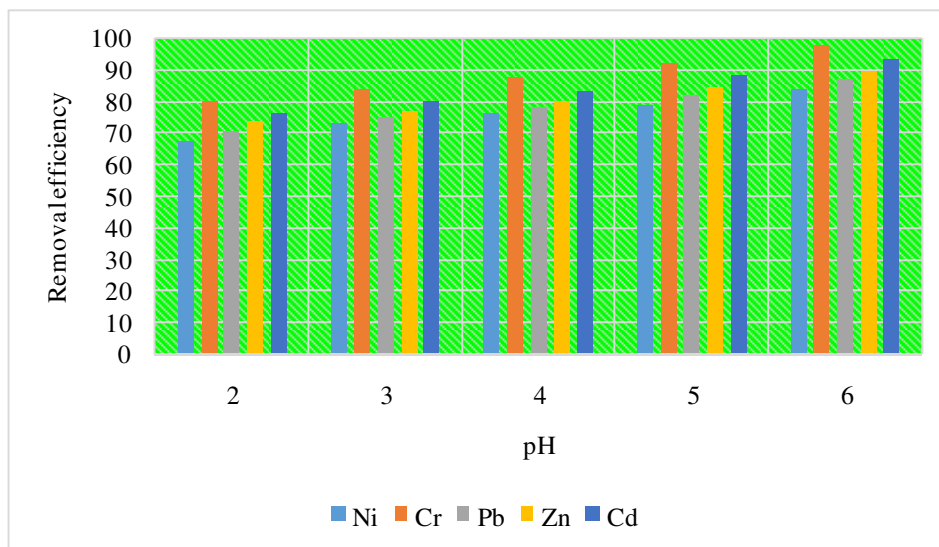


Figure-3
 The effect of pH on the removal efficiency

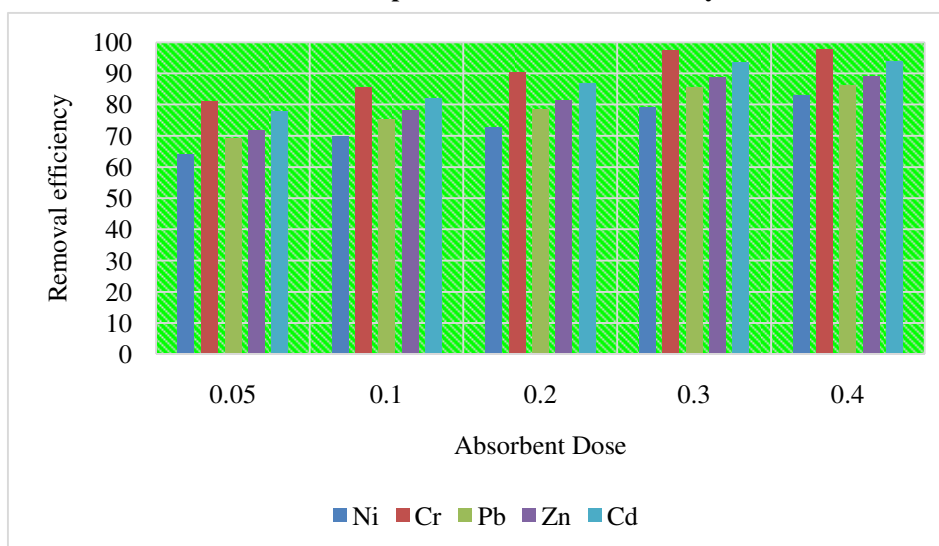


Figure-4
 The effect of amount of adsorbent on the removal efficiency

Figure-5 shows the effect of contact time for the adsorption of Pb, Ni, Zn, Cd and Cr onto zeolite. It can be observed that adsorption of investigated ions increase with the phase contact time for initial concentrations of 50 ppm. For all studied metal ions the sorption occurs most rapidly over the first 20 min. Then it remains constant at all concentrations which indicate the binding sites on the zeolite are fully saturated after this time. Therefore, the phase contact time of 30 min can be assumed to be equilibrium time for the adsorption of Cr and Cd onto zeolite. In case of adsorption of Pb, Zn and Ni time to reach equilibrium conditions was equal to 40 min.

The percentage removal of metal ions by the zeolite regarding to the initial metal ions concentration was presented in figure-6. It was shown that the adsorption capacity increased with increase an initial concentrations of metal ions. This showed that an initial concentration has an important role in the adsorption of listed heavy metal ions onto zeolite. This may be interpreted by a higher chance of collision between them and the adsorbent surface and a higher ioncentration gradient, which makes the mass transfer resistance lower.

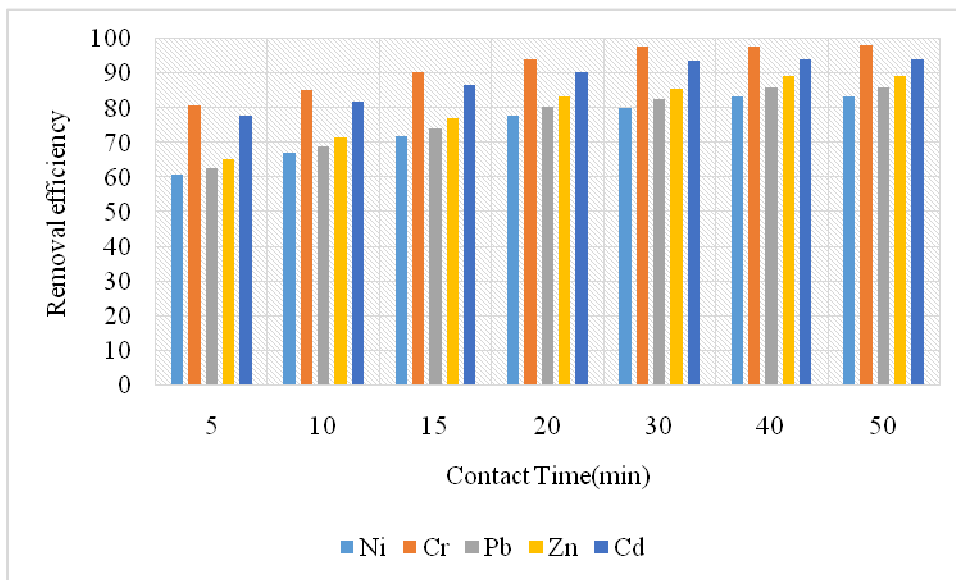


Figure-5
 The effect of contact time on the removal efficiency

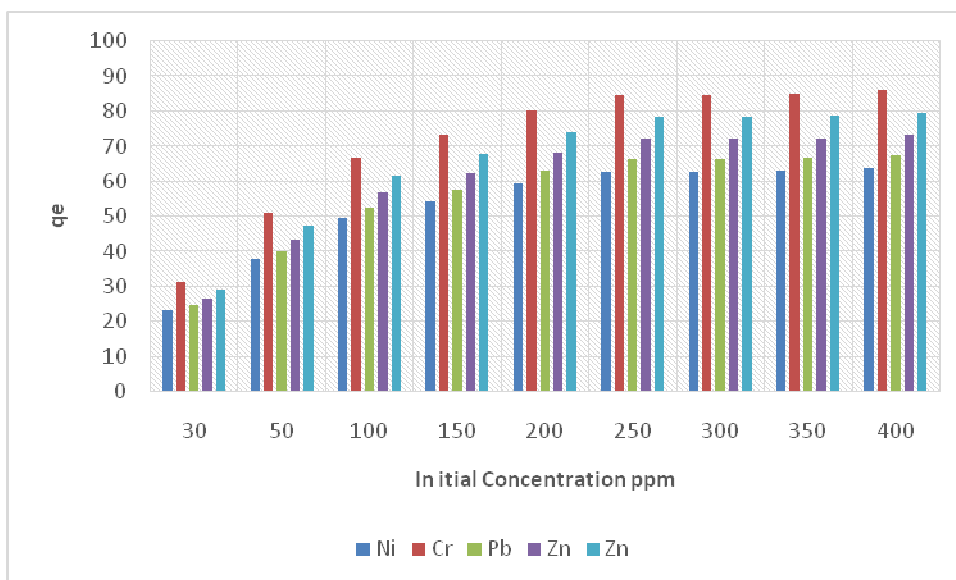


Figure-6
 Effect of metal ions initial concentration on absorption capacity

Adsorption kinetics: To study the adsorption mechanism, the pseudo first order and the pseudo second order equations were applied to the experimental data of initial concentrations. The obtained results are listed in table-1. The determination coefficient R^2 almost equal to 1.00 for adsorption of metal ions confirms that adsorption processes followed the pseudo second order kinetics. It can be observed that the rate constant of the pseudo second order decreases in a gradual way with an increment in the adsorbate initial value, this can be because of competition between higher levels of metal ions for the zeolite active sites (a larger k_2 value shows that to reach a specific fractional uptake, adsorption systems with low concentrations will needed a shorter time).

Adsorption isotherms studies and adsorption mechanism: The Langmuir and Freundlich isotherm models are applied in this study for analyzing experimental sorption equilibrium data and obtaining some important information on the surface properties of the adsorbent and its affinity for the investigated metal ions. As seen from table-2. Freundlich isotherm model fitted the equilibrium data for adsorption of listed above ions onto both zeolite what is confirmed by the correlation coefficient R^2 almost equal to 1.0. The Langmuir-type isotherm hints toward surface homogeneity of the adsorbent while the Freundlich-type adsorption isotherm is an indication of surface heterogeneity of the adsorbent. This draws the conclusion that the small heterogeneous adsorption patches form the surface of adsorbent which are very much similar to each other regarding to adsorption phenomenon. The constants K_F and n were calculated from the slope and intercept of the plot between $\log q_e$ vs. $\log c_e$. It can be observed that $1/n$ values lies in the range $0.1 < 1/n < 1$ for adsorption of metal ions onto zeolite what means that adsorption was favorable.

Table-1
Kinetic parameters for the adsorption

	The pseudo first order			The pseudo second order			
	q1	k1	R2	q2	k2	h	R2
Ni	1.51	0.03	0.7	1.98	0.08	0.3	0.99
Cr	4.25	0.21	0.84	1.12	0.3	0.38	0.99
Pb	1.38	0.02	0.81	2.26	0.5	3.18	0.99
Cd	1.41	0.03	0.86	1.62	0.03	0.5	0.99
Zn	1.35	0.02	0.8	2	0.07	1.2	0.99

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Conclusion

Solid-state fusion reaction with NaOH creates aluminosilicate adsorbent and geopolymer with porous structures, and this way, improves the surface area, pore volume, and the capacity of adsorption for metal ions in aqueous solution. In this study, zeolite of oil shale ash was used to treat oilfield wastewater and remove heavy metal ions. The optimum conditions of sorption were as follows: pH value of 6, a sorbent dose of 0.3 g, contact time of 30 min for Cr and Cd and 40 min for Pb, Zn and Ni. The kinetic data obtained showed that pseudo-second-order equations controlled the adsorption process. Moreover, according to adsorption isotherm investigations, Freundlich equation was proved to be the best in fitting the adsorption process.

Table-2
Langmuir and Freundlich parameters for adsorption

	T(K)	q_{exp}	Langmuir model				Freundlich model		
			q^0	K_L	R_L	R^2	K_F	$1/n$	R^2
Cr(III)	293	19.1	1.55	2.69×10^{-4}	0.61	0.96	1.63	1.83	0.99
	313	17.51	1.17	3.63×10^{-4}	0.54	0.91	1.44	1.81	0.99
	333	16.29	1.47	1.75×10^{-4}	0.71	0.85	1.52	0.89	0.99
Pb(II)	293	12.65	1.37	5.43×10^{-4}	0.59	0.93	0.91	1.33	0.99
	313	10.81	1.2	6.61×10^{-4}	0.54	0.92	0.88	1.43	0.98
	333	9.55	1.82	9.07×10^{-4}	0.46	0.93	0.67	1.64	0.93
Cd(II)	293	36.22	1.55	4.52×10^{-4}	0.63	0.97	0.65	1.16	0.96
	313	32.39	1.95	4.34×10^{-4}	0.64	0.99	0.82	1.16	0.96
	333	29.5	1.55	6.16×10^{-4}	0.55	0.93	0.79	1.25	0.92
Zn(II)	293	28.65	1.82	1.09×10^{-4}	0.05	0.97	4.64	1.26	0.93
	313	27.88	1.49	1.27×10^{-4}	0.05	0.98	4.3	1.27	0.66
	333	26.35	1.32	1.22×10^{-4}	0.05	0.99	3.55	1.29	0.92
Ni(II)	293	55.52	1.56	2.34×10^{-4}	0.7	0.93	1.07	1.93	0.97
	313	53.94	1.83	1.38×10^{-4}	0.08	0.98	1.16	1.95	0.96
	333	51.94	1.33	4.49×10^{-4}	0.92	0.91	1.03	1.99	0.93

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