ISSN No. 2395-0900
International Journal of Engineering Studies and Technical Approach

Removal of Heavy Metals from Wastewater by Using Natural Zeolites as Adsorbent

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ABSTRACT:

Nearly 70% of agricultural lands in India are irrigated with wastewater. Industrial wastewater contains a variety of inorganic pollutants such as heavy metals that make pollution to soil, water, and plant. Methods to remove heavy metals from industrial wastewater are not so effective or they are costly. In this study, three kind of natural Zeolite with four different sizes have been used to investigate their adsorption on five types of important heavy metals. Result shows that the Firouzkoh Zeolite adsorbs heavy metals more than the others. The adsorption efficiency increases with decreasing size. The effect of retention time on adsorption ratio shows that 80% of the Pb is absorbed by Zeolite during early 70 minutes.

Keywords: Adsorption, Heavy metals, Wastewater, Zeolite.

1. INTRODUCTION

In many cities in India, municipal wastewater is used for agricultural irrigation. For instance a significant part of the municipal and industrial wastewater are disposed on it, is widely used for irrigating agricultural lands in producing fruit and vegetables. There is a 9700 ha-land in Tehran, suitable for irrigation from which 6900 ha is irrigated with wastewater. (Nearly 70%). In Shiraz it has been reported that in arid seasons the main discharge of the river is wastewater, which is finally used in agriculture [_13]. In India, municipal and industrial wastewater enters the River and is finally used for agricultural irrigation [_13]. Also wastewater sludge is used as fertilizer in agricultural lands. The application of this wastewater and sludge in agricultural land generates numerous sanitary problems [_8]. Heavy metals enter into the water and soil as solution and cause pollution for surface water, groundwater and soil. These metals also destroy ecosystem in which they enter [_3]. Therefore, they should be removed from water resources. In this way we can reach a stable development without any damage to the environment. Emmerich et al. [_4], for cadmium and nickel, Silvier and Sommers [_12] for cadmium and lead, Petruzzelli et al. [_11] for lead and nickel showed that the application of wastewater with low pH causes a faster movement of the elements towards the low level of the soil profile [_2]. These movements cause contamination of the groundwater and sub surface water. Investigations done by ven der leaden et. al. in 1990 showed that U.S.A. tested aquifers is contaminated by heavy metals [_10]. Chemical deposition, ion exchange process, electrolyze, inverse osmoses, evaporation process, surface adsorption [_14], fluid sand media [_15], wetlands and biosorption [_5] are

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common methods for removal of heavy metals from wastewater [_13]. The common processes for removing heavy metals either do not have necessary efficiency or are costly. For these reasons extensive researcher have been conducted to improve existing methods [_5], [_9]. Zeolite is crystalline solid with small pores. It has pores with dimensions of 3 to 10 Angstroms [Ao]. They are called molecules sieve. All of zeolites have 10-20 percent water in their compositions. They lose their water at heat without any destruction in their structure. This process is returnable [_7]. There is returnable ion exchange, with alkaline elements and it has ion balance. Returnable dehydration along with liquid and gas absorption is a strong reason for formation of the zeolites from pores. Structural analysis using x-ray and Notronmetery_method confirms this issue [_7]. In zeolites Si^{4+} are replaced with Al^{3+} and charge deficit is compensated by Ca^{2+}, Na^{+}, etc. Empirical formula for zeolite is as follows:

$$\mathbf{A_{2/n}\,O\;Al_2Ox\;Sio_2\;yH_2O} \qquad \textbf{(1)}$$

where *A* is an alkaline cation and *n* is cation capacity. The values of *x* and *y* vary from 2 to 10 and 2 to 7, respectively. Zeolites are divided into two groups: natural and synthetic. At present most of the natural types are provided in synthetic form. A Swedish mineralogist named Cronsted discovered the first type of zeolite two centuries ago. Also Dolter has reported the first kind of synthetic zeolite in 1890 [_6]. In spite of the fact that many kinds of natural and synthetic zeolites have been known, only a few of them have industrial application and are important from economic and commercial point of view. Synthetic zeolites include, F, Zeolon, ZSM-S, A, L, X, Y and W and natural zeolites like Clinoptolite, Mordenite, Chabazite and Eerrienite can be named [_13]. In general, commercial application of zeolites is due to three important factors, including chemical structure, availability and economic cost. The important factor in structural stability from thermal, chemical and physical point of view is zeolite chemical composition. On this basis, the more the percentage of Si the more stability to the temperature and chemically active environments [_6]. Zeolites can be found in volcanic environments (under hydrothermal condition), salt lake and sediment layers. The most popular kinds of zeolites are Clinoptilolite, Mordenite, Dachiardite, Analsim, Phillipsite, and Heulandite. They have significant resources in USA, Mexico, Bulgaria, Italy, Russia, Iran and … [_7].

So far, zeolites have been applied in different industries. They are used in petrochemistry and oil industries as a catalyst to separate and purify the gases by using molecule sieve phenomena, solar energy, industrial, ceramic and fire proof industries, washer industries as a replacement for phosphates. They are used also in agricultural industries as a fertilizer and increasing water content, in animal husbandry for absorption of gasses in the animal stomach and more importantly in the treatment of municipal, industrial and nuclear wastewater [_7]. In Romania tuffs including clinoptilolite, activated by a 2-N acid citric for two hours, at 20°c and solid liquid ratio equal to 1.4. It has been used in Coagulation process in water treatment for removing colloids and other contamination and microorganisms. Also application of clinoptilolite tuffs in the filtration process compare to quartz sand filter has decreased the cost of treatment 20-30%. In Ukraine modified clinoptilolite along with large quantity of manganese dioxide are used for removing iron and magnate from artesian wells [_7]. NASA in supporting the long life in space for reuse of human wastewater including urine has used zeolites for adsorption and removing of ammonium ion. Experimental study in pilot plant scale showed that application of clinoptilolite in separation of about 17% wastewater Ammoniac in ammonium ion shape is efficient. Clinoptilolite for having ion exchange replacement property in wastewater treatment has been used in USA. With discharge of ammoniac [in harmless shape] in the atmosphere, it can be reused. Because of magnetic susceptibility and high cation capacity the modified zeolite has been used for treatment of the turbid water, sludge and soil in Russia [_7]. In this research the potential of Iranian natural zeolite for removing of heavy metal from wastewater has been studied.

2. MATERIAL AND METHODS

In this study tests are divided into two groups: physical and chemical tests. The physical tests include measurement of hydraulic conductivity, maximum water content and Bulk specific gravity. The chemical tests include measurement of cation exchange capacity, pounding time and isotherm. All tests were done in 20 ± 5 ^{o}C and in 3 periods. The instrument is used for measurement of hydraulic conductivity in a touched soil sample is a constant head method's [_1]. Five cm of zeolite with a given size was put into the instrument. A geotextile layer and a screen wire were installed at the bottom of the instrument to prevent the flow of soils. The other installed above of zeolite column to prevent movement and turbulence of the surface. Before performing tests samples were washed from bottom. In this way small sizes of zeolite were come out. Then, the water flow was set from up. After equilibrium condition the volume of water in a given time was collected. The following equation was used for computation of hydraulic conductivity:

$$K = 86.4*(V * L) / (A * H * T) \quad (2)$$

where; *K* is hydraulic conductivity (m/day), *V* is volume of collected water (cm3), *L* is the length of zeolite sample (cm), *A* is cross section of area for sample (cm2), *H* is the depth of water (cm) and *T* is duration of test. For measurement of maximum water adsorption (water content), first all of zeolite sample was saturated and after releasing gravity water, it was weighed and was put into oven for 24 hours and in 105 ^{o}C. Samples were weighed and the water contained in to the soil was calculated. Water content can be calculated by the following equation:

$$W = (M_1-M_2)/(M_2-M_3)*100 \quad (3)$$

Where M_1 is weight of sample with container after releasing gravity water, M_2 is weight of sample with container after 24 hours; M_3 is weight of container and *W* is Water content. For measurement of specific gravity used a column with a 5-cm diameter, a 5.2-cm height. It filled with given sample and weighted without any shaking or … then by using specific gravity calculated:

$$B_d = M/V \quad (4)$$

Where; B_d is Bulk specific gravity, *M* is net weight of zeolite in container and *V* is Volume of zeolite. For determination zeolite cation exchange capacity (*CEC*), 0.1 gr of sample was poured in glass container and 10 ml of a solution with 0.1 normal of given cation was included and was shaken in 25 ^{o}C, with a speed of 250 rpm. After clarifying the liquid under strainer and also the zeolite sample was tested and cation concentration was calculated. The remaining metal in solution was then read by atomic absorption instrument and absorbed metal in unique germ absorber was calculated using the following equation:

$$Q = V*(Ci-Cf))/M \quad (5)$$

ISSN No. 2395-0900
International Journal of Engineering Studies and Technical Approach

where; Q is adsorbed metal in the unit weight of absorber (mgr./gr), V is volume of solution (lit), Ci is initial concentration of the metal in the solution (mgr./lit), Cf is final concentration of the metal in the solution (mgr./lit) and M is adsorbed metal (gr). In order to know how many metals are absorbed by strainer or by it a witness in each step was considered. For analysis of exchangeability of the zeolite sample related to cation, the *CEC* of sample in mill equivalent of cation for one gram was calculated. In the pounding time experiment the goal is finding relationship between the adsorbed metal and time of contact. For this means, 5 grams of Analsim zeolite was put in 2 liters Erlen-Mayer. Then 500 cc of solution with a 500-mgr./lit concentration prepared. Zeolite and solution contacted and was put in a shaker. At the distinct time it has been get a 10-ml sample and analyzed with atomic adsorption. Difference between the observed and initial concentration means adsorbed until this time. For calculating retardation factor in the movement of contamination in a porous media, it is necessary understanding sorption isotherm. By means of finding type of isotherm and its coefficients, several repetition of 1 gram Analsim-zeolite has been weighted. Then several solutions with concentration range from 1 mgr./lit to 500 mgr./lit prepared. After contacting zeolite and solution they put in the shaker for 24 hours. The 10-ml sampled and analyzed with atomic adsorption

3. RESULTS AND DISCUSSIONS

The results of the hydraulic conductivity tests are seen in **Fig. 1.** As one can see hydraulic conductivity decreases with increasing diameter of the particles. This trend can be observed for all samples. Figure 1 shows the relationship between hydraulic conductivity and size of the zeolite and type of the zeolite. Also, for large particles, hydraulic conductivity for Clinoptilolite Firouzkoh is more than the other zeolites. The reason is the shape of the Analsim and Semnan Clinoptilolite particles. Since they have higher Si compared to the other, they are made into pieces in such a way that they have sharp points. Therefore, the sharp points occupy the pores. In fact, decrease of hydraulic conductivity is due to reduction of pores.

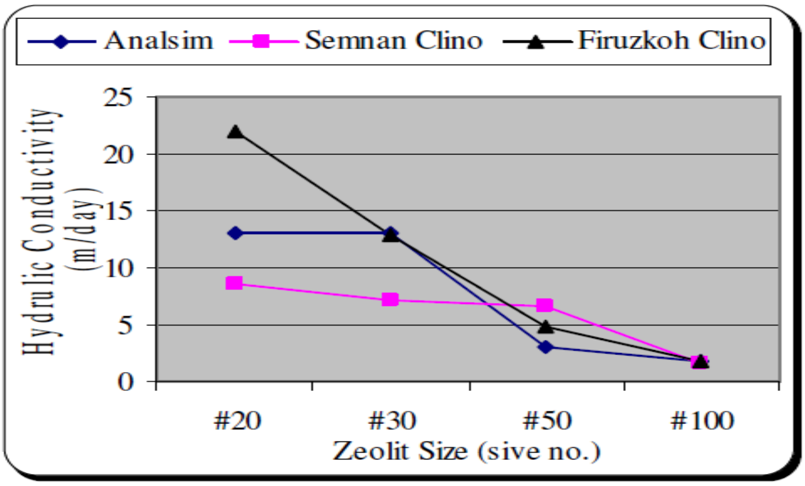

Fig. 1 Hydraulic conductivity in Samples

Figure 2 indicates the results of the water content tests. As one can see water content increases as diameter of particles increases. The reason is that the specific area of particles increases with decreasing diameter of particles, with increasing specific surface area the adsorption of water increases. Figure 2 shows the relationship between water content and size of the zeolite and type of the zeolite. Water adsorption in Clinoptilolite samples is more than Analsim sample. The reason is that the Si amount in Analsim sample is more than that of the Clinoptilolite samples.

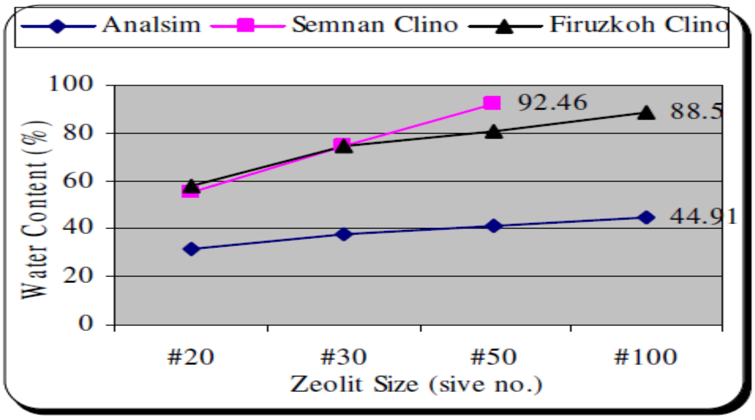

Fig. 2 Water content in Samples

Figure 3 shows the results of bulk specific gravity. The results show that with decreasing diameter of particles the bulk specific gravity increases. The reason is that the micro porosity for small particles is more than that of for large particles. Fig.3 shows the relationship between specific gravity and size of the zeolite and type of the zeolite. The bulk specific gravity for Analsim sample is more than that for two others and for Firouzkoh-clinoptilolite sample is more than Semnan-clinoptilolite. The reason is that the percentage of the Si for Analsim is more the two others. The difference between the zeolites is small and the reason is that the percentage of Si for samples is close.

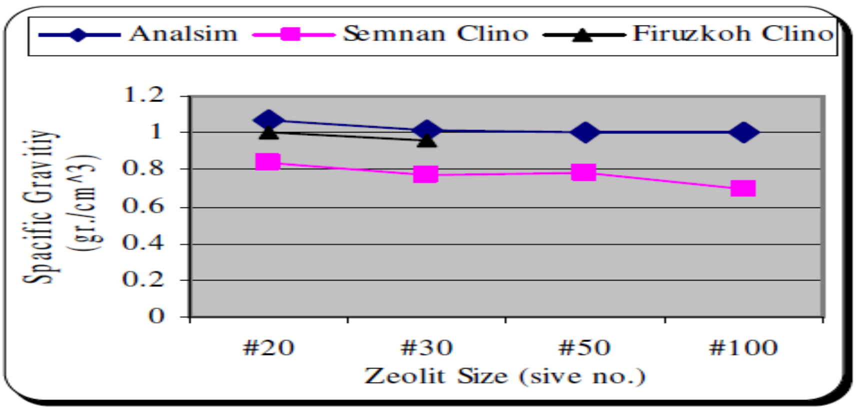

Fig. 3- Specific gravity in Samples

CEC test done on Pb, Zn, Ni, Cu and Fe elements which here you can find Pb and Zn results. **Figure 4 and Figure 5** show the results of tests performed for determination of Pb, Zn adsorption by samples. Based on these results, as diameter of particle decreases, the CEC increases. This trend can be seen for all samples. This is due to increasing specific area index with decreasing diameter of particles. As one can see from Fig. 4, cation absorption for Firouzkoh-Clinoptilolite is more than that for the rest of the samples and almost Semnan-Clinoptilolite sample does not show any adsorption. Maximum adsorption capacity related to Pb has been measured 1.54 meq/gr. It seems the reason is high percentage of Si in Analsim sample compare to two other samples but about the Semnan-Clinoptilolite it is due that it isn't pure and this cause low CEC. Figure 5 shows the results of tests for Zn adsorption. As one can see from this figure all three Zeolites have almost similar adsorption related to Zn. In this case, Firouzkoh Clinoptilolite and Analsim have maximum and minimum adsorption, respectively.

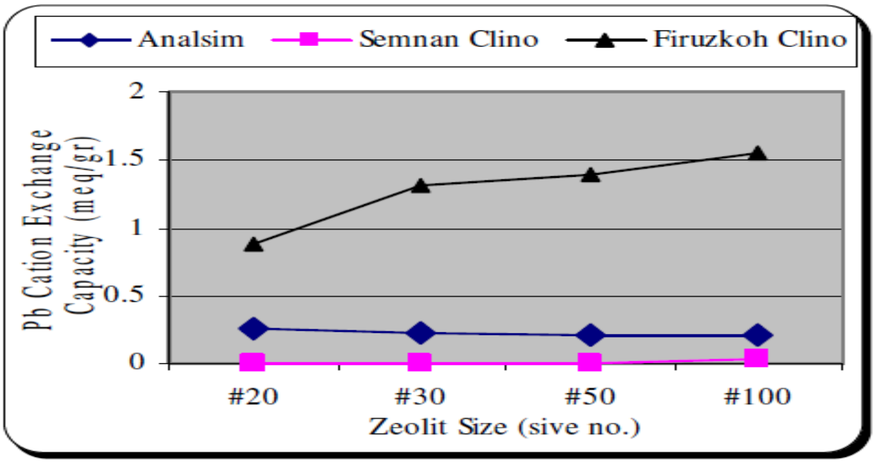

Fig. 4 CEC of Pb in Zeolite Samples

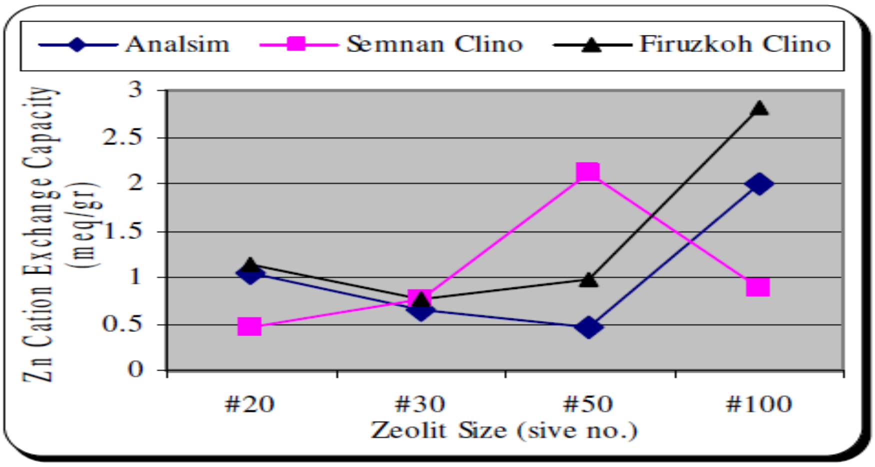

Fig. 5 CEC of Zn in Zeolite Samples

Figure 6 indicates the results of zeolite pounding time. Figure 6 shows relationship between pounding time of Analsim zeolite (mesh no.20) and Pb adsorption. The results of the experiments show that the rate of the adsorption decreased as time goes on. The reason is that at the beginning of the tests all adsorption sites are empty and absorber substance are easily replaced in the empty sites.

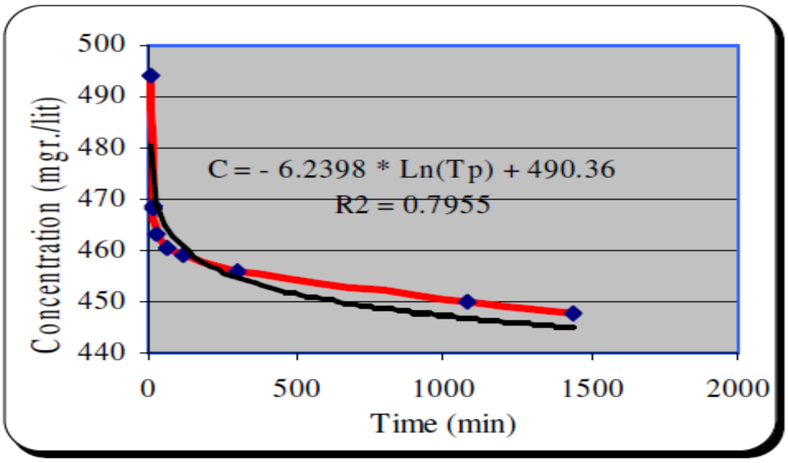

Fig. 6 Pounding time in Analsim for Pb

As time goes on the empty sites of zeolites decreased and therefore the rate of adsorption decreases. As one can see about 80% of the total adsorption happens in less than 70 minutes and after 24 hours the rate of the adsorption is almost insignificant. **Figure 7** shows that after 24 hours, the experiment's line will be nearly horizontal and it means that no adsorption will be occurred.

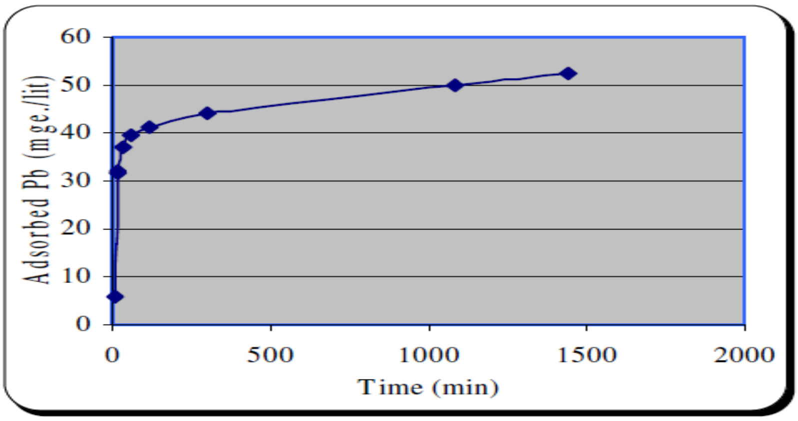

Fig. 7 Adsorbed Pb in Analsim

Figure 8 indicates the results of the isotherm tests. The results show that as the concentration of solution increases the absorption begin to increases and then reach to a maximum value. After this point it has a nearly constant adsorption. Fig. 8 shows the results of adsorption isotherm. As one can see, with increasing concentration of the solution the adsorption increases. Finally, in 150 mg/lit concentration the maximum adsorption happens. Based on Fig. 8 the resulted adsorption isotherm is Langomoyer isotherm.

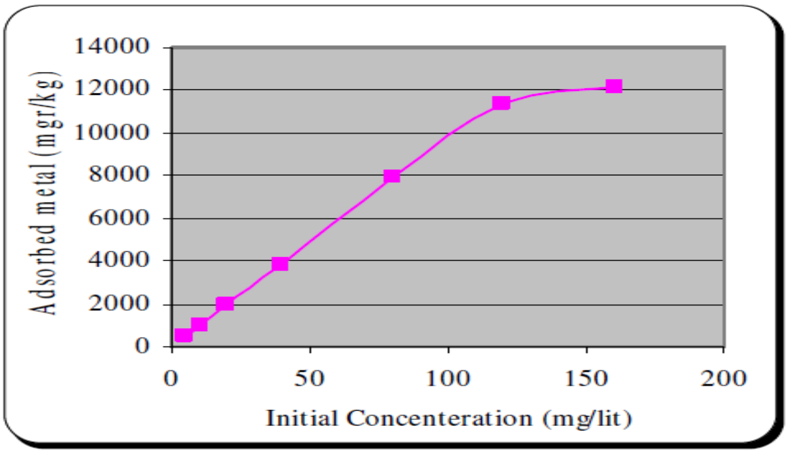

Fig. 8 Adsorption Isotherm for Analsim

4. CONCLUSIONS

Industrial wastewater contains a variety of inorganic pollutants such as heavy metals that make pollution to soil, water, and plant. Methods to remove heavy metals from industrial wastewater are not so effective or they are costly.Here, three kind of natural Zeolite with four different sizes have been used to investigate their adsorption on five types of important heavy metals. Result shows that the Firouzkoh Zeolite adsorbs heavy metals more than the others. The adsorption efficiency increases with decreasing size. The effect of retention time on adsorption ratio shows that 80% of the Pb is absorbed by Zeolite during early 70 minutes.

5. ACKNOWLEDGEMENTS

I am gratefully acknowledgements to my family & friends for their guidance & help in completion of this paper.

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