Journal of Chemical Health Risks 1(1): 11- 18, 2011

Removal of Zn^{2+} and Cr^{6+}From Waste Water Samples, Using Natural Iranian (Aftar) Zeolites

S. Peyrav [1], *R .Zahiri* [2*] *and K. Moradi Hersini* [2]

[1]School of Earth Sciences, Damghan University, Damghan, Iran
[2]School of Earth Sciences, Damghan University, Damghan, Iran

---

Abstract: This paper concerned the removal of Zn^{2+} and Cr^{6+} ions from waste water using a naturally occurring zeolite from semnan region in Iran. A continuous fixed-column study was carried out by using zeolite as a low-cost adsorbent for the removal of Zn^{2+} and Cr^{6+} ions from aqueous solution under the effect of various process parameters such as, grain size and time. The efficiency of removal was higher for Zn than Cr ions. The Zn^{2+} and Cr^{6+} ions uptake by zeolite increased with initial ions concentration and column height, but decreased as the flow rate increased. The adsorption capacity reached a maximum at grain size of 0.71mm.

Keywords: Zeolite, Aftar, Zinc, Chromium

INTRODUCTION

Since Cr (III) is poorly absorbed by any route, the toxicity of chromium is mainly attributable to the Cr (VI) form. It can be absorbed by the lung and gastrointestinal tract, and even, to a certain extent, by intact skin. The reduction of Cr (VI) is considered to serve as a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effect while the reduction of Cr (VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs (Dayan & Paine, 2001). Heavy metal containing wastes are considered to be hazardous to both human life and the environment due to their acute toxicity and non biodegradability, even when the heavy metals are present at trace concentrations. Several methods for removal of metal ions from waste waters have been developed, but most have disadvantages, such as continuous input of chemicals, high cost and even incomplete metal removal (Brown *et al*, 2000).

Recently, there has been a great interest in R&D of low cost alternative adsorbents for treatment of heavy metal waste waters. These investigations include: removal of Cr(VI) (Chen & Ray, 2001), Cu(II) (Karabult *et al*, 2000; Faur-Brasquet , 2002), Cd(II) (Barbier *et al*, 2000; Burns *et al*, 1999), Ni(II) (Yavuz *et al*, 2003), Pb (II) (Evans *et al*, 2002) Zn(II) (Mohan & Singh, 2002), Co(II) (Brigatti *et al,* 2000), As(V) (Garsia *et al,* 1999) and Hg(II) (Pollard *et al,* 1992) with different low-cost adsorbents such as clinoptiolite (Faur-Brasquet *et al*, 2002), coals (Karabult *et al*, 2000; ; Burns *et al*, 1999), montmorilonite (Barbier *et al*, 2000), agriculturalwaste (Mohan & Singh, 2002), sepiolite) (Brigatti *et al,* 2000), and clay (Garsia *et al,* 1999).

Zeolites are a class of materials which have crystallographically well-defined channels and cavities. Although it originally defined as a luminosilicates with anionic frameworks, the definition of zeolites has been expanded to include silicates, aluminophosphates, silicoaluminophosphates, gallosilicates, titanosilicates, metallosulfides, metalooxides, etc (Sun & Seff, 1964).

The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of $Si^{4+}$by Al^{3+}produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cat ion (sodium, potassium, or calcium). These cations

---

Corresponding Author: Zahiri R, Assistant Professor, School of Earth Sciences, Damghan University, Damghan, Iran

are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese (Barer, 1987; Breck & Chem, 1964).

Existence of vast zeolite resources (especially Clinoptilolite) in different areas of Iran such as Semnan, Mianeh, Nain Dezh, Talhe, Rudehen, Taleghan, Tabas, Kerman and Zahedan is the reason of studying zeolit in this research (Kazemian & Faghihian, 1998) to eliminate cat ions of heavy metals.

The studied area is located in Aftar area in Semnan province and is in northwest of Semnan city and west of Aftar country. Aftar mine is located between longitudes of 53° 00' 00" and 53° 02' 44"and latitudes of 35° 37' 40" and 35° 38' 48".This area is Part of South heights of central Alborz and to several decades have been conducted sporadic and small geologic studies in this sector. Aftar mine despite has severe wrinkles and slope classes without too many breakages and disorganization is a surface outcrop throughout its range. Outcrops on the ground appeared well and also on the part is covered a few centimeters of soil surface covers (Eftekharnejad, 2004).

MATERIALS

The solutions were prepared with freshly deionized water and chemicals of analytical reagent grade. The 1.000 g L^{-1} Zn and Cr standard stock solutions were prepared by dissolving 4.0220 g $Zn(NO_3)$ (Merck, Germany) and 5.0910 gr $CrCl_6$ (Merck, Germany), respectively in water and completing the volume to one liter with water.

After zeolites preliminary purification and set up was their mill by using standard sieve 11-ASTM.E mesh.

CHARACTERIZATION TECHNIQUES

Powder X-ray diffraction (XRD) patterns of the adsorbents were obtained using a powder diffractometer (BRUKER-D8) equipped with a Cu Kα radiation. The accelerating voltage and current used were 40 kV and 20 mA, respectively. The chemical compositions of the adsorbents were determined by a BRUKER X-ray reflective fluorescence spectrometer (XRF, axs –S4 EXPLORER). All metal concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-JVC, Integra-XL, Sequntion). The samples were usually diluted five times by deionized water. Therefore, the concentration of metal ion solutions should be in the range of 0–60 mg l^{-1}. The PH values of the aqueous solutions were measured by a JENWAY- PH meter (MP 120).

Based on XRD analyses were diagnosed of dominant zeolite minerals in the region is Clinoptilolite and Heulandite. Fig. 1

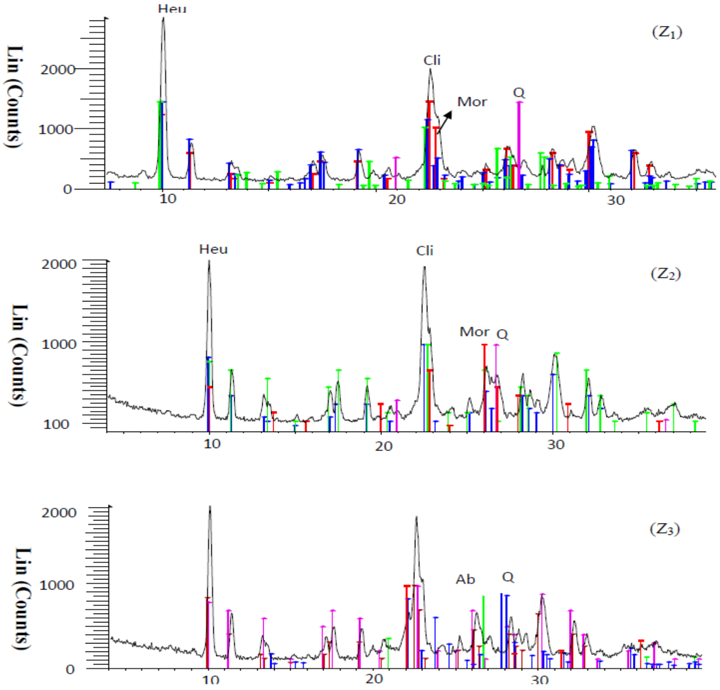


Fig. 1: XRD analysis graph zeoliticrocksamples Aftr. **Cli**:Clinoptilolite- **Heu**:heulandites- **Mor**:Mordenite- **Alb**:Albite- **Q**: Quartz

And according to XRF analysis, composition of zeolits showed in Table 1

Table 1: Chemical composition of the zeolite samples,by X-ray fluorescence.

	Contents wt%		
Components	Z_1	Z_2	Z_3
SiO_2	68.03	70.02	70.20
Al_2O_3	12.48	11.54	11.56
Fe_2O_3	1.29	1.05	1.15
TiO_2	0.21	0.23	0.20
CaO	2.22	2.52	2.01
MgO	1.60	1.05	-
Na_2O	1.97	1.92	2.11
K_2O	2.62	1.93	2.09
Y_2O_3	0.01	0.01	0.01
ZrO_2	0.02	0.02	0.02
SrO	0.19	0.19	0.17
Rb_2O	0.01	0.01	0.01
BaO	0.09	0.09	0.09
SO_3	0.04	0.12	0.59
Cl	0.07	0.07	0.06
LOI	9.15	9.24	8.56
Total	100	100	100

PROCEDURE

The tubes with 25cm length packed of aggregated zeolites were filled three in types as 1mm, 0.71mm and mixed of 1mm, 0.71mm and 0.25mm and was closed two sides with washers.

The water samples contained 100 ppm of Zn (II) and 100 ppm of Cr (VI) passing in pipe's zeolite with the different grain scheme and measured Zn (II) and Cr (VI) levels of output water.

With using falling head (downside) test measured permeability on each crossing of water at the special time in the pipe zeolite. General principles to testing determined the permeability device with the downside potential shown In the Fig. 3.

It initially washed the zeolite within the tube with 0.1 HCl. For this purpose, zeolite containing pipe was connected from one direction with tap and another direction with an output vessel. With Opening tap flowing water through a vertical tube into the sample zeolite

The time t=0 at the initial potential, difference Δh_o registered and allowed water to be flow through the zeolite samples. Final potential difference recorded in time $t=t_f$ that is equal to Δh. According to the following formula can achieve influence quality in the zeolite tube.

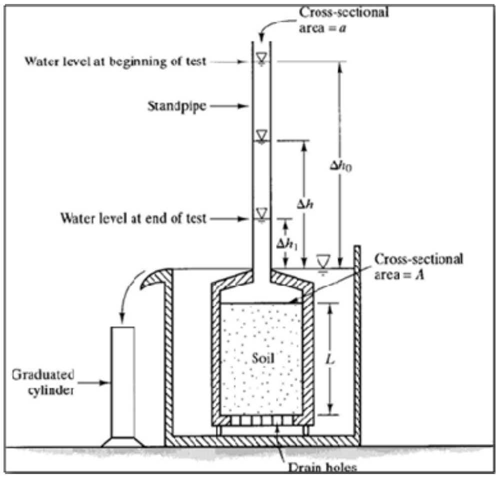


Fig 3: Adsorption picture of how to test using modified fall head

$$K = \frac{a^2 \times l}{A \times t} \times \ln\frac{\Delta h_o}{\Delta h}$$

K: Permeability (cm/sec)
a: Radius of graduated cylinder (cm)
A: Radius of zeolitic tube (cm)
l: Length of zeolitic pipe (cm)
t: Time of experiment (sec)
Δh_o: First head (cm)
Δh: second head (cm)

The test for each element in three stages with three different aggregation 1mm (sample A), 0.71mm (sample B) and mixed 1mm, 0.71mm, and 0.25mm(sample C).

10 times for each stage continuous done in a certain time and each time have been analyzed and compared the output sample.

In all drawn graphs passing water samples showed aggregation 1mm and sample B aggregation 0.71 mm and sample C is a mixed aggregation one mm, 0.71 mm, 0.25 mm.

After passing the water samples containing various heavy metals from the zeolite pipes, water output device was analyzed using ICP set to determine the amount to be absorbed by the zeolite. Furthermore, Removed zeolite of the zeolite tube, they were oven temperature to 105 degrees for 24 hours than powdered and were analyzed by XRF to elemental percentage changes in their study.

RESULTS AND DISCUSSION

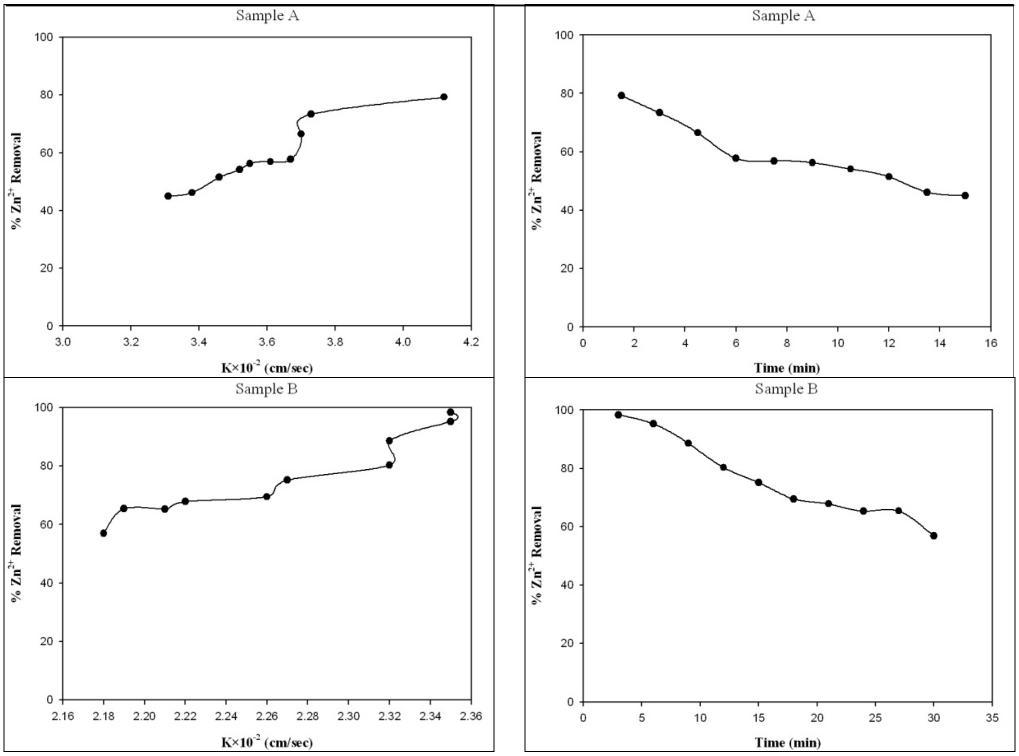
With testing on the permeability of different aggregation, was selected 1mm, 0.71mm and 0.25mm grain size of zeolite category for use in experiments.

Zn^{2+} removal

Water samples with concentrations 100 ppm of zinc after passing through the zeolite tube were also analyzed by ICP. Results indicated that Zn^{2+} has decreased in the water output. Therefore, zeolite can absorb zinc (Fig. 4).

According to the Figure 4, relationships between permeabilities are as follows:

$$K_A > K_B > K_C$$



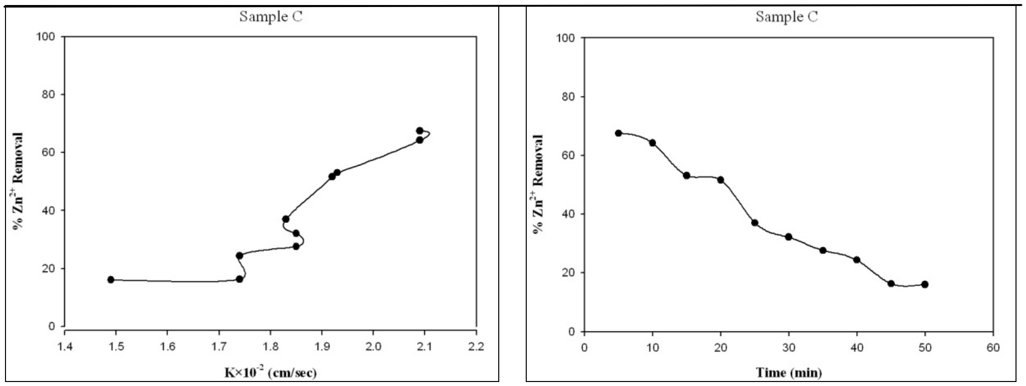


Fig4:Graphs of removalzincbypermeability and time, A. category grain of onemm, B: Categorygrain of0.71mm, C: mixedgrain of 1, 0.71, 0. 25mm.

Rate of zinc removal by different permeability (different aggregation) with according to the Figure 4 to removal zinc is as follows:

B>A>C

According to passed water sample with containing of zinc through the tube zeolite with the different permeability and different aggregation based on the Figure 4 relationship between the times is as follows:

$T_C>T_B>T_A$

The results of water samples by passing aspects of the aggregation of zeolite 0.71 mm as tangible is seen a reduction in zinc concentration in the output water. According to K values and duration of water passing into zeolite samples with different aggregation, zeolite B due to higher absorption and better permeability and less transit time (T) suitable to absorb more zinc. XRF analysis of the used zeolite in experiments after passing water samples can be seen zinc oxide in the composition of this zeolite (Table 2).

Table 2:XRF analysis zeolite of removal zinc in the falling head test with different aggregation

Components	SiO_2	Al_2O_3	ZnO	Fe_2O_3	TiO_2	CaO	Na_2O	K_2O	MgO	ZrO_2	SrO	SO_3	LOI
Z(A)	70.34	10.89	0.22	1.18	0.19	1.98	2.03	1.87	1.13	0.02	0.17	0.24	9.56
Z(B)	71.04	10.90	0.29	1.16	0.20	1.86	1.96	1.87	1.03	0.02	0.17	0.09	9.30
Z(C)	69.72	10.57	0.08	1.19	0.19	2.21	2.04	1.87	1.03	0.02	0.17	1.20	9.46

3.2 Cr^{6+} removal

Results of water sample with 100 ppm concentration Cr^{6+} passes in the trough the tube zeolite in the tube is shown in Figure 3. It can be seen decreased of chromium concentration in the output water.

Water samples with 100ppm concentration of Cr^{6+} after crossing the zeolite tube was ICP analyzed and was seen the concentration of Cr^{6+} decreased in output water. The decrease concentration of Cr^{6+} and absorption by the zeolite of Aftar mine can be seen in Figure 5.

The results of Figure 5 are such that the ratio of permeability in the different aggregation attracted for absorbing the chromium to the as follows:

$K_A>K_B>K_C$

Absorption rate of Cr^{6+} in terms of different permeability (different seed aggregation) with according to the figure 5 to absorb the chromium is as follows:

B>C>A

According to passes water sample through the tube containing chromium zeolite with a grain of a different permeability and different aggregation based on the figure 5, time relationship is as follows:

$T_C>T_B>T_A$

Zeolite with aggregation of 0.71 mm (examples of B) is better to absorb chromium. However, in the graph of absorption with respect to time, water sample containing the chromium in a very long time more of the sample C is passed through. Difference inchromium absorption of zeolite the B and C are not very high but their difference in time is considerable. Considering the factors mentioned is the best aggregation and permeability to the B sample.

The performance in XRF analysis passing zeolite of Aftar mine the water sample containing Cr^{6+} is clear in the table 3. Highest of removal percentage of Cr^{6+} is the zeolite with classified aggregation 0.71 mm.

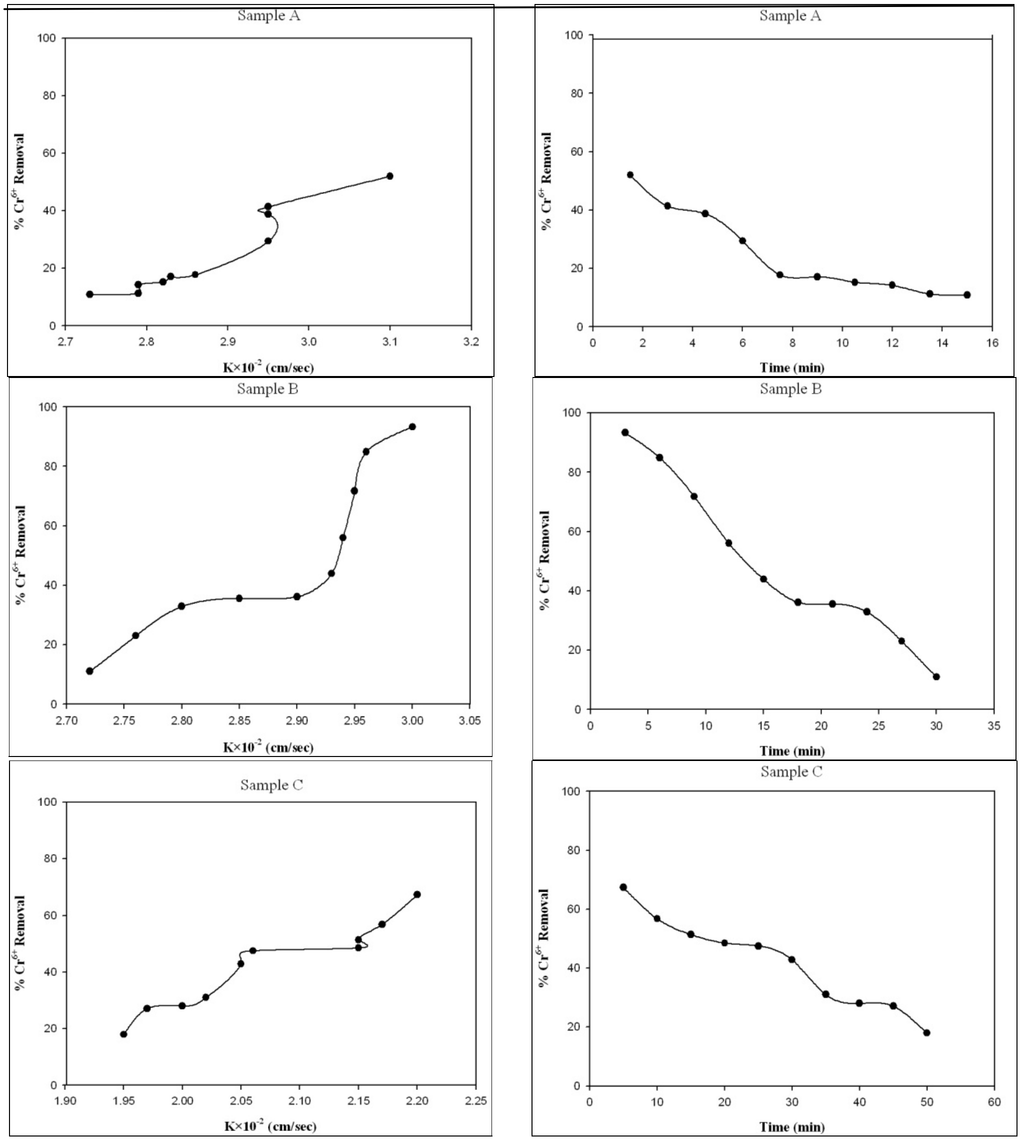


Fig5: Graphs of removal chromium by permeability and time, A. category grain of onemm, B: Categorygrain of0.71mm, C: mixedgrain of 1, 0.71, 0. 25mm.

Table 3**:** XRF analysis zeolite of removal cromiumin the falling head with different aggregation**.**

Components	SiO_2	Al_2O_3	CrO_3	Fe_2O_3	TiO_2	CaO	Na_2O	K_2O	MgO	ZrO_2	SrO	SO_3	LOI
Z(A)	72.24	10.84	0.16	1.38	0.21	2.07	1.91	1.95	1.03	0.03	0.18	0.24	7.48
Z(B)	71.02	11.00	0.22	1.17	0.19	1.83	1.98	1.90	1.04	0.02	0.16	0.07	9.24
Z(C)	71.29	10.87	0.21	1.19	0.20	1.85	1.79	1.91	1.03	0.02	0.17	0.09	9.36

DISCUSSION

According to the results listed above, when each sample water containing Zn^{2+} and Cr^{6+} heavy elements separately using the falling head test passing zeolite into a tube, we will see that the zeolite with a grain Category for these elements has different absorption. Aggregation in 1mm (Sample A) is more sensitive to absorb zinc.

$Zn^{2+} > Cr^{6+}$

According to the time and permeability factor in the removal of heavy metals, this is a more appropriate aggregation best selection zeolite to absorb zinc in aggregation 0.71 mm (Sample B) selected zeolite is as follows.

$Zn^{2+} > Cr^{6+}$

According to some results mentioned above, the aggregation of grain zinc is absorbed well and is suitable for removing it. Aggregation in 1, 0.71 and 0.25 mm (Sample C) are as follows, and once selected zeolite to absorb zinc is better than the chromium.

$Zn^{2+} > Cr^{6+}$

However, zinc removal in the three permeability is much more than the chromium. These results indicate that the competition between two elements, zeolites of Aftar mine the best selection to absorb zinc and also can be used in removing the chromium.

This element is well absorbed. Until in the o.71mm aggregation, element concentration of the output water is fewer devices sensitive. In these cases is considered nearly 100 percent absorbed Zinc. The chromium absorbed to well, but zeolite better operated to absorb zinc.

APPLICATION

To validate the methodology, the proposed method was applied to the wastewater samples for Zn and Cr determination. The wastewater was collected from an electroplating plant. The wastewater samples were filtered through a 0.45 mm membrane filter paper. An aliquot of the filtered sample (10 mL) was put into a 250 mL conical flask and digested with 5 mL mixture of concentrated nitric acid (65%, v/v) and perchloric acid (70%, v/v). When digestion was complete, 10 mL of 0.5 mol L-1 HCl was added to reddisolve the residue and the resultant solution filtered into a 50 mL volumetric flask. Along with the samples, several known amounts of Zn and Cr were spiked to examine the reliability of the method (Table 1).

Table 4. Determination of zinc and chromium in real samples

Metal	Added (µm mL^{-1})	Measured[a] (µm mL^{-1})	Recovery%
Zn^{2+}	0	0.112± 0.024	-
	0.1	0.214± 0.045	101
	0.2	0.321± 0.034	103
Cr^{6+}	0	0.424± 0.034	-
	0.1	0.532± 0.034	108
	0.2	0.627± 0.034	101.5

[a] The results are reported as the average value from five sample measurements.

ACKNOWLEDGMENTS

It necessary has thanks of Mr. Masaodyan responsible ICP units of Damghan University and also of Mrs. Hassan Zadeh responsible XRD and XRF laboratory and Research Deputy Damghan helped us at the implementation of this project.

REFERENCES

Barbier F., G. Due and M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorilonite/ water interface, *Colloid Surface PhysicochemEng Aspect,* **166**, 153–159, 2000.

Barer R.M., Zeolites and Clay Minerals as Sorbent and Molecular Sieves, Academic Press, New York,

Breck D.W. and J. Chem. Edu. 41, 1964. 67

Brigatti M. F., C. Lugli and L. Poppi, Kinetics of heavy metal removal and recovery in sepiolite, *Appl. Clay. Sci.,* **16**, 45–57, 2000.

Brown P. A., S. A. Gill and S. J. Allen. Metal removal from waste water using peat, *Water Res.* **34** (16), 3907–3916,2000.

Burns C. A., P. J. Class, I. H. Harding and R. J. Crawford, Adsorption of aqueous heavy metals onto carbonaceous substrate, *Colloid Surface PhysicochemEng Aspect,* **155**, 63–68, 1999.

Chen D. and A. K. Ray, Removal of toxic metal ions from wastewater by semiconductor photocatalysis, *Chem. Eng. Sci.,* **56**, 1561–1570, 2001.

Dayan, A. D. and A. J. Paine, 2001. "Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000." Human & Experimental Toxicology **20**(9): 439-51.

Eftekharnejad. J. Report of Zeolite mines exploration of Semnan province, industrial and mines organization of semnan province, 2004.

Evans J. R., W. G. Davids, J. D. MacRae and A. Amirbahman, Kinetic of cadmium uptake by chitosan-based crab shells, *Water Res,.***36**, 3219–3226, 2002.

Faur-Brasquet C., Z. Reddad, K. Yavuz O., Y. Altunkaynak and F. Guzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, *Water Res.,* **37**, 948–952, 2003.

Garsia S. A., A. Alastuey and X. Querol, Heavy metal adsorption by different minerals: application to the remediation of polluted soils, *Sci. Total. Environ.,***242**, 179–188, 1999.

Kadirvelu and P. Le Cloirec, Modeling the adsorption of metal ions (Cu^{2+}, Ni^{2+}, Pb^{2+}) onto ACCs using surface complexation models, *Appl. Surf. Sci.* **196** (1–4), 356–365, 2002.

Karabult S., A. Karabahan, A. Denizli and Y. Yurum, Batch removal of copper(II) and zinc(II) from aqueous solution with low-rank Turkish coals, *Separ. Purif.Tech.,* **18**, 177–184 ,2000.

Kazemian H. and H. Faghihian, Ninth article complex of IrrigationandDrainage Iran National Committee, 1998. IrrigationandDrainage Iran National emission, first edation.

Mohan D. and K. P Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste, *Water Res.,* **36**, 2304–2318, 2002.

Pollard S. J. T., G. D. Fowler, C. J. Sollars and R. Perry, Low cost adsorbents for waste and wastewater treatment: A review, *Sci. Total. Environ.,***116**, 31–52, 1992.

Sun T. and K. Seff, Chemical Reviews 94, 1994. 1