S.M. Moosavirad[1], R. Sarikhani[2],
S.Z. Mohammadi[3]

REMOVAL OF SOME HEAVY METALS FROM INORGANIC INDUSTRIAL WASTEWATERS BY ION EXCHANGE METHOD

[1] Department of Mining Engineering, Zarand College,
Shahid Bahonar University of Kerman, Kerman, Iran;
[2] Department of Geology, Faculty of Science,
Lorestan University, Lorestan, Iran;
[3] Department of Chemistry, Payame Noor University, Kerman, Iran
s.m.moosavirad@gmail.com

Removal of heavy metals such as Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) from wastewaters in several industrial areas of Kerman, Iran was evaluated by using ion-exchange method. Dowex 50WX8 (H^+) resin was selected as suitable adsorbent for reduction of toxic elements in wastewater. The most effective sorption was observed within in pH between 4 – 6, fow rate of 4 mL · min^{-1} and amount of 200 mg resin. Sorbent capacities for Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) were 45; 50; 50; 40 and 60 mg/g respectively. The results determine that exchanger resin is extremely effective in lowering the metal content of wastewaters.

Keywords: removal, heavy metal, wastewater, ion exchange method, pollution.

1.Introduction

Humans depend on their surrounding physical environment for the resources. Human exploitation of these resources causes environmental degradation [1]. Anthropogenic influences as well as natural processes degrade surface and groundwater, and impair their use for drinking, industrial, agricultural, recreation or other purposes [2 – 4]. Industries such as mining, steel and electroplating, discharge aqueous effluents containing relatively high levels of heavy metals such as silver, cadmium, copper, cobalt, chromium, zinc, iron and lead. Untreated effluents from these manufacturing processes have an adverse impact on the environment [5,6]. Heavy metals are elements having atomic weights between 63 and 200, and specific gravity greater than 5,0 [7]. Pollution by heavy metals has become a global phenomenon because of its toxicity, persistence for several decades in the aquatic environment, bioaccumulation and biomagnifications in the food chain [8,9]. Zinc is a trace element that is essential for human health. However, too much of zinc can cause health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia [10]. Copper does essential work in animal metabolism, of the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death [11]. Nickel exceeding its critical level can cause serious lung and kidney problems, gastrointestinal distress, pulmonary fibrosis and skin dermatitis [12]. Mercury is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function, chest pain and dyspnoea [13]. Cadmium has been classified by U.S. Environmental Protection Agency (EPA) as a probable human carcinogen. Cadmium exposes human health to severe risks. Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death [14]. Lead can cause damage of central nervous system. Lead can also damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness and irritability, weakness of muscles, hallucination and renal damages [15]. Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the wastewater to protect the people and the environment. Different treatment techniques for treatment of wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Some methods that are being used to remove heavy metal ions include chemical precipitation [16], ion-exchange [17], adsorption [18], membrane filtration [19,20], electrochemical treatment technologies [21], Nanofiltration can remove mentioned components completely or partly [22]. The present note provides the results obtained from the studies on the feasibility of ion exchange method for removal/reduction of toxic heavy metals from wastewaters of several industrial sites in Kerman province, Iran.

2. Experimental

2.1. Sampling and analysis. Seven effluent water samples collected from seven industrial cites were analysed in the laboratory for the major ions/compounds using standard methodology. Wastewater samples for chemical analysis were collected during July, 2012 and the some were used for estimation of the concentration of Cl^-, SO_4^{2-}, HCO_3^-, CO_3^-, NO_3^-, and NO_2^- and some potentially toxic elements such as Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II).

Water samples were kept in 2 l polyethylene plastic bottles cleaned with metal free soap rinsed many times with distilled water. The samples were stored in polyethylene containers, adequately labeled. Water samples were filtered through polycarbonate filter (0,45 mm pore size) and were divided in two parts. One part was used for analysis of anions, while second part treated with 2 ml of concentrated HNO_3 to decrease the pH value to 2 for metal analysis. All samples were stored in the insulated cooler containing ice and delivered on the same day to the laboratory and all the samples were kept at 4°C until processing and analysis were carried out [23]. Temperature, electrical conductivity, and pH were measured in the field. The pH and electrical conductivity were measured with portable ion meters. Chloride was determined by titration and precipitation of AgCl. Sulfate was determined by precipitation of $BaSO_4$ and then by measuring the absorbance with spectrophotometer. Bicarbonate was measured by titration to the methyl orange endpoint. Alkalinity was estimated by titrimetric method. The water samples were analysed for heavy metals according to international standard methods U.S. Environmental Protection Agency (USEPA) 2002; 2011 and World Health Organization (WHO) 1984, 2002 [24 – 27]. The analyses of Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) were performed in the Department of Chemistry, Payame Noor University of Kerman in Iran, using atomic absorption spectrophotometer (AAS) AA-6300 ("Shimadzu", Japan).

2.2. Sample characteristics. Physico-chemical analysis of effluent waters was carried out by adopting standard methods for the examination of water and wastewater as prescribed by American Public Health Association (APHA) [28], American Water Works Association and Water Pollution Control Federation. The metals analyses were carried out by using flame atomic absorption spectrometer SensAA GBC (Dandenong, Australia). Permissible limits of heavy metals in effluent waters listed in Table 1. The instruments were calibrated for the determination of each element by analyzing the standard solution (concentration usually in ppm) of each element. Hollow cathode lamps were used as a source of light for each element. Physico-chemical characteristics of water samples from industrial effluents are provided in Table 2.

According to the EPA specifications (see Table 2), there is some pollution in the examined areas. In this research, removal of some potentially polluting toxic elements by ion-exchange procedure was investigated.

Table 1. Permissible limits of heavy metals in effluent waters (mg/L)

Metals	WHO(1984)	WHO(2002)	EPA(2002)	EPA(2011)
Cu(II)	1,5	1	1	1
Zn(II)	1,5	3	2,5	5
Pb(II)	0,05	0,01	0,01	0,015
Cd(II)	0,01	0,003	0,004	0,005
Ni(II)	0,2	0,02	0,02	0,1

2.3. Mechanism of ion-exchange. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their several advantages, such as high treatment capacity, high removal efficiency and fast kinetics [29]. In ion-exchange, a reversible interchange of ions between the solid and liquid phases occurs, where insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin [30, 31]. Ion-exchange can also be used to recover valuable heavy metals from inorganic effluents [30]. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents.

Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the heavy metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they can effectively remove bulk of the heavy metals from the solution [32]. The most commonly used cation exchangers are strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:

$$n\mathrm{R{-}SO_3H} + \mathrm{M}^{n+} \rightarrow (\mathrm{R{-}SO_3^-})n\mathrm{M} + n\mathrm{H}^+;$$
$$n\mathrm{R{-}COOH} + \mathrm{M}^{n+} \rightarrow (\mathrm{R{-}COO^-})n\mathrm{M} + n\mathrm{H}^+.$$

The uptake of heavy metals ions by ion-exchange resins are rather affected by certain variables such as pH, initial metal concentration and contact time [33, 34].

Table 2. Physico-chemical parameters of water samples from industrial effluents

Parameter	pH	EC(μS/cm)	TSS	Alkalinity	Ni(II)	Cd(II)	Pb(II)	Zn(II)	Cu(II)	CO_3^{2-}	NO_2^-	NO_3^-	SO_4^{2-}	Cl^-
			mg/L											
Ceramic factory (1)	8,01	3210	1605	180	0,074	0,132	0,235	0,102	0,112	ND*	ND*	7	400	982,5
Coal washing factory	7,23	2980	1490	225	0,111	0,061	0,225	0,513	0,053	ND*	ND*	7	1190	502,5
Ferromolybdenum factory	7,76	4600	2300	340	0,109	0,113	0,25	0,055	0,243	ND*	0,22	19	940	1075
Polyethylene factory	8,79	5130	2565	250	0,064	0,081	0,175	0,242	0,061	ND*	0,013	15	210	1600
Ceramic factory (2)	5,37	–	–	400	0,072	0,087	0,275	2,021	0,056	ND*	0,07	145	240	1370
Ceramic factory (3)	6	3670	1835	340	0,072	0,131	0,251	1,328	0,067	ND*	0,04	24,7	260	1300
Coal mining	7,19	29000	14500	100	0,265	0,21	0,75	0,238	0,106	ND*	0,31	112,2	>1000	9820
EPA (2011)	6,5–8,5	–	500	–	0,1	0,005	0,015	5	1	–	1	10	250	250
WHO (2002)	6,5–8,5	–	1000	–	0,02	0,003	0,01	3	1	–	3	50	250	250

* Not Detected.

In this research, Dowex 50WX8 (H^+) type resins are used for removal of heavy metals from wastewater owing to their high treatment capacity, high removal efficiency and fast kinetics. Dowex 50WX8 (H^+) type resins, owing to their high cation exchange capacities can reduce the residual concentration of heavy metals below the discharge limits. They are also widely available as they are commercially produced. Further their regeneration properties provide economical benefits. Taking into consideration of the above mentioned properties, Dowex 50WX8 (H^+) resin has been preferred. Packed technique was used in order to determine the equilibrium data. After defining optimum reaction conditions (pH, resin dosage, contact time), experimental results were applied to the wastewaters [34 – 36]. It is thought that results of this study can be useful for treatment processes of sectors containing heavy metal in their wastewaters. Physical and chemical properties of Dowex 50WX8 (H^+) resin are given in Table 3.

Table 3. Physical and chemical properties of Dowex 50WX8 (H^+) resin

Type	Strong acid cation
Matrix	Styrene-DVB, gel
Functional group	Sulfonic acid
Physical form	Uniform particle size spherical beads
Shipping weight	800 g/L
Total exchange capacity	Minimum 1,9 g-eq/L
Particle size	0,3 –1,2 mm: 90% minimum, <0,3mm: 1% maximum
Particle density	1,30 g/mL
Whole beads	90% minimum
Ionic form as shipped	H^+

2.4. Analytical procedure. Period to dealing with the real samples, the optimum conditions for removal of considered ions with Dowex 50WX8 (H^+) resin were investigated. For this purpose, a glass tube (10 cm length and 5 mm i.d.) packed with 0,2 g of the Dowex 50WX8 resin absorbent is used for removal of Cd(II), Cu(II), Zn(II), Pb(II) and Ni(II) from standard solution (25 ml of the solution containing 125 μg of each ion) is passed through the mini-column at a flow rate of 5 $mL \cdot min^{-1}$. Removal (%) of each element was determined by flame atomic absorption spectrometry (FAAS) separately. The different factors which play a significant role in the removal process includes quantity of resin, sample pH, contact time and flow rate [36].

3. Results and discussion

3.1 Effect of pH. The pH of aqueous solution is an important factor and it influences the metal speciation in aqueous solution and therefore can affect the extent of adsorption [35,37]. Hydronium ion concentration is an important parameter affecting the ion-exchange process. This is partly because hydrogen ions themselves are strongly competing adsorbate and the solution pH influences the ionization of surface functional groups. The pH dependence of ion exchange may suggest that the metal ions are adsorbed according to the ion-exchange mechanism. The effect of pH on the Dowex 50WX8 (H^+) resin surface has been investigated over a pH range of 2,0–10,0 at room the temperature. Constant resin amount (200 mg) was added to all reaction bottles and solutions were agitated at 200 rpm speed. The results are shown in Fig 1. According to the results, 4<pH<6 is the appropriate for removal of heavy metal ions. Therefore, pH 5 was chosen as suitable condition for experiments.

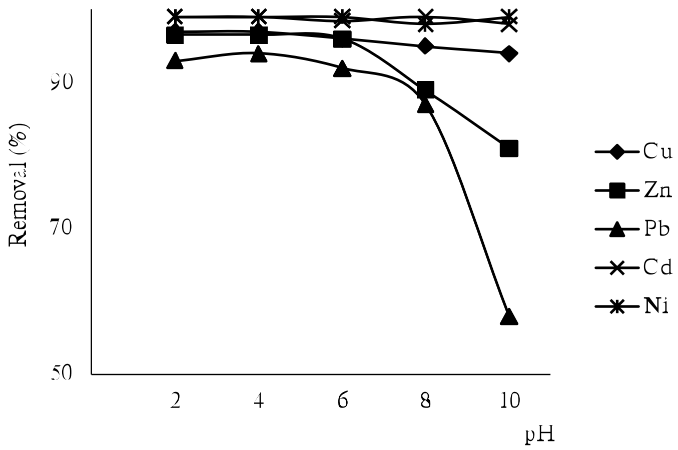

Fig. 1. Effect of pH on removal percentage of heavy metals.

3.2. Effect of flow rate. Appropriate time plays an important role in adsorption of metal ion on solid surface. Percent removal is found to be proportional to contact time up to equilibrium achieved, after which it is independent of time due to the fact that at equilibrium the rate of adsorption and desorption will be same. Fig. 2 represents percent removal of heavy metals versus flow rate and showing the decreasing value of removal with time. Effect of contact time on the adsorption process by resin was studied in the range of 1 to 10 mL/min at room temperature. It can be seen that the adsorption of heavy metals increased up to flow rate of 4 mL/min and at higher flow rate, the adsorption (% removal) decreased. A further increase in contact time had a negligible effect on the percent removal. The percentage metal removal is higher in the beginning due to greater number of resin exchange sites available for the sorption of the metal. It is cleared from figure that maximum removal is achieved for heavy metals (Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II)) in flow rate of 4 mL/min.

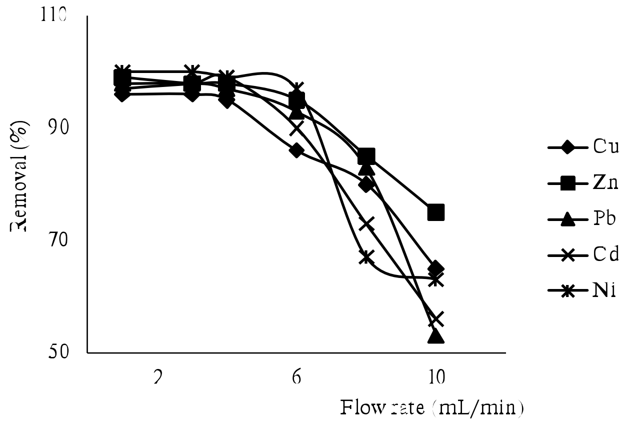

Fig. 2. Effect of flow rate on removal percentage of heavy metals.

3.3 Effect of resin amount. The resin amount is also one of the important parameters to obtain the quantitative uptake of metal ion. The dependence of metal sorption on resin input amount was studied by varying the amount of Dowex 50WX8 (H^+) resin, while the other parameters such as pH, initial metals concentration and reaction time remained constant. The amount of resin in the range of 100–700 mg has been considered during trial turns for quantification of adsorption (% removal) of heavy metals. It was apparent that the adsorption percentage of metal ions increased with higher resin dosages. Fig. 3. represents that 200 mg of resin is needed to separate a quantitative removal of metals.

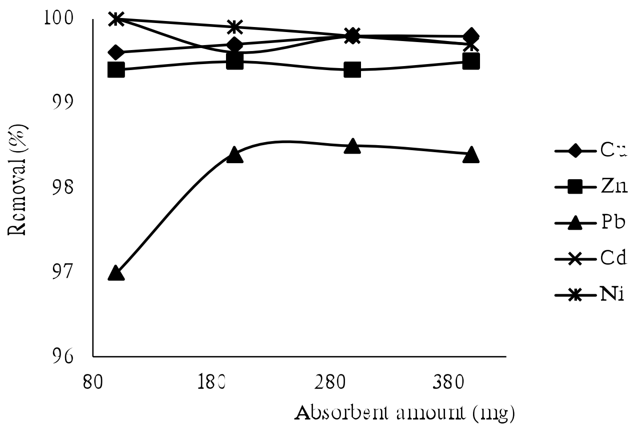

Fig. 3. Effect of resin amount on removal percentage of heavy metals.

This result proved that increasing the amount of adsorbent provides higher removal due to formation of greater adsorption sites [35].

3.4. Adsorption capacity. The adsorption capacity was determined by following the batch experiment at room temperature. Solutions of heavy metal ions at the concentration range of 20 – 180 µg/mL and at the optimum pH were maintained. Solutions were shaken for 30 min with the 200 mg of resin. The metal ions in the supernatant were determined by FAAS and the amount of metals adsorbed per unit mass (q, µg/g) at equilibrium was calculated as

$$q = \frac{v(C_0 - C)}{m}, \qquad (1)$$

where C_0 is the initial concentration of heavy metal ions (µg/mL), C is the equilibrium concentration of heavy metal ions (µg/mL), V is the volume of heavy metal ions solutions (ml) and m is the mass of the resin (g). Adsorption isotherm is described by the following Langmuir [38] equation

$$\frac{C_{eq}}{q} = \frac{C_{eq}}{q_m} + \frac{1}{bq_m}, \qquad (2)$$

where b is a Langmuir constant, q_m is a constant representing adsorption capacity (also known as monolayer coverage of the surface), is a constant related to b and C_{eq} is adsorbate concentration in the solution at equilibrium.

Langmuir constants were determined by using the adsorption data through batch experiment. According to the results the adsorption capacity for Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) is 45; 50; 50; 40 and 60 mg/g respectively.

3.5. Analysis of real samples. Heavy metals in industrial wastewater samples were removed according to the procedure described in before sections. The obtained results are shown in Table 4. According to the experimental conditions, the removal of considered ions present in industrial wastewaters was done successfully.

Table 2 provides the physic-chemical parameters of waste samples collected from seven industrial sites of Kerman province, Iran. According to water quality specifications of EPA and WHO, these wastewaters are polluted with excessive concentrations of certain anions (viz., Cl^- and SO_4^{2-}) and toxic cations (viz., Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II)). These wastewater samples were subjected to ion-exchange treatment for removal of toxic heavy metals (viz., Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II)). The laboratory studies indicate that the maximum removal of heavy metals can be achieved by using Dowex 50WX8 (H^+) resin as the exchanger. Trial turns indicate that, the maximum removal of heavy metals can be achieved by maintaining the pH of the wastewater at 5 and flow-rate at 4 mL/min.

Table 4. Residual concentration of heavy metals in solution

Parameter	Ni(II)	Cd(II)	Pb(II)	Zn(II)	Cu(II)
	mg/L				
Ceramic factory (1)	0,017	0,034	0,023	0,025	0,041
Coal washing factory	0,022	0,008	0,019	0,021	0,012
Ferromolybdenum factory	0,033	0,013	0,028	ND	0,043
Polyethylene factory	0,027	0,004	0,009	0,042	0,031
Ceramic factory (2)	0,019	0,005	0,011	0,417	0,023
Ceramic factory (3)	0,012	0,016	0,017	0,223	0,028
Coal mining	0,178	0,128	0,534	0,174	0,063
EPA (2011)	0,1	0,005	0,015	5	1
WHO (2002)	0,02	0,003	0,01	3	1

Ion exchange treatment to wastewaters from 3 ceramic factories resulted in achieving removal of 73,6 to 83,3% Ni(II), 74,2 to 94,2% Cd(II), 90,2 to 96% Pb(II), 75,5 to 83,2% Zn(II) and 58,2 to 63,4% Cu(II). Effluents from coal washery, after ion-exchange treatment, yielded water containing significantly lower concentrations of heavy metals. Ion-exchange treatment to coal washery effluents reduced the contents of Ni(II), Cd(II), Pb(II), Zn(II) and Cu(II) by 80,2; 86,9; 91,5; 96 and 77,3% respectively. The results are shown in Fig 4. According to the results, wastewater from ferromolybdenum factory also responded positively to ion-exchange treatment and the removal percentages achieved are as follows: Ni(II) (70%), Cd(II) (88,5%), Pb(II) (88,8%), Zn(II) (100%) and Cu(II) (82,3%).

Ion-exchange treatment to wastewater from a polyethylene factory resulted in the removal of Ni(II) by 57,8%, Cd(II) by 95,1%, Pb(II) by 94,8%, Zn(II) by 82,6% and Cu(II) by 50%. Ion exchange treatment reduction to wastewater from coal mine resulted in the reduction of Ni(II) by 32,8%, Cd(II) by 39%, Pb(II) by 28,8%, Zn(II) by 26,9% and Cu(II) by 40,6% only.

Above results indicate that, during ion-exchange treatment to polluted wastewaters from industries, best results can be achieved of Dowex 50WX8 (H^+) resin is chosen as an exchanger. Dowex 50WX8 (H^+) resin has high exchange capacity and provides more exchangeable sites for heavy metal ions for adsorption. During the present studies ion-exchange treatment to wastewaters from coal washery and ceramic, ferromolybdenum and polyethylene factories yielded waters containing significantly lower concentrations of heavy metals. Ion-exchange treatment to run-off from coal mine did not yield satisfactory results. In this case poor adsorption by the resin may be attributed to the presence of the heavy metals mainly as organo-metallic complexes [39].

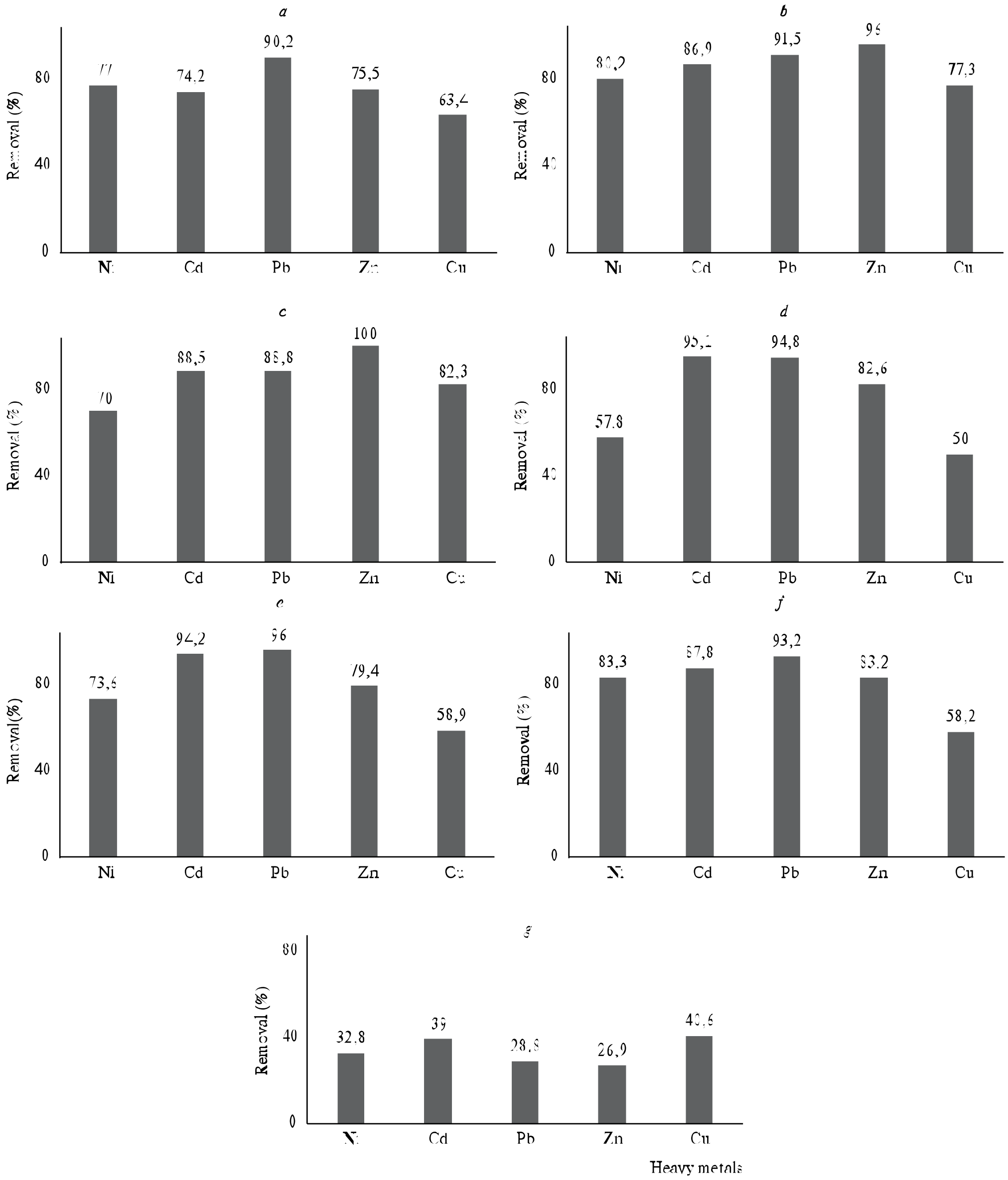

Fig. 4. Removal percentage of heavy metals (mg/L) in industrial areas: a – ceramic factory (1), b – coal wishing factory; c – ferromolibdenum factory; d – polyethylene factory; e – ceramic factory (2); f – ceramic factory (3); g – coal mining.

4. Conclusions

From the data provided above, it is evident that wastewaters from studied factories contain significantly higher concentrations of Pb(II), Cd(II) and Ni(II). Ion- exchange treatment to these wastewaters can significantly lower the concentrations of the heavy metals. Dowex 50WX8 (H^+) resin is found to be an exchanger during laboratory trials for removal of heavy metals from heavy metal-rich wastewaters from industries. Maximum heavy metal binding on Dowex 50WX8 (H^+) resin can be achieved by maintaining the pH of the wastewater in the range 4,0 – 6,0. Langmuir isotherm confirms very well with the laboratory experimental data of the present study. The value of Q_0 is for Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) equals 45; 50; 50; 40 and 60 mg/g under optimum conditions of pH (at 5), flow rate (4 mL/min) and amount of resin (200 mg).

Acknowledgments

The financial support for this work, provided by the Iran National Science Foundation (INSF), Government of Iran (Project-No.90003738). The authors are grateful to Prof. B.Krishna Rao for critical examination of the earlier version of the manuscript. The first author is grateful to Department of chemistry, Payame Noor University of Kerman in Iran, for providing logistic support during the field work and laboratory investigations. The authors also would like to express their gratitude to anonymous reviewers for their constructive comments on the paper.

References

[1] *Pastircakova K.* // Energy Edu. Sci. Technol. – 2004. – **13**. – P. 97 – 104.

[2] *Luo L., Ma Y., Zhang S., Wei D., Zhu Y.-G.* // J. Environ. Manage. – 2009. – **90**. – P. 2524 – 2530.

[3] *Chen W., Chang A.C., Wu L.*// Ecotox. Environ. Safe. – 2007. – **67**. – P. 48 – 58.

[4] *Moosavirad S.M., Janardhana M.R., Khairy Houshang.* //Environ Earth Sci. – 2013.– **67**, N7. – P. 2451 – 2467

[5] *Mishra V.K., Upadhyay A.R., Pandey S.K., Tripathi B.D.*// Biores. Technol. – 2008. – **99**. – P. 930 – 936.

[6] *Fu F., Wang Q.* // J. Environ. Manage. – 2011. – **92**. – P. 407 – 418.

[7] *Srivastava N.K., Majumder C.B.*// J. Hazard. Materials. – 2008. – **151**. – P. 1 – 8.

[8] *Valls M., Lorenzo V.D.*// Fems Microbiol. Rev. – 2002. – **26**. – P. 327 – 338.

[9] *Gochfeld M.*// Ecotox. Environ. Safe. – 2003. – 56. – P. 174 – 179.

[10] *Oyaro N., Juddy O., Murago E.N.M., Gitonga E.* //Int. J. Food Agric. Environ. – 2007. – **5**. – P. 119 – 121.

[11] *Paulino A.T., Minasse F.A.S., Guilherme M.R., Reis A. V. E., Muniz C., Nozaki J.* //J. Colloid Interface Sci. – 2006. – **301**. – P. 479 – 487.

[12] *Borba C.E., Guirardello R., Silva E.A., Veit M.T., Tavares C.R.G.*// Biochem. Eng. J. – 2006. – **30**. – P. 184 – 191.

[13] *Murthy Z.V.P., Chaudhari L.B.*// Chem. Eng. J. – 2009. – **150**. – P. 181 – 187.

[14] *Manzoori J.L., Karim-Nezhad G.* //Anal. Chem. Acta. – 2004. – **521**. – P. 173–177.

[15] *Mohammadi S.Z., Karimi M.A., Afzali D., Mansouri F.* //Desalination. – 2010. – **262**. – P. 86 – 93.

[16] *Aydin F.A., Soylak M.* //Talanta. – 2007. – **73**. – P. 134 – 141.

[17] *Vigneswaran S., Ngo H.H., Chaudhary D.S., Hung, Y.T.* //Physico-chemical treatment processes for water reuse / Eds. L.K. Wang, Y.T. Hung, N.K. Shammas. – New Jersey: Humana Pres, 2004. – Vol. 3. – P. 635 – 676.

[18] *Amara M., Kerdjoudj H.*// Desalination. – 2004. – **168**. – P. 195 – 200.

[19] *Sablani S.S., Goosen M.F.A., Al-Belushi R., Wilf M.* // Ibid. – 2001. – **141**. – P. 269 – 289.

[20] *Benito Y., Ruiz M.L.*//Ibid. – 2002. – **142**. – P. 29 – 234.

[21] *Kurniawan T., Chan A. G. Y.S., Wai-Hung Lo, Babel S.* //J. Chem. Eng. – 2006. – **118**. – P. 83 – 98.

[22] *Bruggen B., Vandecasteele C .* // Environ. Pollut. – 2003. – **122**. – P. 435 – 445.

[23] *Bashkin Radojevic.* Practical Environmental Analysis, MPG Brook Ltd., Badman Cornwal, UK (1999).

[24] *USEPA* Effluent Guidelines and Standards. Sub-Chapter N., 2002. – P. 400 – 424.

[25] *USEPA.*Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020. U.S. Environmental Protection Agency, Cincinnati, Ohio, 2011.

[26] *WHO.* Guidelines for drinking water quality /Recommendations. – Geneva, 1984. – Vol.2 . – 254 p.

[27] *WHO.* Guidelines for drinking water quality /Recommendations. – Geneva, 2002. – Vol.1. – P. 1 – 4.

[28] *APHA.* Standard Methods for the Examination of Water and Wastewaters. American Public Health Association, Washington DC, 1998.

[29] *Kang S.Y., Lee J.U., Moon S.H., Kim K.W.* // Chemosphere. – 2004. – **56**. – P. 141 – 147.

[30] *Ashfaq Nabi S., Naushad M., Khan A.M.* // Colloids and Surfaces, A. – 2006. – **280**. – P. 66 – 70.

[31] *Rengaraj S., Yeon K.H., Moon S.H.*// J. Hazard. Materials. – 2001. – **B87**. – P. 273 – 287.

[32] *Dabrowski A., Hubicki Z., Podko'scielny P., Robens E.*// Chemosphere. – 2004. – **56**. – P. 91 – 106.

[33] *Stafilov T.D., Zendelovska G., Pavlovska Cundeva K.*// Spectrochim. Acta. – 2007. – **B 57**. – P. 907 – 917.

[34] *Gode F., Pehlivan E.* // J. Hazard. Materials. – 2006. – **136**. – P. 330 – 337.

[35] *Alyuz B., Veli S.*//Ibid. – 2009. – **167**. – P. 482 – 488.

[36] *Moosavirad S. M., Shankara M.* //J. Appl. Geochem. – 2010. – **12**. – P. 180–185.

[37] *Sreejalekshmi K.G., Krishnan K.A., Anirudhan T.S.* // J. Hazard. Materials. – 2009. – **161**. – P. 1506 – 1513.

[38] *Langmuir I.*// J. Amer. Chem. Soc. – 1916. – **38**. – P. 2221 – 2295.

[39] *Moosavirad S.M., Shankara M., Janardhana M.R.* //Pollut. Res. – 2010. – **29**. – P. 1 – 4.

Recieved 17.03.2014