Removal of heavy metals from paint industry's wastewater using Leca as an available adsorbent

[1]*M. Malakootian; [2]J. Nouri; [1]H. Hossaini

[1]*Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran*

[2]*Department of Environmental Management, Graduate School of the Environment and Energy, Science and Research Branch, IAU, Tehran, Iran*

ABSTRACT: The ability of light expanded clay aggregate to remove lead and cadmium from paint industry's effluents was studied at different levels of adsorbent, contact time and pH in April 2008. For this purpose, lead and cadmium removal from paint industry effluents were studied in batch reactors. lead and cadmium measurements have been taken with non-flame atomic absorption techniques and test methods were adapted from 19th. Ed. of standard methods for the examination of water and wastewater. In this study, different amounts of Leca (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/L) were investigated. The amount of adsorbed lead and cadmium exposure to Leca increased from 1.41 to 3 mg/g and 0.22 to 0.75 mg/g, respectively. The maximum removal efficiency for Pb was 93.75 % at pH = 7 and exposure to 10 g/L of Leca, while for cadmium, it was nearly 89.7 % at the same condition. In this study, adsorption process of lead and cadmium was fitted with Freundlich adsorption isotherm (R^2_{Pb} = 0.97 and R^2_{Cd} = 0.98). The sufficient contact time was deemed 1-2 h for lead and cadmium. According to the results, Leca is recommended as a low cost and available adsorbent to remove lead and cadmium from industrial wastewater.

Keywords: *Lead, cadmium, adsorption, light expanded clay aggregate*

INTRODUCTION

The release of heavy metals into the environment through industrial effluents is a major concern, worldwide and removal of such pollutants has been a great concern during last decades. Pb (II) and Cd (II) are particularly common heavy metals found in paint industries's wastewater. Heavy metals are not biodegradable and tend to be accumulated in organisms and cause numerous diseases and disorders (Ozer and Pirincci, 2006). Chronic exposure to high amount of lead and cadmium can result in various and considerable damages to systems of the body, including nervous and reproductive systems and kidneys. Moreover, high blood pressure, anemia, lead poisoning, coma and death can be considered among the most substantial consequences (PCS, 2001). Cadmium is an irritant to the respiratory tract and being exposure to this pollutant can lead to anemia, renal damage, osseous disease with the similar symptom as osteoporosis and Itai-Itai disease (Miyahara *et al.*, 1980; SHMRC, 2003). The most widely used methods to

✉ *Corresponding Author Email: *m.malakootian@yahoo.com*
Tel: +098341 320 5074; Fax:+098341 320 5105

remove heavy metals are chemical or electrochemical precipitation (Lai and Sheng, 2003; Mahvi, 2008). Adsorption process using activated carbon, widely used as an adsorbent, is among the most effective techniques for heavy metals removal from waste streams (Jusoh *et al.,* 2007). In the last decades, there have been a great trend for using of low cost absorbents and different studies have demonstrated that natural agents have high removal capacity for divalent heavy metal ions (Ayyappana *et al.*, 2005; Carrillo-Morales *et al.,* 2001; Corami *et al.*, 2008; Inglezakis *et al.*, 2007; Naseem and Tahir, 2001). Different kinds of clays for removal of metal ions from aqueous solution have been studied and many factors effecting the absorbability of dissolved element, including chemical form of metal, pH, contact time, metal concentrations, presence of competing adsorbents, amount of sorbent, temperature, particle size and others have been distinguished (Benjamin *et al.,* 1982; Farrah and Pickering, 1977; Johnson, 1990; Orumwenese Faraday, 1996). Three major kinds of clays, including smectites (such as montmorillonite), kaolinite and micas

have shown good metal removal efficiency. Montmorillonite has the highest cation exchange capacity and its current market price (about US$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon (Virtaa, 2002). In 1989, the removal efficiency of montmorillonite and kaolinite for lead and cadmium was compared and it was found that the adsorption capacity of Pb^{2+} and Cd^{2+} is greater on montmorillonite (Pb: 0.68, Cd: 0.72 mg/g) than kaolinite (Pb: 0.12, Cd: 0.32 mg/g) (Babel and Agustino, 2003). Leca (light expanded clay aggregate) was selected as an adsorbent for removal of metal ions from paint industries effluents. Leca is an aggregate made of expanded clay produced in rotary kiln at the temperature around 1200 °C. Thousands of small bubbles-like spaces will be produced during cooling process inside the clay and also a coarse surface is created. Leca aggregates are round in shape with coarse and disagreeable texture. The exterior color is brown and black with cellular structure inside. Its sponge-like and microscopic surface is considerable. Adsorption mechanism at clay surfaces is strictly related to the dual nature of the surface charge, permanent negative charge arises from non-stochiometric isomorphous substitution of cations of charge +4 and +3 with cations of charge +3 and +2, respectively. But some articles discussed that an adsorption at the layer edges, involving more specific interactions with the surface, is more dependent on the pH and less dependent on ionic strength (Karbassi *et al.*, 2008; Majone and Papini, 2006). Among the most remarkable specifications of Leca are lightness, insulation against thermal and sound, moisture impermeability, incompressibility under permanent and steady pressure, non-decomposition, fire resistance, pH of around 7 and freezing and melting resistance. The aggregates manufactured in Iran are presented in various sizes. Four usual gradations are 0-3 mm, 3-10 mm, 10-20 mm and 0-25 mm. Leca bulk dried density for different gradations is presented in Table 1. This study focuses on the removal of lead and cadmium from Binalood Paint Industry effluent (Kerman, Iran) by the usage of Saveh (a small city of IRAN) Leca as an adsorbent in April 2008.

MATERIALS AND METHODS
Adsorbent preparation
Proposed Leca was provided from Saveh Leca Industry at 3-10 mm size and special weight of 380 kg/m³. The main characteristics of Leca are shown in Table 2.

Table 1: Density of Leca aggregates (LECA Co., 2006)

Leca gradation (mm)	0-3	3-10	10-20	0-25 (mixed)
Weight (kg/m³)	560	380	330	380

Table 2: Typical characteristics of Leca (LECA Co., 2006)

Elements/compounds	Value (wt. %)
Al_2O_3	16.57
SiO_2	66.06
CaO	2.46
Fe_2O_3	7.1
K_2O	2.69
MgO	1.99
MnO_2	0.09
Na_2O	0.69
P_2O_5	0.21
TiO_2	0.78
LOI*	1.36

*Loss on ingnition

Different studies showed that particle size has significant effect on adsorption efficiency. Thus, smaller the particle size, higher the adsorption efficiency. Hence, the particle size decreases the surface area of the mineral due to increase of the incoming ion (Vassilis *et al.*, 2007). Leca was crashed and sieved through a 30 mm mesh (remained on # 20), then crashed materials were washed to remove fines and undesirable materials with dionized water several times and dried in oven at 110 °C for 24 h to obtain constant weight (Chem and Wu, 2001).

Characteristic and preparation of effluent samples
Binalood Paint Industry with 70 tons/month paint productions has approximately a generation of 200 m³/month wastewater. Since, high peak flow rate may be existed in industrial effluents and the concentration of metal ion may be different, therefore, samples were taken from industry equalization tank effluent After pH and temperature measurements, samples were transferred to the laboratory in order to remove supernatant and undesirable suspended materials. Then, each sample was settled 1 h and filtered through a 0.45 µm polycarbonate filter. For preservation of metals content, appropriate amount of HCl was added to each sample until pH decreased to less than 2 and these samples were kept at 4 °C. In order to determine raw wastewater characteristics, prepared samples were analyzed with nonflame atomic absorption techniques and test methods were adapted from 19th Ed. of standard methods to examine water and wastewater (Eaton *et al.*, 1998). In order to determine the effect of different conditions (contact time, pH and adsorbent amount) procedures were based on the other experiments carried out through similar studies

(Malakootian *et al.,* 2006; Nouri *et al.,* 2008; Viraraghavan and Rao, 1991). Moreover, to determine the optimum contact time, 10 g of Leca was added to each jar containing 1000 mL sample with known metal concentration and pH and then shacked at 200 rpm for 3 h. Each 10 min, sample was taken, until it reached to equilibrium level. For determining the effects of different pH on the adsorption rate, each prepared sample was influenced by appropriate amounts of HCl and NaOH solution and its pH adjusted to 3, 7 and 10 and optimum pH was determined for next steps. The adsorption isotherm models and equations in 25 °C ±1, pH=7 and fixed concentration of Pb and Cd were used for different densities of adsorbent (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/L) and 3 h contact time. Then, samples were mixed with a mechanical mixer at 200 rpm speed, centrifuged and filtered. Pb and Cd measurements were done for the effluent and the settled sediments. Sediments were rinsed and filtered with deionized water and after measurement they were used in calculations. To control any leaching interference during the test period, a sample was prepared adding Leca to 1000 cc of deionized water as a blank sample. This study conducted research in 1 to 3 h contact time.

RESULTS AND DISCUSSION

Table 3 shows the average of ten raw wastewater samples before 1 h settling and after transferring to the laboratory. The results showed that Pb and Cd concentrations were 5.6 and 1.8 mg/L, respectively . According to results, the concentrations of heavy metals in wastewater used in agricultural irrigation are more than relevant MCL_S (5 and 0.01 mg/L) and is propounded as the most important environmental problem concerning this wastewater and required specific care (Ayers and Westcot, 1994).

Determination of optimum contact time

Fig. 1 shows that adsorption of Pb and Cd reached equilibrium in the range of 60 to 90 min and 110 to 130 min of contact time, respectively while removal efficiency for Pb and Cd at these contact times was 93.75 % and 89.7 %, respectively. Fig. 1, obviously shows that uptake of Cd and Pb by Leca was rapid within the first 20 min of contact time. The removal rate of Cd and Pb gradually decreased with increase in contact time. Initially, the rate of Cd and Pb was higher because all sites on Leca were vacant and concentration was high, but decrease of sorption sites reduced the uptake rate. As it was shown in the same Fig, desorption will be occurred after saturation. Therefore, considering technical and economical aspects, 1-2 h contact time is recommended for lead and cadmium removal from wastewater by Leca adsorption. Results of this study are in entirely accordance to the results of Inglezakis *et al.* (2007) and Malakootian *et al.* (2006). Inglezakis *et*

Table 3: Raw wastewater characteristics of Binalood Paint Industries

Parameters	Unit	Mean	SD
pH	pH unit	5.7	0.96
Pb	mg/L	5.6	1
Cd	mg/L	1.8	0.9
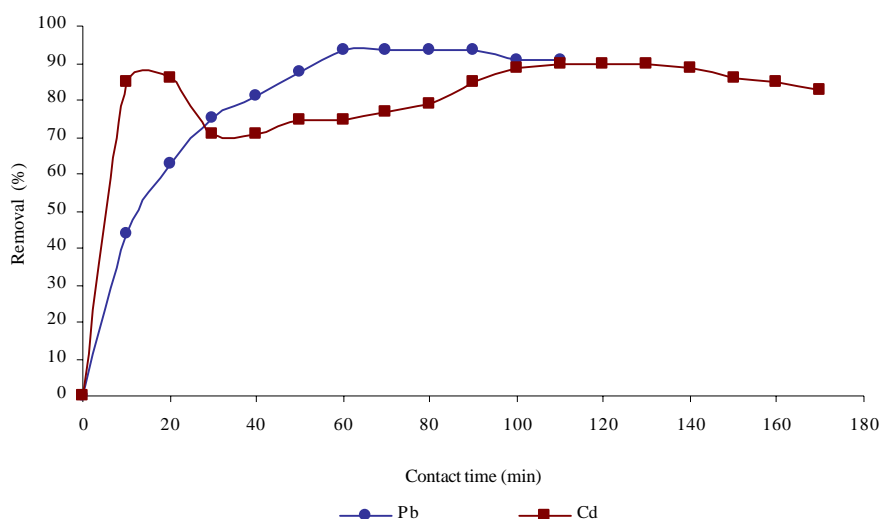
Fig. 1: Optimum contact time of Pb and Cd adsorption on Leca, T = 25 °C, pH = 7

Table 4: Comparing the performance of different supports

| Sorbent support		Q		Removal (%)		Reference
		Cd	Pb	Cd	Pb	
Leca		0.22 to 0.75 mg/g	1.41 to 3 mg/g	89.7	93.75	Current results
Fly ash		-	-	93	-	Viraraghavan and Rao, 1991
Buomass	Crab shell	-	19.83 ± 0.29 mg/g	-	-	Dahiya *et al.,* 2008
	Arca shell	-	18.33 ± 0.44 mg/g	-	-	
Wood ash		0.05-0.019	-	98	-	Malakootian *et al.,* 2006
Wood ash		-	-	-	96.1	Malakootian *et al.,* 2008
Hydroxiapatite		0.058-1.681 mmol/g	-	83	-	Corami *et al.,* 2008
Clinoptilolite		2.40 mg/g	1.60 mg/g	-	-	Zamzow *et al.,* 1990
Montmorillonite		0.72 mg/g	0.68 mg/g	-	-	Srivastava *et al.,* 1989
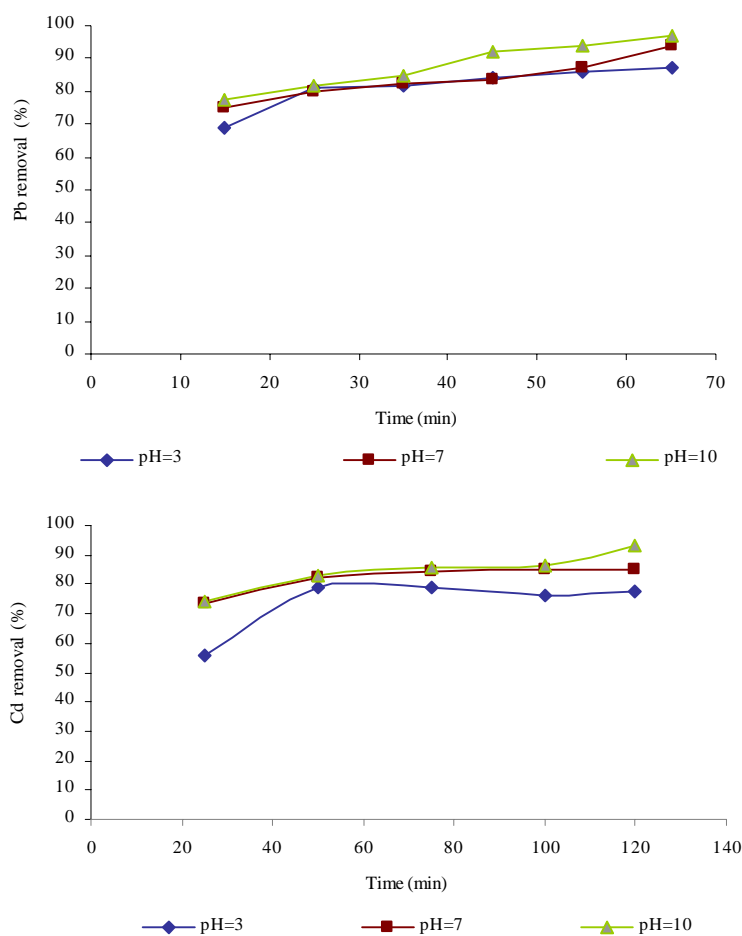
Fig. 2: Effect of pH for Cd and Pb adsorption on Leca

al. (2007) showed that 120 min is a sufficient time for Pb adsorption on Bentonite and Clinoptilolite. The removal of Pb (II) using Bentonite reached 100 % and 55 % for Clinoptilolite at ambient temperature and mild agitation (100 rpm) (Vassilis *et al.,* 2007). Pb removal efficiency was lower than last results obtained on wood ash (96.1 %) due to higher amount of applied wood ash

(Malakootian *et al.,* 2008). Weakly sorption of cadmium attributed with the fact that Cadmium adsorbs rather weakly on organic matter, silicate clay and oxides (Mcbride, 1994). Leca showed higher Cd removal efficiency than other studied minerals material like hydroxiapatite (Cd removal efficiency = 83 %) and it showed lower efficiency than fly ash (Corami *et al.,*
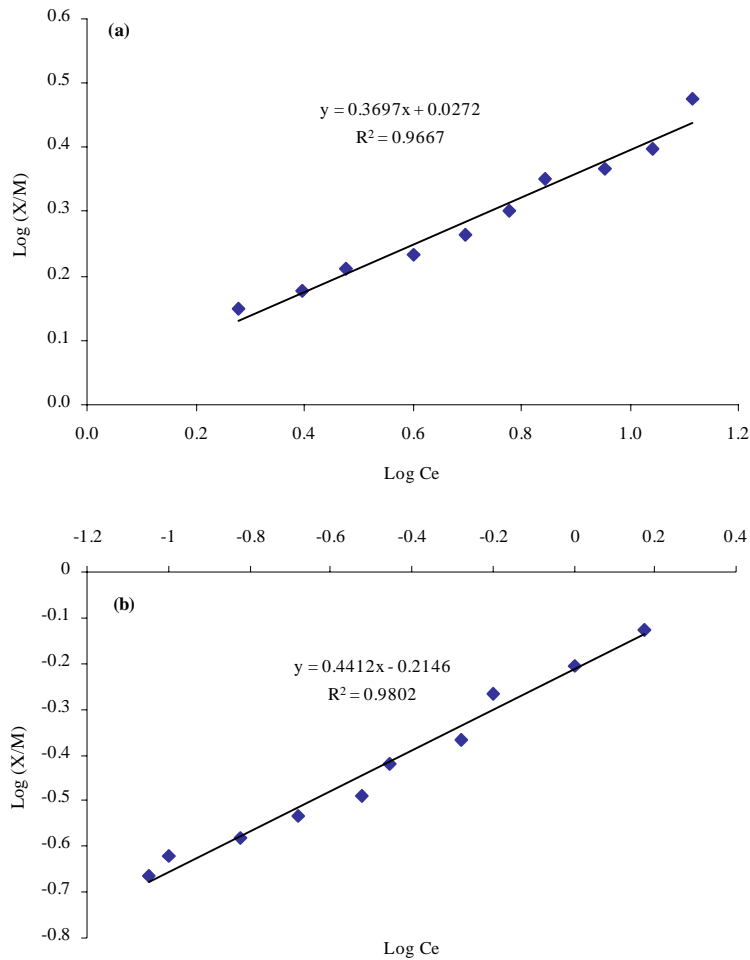
Fig. 3: Freundlich isotherm for metal removal by Leca, pH = 7, T = 25 °C (a: Pb; b: Cd)

Table 5: Freundlich and Langmuir model parameters

Freundlich model	Pb adsorption on Leca	Cd adsorption on Leca
K_F	1.064	0.61
$1/n$	0.369	0.44
R^2	0.97	0.98
Langmuir model	Pb adsorption on Leca	Cd adsorption on Leca
q_m	3.53	0.91
K_L	0.25	2.4
R^2	0.954	0.949

2008; Viraraghavan and Rao, 1991) as a result of fly ash small size classification. Leca in comparaison with wood ash showed better removal efficiency regarding Pb (Malakootian *et al.,* 2008). Table 4 compares the performance of this support compared to others.

Effect of Leca quantity and pH (Fig. 2)

Study of different densities of Leca showed that the amount of adsorbent has a great role in adsorption of Cd and Pb. In this study, different amounts of Leca (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/L) were sampled and the obtained results showed that increasing the amount
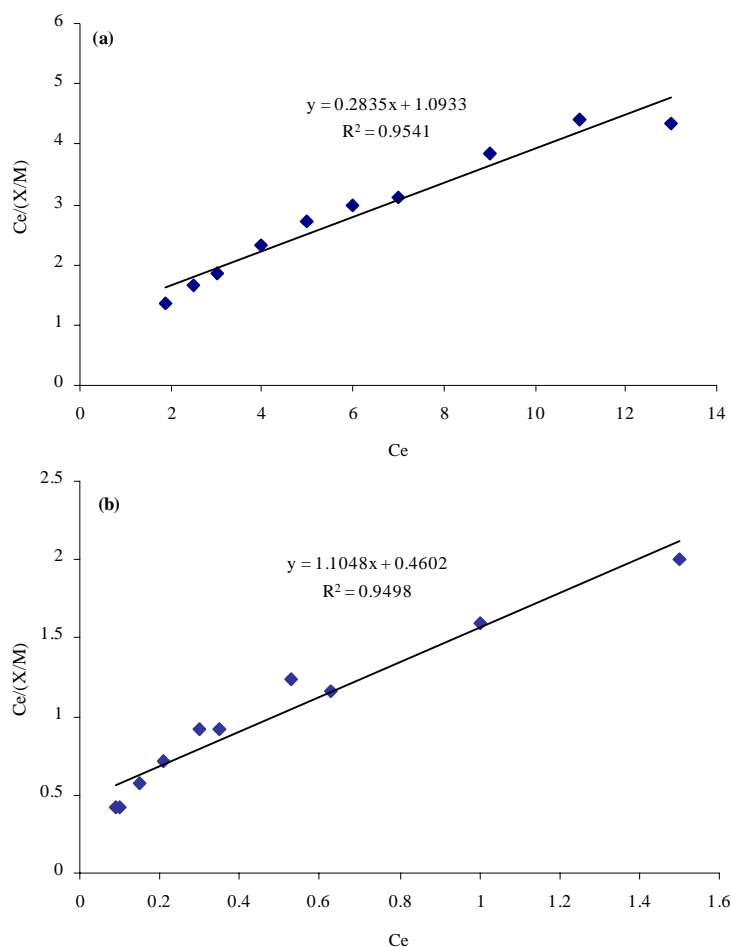
Fig. 4: Langmuir isotherm for metal removal by Leca, pH = 7, T = 25 °C (a: Pb; b: Cd)

of sorbent, the sorption sites were increased, but the residual metal concentration was obviously decreased (regarding high sorption) and limited the sorption efficiency. The results reveal that the unit adsorption (q) was high at low dose and reduced at high dose. The amount of adsorbed Pb (II) and Cd (II) increased from 1.41 to 3 mg/g and 0.22 to 0.75 mg/g, respectively. In this study, by increasing the purposed metal ion by two times of their MCLs for agricultural irrigation usage, 10 g/L Leca was selected. In order to investigate the effect of pH, the same amount of Leca in different PH_s (3, 7 and 10) was studied. The results showed that maximum Pb adsorption was 96.8 % in 10 g/L Leca and pH = 10 and maximum Cd adsorption was approximately 89.7 % at the same condition. Investigation the effects of pH on the adsorption rate of Cd and Pb by Leca was illustrated in Fig. 2 and as it is clear, adsorption is done at various ranges of pH, from 3 to 10 and pH variations

have relatively great effect on the adsorption rate. There was a gradual increase in adsorption rate related to increasing pH from 3 to 10 due to this fact that alkaline condition on sorbent produce more negative charge on the surface (Viraraghavan and Rao, 1991). The maximum removal efficiency of Pb and Cd was at alkaline condition (pH = 10) and these results were in accordance with the results of McBride (1994). Considering these results and the limitations concerning the discharge of acidic and alkaline effluents to the environment, neutral pH is logical and acceptable in the removal process.

Adsorption model (Figs. 3 and 4)

For modeling of the heavy metals adsorption from wastewater, two models (Langmuir and Freundlich) were used. These models are useful in the full scale applications. As Figs. 3 and 4 show, the adsorption of

Pb and Cd by Freundlich isotherm is better explained. The value of Freundlich and Langmuir constant was presented in Table 5. It will be noted that the value of 1/n was between 0 and 1indicating that the sorption of metal ions into Leca was favorable under the mentioned conditions.

Original form   Linearized form
1. Langmuir model

$$q = \frac{q_m . K_L . C}{1 + K_L . C} \qquad \frac{C}{q} = \frac{1}{K_L . q_m} + \frac{1}{q_m} . C$$

2. Freundlich model

$$q = K_F . C^{\frac{1}{n}} \qquad \log q = \log K_F + \frac{1}{n} . \log C$$

Where,

q: The amount of metal ions adsorbed per specific amount of adsorbent (mg/g)

C: Equilibrium concentration (mg/L or mmol/L)

q_m: The amount of metal ions required to form a monolayer (mg/g)

K_L: Langmuir equilibrium constant

(K_F) and (1/n) are indicative isotherm parameters of sorption capacity and intensity, respectively. As a consequence, the Freundlich isotherms for Pb removal by Leca can be represented by the following empirical formula:

$q = 1.064 \, x^{0.369}$

and Cd removal by Leca can be represented as:

$q = 0.61 \, x^{0.44}$

Results showed that Leca as an available, natural and low cost material can be considered as an alternative in the removal of heavy metals from this type of wastewater and similar ones.

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AUTHOR (S) BIOSKETCHES

Malakootian, M., Ph. D., Associate professor, Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran. Email: *m.malakootian@yahoo.com.*

Nouri, J., Ph.D., Full professor, Department of Environmental Management, Graduate School of the Environment and Energy, Science and Research Branch, Islamic Azad University, also as adjunct professor of the Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran. Email: *nourijafar@gmail.com*

Hossaini, H., Postgraduate student, Environmental Health Engineering, Post Graduated Programme, Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran. Email: *hhiwa_kmu@yahoo.com*