

# Rice husk and activated carbon-silica as potential bioadsorbents for wastewater purification

Mousa Mohammadpour<sup>1</sup>, Hossein Babazadeh<sup>1\*</sup>, Ali Afrous<sup>2</sup>, Ebrahim Pazira<sup>3</sup>

1. Department of Water Science and Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

2. Department of Water Engineering, Dezful Branch, Islamic Azad University, Dezful, Iran

3. Department of Soil Science, Science and Research Branch, Islamic Azad University, Tehran, Iran

\*Corresponding Author's Email: h\_babazadeh@hotmail.com

# ABSTRACT

Heavy metals are generally found in industrial wastewaters, affecting human health and living organisms. This study was therefore aimed to use bioadsorbents rice husk and activated carbon-silica to efficiently remove the heavy metals including lead (Pb) and cadmium (Cd) from an aqueous wastewater. The effects of bioadsorbent content, initial concentration, contact time, and pH value on the metal removal were investigated. An increased metal initial concentration lowered the removal efficiency of the bioadsorbents, and pH 6 provided the best condition for the removal of Pb and Cd. The use of rice husk and activated carbon-silica at pH 6 resulted in a maximum metal removal of 81% and 98% for Pb, while 88% and 100% for Cd respectively. The adsorption parameters were then determined by the Langmuir and Freundlich adsorption isotherms, and the experimental data were better fitted in the Freundlich adsorption isotherm model in comparison with the Langmuir adsorption isotherm model.

Keywords: Bio-adsorbent, Cadmium, Freundlich, Langmuir, Lead.

Article type: Research Article.

# INTRODUCTION

Different heavy metals including cadmium (Cd), mercury (Hg), and lead (Pb) are found in industrial wastewaters produced during battery manufacturing processes, mining operations, car radiator manufacturing, paints and pigments production, and ceramic and glass manufacture (Thavamani et al. 2013). Heavy metals can be introduced to human bodies through direct intake or food products and casue severe physiological or neurological damages to the human body and living organisms (Mohan & Sreelakshmi 2008; Imamoglu & Tekir 2008, Pratushet al. 2018). These elements cannot be decomposed in the environment and their intakes should be therfore prevented to minimize the related side-effects (Chuah et al. 2005). Pb and Cd are the most hazardous heavy metals commonly found in industrial wastewaters, and thus their removal is of utmost importance (Wong et al. 2003). Several methods have been used to remove toxic heavy metals from wastewater, such as chemical precipitation, membrane filtration, ion exchange, and carbon adsorption. These methods usually require expensive facilities and have high maintenance costs. In this case, more economical alternative technologies or adsorbents are needed for the treatment of metal-contaminated wastes (Salam et al. 2011). Several adsorbents include bark, coal, lignite, coconut shells, wood, dead biomass, and pecan shell have been used for this purpose as abundant and low cost chelating agents (Chuah et al. 2005). Furthermore, the potential use of eggshell, seaweed, tea waste, fly ash, peat moss, orange peels, animal bones, and coconut husks has been investigated; As well, microorganisms such as fungi, bacteria, yeast, and algae can be used to treat wastewaters containing toxic metal ions; however, this technique is not yet suitable for large-scale applications (Ahmad et al. 2012). Agriculture wastes or by-products

Caspian Journal of Environmental Sciences, Vol. 19 No. 4 pp. 661-672



Received: May 10, 2021 Accepted: Aug. 30, 2021 © The Author(s)

Publisher: University of Guilan, Iran

have been investigated extensively for the removal of heavy metals due to their abundance in nature. In recent years, natural materials have beenapplied as low cost adsorbents, such as rice husk, mud, agricultural wastes, silica, ash, and solid wastes. Recently, attention has been focused on the utilization of unmodified or modified rice husk as a sorbent for pollutant removal. Unmodified rice husk has been evaluated for its ability to bind metal ions. Various modifications have been employed to enhance its sorption capacity for metal ions and other pollutants (Wong *et al.* 2003).

Rice husk is an agricultural waste and containtsabout 20% silica, as a good adsorbent of many metals. One of the characteristics of rice husk is its porous matrix that can be made into activated carbons to use as an adsorbent to remove the heavy metals from the industrial effluents. Activated carbon from cheap and readily available sources likerice husk could be successfully employed for the removal of Pb, Cd, and other toxic heavy metals from aqueous solutions. Rice husk is producedduring rice milling and it is used to producegreen  $CO_2$  and remove pollutionsfrom the environment (Mohan & Sreelakshmi 2008). The OH<sup>-</sup> factor group of the rice husk can interact with metal ions (Salam *et al.* 2011).

Metal separation is significantly influenced by the pH value, adsorbent amount, metal concentration, and contact time (Chuah *et al.* 2005). Al-Zboon *et al.*(2011) used geopolymer as an adsorbent and found that the adsorption efficiency increases from 1% to 90.66% as pH increases from 1 to 5, while it decreases slightly (89.8%) at pH of 6. As a result, the zero point of charge is about pH of 5 and there is an excess of  $H_3O^+$  ions in the solution at low pH values, which make a competition between the positively charged hydrogen ions and Pb<sup>2+</sup> ions for the available adsorption sites on the negatively charged geopolymer surface. Researchers have usedadsorbents forthe removal of heavy metals; for example, the amorphous geopolymer for removal of Cu (Al-Harahsheh *et al.* 2015), and Pb (Al-Zboon *et al.* 2011), peanut husk charcoal and natural zeolite for the adsorption of Cu (II) and Zn (II) (Salam *et al.* 2011) etc.

As seen in the literature and to the best of our knowledge, there is no report dealing with simultaneously use of rice husk and its activated carbon silica as bioadsorbents for wastewater purification. In most of the industrial provinces in Iran, the problem of entering heavy metals to water resources through effluents has been considered a huge environmental challenge. Similarly, the remnants of crops such as rice husk and burning them is regarded as another environmental challenge that can be minimized to a great extent by utilizing the rice husk capacity and, especially, its carbon form during the process of surface adsorption of heavy metals from industrial wastewater. The present study was therefore conducted to evaluate the effectiveness of rice husk and activated carbon for the removal of  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous solutions.

# MATERIALS AND METHODS

#### **Natural and Chemical Materials**

Rice husk was obtained from a local rice milling company in Isfahan, Iran. All chemical reagents used in this study were of analytical grade and purchased from Merck Co. (Darmstadt, Germany).

#### Chemical analysis of rice husk

Chemical analysis was carried out by XRF spectrometry using a Philips Model PW 2400 XRF instrument with a Rh target tube and PW 2540 VTC sample changer. A Philips Model PERL'X3 was used to prepare samples automatically in the form of fused discs (beads).

#### Preparation of silicate from rice husk

The rice husk (3 kg) was washed several times with distilled water and ethanol to remove pollutions. Subsequently, it was dried in an oven at 95°C for 3 h. The rice husk was milled by a simple mill and separated by a mesh-size sifter 30 and 40 with the sizes between 425 and 600  $\mu$ m. The average diameter of particles was about 510  $\mu$ m. The activated carbon of rice husk silica was provided by heating a portion of the rice husk at 400 °C for 4 h.

# Preparation of heavy metals ions (Pb and Cd) stock solutions

The experiments in the present study were performed in a simulated synthesized aqueous solution of Pb and Cd. The stock solution (1000 mg  $L^{-1}$  metals) was then diluted to the desired concentrations using distilled water, and the concentration of heavy metals was measured by a spectrophotometer (Nsaif Abbas & Saeed Abbas 2013).

# Separation of Pb and Cd by the rice husk and activated carbon-silica

To evaluate the efficacy of the bioadsorbents in removing Pb and Cd, the pH values of the solutions containing adsorbents (0.5, 0.75, and 1.0 g L<sup>-1</sup>) and the heavy metals (10, 15, 20, 25, 30, 35, 40, 45 and 50 mg L<sup>-1</sup>) were adjusted to 4, 6, and 8 followed by shaking at 180 rpm for 15, 30, 60, and 120 min. Afterwards, the rice husk and silica were removed from the solution using a filter paper (Whatman No. 42). The bioadsorbent was analyzed by an Atomic Adsorption Spectroscopy apparatus, and the concentration of heavy metals in reaction medium was measured by a spectrophotometer to calculate the bioadsorbent efficiency in separating heavy metals. Experiments were conducted at room temperature ( $25 \pm 1$  °C), over a range of metal concentrations.

# Adsorption isotherm studies

Adsorption isotherm equations include constants that indicate the surface properties and affinity of the adsorbent were usually described by the Langmuir and Freundlich isotherms (Langmuir 1916; Freundlich 1906). Isotherm equation of adsorption is an expression of the relation between the solute concentration in the fluid phase and the amount of solute adsorbed. So, the adsorption isotherms are important in explaining how adsorbates interact with the adsorbents and also are essential for designing targets. Therefore, the correlation of equilibrium data using an equation is critical for practical adsorption operation (Salam *et al.* 2011). Two isotherm equations were adopted in this study, as follows:

# Langmuir adsorption isotherm

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the adsorption energy is constant, and there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is defined as (*Eq. 1*) (Salam *et al.* 2011):

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$$
(1)

where qe is the amount of adsorbed Pb and Cd ions (mg g<sup>-1</sup>), Ce is equilibrium concentration of Pb and Cd ions (mg L<sup>-1</sup>), qm (mg g<sup>-1</sup>) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites, and  $K_L$  (L mg<sup>-1</sup>) is the Langmuir empirical constant related to the energy of adsorption (Table 2).

# Freundlich adsorption isotherm

The isotherm of Freundlich sorption, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies (Salam *et al.* 2011). The Freundlich isotherm is defined as (*Eq.* 2):

$$Logq_e = \frac{1}{n}\log C_e + \log K \tag{2}$$

where qe is the amount of adsorbed Pb and Cd ions (mg  $g^{-1}$ ), Ce is equilibrium concentration of Pb, and Cd ions (mg  $L^{-1}$ ), K<sub>F</sub> is the Freundlich characteristic constant (mg  $g^{-1}$ ), and 1/n is the heterogeneity factor of sorption obtained from intercept and slope of log qe versus log Ce linear plot, respectively.

# Statistical analysis

The mean of data for each variable were statistically analyzed using one-way analysis of variance (ANOVA) based on the GLM procedure of the SAS statistical Package (SAS; version 9.1). Significance of the differences between Initial concentration, adsorbent dosage, pH, contact time and their interactions for the variables were tested using Duncan's Multiple Range (p < 0.05).

# **RESULTS AND DISCUSSION**

# X-Ray Fluorescence (XRF) analysis

The chemical composition of rice husk ash was obtained by XRF technique; Table 1 presents the chemical analysis of the rice husk. As shown in the table, the raw rice husk ash mainly contained silica (94.32%), potassium (2.45%), calcium (0.82%), phosphorus (0.78%), and alumina along with minor levels of iron and magnesium oxides. The

<b>Table 1.</b> The XRF analysis results of ash.										
Composition	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cl	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	$SO_3$
Ash (wt %)	94.32	2.45	0.82	0.78	0.36	0.11	0.19	0.67	0.12	0.18

high  $SiO_2$  content (94.32%) of the rice husk make it a good porous adsorbent for the removal of heavy metals from wastewaters.

# Adsorption studies of Pb and Cd by rice husk and activated carbon Effect of initial pH

It is well known that adsorption of heavy metal ions by solid substrates depends on the pH of the solution. The amount of pH is considered one of the important factors that affect the chemical and biological reactions of the effluents (Zhang & Frankenberger 2003). The effect of initial pH on the adsorption process is presented in Fig. 1. As can be seen, the removal efficiency of Cd (II) and Pb (II) increased with increasing pH and maximum removal efficiency for both Cd (II) and Pb (II) was obtained at pH of 6 which was the initial pH value of the solutions. The lowest removal efficiency was achieved for both ions by the rice husk at pH 4. At pH 6, Cd ion had a higher adsorption rate than the lead ion; the removal efficiency of Cd ion was found to be 88% and 100% by rice husk and activated carbon adsorbents, while in the case of Pb ion, were 81.98% and 98.8% respectively. Also, the high efficiency removal of 87.5% and 100% were observed for Cd ions when the rice husk and activated carbon were applied as adsorbents.

The solution pH is an important factor in the adsorption process, which affects surface charge of the adsorbent and the degree of ionisation and speciation of adsorbate (Imamoglu & Tekir 2008). At low pH values, there is an excess of  $H_3O^+$  ions in the solution, which make a competition between the positively charged hydrogen ions and  $Pb^{2+}$  and  $Cd^{2+}$  ions for the available adsorption sites on the negatively charged adsorbent surface. As the pH elevates, the competition between protons and  $Pb^{2+}$  and  $Cd^{2+}$  for surface sites will decrease. In addition,  $Pb^{2+}$  and  $Cd^{2+}$  ions are the predominating species, which will attract to the surface of adsorbent by columbic forces (Wong *et al.* 2003; Amarasinghe & Williams 2007; Al-Zboon *et al.* 2011). A similar observation was found in the adsorption of lead and chromium (Gupta *et al.* 2003), Zn (II) and Ni (II) (Cetin & Pehlivan 2007). Pham *et al.* (2015) used sugarcane as an adsorbent and found that the optimal pH (6) is appropriate for the removal of cadmium. As the pH upraises, the competition between protons and Pb (II) for surface sites will decrease. Chuah *et al.*(2005) suggested that the contents of amino acids, the active functional groups, and metal oxides in rice husk, may have an effect on the uptake process. Rice husk could exhibit a hydration shell at lower pH positively charged by the hydronium ion, H<sup>+</sup>, in the solution. This restricted the uptake of ions. In general, the adsorption of most metal ions elevates by an increased pH up to a certain value and then decreases with further increase in pH (Ahmaruzzaman 2010).

# Effect of adsorbent dosage

The adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbed material. The concentration of adsorbent particles is effective in the amount of attracted metal ions by the particles of rice husk (Raji & Anirudhan 1997).

The effect of adsorbent dosage on removal of Cd (II) and Pb (II) is presented in Fig. 2, indicating that adsorption elevated by increased adsorbent dosage. The results showed that both adsorbents have the same removal efficiency of Pb and Cd at pH 6 and dose of 1 g  $L^{-1}$ . An elevated adsorbent doses from 0.5 to 1 g  $L^{-1}$  will upraise the removal efficiency in both adsorbents.

It seems that by elevation in adsorbent dose, the specific surface area rises, hence the adsorption occurs more easily. The elevating in removal efficiency of Cd and Pb with carbon dose is probably resulted from the upraised total surface area and activated functional groups on carbons. The obtained results are similar to those reported in some studies (Babel & Kurniawan 2003; Argun *et al.* 2007). Cetin & Pehlivan (2007) found that the rate of removal of metal ions (Zn) elevates by upraised adsorbent dose. Similarly, Gupta *et al.*(2003) used fly ash of sugar industry and found that the dose of 10 g L<sup>-1</sup> resulted in the adsorption capacity of 3.8 mg g<sup>-1</sup>. In another study, Al-Zboon *et al.*(2011) found that the adsorption efficiency elevated from 50.7 to 97.1% as the adsorbent dose rises from 0.03 g (0.6 g L<sup>-1</sup>) to 0.1 g (2.0 g L<sup>-1</sup>), while the adsorption capacity decreased from 84.5 to 48.55 mg g<sup>-1</sup> in

the same doses, respectively. By upraising adsorbent content, the available sites for binding Cd and Pb ions elevates and thereby enhances the adsorption of the solution to the adsorbent. This elevation can be described by the increased area and the available adsorption sites of adsorbent samples (Al-Zboon *et al.* 2011).

In general, the removal efficiency of rice husk strongly depends on the surface activities, in other words, on the specific surface area available for solute surface interaction, which is accessible to the solute. Higher sorption for smaller particle size could be attributed to the larger surface area per unit mass of rice husk. It is expected that adsorption capacity will be raised by a larger surface area, as smal particle sizes elevates the removal efficiency (Al-Zboon *et al.* 2011).





Fig. 1. Effect of initial pH on (a) Pb and (b) Cd removal efficiency (10 mg  $L^{-1}$  concentration, 25°C, dose: 1 g  $L^{-1}$ , and contact time: 120 min). (Means in the same column with different letters are significantly (p < 0.05) different).

# Effect of initial concentration

The effect of initial concentration on the removal efficiency of Cd (II) and Pb (II) ions by rice husk and activated carbon is shown in Fig. 3. The adsorption of Cd (II) and Pb (II) on rice husk decreased from 88% and 81.6% to 20% and 18% by elevating the Cd (II) and Pb (II) concentrations from 10 mg L<sup>-1</sup> to 50 mg L<sup>-1</sup>, respectively. The removal efficiencies by activated carbon at the initial concentration of 10 mg L<sup>-1</sup> for the Pb and Cd ions were 98.8% and 100%, respectively, while at the concentration of 50 mg L<sup>-1</sup> it was decreased to 21.8% and 21.6%,

respectively. Regarding the efficiency of adsorbents in removing heavy metals, similar observations have been reported in the literature (Argun *et al.* 2007; Kumar *et al.* 2008; Al-Zboon *et al.* 2011; Nsaif Abbas & Saeed Abbas 2013). At low initial concentration, the available pores in the adsorbent surface are sufficient to adsorb most of the metal ions and fill the possible available sites, so the adsorption efficiency rises to a certain level. As the initial concentration elevates, the available pores become insufficient to adsorb further metal ions, hence much of the ions remain in suspension and no metal ions can be adsorbed. Several investigations have shown that the removal efficiency of heavy metals is concentration-dependent and there is a dropping trend by the upraised initial concentration (Imamoglu & Tekir 2008).



**Fig. 2.** Effect of adsorbent dosage on (**a**) Pb and (**b**) Cd removal efficiency (10 mg  $L^{-1}$  concentration, 25°C, doses: 0.5, 0.75 and 1 g  $L^{-1}$ , and contact time: 120 min, pH 6). (Means in the same column with different letters are significantly (p < 0.05) different).

The results showed that the removal efficiency of activated carbon in the adsorption of metal ions ( $Pb^{2+}$  and  $Cd^{2+}$ ) from wastewater is higher than that of rice husk. Several factors such as the adsorbent chemical properties, the operating groups in the adsorbent physical structure (high porosity, size particle, high surface area, and etc.) as well as the chemical nature of metal like polarity, molecular weight, and its size might play a role in this result (Shah *et al.* 2015; Tang *et al.* 2017). Gumus & Okpeku (2015) and Sricharoenchaikul *et al.* (2007) found that the activated carbon is widely used due to its large surface areas available for adsorption and high degree of porosity for chemical reactions. The surface area of the adsorbent is an important parameter for adsorption. When the

surface area of adsorbent is high, more adsorbent sites are available for interaction with solid-metal ion. Smaller particle size of adsorbent have more surface area per unit of weight and hence higher percentage of metal removal is expected (Amarasinghe & Williams 2007).





**Fig. 3.** Effect of initial concentration on the (**a**) Pb, (**b**) Cd and (**C**) Pb/Cd removal efficiency with using the rice husk and activated carbon (contact time is 30 min and adsorbent material dose is 1 g L<sup>-1</sup> and pH of 6). (Means in the same column with different letters are significantly (p < 0.05) different).

According to Low *et al.* (1995), the adsorption surface would depend on the equilibrium between sorption competition of all the cations, ionic size, the stability of the bond between metal ions and bioadsorbent, nature of the metal ions and sorbent, as well as interaction and the distribution of the reaction groups on the bioadsorbents. This result indicates that the removal efficiency of  $Cd^{2+}$  by two adsorbents was higher than the  $Pb^{2+}$  ion. This could be likely due to the influence of several factors, such as chemical chemistry of metal (i.e. polarity, molecule weight, and size), the chemical nature of cadmium metal, the radius of metal ions, the nature of paramagnetic and electronegativity in the efficiency, and the adsorption capacity of metals.

The present resluts are in agreement with those of Singanan (2011), who reported the maximum efficiencies of lead and cadmium removal by biocarbon as 95% and 98%, respectively, and Anwar *et al.* (2009) who performed a batch adsorption study and reported an increase of 88% and 86% in Cd and Pb removal, respectively. In general, sufficient adsorption sites are available at lower initial concentration, but at higher concentration, metal ions are greater than adsorption sites. Thus, it can be deduced that removal of cadmium and lead is highly concentration-dependent.

# Effect of the contact time

The effect of the contact time on the adsorption of cadmium and lead are shown in Fig. 4. As can be seen, the adsorption of Cd and Pb metal ions elevated by an increased contact time and reached to a maximum value after 30 min, and it remained constant thereafter. The lowest removal efficiency of lead (69%) and cadmium (76.5%) was observed at 15 min contact time for raw husk; whilst, activated carbon resulted in the highest removal efficiency of lead (94.8 %) and cadmium (96.6%) at contact time of 30 min. At the initial contact times, the adsorption speed was very high, so that in the first 15 min, higher than 70% of Pb and Cd concentrations were adsorbed and in the another 15 min, contact time led to a higher than 80% removal of Pb and Cd. This could be probably related to the completion of the adsorption capacity of the adsorbents. In general, adsorbent saturation reduces metal adsorption from the solution and two solid and fluid phases are almost balanced. In this case, the adsorption rate of metal ion to the adsorbent surface is equal to the rate of ion's return from the adsorbent particles surface into the solution. In other words, the adsorption occurs in two fast and slow stages. In the first stage, the attracting action is quickly performed on the adsorbent surface because the majority of the adsorbent sites are empty. Over time and gradual filling of these sites, the penetration of the metal ion among the adsorbed ions and its connection to the empty surfaces make the adsorption process slow, and this is the slow stage of the internal mass transfer. Also, by upraising the metal ion concentration, the amount of adsorption elevateds and ultimately the amount of adsorption reaches a fixed amount when the adsorbent is saturated. Therefore, a further elevate in the concentration, no more affects is found on the surface area of adsorption (Amarasinghe &Williams 2007).

Similar results were reported by Sharma et al. (2008), Mousa et al. (2013), and Abdulrazak et al. (2017). Cetin & Pehlivan (2007) found that the maximum removal of Zn (II) and Ni (II) ions by fly ash was achieved after 1 h. Gupta et al. (2008) reported that the equilibrium contact time for the lead was 60 min. Ajmal et al. (2003) found that the adsorption of Pb (II) metal ions on geopolymer increases by the elevated contact time and reaches a maximum value after 120 min, therafter remains constant.

To determine the adsorption isotherms, rice and activated carbon were used as an adsorbent. Then, the related tests were carried out at pH 6 and with different saturations of lead and cadmium. The data from isotherms adsorption experiments were fitted with Langmuir and Freundlich isotherms simulations and the constants of each simulation and their correlation coefficients were obtained. The results of the fitting of the related parameters of Langmuir and Freundlich isotherms are summarized in Tables 2-3. The correlation coefficients by Freundlich isotherms for Pb were found to be 0.932 and 0.954 in rice husk and activated carbon, respectively. In the case of Cd, these coefficients were found to be 0.952 and 0.984 respectively.

In addition, the results of the adsorption isotherm showed that correlation coefficients by Freundlich and Langmuir for cadmium were higher than those of lead. Considering the regression coefficients (Tables 2-3), for two adsorbents (rice husk and activated carbon), the Freundlich isotherm is fitted better than the Langmuir one. Therefore, for predicting the behavior of lead and cadmium adsorption from industrial effluents by adsorbent rice husk and activated carbon, the results of this study were similar to those of Li et al. (2007). Hence, the Freundlich isotherms were selected and suggested because of the high correlation coefficient by Freundlich isotherms compared to Langmuir ones.

....

. .

Table 2 . Parameters of Langmuir model.										
		pH = 6			$\mathbf{pH} = 4$	ļ	<b>pH</b> = 8			
Adsorbents	R <sup>2</sup>	$q_m(mgg^{\text{-}1})$	$K_L (L mg^{-1})$	R <sup>2</sup>	$q_m(mg~g^{\text{-}1})$	$K_L (L mg^{-1})$	R <sup>2</sup>	$q_m(mg~g^{\text{-}1})$	$K_L (L mg^{-1})$	
$Pb^{a}$	0.9124	38.31	0.138	0.77	6.70	1.20	0.85	7.710	0.50	
$Pb+C^b$	0.9075	33.78	0.402	0.58	8.95	3.93	0.69	10.40	0.81	
Cd <sup>c</sup>	0.9376	41.66	0.158	0.87	5.81	0.11	0.74	9.88	1.10	
$Cd+C^d$	0.9332	35.71	0.609	0.85	5.12	1.25	0.75	10.72	3.51	

<sup>a</sup>Rice Husk Adsorbent for lead metal (Pb)

<sup>b</sup>Activated Carbon Adsorbent for lead metal (Pb+C)

°Rice Husk Adsorbent for cadmium metal (Cd)

<sup>d</sup>Activated Carbon Adsorbent for cadmium metal (Cd+C)

Table 3. Parameters of Freundlich model.									
	<b>pH</b> = 6				pH	= 4	<b>pH</b> = 8		
Adsorbents	R <sup>2</sup>	Ν	$K_L (L mg^{-1})$	R <sup>2</sup>	n	$K_L (L mg^{-1})$	R <sup>2</sup>	n	$K_L (L mg^{-1})$
Pb <sup>a</sup>	0.9324	1.45	1.97	0.76	31.74	2.15	0.96	9.95	2.03
Pb+C <sup>b</sup>	0.9544	1.89	2.62	0.8	48.30	2.50	0.89	1.04	2.370
Cd <sup>c</sup>	0.9527	1.52	2.17	0.96	5.77	1.57	0.92	14.45	2.41
$Cd+C^d$	0.9845	2	2.96	0.96	24.09	1.88	0.91	3.80	2.68

<sup>a</sup>Rice Husk Adsorbent for lead metal (Pb) <sup>b</sup>Activated Carbon Adsorbent for lead metal (Pb+C)

°Rice Husk Adsorbent for cadmium metal (Cd)

dActivated Carbon Adsorbent for cadmium metal (Cd+C)



**Fig. 4.** Effect of contact time on the (a) Pb and (b) Cd removal efficiency using the rice husk and activated carbon (Initial concentrations of Pb and Cd are 10 mg  $L^{-1}$ , pH 6, and adsorbent material dose is 1 g  $L^{-1}$ ). (Means in the same column with different letters are significantly (p < 0.05) different).

#### CONCLUSION

In conclusion, results showed that the removal efficiency of  $Cd^{2+}$  and  $Pb^{2+}$  by rice husk and activated carbon from aqueous solutions are affected by pH, contact time,  $Cd^{2+}$  and  $Pb^{2+}$  initial concentration, and adsorbent dosage. The optimum pH and adsorbent dosage for  $Cd^{2+}$  and  $Pb^{2+}$  removal were 6 and 1 g L<sup>-1</sup>, respectively. An equilibrium time of 120 min was required for the adsorption of Pb and Cd ions onto rice husk and activated carbon. The highest removal efficiency by rice husk and activated carbon was observed in the initial concentration of 10 mg L<sup>-1</sup>. The rice husk and activated carbon have therefore high potential to remove cationic species from industrial wastewater, and activated carbon showed a higher efficiency than rice husk. In additon, adsorption parameters were determined by the Langmuir and Freundlich isotherms, and the experimental data (regression coefficients) were well fitted in the Langmuir equation.

Langmuir correlation coefficients were found to be 0.912 for Pb, 0.907 for Pb+C, 0.937 for Cd, and 0.933 for Cd+C, and also Freundlich correlation coefficients were 0.932 for Pb, 0.954 for Pb+C, 0.952 for Cd, and 0.984 for Cd+C. To predict the behavior of lead and cadmium adsorption from industrial effluents, the Freundlich were selected and suggested because of the better correlation coefficient than those of Langmuir ones.

#### ACKNOWLEDGEMENTS

The authors would like to express their gratitude to Islamic Azad University, Science and Research Branch, Department of Water Engineering Sciences and the Isfahan University of Technology for the support of our work.

#### REFERENCES

- Abbas, MN & Abbas, FS 2013, Utilization of Iraqi Rice Husk in the Removal of Heavy Metals from Wastewater. *Research Journal of Environmental and Earth Sciences*, 5: 370-380.
- Abdulrazak, S, Hussaini, K & Sani, HM 2017, Evaluation of removal efficiency of heavy metals by low-cost activated carbon prepared from African palm fruit. *Applied Water Science*, 7: 3151-3155.
- Ahmad, M, Usman, AR, Lee, SS, Kim, SC, Joo, JH, Yang, JE & Ok, YS 2012, Eggshell and coral wastes as low cost sorbents for the removal of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup> from aqueous solutions. *Journal of Industrial and Engineering Chemistry*, 18: 198-204.
- Ahmaruzzaman, M 2010, A review on the utilization of fly ash. *Progress in energy and combustion science*, 36: 327-363.
- Ajmal, M, Rao, RAK, Anwar, S, Ahmad, J & Ahmad, R 2003, Adsorption studies on rice husk: Removal and recovery of Cd (II) from wastewater. *Bioresource technology*, 86: 147-149.
- Al-Harahsheh, MS, Al Zboon, K, Al-Makhadmeh, L, Hararah, M & Mahasneh, M 2015, Fly ash based geopolymer for heavy metal removal: A case study on copper removal. *Journal of Environmental Chemical Engineering*, 3: 1669-1677.
- Al-Zboon, K, Al-Harahsheh, MS & Hani, FB 2011, Fly ash-based geopolymer for Pb removal from aqueous solution. *Journal of hazardous materials*, 188: 414-421.
- Amarasinghe, BMWPK & Williams, RA 2007, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, 132: 299-309.
- Anwar, J, Shafique, U, Salman, M, Zaman, Waheed & Memoona, M 2009, Adsorption study of cadmium (II) and lead (II) on radish peels. *Journal of Scientific Research*, 39: 29.
- Argun, ME, Dursun, S, Ozdemir, C & Karatas, M 2007, Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*, 141: 77-85.
- Babel, S & Kurniawan, TA 2003, Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of hazardous materials*, 97: 219-243.
- Cetin, S & Pehlivan, E 2007, The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 298: 83-87.
- Chuah, TG, Jumasiah, A, Azni, I, Katayon, S & Choong, ST 2005, Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. *Desalination*, 175: 305-316.
- Freundlich, HMF 1906, Uber die adsorption in losungen, zeitschrift fur phtsikalische chemie. *American Chemical Society*, 62: 121-125.
- Gumus, RH & Okpeku, I 2014, Production of activated carbon and characterization from snail shell waste (Helix pomatia). *Advances in Chemical Engineering and Science*, 5: 51.
- Gupta, VK & Rastogi, A 2008, Biosorption of lead (II) from aqueous solutions by non-living algal biomass Oedogonium sp. and Nostoc sp.—a comparative study. *Colloids and Surfaces B: Biointerfaces*, 64: 170-178.
- Gupta, VK, Jain, CK, Ali, I, Sharma, M & Saini, VK 2003, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste. *Water Research*, 37: 4038-4044.
- Imamoglu, M & Tekir, O 2008, Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *Desalination*, 228: 108-113.
- Kumar, R, Bishnoi, NR & Bishnoi, K 2008, Biosorption of chromium (VI) from aqueous solution and electroplating wastewater using fungal biomass. *Chemical Engineering Journal*, 135: 202-208.
- Langmuir, I 1916, The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American chemical society*, 38: 2221-2295.
- Li, Q, Zhai, J, Zhang, W, Wang, M & Zhou, J 2007, Kinetic studies of adsorption of Pb (II), Cr (III) and Cu (II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials*, 141: 163-167.
- Low, KS, Lee, CK & Leo, AC 1995, Removal of metals from electroplating wastes using banana pith. *Bioresource Technology*, 51: 227-231.

- Mohan, S & Sreelakshmi, G 2008, Fixed bed column study for heavy metal removal using phosphate treated rice husk. *Journal of Hazardous Materials*, 153: 75-82.
- Mousa, WM, Soliman, SI, El-Bialy, AB & Shier, HA 2013, Removal of some heavy metals from aqueous solution using rice straw. *Journal of Applied Sciences Research*, 9: 1696-1701.
- Pham, TT, Hoang, MT, Nguyen, MK, Dinh, TH, Han, LP & Bruggen, BV 2015, Evaluation of chemical modified sugarcane bagasse for cadmium removal in aqueous environment. *International Proceedings of Chemical*, *Biological and Environmental Engineering*, 88: 6-10.
- Pratush, A, Kumar, A & Hu, Z 2018, Adverse effect of heavy metals (As, Pb, Hg, and Cr) on health and their bioremediation strategies: A review. *International Microbiology*, 21: 97-106.
- Raji, C & Anirudha, TS 1997, Chromium (VI) adsorption by sawdust carbon: Kinetics and equilibrium.
- Salam, OEA, Reiad, NA & ElShafei, MM 2011, A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. *Journal of Advanced Research*, 2: 297-303.
- Shah, I, Adnan, R, Ngah, WSW & Mohamed, N 2015, Iron impregnated activated carbon as an efficient adsorbent for the removal of methylene blue: regeneration and kinetics studies. *PlOS one*, 10.
- Sharma, YC, Upadhyay, SN & Weng, CH 2008, Studies on an economically viable remediation of chromium rich waters and wastewaters by PTPS fly ash. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317: 222-228.
- Singanan, M 2011, Removal of lead (II) and cadmium (II) ions from wastewater using activated biocarbon. *Science Asia*, 37: 115-119.
- Sricharoenchaikul, V, Pechyen, C, Aht-ong, D & Atong, D 2007, Preparation and characterization of activated carbon from the pyrolysis of physic nut (*Jatropha curcas* L.) waste. *Energy & Fuels*, 22: 31-37.
- Tang, C, Shu, Y, Zhang, R, Li, X, Song, J, Li, B, Zhang, Y & Ou, D 2017, Comparison of the removal and adsorption mechanisms of cadmium and lead from aqueous solution by activated carbons prepared from Typha angustifolia and Salix matsudana. *RSC Advances*, 7: 16092-16103.
- Thavamani, SS & Rajkumar, R 2013, Removal of Cr (VI), Cu (II), Pb (II) and Ni (II) from aqueous solutions by adsorption on alumina. *Research Journal of Chemical Sciences*, 2231: 606X.
- Wong, KK, Lee, CK, Low, KS & Haron, MJ 2003, Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. *Process Biochemistry*, 39: 437-445.
- Zhang, Y & Frankenberger, WT 2003, Factors affecting removal of selenate in agricultural drainage water utilizing rice straw. *Science of the Total Environment*, 305: 207-216.

Bibliographic information of this paper for citing:

Mohammadpour, M, Babazadeh, H, Afrous, A, Pazira, E 2021, Rice husk and activated carbon-silica as potential bioadsorbents for wastewater purification. Caspian Journal of Environmental Sciences, 19: 661-672

Copyright © 2021