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[Research]

Effects of pH, particle size and porosity of raw rice husk and its silica on removing lead and hexavalent chromium from aqueous solution

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ABSTRACT

Adsorbent properties and aqueous characteristics are very important parameters in the removal efficiency (RE) of environmental pollutants. The main goal of this study was to investigate the effects of pH, particle size and porosity of raw rice husk and its silica on removing lead and hexavalent chromium (Cr^{+6}) from aqueous solution. The raw rice husk was collected from north of Iran and the rice husk silica was prepared at 800ºC after acid leaching. The effects of the adsorbent particle sizes (0.07-0.1, 0.1-0.5, 0.5-1.0 and 1.0-1.5 mm), porosity and pH from 2 to 8 were investigated by varying any of the process variables while keeping the other variables constant (adsorbent dosage = 1.5 $g.l^{-1}$, contact time = 60 min, chromium and lead initial concentration = 5 $mg.l^{-1}$). The results of this study showed that the RE of Cr^{+6} is intensively pH - dependent. Using 1.5 $g.l^{-1}$ adsorbents, particle size = 0.5 - 1.0 mm, 5.0 $mg.l^{-1}$ initial concentration of Cr^{+6} and 60 min contact time, the maximum RE obtained by raw rice husk and its silica at pH 2 were up to 98.8 and 88.4%, respectively. However, at the same condition with changing pH (pH 7), the maximum RE decreased up to 69.4 and 60.4%, respectively. Moreover, a positive strong significant correlation was detected between decreasing the adsorbents particle sizes and lead removal efficiency in the two adsorbents ($P < 0.01$). The scanning electron microscope images of the two adsorbents showed that silica derived from raw rice husk has more porosity. In conclusion, the acidic condition of aqueous for Cr^{+6} and neutral condition for lead, increases the adsorbents porosity, while decreased adsorbent particle sizes causes an elevation in the RE of the two pollutants.

Key words: Hexavalent chromium, Lead; Particle size, Removal efficiency, Rice husk silica.

INTRODUCTION

Over the course of the recent decades, human activities have led to a significant increase in environmental pollution. This is also why control and treatment of pollutants are the most important environmental challenges today. Lots of studies have reported a relationship between environmental pollution levels and human health problems (Koop *et al.* 2010; Mehdinia 2011). Heavy metals are some of the most important environmental pollutants which have some hazardous effects on human health at exceeded concentrations (Kobya *et al.* 2004). Currently, several methods have been used to remove heavy metals from the environment. Some of the most important methods utilized in removing them work by adsorption (Abdel Ghani *et al.* 2007; Mehdinia *et al.* 2014). Activated carbon has been generally used for adsorption of heavy metals from aqueous. Since the use of commercial activated carbon to remove pollutants is expensive, investigators are searching for other cost-effective adsorbents. Recently, wide attention has been devoted to the study of the heavy metals removal from water and wastewater with the application of agricultural wastes (Mahvi 2002; El-Ashtoukhy *et al.* 2004; Demirbas *et al.* 2004; Gueu *et al.* 2007; Shamohammadi *et al.* 2008; Montazeri *et al.* 2009; Khazaei *et al*. 2011; Salari *et al.* 2012; Kafia & surci 2012; Ghaneian *et al.* 2014; Mohseni *et al.* 2016). Adsorbent properties such as porosity, particle size, surface area and pore radius size as well as the properties of water and wastewaters such as pH and temperature are very important in determining the removal efficiency of pollutants. Therefore, this study investigates the effects of pH, particle size and porosity of raw rice husk and its silica on removing the lead and hexavalent chromium from water and wastewaters.

MATERIALS AND METHODS

Preparation of adsorbents

This research as an experimental study, was carried out in the School of Health, Semnan University of Medical Sciences in 2014. Raw rice husk was collected from the north of Iran. Rice husk silica was prepared according to Jamwal & Mantri method (2007). In this method, the rice husk was first washed with tap water to remove contaminants and was then oven-dried at 110°C for 24 h. It was then subjected to acid leaching by reflux in 3% hydrochloric acid and 10% sulphuric acid for 2 h, at a ratio of 50 g husk per liter. The husk was completely washed with distilled water and oven-dried at 100°C for 4 h. Eventually, the clean and dried husk was burned inside a muffle furnace at 800°C in static air for 4 h.

Batch adsorbent experimental

According to Souag *et al.* (2007), synthetic solution containing lead and chromium were prepared by dissolving a known amount of analytical-grade lead chloride and potassium dichromate in distilled water. The effects of the adsorbent particle sizes (0.07-0.1, 0.1-0.5, 0.5-1.0 and 1.0-1.5 mm), porosity and pH from 2 through 8 were investigated by varying any of the process variables while keeping the other variables constant (adsorbent dosage = 1.5 $g.l^{-1}$, contact time = 60 min, chromium and lead initial concentration = 5 $mg.l^{-1}$). The pH was adjusted from 2.0 through 8.0 by adding 0.1M HCl and 0.1M NaOH. All experiments were carried out in batch reactors at room temperature of 25 ± 2°C. All experiments were carried out at three times and the averages were reported as results.

Data analysis

The concentration of lead and hexavalent chromium before and after the adsorption process were measured using atomic adsorption (Perkin Elmer-100 model). Wavelengths of 283.3 and 357.9 nm and detection limits of 0.05 and 0.02 $mg.l^{-1}$ were used for measurment of lead and Cr^{+6}, respectively. Removal efficiency of the adsorbents was determined by the following formula:

$$RE= \frac{Ci-Co}{Ci} \times 100$$

where, C_i and C_o are the concentration of lead and hexavalent chromium before and after adsorption operating time, respectively (Mehdinia *et al.* 2011; Mehdinia *et al.* 2013).
The surface morphology of the adsorbents were observed under a scaning electron microscope (SEM), using LEO operated at an accelerating voltage of 15 kV (Ros *et al.* 2007).

RESULTS AND DISCUSSION

Effect of particle size

The results of this study showed that the removal efficiency of hexavalent chromium is dependent on the particle sizes of raw rice husk and its silica. Using 1.5 $g.l^{-1}$ of the adsorbents, 5.0 $mg.l^{-1}$ initial concentration of Cr^{+6} and 60 min contact time, the maximum removal efficiency of up to 98.8 and 88.4% was obtained at particle size of 0.07-0.1 mm by the application of raw rice husk and its silica, respectively. However, at the same condition but with changing the particle size to 1.0-1.5 mm, the maximum removal efficiency decreased up to 63.3 and 61.4%, respectively. The result of removal efficiency of Cr^{+6} using raw rice husk and its silica of different particle sizes and 5.0 $mg.l^{-1}$ initial concentration, 60 min contact time and 1.5 $g.l^{-1}$ adsorbents dosage are shown in Fig. 1.

This result is supported by Choudhury *et al*. (2012) who studied the adsorption of Cr (III) from aqueous solution using groundnut shell. They reported that: "The lower the particle size, the higher the chromium removal (%). By decreasing in particle size, the removal of chromium (III) increased from 47 to 97%".

Moreover, Wong *et al*. (2003) and Munaf & Zein (1997) reported that by elevating the adsorbent particle size, the removal efficiency of heavy metals will be decreased.

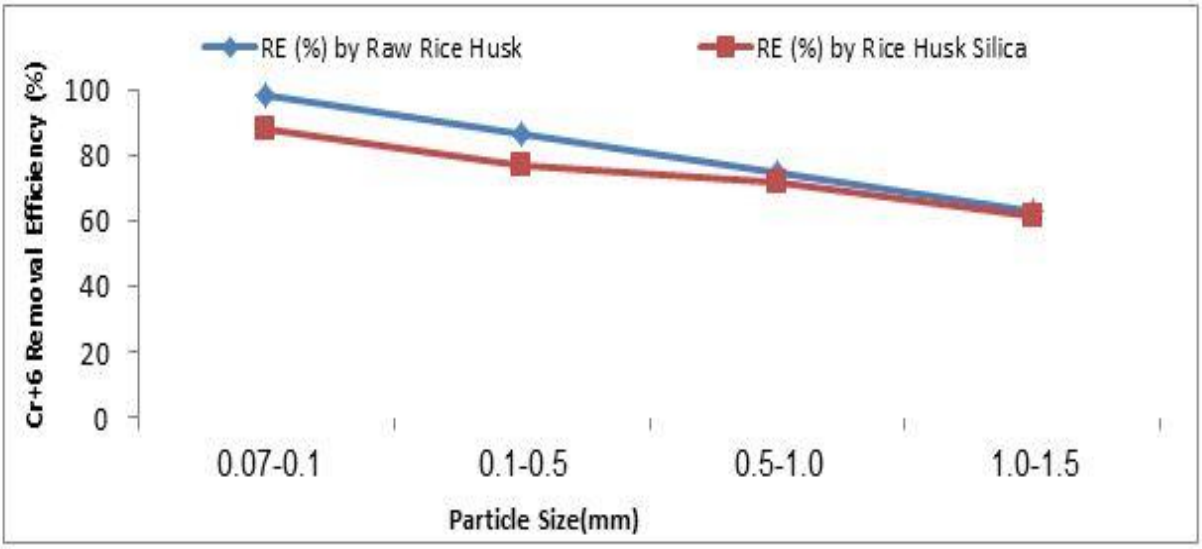


Fig. 1. Removal efficiency of Cr^{+6} using raw rice husk and its silica with different particle sizes, 5.0 $mg.l^{-1}$ concentration, 60 min contact time and 1.5 $g.l^{-1}$ adsorbent dosage.

In addition, in this research, we studied the correlation between decreasing adsorbents particle size and removal efficiency of lead using the Pearson's correlation analysis.

So that, we assessed the correlation between decreasing the raw rice husk and its silica particle sizes (0.07-0.1, 0.1-0.5, 0.5-1.0 and 1.0-1.5 mm) as well as removal efficiency of lead at pH 6, adsorbents dosage = 1.5 $g.l^{-1}$, contact time = 60 min and initial concentration of lead = 5.0 $mg.l^{-1}$. A positive strong significant correlation was detected between decreasing the adsorbent particle sizes and lead removal efficiency in both adsorbents ($P < 0.01$).

The results showing the correlation between decreasing particle sizes and lead removal efficiency is illustrated in Fig. 2.

These effects could be due to the fact that the smaller adsorbent particles offer larger surface areas and greater numbers of adsorption sites (Choudhury *et al*. 2007).

Effect of pH

The results of this study showed that the removal efficiency of hexavalent chromium is intensively pH-dependent. Using 1.5 $g.l^{-1}$ adsorbents, 5.0 $mg.l^{-1}$ initial concentration of Cr^{+6} and 60 min contact time, the maximum removal efficiency of 98.8 and 88.4% by the application of raw rice husk and its silica, were obtained at pH 2, respectively. However, at the same condition only by changing pH values, the removal efficiency decreased as the maximum RE at pH 7 reached up to 69.4 and 60.4, respectively. Unlike chromium, lead removal efficiency is not so pH-dependent. Using 1.5 $g.l^{-1}$ of the adsorbents, particle size = 0.5-1.0 mm, 5.0 $mg.l^{-1}$ initial concentration of lead and 60 min contact time, maximum removal efficiency of 69 and 97.4% were obtained by the application of raw rice husk and its silica, respectively at pH 6.

Therefore the removal efficiency did not

Change by changing pH values. Hasan *et al.* (2004) studied the removal of hexavalent chromium from aqueous solutions using agricultural waste 'maize bran'. They reported that the initial removal of hexavalent chromium increased by an increase in pH from 1.4 to 2.0, thereafter removal started to decrease by elevating pH from 2.0 to 8.5. This could be that since hexavalent chromium occurs in the form of oxyanions for example $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, etc. in acidic medium and the lowering of pH causes the surface of the adsorbent to be protonated to a higher amount, consequently a strong attraction exists between these oxyanions of hexavalent chromium and positively-charged surface of the adsorbent. Hence, the removal efficiency increases by a decrease in the pH of the aqueous (Hasan *et al.* 2008).

Demirbas *et al.* (2004) studied the removal of hexavalent chromium by three types of carbon at different pH levels at an initial concentration of 105 mg.l^{-1} and particle sizes of 1.0 to 1.25 mm. They reported that optimum removal efficiency was observed at pH 1.0. They also reported that the dominant form of hexavalent chromium at pH 2 is $HCrO_4^-$. Increasing in the pH will shift the concentration of $HCrO_4^-$ to other forms, $CrO_4^{2-}$and $Cr_2O_7^{2-}$.

The results of lead and hexavalent chromium removal efficiency using raw rice husk and its silica with different solution pH, 5.0 mg.l^{-1} initial concentration, 60 min contact time and 1.5 g.l^{-1} adsorbent dosages are shown in Fig. 3.

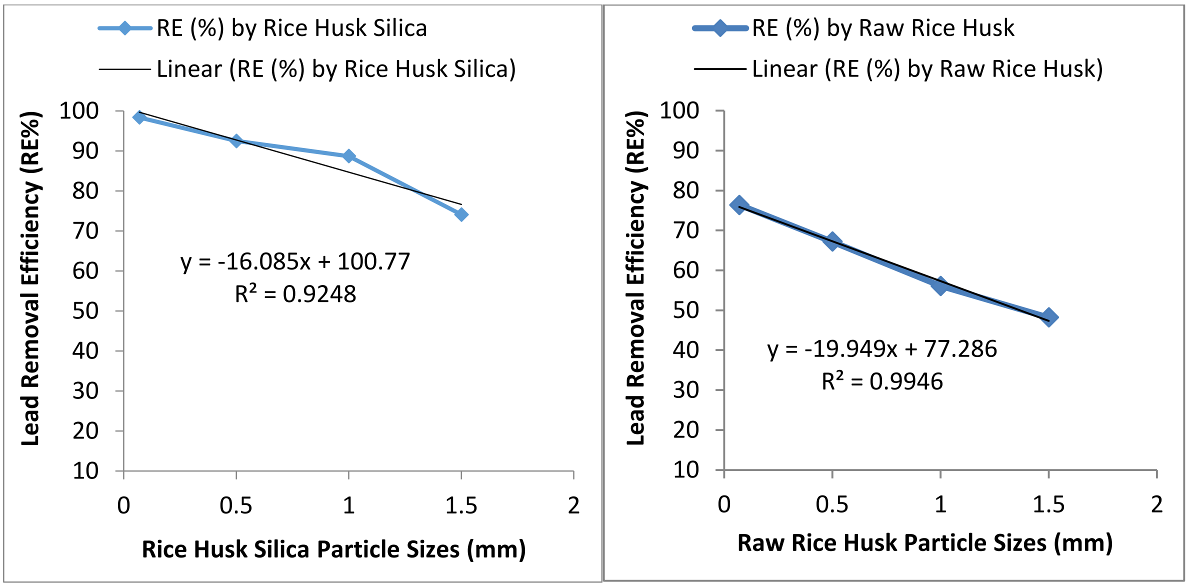


Fig. 2. The correlation between decreasing in particle sizes and lead removal efficiency at pH 6, adsorbents dosage of 1.5 g.l^{-1}, initial concentration of lead = 5 mg.l^{-1} and contact time of 60 min by the two adsorbents.

Effect of adsorbent morphology

Scanning electron microscope (SEM) shows the morphologic images of the raw rice husk and the silica derived from modified rice husk. It showed that when the rice husk goes under on acid leaching and incineration at high temperature, it reduces the crystallization of cells and increases its porosity. This phenomenon can thus increase the potential of adsorbents to remove environmental pollutants. Mehrasbi & Farahmandkia (2008) reported that modification of banana shell using acidic an alkaline agents results in increased porosity and surface area of the adsorbent (Mehrasbi & Farahmandkia, 2008). This result is also supported by Wang Ngah & Hanafiah (2008) who investigated the removal of the heavy metal ions from wastewater using chemically-modified plant wastes as adsorbents.

In order to compare the shape and pores of the raw rice husk with its silica, SEM images of rice husk silica with magnification of (a) 1000 and (b) 2000 are shown in Fig. 4 while the SEM images of raw rice husk with magnification of (c) 500 and (d) 1000 are shown in Fig. 5.

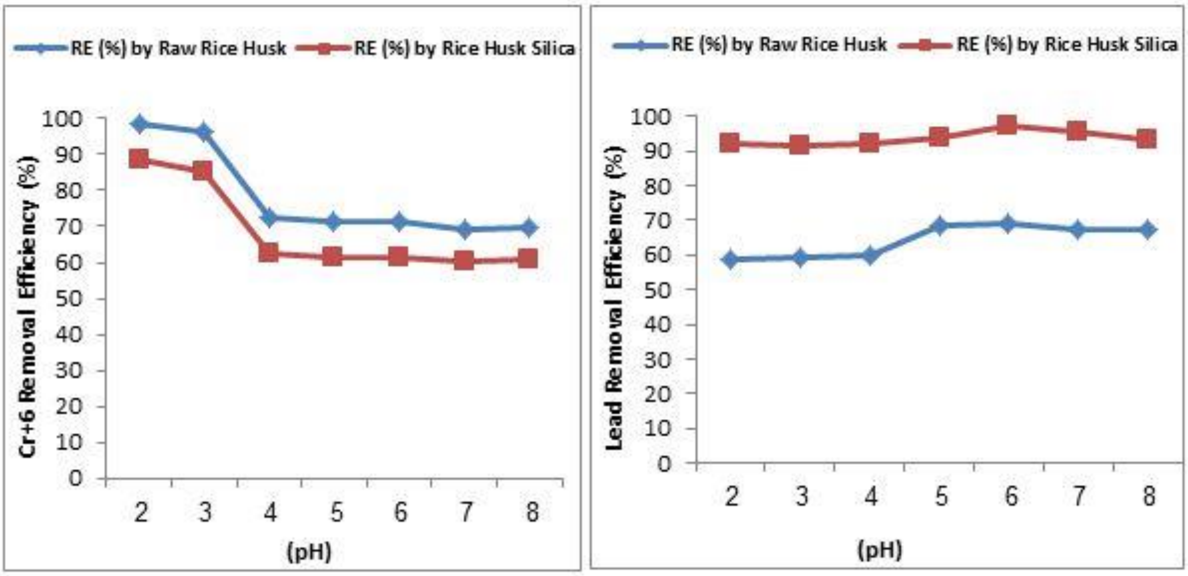
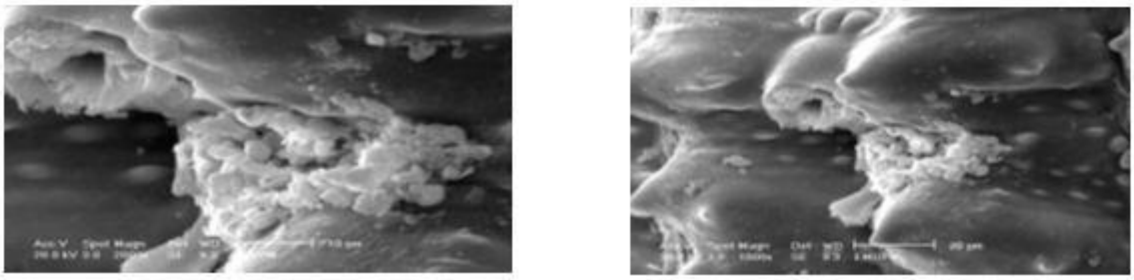
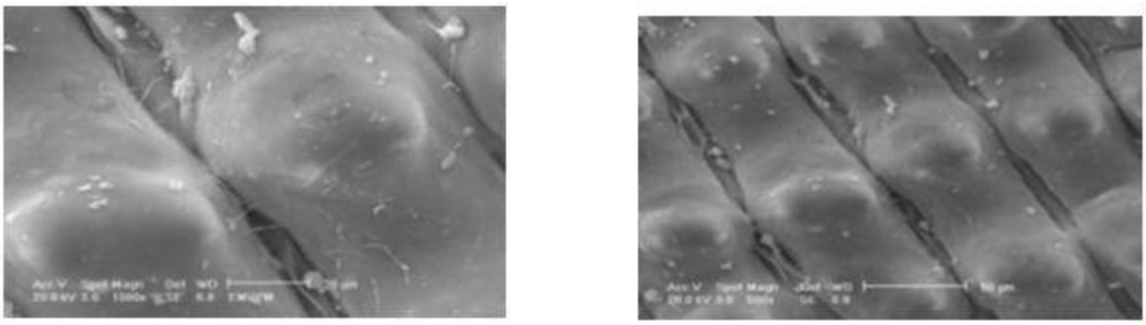


Fig. 3. Removal efficiency of lead and Cr^{+6} using raw rice husk and rice husk silica with different solution pH and 5.0 $mg.l^{-1}$ initial concentration, 60 min contact time and 1.5 $g.l^{-1}$ adsorbents dosage.



(a) (b)

Fig. 4. Scanning electron microscope (SEM) images of silica derived from raw rice husk with magnification of 1000 (a) and 2000 (b).



(c) (d)

Fig. 5. Scanning electron microscope (SEM) images of raw rice husk with magnification of 500 (c) and 1000 (d).

CONCLUSION

The results of this study showed that the removal efficiency of hexavalent chromium and lead from aqueous with the application of raw rice husk and its silica increase using smaller particle sized adsorbents. A strong positive significant correlation was observed between decreasing adsorbents particle sizes and lead removal efficiency.

According to the results of this study, acidic condition of aqueous for Cr^{+6} and neutral condition for lead, by increasing in adsorbents porosity and decreasing in adsorbents particle sizes result in elevation of the removal efficiency by the both adsorbents.

Competing interests

The authors declare that they have no competing interests.

ACKNOWLEDGEMENTS

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REFERENCES

Abdel-Ghani, NT, Hefny, M & El-Chaghaby, GAF 2007, Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science and Technology,* 4: 67-73.

Choudhury, TR, Pathan, KM, Nurul, Amin, M, Ali, M, Quraishi, SB & Mustafa, AI 2012, Adsorption of Cr (III) from aqueous solution by groundnut shell. *Journal of Environmental Science and Water Research,* 1: 144-150.

Demirbas, E, Kobya, M, Senturk, E & Ozkan, T 2004, Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA*, 30: 533-540.

El-Ashtoukhy, ESZ, Amin, NK & Abdelwahab, O 2008, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination,* 223: 162-173.

Ghaneian, M, Jamshidi, B, Amrollahi, M, Dehvari & M, Taghavi, M 2014, Application of biosorption process by pomegranate seed powder in the removal of hexavalent chromium from aquatic environment. *Koomesh,* 15: 206-211.

Gueu, S, yao, BA, douby, K & Ado, G 2007, Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree.*Journal of Environmental Sciences and Technology,* 4: 11-17.

Hasan, SH, Singh, KK, Prakash, O, Talat, M & Ho, YS 2008, Removal of Cr (VI) from aqueous solutions using agricultural waste 'maize bran. *Journal of Hazardous Materials,* 152: 356–365.

Jamwal, RS & Mantri, S 2007, Utilization of rice husk for derivation chemicals, extracts from *Nandini Chemical Journal*, http://www. nandinichemical.com/ 2007 febjournal.html.

Kafia, M, Surci, S 2012, Agricultural wastes as low cost adsorbent for Pb removal: kinetic, equilibrium and thermodynamics. *International Journal of Chemistry,* 3: 103-112.

Khazaei, I, Aliabadi, M, Hamed & Mosavian, HT 2011, Use of agricultural waste for removal of Cr (VI) from aqueous solution. *Iranian Journal of Chemical Engineering,* 8: 11-23.

Kobya, M, Demirbas, E, Senturk, E & Ince, M 2004, Adsorption of heavy metals ions from aqueous solutions by activated carbon prepared from apricot stone, *Bioresource Technology,* 96: 1518-1521.

Koop, G, McKitrick, R & Tole, L 2010, Air pollution, economic activity and respiratory illness: evidence from Canadian cities, 1974–1994. *Environmental Modeling and Software,* 25: 873–885.

Mahvi, AH, Bita, B & Saeidi, A 2002, Heavy metal removal from industrial effluents by natural fibers. *Water and Wastewater,* 43: 2-5.

Massoudinejad, MR, Manshouri, M, Khatibi, M, Adibzadeh, A & Amini, H 2008, Hydrogen sulfide removal by *Thiobacillus thioparus* bacteria on seashell bed biofilters. *Pakistan Journal of Biological Sciences,* 11: 920-924.

Mehdinia, SM 2011, Removal of hydrogen sulfide by physico - biological filteration system, using mixed rice husk silica and dried activated sludge. PhD Dissertation, University Putra Malaysia, 14.

Mehdinia, SM, Abdul, Latif, P, Makmom, Abdullah, A & Taghipour, H 2011, Synthesize and characterization of rice husk silica to remove the hydrogen sulfide through the physical filtration system. *Asian Journal of Scientific Research,* 4: 246-254.

Mehdinia, SM, Abdul-Latif, P & Taghipour, H 2013, Removal of hydrogen sulfide by physico biological filter, using mixed rice husk silica and dried activated sludge. *Clean Soil, Air, Water*, 41: 949-954.

Mehdinia, SM, Moeinian, Kh & Rastgoo, T 4014, Rice husk silica adsorption for removal of hexavalent chromium pollution from aquatic solutions. *Iranica Journal of Energy & Environment,* 5: 218-23.

Mehrasbi, MR & Farahmandkia, Z 2008, Heavy metal removal from aqueous solution by adsorption on modified banana shell. *Iranian Journal of Health and Environment,* 1: 57-66.

Mohseni, SN, Amooey, AA, Tashakkorian, H & Amouei, AI 2016, Removal of dexamethasone from aqueous solutions using modified clinoptilolite zeolite (equilibrium and kinetic), *International Journal of Environmental Science* and *Technology,* 13: 2261- 2268.

Montazeri, N, Baher, E, Barami, Z & Ghochi-Baygi, M 2009, Kiwi Role in Eliminating Environmental Pollution and Its Affecting Factors. *Journal of Sciences and Techniques in Natural Resources,* 5: 118-128.

Munaf, E & Zein R 1997, The use of rice husk for removal of toxic metals from wastewater. Environmental Technology, 18: 359-362.

Ros, A, Montes-Moran, MA, Fuente, E, Nevskaia, DM & Martin, MJ 2006, Dried sludge and sludge-based chars for H_2S removal at low temperature: influence of sewage sludge characteristic. *Environmental Science* and *Technology,* 40: 302-309.

Salari, B & Shahmohammadi, M 2012, Examination of kinetic the removal of nickel from aqueous solutions by Rafsanjan pistachio shells. *Journal of Environmental Studies,* 60: 149-156.

Shamohammadi, Z, Moazed, H, Jaafarzadeh, N & Haghighatju, P 2008, Removal of low concentrations of cadmium from water using improved rice husk. *Water and Wastewater,* 67: 27-33.

Souag, R, Touaibia, D, Benayada, B & Boucenna, A 2009, Adsorption of heavy metals (Cd, Zn and Pb) from water using keratin powder prepared from Algerian sheep hoofs. *European Journal of Scientific Research,* 35: 416-425.

Wan, Ngah, WS, Hanafiah, MA 2008, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology*, 99: 3935-3948.

Wong, KK, Lee, CK, Low, KS, Haron, MJ 2003, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere,* 50: 23-28.

بررسی تاثیر pH، اندازه ذرات و تخلخل شلتوک خام برنج و سیلیکای حاصل از آن در حذف کروم شش ظرفیتی و سرب از محلول‌های آبی

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چکیده

خصوصیات مواد جاذب و ویژگی‌های محلول پارامترهای بسیار مهمی در کارایی حذف آلاینده‌های زیست محیطی می‌باشند. هدف این مطالعه بررسی تاثیر pH، اندازه ذرات و تخلخل شلتوک خام و سیلیکای حاصل از آن در حذف سرب و کروم شش ظرفیتی از محیط‌های آبی بوده است. شلتوک خام از منطقه شمال ایران جمع‌آوری گردید و سیلیکای شلتوک برنج پس از مرحله اسید شویی و احتراق در دمای ۸۰۰ درجه سانتی گراد در کوره تهیه گردید. تاثیر اندازه ذرات جاذب (۰/۰۷- ۰/۱،۰/۱- ۰/۵، ۰/۵-۱/۰ و ۱/۰-۱/۵میلی متر)، تخلخل و pH محلول از ۲ تا ۸ مورد مطالعه قرار گرفت. در این تحقیق هریک از متغیرها با ثابت در نظر گرفتن سایر پارامترها (جرم مواد جاذب ۱/۵ گرم در لیتر، مدت زمان تماس ۶۰ دقیقه و غلظت اولیه سرب و کروم برابر با ۵ میلی‌گرم درلیتر) مورد بررسی قرار گرفتند. نتایج این تحقیق نشان داده است که راندمان حذف کروم شش ظرفیتی به شدت به pH وابسته می‌باشد. با کاربرد ۱/۵ گرم در لیتر مواد جاذب، با اندازه ذرات ۰/۵-۱/۰ میلی‌متر، ۵/۰ ، با غلظت اولیه ۵/۰ میلی‌گرم در لیتر کروم شش ظرفیتی و در زمان ماند ۶۰ دقیقه، راندمان حذف برای شلتوک خام و سیلیکای حاصل از آن به ترتیب برابر با ۹۸/۸ و ۸۸/۴ درصد در pH حاصل گردید، در حالیکه در شرایط مشابه با تغییر pH به ۷ راندمان حذف به ترتیب به ۶۹/۴ و ۶۰/۴ کاهش یافت. همچنین مطالعه حاضر نشان داده است که یک همبستگی مثبت و قوی بین کاهش اندازه ذرات مواد جاذب و افزایش راندمان حذف سرب وجود دارد ($P < 0.01$). بررسی میکروسکوپ الکترونی مواد جاذب نشان داده است که سیلیکای حاصل از شلتوک برنج دارای میزان تخلخل بیشتری نسبت به شلتوک خام می‌باشد. مطالعه حاضر نشان داده است که شرایط اسیدی محیط‌های آبی برای حذف کروم شش ظرفیتی و شرایط خنثی برای حذف سرب، افزایش میزان تخلخل مواد جاذب و کاهش اندازه ذرات مواد جاذب باعث افزایش راندمان حذف این دو آلاینده می‌گردند.

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