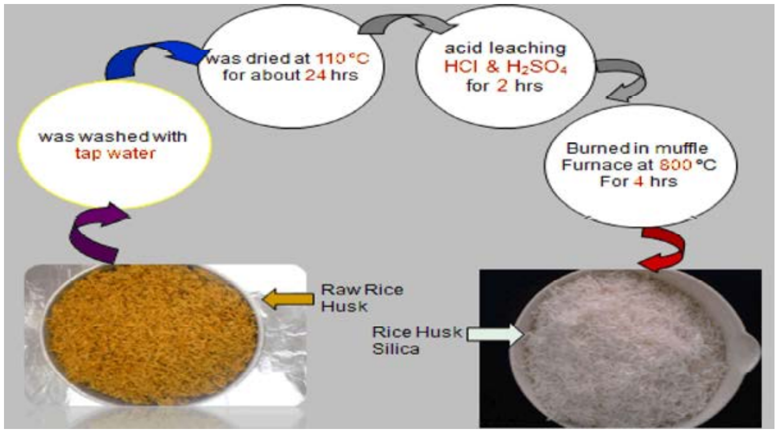


Fig. 1: A schematic process to preparation of silica from raw rice husk

MATERIALS AND METHODS

The batch removal of Cr^{+6} from aqueous solution using three low-cost adsorbents: raw rice husk, rice bran and rice husk silica under different experimental conditions were investigated. The raw rice husk and rice bran was collected from North of Iran and the rice husk silica was prepared according to the method proposed by Jamwal and Mantri [20]. Base on this method, the raw rice husk was first washed with tap water to remove the contaminants and then it was dried in an oven at 110°C for 24 hrs. After that, it was subjected to acid leaching by refluxing it in 3% (v/v) chloridric acid (HCL) and 10% (v/v) sulphuric acid (H_2SO_4) for 2 hours and at a ratio of 50 g husk/L. The husk was thoroughly washed with distilled water and then dried in an air oven at 100°C. Finally, it was burned inside a muffle furnace at temperature of 800°C for 4 hours in static air. A schematic process to preparation of silica from raw rice husk is showed in Figure (1).

In this study, the effects of four parameters: contact time (30, 45, 60, 75 and 90 min), pH values (2, 3, 4, 5, 6, 7, 8 and 9), adsorbents dosages (0.5, 1.0 and 1.5 g/L) and initial concentration of Cr^{+6} (1.0, 5, 10 and 15 mg/L) were investigated by varying any of the process parameters and keeping the other parameters constant. The experiments were carried out in batch reactors and at room temperature of 25±2°C. The synthetic solution containing chromium was ready by dissolving the known amount of analytical-grade potassium dichromate in distilled water. The concentrations of chromium were measured using a standard method of atomic adsorption. The Eq. (1) was used to determination of removal efficiency:

$$RE(\%) = \frac{(C_0 - C)}{C_0} \times 100$$

where RE is the removal efficiency (%), C_o and C are the inlet and outlet concentration of hexavalent chromium (mg/L) [21-24].

RESULTS AND DISCUSSION

The physico-chemical characteristics of the adsorbents showed that carbon is the highest element percentage of the CHN analysis in the raw rice husk, but the silica derived from rice husk showed a high percentage of SiO_2 up to 94.24%. Some of the important physico-chemical characteristics of the rice husk silica and raw rice husk used in this study are summarized in Table 1.

The Scanning Electron Microscope (SEM) of the adsorbents showed that, when the raw rice husk goes under on the acid leaching and combustion processes at high temperature, it reduces the crystallization cells and increases its porosity. This issue can increase the adsorption rate of the adsorbents (Figure 2).

For the investigation of the effect of pH, hexavalent chromium removal experiments at various values of pH 2, 3, 4, 5, 6, 7, 8 and 9 while keeping the other parameters constant (initial concentration of hexavalent chromium = 5.0 mg/L, adsorbents dosage = 1.0 g/L and contact time = 60 min) were studied. The results of removal efficiency of hexavalent chromium at different values of pH by the three adsorbents are shown in Figure 3.

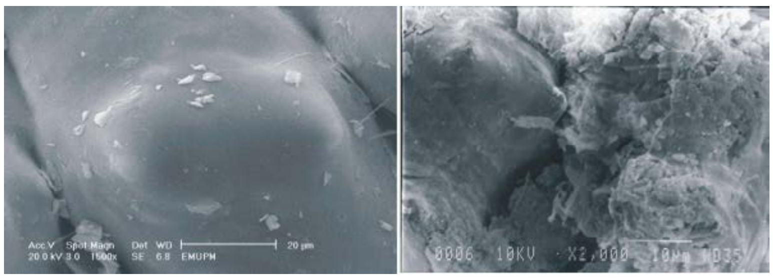
The removal efficiency of Cr^{+6} at different contact times (30, 45, 60, 75 and 90 min), pH=2, adsorbents dosage = 1.0 g/L, initial concentration of Cr^{+6} = 5.0 mg/L by the three adsorbents is shown in Figure 4.

Effects of the adsorbents dosages (0.5, 1.0 and 1.5 g/L) on removal efficiency of hexavalent chromium at pH = 2, initial concentration of hexavalent chromium = 5.0 mg/L and contact time = 60 min are shown in Figure 5.

Table 1: Some of the important physico-chemical properties of the rice husk silica and raw rice husk used in this study

Raw Rice Husk			Rice Husk Silica		
Physico-chemical characteristics	Unit	Value	Physico-chemical characteristics	Unit	Value
Density	(g/L)	93.3	Density	(g/L)	44.5
pH	-	6.7	pH	-	7.5
C	(%)	35.92	C	(%)	0.09
H	(%)	4.84	H	(%)	0.16
N	(%)	0.42	N	(%)	0.14
SiO_2	(%)	NM*	SiO_2	(%)	94.24

NM* = not measured



a) Raw rice husk b) Rice husk silica

Fig. 2: Scanning Electron Microscope (SEM), a) raw rice husk and b) rice husk silica

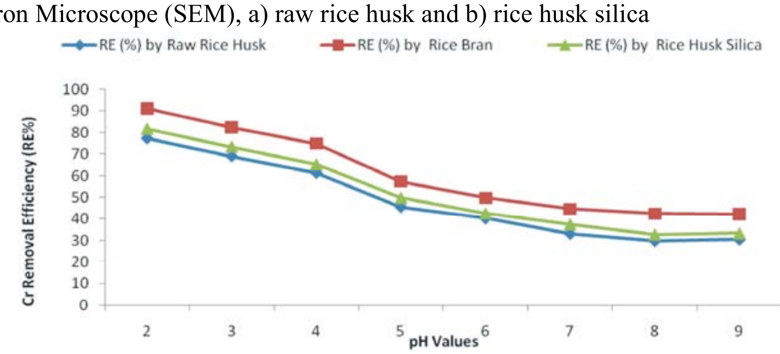


Fig. 3: Cr^{+6} removal efficiency by raw rice husk, rice bran and rice husk silica at variable pH values, adsorbents dosage of 1.0 g/L, 5.0 mg/L initial concentration of Cr^{+6} and 60 min of contact time.

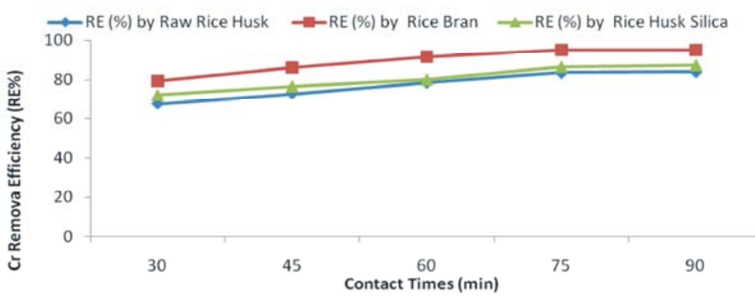


Fig. 4: Removal efficiency of $Cr^{+6}$with variable contact times at pH = 2, adsorbent dosage = 1.0 g/L and initial concentration = 5.0 mg/L by three adsorbents.

In addition, in this research the correlation between increasing of initial concentration of Cr^{+6} and removal efficiency was studied using the Pearson correlation analysis. For this purpose the correlation between increasing of initial concentration of Cr^{+6} (1, 5, 10 and 15 mg/L) at pH = 2, adsorbents dosage = 1.0 g/L and contact time = 60 min were studied. The results are illustrated in Figure 6.

The experimental data were also fitted using two adsorption models including Freundlich and Longmuir. The constants coefficients for Freundlich and Langmuir adsorption isothermsare summarized in Table 2.

The value of media pH is very important to remove Cr^{+6}, which is the toxic type of chromium. The result of this study showed that the adsorption of hexavalent chromium is highly pH-dependent and the best pH for

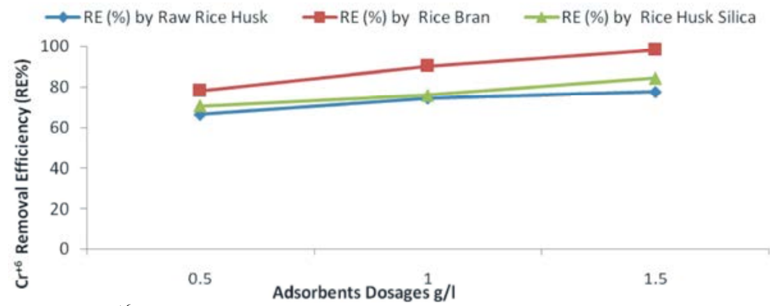


Fig. 5: Removal efficiency of Cr^{+6} with different dosages of the adsorbents at pH = 2, initial concentration of Cr^{+6} = 5.0 mg/L and contact time = 60 min by the three adsorbents.

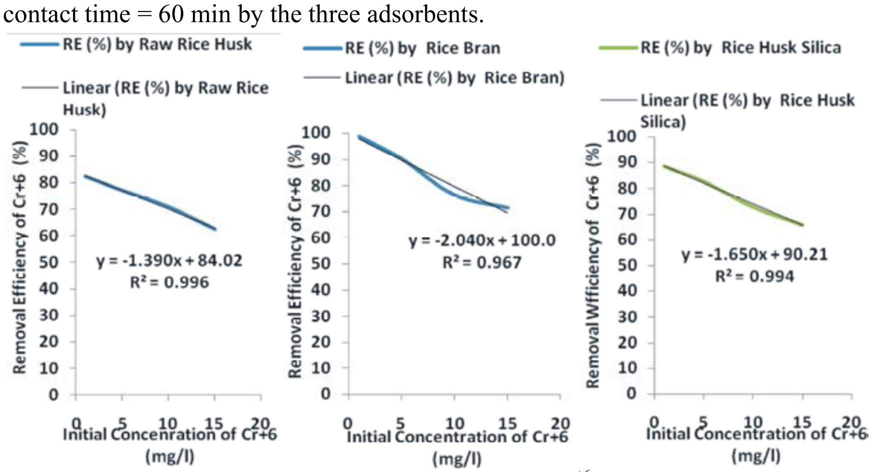


Fig. 6: The correlation between increasing of initial concentration of Cr^{+6} and removal efficiency at pH = 2, adsorbents dosage of 1.0 g/L and contact time of 60 min by the three adsorbents.

Table 2: Constants coefficients for Freundlich and Langmuir adsorption isotherms

	Langmuir Coefficients			*Freundlich Coefficients*		
Adsorbents	q_{max}(mg/g)	b (l/mg)	R^2	K (mg/g)	n	R^2
Raw rice husk	*13.30*	*0.38*	*0.9978*	*3.87*	*1.39*	*0.9865*
Rice bran	*7.13*	*16.28*	*0.9884*	*5.85*	*2.60*	*0.9966*
Rice husk silica	*9.18*	*0.98*	*0.9386*	*3.82*	*1.57*	*0.9801*

q_{max} = Amount adsorbed on the surface; b = Isotherm constant; K, n = Isotherm constants

the removal of hexavalent chromium was found to be acidic condition at pH value of 2 for the three adsorbents. This result is in agreement with reported data by Khazaei *et al*. [14] which showed the optimum initial pH was observed at pH = 2.0 to remove hexavalent chromium using agricultural waste. Demirbas *et al*. [8] reported an optimum pH of 1.0 for adsorption of hexavalent chromium ions from aqueous solutions using activated carbons prepared from agricultural wastes. However to remove cadmium, zinc and lead, Kafika *et al*. [16] have reported an increasing of heavy metals adsorption with increasing of pH.

In this study, the maximum removal efficiency of hexavalent chromium was obtained by rice bran up to 98.8% at 5.0 mg/L initial concentration of hexavalent chromiun, 60 min of contact time, pH = 2 and adsorbents dosage of 1.0 g/L. However, at the same condition the maximum removal efficiency by raw rice husk and rice husk silica obtained 82.3 and 88.4%, respectively. A removal efficiency of hexavalent chromium up to 42% with 30 min contact time using activated carbon derived from rice husk was obtained. However, a maximum removal efficiency of hexavalent chromium up to 61% with 180 min contact time was reported[25]. Moreover, a negative strong significant correlation between increasing of initial concentration of hexavalent chromium and removal efficiency was detected by the three adsorbents ($p<0.01$). Khazaie *et al*. [14] reported a decreasing removal adsorption of hexavalent chromium with increasing of initial concentration. They pointed out that "at low concentrations the ratio of available surface to initial hexavalent chromium is larger; therefore, the removal becomes independent of initial concentrations. However, in the case of higher concentrations this ratio is low; the percentage removal then depends upon the initial concentration" [14].

CONCLUSION

Based on obtained results, raw rice husk and adsorbents prepared from it such as rice bran and rice husk silica could be considered as effective and inexpensive adsorbents for the removal of hexavalent chromium from aquatic solutions. High removal efficiency, easy and inexpensive way to preparation of the adsorbents from raw rice husk could be the advantages of their application in removal of heavy metals.

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