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Using Modified Concrete for Removing Chromium From Wastewater

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Abstract

Background: Annual large amounts of wastewater can be entered into the environment from domestic, agricultural, and industrial sources that contain high concentrations of chemical materials and heavy metals. Chromium (Cr) is one of the most important environmental pollutants, which can cause pollution of water resources and disorder in the metabolic activities of living organisms.
Objectives: In this study, we used the alteration in the concrete structure by iron oxide nanoparticles and rice husk ash (RHA) to remove Cr as a heavy metal from sewage.
Methods: Rice husk ash was used in the structure of concrete as a forty percent by cement weight. Samples were made according to sewage condition and concrete required strength of purification pools. Samples' surface was covered with nanoparticle, RHA, RHA and nanoparticle. Different sewage concentrations of Cr were made from the range of 1 to 1000 ppm. The effects of parameters, such as contact time, adsorbent dose, pH, concentration of Cr in sewage, and Cr absorption were examined.
Results: The maximum absorption was obtained 99.7%, in the contact time of 6 hours, dose of adsorbent 20 mg/L, pH 3, and Cr concentration in sewage 10 ppm at the laboratory temperature. Cr absorption followed the Freundlich model of adsorption.
Conclusions: The combination of nanoparticles and RHA showed well efficiency for Cr absorption from sewage.

Keywords: Concrete, Iron Oxide Nanoparticles, Surface Adsorbent, Rice Husk Ash, Chromium (+6)

1. Background

The existence of heavy metals in sewage is one of the major reasons of water pollution (1). Some heavy metals are toxic such as mercury, lead, cadmium, copper, chromium (Cr) and nickel even in small quantities (2-4). Chromium can be produced from industrial processes such as the leather tanning process, metalworking, manufacturing paints and paper. Mainly there are two valences of Chrome, III and VI (5). Many methods have been reported for restoration and removal of Cr from the aqueous phase such as physical, chemical and biological methods in which the filtration, adsorption, reverse osmosis, ion exchange, electro-dialysis, chemical precipitation and biological absorption were noted (6-8). The US environmental protection agency standard limit has determined that the hexavalent Cr in surface water was 0.1 mg/L and for drinking water 0.05 mg/L (9). Effect of different parameters such as an initial concentration of Cr and nickel, pH, contact time, amount of nanoparticles and temperature has been studied by Akhbarizade et al. (9, 10). An absorption rate decreased with increasing concentration, amount of adsorbent, contact time and temperature. This study showed that by increasing the contact time the absorption was increased due to the increased risk of pollutant contact with the surface adsorbent. The absorption rate was high in the early times, but decreased over time, which indicates that the reaction has reached equilibrium. Results in the study of Singh et al. (2008) on removing Cr (VI) by using iron zero-valent nanoparticles showed that by increasing the contact time between the absorber and Cr (VI), the removal efficiency was increased (11). The results showed that the Cr removal rate increased with decreasing pH due to the increase in $Hcro_4^-$ and Cro_4^{2-} ions that increase the ions in the environment, and Cr can be absorbed more easily. Hu et al. in other study achieved similar results (12). The maximum absorption rate was achieved in the initial concentration of 50 mg/L, the amount of adsorbent 0.15 g at 70°C and pH 2.6. Samarghandi et al. studied the decreasing efficiency of Cr (VI) with increasing pH at constant conditions from 57.65% to 30.63% and from 79.5 %to 68.67%, respectively in aerobic and anaerobic conditions (13, 14).

2. Objectives

This study aimed to evaluate the absorption of Cr from aqueous solution by iron nanoparticles and RHA and determine the effect of the adsorbent concentration, initial concentration of Cr, pH, and contact time, and finally to determine the suitable adsorption isotherm.

3. Methods

3.1. The Method of Preparing Samples

In this study, we used gravel with an average size of 19 mm, sand 0 - 5 mm, Portland cement type 2 and RHA that is shown in (Table 1). Active carbon was used due to its adsorbent properties for Cr (+ 6) (15). Portland cement type 2 used according to definition of the type of sample use for municipal wastewater treatment, has good resistance because the cement was constantly exposed to moisture and frost (16). Concrete adhesive solution was used for installing nanoparticles on the surface.

Diameter and height of the mold concrete were 16 and 3cm, respectively. According to the equation (1) the amount of materials presented in Table 2:

Concrete volume = $V = \pi r^2 \times H = 0.0006\ m^3$

Table 3 shows the species of molds, which have been made.

3.2. Nanoparticles

Nanoparticles of Fe2O3 by specifications: SSA > 30 m^2/g, APS < 30 nm, and purity 99%. Appearance Red powder was also used.

3.3. The Method of Adsorbent Preparation

The best and most economic temperature was also suitable for the production of ash, homogeneous, with maximum activity and high quality rice husk were conducted when the ash was grind and used in concrete (17). Nanoparticles on the surface of the samples were used in the form of solution. The nanoparticle solution was poured on surface coated with glue. This method, due to economic justification as well as the homogeneous distribution of nanoparticles was considered the optimal method.

3.4. Experimental Method

Synthetic sewage was made by dissolving Cr in water with 10 ppm concentration and was poured on each 4 type's sample (with husk ash, with nanoparticles, without absorber, with husk ash and nanoparticles). pH of the solution was prepared by hydrochloric acid 2 M and NaOH 2 M at different intervals. The amounts of sewage chromium were measured by atomic absorption. The removal rate was calculated according to the equation (2) and the optimal values for the best removal were obtained.

$R = 100 \times (C_0 - C_e) / C_0$

That C_0 and C_e were the initial and final concentrations of Cr, respectively.

4. Results

In this study, Cr removal from wastewater by using concrete modified with nanoparticles of iron oxide and RHA was investigated. The 8 molds (Table 3) was dipped in sewage and remained for 6 hours (according to the contact time in an equilibrium tank).

The results of the current study showed that the sample number 4 had a higher absorption. Then, it was selected for the rest of the experiments.

4.1. Determination of the Optimum Parameters

Firstly, the optimum pH was found. For this purpose, pH 3, 5, 7.5 and 9 were selected for the sample number 4. The optimum pH happened in pH 3 (the other parameters were fixed, such as the contact time of 6 hours, and Cr concentration of 10 mg/L).

The removal rate of 99.7% was achieved for 10 mg/L initial concentration of Cr by considering the optimum of other parameters.

4.2. Adsorption Isotherm

One of the important studies of the adsorption process is the study of the absorption kinetics. Because in the study of absorption kinetics, the mechanisms of absorption have shown with time (18, 19). Table 4 shows Langmuir and Freundlich models' parameters at different concentrations. The results showed that the Freundlich model was better for this kinetic.

5. Discussion

Studies on the laboratory scale showed that the concrete serve as the most widely used building material and as the main materials in water and waste treatment can be a suitable surface for coating iron nanoparticles. Using concrete adhesive as one of the simple and low cost methods compared to other coating processes can be helpful combined with concrete to stabilize the nanoparticles in a long time. The combination of nanoparticles and husk showed well efficiency for Cr absorption. Results of this study showed that by increasing the concentration of Cr from 50 to 100 ppm, the removal rate was decreased. Ghanizadeh et al. showed that the Cr (VI) removal efficiency reduced with increase in the initial concentration of pollutant (20). Owlad et al. found that in Cr removal by activated carbon that increases the initial concentration of Cr led to the saturation of the active sites of absorption and increasing the concentration of pollutants which could lead to a decrease in absorption amount of it (21). This study showed that by increasing the contact time, the absorption was increased (22) due to the increased risk of pollutant contact with the surface adsorbent. The absorption rate was high in the early times, but decreases over time, which indicates that the reaction has reached equilibrium. Results of the Singh et al. study (2008) on removing Cr (VI) by using zero-valent iron nanoparticles showed that by increasing the contact time between the absorber and Cr (VI), the

Table 1. Concrete Mix Design

Materials	Concrete Density (Kg/m^3)	Water (L/m^3)	Sand (Kg/m^3)	Gravel 19 mm (Kg/m^3)	Cement (Kg/m^3)
Amount of weight	2345	190	902	1012	312

Table 2. Amount of Materials Weight for a Mold

Materials	Required Surface, Sample one Side Area (m^2)	Water (L)	Sand (Kg)	Gravel 19 mm (Kg)	Cement (Kg)
Amount of weight	0.02	0.12	0.54	0.61	0.19

Table 3. Species of Molds

Mold Number	Specie of Mold
1	Concrete made by RHA and 30 mg/L nanoparticle concentration
2	Concrete made by 30 mg/L nanoparticle concentration
3	Concrete made by 20 mg/L nanoparticle concentration
4	Concrete made by RHA and 20 mg/L nanoparticle concentration
5	Concrete made by 40 mg/L nanoparticle concentration
6	Concrete made by RHA and 40 mg/L nanoparticle concentration
7	Concrete without adsorbent
8	Concrete made by RHA

Table 4. Freundlich and Langmuir Adsorption Isotherms

Isoterm	Parameters	
	q_{max} (mg/g)	R^2
Freundlich	2.489	0.9996
Langmuir	3.225	0.9857

removal efficiency was increased (11). The results showed that the removal rate increased with decreasing pH due to increased Hcro4- and Cro_4^{2-} ions that increase the ions in the environment, and it can cause the easier absorption. Hu et al. in other study achieved similar results (12). In comparison with other studies conducted in this field, the findings of the current study show that the optimal condition is an acidic environment in which the removal efficiency increases significantly. Also, Freundlich and Langmuir isotherm models are the most appropriate models to demonstrate the adsorption mechanism (23). In a study by S. Hashemian Ghahfarokhi et al. (2012), similar results were obtained (24). It seems that the equilibrium tank that is used in sewage and industrial wastewater treatment using concrete modified by nanoparticles of Fe_2O_3 and RHA can be suggested as a suitable solution for removing heavy metals such as Cr.

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Footnotes

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