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MODIFIED CONCRETE ABILITY FOR REMOVING CADMIUM (II) FROM WASTEWATER

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Abstract

Cadmium is found in high concentrations in industrial wastewater. In this study, using two adsorbent in concrete has been discussed. The solutions of iron nanoparticle as the first absorbent have been used in amounts of 20, 30 and 40 mg/l. The rice husk as the second adsorbent was converted to rice husk ash in 500 to 650 ^{oC}. The rice husk ash mixed to 40% by weight of cement in the concrete structure. Samples, with nanoparticle, with rice husk, and combination nanoparticles and rice husk, were constructed. The samples under the different conditions such as pH, contact time, concentration of absorbent and cadmium concentrations in solution were examined. The maximum absorption 97.5% could be occurred in optimum contact time 6 hours, absorbent concentration 40 mg /l, the optimum pH 3 and wastewater concentration 10 ppm. To remove cadmium, modified concrete can be suggested as new and efficient method.

Keywords: *Cadmium (II), concrete, iron nanoparticle, rice husk.*

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Introduction

Any impurities in groundwater and surface water that are harmful to living organisms, is called water pollution (Hart, 2004). In scientific reports, many cases of poisonings due to the various metals such as lead, mercury, cadmium, chromium, etc. which should be an important warning for control pollution industries, be considered (IPCS, 1991; Niyaz Zade and Samnar Sha, 1986). Cadmium is a one of hazardous and toxic environmental pollutant. Much of cadmium from electroplating operations enters into the aqueous environment. Various methods used for removing heavy metal ions from aqueous solution include chemical precipitation (Mandal, 2008), electrochemical methods (Alvarez-Ayuso et al, 2007), membrane processes (Yang et al., 2005), solvent extraction (Mandal and Mayadevi, 2008), adsorption (Ramos-Ramirez et al., 2009) and Biological methods (Mohan and Singh, 2002; Özcan and Özcan., 2004; Pehlivan and Arslan., 2007). Most methods are particularly reliable but require high installation cost and time .Adsorption, which is a more sophisticated technique, allowing the recovery of metallic ions, though is sometimes more expensive than other techniques. Studies on treatment of effluents containing heavy metals have showed that adsorption to be a highly effective technique for removing heavy metals from aqueous solutions. Moreover, adsorption is more economic process,

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simple to design and easy to operate (Wei et al., 2009).In recent years, various adsorbent have been used for removal of cadmium (Π) from aqueous solutions. A number of adsorbent materials such as zeolites (Bruna et al, 2009), activated carbon (Babel and Kurniawan, 2004), kaolinite (Mor et al, 2007) and nano adsorbent has been used in heavy metal removal from aqueous solutions. In this study iron oxide nanoparticles have been used as adsorbent. Iron oxide nanoparticles were chosen between the metal nanoparticles because; they are inexpensive, non-toxic, fast response and high ability to absorb heavy metals from wastewater (Kanel et al, 2005). Magnetic iron nano particles, using the mechanism of adsorption, ion exchange and electrostatic forces can be controlled and used to remove heavy metals from aqueous solutions. Adsorption characteristics of used cement for phosphorus removal from wastewater have been researched. Actually, using cement was chosen as the experimental material, and the effects of main influencing factors, such as dosage, temperature, pH and vibration time, on phosphorus adsorption characteristics were evaluated (Yanran et al, 2013). Immobilization mechanisms of Cr and Pb studied in cement solidified municipal solid waste incineration fly ash. The objective of this study is to investigate the mechanisms of solidification/stabilization on municipal solid waste incinerator (MSWI) fly ash using cement. (Yan et al, 2013). The mechanical properties rice husk ash concrete irrigation channels have been investigated in environments containing sulfated, studies conducted in the field of modified concrete. The results of tests on cubic samples with dimensions of 70 mm and cylindrical samples with a diameter of 50.8 and 101.6 mm height, Which were kept at 180 day in the different solutions it showed that in concrete samples with different percentages of rice husk alternative, the process compressive strength, tensile strength and concrete durability in sulfate environments slope is faster more than control samples (Abedi and Fathi, 2004). Liu studied about coating Fe_3O_4 Magnetic Nanoparticles with humic acid for high efficient removal of heavy metals in water. Sorption of the heavy metals to Fe_3O_4/HA reached equilibrium in less than 15 min, and agreed well to the langmuir adsorption model with maximum adsorption capacities from 46.3 to 97.7 mg/g. The Fe_3O_4/HA was able removed over 99% of Hg(II) and Pb (II) and over 95% of Cu (II) and Cd (II) in natural and tap water at optimized pH (Liu et al , 2008). The aim of this research was to use of absorbent materials (iron oxide nanoparticle and rice husk ash) to remove cadmium from the wastewater in discontinuous system. The impacts of important factors such as pH, initial concentration, amount of adsorbent and contact time on Cadmium removal process, were investigated. Other objectives of this study prepared samples concrete, by which can be operation wastewater treatment performed in a short time.

Materials and methods

Method of preparing the sample

In this research used gravel with an average size of 19 mm, sand 0-5 mm, Portland cement type 2 and ACRA (Table 1). The main aim of using active carbon is adsorbent properties for Cadmium.

Concrete density	Water	Sand	Gravel 19 mm	Cement	Materials
Kg/m^3	L/m^3	Kg/m^3	Kg/m^3	Kg/m^3	
2345	190	902	1012	312	amount of weight

Table 1 *Mixing ratio by weight values in m^3.*

Portland cement type 2 used according to definition of the type of use sample for municipal wastewater treatment, is good resistance that the cement in terms of exposure to moisture and frost constantly. Concrete adhesive solution has been used for installing nanoparticles on the surface. Then mold with diameter 16 cm and concrete height 3 cm has been made. The species of different samples have been numbered: number1, 2, 3 including the rice husk and nanoparticle with concentration of 40, 30 and 20 mg/l, respectively. The samples including nanoparticle with concentration of 40, 30 and 20mg/l has been named number 4, 5 and 6. The sample number 7 had rice ash and number 8 was without sorbents. Iron nanoparticle with this properties: Appearance = Red powder, SSA = >30m^2/g , APS <30nm, purity = 99%,.Nano powder=Fe_2O_3 has been used. All materials were Merk. Rice husk from local factories around the city of Shiraz was prepared. Then, rice husk was cremated by furnace in the optimum temperature of 500 to 650 °C and in time 2 hours. For the production of adhesive solution, initially the cross-section of sample was calculated. Amount of adhesive solution by 20cc were obtained for each, after pouring solution of adhesive on the surface of concrete sample, this solution was dried for 1 to 2 minutes at in the laboratory temperature.

Experiments

Samples were prepared with different concentrations of nanoparticle synthetic wastewater that made by dissolving cadmium in water with concentration of 10 ppm. Then, this wastewater on the samples (samples with nanoparticle, the rice husk, the rice husk and nanoparticle and without sorbents) was poured, and for different contact times were in conditions of laboratory the amount of wastewater created as standard control samples were considered. A portion of the produced artificial sewage solution was also kept as a standard control sample. pH of the solution is determined by the pH meter model PHS-3F and profit (2 molar) and chloridric acid (2 molar) were prepared at different pH. At the end of the first and final amount of the cadmium concentration was measured by atomic absorption (SensAA atomic absorption spectrometer made in Australia equipped with deuterium lamp to correct sample adsorption, and cadmium cathode lamp to measure adsorption by air-acetylene flame).
The removal rate calculated and was obtained optimum amounts; the removal rate according to equation [1] was obtained:

$$\mathbf{R} = \frac{(\mathbf{C_0} - \mathbf{C_e})}{\mathbf{C_0}} \times 100 \qquad [1]$$

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where, **R** is the percent removal, C_0 initial concentration of cadmium and C_e is final concentration of cadmium.

Data obtained from experiments

In the first experiment, contact time with the adsorbent synthetic wastewater were studied under the other parameters consider on the constant values (pH =7.5, the initial concentration of cadmium wastewater (10 ppm) and room temperature). These proceedings, for 10 and 30 minute contact times and as well as for 2 and 6 hours were repeated. The process of absorption was measured by atomic absorption spectrometry. Finally, removal efficiency of cadmium in 24, 6, 2 hours and 30, 10 minutes contact times was studied

According to the results, the sample 1 (concrete includes the rice husk and nanoparticle with concentration of 40 mg/l) in the all contact times, have been shown higher adsorption. Then the sample 1 has been chosen for the other experiments. To assess the data accuracy and the measurements repeatability three determinations were made for each sample.

Results and discussion

Effect of contact time

According to the Figure 1, with increasing contact time, adsorption efficiency increases. The reason it can be, the pollutant was contact increased with the surface of adsorbent. The adsorption rate in initial times is high, but after a while reduced, which indicates that the reaction is reached to equilibrium. So, 60 minutes was chosen as the optimum contact time for all experiment. (By according the real rest time in equilibrium tank)

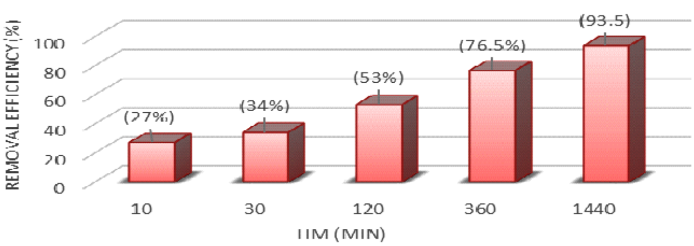

Figure 1
Removal cadmium percentage in different times.

Effect of pH

According to the results showed in the Figure 2 cadmium removal efficiency decreases with increasing pH, because hydrogen ions strongly with metal ions compete for occupy adsorption sites.

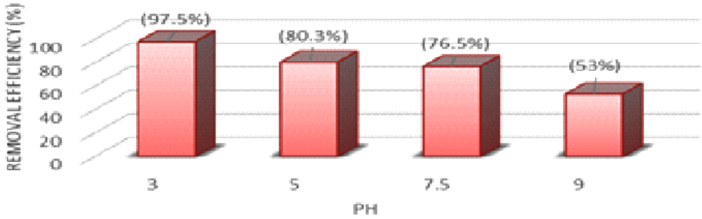

Figure 2
Removal cadmium percentage in different pH.

According to Figure 2, it was found that absorption of cadmium on absorbent increases with decreasing pH, which are due to the increase in hydrogen ions and cadmium ions. The results of study with Malekotian and Khazaie (2015) showed that the removal rate increased with decreasing pH (Malekotian and Khazaie, 2015; Mahdi Nia et al., 2015).

Effect of initial concentration

In Figure 3, the initial concentration of cadmium in the removal percentage is plotted. According to the Figure 3, the initial concentration of cadmium increased from 10 to 100 mg, the adsorption efficiency decreases. Cadmium removal rate from water by using granulated activated carbon studied by Tilaki et al. (2003). It was determined, and that the cadmium removal with increasing the cadmium initial concentration decreases (Tilaki et al, 2003). Removal of Cd (Π) ion was carried out at different initial concentrations ranging from 1, 5, 10, 100 and 1000 mg/L. According to these diagrams, optimum conditions are obtained in the contact time of 6 hours and pH 3, in the cadmium of initial concentration (selected 10 ppm).

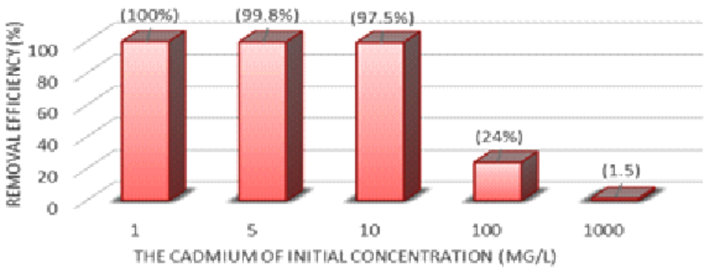

Figure 3
Removal cadmium percentage in the different initial concentration.

Equilibrium adsorption

Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation.

$$\mathbf{q_e} = \frac{\mathbf{K_L\, q_m\, C_e}}{1+\mathbf{K_L\, C_e}} \qquad [2]$$

where, $\mathbf{K_L}$ is the adsorption equilibrium constant including the affinity of binding sites(L/mg), $\mathbf{q_m}$ is the maximum adsorption capacity (mg/g), $\mathbf{C_e}$ the equilibrium

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metal ion concentration in the solution (mg/L) , and q_e is the amount of adsorbed ion at equilibrium point(mg/L). It represents a particle limiting adsorption capacity when the surface is fully covered with ions. The q_m and K_L can be determined from the linear plot of equation [3].This equation can be written as follows (Toth, 1995; Parida et al., 2006):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \qquad [3]$$

Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface. The Freundlich model in linear form is (Jaroniec, 1983):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad [4]$$

where, K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively (Moradi et al, 2004). Linear plots of l/q_e versus l/C_e and $\ln q_e$ versus $\ln C_e$ were drawn.

According to table 2, Freundlich model due to having higher R^2, as compared with the langmuir model, with of data was more compatible. So can be concluded that freundlich model describes of data as well.

Table 2
Result of isotherm.

R^2	Isotherms
0.9952	Langmuir
0.9968	Freundlich

Conclusion

Removal of Cd (Π) ion from aqueous solutions at different conditions such as contact time, pH and initial concentration were studied to investigate optimum values of the mentioned parameters for adsorption of Cd (II). Almost 97.5% Cd(II) removed under these conditions: pH=3, initial concentration of Cd,10mg/L; concentration of adsorbent,40mg/L; contact time and 6 hours .The adsorption data fitted well with the Freundlich isotherm equation. Using iron nanoparticle in this study, due to having the high of surface to weight of ratio and high density of reaction sites, increased absorption capacity. According to results, concrete using by the nanoparticles of cover and other absorbent materials used in water and wastewater treatment. It is possible to using concrete adhesive of solution. Also, the use of rice bran, as inexpensive adsorbent, available and high adsorption of performance, can increase cadmium removal percentage. In Malekotian and Khazayi study in 2015 year, cadmium adsorption of capacity by zero-valent iron nanoparticle increased with pH decreasing (Malekotian and Khazayi, 2015). Also, the cadmium removal of maximum by the rice husk absorbent in the low pH obtained (Mahdi Nia et al, 2015). Therefore, it could be concluded that the maghemite nanoparticles presents a good potential for treatment of Cd (II) wastewater. However, further research should improve the sorption capacity of maghemite nanoparticles to be applied for continuous removal of heavy metal in large-scale.

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