Removal of cadmium from industrial wastewater by steel slag

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Abstract

Introduction: The steel slag is the main by-product of steel industry. The aim of this study using the steel slag as a low-cost absorbent in order to remove cadmium pollutant from industrial wastewater.

Methods and Materials: Some factors that affect the process of cadmium removal by steel slag such as PH, contact time, absorbent dosage and cadmium initial concentration has been studied. Standard solution of synthetic wastewater including cadmium has been prepared by adding Chloride Cadmium to distilled water and concentrations in the range of 5-25 mg/l have been reached.

Results: The results show that in optimum conditions, the removal of cadmium from aqueous solution with concentration about 25mg/l and 60min contact time is about 99%. The experimental data of adsorption equilibrium have been analyzed according to adsorption kinetics models and Freundlich and Longmuir adsorption isotherms. The physical, chemical and morphological features of the steel slag have been determined by XRD, XRF and SEM techniques, too.

Conclusions: The result of the experiments determined that the steel slag could be used as an effective and low-cost method in removing cadmium from industrial wastewater.

Keywords: slag steel, cadmium, adsorption, the kinetic model, the isotherm model.

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Introduction

One of the main environmental pollutants is heavy metals in the industrial effluent that are among the first important group of toxic pollutants due to their polluting intensity [1]. The heavy metals are decomposable and gather in the human body through food chains [2]. Cadmium is among the heavy metals which are found in industrial effluent including metal processing, electroplating industries, textile, alloy industry and composting [3], [4]. Different methods have been analyzed in order to remove the heavy metals such as: the reverse osmosis process, electro dialysis, ion exchange, etc…. [5], [6]. Such processes have some special deficits due to their inability to remove of heavy metals fully and also their high expense. One of the methods in metal removal is adsorbent by active carbon. Generally, adsorbent is the process of substance accumulation in the joint section of two phases. The active carbon is an effective substance used in the removal of cadmium. Since carbon regeneration is expensive, researchers always try final use and low-cost adsorbents [7]. Researchers emphasize on using mineral substances like steel slag as a new method in industrial effluent treatment [8]. For the first time, Ramakrishna and Viraraghavan (1997) studied dye removal by steel slag [9]. Lu, et al (2008) studied phosphate removal from water solution by slag [8]. In another study, Kim, et al (2008) studied mechanism of copper removal using steel slag [2]. Also, Liu, et al (2009) analyzed metal removal using steel slag [10]. This study following other studies had been done in order to access desirable condition for waste treatment containing cadmium using low-cost substances and minerals.

Methods and Materials

The work style

This research was an applied-foundation study accomplished in pilot plant and in a discontinuous system. The effective factors on this process included PH values 3, 5, 6/5, 7 and 10, initial concentration of metal solution at values 5,10,15,20 and 25 mg/l, adsorbent in dosage of 0/5, 2, 3 g and contact time of 15, 30, 60, 90 and 120 min were analyzed in isolated stages .In this study, steel slag was used as adsorbent because of vast production of the slag in the industry of Ahvaz. Standard solution of synthetic wastewater including cadmium was prepared by adding Chloride Cadmium to distilled water and concentrations was reached in the range of 5-25 mg/l. In all experiments first the slag was sieved by a mesh 35 to access homogeneous particles. Then it has been washed by distilled water several times in order to remove the dust and other pollutants and then dried to reach a fixed weight in 105°c. After each test, the samples were caused to pass a whatman paper 40 using vaccum pump and bokhner cone in order to separate the slag from the samples. The concentration of remaining cadmium in solution was measured by a spectrophotometer plant .The absorbent percentage was estimated by following equation:

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \qquad (1)$$

According to equation (1), where c_0 and c_e are initial and final concentration of cadmium in solution, respectively. In this study all tests have been done carefully by using of mentioned standard methods in reliable references like standard method. It is needed to mention that all the test repeated three times and average of data and results has been used.

The physical, chemical and morphological characteristics of the steel slag were defined by XRD, XRF and SEM [11] .In Table 1, the characteristics of used apparatus in this research has been demonstrated.

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Table1: The characteristics of used apparatus in this research

Model apparatus	Name apparatus
Siefret ID3003(Germany)	x-ray diffraction(XRD)
Sequential WDX(Germany)	x-ray fluorescence(XRF)
Xl30(fillips Netherland)	Scanning electron microscopy(SEM)

Results

Analyzing the physical, chemical and morphological characteristics of the slag

When the physical structure of the slag was accomplished by XRD, the result showed that the slag has an irregular and non-crystal shape Fig. l. The result of analysis by XRF drawn is in Table 2. According to results, the steel slag is a non-metal compound consisting of chemical compounds, such as Cao, etc. An image of the slag surface before the adsorbent process is drawn in Fig.2-a, and the image of slag after the adsorbent drawn in Fig.2-b indicating that the adsorbent has been made and the apertures filled by cadmium.

PH effect and estimating the optimum PH

As seen in the Fig.3, the cadmium adsorbent increases as PH increases causing low PH condition H^+ ions to compete with cadmium ions on the adsorbent places and reduce the cadmium adsorbent capacity by occupying the adsorbent places.

The effect of cadmium initial concentration on adsorbent and optimum concentration

In order to study the effect of initial concentration of metal solution with 5 to 25 mg/l, firstly 0/5 g of adsorbent was taken and mixed with 50ml of mentioned cadmium solution and the adsorbent percentage of cadmium in 30 min was recorded (Fig.4).

Effect of adsorbent dosage and estimating the optimum adsorbent estimating

The effect of adsorbent dosage on adsorbent of cadmium is drawn in Fig.5.In this test, various amount of slag weighting 0/5, 2 and 3gr was exposed to 50 ml of cadmium solution with concentration 25 mg/l for 30 min. The results show that by increasing the amount of adsorbent the amount of adsorbed cadmium increases, too. It is obvious that by increasing the adsorbent quantity the accessible adsorbent places would increase so the adsorbent efficiency becomes more.

The effect of the adsorbent contact time on adsorbent and estimating the optimum exposure time

Analyzing the contact time due to Fig.6 shows that the minimum adsorbent of cadmium takes place in 60 min, it means that by increasing the exposure time up to 60 min, the adsorbent dosage increases, too, but after 60 min the adsorbent decreases by increasing the time. In other words, after 60 min there is an equilibrium between the solid phase. Or, it' s possible that cadmium has been adsorbed to the adsorbent completely. Or maybe the time doesn't effect the removal process after equilibrium time.

Adsorbent isotherms

Nowadays, various equations and isotherm are developed to depict the adsorbent behavior. In this study, the Frounlich and Langmuir isotherms have been analyzed and the experimental result with so-called equation been compared.

Langmuir isotherm

The general Langmuir equation as follows [11]:

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$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m k_l c_e} \qquad (2)$$

Froundlich isotherm

The linear Froundlich equation is as follows [13]:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \qquad (4)$$

This is an experimental model. Kf equation (4) is Froundlich constant value that depends on the adsorbtion capacity by the adsorbent. The result is shown in Fig.8. If the value in Froundlich equation equals $1 < n < 3$ then it shows that metal absorbent on the cadmium adsorbent isotherm is so desirable [12].Table 3 analyzed the results and various isotherm constants.

Adsorption Kinetics

Various kinetic models have been reported for comparing experimental data related to adsorbent of pollutants on the surface of adsorbents, including: Kinetic pseudo-first order model and pseudo-second order model. In this study, the data derived from experimental test results was compared to the mentioned equation.

Pseudo-first order model

The equation of pseudo –first order model was as follows [13]:

$$\log(q_e - q_t) = \log q_e - k_1 t/2/303 \qquad (5)$$

Pseudo – second order model

The linear form of pseudo-second order model is as follows [13]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \qquad (6)$$

According to equation (6), second order model with linear value t/q_t is obtained in terms of t. K_2 is constant speed of pseudo-second order resemblance model, g/mg/min, qe is balanced adsorbent capacity, mg/g that is obtained from gradient and width of origin of equation (6).The results are shown in Fig.10.The parameters related to pseudo-second order model are shown in Table 4, by these parameters we can concluded that data correspond to second order resemblance model, because R^2 value is desirable .

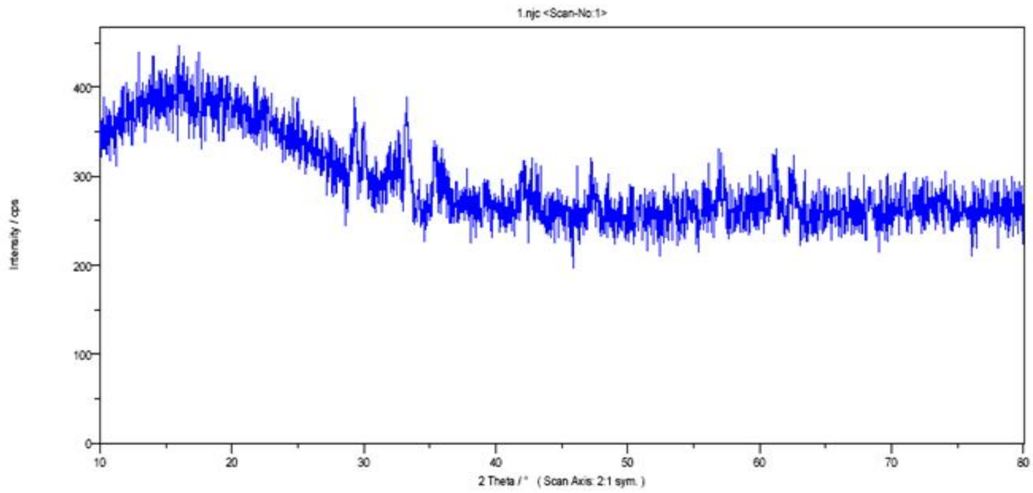

Fig. 1: XRD pattern of steel slag

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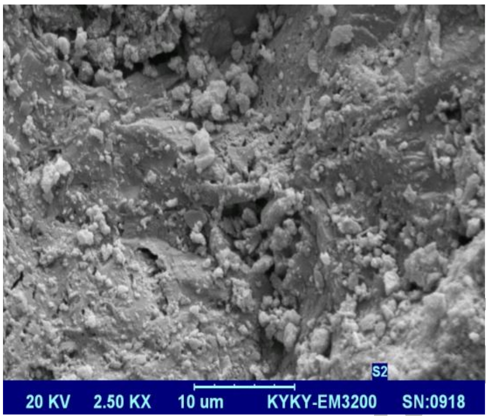
Table 2: The result of analyze by XRF

Ingredient	Contents (%)
Cao	41/3
Fe_2O_3	19/1
SiO_2	14/64
Al_2O_3	9/51
Mg O	6/3
Mn O	1/4
Cr_2O_7	./11
The other Compsition	2/94

(a) (b)



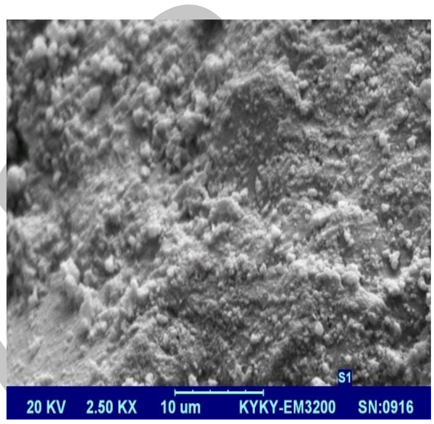


Fig.2: SEM image of steel slag

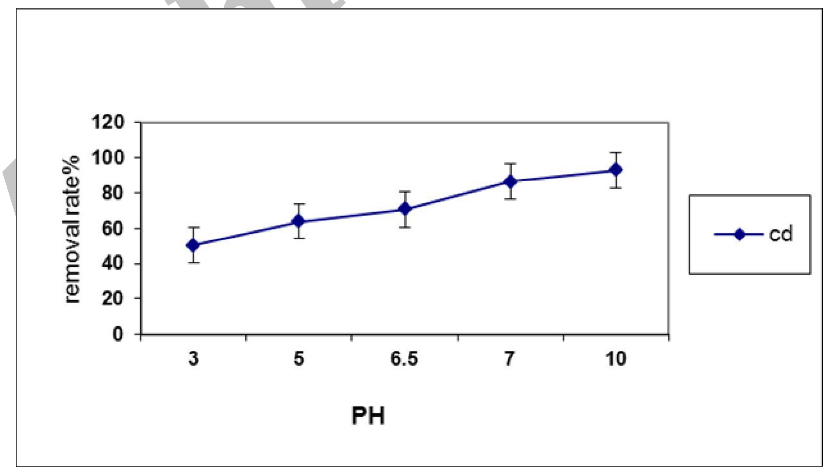


Fig.3: Effect of PH

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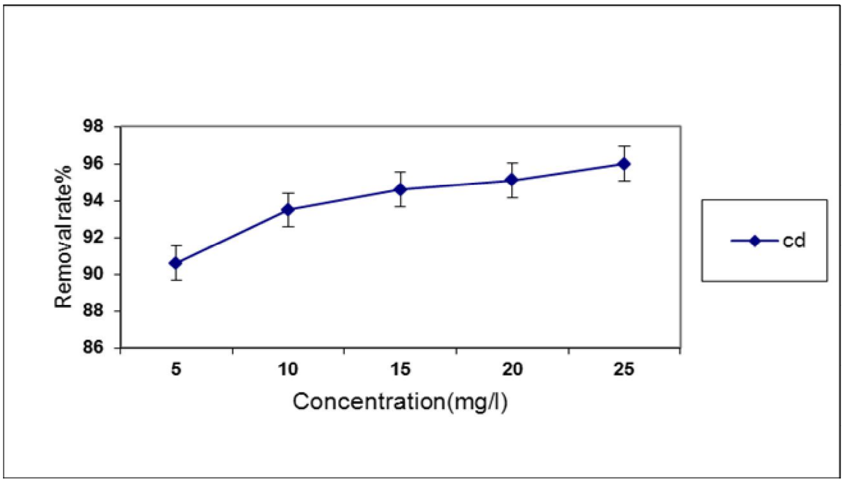

Fig.4: Effect of cadmium initial concentration on adsorbent

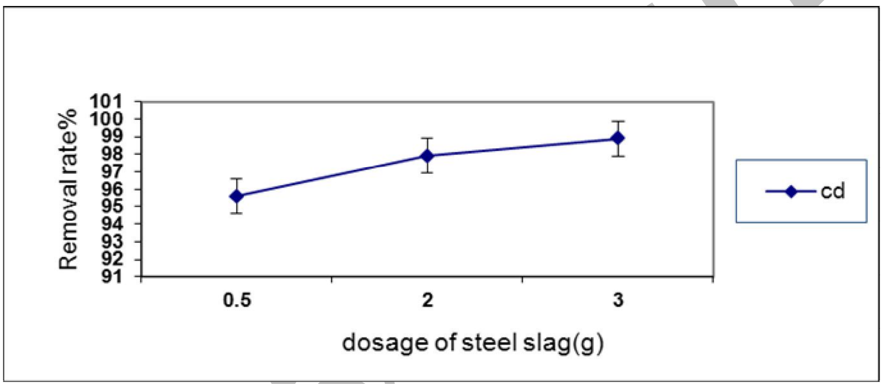

Fig.5: Effect of steel slag dosage

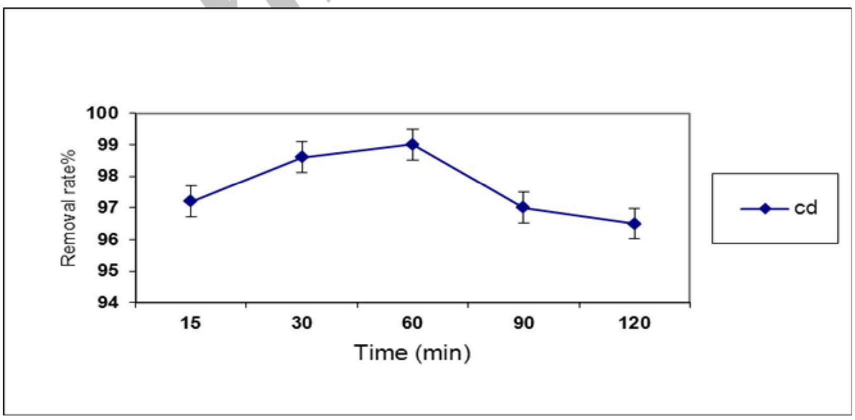

Fig.6: Effect of contact time on adsorbent

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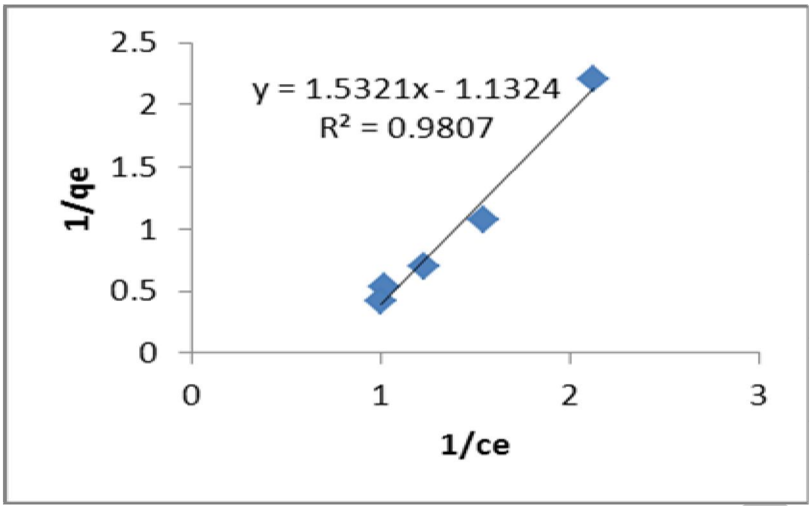

Fig.7: Langmuir adsorbent isotherm cadmium

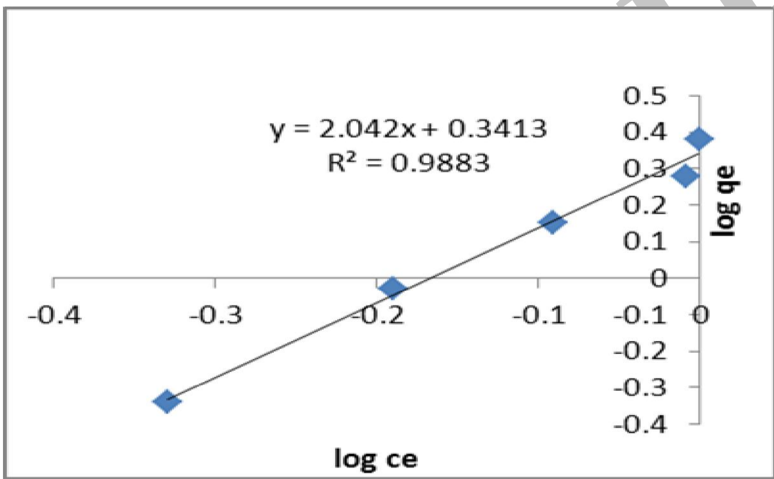

Fig.8: Froundlich adsorbent isotherm cadmium

Table3: The results and various analyzed isotherms adsorbent

Isotherm	Parameter	Cadmium
Langmuir	q_m	./88
	K_1	./739
	R^2	./980
	R_L	./05
Froundlich	n	./49
	k_f	2/19
	R^2	./988

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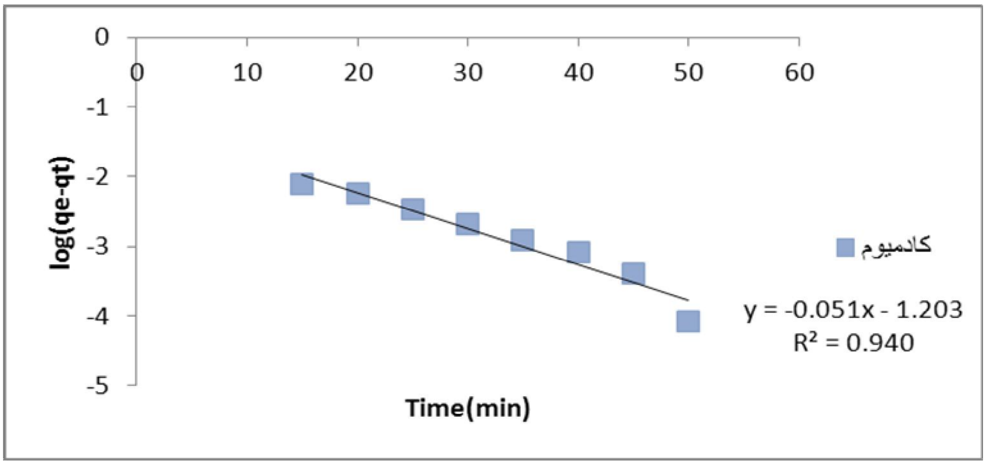

Fig .9: pseudo-first order model of steel slag adsorbing cadmium

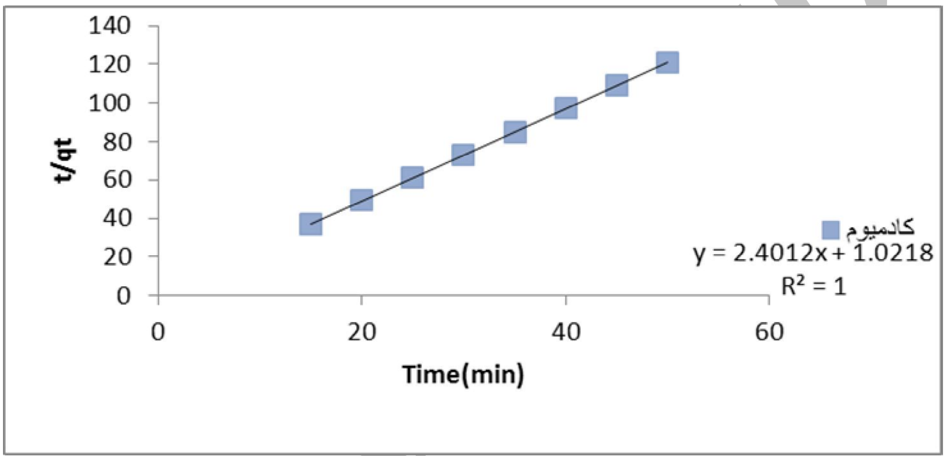

Fig: 10: pseudo- second order model of steel slag adsorbing cadmium

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Table 4: The kinetic data estimated by various models for cadmium

kinetic models	Parameter	Cadmium
pseudo-first order	q_e K_1 R^2	./117 ./062 ./940
Pseudo-second order	q_e K_2 R^2	5/64 ./416 1

Discussion

According to pictures by SEM, the slag has apertures and it has pervious inner structure. An image of the slag surface before the adsorbent process is drawn in Fig.2-a, and the image of slag after the adsorbent drawn in Fig.2-b indicating that the adsorbent has been made and the apertures filled by cadmium. In order to study the PH effect of water solution on the absorbent efficiency , 0/5gr adsorbent with 50ml of cadmium solution 10 mg/l has been done in different PH between 3-10 and contact time 30 min and mixing speed 120rpm .The adsorbent amounts were measured after the test completed.

As seen in Fig.4, the adsorbent percentage increases when the cadmium initial

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Concentration increases. As a result, the optimum concentration is reported to be 25 mg/l. Because of this adsorbent places aren't saturated till concentration 25mg/l and the adsorbent can adsorb metal. According to equation (2), c_e is balanced concentration in terms of mg/l, q_e is cadmium adsorbent amount in terms of mg/g, q_m and K_1 are Langmuir constant, which are obtained from equation width of origin and gradient of Fig.7, respectively, and their values are shown in Table 3.One of the main characteristics of Langmuir isotherm and optimum adsorbent could be expressed using non-dimension factor called segregation factor, R_L, that its equation is as follows:

$$R_L=\frac{1}{(1+K_1+C_0)} \quad (3)$$

According to equation (3), c_0 is cadmium initial concentration in solution in terms of mg/l, K_1 is Langmuir constant l/mg , and the R_L value indicates the isotherm sort so that $R_L= 0$ is irreversible , $0< RL <1$ is desirable and $R_L=1$ is linear and $R_L>1$ shows that the isotherm is undesirable [12]. The RL value for cadmium is shown in Table.3 and indicates that the model of Langmuir isotherm of cadmium is desirable.

According to Table 3, for cadmium, $n<1$ concludes that the adsorbent data doesn't correspond to Froundlich adsorbent isotherm.

According to equation (5), q_e is the adsorbent capacity of slag on equilibrium state , mg/g , qt is adsorbed cadmium within t , mg/g , K_1 is the constant speed of. pseudo- first order resemblance , min^{-1} . q_e obtained from gradient and width of origin of equation (5) .the results are shown in Fig.9.The parameters related to pseudo- first order model are shown in Table 4. By these parameters, we could concluded that data don't correspond to first order model because R^2 is not desirable.

Conclusions

In this study, the physical, chemical and morphological characteristics of the steel slag were analyzed. The results show that the steel slag has an irregular and non-crystal structure. Cao is the main substance in the chemical compound of the slag that makes it alkaline. Also it can adsorb metals due to its pores and pervious inner structure. In this study we analyzed the effect of various factors including PH, initial concentration of solution, the adsorbent dosage and contact time on cadmium adsorbent on the slag. The optimum adsorbent for cadmium is PH=10.The optimum initial concentration in cadmium solution, the adsorbent amount and the exposure time estimated was: 25 mg/lit, 3g and 60 min, that we can conclude that adsorbent of cadmium has a direct relation by increasing initial concentration of solution and the amount of adsorbent. The balanced and experimental data were analyzed from Froundlich and Langmuir isotherms, the results showed that experimental data correspond to Langmuir isotherm model. The kinetics models pseudo-first order and pseudo-second order resemblance were analyzed and the results show that the kinetic pseudo-second order model correspond to experimental data in the best manner. In a study conducted by Ortiz, et al (2001) on Nickel adsorbent by the steel slag, they concluded that the adsorbent speed decreases as the temperature increases and PH reduces and the adsorbent equilibrium data follow Froundlich isotherm model [14]. In a study by Kim, et al (2008) on Cu^{+2} removal using steel slag, they concluded that the adsorbent would increase as PH of solution increases, and the adsorbent equilibrium data follow Langmuir isotherm model [2]. In another study by Liu, et al (2009) on heavy metal removal by steel slag , the results showed that the steel slag is an effective adsorbent in removing heavy metals from water solutions and that Cr^{+3} shows the most adsorbent percentage ,

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%99; and data correspond to Froundlich and Langmuir isotherm model [10]. In the research made by Huifen, et al (2011) for Cu^{+2} , Cd^{+2} , Pb^{+2} , and Zn^{+2} removal by steel slag as an adsorbent , the results show that removal of Cu^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} is %99/24 , %99/08 , %98/75 and % 98/73, respectively .So the results show that the steel slag is a suitable adsorbent for wastewater treatment containing Cu^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} [15]. Chen ,et al (2001) conducted a research on heavy metal adsorbent by electrical arc slag and concluded that the optimum PH in Zn^{+2} and Pb^{+2} adsorbent process is 7 and equilibrium data correspond Froundlich and Langmuir isotherm model and electrical arc slag is a suitable adsorbent in removing heavy metals from the wastewater [5]. Due to these reports and results, the steel slag is an effective adsorbent in cadmium removal from synthetic effluent and it could be used as an adsorbent in removing heavy metals from polluted water and effluents.

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