Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 15 (1) 105-112: Spring 2018
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

The Use of Corn cob Micro Powder as a Low Cost Adsorbent, for the Removal of Co^{2+} Ion from Aqueous Solutions and from the View Point Thermodynamics

Gholamali Haghdoost *

Department of Chemistry, Kazerun Branch, Islamic Azad University, Kazerun, Iran

Received November 2018; Accepted December 2018

ABSTRACT

Corn cob as a low cost adsorbent were used in the present work for the removal of toxic heavy metal Co^{2+} from aqueous solutions. Bath experiments were used to determine the best adsorption conditions. The equilibrium adsorption level was determined as a function of solution pH, temperature (T), contact time (t_c), initial adsorbate concentration, and adsorbent dosage. Effective removal of metal ions was demonstrated at pH values of 8. Metal adsorption onto corn cob was evaluated by Langmuir and Freundlich isotherms. Results indicate that the Langmuir isotherm model is the most suitable one for the adsorption process using corn cob (R^2=0.9503), thus indicating the applicability of monolayer coverage of Co^{+2} ion on corn cob surface. The relationship between thermodynamic parameters was used to predict the absorption process. According to Thermodynamic analysis, the process endothermic and natural (ΔH^o= -18.7 J mol^{-1} and ΔS^o = -47.6 J mol^{-1} K^{-1}).

Keywords: Cobalt (II); Adsorption; Thermodynamic; Corn cob.

INTRODUCTION

Toxic heavy metals pollution is one of the influential environmental problems, because they are non degradable and harmful for public health, even at very low concentrations. Cobalt is one of several commonly occurring toxic metals. It is an animal carcinogen producing cancer at various sites. Exposure to cobalt is extremely irritating to the skin both on contact and by provoking an allergic reaction which sensitizes the skin to further contact. It is also irritating to the eyes and mucous membrane, causing severe discomfort in the nose, often leading to perforation of the nasal septum. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m^3 in the U.S. The use of activated carbons to remove cobalt from water was proposed because of their high surface areas and active functional groups leading to a search for low-cost adsorbents in recent years [2-5].

Indeed agricultural waste for example, has two advantages. First, waste material is converted to useful, value-added adsorbents. Disposal of agricultural by-products has become a major costly waste disposal problem. Second, produced activated carbons are used for removing organic chemicals and metals from wastewater [6-8]. Removal of toxic heavy metals from wastewater is an important environmental challenge. In the present study, corn cob prepared used as an adsorbent to remove cobalt from aqueous solutions. The adsorption of cobalt ions

*Corresponding author: haghdoost1352@yahoo.com

onto corn cob was studied in batch equilibrium conditions. The effects of different parameters including pH, initial metal ion concentration, contact time, corn cob dosage and temperature were investigated. Langmuir and Freundlich isotherm models were used to analyze the equilibrium data.

EXPERIMENTAL

Apparatus and Materials

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used for measuring the concentration of Co^{2+} ion in studied solutions, a 820 A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neolab model (India) was used to measure contact time in solution. All chemical materials used in this study were of analytical grade. Corn cob prepared by chemical activation with KOH was characterized. Cobalt nitrate, was purchased from Merck Company.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to determine the Co^{2+} ions adsorption isotherm onto corn cob and its thermodynamic properties. Co^{2+} ions stock solution (100 mg. L^{-1}) was prepared by dissolving the appropriate quantity of Co $(NO_3)_2$ salt in deionized water.

Adsorption isotherms were obtained by using initial Co^{2+} ion concentration, M_o, and its equilibrium concentration, M_e, at 298 K. The effect of pH on the Co^{2+} ions adsorption onto corn cob was conducted in a pH range of 4-10. The pH of solutions was adjusted by 0.1 M HCl or 0.1 M NaOH solutions. For every experiment, 100 ml of the solution with Co^{2+} concentration of 10 mg.L^{-1} was mixed with 50 mg of corn cob in a 250 ml glass conical flask. The flask was shaken in a thermostatic orbit shaker at 220 rpm for 60 min. The mixed was filtered through a 0.45 μm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A_e = \frac{A_0 - A_e}{A_0} \times 100 \qquad (1)$$

Where M_o and M_e are the initial and final concentration of Co^{2+} ion in solution (mg L^{-1}), respectively. Q_e, amount adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}) was calculated using the following equation:

$$Q_e = \frac{(M_0 - M_e)V}{W} \qquad (2)$$

Where W is the mass of corn cob (g) and V is the volume of the solution (L). To evaluate the thermodynamic properties of the adsorption process, 50 mg of corn cob was added into the 100 ml solution with pH of 8.0 and initial Co^{2+} concentration ranging from 10 mg. L^{-1} in every experiment. Each solution was shaken continuously for 60 min [9-11].

RESULTS AND DISCUSSTON

Adsorption Study

Surface morphology

Figures 1 and 2 show the SEM images of corn cob before and after adsorbents. Corn cob surface morphology before and after the absorption process in Figure 1 and 2 is shown. It is apparent porosity of the adsorbent and is the reason for the sinking of many metal ions absorbed by the absorbent biological. By comparing Figures 1 and 2 can be said that the difference created in the image after the capture metal ions adsorbed on the surface SEM evidence is catchy.

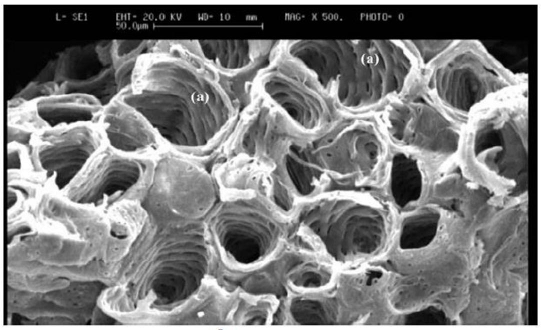

Fig. 1. SEM image of adsorbent of corn cob before biosorption.

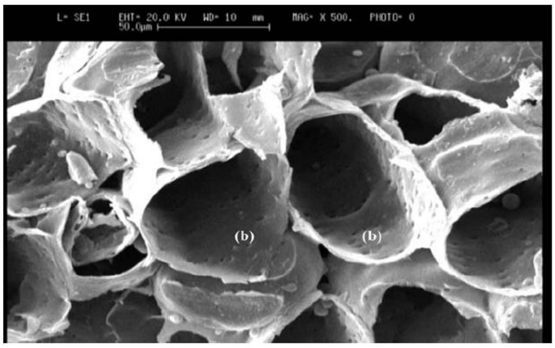

Fig. 2. SEM image of adsorbent of corn cob after biosorption.

The Effect of pH

Solution pH is one of the most important parameters to determine. The pH is one of most important environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals. The pH value of the solution is an important controlling parameter in the adsorption process [12]. Table 1 and fig. 3 illustrate the effect of the pH of the solution on the adsorption percentage of Co^{2+} ion adsorbed onto corn cob. The best results were obtained at pH=8 for Cobalt. The decrease of the adsorption percentage in acidic pH can be attributed to the repulsion between positive charge surface of corn cob and Co^{2+}. Increase in metal removal with increase in pH can be explained on the basis of a decrease in competition between proton and metal cautions for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH is due to formation of soluble hydroxyl complexes.

Table 1. The effect of initial pH of the solution on the adsorption percentage (%A) of Co^{2+}

(M_o=10 mg.L^{-1}, $W_{com\ cob}$=50 mg, T=298 K, t_c=60 min)

pH	%A
4	48.00
5	51.00
6	58.20
7	63.00
8	78.00
9	73.10
10	70.80

The Effect of Dosage

The effect of corn cob dosage on the adsorption percentage of Co^{2+} ion are shown in table 2 and plotted in fig. 4. We concluded that the dosage of 50 mg of corn cob was the most suitable. After optimum dosage, all active sites are entirely exposed and the adsorption on the surface is saturated.

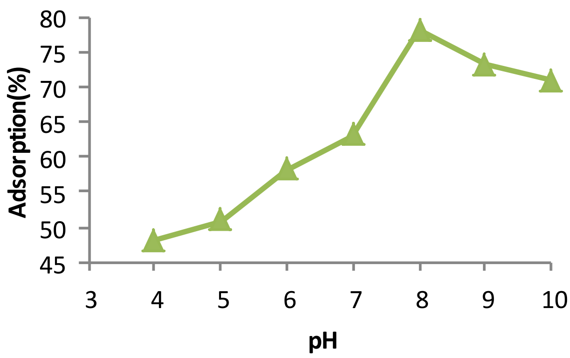

Fig. 3. The effect of initial pH of the solution on the adsorption percentage of Co^{2+}

(M_o=10 mg.L^{-1}, $W_{com\ cob}$=50 mg, T=298 K, t_c=60 min).

Table 2. The effect of corn cob dosage on the adsorption percentage (%A) of Co^{2+} ($Mo=10$ mg.L^{-1}, pH=8, T=298 K, tc=60 min)

Wcorn cob / mg	%A
10	28.00
20	40.10
30	45.80
40	53.60
50	61.80
60	61.80

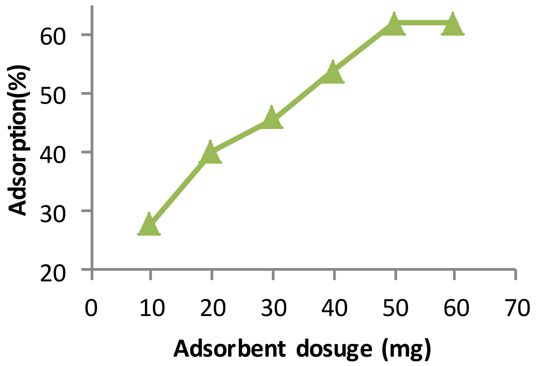

Fig. 4. The effect of corn cob dosage on the adsorption percentage (%A) of Co^{2+} ($Mo=10$ mg.L^{-1}, pH=8, T=298 K, tc=60 min).

The Effect of Temperature

Table 3 and fig. 5 show that the adsorption percentage decrease with increasing temperature. Therefore, it may be concluded that the interaction between Co^{2+} ions and corn cob is exothermic in nature. Adsorption decrease may be due to increase the electrostatic repulsion between of the Co^{2+} ions.

Table 3. The effect of temperature on the adsorption percentage (%A) of Co^{2+} ($M_o=10$ mg.L^{-1}, $W_{\text{com cob}}=50$ mg, pH=8, $t_c=60$ min)

T / K	%A
298	87.00
308	83..00
318	80.10
328	73.60
338	72.00
348	68.80

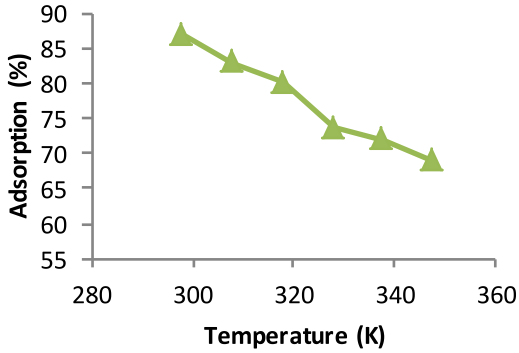

Fig. 5. The effect of temperature on the adsorption percentage of cobalt ion onto corn cob ($M_o=10$ mg.L^{-1}, $W_{\text{com cob}}=50$ mg, pH=8, $t_c=60$ min).

The Effect of Contact Time

The effect of contact time, tc, on the adsorption percentage of Co^{2+} ion onto corn cob are shown in table 4 and plotted in fig. 6. A rather fast up take occurs during the first 50 min of the adsorption. It becomes slower as the adsorbed amount of Co^{2+} ion reaches its equilibrium value. It can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special one atom layered structure of corn cob [13]. At first adsorption capacity was a slow process then increases rapidly, it attains equilibrium and saturation gives constant adsorption value. The optimum contact time was obtained as 65 min.

Table. 4. The effect of contact time, t_c, on the adsorption percentage (%A) of Co^{2+} ions ($M_o=10$ mg.L^{-1}, $W_{\text{com cob}}=50$ mg, pH=8, T=298 K)

tc/min	%A
5	35.00
20	41.00
35	48.10
50	53.00
65	60.20
80.	60.20

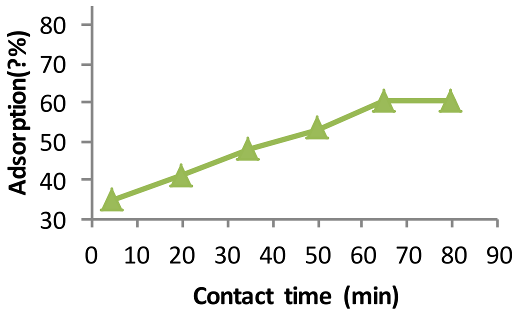

Fig. 6. The effect of contact time on the adsorption percentage of Co^{2+} ion onto corn cob
(M_o=10 mg.L^{-1}, $W_{corn\ cob}$=50 mg, pH=8, T=298 K).

Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which express the surface properties of the adsorbent and so on the percentages adsorption of Co^{2+} ion corn cob as a function of initial concentration of Co^{2+} ions are given in table 5.

Equilibrium data of adsorption process can be analyzed on the basis of Freundlich and Langmuir models. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The Freundlich isotherm equation is used for the description of monolayer (chemisorption) and multilayer (physisorption) adsorption [14]. The linear form of Freundlich isotherm is given by the equation:

$$\log Q_e = \log P + \frac{1}{n} \log C_e \tag{3}$$

Table 5. Adsorption data for Co^{2+} adsorption onto corn cob
(pH=8, t_c=65 min, T=298 K, $W_{corn\ cob}$ =50 mg)

Parameter	Value					
M_0 /mg L^{-1}	2	4	6	8	10	12
%A	57.00	61.00	65.40	71.00	78.00	83.40
Me / mg L^{-1}	0.86	1.57	2.06	2.32	2.20	2.00
Q_e / mg g^{-1}	2.28	4.88	7.87	11.36	15.60	20.00
log Me	-.07	0.19	0.32	0.37	0.34	0.30
log Q_e	0.36	0.69	0.90	1.06	1.19	1.31
1/Me /L mg^{-1}	1.1	0.64	0.48	0.43	0.45	0.50
1/Q_e /g mg^{-1}	0.48	0.29	0.15	0.10	0.07	0.05

Where P (L/g) and n are the Empirical Freundlich constant or capacity factor and adsorption intensity. The values of P and n are determined from the intercept and slope of a plot of log Q_e versus log Me (table 5 and fig. 7) that were used to calculate the values of P and n (table 6)).

The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface without any interaction between adsorbed ions and with uniform binding sites and equivalent sorption energies [15]. The linear Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$\frac{1}{Q_e} = \frac{1}{bQ_m}\left(\frac{1}{C_e}\right) + \frac{1}{Q_m} \tag{4}$$

Where Q_m (mg g^{-1}) is the maximum metal ion to adsorb onto 1 g adsorbent and b (L/mg) is the Langmuir constant related to adsorption capacity and energy of adsorption. The slope and intercept of plot of 1/Q_e versus 1/M_e is shown in fig. 8 that were used to calculate the values of b and Q_m (table 6).

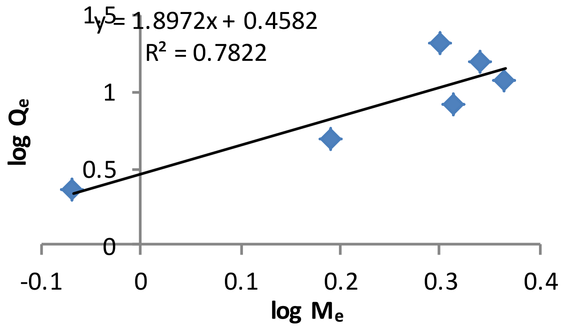

Fig. 7. Freundlich isotherm for cobalt ion adsorption onto corn cob.

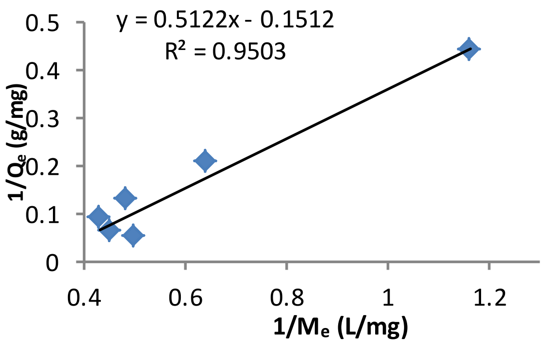

Fig. 8. Plot of $(1/Q_e)$ versus $(1/M_e)$ for Co^{+2} adsorption onto corn cob.

Table 6. The resultant values for the studied isotherms in connection to Co^{+2} ion adsorption onto corn cob at 298 K

Isotherm Value	Parameter
Freundlich	
2.90	P /(L g^{-1})
0.53	n
0.87	R^2
Langmuire	
0.30	b / (L mg^{-1})
6.62	Q_m /(mg g^{-1})
0.95	R^2

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is favorable or unfavorable. The essential characteristic separation constant factor, R_L, for the Langmuir adsorption is defined as follows:

$$R_L = \frac{1}{1+bC_0} \tag{5}$$

The value of R_L illustrate the shape of the isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$) [16]. The calculated R_L values versus initial Co^{2+} concentration are given in table 7, indicating that the Langmuir adsorption of Co^{2+} onto corn cob is favorable.

Table 7. Separation factor for the adsorption of Co^{2+} onto corn cob in terms of initial concentration of Co^{2+}

Mo / mg L^{-1}	R_L
2	0.63
4	0.50
6	0.36
8	0.30
10	0.25
12	0.22

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o [16-18]. Where K_o is defined as follow:

$$K_0 = \frac{a_S}{a_e} = \frac{Q_e}{M_e} = \frac{M_0 - M_e}{M_e} \tag{6}$$

Where a_S and a_e are the activity of adsorbed Co^{2+} and the activity of Co^{2+} in solution at equilibrium, respectively. The adsorption standard free energy change (ΔG^0) is calculated according to:

$$\Delta G^0 = -RTlnK_0 \tag{7}$$

The average standard enthalpy change (ΔH^o) and the average standard entropy change (ΔS^o) are obtained from the plot of equation (8):

$$lnK_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

In order to obtain the values of ΔH^o and ΔS^o, was plotted $\ln K_o$ against 1/T (table 8, fig. 9).

Table 8. The effect of temperature on K_o values (M_o=10 mg.L^{-1}, pH=8, $W_{corn\ cob}$ =50 mg, t_c=65 min)

T/K	%A	K
298	89	8.9
308	83	4.88
318	78	3.55
328	76.6	3.27
338	72	2.57
348	68	2.13

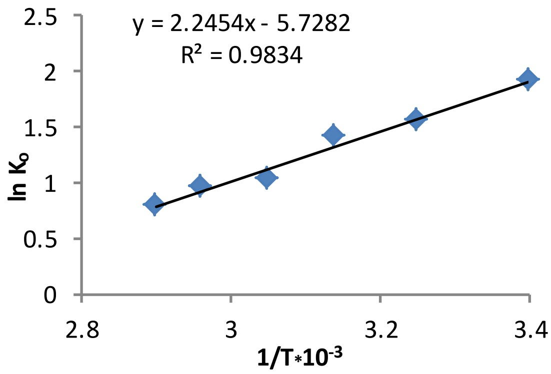

Fig. 9. The effect of temperature on equilibrium constant values.

Table 9. Thermodynamic parameters for adsorption Co^{+2} ions onto corn cob

T/K	ΔG^o/kJ.mol^{-1}	ΔH^o/J.mol^{-1}	ΔS^o/J.mol^{-1} K^{-1}
298	-4.71	-18.7	-47.6
308	-4		
318	-3.7		
328	-2.81		
338	-2.64		
348	-2.29		

The obtained values of thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) are listed in table 9. The negative value of ΔH^0 suggests that the interaction of adsorbed Co^{+2} with corn cob is an exothermic process, which is supported by the decreasing the amount of Co^{+2} ions adsorption with increasing temperature. The negative value of ΔS^o indicates a increased randomness and mobility at the adsorbent-solution interface during the adsorption of Co^{+2} ions onto corn cob. The negative values of ΔG^0 reveals the fact that the adsorption process is spontaneous.

CONCLUSION

The results of this work show that corn cob is an effective adsorbent for removal of Co^{2+} ion from aqueous solution. Results showed that the Langmuir isotherm model was fitted well with adsorption data, thus indicating the applicability of monolayer coverage of Co^{2+} ion on corn cob surface. Thermodynamic analysis showed that the adsorption process is exothermic and spontaneous in nature.

REFERENCES

[1]. M. Nasiruddin Khan, M. Farooq Wahab, J. Hazard. Mater. 141 (2007) 237-244.
[2]. R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, Separation and Purification Technology. 45 (2005) 41-49.
[3]. T. Vaughan, W.S. Chung, W.E. Marshall, Technology. 78 (2001) 131-139.
[4]. W.T. Tsai, W. C.Y. Chang, C, S.Y. Wang, C.F. Chang, S.F. Chien, H.F. Sun, Technol. 78 (2001) 203–208.
[5]. A. Hashem, E.S. Abdel-Halim, K.F. El-Tahlawy, A. Hebeish, Technol. 23 (2005) 367-380.
[6]. O. Yavuz, Y. Altunkaynak, F. Guzel, Water Res. 37 (2003) 948-952.
[7]. S. Cetin, E. Pehlivan, Colloid Surface A. 298 (1-2) (2007) 83-87.
[8]. Z. Shamohammadi, J. of Water and Wastewater. 75 (2010) 45-50.

[9]. S. Bagheri, H. Aghaei, M. Ghaedi, M. Monajjemi, K. Zare, Eurasian Journal of Analytical Chemistry. 13(3) (2018) 1-10.

[10]. M. Ghaedi, B. Sadeghian, A.A. Pebdani, R. Sahraei, A. Daneshfar, C. Duran, Chem. Eng. J. 187 (2012) 133–141.

[11]. E. Alipanahpour, M. Ghaedi, A. Ghaedi, A. Asfaram, M. Jamshidi, M.K. Purkait, Journal of the Taiwan Institute of Chemical Engineers. 59 (2016) 210-220.

[12]. K. Vijayaraghavan, H.Y.N. Winnie, R. Balasubramanian, Desalination. 266 (2011) 195-200.

[13]. A. Abdul Halim, H. Abdul Aziz, M.A.M. Johari, K.S. Ariffin, Desalination. 262 (2010) 31-35.

[14]. M. Kilic, E. Apaydin-Varol, A.E. Putun, J. Hazard. Mater. 189 (2011) 397-403.

[15]. R. Bazargan-Lari, M.E. Bahrololoom, A. Nemati, J. Food. Agri. Environ. 9 (2011) 892-899.

[16]. H.M. Mozammel, O. Masahiro, S.C. Bahattacharya, J. Biomass. Bioenergy. 22 (2010)397-400.

[17]. H. Demiral, I. Demiral, B. Karabacakoglu, F. Tumsek, Chem. Eng. Res. Des. 89 (2011)206-213.

[18]. M. Yimenez-Reyes, M. Solache-Rios, J. Hazard. Mater. 180 (2010) 297-302.