Determination of equilibrium, kinetic and thermodynamic parameters for the adsorption of cadmium (II) onto Castanea sativa shell

G. Vázquez, R. Fernández-Bea, M. S. Freire, J. González-Álvarez, G. Antorrena

Department of Chemical Engineering, University of Santiago de Compostela , School of Engineering, Rúa Lope Gómez de Marzoa, 15782 Santiago de Compostela, Spain

Abstract

A study on the removal of Cd (II) ions from aqueous solutions by *Castanea sativa* shell was conducted in batch conditions. The influence of different parameters such as adsorption time, temperature and initial concentration of Cd ions on cadmium uptake was evaluated. Results indicated that cadmium adsorption could be described by the Freundlich adsorption model in the studied concentration range of cadmium (II) ions at all the temperatures essayed, predicting the heterogeneity of the shell. The kinetics of the adsorption process followed the pseudo-second order model, with cadmium sorption capacity decreasing slightly with increasing temperature at 15.3 mg/L. Equilibrium sorption capacity increased with increasing the initial cadmium concentration. Using the second-order kinetic constants, which decreased with decreasing temperature, the energy of adsorption was calculated as equal to 19.2 kJ/mol.

Keywords: cadmium adsorption, chestnut shell, equilibrium, kinetics, thermodynamic parameters

1. Introduction

In view of their toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters before they are released into the environment. Different technologies have been developed to remove toxic metal ions from water; among these, adsorption as compared to others methods, appears to be an attractive process in view of its high efficiency, easy handling and cost-effectiveness as well as the availability of different adsorbents.

Castanea sativa shell is generated as a residue of a food factory during the peeling process in the “marrón glace” production. Apart from its use as fuel, the shell has little application, and although other similar lignocellulosic materials have received considerable attention as adsorbents of cations from wastewaters, there is no much information in the literature on the utilization of chestnut shell as adsorbent. Therefore, in this work, we proposed the study of the adsorption of cadmium ions from aqueous solutions onto the chestnut shell.

There are several parameters which determine sorption rate, like structural properties of the adsorbent, metal ion properties, initial concentration of metal ions, pH and temperature (Ünlu and Ersoz, 2006). In general, the characteristics of the adsorption behaviour are inferred in terms of both adsorption kinetics and equilibrium isotherms. They are also important tools to understand the adsorption mechanism for the theoretical evaluation and interpretation of thermodynamic parameters.

Two adsorption models have been applied to evaluate the experimental data: the Lagergren pseudo-first order kinetic model and the Ho's second-order rate equation. The dynamic behaviour of the adsorption was investigated analysing the effect of concentration (15.3, 50.5 and 87.3 mg/L) at 25ºC and temperature (15, 25 and 35ºC) at an initial cadmium concentration of 15.3 mg/L. In addition, Langmuir and Freundlich isotherms were used to describe the adsorption equilibrium at the three temperatures essayed.

2. Experimental

Chestnut shell was supplied by a food factory (Galicia, NW of Spain), which produces chestnut derivatives. Firstly, it was air-dried till equilibrium moisture content, ground in a hammer mill and sieved to a particle size less than 2 mm. Then it was treated with formaldehyde in acid-medium to polymerise and immobilise the water-soluble phenolic compounds (Vázquez *et al*., 1994).

Adsorption experiments were conducted in a series of Erlenmeyer flasks covered with parafilm® to prevent contamination. 100 mL of cadmium ion solution of known concentration were transferred to the flasks together with 1g of pre-treated chestnut shell, and placed in a water bath shaker maintained at the desired temperature. When the adsorption process was completed, the solutions were filtered and analyzed for residual cadmium (II) ion concentrations by atomic absorption spectrometry. The equilibrium adsorption experiments at the three temperatures essayed (15, 25 and 35ºC) and at different initial cadmium concentration were performed for 4 days.

3. Results and discussion

Kinetic modelling*: *Effect of contact time and initial concentration of cadmium ions
Cadmium ion uptake capacities of the shell were determined as a function of time to determine an optimum contact time for the adsorption of cadmium on chestnut shell. Figure 1 shows the time course of the adsorption process at 25ºC for the three initial concentrations of the cation essayed. As it can be seen, the amount of cadmium

adsorbed increased rapidly with time at the beginning and became slow towards the end of the process. Independently of the initial concentration, for a contact time of 4 days, the maximum removal at each concentration was attained; therefore, this time was selected as the optimum contact time for the study of the adsorption equilibrium. The efficiency of adsorption was increased not only with increasing contact time but also with increasing initial cadmium concentration. Higher cadmium adsorption at higher cadmium solution concentration may be because of the higher metal to adsorbent ratio (Ofojama and Ho, 2006).

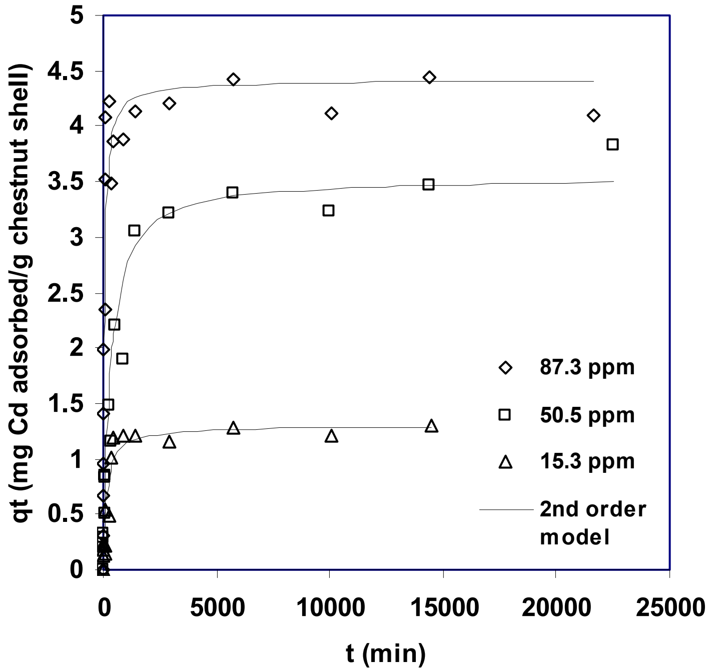

Figure 1. The effect of contact time for the adsorption of cadmium (II) onto *Castanea sativa* shell at 25ºC and various initial concentrations

In order to analyse the sorption kinetics of Cd (II) ions, the Langergren pseudo-first order kinetic model and Ho´s second-order rate equation were applied to data. The pseudo-second order reaction model (Figure 1), based on the assumption that the rate limiting step may be the bioadsorption (Aksu, 2001), provided the best description of the data with correlation coefficients higher than 0.99 for all initial cadmium concentrations. The rate constant (k_2), correlation coefficients of the plots together with the initial sorption rate (h_0) and equilibrium sorption capacity (q_e) are given in Table 1.

Table 1. Second-order rate constants for the adsorption of Cd (II) on chestnut shell at 25ºC and various initial concentrations

C_0 (mg/L)	k_2 ($g \cdot min^{-1} \cdot mg^{-1}$)	q_e ($mg \cdot g^{-1}$)	h_0 ($mg \cdot g^{-1} \cdot min^{-1}$)	r^2
15.3	$5.32 \cdot 10^{-3}$	1.29	$8.91 \cdot 10^{-3}$	0.9910
50.5	$9.46 \cdot 10^{-4}$	3.54	$1.19 \cdot 10^{-2}$	0.9912
87.3	$4.53 \cdot 10^{-3}$	4.41	$8.81 \cdot 10^{-2}$	0.9992

As it can be observed, the values of the initial rate constant and the equilibrium sorption capacity obtained from model equations were affected by the initial concentration. Thus, both parameters increased, respectively, from $8.91 \cdot 10^{-3}$ to $8.81 \cdot 10^{-2}$ $g.min^{-1}.mg^{-1}$ and from 1.3 to 4.4 mg/g with an increase in initial cadmium concentration from 15.3 to 87.3 mg/L. However, the dependence of the second-order model constant with the initial concentration was unexpected (minimum at the intermediate concentration).

Kinetic modelling*: *Effect of temperature
The effect of temperature on the uptake of cadmium on chestnut shell is shown in Figure 2 for an initial cadmium concentration of 15.3 mg/L. As it can be observed, the variation in temperature from 15 to 35ºC did not influence the time required to reach saturation. Experimental data were also applied to the pseudo-second order kinetic model and it is clear from the figure that experimental and theoretical values are in accordance with each other. The correlation coefficients were also very high with values higher than 0.99 (Table 2).

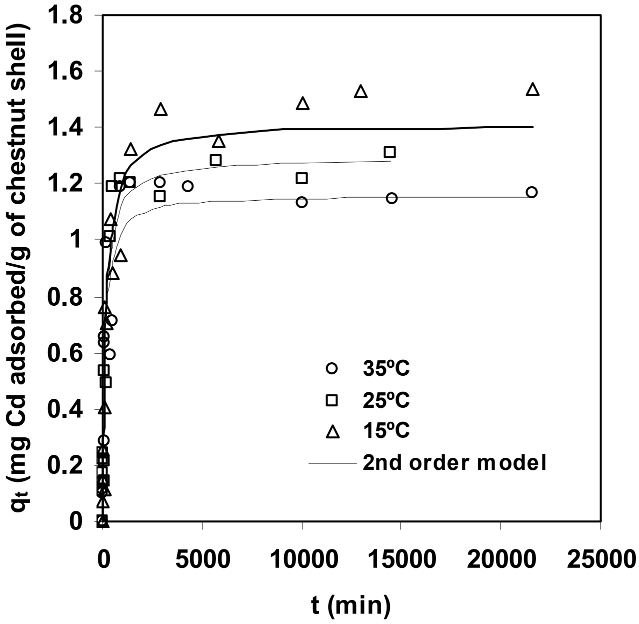

Figure 2. The effect of contact time for the adsorption of cadmium (II) onto *Castanea sativa* shell at an initial concentration of 15.3 mg/L and various temperatures

The data listed in Table 2 show that the initial sorption rate and rate constant correlate positively with temperature, thus these parameters varied from $8.39 \cdot 10^{-3}$ to $9.53 \cdot 10^{-3}$ $mg \cdot g^{-1} \cdot min^{-1}$ and $4.2 \cdot 10^{-3}$ to $7.1 \cdot 10^{-3}$ $g \cdot mg^{-1} \cdot min^{-1}$, respectively, when temperature raised from 15 to 35ºC. However, the equilibrium sorption capacity decreased with increasing temperature although very slightly.

Table 2. Second-order rate constants for the adsorption of Cd (II) on chestnut shell at an initial concentration of 15.3 mg/L and various temperatures

Temperature (ºC)	k_2 ($g.min^{-1}.mg^{-1}$)	q_e ($mg \cdot g^{-1}$)	h_0 ($mg \cdot g^{-1} \cdot min^{-1}$)	r^2
15	$4.19 \cdot 10^{-3}$	1.42	$8.39 \cdot 10^{-3}$	0.9941
25	$5.32 \cdot 10^{-3}$	1.29	$8.91 \cdot 10^{-3}$	0.9910
35	$7.06 \cdot 10^{-3}$	1.16	$9.53 \cdot 10^{-3}$	0.9960

A linear relationship between the rate constant and the reciprocal absolute temperature, with a correlation coefficient of 0.9954, was found (Figure 3). Therefore, the variation of the pseudo-second order rate constants with temperature could be represented in an Arrhenius form. The rate constant of sorption, k_0, took the value of 12.72 $g \cdot mg^{-1} \cdot min^{-1}$ and the activation energy for sorption, E, a value of 19.2 kJ/mol, which is inside the range (8-22 kJ/mol) of diffusion-controlled processes (McKay *et al.,* 1981; Ho and McKay, 1998). These results suggested that the rate-controlling step for the adsorption of cadmium on chestnut shell is likely not chemical in nature.

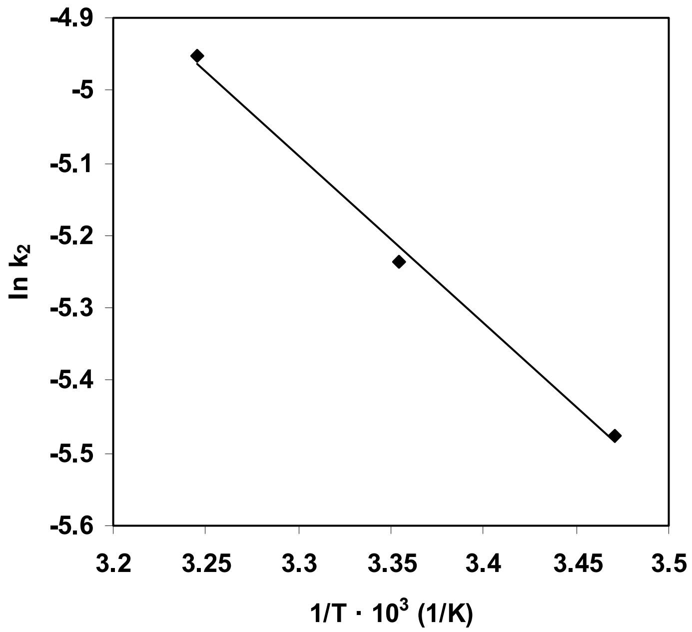

Figure 3. Relationship between rate constant and temperature (Arrhenius plot)

Equilibrium modelling: Effect of temperature

The equilibrium distribution of cadmium between the chestnut shell and the solution is important to determine the maximum sorption capacity of the shell for Cd (II). To assess the Langmuir and Freundlich isotherms and their ability to correlate experimental results, the theoretical plots from each isotherm have been performed at the three temperatures essayed. The correlation coefficients were higher than 0.99 for Freundlich isotherm and lower than 0.98 for Langmuir. Therefore, on the comparison of these r^2 values, it can be concluded that Freundlich equation represents a better fit to the experimental data than the Langmuir equation. This result also predicts the heterogeneity of the adsorption sites on chestnut shell.

Freundlich isotherm together the experimental data obtained at the three temperatures of 15, 25 and 35ºC are given in the Figure 4 and the adsorption constants evaluated from the isotherms with the correlation coefficients are shown in Table 3.

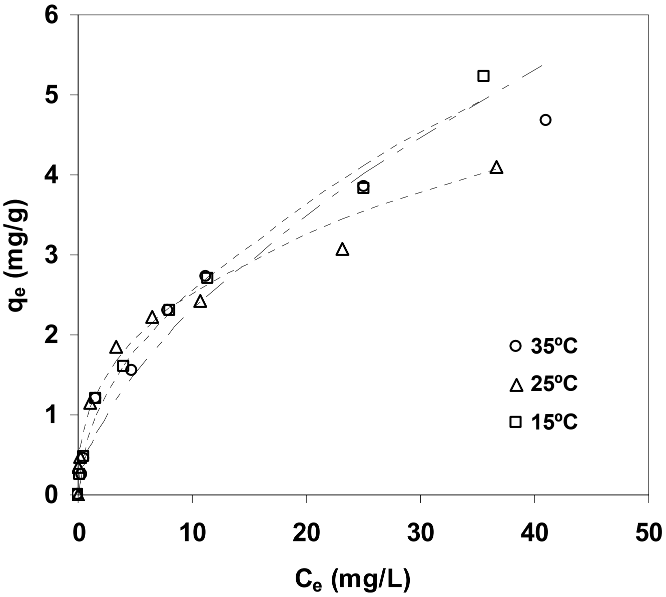

Figure 4. Freundlich adsorption isotherms for the adsorption of cadmium (II) ions on chestnut shell at different temperatures

The value of K_F, 1.08 $mg^{1-1/n} \cdot g^{-1} \cdot L^{1/n}$ (at 25ºC), which indicates the cadmium adsorption capacity of the chestnut shell, is comparable with some of those reported for other types of biomass (for example, 1.5 and 1.63 for walnut shell and waste tea, respectively; Orhan and Büyükgüngör, 1993). The values of n, which are greater than unity, indicate that cadmium (II) ions are favourably adsorbed by *Castanea sativa* shell at all the temperatures studied.

As can be seen in Table 3, the maximum value for K_F was obtained at 25ºC. This indicates that the dependence of Freundlich constants with temperature is quite inconsistent, confirming that it is necessary an exhaustive study about the influence of temperature on the cadmium adsorption process.

Table 3. Parameters of the Freundlich isotherm for the adsorption of Cd (II) on chestnut shell at an initial concentration of 15.3 mg/L and different temperatures.

Temperature (ºC)	K_F ($mg^{1-1/n}.g^{-1}.L^{1/n}$)	1/n	r^2
15	0.772	0.52	0.9928
25	1.077	0.37	0.9926
35	0.582	0.60	0.9891

4. Acknowledgements

Authors are grateful to Ministerio de Educación y Ciencia, Plan Nacional de I+D+I (Project AGL2005-00273) and to Xunta de Galicia (Project PGIDIT06PXIC265046PN) for financial support.

5. References

Aksu, Z. (2001) *Sep Purif. Technol.*, 21, 285-294.

Ho, Y. S. and McKay, G., (1998) *Chem. Eng. J.*, 70, 115-124.

McKay, G., Allen, S. J., McConvey, I. F. and Otterburn, M. S., (1981) *J. Colloid Interf. Sci.*, 80(2), 323-339.

Ofojama, A. E. and Ho, Y-S. (2007) *Int. J. Environment and Pollution*, in press

Orhan, Y. and Büyükgüngör, H. (1993) *Water Sci. Technol.* 28(2), 247-255.

Ünlü, N., and Ersoz, M., (2006) *J. Hazard. Mater.*, 136(2), 272-280.

Vázquez, G., Antorrena, G. González, J. and Doval, M. D. (1994) *Bioresource Technol.* 48, (1994) 251-255.