Preparation of an activated carbon / β-C*yclodextrin* composite material with high adsorption capacity of Pb^{2+} using an hydrothermal method

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Abstract

β-cyclodextrin (β-CD) and activated carbon (AC) were used as starting material to hydrothermally synthesize new hybrid material. It was found that hybrid carbon material, rich in oxygen-containing functional groups like -C=O-, -OH, etc., can be effectively well-dispersed on the surface and at the entrance of the pores of AC. The carbon composite that was obtained exhibited a remarkably enhanced adsorption capacity for Pb (II) per unit mass, reaching a value twice that of non modified AC. The high specific adsorption capacity of the composite can be explained by the abundant surface oxygen-containing functional groups and the relatively well-developed pore structure. In addition to this, the adsorption process studied was best described by the pseudo-first and pseudo-second order kinetic model.

Keywords: *Activated carbon, β-cyclodextrin, Adsorption, lead (II), modeling, Non-linear method.*

I. Introduction

The excess of Pb^{2+} ions released in environment from many activities such as agriculture and chemical industry, mining, and metal processing is very harmful to human and animal health. A low lead concentration of 0.006 mg/L blood can damage fetal brain, causing diseases to kidney, circulatory and nervous systems, etc. Therefore it is necessary to treat lead-containing wastewaters prior to any discharge into the environment [1]. Several conventional methods, such as chemical precipitation as hydroxides, carbonates or sulphides and subsequent liquid–solid separation, sorption, membrane processes, reverse osmosis, electrolytic recovery and liquid–liquid extraction, may be used for the removal of such pollutants [2, 3]. However, these technologies are either expensive for the treatment and disposal of the secondary toxic sludge or non effective when the toxic metal is present in wastewaters at low concentrations [4]. Alternatively, adsorption is one of the preferred methods for the treatment of wastewater because of its efficiency and simplicity. A successful adsorption process depends on the adsorption performance of the adsorbents. Various conventional adsorbents such as activated carbon have been reported for the removal of heavy metals from wastewaters [5, 6]. Commercial activated carbons are mostly prepared from coal, wood, peat and coconut shells [7]. Research on Hybrid materials are a new class of functional materials that have attracted tremendous interest in recent years [8-10].The combination of biomaterials β- cyclodextrin which is one of the most accessible, the lowest-priced and generally the most useful compounds [11]. Clearly the following figure 1 illustrates new possibilities for the preparation of novel functional materials, involving AC.

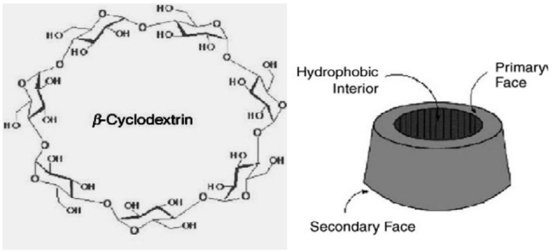

Figure. 1 Chemical structure of β-cyclodextrin.

The purpose of this study was to develop a new composite that combined abundant oxygen-containing functional groups with a highly developed pore structure as well as a high adsorption capacity for Pb (II) ions.

II. Materials and methods

II.1 Preparation of the adsorbent

The adsorbent support used in this study was commercial activated carbon supplied by Panreac Quimica Sa (E-08110 Montcada i Reixac [Spain]).
The method used for the preparation of the adsorbent consisted of mixing 10 g of AC with 10 g of β-CD, 150 mL of toluene and 5 mL of H_2SO_4. The obtained material-solution mixture was brought at temperature of 110°C, maintaining stirring for 24 hours. The material was then filtered and the recovered composite was washed extensively with distilled water. The washing was stopped when the conductivity of the wash water was practically identical to that of the distilled water used. The washed solid was then dried in an oven at 100°C for 24 hours.

II.2 Adsorption tests

All the compounds were purchased from BIOCHEM and used with no further purification. The experiments were carried out using distilled water. The adsorption process experiments were carried out batch wise in a reactor. The stock solution with a desired amount of nitrate lead was prepared by dissolving it in distilled water before adding a quantity of the prepared composite. The solution pH was adjusted at the desired value by using either 0.1 M NaOH or 0.1 M HNO_3. The concentration of the non adsorbed Pb(II) ions in the solution were determined by an atomic absorption spectrophotometery (AAS).The adsorbed quantities of metal ions at different time were determined by means of the following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{m} \qquad (1)$$

Where q_e is the amount of ions adsorbed per mass unit of prepared material, c_0 is the initial metal ions concentration (mg L^{-1}), C_e the equilibrium metal ions concentration (mg L^{-1}). V the volume of the aqueous phase (L) and m is the weight of material used (g).

II.3 Characterization methods

The chemical and physical characterizations of prepared materials were analyzed by different techniques such as:

- **FTIR spectroscopic:** which is defined as one of the most widely used methods for the qualitative analysis of organic matter. The different samples were prepared by pellets method and analysis was performed by 64 scans using IR AFFINITY-1 SHIMADZU, Spectra were recorded in the 4000-400 cm^{-1} range with a 4 cm^{-1} resolution.
- **Method of displacement liquid:** this method was used for physical characteristics determination such as apparent density, real density, total pore volume and porosity of different materials. The apparent density was calculated by filling a calibrated cylinder with a given activated carbon weight and tapping the cylinder until a minimum volume was recorded. This density was referred as tapping or bulk density of adsorbent. For the real density the pycnometer method was used and consisted in filling a pycnometer with the activated carbon, then adding a solvent (methanol) to fill the void; at each step the weight was determined. The pore volume and the porosity were determined by using a volumetric method consisting in filling a calibrated cylinder with a $V1$ volume of activated carbon (mass $m1$) and solvent (methanol) until volume $V2$ (total mass $m2$) was reached. Knowing the density of solvent, porous volume and porosity of the adsorbent were readily calculated.

III. Results and discussion

III. 1 Characterization results

A. FTIR

To further exhibit the functional groups involved on adsorbent used in this study, FTIR spectra of AC and modified AC with β-cyclodextrin were compared and are shown by Figure 2. In the case of AC, The band at around 3523 cm^{-1} was typically attributed to hydroxyl groups. The region of the spectrum of 2376 cm^{-1} could be attributed to CH_2 asymmetric stretching vibration. The region of the spectrum of 1683 cm^{-1} was attributed to axial deformation of carbonyl groups (C=O). Comparing the FTIR spectra of the modified AC-β-cyclodextrin (b) with the native AC (a), showed the appearance of an intensive absorption band at 1712 cm^{-1} in (b) which was absent in (a), and this band was due to the C=O stretching vibration of ester groups and

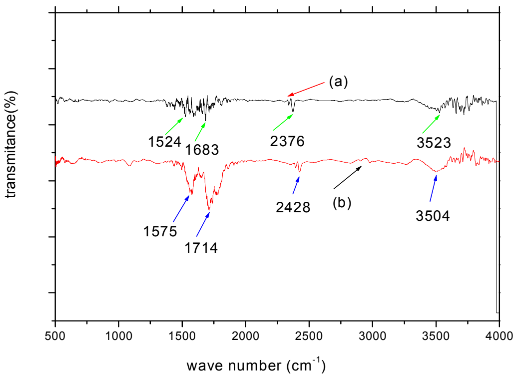

Figure. 2, Spectra FTIR of AC (a) and AC- β-CD (b)

The performance and high efficiency of adsorbent depend also on physical characteristics which, in the present study, included real density, total pore volume and porosity of materials used were determined and the results are presented in Table 1.

Table.1, physical characteristics of AC and AC- β-CD

Adsorbents	Apparent density (g/ cm^3)	Real density (g/ cm^3)	Total Pore Volume (cm^3/g)	Porosity
AC	0.32	0.93	2.05	65.4
AC-β-CD	0.40	0.98	1.45	58.2

The results of the physical characterization indicate that the physical characteristics of the AC and AC- β-CD depend on the nature of material. These results also show that the modification of AC reduced their total pore volume and their porosity. This diminution was due to the incorporation of the biopolymer β-cyclodextrin in the pores of the AC.

III.2 Adsorption performance

Based on a literature review it is well known, that adsorption performance of an adsorbent is closely related to its surface chemistry such as nature and number of surface bound functional groups [12]. Effects of modification of activated carbon with β-cyclodextrin and toluene agent in the removal of Pb^{2+} from aqueous solution was studied under identical conditions. As shown in Figure 3 the modification carried out onto activated carbon exhibited a considerably high efficiency in removing Pb^{2+} ions from aqueous solution, with the uptake Pb^{2+} passing from 10.57 to 21.20 mg/g. These results confirmed that the presence of the abundant surface oxygen involved after modification with β-cyclodextrin biopolymer was essential for the uptake of Pb^{2+} ions. This also was confirmed by the FTIR results. The sorption efficiency of Pb(II) increased gradually with increasing contact time and reached a plateau afterwards. An increase in initial Pb(II) concentration led to an increase in the sorption capacity of adsorbents used. The equilibrium time required for the metal ion was short. According to the results, the equilibrium time was fixed at 1 h for the rest of the batch experiments to make sure that equilibrium was reached. The majority of Pb(II) was removed within the first 10 min.

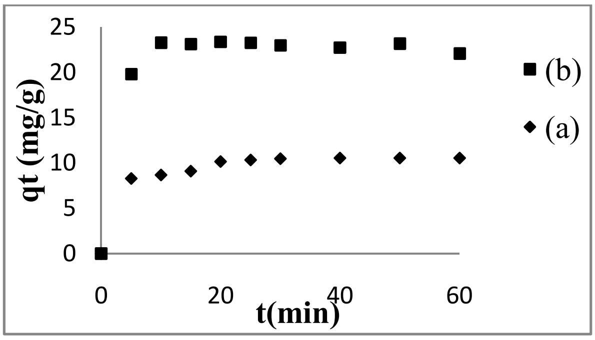

Figure. 3, Evolution of the Pb^{2+} sorption amount on agitation time by AC (a) and AC- β-CD (b)

III.3 Sorption mechanism

The sorption mechanism involved chemical bonding and ion exchange. The sorption mechanisms could be explained by the presence of several interactions, such as complexation, ion exchange due to a surface ionization, and hydrogen bonds. In general, solution pH not only influenced the properties of the adsorbent surface, but also affected the adsorbate speciation of different compounds in solution. The change in pH affected the adsorptive process through dissociation of functional groups on the solid surface active sites. Therefore, this led to a change in reaction kinetics and equilibrium characteristics of adsorption process. At the end of each experiment, the pH of the equilibrium solution was systematically measured, permitting to observe a decrease in this parameter compared to the original pH. This reduction in pH was due to the dissociation of the functional groups located at the AC-β- CD. Thus, some of the adsorbed Pb(II) ions could be attributed to a ionic exchange and the other part of the adsorbed Pb(II) ions to the various oxygen atoms of the β-CD functional groups, which had pairs of free electrons that could covalently bind to the Pb(II) ions. The same results were reported by [13].

Table 2. Kinetic parameters for adsorption of lead (II) onto AC and AC- β-CD using the non-linear method

Pseudo –first-order model				
Materials	k_1 (min^{-1})	$q_{e\ (cal)}$ (mg/g)	$q_{e\ (exp)}$ (mg/g)	R^2
AC	0.27	10.25	10.57	0.97
AC-β-CD	0.55	21.12	21.20	0.99
Pseudo-second-order model				
Materials	k_2 (g/mg/min^{-1})	$q_{e(\text{cal})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	R^2
AC	0,047	10.96	10.57	0.98
AC-β-CD	0.135	21.40	21.20	0.99

The FTIR spectra of the AC- β- CD had clearly elucidated the nature of the functional groups (-OH and –C=O) located on the surface and which were involved in the sorption mechanism for the removal of Pb(II) ions.

III.4 Adsorption Kinetics

Kinetic study is an important part of researches in adsorption area because the mechanism of the process can be performed by kinetic constants. Knowledge about kinetic parameters provides valuable insight into the reaction pathway, as well as the rate of adsorption which controls the resistance time is determined by kinetics [14]. In the present study, two kinetic models had been used to fit the experimental rate data.

The pseudo-first -order rate expression of lagergren is a widely used kinetic model for adsorption data analysis. This Kinetic model is used for reversible reaction with an equilibrium being established between liquid and solid phases [15]. It is represented by the following equation [14]:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (2)$$

Where q_t is the metal uptake capacity (mg/g) at any time t, q_e denotes the metal uptake capacity (mg/g) at equilibrium and k_1 (1/min) is the observed rate which was mistakenly. Most of the sorption systems followed a pseudo-second-order kinetic model which is based on the assumption that the rate- limiting factor may be chemisorptions [16]. The rate law for this system is expressed as [17]:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \qquad (3)$$

Table 2, shows the pseudo-first order and pseudo-second-order rate parameters obtained by using the non-linear method. The correlation coefficients are greater than 0.975 in all the cases. The theoretical $q_{e\ (cal)}$ values agreed perfectly with the experimental $q_{e(exp)}$ values. This suggested that the sorption kinetics system studied was described by both pseudo-first and pseudo-second-order models.

III.5 Intraparticle diffusion model

Intraparticle diffusion model assumes that the film diffusion is negligible and Intraparticle diffusion is the only rate controlling step, which is usually true for well-mixed solutions. The Intraparticle diffusion model is a single-resistance model in nature and can be derived from Fick's second law under two assumptions: first, the Intraparticle diffusivity is constant; second, the uptake of sorbate by the adsorbent is small relative to the total quantity of sorbate present in the solution [18]. The mathematical expression thus obtained for the Intraparticle diffusion model is:

$$q_{t=}K_{id}\, t^{\frac{1}{2}} \qquad (4)$$

Where q_t and K_{id} are the amount sorbed (mg/g) at time t and Intraparticle rate constant (mg/g min$^{(1/2)}$) respectively. Equation (4) indicates that a plot of q_t(m/g) versus the square root of time ($t^{1/2}$), would yield a straight line passing through the origin if the adsorption process obeys the Intraparticle diffusion model. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The deviation of straight lines from the origin (Figure 4) provides information about the thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger the intercept is the higher the external resistance [19].

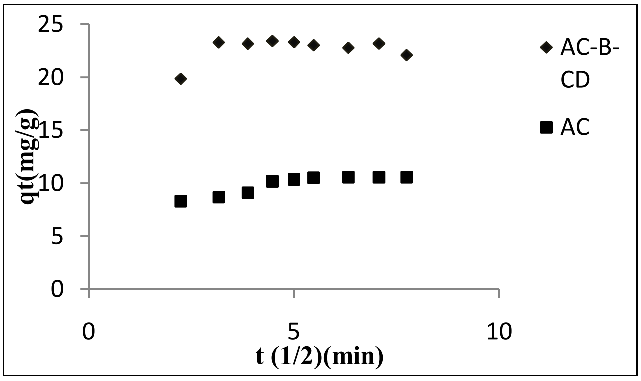

Figure.4 Intra-particle diffusion plot for the removal of lead.

responsible for the adsorption of Pb(II) on AC and AC-β-CD, attempts were made to calculate the coefficients of the process as reported by Chabani et al. [20] and Gupta et al. [21]. Assuming spherical geometry for the adsorbents particles, the overall rate constant of the process can be correlated with the pore diffusion coefficient (D_{ip}) and the film diffusion coefficient (D_f) independently as described below:

$$D_{ip}=\frac{0.03\, r^2}{t_{1/2}} \qquad (5)$$

$$D_f = 0.23\left[\left(\frac{r\,\varepsilon}{t_{1/2}}\right)\left(\frac{q_e}{C_0}\right)\right] \qquad (6)$$

where r is the radius of the sorbent, ε the film thickness (10^{-3} cm) [20, 21], q_e the amount of metal sorbed (mg/g), C_0 the initial concentration and $t_{1/2}$ is the time for half sorption (min) of Pb(II). If film diffusion was to be the rate-determining step in the adsorption of Pb(II) on the surface of AC and AC-β-CD, the value of the film diffusion coefficient (D_f) should be in the range 10^{-6} to 10^{-8} cm^2/s. If pore diffusion was to be rate limiting, the pore diffusion coefficient (D_{ip}) should be in the range 10^{-11} to 10^{-13} cm^2/s [22, 23]. In this study, the obtained values of D_f and D_{ip} (Table 3) were of the order of 10^{-8} cm^2/s, indicating that the boundary layer was the only rate controlling step.

Table 3. Diffusion coefficients for AC and AC- β-CD

Adsorbent	D_f (cm^2/s)	D_{ip} (cm^2/s)
AC	0.9 10^{-8}	1.7 10^{-8}
AC-β-CD	0.22 10^{-8}	2.1 10^{-8}

IV. Conclusion

In this study, new adsorbent was prepared by modifying AC with β-cyclodextrin. The FTIR spectra of the AC- β- CD had clearly elucidated the nature of the functional groups (-OH and –C=O) located on the surface and which were involved in the sorption mechanism for the removal of Pb(II) ions.

The equilibrium time required for the metal ion was short. The majority of Pb(II) was removed within the first 10 min. The sorption kinetics system studied was described by both pseudo-first and pseudo-second-order models.

The sorption mechanisms could be explained by ions exchange and the other part of the adsorbed Pb(II) ions could be due to the various oxygen atoms of the β-CD functional groups, which had pairs of free electrons that could covalently bind to the Pb(II) ions. In this study, the pore diffusion coefficient (D_{ip}) and the film diffusion coefficient (D_f) were calculated. The results indicated that the boundary layer was the only rate controlling step.

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