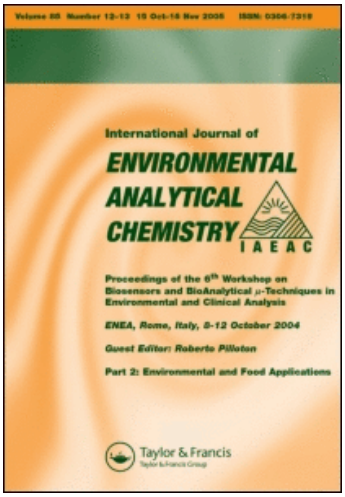

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Monitoring of Zn(II) and Cd(II) adsorption on activated carbon from aqueous multicomponent solutions by differential pulse polarography (DPP)

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Monitoring of Zn(II) and Cd(II) adsorption on activated carbon from aqueous multicomponent solutions by differential pulse polarography (DPP)

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The adsorption process of Zn(II) and Cd(II) from aqueous solution has been investigated from both kinetic and equilibrium standpoints, using differential pulse polarography (DPP) on a mercury dropping electrode as the analytical technique. With such an aim, adsorption experiments were performed using not only a single metal ion–Zn(II) or Cd(II) solution but also a multi-component ion metal–Zn(II), Cd(II) and Hg(II) solution. The influence of the pH change in the multi-component ion metal solution on the adsorption of Zn(II) and Cd(II) was also studied. The adsorption processes is relatively fast for Zn(II) and Cd(II). The presence of two foreign ions in the solution slightly speeds up the adsorption process for Zn(II) and significantly slows it down for Cd(II). The adsorption isotherms are similarly shaped for Zn(II) and Cd(II). The addition of the foreign ions has a more unfavourable effect on the adsorption for Cd(II) than for Zn(II). At pH 2, neither Zn(II) nor Cd(II) is adsorbed practically on the carbon. The voltammetric approach has proved to be a fast and efficient method that, at the same time, enables one to monitor the adsorption of Zn(II) and Cd(II) with potential on-line application, which could be useful in waste-water treatment.

Keywords: Zn(II); Cd(II); Adsorption; Differential pulse polarography; Activated carbon

1. Introduction

The study of the adsorption of metal ions on solid surfaces has gained research interest in recent years. This is mainly due to the environmental implications of the adsorption process, which is decisive in the physico-chemical speciation of metal ions in natural and residual waters. Adsorption–desorption equilibria control important phenomena

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in terms of mobility and bioavailability of elements in natural aqueous media. Adsorption on solid surfaces has also been proposed for the elimination of metal ions from polluted waters, this area being connected with the analytical preconcentration of metal ions.

Interactions of different metal ions, mainly heavy elements, with various kinds of natural solid surfaces, including vermiculite [1], goethite [2], marine particles [3, 4] and metal oxides [5, 6], have been studied previously. Chemically prepared sorbents from natural organic wastes, including cactaceus pulp, rice and groundnut husk, bark or sunflower stalks [7, 8] have also been used frequently. In the field of modified sorbent materials, activated carbon is a preferred option due to its proven ability to remove organic compounds and inorganic ions from aqueous solutions [9]. The useful properties of such a carbonaceous material include a high surface area, well-developed microporous structure, high adsorption capacity, and high degree of surface reactivity [10]. Moreover, activated carbon is a widely available material, easily prepared from a variety of residual products from the food processing and other industries. Activated carbon prepared from pecan shells has been used by Dastgheib and Rockstraw [11] to describe the adsorption isotherms of binary metal ion solutions. Kadirvelu and Namasivayam [12] assayed activated carbon from coconut coirpith for adsorption of Cd(II) from aqueous solutions. Bagasse pitch from sugar-refining industries was converted to activated carbon and tested for metal ion adsorption by Mohan and Singh [13]. Commercial granulated activated carbon has also been used by a number of authors in the adsorption of metallic ions [14, 15]. Enhancement of the adsorption efficiency has been attained by chemical modification of activated carbon [16–18]. For instance, sulphur compounds (i.e. H_2S and SO_2) have been used to increase the adsorption ability of commercial activated carbon toward Cd^{2+}, Hg^{2+}, and Pb^{2+} from aqueous solutions [19–24]. The use of activated carbon cloths [25, 26] and flow through activated carbon electrodes [27] for a more efficient contact has also been reported. Our group has previously reported [28] the adsorption kinetics of Zn(II) onto activated carbon surfaces.

Spectrochemical techniques are preferred to follow the adsorption of metal ions from aqueous solutions onto activated carbon and other above-mentioned solid surfaces. Such techniques include UV/Vis spectrophotometry [19, 22], flame and graphite furnace atomic absorption [11, 13, 14, 16–18, 20–27], ICP-AES and ICP-MS [4, 15, 27], and radiotracers [2, 4]. In contrast, electrochemical techniques have been used less often for such purpose. Abate *et al*. [1] used anodic stripping voltammetry to study the extent of Cd(II) and Pb(II) adsorption onto vermiculite. Pesavento *et al*. [14] combined voltammetric and spectrophotometric techniques for monitoring the adsorption of Cu(II) and Pb(II) onto activated carbon. Despite its minor use, however, electroanalytical techniques are attractive for these kinds of studies because of its inherent feasibility for on-line monitoring of adsorption phenomena, since the working electrode can be introduced in the medium without process perturbation.

In this work, we demonstrate the applicability of differential pulse polarography to the study of the adsorption of Zn(II) and Cd(II) on activated carbon from aqueous solutions containing either Zn(II) or Cd(II), or Zn(II), Cd(II) and Hg(II). Mercury has been used for testing the interference mainly because, like cadmium, it is a toxic metal. Furthermore, mercury is present in the environment, not only in the atmosphere because of its high volatility, but also in aqueous medium and in sediments [29]. Moreover, for the selected metals and their compounds, some trends are observed in

the variation of physico-chemical properties, for instance, in atomic and molecular sizes, which may help in the interpretation of the adsorption results. Adsorption kinetic and equilibrium experiments have been carried out at two pH values, i.e. at an unmodified solution pH and at pH 2. The results obtained may be applied to other heavy metals, provided that they are amenable to electrochemical detection. Our work is now aimed at designing an on-line voltammetric analyser for monitoring a functional purification water system to be checked under real operation conditions, and also for the chemical modification of the activated carbon to enhance its original adsorption potential toward heavy metals in aqueous solution.

2. Experimental

2.1 *Materials, instruments, and reagents*

Commercial activated carbon (average particle size, 1.5 mm, from Merck) was used. The carbon was characterized by the physico-chemical procedures of elemental analysis, gas adsorption (N_2, 77 K; CO_2, 273 K), mercury porosimetry, density measurements, and FT-IR spectroscopy. Proximate analysis data (moisture, volatile matter and ashes) were determined in a Mettler TA-3000 system, using a previously set-up thermogravimetry method [30], while the carbon fixed content was obtained by difference. Elemental analysis (C, H, N, S) was carried out in the Instituto Nacional del Carbon (CSIC, Oviedo, Spain) by using a LECO microanalyser. The N_2 isotherm was measured in a Quantachrome apparatus, Autosorb-1, and the CO_2 isotherm in a Micromeritics ASAP2000 surface area analyser. The mercury porosimetry was carried out in a Quantachrome porosimeter, Autoscan-60. The mercury density was measured as usual. For the helium density, a Quantachrome steropycnometer was used. The FT-IR spectrum was recorded on a Perkin-Elmer 1720 spectrophotometer in the wavenumber range of 450–4000 cm^{-1}. Fifty scans were taken at a 2 cm^{-1} resolution. The carbon : KBr used in the preparation of the disc was 1 : 400. The data obtained in the characterization study of the carbon are listed in table 1.

Voltammetric measurements were performed using Princeton Applied Research (PAR) 384B equipment, connected to a 303A polarographic stand. The analytical cell consists of a static mercury drop electrode (SMDE), operating in dropping mode (medium size), a 3 M KCl Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. Analytical glass cells were cleaned by first heating to 60°C in a 1 : 10 nitric acid : water bath for 5 days, then rinsed with ultrapure water and dried.

All chemicals were of analytical grade. Nitric acid was produced by a quartz sub-boiling system (Kürner, Rosenheim, Germany). Ultrapure water ($R > 13\,M\Omega$), as obtained from a MilliQ (Millipore) system, was used to prepare all the metallic ion solutions.

2.2 *Procedures*

Using test tubes fitted with Bakelite screw-on caps to avoid solvent losses by evaporation, individual adsorption experiments were carried out by adding an exactly weighed amount of activated carbon (i.e. 0.10 g in the kinetic experiments and 0.01–1 g in the adsorption equilibrium experiments) and 25 mL of metal ion solutions. Then, the

Table 1. Chemical and physical properties of the activated carbon[a].

Proximate analysis (wt%)	Moisture	2.62
	Volatile matter	3.98
	Fixed C	88.49
	Ashes	4.91
Elemental analysis (wt%)	C	88.17
	H	0.80
	N	0.63
	S	0.88
	O	3.34
Textural data	S_{BET}	$805\,m^2\,g^{-1}$
	V_{mi}	$0.39\,cm^3\,g^{-1}$
	V_{me}	$0.11\,cm^3\,g^{-1}$
	W_0	$0.16\,cm^3\,g^{-1}$
	$V_{me\text{-}p}$	$0.16\,cm^3\,g^{-1}$
	$V_{ma\text{-}p}$	$0.20\,cm^3\,g^{-1}$
	V_T	$0.84\,cm^3\,g^{-1}$
Densities ($g\,cm^{-3}$)	ρ_{He}	2.08
	ρ_{Hg}	0.76
Surface groups	$3739\,cm^{-1}$	$\nu(O–H)_{free}$
	$3428\,cm^{-1}$	$\nu(O–H)_{associated}$
	$1701\,cm^{-1}$	$\nu(C=O)$
	$1550\,cm^{-1}$	$\nu(C=C)$
	$1146\,cm^{-1}$	$\nu(C–O)$

[a] The textural data were obtained from the N_2 adsorption isotherms at 77 K: S_{BET} ($P/P^0 = 0.05 - 0.35$, $a_m = 16.2\,Å^2$), V_{mi} (volume adsorbed, V_{ad}, at $P/P^0 = 0.10$) and V_{me} (V_{ad} at $P/P^0 = 0.95 - V_{ad}$ at $P/P^0 = 0.10$), the CO_2 adsorption isotherms at 273 K: W_0 (Dubinin–Radushkevich equation), mercury intrusion curves: $V_{me\text{-}p}$, $V_{ma\text{-}p}$, and the helium and mercury density values (ρ_{He} and ρ_{Hg}): $V_T = 1/\rho_{Hg} - 1/\rho_{He}$. V_{mi}, V_{me}, and W_0 are expressed as liquid volumes.

tubes were placed in a shaker bath (Unitronic-Orbital C, Selecta), containing water at 25°C and working with a constant agitation of 50 oscillations/min. The contact between the liquid and solid phases was maintained up to a different time between 0.5 and 360 h in the kinetic study and until equilibration was reached in the adsorption system, which took approximately 330 h, when measuring the adsorption isotherms. Adsorption experiments were performed at two pH values, i.e. at unmodified solution pH and at pH 2. This pH value was fixed in the solution by adding concentrated HCl solution, as supplied by Probus (Spain).

A certain amount of supernatant solution was taken for Zn(II) and Cd(II) differential pulse voltammetric analysis. Ten millilitres of sample were placed in the analytical cell. Suprapur HCl (Merck) was then added for pH 2 adjustment. The analytical parameters were as follows: purging time, 240 s; start potential, −0.4 V; final potential, −1.2 V; drop time, 1 s; pulse height, 20 mV; sweep rate, $4\,mV\,s^{-1}$. Quantitative measurements were performed by Zn(II) and Cd(II) standard additions. The analytical performance of the method was confirmed by daily evaluation of the recovery from 10^{-4} M Zn(II) and Cd(II) standard solutions, which was always within the $100 \pm 5\%$ range. Detection limits were estimated from the signal/noise ratio to be around 5×10^{-7} M, far lower than the analytical signals measured in this study. No interference from water-soluble compounds of the activated carbon was observed. As an example, a sample polarogram showing the Zn(II) and Cd(II) voltammetric responses for a particular adsorption experiment is shown in figure 1.

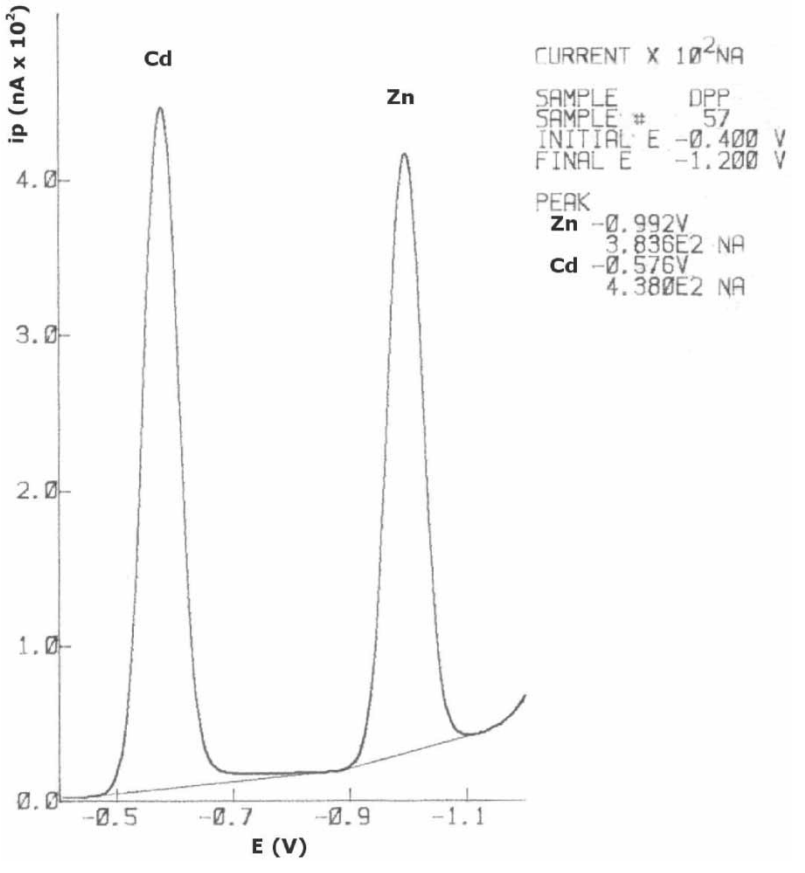

Figure 1. Zn(II) and Cd(II) differential pulse voltammetric response during an adsorption kinetic experiment. Initial concentration: 10^{-4} M each (chloride salts). Adsorption time: 240 h.

3. Results and discussion

3.1 *Properties of the adsorbent*

As shown in table 1, the adsorbent used in this study is typical activated carbon, its fixed carbon content being as high as 88.49 wt%. On the other hand, the material possesses well-developed surface area and porosity, in particular, in the micropore region (N_2 adsorption). The values of $V_{me} = 0.11\,cm^3\,g^{-1}$ and $V_{me\text{-}p} = 0.16\,cm^3\,g^{-1}$ indicate that the volume of mesopores is significant in the carbon. It is a relevant textural property for the adsorption from the liquid phase as such pores act as the channels leading to the micropores, where the surface area concentrates, and most adsorption occurs. The total pore volume is $0.84\,cm^3\,g^{-1}$. As inferred from the FT-IR spectrum registered for the carbon, which is omitted for the sake of brevity, O–H, C=O, C=C and C–O bonds containing surface functional groups or chemical structures are present in the carbon. The presence of C=O and C–O bonds is consistent with its high oxygen content (i.e. 3.34 wt%). Finally, as expected for porous solids, ρ_{He} is higher than ρ_{Hg}.

3.2 *Adsorption kinetics*

The plots of concentration (C) against time (t) for the various Zn(II) containing solutions are shown in figure 2. When the single metal ion solution is used, the adsorption process of Zn(II) is relatively fast as it occurs largely before approximately 150 h have elapsed (notice that even at short contact times, the concentration of the Zn(II) solution is already below 9×10^{-5} mol L^{-1}). At longer times between 150 and 350 h, the change produced in such a concentration is of little significance. As a result of the adsorption, the concentration of Zn(II) in the remaining solution is reduced to about half of that in the starting solution. Considering the ratio of 25 mL Zn(II) solution to 0.10 g of carbon, the effectiveness of the carbon substrate for the uptake of Zn(II) is around 12.5 μmol g^{-1}.

For the multi-component ionic solution, the C–t plot displays a similar shape to that obtained when the Zn(II) solution is used. However, the former curve is situated slightly below the latter in a wide time range (i.e. until $t \approx 150$ h). At short contact times, the concentration of Zn(II) becomes lower than 8×10^{-5} mol L^{-1}. From these results, it is clear therefore that the adsorption of Zn(II) is a somewhat faster process when the ionic strength increased in the Zn(II) solution. The speeding up of the process is surely connected with the change produced in the degree of electrostatic interaction in the bulk of the solution when Cd(II) and Hg(II) are present in this solution. The repulsive interactions between ions with the same charge will depend not only on their concentration (i.e. as the concentration increases, the degree of interaction must be larger) but also on the ionic size. Thus, an increase in the ionic size will decrease

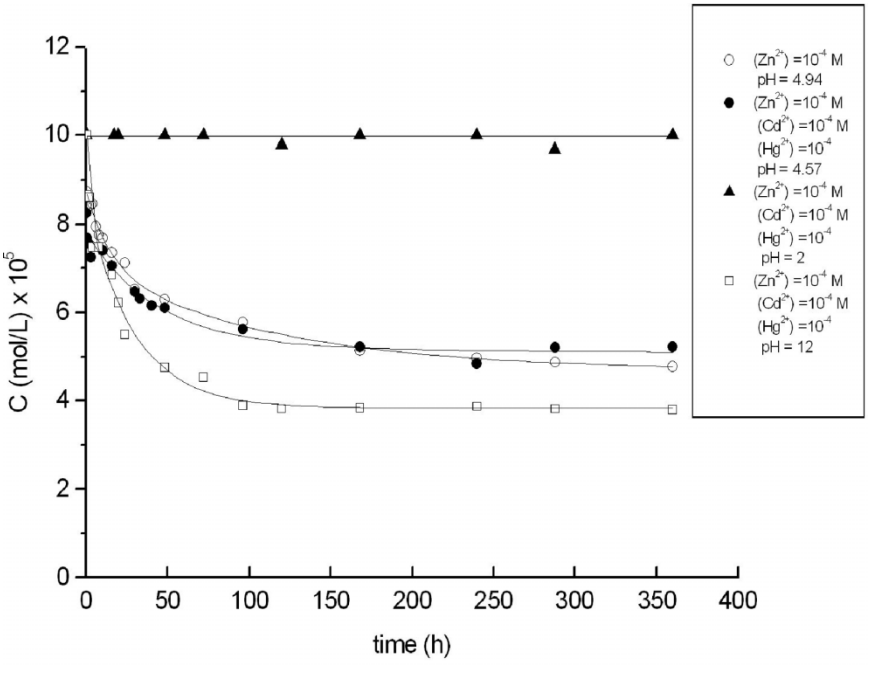

Figure 2. Kinetic evolution of Zn(II) adsorption onto the activated carbon. The legend indicates initial concentrations and sample compositions (chloride salts).

the intensity of such interactions, and this facilitates the diffusion of Zn^{2+} in the solution and its approach to the adsorbent surface. Speciation of the metals in aqueous solution is another factor that must influence the electrostatic interaction and hence adsorption kinetics. In that connection, it should be borne in mind that in aqueous solution, $ZnCl_2$ is highly dissociated [31], a large proportion of $CdCl_2$ is found undissociated, and only a very small amount of $HgCl_2$ is as Hg^{2+}; most of $HgCl_2$ in solution is present as undissociated compound molecules [32]. Moreover, the three metal chlorides form auto-complexes, i.e. species of the form MCl^+, MX_3^-, MX_4^{2-}, etc. [31, 32].

As inferred also from figure 2, the adsorption of Zn(II) practically does not occur at pH 2 (the *C–t* plot obtained at this pH value stands nearly parallel to the abscissa axis in the entire time interval studied). The dramatic effect of a great presence of H_3O^+ ions in the multi-component ionic solution on the adsorption of Zn(II) is attributable to a strong competitive effect between H_3O^+ and Zn^{2+} for surface active sites of the activated carbon. The preferable adsorption of H_3O^+ to the detriment of the adsorption of Zn^{2+} is consistent with the fact that H_3O^+ is an abnormally more mobile ion [33] than Zn^{2+} and also with the smaller size and higher concentration of H_3O^+ (i.e. both factors favour the ionic exchange process) as compared with Zn^{2+}; the ionic charge is however higher for Zn^{2+} than for H_3O^+. A decrease in the adsorption at pH 2 was also observed before when investigating the adsorption of various metal ions on heat-treated and sulphurized activated carbon [22].

The resultant *C–t* plots for the adsorption of Cd(II) are shown in figure 3. In comparison with the above-mentioned results obtained for Zn(II), one should note the more significant decrease produced in *C* for Cd(II) a short contact time

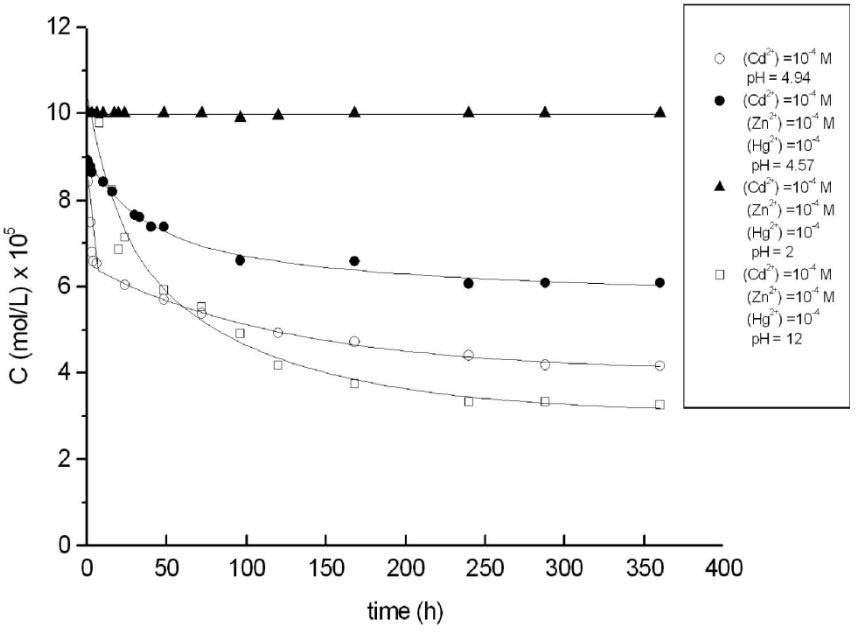

Figure 3. Kinetic evolution of Cd(II) adsorption onto the activated carbon. The legend indicates initial concentrations and sample compositions (chloride salts).

(i.e. until $t \approx 10$ h) between the Cd(II) solution and the adsorbent. At such times, therefore, the adsorption process accelerates for Cd(II). This is in agreement with the somewhat higher diffusivity at an infinite dilution for Cd(II) (0.719×10^{-5} cm^2 s^{-1}) than for Zn(II) (0.703×10^{-5} cm^2 s^{-1}) [34]. At higher solution concentrations, such as those used in the present study, the ionic size may also influence the kinetics of the adsorption process of these metal ions. Thus, because Cd(II) is a significantly larger ion than Zn(II) (the ionic radius is 1.03 and 0.83 Å, respectively) [35], a decrease in the degree of electrostatic interaction and as a result an increase in the diffusion are expected to occur in the solution of Cd(II), the process then being faster for this ion than for Zn(II). The effectiveness of the carbon substrate for Cd(II) adsorption is around 13.7 μmol g^{-1}.

It should also be noted that when Zn(II) and Hg(II) are present in the Cd(II) solution, the adsorption process is significantly slower than when such a solution only contains Cd(II). In the case of Cd(II), which possesses an intermediate size to the sizes of Zn(II) and Hg(II) (i.e. the ionic radius is 1.12 Å for Hg^{2+} [35]), the effect of the size of these foreign ions on the adsorption kinetics of Cd(II) must balance, and therefore the predominant effect is merely that associated with the higher ionic concentration of the multi-component solution. Since the ionic disorder in the bulk of the solution must increase with increasing solution concentration, the adsorption process should be slower when the multi-ionic solution is used, and this is reflected by the adsorption results obtained in this study. In fact, for long contact times (i.e. $t > 50$ h) the rate of adsorption is also higher for the solution of only Cd(II), as revealed by the noticeably greater slope of the C–t plot obtained for such a solution/carbon adsorption system (figure 3). At pH 2, the adsorption of Cd^{2+}, as for Zn(II), is almost negligible, and therefore the process kinetics do not deserve to be discussed any further.

3.3 *Adsorption isotherms*

The adsorption isotherms (i.e. the plots of X_e against C_e, X_e and C_e being the amount of metallic ion adsorbed per gram of adsorbent and the equilibrium concentration, respectively) determined for Zn(II) are shown in figure 4. The isotherm measured at pH 2 has been omitted as the adsorption of Zn(II) is very low at this pH value. From these results, it is evident that the pH change in the Zn(II) solution between ≈4.94 (i.e. the pH of the initial Zn(II) solution) and 2, and hence a great presence of protons in the Zn(II) solution has a strong unfavourable effect on the adsorption of this metal ion. When investigating the adsorption of Pb(II) and Cu(II) also on granular activated carbon (Filtrasorb 300, Chemviron) by complexation with surface functional groups, an important competitive effect was also reported by Pesavento *et al.* [14], even when, in their study, the decrease in pH was less significant (i.e. between 6 and 4.20, at most). It was also found by these authors that the concentration of active sites in the aforementioned carbon is much lower than that of the total protonable sites and that, as a result, only a fraction of the protonable sites is able to combine with the heavy metal ions.

The isotherm obtained for the single metal ion–Zn(II) solution clearly displays two more sloping rises which commence at C_e values of 1.5–2.0×10^{-5} mol L^{-1} and $\approx 6.5 \times 10^{-5}$ mol L^{-1} and two not-too-flat 'plateaus' situated at 1.5–2.0×10^{-5} mol L^{-1} and 1.5–2.0×10^{-5} and 6.5×10^{-5} mol L^{-1}. When studying the adsorption of organic

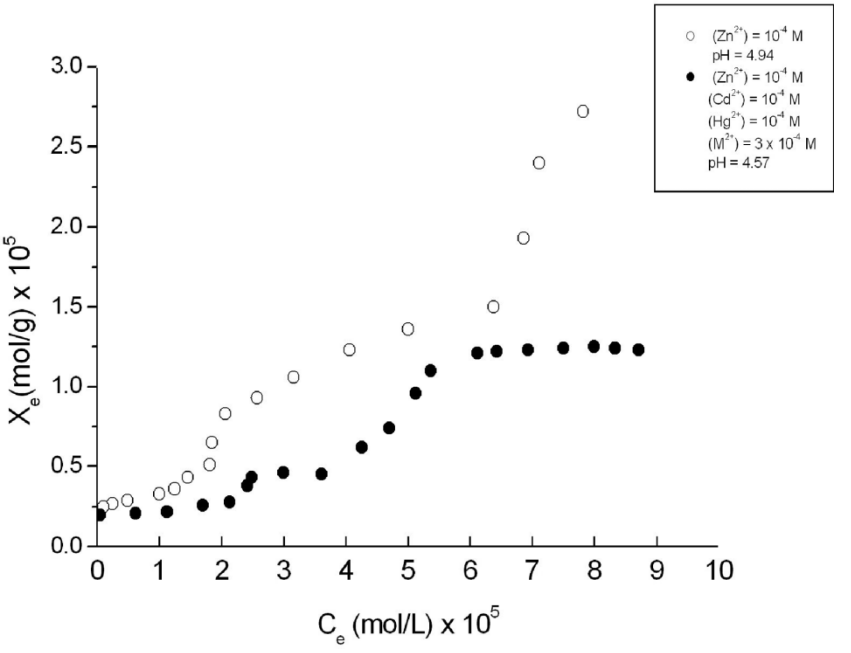

Figure 4. Adsorption isotherms for Zn(II). The legend indicates initial concentrations and sample compositions (chloride salts).

solutes, a second rise in the adsorption isotherm was attributed earlier by Giles *et al.* [36] to the development of a fresh surface on adsorption. The fresh surface may be: (1) the exposed parts of the adsorbate layer already present; (2) new (probably) more crystalline regions of the substrate structure into which the solute begins to penetrate; or (3) part of the original surface. On the other hand, the length of the plateau was associated by the same authors with the energy barrier that has to be overcome before additional adsorption can occur on new sites, after the surface has become saturated to the first degree.

From the adsorption isotherm obtained for the single metal ion–Zn(II) solution, it becomes apparent that the adsorption of Zn(II) on the surface of the activated carbon occurs in two different stages. Furthermore, the magnitude of the two rises denotes that the affinity of Zn(II) toward the adsorbent is higher for the second one. Moreover, the length of the plateau is larger for that at higher C_e values. These results suggest that, after a preceding degree of adsorption has been completed, the adsorption of Zn(II) occurs on the fresh surface, which is only accessible to this metallic ion when the Zn(II)-to-carbon ratio is higher. Perhaps such a surface is more active to the adsorption of Zn(II), and as a result the Zn(II) aquo-cation loses water molecules from its coordination shell, the adsorbate/adsorbent affinity then being higher.

The presence of Cd(II) and Hg(II) in the Zn(II) solution markedly influences the adsorption of this metal ion. Thus, in the isotherm determined for the multi-component ionic solution (figure 4), the first rise is less sloped, the second plateau is shorter, and the second rise commences at a lower C_e value; at a high C_e, a further long plateau is defined. Accordingly, a higher content of metallic ions in the Zn(II) solution seems to facilitate the access of fresh surface to Zn(II), to the detriment of the

Zn(II)/carbon affinity. However, the fact that the amount of Zn(II) adsorbed at low C_e values (i.e. up to $\approx 1.25 \times 10^{-5}$ mol L^{-1}) decreases only slightly in comparison with the single metal ion solution suggests that the affinity of Zn(II) at low metal ion/carbon ratios is higher for Zn(II) than for Cd^{2+} and Hg^{2+}, which is consistent with the smaller ionic size, and hence higher ionic potential, for Zn(II) than for Cd(II) and Hg(II). Otherwise, the adsorption of Zn(II) should occur on surface active sites other than those involved in the adsorption of Cd(II) and Hg(II). If so, the adsorption behaviour of the various metals would be connected with the dependence of speciation [31, 32] on each metal chloride. Thus, the chemical species present in solution, depending on their ionic or covalent character, would adsorb on different surface sites of the adsorbent. The ionic species should interact preferably with hydrophilic groups (namely, functional groups and heteroatoms) and the covalent species with hydrophobic portions of the carbon structure.

From figure 4, it also follows that in a wide C_e interval, the amount of adsorbed Zn(II) is significantly smaller for the multi-component ionic solution. This fact denotes competition for, or hindrance to, the adsorption between the Zn(II) ion and the Cd(II) and Hg(II) ions. The competition effect must be very strong above ($C_e \approx 6 \times 10^{-5}$ mol L^{-1}) as X_e remains steady, without further increasing with C_e. For $C_e \approx 6.5 \times 10^{-5}$ mol L^{-1}, X_e is practically the same regardless of the single or multi-solute solution used. This is quite a remarkable finding, as it means that at such a C_e value, X_e does not depend on the presence of Cd(II) and Hg(II) in the Zn(II) solution.

The adsorption isotherms measured for the single metal ion–Cd(II) solution (figure 5) as a whole have a similar shape to that obtained for Zn(II) (figure 4). Different features

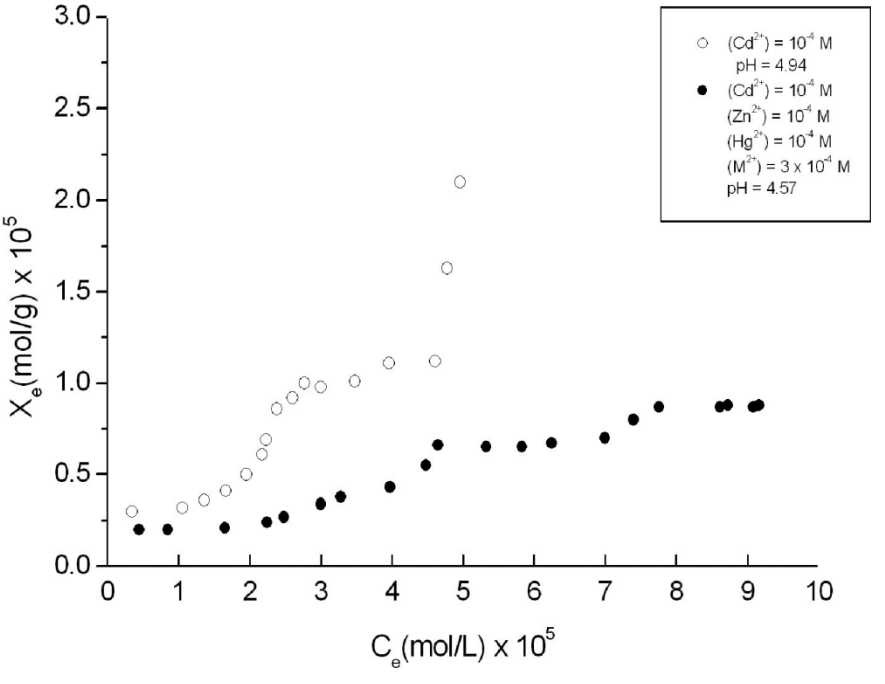

Figure 5. Adsorption isotherms for Cd(II). The legend indicates initial concentrations and sample compositions (chloride salts).

worth noting are the significantly shorter second plateau and also the more marked rises in the isotherm for Cd(II). These results are consistent with an easier loss of coordination water molecules for Cd(II) than of Zn(II), which can be accounted for in terms of the larger ionic size of Cd(II).

The effect of the presence of Zn(II) and Hg(II) in the Cd(II) solution on the adsorption of this metal ion is much stronger than for Zn(II). Thus, the isotherm rises are less pronounced for Cd(II). These results are compatible with a stronger ionic competition effect for the adsorption in the case of Cd(II) than for Zn(II). Such an effect must be mainly associated with the presence of Zn(II) in the Cd(II) solution as the ionic size is smaller for Zn(II) than for Cd(II). Thus, the affinity toward the adsorbent will be higher for Zn(II) than for Cd(II), and the exchange process will also be favourable for Zn(II). Using a different couple of metallic ions, the complete replacement of Pb(II) (ionic radius = 1.32 Å) by Cu(II) (ionic radius = 0.72 Å [35]) at sufficiently high concentrations has been observed before [14], thus demonstrating that the two metals compete at least for some interaction sites. Finally, it should be noted that for Cd(II), there is a C_e value (4.5×10^{-5} mol L^{-1}) as well at which the unfavourable effect of Zn(II) and Hg(II) on the adsorption of Cd(II) is less significant.

The Langmuir equation [37] was applied to analyse the adsorption equilibrium for Zn(II) and Cd(II),

$$C_e/X_e = 1/(X_m b) + C_e/X_m, \quad (1)$$

where X_m and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. Specifically, X_m is the amount of metal ion necessary for the formation of the monolayer, and b is a constant related to the intensity of the adsorption. In the present study, owing to the peculiar shapes of the adsorption isotherms with various branches (see figures 4 and 5), equation (1) was applied only to the first. The C_e range of application of this equation depends on the composition of the initial solution, being wider for the multi-component ionic systems (2.13×10^{-5} mol L^{-1}, Zn^{2+}; 2.24×10^{-5} mol L^{-1}, Cd^{2+}) than for the single metal ion systems (1.24×10^{-5} mol L^{-1}, Zn^{2+}; 1.66×10^{-5} mol L^{-1}, Cd^{2+}) and also for cadmium than for zinc. The plot of C_e/X_e *versus* C_e yields a straight line with slope $1/X_m$ and intercept $1/(X_m b)$; R^2 ranged between 0.994 and 0.999. The resultant X_m values, which are given in mg g^{-1} for comparison purposes, are 0.25 and 0.19 mg g^{-1} for zinc and 0.43 and 0.29 mg g^{-1} for cadmium. Accordingly, X_m is lower for zinc than for cadmium and for the multi-component ionic systems than for the single metal ion systems. As expected, the values of X_m obtained here are lower than those reported previously for other carbonaceous adsorbents [12]. In the case of Cd(II), as a guide, X_m was 3.27 mg g^{-1} for peach-stone carbon and 2.70 mg g^{-1} for almond-shell carbon [38]. On the other hand, the competition effect due to the presence of interference ions in the Zn^{2+} or Cd^{2+} solution is stronger for Cd^{2+} than for Zn^{2+}. The percentage decrease in X_m is 33 for Cd^{2+} and 24 for Zn^{2+}.

4. Conclusions

Differential pulse voltammetry on a mercury dropping electrode has proved to be a fast, reliable and convenient tool for studying the adsorption kinetics and equilibrium

of Zn(II) and Cd(II) from both single- and multi-component ionic aqueous solutions on activated carbon. The carbon used is an efficient material to remove significant amounts of Zn(II) and Cd(II), its adsorption capacity being around 12.5 and 13.7 $\mu mol\, g^{-1}$ for Zn(II) and Cd(II), respectively. The presence of foreign ions in the Zn(II) solution slightly speeds up the adsorption processes for Zn(II) and significantly slows it down for Cd(II). Their unfavourable effect on the adsorption is stronger for Cd(II) than for Zn(II). The decrease in pH of the sample solution to 2 renders the adsorption of Zn(II) and Cd(II) negligible.

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References

[1] G. Abate, J. Lichtig, J.C. Masini. *Talanta*, **58**, 433 (2002).
[2] M. Bäckström, M. Dario, S. Karlsson, B. Allard. *Sci. Tot. Environ.*, **304**, 257 (2003).
[3] J.M. Garnier, M.K. Pham, P. Ciffroy, J.M. Martin. *Environ. Sci. Technol.*, **31**, 1597 (1997).
[4] V. Hatje, T.E. Payne, D.M. Hill, G. McOrist, G.F. Birch, R. Szymczak. *Environ. Int.*, **29**, 619 (2003).
[5] N.Z. Misak, H.F. Ghoneimy, T.N. Morcos. *J. Colloid Interf. Sci.*, **184**, 31 (1996).
[6] P. Trivedi, L. Axe. *Environ. Sci. Technol.*, **35**, 1779 (2001).
[7] S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry. *Sci. Tot. Environ.*, **116**, 31 (1992).
[8] G. Carrillo-Morales, M.M. Dávila-Jiménez, M.P. Elizalde-González, A.A. Peláez-Cid, *J. Chromatogr. A*, **938**, 237 (2001).
[9] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla. In *Chemistry and Physics of Carbon*, L.R. Radovic (Ed.), Vol. 27, Marcel Dekker, New York (2000).
[10] R.C. Bansal, J.B. Donnet, F. Stoeckli. *Active Carbon*, Marcel Dekker, New York (1988).
[11] S.A. Dastgheib, D.A. Rockstraw. *Carbon*, **40**, 1853 (2002).
[12] K. Kadirvelu, C. Namasivayam. *Adv. Environ. Res.*, **7**, 471 (2003).
[13] D. Mohan, K.P. Singh. *Water Res.*, **36**, 2304 (2002).
[14] M. Pesavento, A. Profumo, G. Alberti, F. Conti. *Anal. Chim. Acta*, **480**, 171 (2003).
[15] J.P. Chen, M. Lin. *Water Res.*, **35**, 2385 (2001).
[16] J. Rivera-Utrilla, M. Sánchez-Polo. *Water Res.*, **37**, 3335 (2003).
[17] T.C. Miller, J.A. Holcombe. *Anal. Chim. Acta*, **455**, 233 (2002).
[18] L. Monser, N. Adhoum. *Sep. Purif. Tech.*, **26**, 137 (2002).
[19] C. Valenzuela-Calahorro, A. Macías-García, A. Bernalte-García, V. Gómez-Serrano. *Carbon*, **28**, 321 (1990).
[20] A. Macías-García, C. Valenzuela-Calahorro, V. Gómez-Serrano. *Carbon*, **31**, 1249 (1993).
[21] A. Macías-García, C. Valenzuela-Calahorro, A. Espinosa-Mansilla, V. Gómez-Serrano. *An. Quim.*, **91**, 547 (1995).
[22] V. Gómez-Serrano, A. Macías-García, A. Espinosa-Mansilla, C. Valenzuela-Calahorro. *Water Res.*, **32**, 1 (1998).
[23] A. Macías-García, V. Gómez-Serrano, M.F. Alexandre-Franco, C. Valenzuela-Calahorro. *J. Hazard. Mat.*, **B103** 141 (2003).
[24] A. Macías-García, C. Valenzuela-Calahorro, A. Espinosa-Mansilla, A. Bernalte-García, V. Gómez-Serrano. *Carbon*, **42**, 1755 (2004).
[25] C. Faur-Brasquet, Z. Reddad, K, Kadirvelu, P. Le Cloirec. *Appl. Surf. Sci.*, **196**, 356 (2002).
[26] B.M. Babic, S.K. Milonjic, M.J. Polovina, S. Cupic, B.V. Kaludjerovic. *Carbon*, **40**, 1109 (2002).
[27] H. Oda, Y. Nakagawa. *Carbon*, **41**, 1037 (2003).
[28] R. Pardo-Botello, C. Fernández-González, E. Pinilla-Gil, E.M. Cuerda-Correa, V. Gómez-Serrano. *J. Colloid Interf. Sci.*, **277**, 292 (2004).
[29] X. Doménech. *Química de la Hidrosfera: Origen y Destino de los Contaminantes*, Miraguano Eds, Barcelona (1998).
[30] C. Valenzuela, A. Bernalte. *Bol. Geol. Min.*, **196**, 58 (1985).
[31] H. Remy. *Treatise on Inorganic Chemistry*, Vol. 2, Elsevier, Amsterdam (1956).

[32] J.C. Bailar Jr, H.J. Emeléus, R. Nyholm, A.F. Trotmant-Dickenson (Eds). *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford (1973).
[33] N.N. Greenwood, A. Earnshaw. *Chemistry of the Elements*, Pergamon Press, Oxford (1989).
[34] D.R. Lide (Ed.). *Handbook of Chemistry and Physics*, 82nd Edn, CRC Press, Boca Raton, FL (2002).
[35] J. Emsley. *The Elements*, Clarendon Press, Oxford (1989).
[36] C.H. Giles, T.H. MacEwans, S.N. Nakhwa, D. Smith. *J. Chem. Soc.*, **786**, 8973 (1960).
[37] I. Langmuir. *J. Am. Chem. Soc.*, **40**, 1361 (1918).
[38] M.A. Ferro-García, J. Rivera-Utrilla, I. Bautista-Toledo. *Carbon*, **26**, 263 (1988).