The adsorption of cadmium(II) on an activated carbon was investigated by determining the adsorption isotherm from a 0.1 M NaNO₃ solution. Different acidities, from pH 5 to 7.5, were separately examined. Increasing concentration of cadmium(II) were added to the solution, and the concentration of metal ion adsorbed in the carbon phase was determined after equilibration at 20°C. The data were treated according to the Ruzic linearization method, in order to evaluate the concentration of the active sites ($c_L$) in the carbon phase, able to bind cadmium(II), and the conditional adsorption coefficient $\beta_c$. This was found to strongly depend on the acidity of the solution phase, and this dependence was examined on the basis of a model involving the combination of cadmium(II) with protonated sites. Quantities related to the complexation constant $\beta_i$ and the protonation constant $K_{a_i}$ were evaluated from these quantities on the basis of the Gibbs-Donnan model for the ion exchange solids. They allow one not only to describe the adsorption process, but also to make predictions. It has been found that the adsorption of cadmium(II) on the considered activated carbon can be described by two adsorption equilibria. One involves carbon sites at low concentration (0.00038 mmol g⁻¹) but with a high complexation constant (log $\beta_i$ =6.75), the other involves carbon sites which are present at much higher concentration (0.019 mmol g⁻¹), with a lower complexation constant (log $\beta_i$ =3.62). The interaction sites of cadmium(II) are at a much lower concentration than the protonation sites, which is 0.51 mmol g⁻¹.

**KEYWORDS:** Activated carbon, Cadmium adsorption, Ruzic linearization, Active sites on carbon.
In this paper the adsorption of the toxic metal ion cadmium(II) on the activated carbon FILTRASORB 300 supplied by CHEMVIRON is examined, to show the possibilities of the proposed characterization method.

**The model for the adsorption of metal ions on activated carbon**

It is assumed that the adsorption of metal ions in the carbon phase takes place through combination of the metals with ion exchange interaction sites, which are considered as “ligands” of the metal ion, and whose combination with the metal can be described exactly as the complexation in the solution phase. This model, which is the Gibbs-Donnan model, was successfully used by Marinsky and other researchers for the description of the adsorption of metal ions on ion exchange resins and other substances [5, 6, 7]. It is here applied for describing the metal adsorption on the activated carbon, since it is known that this solid is an ionic exchanger. The carbon is probably a much less hydrophilic phase than, for instance, the ion exchange resins, but the model could be applied also to hydrophobic ion exchangers [6]. The most important point of the Gibbs-Donnan model is that it predicts the existence of a potential difference at the interface ion exchanger-solution, due to the different mobility of the ions through the phases. Then the following equilibrium holds for all the electrolytes able to diffuse through the phases:

\[ a_{C,A} = a_{C} a_{A} \] equation (1)

where \( a \) indicates the activity, the symbols with the over bar are relative to the species in the solid phase, and A and C are an anion and a cation, monovalent for simplicity.

The concentration of the interaction sites in the solid phase is experimentally determined by titrating them with the metal ion of interest, which is added at known concentration to an aqueous suspension of the activated carbon. The concentration of metal ion adsorbed in the solid phase after equilibration is measured, obtaining an adsorption function similar to the Langmuir adsorption isotherm, in agreement with the model hypothesis that the adsorption takes place through combination on interaction sites. The experimental data are treated according to a method previously suggested to titrate unknown soluble ligands in natural waters, obtaining significant results with a limited number of data points [8, 9, 10]. Also the conditional adsorption constant can be determined by the proposed procedure. This quantity is a measure of the “strength” of the adsorption, and allows one to quantitatively predict the adsorption.

For simplicity, the association metal ion/active site in the carbon phase is also called “complex”, and a simple case in which only a 1 to 1 (metal to site) complex is formed in the solid is considered.

It is understood that these interaction sites may have also different structures, provided that the respective complexation coefficients with the metal ion are not significantly different considering the experimental uncertainty. The adsorption reaction can be represented as following

\[ \text{M} + \text{L} \xleftrightarrow{\text{ML}} \beta_c = \frac{[\text{ML}]}{[\text{M}] [\text{L}^*]} \] equation (2)

Here too the over bar indicates the species in the solid phase, and the concentration is in mmol per gram of solid in the solid phase (w g of carbon phase) and in mmol per ml in the solution phase (V ml of solution). \( \beta_c \) is a conditional coefficient, depending on the acidity and ionic composition of the solution, according to the Gibbs-Donnan model, as discussed below. \( c_{L^*} \) is the concentration of the interaction site not complexed with the considered metal, while \( \text{L} \) is the form of the interaction site which actually combines with the metal ion. It is possible that it combines also with the proton, depending on the conditions, and in particular on the acidity of the solution. For this reason \( \beta_c \) may depend on the acidity, as it happens in the case of ligands in aqueous solution. The ligand site is at different protonation states. \( \beta \) is the corresponding adsorption constant, independent of the acidity.

The following mass equilibria hold

\[ c_{\text{M}} = [\text{M}] + [\text{ML}] \frac{w}{V} \] equation (3)

\( V \) is the volume of the solution phase (in ml) and \( w \) the amount of activated carbon (in g)
From which it is seen that
\[ \beta = \beta_c \alpha. \]

It has been proposed that the value of \( c_L \), the concentration of the active groups in the carbon phase, can be evaluated together with \( \beta_c \), using the following relation, which has been previously suggested by Ruzic [8], and is now widely used

\[ \frac{[M]}{[ML]} = \frac{1}{c_L \beta_c} + \frac{[M]}{c_L} \]  
equation (6)

Of course this relationship holds at constant pH, since \( \beta_c \) is constant at this condition. \([M]\) is the concentration of the metal in the solution phase, in the absence of any complexing substance in the solution phase. It is determined experimentally by the usual methods for the determination of the concentration of metal ions in solution. \([ML]\) is determined by eq. 3, once \([M]\) is known. An equation similar to eq. 6 has been previously suggested for the determination of the concentration of complexing substances in aqueous solution, by a procedure which has been defined “ligand titration” [8, 9, 10].

Of course the function \([M]/[ML]\) vs. \([M]\) (equation 6) is a straight line only if \( \beta_c \) is really constant during the titration of the active groups with the metal ion. It is well known that this can be not true in the case of other ion exchange solids, for instance ion exchange resins [11, 12].

**The model for the effect of the acidity of the aqueous phase on the adsorption of metal ions on activated carbon**

If the active site can combine with the metal, and also with proton, the following protonation reaction, which is considered for the sake of simplicity, must be taken into account:

\[ H + L \rightleftharpoons HL \]  
\[ K_a = \frac{[HL]}{[H][L]} \]  
\[ \alpha_L = \frac{[L] + [HL]}{[L]} = 1 + K_a[H] \]  
\[ \beta_c = \frac{1}{1 + K_a[H]} \]  
\[ \beta = \frac{1}{\beta_c} + \frac{K_a[H]}{\beta} \]  

Thus \( \beta \) and \( K_a \) can be evaluated from \( \beta_c \) obtained by the ligand titration at different pH, from eq. 9, by non linear regression or by linearization of the function, according to

According to the Gibbs-Donnan model (eq. 1) the adsorption constant \( \beta \) depends on the ionic composition of the solution and solid phases as following

\[ c_L = c_{L} + [ML] \]  
\[ c_{L} = \alpha_L[L] \]  
\[ \alpha_L = 1 + \frac{K_a[H]}{\beta} \]  
\[ \beta = \frac{1}{\beta_c} + \frac{K_a[H]}{\beta} \]  
\[ \beta_c = \frac{1}{1 + K_a[H]} \]  
\[ \beta = \frac{1}{1 + K_a[H]} + \frac{K_a[H]}{\beta} \]
Where \( \beta_i \) is the intrinsic complexation constant of the metal with the active sites in the carbon phase. It has been found to be independent of the conditions in the case of ion exchange resins \([7, 11, 12]\). On the contrary \( \beta_c \) is constant only if \( |C| \) is constant, the other quantities, \([H] \) and \([C] \), being constant during a particular titration. In this research \( |\bar{C}| \) is assumed to be constant, but this hypothesis must be checked.

According to the Gibbs-Donnan model (eq. 1), also \( K_a \) depends on the ionic compositions of the two phases

\[
K_a = K_a |\bar{C}|/|C| \tag{12}
\]

where \( C \) indicates the counter ion concentration in the two phases.

\( K_{ai} \) is the intrinsic protonation constant, and is independent of the ionic compositions of the phases.

Considering also the effect of the ionic composition of the phases, the relationship between the adsorption coefficient experimentally determined, and which must be used for predictions, \( \beta_c \), and the variables is

\[
\beta_c = \frac{\beta_i |\bar{C}|}{1 + |H| K_{ai} |\bar{C}|/|C|} \tag{13}
\]

It must be taken in mind that the activity, not the concentration of the counter ion in the two phases should be considered, when eq. 1 is used. The concentration is reported for convenience.

\( \beta_i \) is the intrinsic complexation constant of that metal with that activated carbon. It is independent of the acidity and of the ionic composition of the two phases, and can be used for the evaluation of the adsorption coefficients \( \beta_c \) at particular conditions (acidity and counter ion concentration).

**EXPERIMENTAL**

**Reagents**

The activated carbon used in this study was FILTRASORB 300 supplied by CHEMVIRON, 8-30 mesh. It was used without further washing and stored in a closed bottle. The surface characteristics are herein summarized.

Average specific surface, measured by the nitrogen-BET method is 1000 m\(^2\)/g.

Iodine number 950 mg/g, the minimum methylene number 230 mg/g, effective diameter 0.8-1 mm, wet carbon particles density 1.2 mg/ml. All the experiments were done with the carbon fraction obtained with a 70-140 mesh sieve.

Analytical grade reagents were used. Stock solutions of cadmium(II) were prepared from weighted amounts of Cd(NO\(_3\))\(_2\) by dilution with milli-Q water, and checked by FA-AAS with standard method.

**Equipment**

pH measurements were done with a PHM 84 RESEARCH pHmeter (Radiometer), and a combined glass electrode, standardized in H\(^+\) activity.

The metal concentrations were determined with a Shimadzu model 6601G Graphite Atomic Absorption Spectrophotometer, with pyrolitic tubes and with the procedure indicated by the instrument producer. Also voltammetric methods were used, with an Amel mod 433 Polarographic Analyzer. The measurements were done in DPV (starting potential: -0.200 V, end potential: -0.900 V, scan rate 50 mV s\(^{-1}\), pulse height 50 mV) or in ASDPV (deposition potential: -0.900 V, deposition time: 120 s) at a static mercury drop electrode (SDME) as working electrode, a saturated KCl AgCl/Ag as reference electrode and a platinum electrode as counter electrode. Determinations were done by the standard additions method.
Procedure for the determination of the adsorption isotherms

The adsorption isotherms were obtained in 0.1 M NaNO₃, at room temperature (20°C), by placing into 30 mL polyethylene (PE) tubes constant amounts of carbon (5 g/L) in 0.1 M NaNO₃ solution (20 mL) and increasing the metal concentration at constant pH. The experiments were performed at different pH values. pH was never greater than 7.5 for cadmium(II) in order to prevent hydrolysis and/or hydroxides precipitation. The investigated concentration ranges varied from a few tens of ppb to a few hundreds of ppm. The tubes were equilibrated for at least four hours (usual equilibration time 10 hours), and then were centrifuged at 12000 rpm for ten minutes. Proper volumes of clear solution were analysed by EA-AAS and/or voltammetry, as described above.

Procedure for the investigation of the protonation of the activated carbon

The maximum capacity of the carbon for H⁺ was determined by adding an excess of acid to the sample and measuring the excess at different conditions. For example, 3 ml of standard HNO₃ 0.196 M were added to 25 ml of 0.1 M NaNO₃ solution, containing in suspension 0.205 g of activated carbon. After equilibration (normally 4 hours) an aliquot of the clear solution was separated and the H⁺ excess was determined by titration with standard NaOH.

RESULTS AND DISCUSSION

It has been found that the equilibration time for the adsorption of cadmium(II) on the considered activated carbon was 4 hours, but the equilibration time actually used in the experiments was always 10 hours, in order to be sure that the equilibrium was attained.

The concentration of the active sites in the carbon phase, able to bind cadmium(II), was determined by titration of the activated carbon with the metal ion at different conditions, as reported in the experimental part. Each titration was carried out at constant pH and ionic composition of the solution, by varying the concentration of the metal in the range 2 \times 10^{-7} to 5 \times 10^{-4} M. Different subsamples were added with different concentration of cadmium(II), and equilibrated with the same amount of carbon (0.1 g in 20 ml of solution). The concentration of the metal ion in the liquid phase after equilibration was determined by ETA-AAS or voltammetric techniques, and the concentration of adsorbed metal was obtained by difference.

For convenience, in the data treatment two different concentration ranges were separately considered: 1-10 \times 10^{-4} M and 1-10 \times 10^{-7} M.

As an example, some adsorption isotherms of cadmium(II) the highest concentration range of titrant metal, from 1 \times 10^{-4} to 9.7 \times 10^{-4} M, and at different pH, are reported in Fig 1.
Fig.1 – Adsorption isotherms of cadmium(II) on activated carbon in 0.1 M NaNO₃, at different pH, and for titrant concentration from 1.18 10⁻⁴ M to 1.01 10⁻³ M

The subscript “1” indicates the parameters determined in this concentration range. A constant concentration of adsorbed metal ion in function of increasing concentration of added metal was never obtained, not even at the highest concentrations, so that the total concentration of the active sites for cadmium in the considered carbon was always determined using the Ruzic linearization (equation 10). In all the cases the function [M]/[ML] vs. [M] was an acceptable straight line, indicating that in each titration the conditional adsorption coefficient β₁ is actually constant. Considering equation 13, this means that [C], the counter ion concentration in the carbon phase, or also the ratio [C]/[C], is constant during a particular titration. A reason for this is discussed below.

The values of c₁₁ and β₁ obtained from the parameters of the straight line at the different conditions are reported in Table 1.

The total concentration of the active sites found by the ligand titration is independent of the conditions, at least for pH lower than around 7.5, the variations being ascribable to the irreproducibility of the method. The average value (and the standard deviation) is 0.019(0.004) mmol/g. The considerably higher c₁ obtained at pH=8.2 is probably due to the precipitation of the hydroxide which takes place at the high concentration and pH considered. However such concentrations are not realistic in the environmental water samples.

The conditional adsorption coefficient significantly increases with the pH, reflecting the fact that the adsorption of cadmium(II) is promoted at higher pH, as previously observed for example in Ref. [3].

<table>
<thead>
<tr>
<th>pH</th>
<th>c₁₁</th>
<th>β₁c₁₁</th>
<th>log β₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.60</td>
<td>1.67(0.26) 10⁻²</td>
<td>1.20(0.27) 10¹</td>
<td>2.86</td>
</tr>
<tr>
<td>6.03</td>
<td>1.19(0.33) 10⁻²</td>
<td>2.74(0.74) 10¹</td>
<td>3.36</td>
</tr>
<tr>
<td>6.40</td>
<td>1.90(1.10) 10⁻²</td>
<td>4.16(0.16) 10¹</td>
<td>3.34</td>
</tr>
<tr>
<td>6.50</td>
<td>2.11(0.30) 10⁻²</td>
<td>3.82(0.50) 10¹</td>
<td>3.26</td>
</tr>
<tr>
<td>6.60</td>
<td>1.74(0.30) 10⁻²</td>
<td>3.15(0.84) 10¹</td>
<td>3.26</td>
</tr>
<tr>
<td>7.00</td>
<td>1.90(0.25) 10⁻²</td>
<td>1.04(0.35) 10²</td>
<td>3.74</td>
</tr>
<tr>
<td>7.30</td>
<td>5.27(4.31) 10⁻²</td>
<td>6.19(3.31) 10¹</td>
<td>3.07</td>
</tr>
<tr>
<td>7.30</td>
<td>2.50(0.25) 10⁻²</td>
<td>1.09(0.22) 10²</td>
<td>3.64</td>
</tr>
<tr>
<td>7.60</td>
<td>2.30(0.30) 10⁻²</td>
<td>2.51(0.65) 10²</td>
<td>4.04</td>
</tr>
<tr>
<td>8.20</td>
<td>9.89(0.61) 10⁻²</td>
<td>4.21(0.31) 10²</td>
<td>3.63</td>
</tr>
</tbody>
</table>
This is described in the model by eq. 12, which can be conveniently transformed as following:

\[
\frac{1}{\beta C_{L1}} = \frac{1}{\beta C_{L1}(C_l/C_0)^m} + \frac{[H]K_{a1}(C_l/C_0)}{\beta C_{L1}(C_l/C_0)^m}
\]

\text{equation (13a)}

The parameters of eq. 13a, obtained by the linear regression, by plotting \(1/\beta_{c1}c_{L1}\) vs \([H]\), are:

\[
\frac{1}{\beta_{c1}c_{L1}} = 1.29(0.46)10^{-2} + 2.81(0.50)10^4[H] \quad (R^2=0.819)
\]

From which it is found that:

\[
\beta_{1c L1}(C_l/C_0)^m = 7.77(2.77)10^4
\]

\[
\beta_{1c L1}(C_l/C_0)^{m1}/K_{a1} = 3.55(1.27)10^5
\]

\[
K_{a1}(C_l/C_0) = 2.19(0.28)10^6
\]

as \(c_{L1}\) is known, it can be evaluated that:

\[
\beta_{1c}(C_l/C_0)^m = 4.09 10^3
\]

These parameters are a useful description of the sorbing properties of the considered activated carbon, and they allow the evaluation of \(\beta_{c1}\) at different conditions by eq. 13.

An example of active sites titration at much lower titrant concentration is reported in Fig. 2.

The adsorption isotherms were obtained at different pH, and for cadmium additions from \(3.11 10^{-7}\) to \(3.20 10^{-6}\) M. The parameters determined at these concentrations are indicated by the subscript “2”. At these concentrations too a marked effect of the solution pH is observed, causing an increase of the adsorption at increasing pH.

In Table 2 the results obtained by the Ruzic linearization are reported. Due to the poor reproducibility of the experimental determination of the metal concentration in the solution phase at the low concentrations here considered, the concentration of the active sites could be determined with sufficient precision only at pH=5.7. At the other acidities the slope of the Ruzic function was not significantly different from 0, so that \(c_{L1}\) could not be evaluated.

The variation of \(\beta_{c2}c_{L2}\) with the acidity, according to eq. 13a, was as following:

\[
\frac{1}{\beta_{c2}c_{L2}} = 4.64(0.43)10^{-3} + 2.78(0.37)10^2[H] \quad (R^2=0.999)
\]
Fig. 2 – Adsorption isotherms of cadmium(II) on activated carbon in 0.1 M NaNO₃, at different pH, and for titrant concentration from 3.11 × 10⁻⁷ M to 3.20 × 10⁻⁶ M

Table 2 - Results of the Ruzic linearization of the titration of activated carbon at different pH with cadmium(II), at titrant concentration from 3.11 × 10⁻⁷ M to 3.20 × 10⁻⁶ M, in NaNO₃ 0.1 M. (The standard deviation is in parenthesis).

<table>
<thead>
<tr>
<th>pH</th>
<th>c₁₂</th>
<th>β₂c₁₂</th>
<th>β₂c₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.72</td>
<td>1.71(1.10) × 10⁻⁴</td>
<td>2.59(1.02) × 10⁷</td>
<td>1.53 (1.20) × 10⁶</td>
</tr>
<tr>
<td>5.70</td>
<td>3.83 (0.48) × 10⁻⁴</td>
<td>1.02 (0.19) × 10³</td>
<td>2.67 (0.61) × 10⁶</td>
</tr>
<tr>
<td>6.89</td>
<td>Not evaluable</td>
<td>1.86 (0.22) × 10³</td>
<td>Not evaluable</td>
</tr>
</tbody>
</table>

From the parameters of the straight line obtained from eq. 13a, it is found that

\[ \beta_2 c_{1,2} ([C]/[I])^{m} = 2.15 (0.20) \times 10^{3} \]

\[ \beta_2 c_{1,2} ([C]/[I])^{m-1} / K_{a,2} = 3.59 (0.05) \times 10^{-3} \]

\[ K_{a,2} ([C]/[I]) = 6.01 (0.56) \times 10^{5} \]

Assuming that \( c_{1,2} = 3.8 \times 10^{-4} \text{ mmol/g} \), it is found that

\[ \beta_2 ([C]/[I])^{m} = 5.67 (0.54) \times 10^{6} \]

This value is very high, much higher than that of the sites at higher concentration found above. Moreover the protonation constant of the site at low concentration is one order of magnitude lower than that of the sites at lower concentration, so that the proton competes with cadmium(II) at a lower extent when the sites at low concentration are involved.

When these strong sites are saturated, at higher metal ion concentration, the sites at larger concentration but with lower conditional coefficient will be occupied.

The fact that sites with different affinity for the metal ion are present in the same sorbing material is not surprising, since different density and spatial distribution of the donor atoms can be expected.
Protonation of the activated carbon

The maximum capacity of the activated carbon for $\text{H}^+$ was determined as described in the experimental part, at different conditions, and in particular at different excess of acid. Similar results were obtained, and the average value of the proton exchange capacity was $0.51 \pm 0.06 \text{ mmol/g}$. This is in agreement with the values obtained for the surface charge evaluated by other researchers in the case of similar activated carbons [3].

It must be noticed that the concentration of the interaction sites of cadmium are at considerably lower concentration in the carbon phase than the protonation sites. The total ion exchange capacity does not correspond to the capacity for cadmium(II). Probably the sites able to interact with cadmium(II) not only contain protonable donor groups, for instance carboxyl and hydroxyl groups, but they have also a proper special structure, suitable for the combination with cadmium. Sites of different structure are present, with different affinity for cadmium. They have also different protonation constants, which have been determined together with the adsorption of cadmium(II).

The conditional constant $\beta_c$

Some comments must be done about the fact that the conditional constant $\beta_c$ obtained at constant acidity and ionic composition is really constant during the titration. This is an experimental observation obtained from the Ruzic linearization, and in particular to the fact that the function was always a straight line. $\beta_c$ is correlated to the intrinsic constants $\beta_i$ and $K_{ai}$ through eq. 13, and it should depend on $[\text{H}^+]$ and on the concentration of the counter ion in the solid phase and in the solution phase. $[\text{H}^+]$ is constant in each titration experiment, and the same must be true for the counter ion concentrations in the two phases.

It is also possible that not the single activity, but the ratio of the activities of the counter ion in the two phases $[\text{C}] / [\text{C}]$ is constant. This may happen when the counter ions in the solid phase are not free. It is not unreasonable to suppose that the alkaline metals are present in the solid phase mainly linked to sites, because of the very lipophilic nature of carbon, involving the presence of only a small amount of free water. In this case the counter ion is only present in the solid phase as a free ion because of the diffusion. For this reason at the equilibrium its activity must be equal in the two phases. If this explanation holds, also the effect of the ionic composition of the solution phase should be limited, and have only an effect on the activity coefficients of the ions in the solution phase. Some preliminary experiments at ionic composition of the aqueous phase different from 0.1 M NaNO$_3$ seem to support this interpretation, but further investigation is required to confirm this point.

An important consequence is that the intrinsic complexation and protonation constants are equal to the parameters evaluated by the proposed analysis of data, since $[\text{C}] / [\text{C}]$.

CONCLUSIONS

Two kinds of binding sites for cadmium(II) are present in the considered activated carbon, indicated by the subscript numbers 1 and 2. They were characterized by determining their concentration and the corresponding complexation constants. Also the protonation constant of the site was evaluated, which explains the effect of the acidity. One kind of site, indicated by 2, is at low concentration, but has a very high complexation constant, and is responsible for the adsorption of cadmium(II) at concentration as low as about 30 ppb. The other kind of site is at much higher concentration and has a lower complexation constant. The knowledge of the parameters makes it possible to evaluate the adsorption coefficients at the particular conditions considered, and the fraction of metal ion adsorbed onto carbon at these conditions, since the following relation holds

$$ f = \frac{1}{1 + \frac{V}{w(\beta_{c2}[L_2] + \beta_{c1}[L_1])} } $$

The meaning of the symbols has been explained above. The total concentration of the sites $c_{1,2}$ can be of help to evaluate the concentration of the free sites $L_i$. At concentration of metal ion higher that about $1 \times 10^{-3}$ M, sites 2 are negligible, while at concentration lower that about $1 \times 10^{-6}$ M, sites 1 are not occupied, and can be neglected.
REFERENCES