



## A descriptive model for metallic ions adsorption from aqueous solutions onto activated carbons

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### ABSTRACT

The design of adsorber units is mainly dependent on the equilibrium adsorption capacity of the sorbent in the working conditions. At the moment, these data are available in a limited number of experimental conditions and, for the case of activated carbon, there are no predictive models to assess the adsorption capacity as a function of the process parameters. This makes the adsorber design a complex and approximated task. In this work, a model for the description of metallic ions adsorption onto activated carbon is presented. The model starts from an evaluation of ion speciation and it considers the approach of the multi-component Langmuir model to correlate the metal uptake to the ion concentration in solution. The model has been used to analyse available experimental data on the adsorption of As(V), Cd(II), Cr(III) and Cr(VI) ions on activated carbon. A good matching between experimental results and model predictions has been obtained for all the investigated conditions.

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### 1. Introduction

The contamination of natural and industrial waters by heavy metals is recognized as a major environmental concern due to the impact and persistence of these pollutants [1–4]. Major anthropogenic heavy metal sources include industrial processes, fossil-fuel combustion, waste incineration and disposal, transportation and agriculture.

Activated carbon adsorption is widely used to remove pollutants from waters and wastewaters due to its good removal efficiencies and to its great versatility.

The performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute–solvent–sorbent interactions and on the transport phenomena involving the diffusive–convective transport within the porous media. The equilibrium conditions are the most significant limits for the application of a given sorbent since the uptake of metallic ions may change within orders of magnitude by varying the process parameters, such as concentration, pH, ionic strength, temperature and chemical composition of the aqueous solution [5]. These parameters also affect the characteristics of the carbon–water system, which consists in both carbon hydrolysis and surface red-ox reactions [6–9].

Indeed, the dynamic of a fixed bed adsorption column is usually characterised by the occurrence of pH, salinity or temperature

profiles and the classical approach of the local equilibrium for adsorption kinetics [5,10] requires the correct estimation of the equilibrium adsorption capacity in function of the local value of the process parameters. This is the main reason why a trial-and-error or a rule-of-thumb approach is usually considered in the design of industrial adsorbers.

Several models have been developed in the past to describe the adsorption of metallic ions with the aim to provide accurate methods for process design and optimization [5,10–13]. These models are based on the hypothesis that adsorption is the result of acid/base reactions between the ionic species and the ionized surface sites of the adsorbent and they are also defined as surface complexation models. They are usually coupled with models for the description of the electrostatic field around the adsorbing surface (the most famous of which is the triple layer model, TLM) to address the effect of electrostatic potential near the sorbent surface. As a consequence, these models require the evaluation of both chemical and electrostatic parameters and, usually, the surface ionization constants are evaluated starting from the adsorption isotherms and from a surface characterization of the sorbent. Hence, these models are particularly useful for those materials that present a homogeneous surface structure. Anyway, a critical analysis of surface complexation models applied to the simple case of oxide and hydroxide sorbents has been reported by Zuyi et al. [14] who clearly point out their theoretical limits claiming for the necessity of a deeper analysis of surface properties.

On the contrary, activated carbons, that are by far the most used sorbent in water treatments, are complex materials with a

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non-homogeneous structure deriving from the raw material and from the activation process. In fact, on the one hand, the raw materials may lead to the presence of impurities in the structure of the graphitic layer such as nitrogen, sulphur and oxygen atoms as well as ashes. On the other hand, a given activation process creates a peculiar pore size distribution and a series of C–O bonds resulting in different surface functional groups of the generic form  $\text{CO}_x\text{H}_y$ , also responsible for the acid–base behavior of the activated carbons shown during the hydrolysis phenomena [8]. Furthermore, Alfarrá et al. [15] stressed that the metal–surface interactions mainly depend on the hard–soft character of the adsorbed ions and the surface active sites, and they can be essentially considered in light of an extension of the HSAB theory developed by Pearson [16].

This result shows that the complexity of active site–solute interactions cannot be reduced to acid–base reactions due to surface hydrolysis only but it has to account for more complex mechanisms involving Lewis acid and base functional groups characterized by the absence of a net electric charge and represented by heteroatomic bonds (C–N, C–Cl, C–S) or by the ashes themselves.

Anyway, some attempts to use the surface complexation models are reported in the literature [5,10,13] under the assumptions that the carbon has a unique, uniform value of the surface potential, that acid/base reactions involve only dissociated and hydrolyzed cations and that the surface hydrolysis gives rise to one type of hydrolyzed surface site only. Nevertheless, a rigorous application of these models requires the assessment of the properties of different active sites vis-à-vis all the adsorbable species as well as a local distribution of the surface electrostatic field. The overall complexity of the model sharply increases and, even if it is applied to a given activated carbon and a given metal ion, the surface complexation model can hardly be extended to different activated carbons and to multi-component adsorption.

Another critical issue of metallic ion adsorption deals with the analysis of the effect of temperature on adsorption. This appears to be a critical factor in the interpretation of experimental results as in some cases adsorption capacity increases with temperature, in contradiction with the intrinsic exothermicity of adsorption phenomena [17–20]. At this moment, the assessment of temperature effects is still a debated question.

For these reasons a simplified approach can be considered in order to provide for sufficiently accurate design equations in absence of a rigorous theoretical model. For a given sorbent this approach is based on three different steps:

1. A properly designed matrix of experiments which is able to address the effect of each variable (temperature, pH, salinity, solute concentration, presence and concentration of ligands, etc.) on the adsorption capacity;
2. A speciation analysis which provides for the determination of ion distribution in solution at equilibrium conditions;
3. The assessment of an adsorption model which can be applied under reasonable restrictive hypotheses and which requires the smallest number of adjustable parameters for data fitting. The model has to take into account the presence of different types of active sites on carbon surface and the simultaneous presence of several metallic ions in solution.

The main goal of this approach is to provide for an estimation of adsorption capacity in a very wide range of working conditions thus allowing a correct evaluation of metal uptake and a reliable reactor design. The required experimental analysis and ion speciation results (steps 1–2) of the adsorption of As(V), Cr(III), Cr(VI) and Cd(II) has been formerly reported [19–23]. In this paper, the multi-component Langmuir model has been used as the adsorption model for the description of experimental data (step 3), covering a wide range of working conditions. The model equation is used to

correlate experimental results in terms of concentration of ions in solution, pH, salinity and temperature, to the overall adsorption capacity.

## 2. Adsorption model

The adsorption of ions on the surface of activated carbons is the result of the interactions between the aqueous solution and the various active sites on the carbon surface. Activated carbon can be represented as a complex and irregular amorphous carbon matrix with a fraction of graphite (known as *graphitic layer*) which contains several impurities such as ashes or heteroatoms of oxygen, nitrogen, and sulphur, and with several surface functional groups mainly consisting in C–O bonds [8,15]. Surface functional groups are originated from the activation process of the raw materials and are responsible for the surface hydrolysis of the activated carbons in aqueous solutions [5]; the structure and the distribution of these functional groups, denoted as  $\text{CO}_x\text{H}_y$ , are well described by Boehm [8]. The presence of surface heteroatoms and the structure of the graphitic layer itself, as well as the ashes properties, determine the occurrence of active sites acting as Lewis acids or bases, able to capture ions with base or acid character [15].

Furthermore, activated carbons also show reducing properties, mainly due to lactonic and phenol functional groups and to the graphitic layer itself. Lakatos et al. [9] pointed out the role of surface functional groups with reducing properties in determining the adsorption of chromium ions. During an adsorption experiment, the occurrence of surface reduction reactions can be only deduced by analysing the ion speciation in solution. For example, for the case of Cr(VI) adsorption, the occurrence of surface reduction reactions is inferred from the presence of Cr(III) ions in acidic solution deriving from Cr(VI) reduction reaction on the carbon surface [9,21,24].

To sum up, the carbon surface presents different types of adsorbing active sites that can be distinguished as follows:

1.  $\text{CO}_x\text{H}_y$  surface functional groups with acid properties, which, by substitution reactions, may complexate the cations [5];
2.  $\text{CO}_x\text{H}_y$  surface functional groups with basic properties, which may react directly with cations by addition reactions and, after reaction with  $\text{H}^+$ , may also react with anions [25–26];
3. Lewis acid sites, which tend to react with anions and other nucleophilic substances in the solution [15];
4. Lewis base sites, with a more pronounced tendency to adsorb cations or other electrophilic substances [15];
5. functional groups with reducing properties (e.g. [9]).

The interactions between activated carbon and metal aqueous solution involve all the ionic species of the metal and all the other ions dissolved in water. Hence, the adsorption process mainly depends on the complete water speciation.

The water speciation analyses are based on mass and charge balance equations and equilibrium reactions. For the case of metallic

**Table 1**  
Adsorption pseudo-reactions.

k	Active site	Chemical species	Reaction	Expression
1	$\sigma\text{H}$ –acid	Cations $\text{P}^+$	Substitution	$\sigma\text{H} + \text{P}^+ = \sigma\text{P} + \text{H}^+$
2	$\sigma\text{H}$ –basic	Cations $\text{P}^+$	Addition	$\sigma\text{H} + \text{P}^+ = \sigma\text{HP}^+$
3	$\sigma\text{H}$ –basic	Anions $\text{Q}^-$	Protonation	$\sigma\text{H} + \text{H}^+ = \sigma\text{H}_2^+$
			Addition	$\sigma\text{H}_2^+ + \text{Q}^- = \sigma\text{H}_2^+\text{Q}^-$
4	$\sigma_n$ nucleophilic	Cations $\text{P}^+$	Addition	$\sigma_n + \text{P}^+ = \sigma_n\text{P}^+$
5	$\sigma_e$ electrophilic	Anions $\text{Q}^-$	Addition	$\sigma_e + \text{Q}^- = \sigma_e\text{Q}^-$

**Table 2**  
Langmuir multi-component competitive model equation for different adsorption mechanisms.

k	Langmuir model equation
1	$\omega_i^{(1)} = \omega_{\max}^{(1)} \frac{K_i^{(1)}[M_i^+]}{1 + K_H^{(1)}[H^+] + \sum_{i=1}^m K_i^{(1)}[M_i^+] + \sum_{j=1}^y K_j^{(1)}[Y_j^+]} \quad (1)$
2	$\omega_i^{(2)} = \omega_{\max}^{(2)} \frac{K_i^{(2)}[M_i^+]}{1 + K_H^{(2)}[H^+] + \sum_{i=1}^m K_i^{(2)}[M_i^+] + \sum_{j=1}^y K_j^{(2)}[Y_j^+]} \quad (2)$
3	$\omega_i^{(3)} = \omega_{\max}^{(3)} \frac{K_H^{(3)}[H^+] K_i^{(3)}[A_i^-]}{1 + K_H^{(3)}[H^+] \left(1 + \sum_{i=1}^a K_i^{(3)}[A_i^-] + \sum_{j=1}^x K_j^{(3)}[X_j^-] + K_{OH^-}^{(3)}[OH^-]\right)} \quad (3)$
4	$\omega_i^{(4)} = \omega_{\max}^{(4)} \frac{K_i^{(4)}[M_i^+]}{1 + K_H^{(4)}[H^+] + \sum_{i=1}^m K_i^{(4)}[M_i^+] + \sum_{j=1}^y K_j^{(4)}[Y_j^+]} \quad (4)$
5	$\omega_i^{(5)} = \omega_{\max}^{(5)} \frac{K_i^{(5)}[A_i^-]}{1 + K_{OH^-}^{(5)}[OH^-] + \sum_{i=1}^a K_i^{(5)}[A_i^-] + \sum_{j=1}^x K_j^{(5)}[X_j^-]} \quad (5)$

ions, the latter are typically available as: (i) complexation reactions of a given metal with the different kinds of ligands; (ii) precipitation reactions and (iii) red-ox reactions between the different oxidation states [27–29]. These relations correlate the activities of the ionic species in solution at equilibrium conditions and thus, appropriate methods for the estimation of activity coefficients in non-ideal electrolytic solutions are required. Computational methods and dedicated software (e.g. MINEQL+) are currently available for the speciation analysis of aqueous solutions.

The generic adsorption mechanism which describes the interaction between an ionic species and the carbon surface is usually named *adsorption pseudo-reaction*.

In principle, the interactions between the solid surface and the aqueous solution involve all the different species in solution even if the contribution of molecular species of metals appears to be negligible [5,29].

Table 1 resumes the possible adsorption reactions, identified by the progressive number *k*, coupled with the indication of the active site, the chemical species involved and the expression of the pseudo-reactions. Here,  $\sigma_H$  denotes the  $CO_xH_y$  functional groups with acid/base behaviour,  $\sigma_e$  are the Lewis acid sites and  $\sigma_n$  are the Lewis base ones.  $P^+$  stands for the generic cation in solution, and it includes metallic cations,  $M_i^+$  ( $i = 1, \dots, m$ ),  $H^+$  ions and all the other cations present in solution,  $Y_j^+$  ( $j = 1, \dots, y$ ).  $Q^-$  stands for the generic anion, and it includes metallic anions,  $A_i^-$  ( $i = 1, \dots, a$ ),  $OH^-$ , and all the other anions in solution,  $X_j^-$  ( $j = 1, \dots, x$ ).

In synthesis, the adsorption process can be considered as a network of parallel–consecutive adsorption reactions with the ionic species and the active sites as reagents and the adsorbed species as products.

The multi-component Langmuir adsorption model [5] can be used to correlate the equilibrium concentration of ions in solution to the adsorption capacity of the activated carbon. This model is formulated under several restrictive hypotheses among which the monolayer coverage of carbon surface, the constancy of adsorption energy for each type of active site and the absence of interferences between different solutes toward the carbon adsorption.

The presence of many chemical species in solution, all potentially adsorbed on carbon surface, is taken into account by admitting

**Table 3**  
Run matrix for metal adsorption experimental data employed in the model test.

Metal	Ionic species	[M] (mg/l)	pH	<i>T</i> (°C)	Salinity (M)	Ref.
As(V)	$i = 3$ ( $H_2AsO_4^-$ , $HAsO_4^{2-}$ , $AsO_4^{3-}$ )	0–5	2–11	10–55	0–0.6	[19,20]
Cd(II)	$i = 1$ ( $Cd^{2+}$ )	0–40	2–7.5	10–40	0–0.5	[22,23]
Cr(III)	$i = 1$ ( $Cr^{3+}$ )	0–30	2–3	10–55	–	[19,21]
Cr(VI)	$i = 1$ ( $CrO_4^{2-}$ )	0–30	7–11	10–55	0–0.5	[19,21]

the competition among them for the same active sites according to the mechanisms previously discussed. Table 2 reports, for each mechanism referred to in Table 1, the corresponding expression of the Langmuir multi-component model [5,10] applied to the generic metallic cation  $M_i^+$  or anion  $A_i^-$ . A detailed list of adsorption mechanisms and pseudo-reactions are reported in Appendix A.

In all the expressions, the term  $\omega_i^{(k)}$  refers to the adsorption capacity of activated carbon for the generic species *i*, bonded to the carbon surface according to the particular *k*th mechanism. Similarly, the term  $\omega_{\max}^{(k)}$  refers to the maximum adsorption capacity on that active site, while  $K_i^{(k)}$  is the equilibrium constant for the *k*th adsorption pseudo-reaction involving the *i*th species. As adsorption is an exothermic, spontaneous process, the adsorption reaction constants  $K_i^{(k)}$  can be expressed as:

$$K_i^{(k)} = \exp \left[ \frac{-\Delta G_i^{(k)}}{RT} \right] \quad (6)$$

with a pseudo-Gibbs free energy of reaction  $\Delta G_i^{(k)} < 0$ .

Moreover, starting from Eqs. (1)–(5) it is also possible to estimate the adsorption of the single *i*th species on the activated carbon, denoted as  $\omega_i$ , by summing the contributions  $\omega_i^{(k)}$  of each adsorption mechanism:

$$\omega_i = \sum_k \omega_i^{(k)} \quad (7)$$

Similarly, the contribution to adsorption of all the metallic ions on a given active site, indicated as  $\omega^{(k)}$ , is the summation upon *i* of the  $\omega_i^{(k)}$ :

$$\omega^{(k)} = \sum_i \omega_i^{(k)} \quad (8)$$

Consequently, the total adsorption capacity of activated carbon ( $\omega$ ), can be expressed as

$$\omega = \sum_i \sum_k \omega_i^{(k)} = \sum_k \omega^{(k)} = \sum_i \omega_i \quad (9)$$

**Table 4**  
Regression and statistical parameters in adsorption model Eqs. (6) and (12).

	Parameters				F	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Normality test, P
	Mean	Stand. error	T	Dependency				
$\omega_{\max}$ , mg/g	2.5	0.08	31.9	0.65				
$\Delta G_{\text{AsO}_4^{3-}}$ , kJ/mol	-41.66	0.29	141.4	0.70				
$\Delta G_{\text{HAsO}_4^{2-}}$ , kJ/mol	-21.26	1.21	17.57	0.65				
$\Delta G_{\text{H}_2\text{AsO}_4^-}$ , kJ/mol	-21.53	0.33	64.90	0.27	379.22	0.9024	0.9001	>0.01
$\Delta G_{\text{OH}^-}$ , kJ/mol	-29.69	0.90	33.11	0.60				
$\Delta G_{\text{Cl}^-}$ , kJ/mol	-14.50	1.000	120	0.20				

### 3. Model application and case studies

The application of the model to predict the adsorption phenomena in a generic metal-containing solution requires the assessment of the parameters  $\omega_{\max}^{(k)}$  and  $K_i^{(k)}$ . Currently, the absence of theoretical methods to estimate these parameters makes unreliable any attempt to obtain a general predictive model. For this reason, at the moment, the model can be applied only to the analysis of adsorption mechanisms starting from the description of a proper set of experimental data.

The adsorption of metallic ions from aqueous solutions onto activated carbons can be experimentally studied by classical equilibrium and kinetic tests.

The former are easier, faster and more cost effective. Hence they are usually preferred to kinetic tests that are usually used to characterise the adsorption rates and the process dynamics of adsorption reaction.

Equilibrium experiments mainly consist in batch tests used to determine the so-called adsorption isotherm. Due to the current limitations in the analytical technique, the adsorption isotherm results in the correlation of the equilibrium concentration of total dissolved metal,  $c$  (usually expressed as M, or mg/l units) with the metal uptake on the carbon,  $\omega$  (usually expressed as mg/g or g/g). Indeed, current methods for metal analyses in aqueous solution provide for the overall concentration of a metal, and in the best cases (e.g. Cr(VI) and Cr(III); Fe(II) and Fe (III), As(III) and As(V)), it is possible to distinguish between different valence states. Furthermore, to measure the metal uptake on the sorbent, proper elution solvents are used. In this case the evaluation of the overall metal content, regardless of the metal valence state, is the only significant analysis. However, albeit the computational difficulties, methods for metal ion speciation in waters are currently available [5,29].

Equilibrium tests are carried out in model aqueous solutions consisting in distilled water containing the solute metal, eventually an acid (usually HCl, or HNO<sub>3</sub>) or a basis (usually KOH or NaOH) used to adjust solution pH, and a salt used to alter solution salinity (often NaCl or NaNO<sub>3</sub>). Then, the carbon is added to the solution and the test is prolonged until the equilibrium is reached.

The model application requires a suitable experimental run matrix, assessing the effect of concentrations, pH, temperature, salinity and sorbent properties on adsorption. For this reason, an accurate definition of the experimental plan is necessary, since physically and statistically significant experimental data are

mandatory for the model application. The effect of each parameter on the adsorption capacity can be correctly analysed only if its value varies appreciably within the experimental conditions.

In particular, it is worth underlining that the effect of sorbent properties on the adsorption process is a complex features that includes the surface hydrolysis and reduction reactions, the potential release of substances to the aqueous solution and the adsorption of any ion dissolved in solution.

The description of experimental data with the proposed model implies the application of non-linear regression analysis by means of the Eqs. (1)–(10), for the estimation of model parameters.

This regression analysis correlates the concentration of all the ions dissolved in solution, the temperature and the adsorption capacity. Temperature has to be directly considered as it influences both the ion speciation and the adsorption mechanism (since it determines the value of the adsorption pseudo-reaction equilibrium constant  $K_i^{(k)}$  as reported in Eq. (6)).

In this sense, it has to be observed that the adsorption reactions for cations on the  $\sigma_H$  and  $\sigma_n$  sites give rise to formally identical adsorption equations (Eqs. (1), (2) and (4)) and the regression data for cation adsorption as the sum of these three contributions becomes insignificant. Thus, to assure a more reliable statistical description of experimental data, an overall cation adsorption pseudo-reaction is considered as the sum of the three distinct contributions:



Hence the expression of Langmuir model can be written in a general way:

$$\omega_i^{(*)} = \omega_{\max}^{(*)} \frac{K_i^{(*)} [M_i^+]}{1 + K_H^{(*)} [H^+] + \sum_{i=1}^m K_i^{(*)} [M_i^+] + \sum_{j=1}^y K_j^{(*)} [Y_j^+]} \quad (11)$$

Under this assumption,  $\sigma'$  represent both  $\sigma_H$  and  $\sigma_n$  active sites and the constant  $K_i^{(*)}$  represent an average value of the  $K_i^{(k)}$  constant for Eqs. (1), (2) and (4). Hence,  $K_i^{(*)}$  has only a statistical meaning.

On the contrary, since the pseudo-reactions involving the anions (Eqs. (3) and (5) of Table 1) are different, their contributions can be individually recognized. However, it has to be observed that the contribution of basic active sites  $\sigma_H$  to the adsorption of anions is significant only if  $H^+$  and  $A_i^-$  concentrations in solution are both significant.

**Table 5**  
Regression and statistical parameters in adsorption model Eqs. (6) and (13).

	Parameters				F	R <sup>2</sup>	R <sup>2</sup> <sub>adj</sub>	Normality test, P
	Mean	Stand. error	T	Dependency				
$\omega_{\max}$ , mg/g	11.80	2.86	3.46	0.70				
$\Delta G_{\text{Cd}^{2+}}$ , kJ/mol	-19.57	0.95	18.40	0.65				
$\Delta G_{\text{CdCl}^+}$ , kJ/mol	-25.04	1.10	16.68	0.67	58.47	0.889	0.84	0.24
$\Delta G_{\text{H}^+}$ , kJ/mol	-38.60	0.93	41.20	0.6				
$\Delta G_{\text{Na}^+}$ , kJ/mol	-8.44	0.88	8.30	0.47				

**Table 6**  
Mean value and standard error of parameters in Eqs. (6), (14) and (15) from data regression analysis.

	Parameters				<i>F</i>	<i>R</i> <sup>2</sup>	<i>R</i> <sub>adj</sub> <sup>2</sup>	Normality test, <i>P</i>
	Mean	Stand. error	<i>T</i>	Dependency				
<b>Trivalent chromium</b>								
$\omega_{\max}$ , mg/g	23	3.2	10	0.98	49.2	0.70	0.69	>0.01
$\Delta G_{\text{Cr}^{3+}}$ , kJ/mol	-15.63	1.2	8.49	0.96				
$\Delta G_{\text{H}^+}$ , kJ/mol	-16.74	0.25	7.66	0.96				
<b>Hexavalent chromium</b>								
$\omega_{\max}$ , mg/g	14.04	1.54	7.21	0.95	244	0.85	0.845	>0.01
$\Delta G_{\text{CrO}_4}$ , kJ/mol	-19.53	0.68	28.66	0.96				
$\Delta G_{\text{OH}^-}$ , kJ/mol	-29.70	0.50	36.88	0.7				
$\Delta G_{\text{Cl}^-}$ , kJ/mol	-14.50	0.90	48.30	0.96				

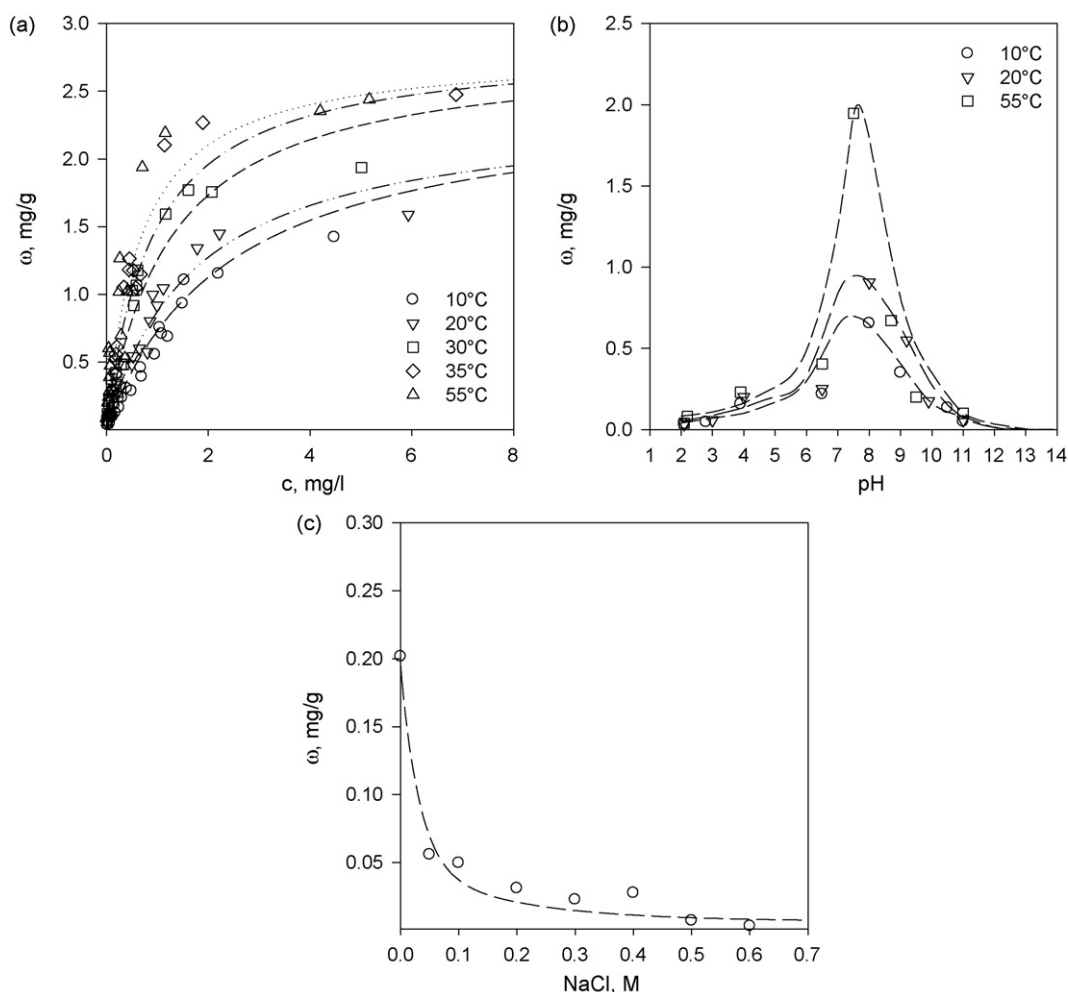
### 3.1. Case studies

The descriptive capacity of the proposed model has been tested on the experimental results available for As(V), Cd(II), Cr(VI) and Cr(III) ions adsorption [19–23]. In all these studies the sorbent was the Aquacarb 207EA<sup>TM</sup>, a commercially available non-impregnated granular activated carbon produced by Sutcliffe Carbon, whose chemical and physical properties have been reported in Di Natale et al. [21].

Table 3 reports the experimental conditions used to test the proposed model. The metal ionic species which are present in solution, as derived from the speciation analysis, are also reported.

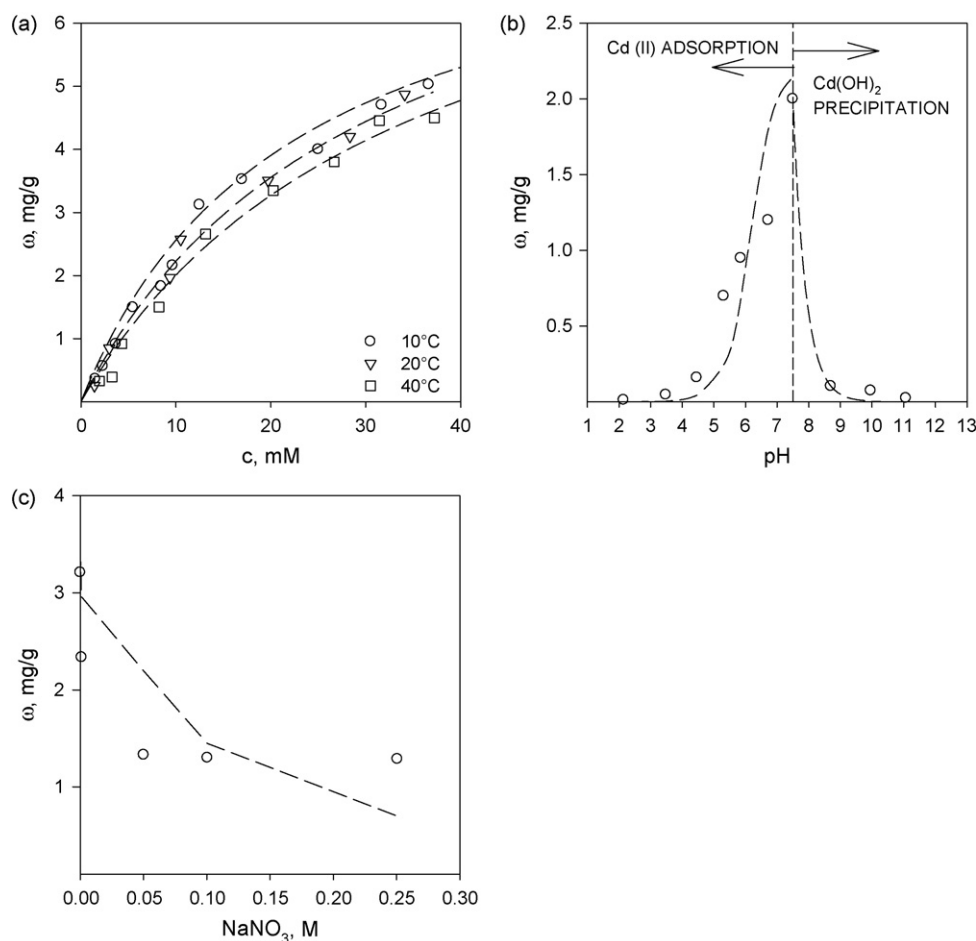
Blank experimental tests on aqueous solutions containing only the activated carbon and the pH and salinity solution controlling agents (NaOH, KOH, HNO<sub>3</sub> and NaCl) have shown that Na<sup>+</sup>, K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are not adsorbed on carbon surface while Cl<sup>-</sup> is captured [20]. Hence, in the following, the adsorption of Na<sup>+</sup>, K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions is neglected in the model application. Furthermore, the release of any inorganic cation or anion from the carbon to the solution is negligible.

The ion speciation of metals has been calculated by mass and charge balance equations coupled with the equations representative of chemical equilibria. Davies's formula [5,29] has been used for the evaluation of the activity coefficients of the ionic species. The



**Fig. 1.** Adsorption capacity of As(V) ions as a function of: (a) temperature (pH = 8 ± 0.4); (b) pH (*T* = 10, 20 and 55 °C), and (c) ionic strength (*T* = 25 °C, pH 8). Comparison between experimental data (symbols) and model results (lines).





**Fig. 2.** Adsorption capacity of Cd(II) ions as a function of: (a) temperature ( $\text{pH} = 7.5 \pm 0.3$ ); (b) pH ( $T = 20^\circ\text{C}$ ), and (c) ionic strength ( $T = 25^\circ\text{C}$ ,  $\text{pH} 7.5$ ). Comparison between experimental data (symbols) and model results (lines).

regression analysis of experimental data is carried out with the SPSS software SigmaPlot 10.0<sup>®</sup> which uses the Levenberg–Marquart algorithm for the estimation of the regression parameters for optimal data fitting. The statistical analysis parameters are reported in Tables 4–6.

### 3.2. Arsenic As(V)

The adsorption of As(V) ions involves the series of dissociation products of arsenic (V) acid, in the chemical form of anions, as reported in Table 3. Red-ox phenomena as well as precipitation reactions have not been observed [21,27–29].

The model equations are reduced to Eqs. (3) and (5) of Table 2, coupled with Eq. (8) in order to take into account the adsorption of all arsenic ionic species. Arsenic speciation analysis shows that for  $\text{pH} < 3$  the arsenic acid dissociation is negligible and the corresponding carbon adsorption capacity is small. Therefore, the contribution of basic protonated sites to adsorption is neglected and the adsorption model is thus reduced to the unique Eq. (5), which becomes:

$$\omega = \omega_{\max} \frac{K_1[\text{H}_2\text{AsO}_4^-] + K_2[\text{HAsO}_4^{2-}] + K_3[\text{AsO}_4^{3-}]}{1 + K_1[\text{H}_2\text{AsO}_4^-] + K_2[\text{HAsO}_4^{2-}] + K_3[\text{AsO}_4^{3-}] + K_{\text{Cl}}[\text{Cl}^-] + K_{\text{OH}}[\text{OH}^-]} \quad (12)$$

A complete set of experimental data on As(V) ions adsorption on activated carbon is reported in [20]. The non-linear regression analysis on experimental data has been performed by means of Eq. (12) coupled with Eq. (6), by determining the values of the parameters  $\omega_{\max}$ ,  $\Delta G_i$  ( $i = 1, \dots, 3$ ),  $\Delta G_{\text{OH}}$  and  $\Delta G_{\text{Cl}}$ . The regression and statistical analysis parameters are reported in Table 4.

In Fig. 1 the experimental data at different temperature (with an equilibrium  $\text{pH} = 8 \pm 0.4$ ), pH (with  $T = 10, 20$  and  $55^\circ\text{C}$ ) and salinity ( $T = 25^\circ\text{C}$ ,  $\text{pH} 8$ ) have been compared to model equations.

In all the investigated conditions, there is a good agreement between the experimental data and the descriptive model. In particular, even under the assumption of exothermicity, the model correctly describes the increase of adsorption capacity with temperature which appears to be related to the increasing concentration of arsenic anionic species.

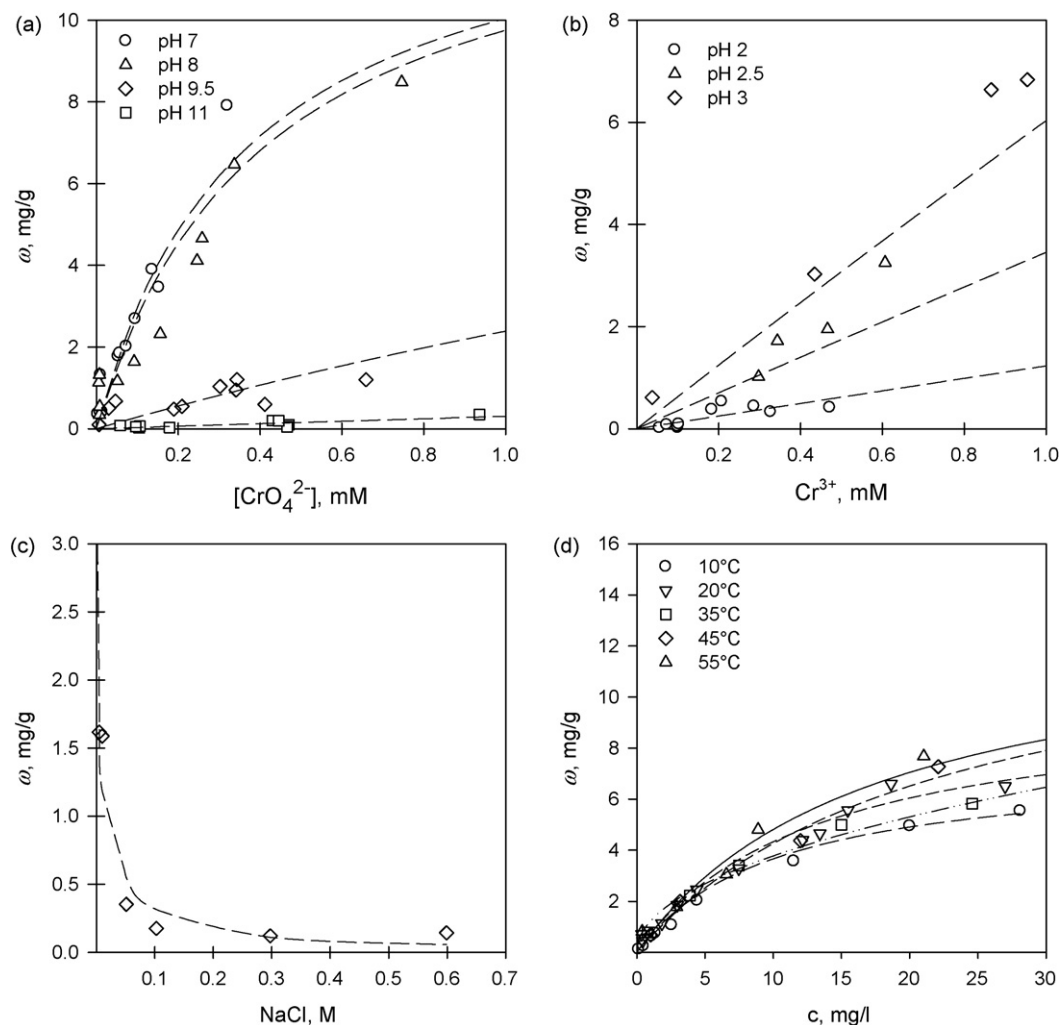
### 3.3. Cadmium Cd(II)

In this case, cadmium is present only as  $\text{Cd}^{2+}$  and the adsorption model equation can be derived from Eq. (11) as

$$\omega = \omega_{\max} \frac{K_1[\text{Cd}^{2+}]}{1 + K_1[\text{Cd}^{2+}] + K_{\text{H}}[\text{H}^+]} \quad (13)$$

Experiments show that, for the concentration range investigated, the precipitation of  $\text{Cd}(\text{OH})_2$  occurs for  $\text{pH} > 8$ .

Experimental data on Cd(II) adsorption on activated carbon are reported in Di Natale et al. [22,23]. The regression analyses of experimental data are carried out by means of Eqs. (6) and (12) and the values of regression and statistical analysis parameters are reported in Table 5.



**Fig. 3.** Comparison between experimental data (symbols) and model results (lines) for: (a) Cr(VI) adsorption isotherms as a function of pH ( $T=25^\circ\text{C}$ ), (b) Cr(III) adsorption isotherms as a function of pH ( $T=25^\circ\text{C}$ ), (c) Cr(VI) adsorption as a function of ionic strength ( $T=25^\circ\text{C}$ ,  $\text{pH}=7\pm 0.3$ ), and (d) total chromium adsorption isotherms as a function of temperature ( $\text{pH}=7\pm 0.3$ ).

The comparison of experimental data obtained at different temperature (equilibrium  $\text{pH}=7.5\pm 0.3$ ),  $\text{pH}$  ( $T=20^\circ$ ) and salinity ( $T=25^\circ\text{C}$ ,  $\text{pH}=7.5$ ) values and the model results are reported in Fig. 2. The effect of  $\text{pH}$  and temperature is well described by the model while less good results can be obtained for high salinity solutions. In this case cadmium cations like  $\text{CdNO}_3^+$  or  $\text{CdCl}^+$  can be present at high salt concentrations and Eq. (13) must be corrected accordingly; nevertheless at this moment the experimental data are not sufficient to provide for a correct modelling analysis.

#### 3.4. Chromium Cr(III) and Cr(VI)

The chromium speciation in aqueous solution is strongly related to the  $\text{pH}$  and red-ox reactions. For  $\text{pH}<3$ , chromium is present as  $\text{Cr}^{3+}$  trivalent chromium cations, and for  $\text{pH}>8$  as the Cr(VI) ion  $\text{CrO}_4^{2-}$ . In all experimental conditions investigated, the precipitation reactions are absent [27–29]. As for the case of Cd(II), for Cr(III) ions, the equation of the model can be written by applying Eq. (11), which becomes:

$$\omega = \omega_{\max} \frac{K_1[\text{Cr}^{3+}]}{1 + K_1[\text{Cr}^{3+}] + K_H[\text{H}^+]} \quad (14)$$

For the case of Cr(VI) ions the equations can be derived by Eqs. (3), (5) and (8). As for As(V) ions, it is worth noticing that in the investigated conditions the contribution of  $\sigma\text{H}$  sites to adsorption

of Cr(VI) ions is neglected due to the insignificant concentration of  $\text{H}^+$  ions. Thus, the adsorption model only considers the adsorption of chromate anions on Lewis acid sites, given by equation:

$$\omega = \omega_{\max} \frac{K_1[\text{CrO}_4^{2-}]}{1 + K_1[\text{CrO}_4^{2-}] + K_{\text{OH}}[\text{OH}^-] + K_{\text{Cl}}[\text{Cl}^-]} \quad (15)$$

Experimental data on Cr(III) and Cr(VI) ions adsorption on activated carbon are reported in Di Natale et al. [19,21]. The estimated parameters for both regression analyses are reported in Table 6 and the comparison among model regression and experimental data at different equilibrium  $\text{pH}$  ( $T=25^\circ$ ) for Cr(III) and Cr(VI) and the effect of solution salinity ( $T=25^\circ\text{C}$ ,  $\text{pH}=7.5$ ) on Cr(VI) are reported in Fig. 3.

#### 4. Conclusions

In this work, a model for the description of metallic ions adsorption onto activated carbon is presented. This model starts from an evaluation of ion speciation and it considers the presence of both the  $\text{CO}_x\text{H}_y$  acid–base sites and Lewis acid/base active sites on the activated carbon surface. A multi-component Langmuir adsorption model is used to describe experimental results, by correlation of ions concentration to the overall adsorption capacity. In order to test its descriptive capacity, the model is applied to available experimental results on the adsorption of arsenic, cadmium and

chromium in model aqueous solution. Model parameters are calculated as the best fitting of experimental data by using an appropriate non-linear regression algorithm.

A good matching between experimental results and model predictions has been obtained for all the investigated conditions, giving a physically meaningful interpretation of concentration, temperature, pH and salinity effects on adsorption capacity.

Indeed, it is worth noticing that one of the key assumptions of the Langmuir model is that the site–solute interaction is a specific property of the solute and the sorbent site, independently from the presence of any other solute and from the occurrence of lateral interactions between adsorbed solutes.

This assumption leads to the fundamental results that the Gibbs' energy and the  $K_i^{(k)}$  values for the uptake of a given pair of adsorbate and activated carbon can be considered as a characteristic property of the pair itself.

When applied to the reported case studies, this means that the Gibbs' energy for those common ions (such as  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{H}^+$ ), that appear in the adsorption of several metals, should be similar.

By analysing the results reported in Tables 4–6, it is clear how this assumption is strictly verified for the case of  $\text{OH}^-$  and  $\text{Cl}^-$  anions (that are present in the adsorption models for arsenic and hexavalent chromium) but not for the  $\text{H}^+$  (common to cadmium and trivalent chromium).

Indeed, this result is not surprising. For the case of  $\text{OH}^-$  and  $\text{Cl}^-$  anions, the adsorption model can be referred to two different mechanisms of uptake: the capture on  $\text{CO}_x\text{H}_y$  hydrolyzed basic sites and Lewis bases. In both cases, only these last sites seem to be involved. Since both the case studies confirm the same value of the Gibbs' energy of adsorption for  $\text{OH}^-$  and  $\text{Cl}^-$ , it is possible to state that the capture of chlorides and hydroxides is likely to occur on the same active sites.

On the other hand, when the adsorption of  $\text{H}^+$  ions is considered, it has to be recalled that the cation adsorption model is intrinsically not able to make any distinction between active sites or between substitution and addition reaction mechanisms (Tables 1 and 2). Hence, for cations, the adsorption isotherm model represents the averaged results of all the uptake mechanisms and it must be taken into account that the competitive adsorption of  $\text{H}^+$  and, eventually, of any other cation, is strictly dependent on the specific metal to be captured.

In addition, the model allows to estimate a solute/sorbent affinity scale based on the value of the  $\Delta G_i$ . By analysing the results in Tables 4–6, it appears that there is a larger affinity of the activated carbon toward ions with larger electrical charges ( $\text{AsO}_4^{3-} > \text{HAsO}_4^{2-} > \text{H}_2\text{AsO}_4^-$ ) and that the arsenic ions are more strongly bonded to the activated carbon with respect to cadmium and chromium ions. Anyway, the overall adsorption capacity of a sorbent also depends on the availability of active sites and, in this sense, by comparing the tabled values of the  $\omega_{\max}$  in terms of moles adsorbed per gram of activated carbon, it appears that there is a larger concentration of active sites for Cr(III) adsorption ( $\omega_{\max} = 0.44$  mmol/g) rather than for Cr(VI) ( $\omega_{\max} = 0.27$  mmol/g), Cd(II) ( $\omega_{\max} = 0.105$  mmol/g) and As(V) ( $\omega_{\max} = 0.03$  mmol/g).

Finally, it has to be noted that, even if, in these case studies the Langmuir model proven to be valid, the general framework of the study sets aside from the choice of the adsorption model.

Indeed, this framework can be summarized with the following steps:

1. experimental analysis with significant variation of process parameters;
2. ion speciation analysis in solution at equilibrium;
3. assessment of the adsorption model;
4. regression analysis;

5. critical analysis of the model result and verification of model assumptions.

Hence, if the Langmuir assumptions are not verified, a different adsorption model can be chosen and the mathematical expression of the adsorption isotherms changes accordingly, but the general structure of the model remains unchanged.

## Appendix A. Adsorption mechanisms model

### A.1. Cation adsorption

The adsorption of cations occurs on two different kinds of active sites, the Lewis bases,  $\sigma_n$ , and the  $\text{CO}_x\text{H}_y$  surface groups,  $\sigma\text{H}$ . The classical procedure used for multi-component Langmuir adsorption [5] is followed.

The adsorption pseudo-reactions for the basic  $\sigma\text{H}$  and the  $\sigma_n$  sites (mechanisms #2 and 4 in Table 1) follow the same reactions of addition of the N species of metal cations,  $\text{M}^+$ , in competition with Q species,  $\text{Y}^+$ , and with  $\text{H}^+$ . For the sake of brevity, only the mechanisms for  $\sigma_n$  is reported here:



The corresponding mass-action law for these reactions is (written for (A1) reaction as example):

$$K_i^{(4)} = \frac{\{\sigma_n\text{M}_i^+\}}{\{\sigma_n\}\{\text{M}_i^+\}} \quad (\text{A4})$$

where square brackets denotes molar concentrations in solutions and braces refer to molar concentration on the carbon surface.

The maximum concentration of  $\sigma_n$  active sites is

$$\{\sigma_{\max}^n\} = \{\sigma_n\} + \sum_i \{\sigma_n\text{M}_i^+\} + \{\sigma_n\text{H}^+\} + \sum_j \{\sigma_n\text{Y}_j^+\} \quad (\text{A5})$$

The solution of the system of equations given by the mass-action laws for the adsorption pseudo-reactions (A1)–(A3) and the mass balance (A5) in terms of superficial concentration of sites occupied by the metal ions, results to be:

$$\frac{\sum_{i=1}^N \{\sigma_n\text{M}_i^+\}}{\{\sigma_{\max}^n\}} = \frac{\sum_{i=1}^N K_i^{(4)} [\text{M}_i^+]}{1 + \sum_{i=1}^N K_i^{(4)} [\text{M}_i^+] + \sum_{j=1}^Q K_j^{(4)} [\text{Y}_j^+] + K_{\text{H}}^{(4)} [\text{H}^+]} \quad (\text{A6})$$

Finally, by multiplying and dividing the left-hand-side of the (A6) for the molecular weight of the adsorbed metal, the adsorption capacity in terms of gram of adsorbed metal per gram of solute is obtained (Eq. (4) in Table 2).

For the case of acid  $\text{CO}_x\text{H}_y$  sites, the capture of cations follows substitution reaction mechanisms such as



With

$$\{\sigma\text{H}_{\max}\} = \{\sigma\text{H}\} + \{\sigma^-\} + \sum_i \{\sigma\text{M}_i^+\} + \sum_j \{\sigma\text{Y}_j^+\} \quad (\text{A10})$$



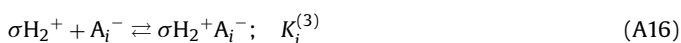
It can be easily demonstrated that the solution of the corresponding system of equation has the same form of Eq. (A6) and Eq. (1) in Table 2.

## A.2. Anion adsorption mechanisms

The adsorption of anions occurs on two different kinds of activate sites, the Lewis acids,  $\sigma_e$ , and the base  $\text{CO}_x\text{H}_y$  hydrolyzed surface groups,  $\sigma\text{H}$ . As regards to the  $\sigma_e$  sites (mechanism #5 in Table 1), the adsorption is represented by the following set of pseudo-reactions whose equilibrium constants are denoted  $K^{(5)}$ . For the case of N metal anionic species,  $\text{A}_i^-$ , competing with Q anions  $\text{X}^-$  and with the hydroxides,  $\text{OH}^-$  the system is:



The mass balance and the mass action law equations for this system are similar to that obtained for cation addition adsorption mechanism and they are not reported here. For the adsorption of  $\text{A}_i^-$ ,  $\text{X}_j^-$  and  $\text{OH}^-$  on the  $\text{CO}_x\text{H}_y$  hydrolyzed surface groups (mechanisms #3 in Table 1), the adsorption pseudo-reactions scheme is represented by



The maximum concentration of active sites on the solid is

$$\{\sigma_{\text{max}}\} = \{\sigma\text{H}\} + \{\sigma\text{H}_2^+\} + \sum_i \{\sigma\text{H}_2^+\text{A}_i^-\} + \{\sigma\text{H}_2^+\text{OH}^-\} + \sum_j \{\sigma\text{H}_2^+\text{X}_j^-\} \quad (\text{A18})$$

The solution of the system of equations given by the mass-action laws for the adsorption pseudo-reactions (A14)–(A17) and the mass balance Eq. (A18) results to be:

$$\frac{\sum_i \{\sigma\text{H}_2^+\text{A}_i^-\}}{\{\sigma_{\text{max}}\}} = \frac{K_{\text{H}}^{(3)}[\text{H}^+] \sum_{i=1}^N K_i^{(3)}[\text{A}_i^-]}{1 + K_{\text{H}}^{(3)}[\text{H}^+] \left( 1 + \sum_{i=1}^N K_i^{(3)}[\text{A}_i^-] + \sum_{j=1}^Q K_j^{(3)}[\text{X}_j^-] + K_{\text{OH}}^{(3)}[\text{OH}^-] \right)} \quad (\text{A19})$$

Multiplying and dividing the left-hand-side of the (A13) for the molecular weight of the adsorbed metal, the adsorption capacity in terms of gram of adsorbed metal per gram of solute is obtained (Eq. (3) in Table 2).

## Appendix B. Regression analysis

The curve fitting of experimental data is carried out with the SPSS software SigmaPlot 10.0<sup>®</sup>, that uses the Levenberg–Marquardt algorithm [30] to find the coefficients (i.e. the regression parameters) of the independent variables ( $M_i$ ,  $A_i$ ,  $\text{OH}^-$ ,  $T$ ) that give the best fit between the equation and the data. This algorithm seeks the values of the parameters that minimize the sum of the squared differences between the values of the observed and predicted values of the dependent variable.

$$S = \sum_{i=1}^n w_i (\omega_i - \omega_{ri})^2$$

where  $\omega_i$  are the observed values of the dependent variable for the  $i$ th experiment and  $\omega_{ri}$  are the corresponding predicted values.  $w_i$  is the function used to weight the residuals. In this work the raw residuals are eventually considered and, thus,  $w_i$  is set to 1.

The SigmaPlot<sup>®</sup> also allows a statistic analysis of the non-linear regression. In particular, for the sake of brevity, in Tables 4–6 of the paper only the values of some parameters for As(V), Cd(II) and Cr(III)–Cr(VI) analysis, respectively, have been reported: the coefficient of determination  $R^2$ , the adjusted coefficient of determination  $R_{\text{adj}}^2$ , the mean value and standard error in determination of the parameters, the parameter dependency, the normality, the  $T$ -statistic and the  $F$ -statistic tests. The meanings of these parameters are reported in classical statistical works [31,32]. The accuracy of data regression is confirmed by the high value of the coefficient of determinations  $R^2$  and  $R_{\text{adj}}^2$ , while the significance of the parameters set is claimed by the high values of  $T$ -statistic, the parameter dependencies and the  $F$ -tests. The high values of  $T$ -statistic test shows that the independent variable can be used to predict the dependent one. The dependence of each parameter is sufficiently far from 1 to assure that the model parameters are weakly dependent on one another and all the parameters are strictly necessary for the regression model. Finally, the high value of the  $F$ -test shows the ability of the chosen set of independent variables to predict the dependent variable.

## Notation

[X]	concentration of the species X (M or mg/l)
$\omega$	total adsorption capacity of activated carbon (mg/g)
$\omega_i^{(k)}$	adsorption capacity for the species $i$ ( $i = 1, \dots, n$ ), according to $k$ th mechanism ( $k = 1, \dots, n$ ) (mg/g)
$\omega_i$	adsorption capacity for the single $i$ th specie (mg/g)
$\omega^{(k)}$	adsorption capacity for the active sites adsorbing according to the $k$ th mechanism (mg/g)
$\omega_i^{(*)}$	adsorption capacity for the $i$ th cationic species
$\omega_{\text{max}}$	maximum adsorption capacity (mg/g)
$\omega_{\text{max}}^{(k)}$	maximum adsorption capacity for the $k$ th mechanism (mg/g)
$K_i^{(k)}$	equilibrium constant for the $k$ th adsorption pseudo-reaction involving the $i$ th species
$K_i^{(*)}$	equilibrium constant for $i$ th cationic species adsorption
$K_{\text{H}}$	equilibrium constant for $\text{H}^+$ species adsorption
$K_{\text{OH}}$	equilibrium constant for $\text{OH}^-$ species adsorption
$\Delta G_i^{(k)}$	free energy of Gibbs for the $k$ th pseudo-reactions (kJ/mol)
$\sigma\text{H}$	acid/base sites
$\sigma_n$	Lewis base active sites
$\sigma_e$	Lewis acid active sites
$\sigma'$	cation adsorption sites
$\text{P}^+$	generic cation in solution
$M_i^+$	metallic cation in solution ( $i = 1, \dots, m$ )
$Y_j^+$	generic cation in solution ( $j = 1, \dots, y$ )
$\text{Q}^-$	generic anion in solution
$A_j^-$	metallic anion in solution ( $i = 1, \dots, a$ )
$X_j^-$	generic anion in solution ( $j = 1, \dots, x$ )
$\text{H}^+$	hydrogen ion (proton)
$\text{OH}^-$	hydroxide ion

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