

# Removal of chromium ions from aqueous solutions by adsorption on activated carbon and char

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## Abstract

Adsorption isotherms of chromium ions in aqueous solution have been experimentally measured on a granular activated carbon (GAC) and on a char of South African coal (CSAC). Experimental results show that the adsorption capacity for the GAC strongly depends on solution pH and salinity, with maximum values around 7 mg/g at neutral pH and low salinity levels. On the contrary, the CSAC shows a smaller adsorption capacity, near 0.3 mg/g, which slightly decreases by increasing pH and salinity levels. Chromium adsorption mainly depends on the availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the Cr(VI) which lead to the formation of Cr(III). The reduction of Cr(VI) and the following sorption of Cr(III) cations appears as the leading mechanism for chromium uptake on the CSAC. A similar behaviour can be observed for the GAC at pH below 3. On the contrary, at pH > 7, the multicomponent competitive adsorption of Cr(VI), OH<sup>-</sup> and Cl<sup>-</sup> has to be considered.

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## 1. Introduction

Chromium compounds are among the most dangerous inorganic water pollutants. They are constantly released into the aquatic environment by natural processes (mainly by volcanic activity and weathering of rocks [1]) and by anthropic sources, which in the last twenty years have become of leading importance in the worldwide emission balance of these substances [2]. Chromium compounds mainly occur in the environment as trivalent, Cr(III), and hexavalent, Cr(VI), chromium. Trivalent chromium is an essential element in humans and is much less toxic than the hexavalent one, which is recognised as a carcinogenic and mutagenic agent [3]. However, due to the possible oxidation of the Cr(III) to the harmful Cr(VI), environmental regulations usually define limiting values for both the total and the hexavalent chromium concentration in waters. European Union environmental regulations consider chromium as a primary hazardous pollutant (e.g. Directives 91/271/CEE and 96/61/CE) and

in recent times, through the Directive 2000/60/CE, have also imposed the cessation or phasing out of discharges, emissions and losses of such priority pollutants within 2020. Current Italian regulations on chromium concentration in wastewaters are fixed to 200 µg/l for Cr(VI) and 2 mg/l for total chromium (D. Lgs 152/99) while for groundwater remediation (D.M. 471/99) the maximum allowed value for Cr(VI) is 5 µg/l.

Depuration technologies usually adopted to remove chromium from industrial wastewaters include precipitation, membrane filtration, solvent extraction with amines, ion exchange, activated carbon adsorption, electro-deposition, and various biological processes [4–14]. Among them, activated carbon adsorption seems to be an attractive choice for chromium removal both for its removal efficiency and for the rapid adaptation to pollutant loading alteration [6,15,16]. For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters [7,17–19]. However, commercially available activated carbons may be expensive and, for this reason, the knowledge of the optimal working conditions to maximize the sorbent capture capacity is required. Similarly, the production of low cost, disposable sorbents for chromium removal is also worth considering [4,5].

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### Nomenclature

|                          |  |
|--------------------------|--|
| $b$                      | Freundlich model parameters ( $\text{mg/g mM}^{-n}$ )    |
| $K$                      | Langmuir model parameters ( $\text{l/mol}$ )             |
| $n$                      | Freundlich model parameters                              |
| $\text{pH}_{\text{PZC}}$ | pH value of the point of zero charge                     |
| $[x]$                    | molar concentration of the species $x$ ( $\text{mg/l}$ ) |

### Greek letters

|                       |   |
|-----------------------|---|
| $\omega$              | adsorption capacity ( $\text{mg/g}$ )       |
| $\omega_{\text{max}}$ | Langmuir model parameters ( $\text{mg/g}$ ) |

The values of process parameters (solute concentration, pH, salinity, temperature, solution composition) severely affect the equilibrium adsorption capacity of a given sorbent, determining a strong variation of the overall removal efficiency of the process [4,5,20–26] and playing a crucial role in the industrial scale up of adsorption units [27,28]. In this sense, it is worth noticing that almost all the thermodynamic results in literature are focused on model aqueous solution [4,5,20–25] with few studies on saline solutions [26] and on pilot plant applications (e.g. [29–32]). Even if this simplification can be considered as too restrictive for the industrial scale-up, the high variability of natural and industrial waters is a severe limitation to the extension of pilot plant results to different working conditions. For this reason, the study of adsorption in model aqueous solutions allows a more interesting and reliable analysis of adsorption phenomena and a more meaningful method for the comparison of sorbents adsorption capacity.

This work concerns the uptake of chromium ions in aqueous solutions by a non-impregnated activated carbon (Aquacarb 207EA<sup>TM</sup> commercialised by Sutcliffe Carbon—named GAC in the following) and a char derived from South African coal (CSAC). In particular, the attention has been focused on the adsorption thermodynamics. Experimental runs have been carried out at ambient temperature (20 °C) by varying chromium concentration, pH and solution salinity.

## 2. Materials and methods

### 2.1. Sorbents characteristics

Aquacarb 207EA<sup>TM</sup> is a commercially available non impregnated granular activated carbon, produced by Sutcliffe Carbon starting from a bituminous coal. This material has a narrow particle diameter distribution between 0.8 and 1.4 mm, with an average diameter of 1.2 mm. The char of South African coal has a higher average particle diameter, around 2.25 mm, and a wider particle diameter distribution, with more than 90% of the material almost uniformly distributed between 1.3 and 3.2 mm.

The main chemical and physical characteristics of the two materials are listed in Table 1.

The textural properties of the sorbents have been studied by means of mercury porosimetry (Carlo Erba Porosimeter 2000), BET (Carlo Erba SORPTOMATIC 1900) and SEM (Environ-

Table 1  
Characteristics of the sorbents

|  | Name             |                    |
|--|------------------|--------------------|
|  | Aquacarb 207EA   | Char of S.A. coal  |
| Origin   | Bituminous coals | South African coal |
| Activation method                                  | Steam activation | –                  |
| Density ( $\text{kg/m}^3$ )                        | 480–520          | 641                |
| Effective density ( $\text{kg/m}^3$ )              | 950              | 1850               |
| Average diameter (mm)                              | 1.20             | 2.27               |
| Porosity (%)                                       | 16.8             | 20                 |
| BET surface area ( $\text{m}^2/\text{g}$ )         | 950              | 11.4               |
| External surface area ( $\text{m}^2/\text{g}$ )    | 401              | 8.83               |
| Micropore surface area ( $\text{m}^2/\text{g}$ )   | 549              | 2.56               |
| Adsorption average pore diameter (4V/A by BET) (Å) | 24.5             | 16.3               |
| Humidity (% w/w)                                   | 5                | 5                  |
| Ultimate analysis (% w/w) on dry basis             |                  |                    |
| Carbon   | 87.00            | 77.02              |
| Hydrogen   | 0.17             | 1.55               |
| Oxygen   | 2.00             | 2.63               |
| Nitrogen   | 1.10             | 1.80               |
| Sulphur  | n.d.             | 0.77               |
| Ash  | 9.58             | 16.23              |
| $\text{pH}_{\text{PZC}}$                           | 8.00             | 8.85               |
| Boehm's titration analysis (acid/base adsorption)  |                  |                    |
| HCl (mequiv./g)                                    | 2.44             | 3.97               |
| $\text{NaHCO}_3$ (mequiv./g)                       | –                | –                  |
| $\text{Na}_2\text{CO}_3$ (mequiv./g)               | 0.36             | 0.30               |
| NaOH (mequiv./g)                                   | 0.40             | 0.34               |

mental Scanning Electron Microscope Philips XL30) analyses. The BET surface areas result of about 950  $\text{m}^2/\text{g}$  for the GAC and 11.4  $\text{m}^2/\text{g}$  for the CSAC while the averaged micropore diameters are 26 Å for the GAC and 16.3 Å for the CSAC.

The chemical composition of the sorbent has been evaluated by elemental analysis (Perkin-Elmer 2400 series, CHNS Analyser) which also shows that the two materials have high ash content.

Both carbons are slightly basic in nature as shown by the value of their  $\text{pH}_{\text{PZC}}$  [33] and by Boehm's titration analyses [34] for the characterization of surface functional groups, which also show that, the surface acidic groups on the carbons are mainly represented by lactones and phenols.

### 2.2. Sorption procedure

The stock solutions of test reagent are prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  in double distilled water to obtain total chromium concentration levels ranging from 5 to 50 mg/l. The pH values of the initial solutions are adjusted by adding  $\text{HNO}_3$  (0.1 M) or  $\text{KOH}$  (0.1 M) but they are not further altered during the experimental runs. Solution salinity has been modified by adding sodium chloride. The experimental runs have been carried out in batch mode at the constant temperature of 20 °C in a PID controlled thermostatic oven. Each sample consists of a 200 ml aqueous solution at the desired concentration of chromium, put

in contact with a mass of sorbent ranging between 0.5 and 10 g. Before each experimental run, the sorbents have been carefully rinsed with distilled water and oven dried for 48 h at 80 °C.

Preliminary tests show that a contact time of 60 h is required to reach equilibrium conditions without additional stirring. At equilibrium conditions, both the chromium concentrations in solution and on the carbon surface have been measured. The solution is filtered in a Hirsch funnel ceramic filter with the aid of a vacuum pump which assures a very rapid and efficient separation of the granular material. The filtered solution is then analysed for pH and total and hexavalent chromium concentrations while the carbon is leached with nitric acid solution to obtain the complete desorption and to give a direct measure of the uptake of chromium on the solid surface. The accuracy of the experimental runs is checked by allowing a maximum error of 5% in the chromium material balance.

### 2.3. Analytical methods

The total chromium concentration in solution has been measured by means of air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer (Standard Method 3111B in Clesceri et al. [35]), with chromium standard solution provided by Sigma Aldrich. Dilution, where required, have been carried out with 1 M HNO<sub>3</sub> in distilled water.

The concentration of hexavalent chromium has been measured by UV–Vis absorption spectrophotometry by means of complexation with diphenylcarbazide (Standard method 3500-Cr-B, in Clesceri et al. [35]) with a Perkin-Elmer Lambda EZ-150 spectrophotometer.

The concentration of trivalent chromium in solution is calculated as the difference between total and hexavalent chromium concentration.

The amount of adsorbed chromium has been measured by leaching the solid material with 100 ml nitric acid aqueous solution (HNO<sub>3</sub>, 1 M) for 24 h, which assures a complete desorption of chromium from carbon surface. Then, the solution has been analysed by means of AAS-F.

The solution pH is determined by Orion EA920 ion-Analyser.

### 2.4. Quality assurance/quality control

To establish the accuracy, reliability, and reproducibility of the collected data, all batch isotherm tests were recorded in triplicate and average values only are reported. Blank tests have been run in parallel. All the labware used in the study has been previously soaked in 1 M HNO<sub>3</sub>, triply rinsed with distilled water and oven dried. All the chemicals used in this work are AR grade supplied by Sigma–Aldrich.

Experimental runs have been performed by using a chromium containing solution without addition of sorbent. The experiments confirm that the initial chromium concentration, the pH and the Cr(III)/Cr(VI) ratio remain unchanged during the experiment. Hence the reduction of chromium concentration, the pH variation and the occurrence of redox reactions during adsorption tests are only related to the presence of the sorbent.

The accuracy of analytical techniques has been checked by determination of the relative standard deviation (R.S.D.) of the sample analysis. Typical values of the R.S.D. for both total and hexavalent chromium are below 7% while for the standard solution they are lower than 5%.

Regression analysis of experimental data has been carried out with the statistic software Sigma Plot V9.0 for Windows (SPSS Inc.). The correlation coefficient ( $R^2$ ) and the standard error in parameter evaluation have been reported to characterize the precision of optimal data fitting analysis.

## 3. Experimental results

### 3.1. Effect of pH and chromium concentration

The effect of solution pH on chromium capture is firstly analyzed by considering eight solutions with the same chromium concentration and carbon dosage and different initial pH values. Experimental results (reported in Fig. 1 in terms of adsorption capacity as a function of the equilibrium pH) reveal that the GAC reaches a maximum value of adsorption capacity between pH 5 and 8, while the CSAC shows an almost monotonic decrease of adsorption capacity at increasing pH.

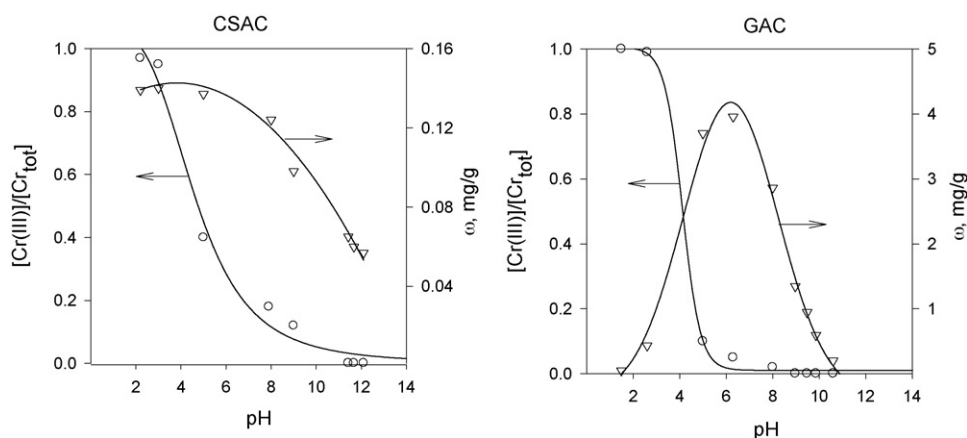


Fig. 1. Total chromium adsorption capacity and trivalent chromium percentage for aqueous solution with  $c^0 = 25$  mg/l at different equilibrium pH levels.

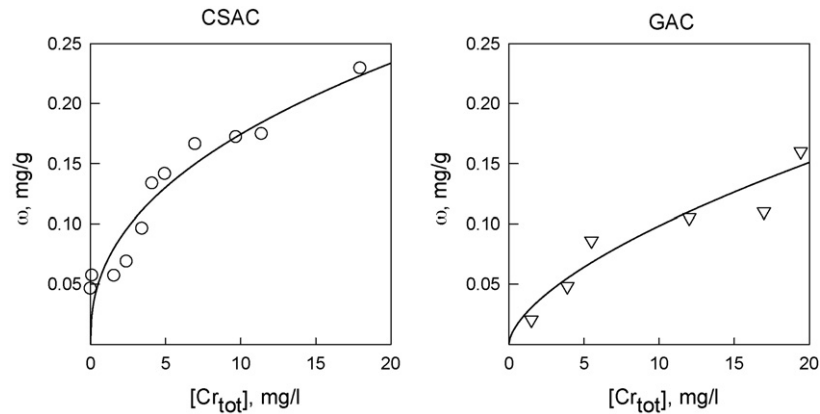


Fig. 2. Adsorption isotherms at  $\text{pH} = 2 \pm 0.1$  at  $T = 20^\circ\text{C}$ .

Fig. 1 also reports the fraction of trivalent chromium in solution highlighting that for pH values below 3 all the chromium is in trivalent form for both the sorbents, while at pH 7 trivalent chromium is absent for the GAC while it still accounts for 20% of the total chromium concentration for the CSAC. At higher pH values only hexavalent chromium is present in solution.

Further details on the effect of pH are obtained from the description of the adsorption isotherms obtained from experimental runs carried out at five equilibrium pH values between 2

and 11 and reported in Figs. 2–6. As previously reported (Fig. 1) experimental data show the simultaneous presence of Cr(III) and Cr(VI) ions. Therefore, although the adsorption isotherms are described in terms of total chromium concentration, the weight percentage of Cr(III) at equilibrium is indicated when both Cr(III) and Cr(VI) are present in solution.

Fig. 2 reports the adsorption isotherm at pH 2 ( $\pm 0.1$ ) and shows no remarkable difference between the GAC and the CSAC: the adsorption capacity is around 0.1–0.2 mg/g for both

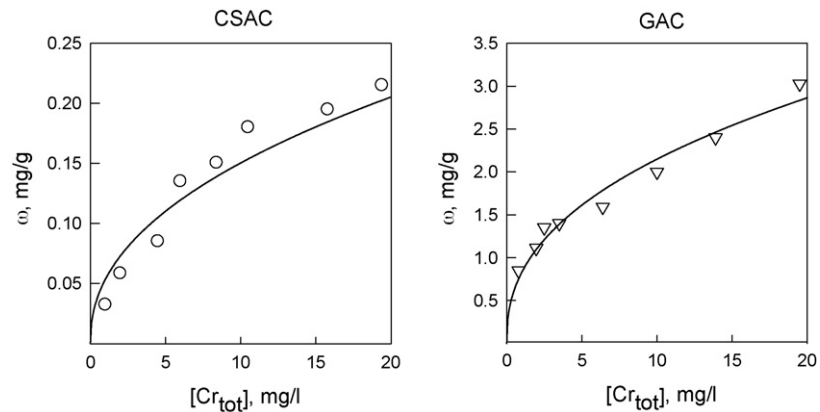


Fig. 3. Adsorption isotherms at  $\text{pH} = 3 \pm 0.2$  at  $T = 20^\circ\text{C}$ .

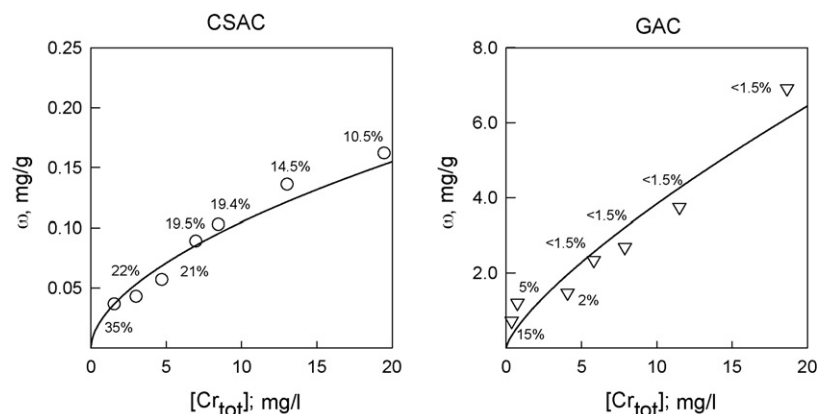


Fig. 4. Adsorption isotherms at  $\text{pH} = 7.5 \pm 0.3$  at  $T = 20^\circ\text{C}$ . The label on each symbol represents the trivalent chromium concentration in solution with respect to the total chromium concentration.

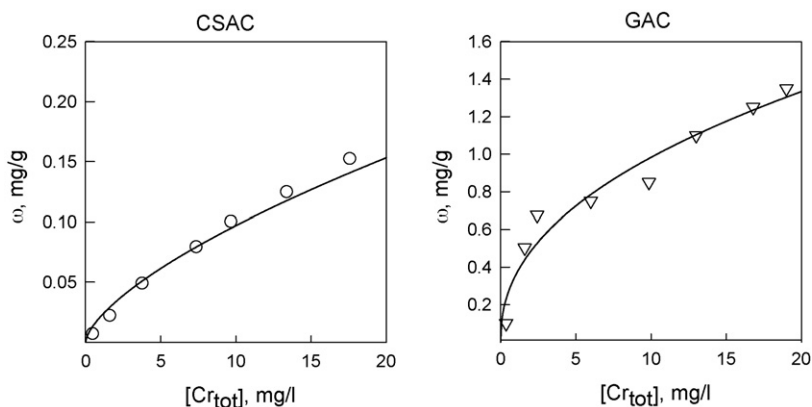


Fig. 5. Adsorption isotherms at  $\text{pH}=9 \pm 0.15$  at  $T=20^\circ\text{C}$ .

the sorbents. In this case all the chromium is in trivalent form. This condition is still verified at  $\text{pH} 3 (\pm 0.2)$  for which experimental results show that the adsorption capacity is almost unchanged for the CSAC while it becomes almost ten times higher for the GAC (Fig. 3).

At pH levels near the neutrality (Fig. 4), the adsorption capacity of the CSAC is further reduced while that of the GAC reaches a maximum value of approximately 6 mg/g. In this case, almost all the chromium is present as Cr(VI) when GAC is used, while for the case of the CSAC, the Cr(III) weight percentage varies from 10 to 30%.

Finally, Figs. 5 and 6 describe the adsorption capacity in alkaline solutions where only Cr(VI) is present in solution. For both the sorbents the adsorption capacities progressively decrease and at  $\text{pH} 11 (\pm 0.1)$  they are reduced to a few hundredth milligrams per gram.

### 3.2. Effect of solution salinity

To analyze the effect of solution salinity experiments have been carried out on six aqueous solutions containing the same chromium concentration and carbon dosage at different salinity levels, obtained by addition of different amount of NaCl.

Experimental results, described in terms of adsorption capacity versus the solution salinity, are reported in Fig. 7. The

equilibrium pH is always near neutrality (6.8–7.3) and only Cr(VI) is present at equilibrium.

For the case of GAC the increase of solution salinity leads to a significant decrease of the adsorption capacity. Actually, for a solution containing 0.1 M of sodium chloride it becomes less than 1% of the adsorption capacity in distilled water. On the contrary, the adsorption capacity of the CSAC coal decreases only by 50% for a sodium chloride concentration as high as 0.6 M.

## 4. Discussion

The metallic ions uptake on carbons mainly depends on the ions concentration, and on adsorption and reduction phenomena which simultaneously take place on the carbon surface [15,16,24,25]. All these phenomena are strongly related to solution pH.

The characteristics and the concentration of ionic species in solution obviously represent the driving force for adsorption phenomena. For this reason, the speciation analysis of the equilibrium solution is the first step to understand experimental data. Trivalent and hexavalent chromium speciations have been calculated by using chromium mass balance and electric neutrality equations coupled with the equations representative of chemical equilibria [15]. Davies's Formula [15] has been used for the

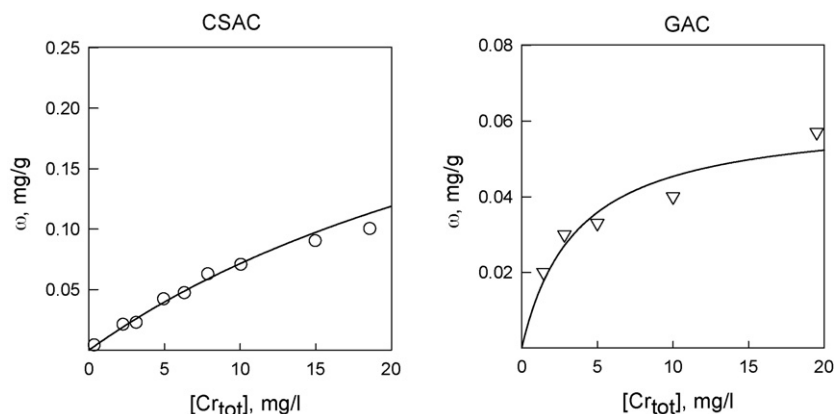


Fig. 6. Adsorption isotherms at  $\text{pH}=11 \pm 0.1$  at  $T=20^\circ\text{C}$ .

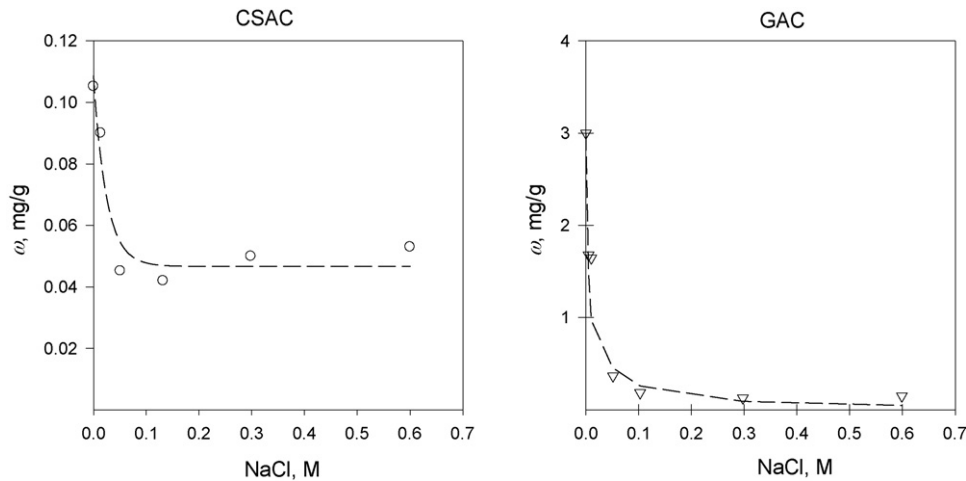


Fig. 7. Chromium adsorption isotherms as a function of solution salinity for an initial chromium concentration of 8 mg/l at  $T = 20^\circ\text{C}$  and  $\text{pH} = 7$ . CSAC:  $m/V = 25$  g/l; GAC:  $m/V = 5$  g/l.

evaluation of the activity coefficients of the ionic species. Trivalent and hexavalent chromium speciations have been reported in Fig. 8 for the case of a total chromium concentration of 0.5 mM ( $\sim 25$  mg/l). Speciation analyses shows that at pH higher than 7 Cr(VI) is mainly present as  $\text{CrO}_4^{2-}$  while at pH lower than 3 the trivalent chromium is mainly represented by  $\text{Cr}^{+3}$ .

The presence of acid and basic functional groups on the surface of carbons [34,36] assures that these materials are able to capture metallic cations [15,16] by surface complexation and cation exchange mechanisms [16,24,37]. The adsorption of anions is more complicated but it can be related to surface complexation reactions with protonated activated sites [25,39] or eventually to the presence of basic or electrophilic surface

sites [40]. As a general rule, the adsorption of cations decreases by increasing the concentration of competitive cations in solution, first of all  $\text{H}^+$ . A similar behavior involves anion adsorption which eventually decreases at higher pH due to the competition with  $\text{OH}^-$  anions [15,16]. The assessment of these competitive phenomena depends on the specific interactions between the ions and the adsorption sites. The HSAB theory developed by Pearson [41] and extended to activated carbon adsorption by Alfarrá et al. [36] gives a possible explanation of the affinity between metallic ions and surface groups, also including the graphitic basal plane itself. According to this theory,  $\text{Cr}^{+3}$  is a hard acid and  $\text{CrO}_4^{2-}$  is a hard basis. Hence, their adsorption capacity appears to be mainly related to the concentration of oxidized

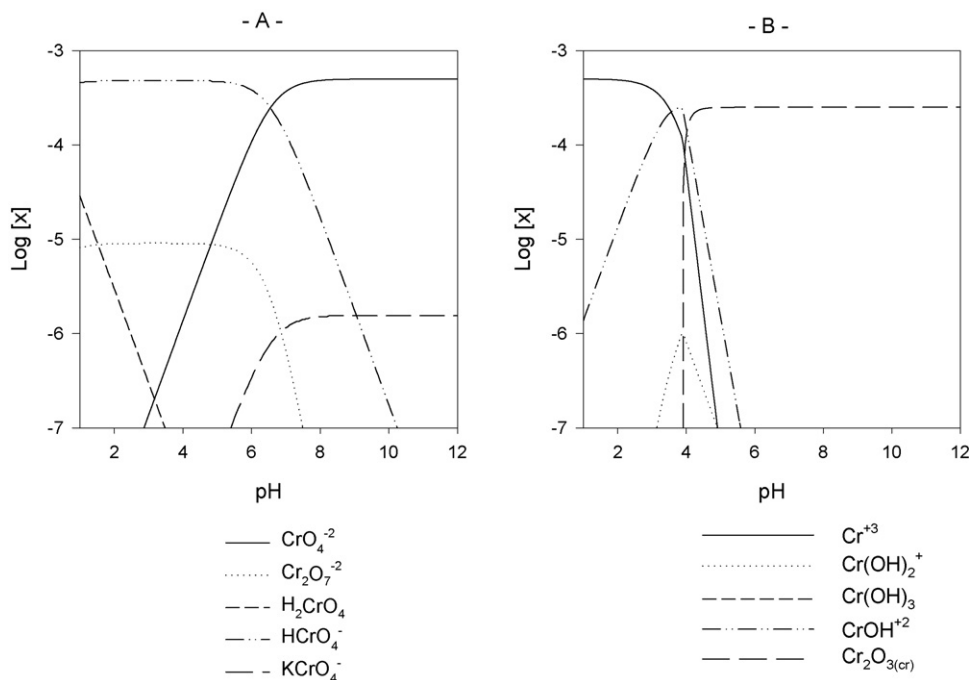


Fig. 8. Speciation of hexavalent (A) and trivalent (B) chromium as a function of pH for a total chromium concentration of 0.5 mM obtained from chemical equilibrium analysis (values of the thermodynamics constant for ion complexation taken from Stumm and Morgan [15]).



Table 2  
Values of the parameters for Freundlich model (Eq. (1))

| pH  | CSAC                           |                   |            | GAC                            |                    |       |
|-----|--------------------------------|-------------------|------------|--------------------------------|--------------------|-------|
|     | $b, \text{mg/g (mmol/l)}^{-n}$ | $n$               | $R^2 (\%)$ | $b, \text{mg/g (mmol/l)}^{-n}$ | $n$                | $R^2$ |
| 2   | $0.501 \pm 0.046$              | $0.665 \pm 0.056$ | 96.10      | $0.323 \pm 0.018$              | $0.740 \pm 0.046$  | >99   |
| 3   | $0.401 \pm 0.052$              | $0.670 \pm 0.110$ | 83.40      | $5.747 \pm 0.879$              | $0.605 \pm 0.092$  | 84.30 |
| 7.5 | $0.290 \pm 0.029$              | $0.668 \pm 0.071$ | 94.20      | $12.65 \pm 0.797$              | $0.611 \pm 0.038$  | 99.00 |
| 9   | $0.3058 \pm 0.024$             | $0.683 \pm 0.057$ | 98.30      | $2.785 \pm 0.240$              | $0.687 \pm 0.060$  | 98.30 |
| 11  | $0.206 \pm 0.119$              | $0.685 \pm 0.040$ | 98.35      | $0.180 \pm 0.083$              | $0.685 \pm 0.0582$ | >99   |

Table 3  
Values of the parameters for Langmuir model (Eq. (2))

| pH  | CSAC                                |                     |            | GAC                                 |                     |            |
|-----|-------------------------------------|---------------------|------------|-------------------------------------|---------------------|------------|
|     | $\omega_{\text{max}} (\text{mg/g})$ | $K (\text{M}^{-1})$ | $R^2 (\%)$ | $\omega_{\text{max}} (\text{mg/g})$ | $K (\text{M}^{-1})$ | $R^2 (\%)$ |
| 2   | $0.290 \pm 0.03$                    | $7323 \pm 311$      | 99.23      | $2.18 \pm 0.24$                     | $315 \pm 16.8$      | 93.10      |
| 3   | $0.285 \pm 0.05$                    | $6408 \pm 226$      | 99.47      | $2.21 \pm 0.32$                     | $37750 \pm 4769$    | 99.45      |
| 7.5 | $0.285 \pm 0.06$                    | $3166 \pm 152$      | 99.60      | $7.20 \pm 0.35$                     | $15334 \pm 974$     | 98.58      |
| 9   | $0.282 \pm 0.05$                    | $2485 \pm 21.5$     | 99.98      | $7.15 \pm 0.51$                     | $1875 \pm 251$      | 97.98      |
| 11  | $0.279 \pm 0.08$                    | $1678 \pm 77.5$     | 99         | $7.13 \pm 1.02$                     | $27 \pm 1.1$        | 99.10      |

functional groups rather than to the carbon surface area [25,36]. For Cr(III) uptake, these considerations appear to be confirmed by noticing that the differences in the adsorption capacities are at most of one order of magnitude despite the large disparity in surface areas (GAC:  $950 \text{ m}^2/\text{g}$ ; CSAC:  $11.4 \text{ m}^2/\text{g}$ ).

The reducing properties of carbon superficial groups, such as phenols, are well known [24,25]. The reduction of Cr(VI) to Cr(III) preferentially happens at acidic conditions [15,16]. As a consequence, during the experiments, starting from a solution which contains only Cr(VI), the progressive and complete reduction to Cr(III) is observed by decreasing pH (Fig. 1). The reducing properties of the GAC are lower than that of the CSAC which reduces Cr(VI) even at neutral pH levels. Moreover, the reduction of Cr(VI) on the carbon surface appears to be an irreversible phenomenon as, after reduction, small amounts of

Cr(III) are released back in solution at pH levels lower than 8, until, below pH 3, almost all the Cr(VI) is reduced to Cr(III) and desorbed. This appears to be related to the combination of the higher reducing capacity [15] and the lower cation uptake which occurs at acid pH levels [15,16].

To sum up, the mechanisms of chromium uptake on the GAC and the CSAC at different pH and salinity levels can be described as follows:

1. Dissolution of potassium dichromate salt and formation of Cr(VI) anions.
2. Cr(VI) anions are adsorbed by the protonated basic surface groups and the electrophilic surface groups of the carbons [36,39,40]. Competition phenomena occur with  $\text{OH}^-$  and  $\text{Cl}^-$  ions.

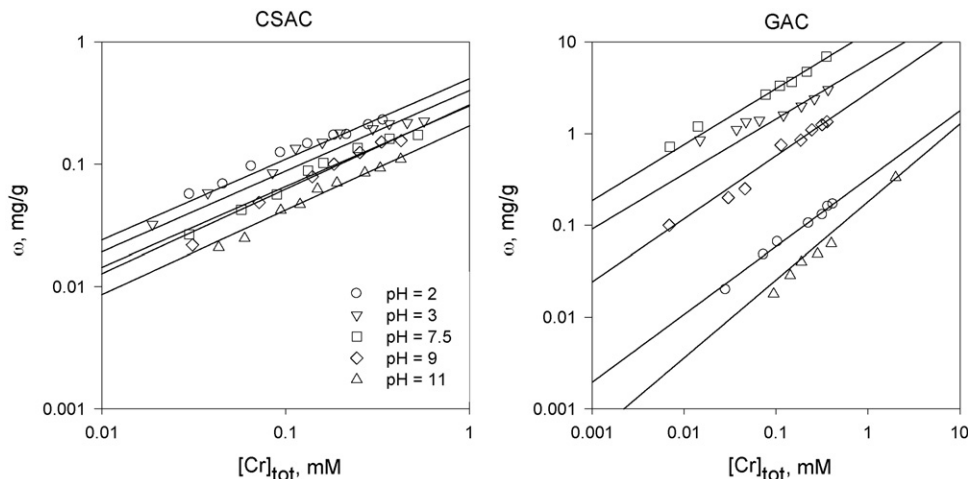


Fig. 9. Linearised Freundlich model for chromium adsorption on CSAC and GAC.

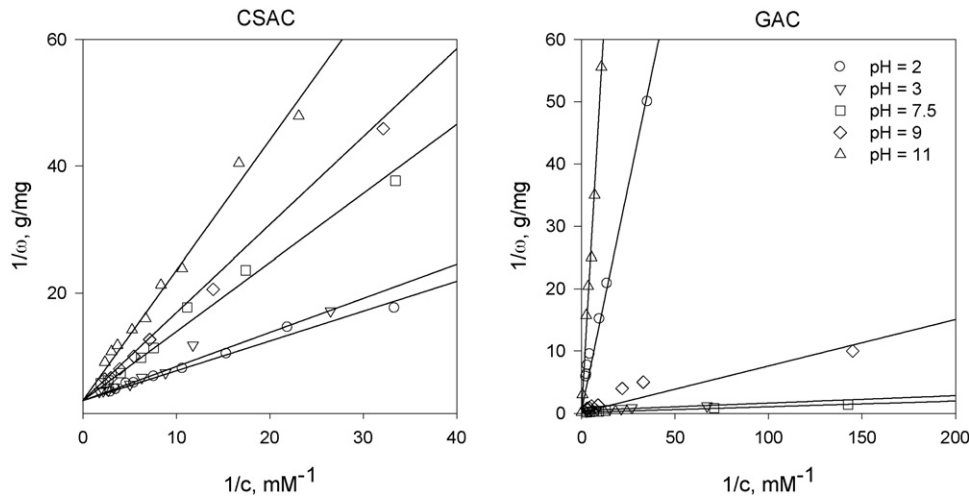


Fig. 10. Linearised Langmuir plots for chromium adsorption on CSAC and GAC.

- In parallel, Cr(VI) is reduced to Cr(III) cations on phenolic surface groups. This reaction pattern is favoured at acid pH [15,24].
- Cr(III) cations are released back in solution [24,25].
- Cr(III) cations are captured by sorption and ion exchange on the weak acid surface groups [16,24,25] or on the basal plane sites on the carbon [38]. Their adsorption is in competition with H<sup>+</sup> or Na<sup>+</sup> ions.

According to these mechanisms, for acidic solution, where Cr(VI) is almost completely reduced to Cr(III) cations, the adsorption capacity is expected to increase at higher pH, while, for alkaline solutions, the adsorption of Cr(VI) anions has to decrease by increasing pH and salinity levels. This holds true for the GAC, while the behavior of the CSAC seems to be quite different as its adsorption capacity monotonically decreases at increasing pH.

In this case the adsorption mechanism seems to be mainly related to the reduction of Cr(VI) and the adsorption of Cr(III). The decrease of pH leads to an increase of Cr(III) formation and to higher driving forces for cation adsorption. Moreover, the similar values of chromium uptake at pH 2 and 3 and at different salinity levels show a small extent of competitive effect between H<sup>+</sup>, Na<sup>+</sup> and Cr<sup>3+</sup> cations.

Furthermore, the regression analysis of experimental results has been carried out by considering both the Langmuir and Freundlich models [16]. To simplify the regression analysis, both the models are applied in their linearised forms (Eqs. (1) and (2)). For the case of Freundlich equation, this results in the correlation between the decimal logarithm of the total chromium concentration and the adsorption capacity (Eq. (1)). For the Langmuir model, the linearization appears as a correlation between the inverse of chromium concentration and of the adsorption capacity (Eq. (2)):

$$\log_{10} \omega = \log_{10} b + n \log_{10} [\text{Cr}]_{\text{tot}} \quad (1)$$

$$\frac{1}{\omega} = \frac{1}{K\omega_{\text{max}}} \frac{1}{[\text{Cr}]_{\text{tot}}} + \frac{1}{\omega_{\text{max}}} \quad (2)$$

The values of the regression parameters with their error of determination and the value of the correlation factor  $R^2$  are reported in Table 2 for the Freundlich model and in Table 3 for the Langmuir one while Figs. 9 and 10 report the plots of the linearised Freundlich and Langmuir models applied to the experimental data. The regression analysis gives better results for the Langmuir model which also allows a more interesting interpretation of experimental data. In fact, for the case of the CSAC the Langmuir model gives an almost constant value of the maximum adsorption capacity at all the pH levels, confirming that the adsorption mechanism remains unchanged with pH.

On the contrary, for the GAC different values of  $\omega_{\text{max}}$  are obtained for acid and basic pH levels. In particular, the adsorption capacity for Cr(VI), at pH > 7, is around 7.2 mg/g while for Cr(III) cations it is around 2.2 mg/g. This seems to confirm that Cr(VI) and Cr(III) adsorption on the GAC follows different reaction mechanisms and different active sites.

## 5. Conclusions

This paper reports the experimental results on the adsorption of chromium from aqueous solutions onto a non-impregnated granular activated carbon (Aquacarb 207EA<sup>TM</sup>) and a char of South African coal at different pH and salinity levels.

Experimental results point out that the adsorption capacity of the CSAC is mainly related to the reduction of Cr(VI) and the consecutive adsorption of Cr(III) cation on weak acidic surface groups, as suggested by Lakatos et al. [24]. A similar behaviour is observed for GAC adsorption at acid pH, while at pH > 7 the adsorption of CrO<sub>4</sub><sup>2-</sup> anions in competition with OH<sup>-</sup> and Cl<sup>-</sup> anions can be considered.

The adsorption behaviour of the two sorbents is confirmed by the application of Langmuir model to the regression analysis of experimental data. The Freundlich model also gives a



good interpretation of experimental data but its results are less significant than the Langmuir ones.

The analyses of the adsorption capacities for the two sorbents have shown that the maximum adsorption capacity for the GAC is around 7 mg/g while it is around 0.3 mg/g for the CSAC. Typical values of Cr(VI) adsorption capacities [4] usually range between 0.7 and 22 mg/g although maximum values as high as 40 mg/g have been obtained for saw dust. Trivalent chromium adsorption capacities at neutral pH usually lies between 7 and 80 mg/g [5], but experimental data at lower pH levels result similar to those observed in this work (e.g. [5,20,23]).

Finally, from an operational point of view it is necessary to highlight that the applicability of a given process for wastewater treatment and for natural water bodies remediation cannot ignore the costs of this process. In the case of adsorption, these are mainly related to the unit cost of the sorbent. Recent estimates show that the unit cost per ton of a granular non-impregnated activated carbon is around 1000 euros, while that of coal is around 10 euros. In this sense, the performance of char in trivalent chromium capture for acid solutions can be considered as an interesting alternative to the expensive activated carbon. On the contrary, the selection of the optimal sorbent for natural water bodies' remediation is still a debated question. In fact, while the high differences in adsorption capacities observed at neutral pH make the use of activated carbon more cost-effective, the high water flow rates to be treated and the strong effect of solution salinity on GAC adsorption might suggest the use of the low-cost char.

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