



## Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones

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### ABSTRACT

Some granular activated carbons (GACs) were prepared from cherry stones (CS), an agricultural waste, by thermal methods following pyrolysis in nitrogen and subsequent activation (with air, carbon dioxide and steam) or single-step activation in steam. A GAC prepared by activation with carbon dioxide was further treated with several oxidizing agents (air, air–ozone mixture, nitric acid and hydrogen peroxide). The non-oxidized GACs produced have surface areas ranged from 508 to 901 m<sup>2</sup>/g and show a predominantly micro- and macropores structure. Oxidation treatments, especially with nitric acid and ozone, led to the fixation of high amounts of acidic surface oxygen complexes (SOCs), thus making the carbon surface more hydrophilic. Contrary to oxidation with the other agents, the ozone treatment, at the conditions applied in this work, does not decrease the GAC surface area. Both, the non-oxidized and the oxidized GACs were used as adsorbent to study the adsorption of Cu(II) from aqueous solution. Adsorption isotherms were obtained at 25 °C and data were well fitted to the Langmuir equation. The results show that the Cu(II) uptake of the non-oxidized GACs is not great, but similar to that of the commercial grade Filtrasorb 400. The adsorption capacity for Cu(II) could be greatly enhanced by GAC oxidation, especially with nitric acid and ozone treatments. The larger adsorption capacity of the oxidized GACs has been attributed to oxygen functionalities (mainly carboxylic) fixed on the GAC surface, which can remove Cu(II) species from water by both ion-exchange and surface complexation mechanisms. The ozonated GAC was also evaluated for the adsorption of Co(II) species from single solute and Cu(II)–Co(II) binary mixture solutions. The functionalization of GAC by the ozone treatment improved the adsorption of both Cu(II) and Co(II) regardless of the fact that they were in single solute or binary systems.

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### 1. Introduction

There is great concern about pollution of water by heavy metals. Some of them are very toxic even at very low concentrations (e.g., mercury, cadmium and lead) and have poisoning effects on human being. Contrary to biodegradable organic matter, heavy metals are not eliminated by natural processes from aquatic ecosystems as they are not biodegradable. Therefore, scientists and engineers are encouraged to investigate and develop novel cost-effective methods aimed to remove colloid and dissolved metals from water, including precipitation, membrane separation, ion exchange, evaporative recovery, reductive electrolysis and adsorption technologies [1]. Particularly, adsorption processes using ion-exchange resins, zeolites, clays and activated carbons have proven to be effective

for achieving high levels of metals removal [2]. Recently, the use of low-cost activated carbons prepared from agricultural wastes is receiving special attention because of the expensiveness of other conventional adsorbents [3].

Broadly speaking, the performance of the adsorption of metals species from water on activated carbon depends on three types of factors: properties of the activated carbon itself, as surface area, pore size distribution, amount of surface oxygen complexes (SOCs) and point of zero charge (PZC); properties of metal species as solubility, ion size and ability to interact with SOC of carbon; and properties of the solution as pH, ionic strength and presence of other solutes that could compete with the target metal species for the adsorption sites [4]. The adsorption of metal ions onto activated carbon has been explained based on various mechanisms such as electrostatic attraction to the carbon surface, ion-exchange and metal surface complexes formation [5–8]. In general, these mechanisms are favoured by a polar carbon surface with low PZC and high concentration of acidic SOC such as carboxylic and

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lactone-type groups. Surface acidic treatments confer these properties to activated carbon, thereby enhancing metal uptake. With this purpose various oxidizing agents have been used, including nitric acid, sulphuric acid, sodium hypochlorite, potassium permanganate, hydrogen peroxide, oxygen plasma and ozone [9]. Particularly, ozone has been successfully applied to enhance the adsorption of Hg(II), Cd(II) and Cr(III) species onto a granular activated carbon (GAC) [10,11]. Ozone seems to be a good choice for tailoring activated carbons aimed to selectively improve the adsorption of metal ions while keeping unmodified the pore texture of the carbon, because, contrary to other oxidizing agents, ozone is able to fix a high concentration of acidic SOC on the carbon surface without destroying significantly its porosity [12].

Cherry stone (CS) is an agricultural waste with desirable properties to be used as raw material in the manufacture of activated carbon [13–18]. As part of a continuing work, this research is focused on the removal of metals from aqueous solution by adsorption onto activated carbons prepared from CS. The impact of the activation methods to prepare the activated carbons and the subsequent functionalization of the carbons with oxidizing agents (air, ozone, nitric acid and hydrogen peroxide) on the adsorption of Cu(II) and Co(II) ions from aqueous solution have been investigated.

## 2. Experimental

### 2.1. Activated carbons

Some GAC samples were prepared in the laboratory from CS. This starting material was obtained from the Asociación de Cooperativas Valle del Jerte (Extremadura, Spain) one of the Europe's leading producers of kirsch. The as-received CS were air-dried, crushed and sieved to particle size 1–2 mm before GAC samples preparation. GAC samples were obtained by physical activation of CS using one-stage and two-stage thermal methods. Accordingly, four types of GAC were prepared as follows: A3 samples were obtained by carbonization of CS in nitrogen at 600 °C for 2 h followed by activation in air at 400 °C for 3 h; C2 and C3 samples were prepared by carbonization of CS in nitrogen at 900 °C for 2 h and further activation in CO<sub>2</sub> at 850 °C for 2 and 3 h, respectively; S3 samples were obtained by carbonization of CS in nitrogen at 900 °C for 2 h followed by activation in steam at 850 °C for 3 h; finally, CS3 samples were prepared by direct activation of CS in steam at 850 °C for 3 h.

Various samples of C2 were further subjected to oxidation using air, air–ozone mixture, hydrogen peroxide and nitric acid. Treatments with air and air–ozone mixture (1.5 vol.% O<sub>3</sub>) were carried out in a stainless steel fluidized bed reactor at 300 °C for 24 h and at room temperature for 1 h, respectively. For the nitric acid and hydrogen peroxide treatments, C2 samples were immersed into a flask containing 100 mL of an aqueous solution (HNO<sub>3</sub> 5N or H<sub>2</sub>O<sub>2</sub> 5N) and stirred under reflux (for nitric acid treatment) or at room temperature (for hydrogen peroxide treatment) for 10 h. Sample codes of oxidized GAC samples are as follows: C2-air, C2-O<sub>3</sub>, C2-HNO<sub>3</sub> and C2-H<sub>2</sub>O<sub>2</sub>. In addition to the lab-prepared GAC samples, the commercial grade Filtrasorb 400 (Calgon Corp., USA) was used for comparative purposes. The as-prepared CS-GAC samples and the as-received Filtrasorb 400 were washed with boiled distilled water, dried and sieved to a particle size range of 1.0–1.6 mm before characterization and use in adsorption experiments.

The characterization of porous texture of GAC samples was accomplished by adsorption of nitrogen at 77 K (Autosorb-1, Quantachrome) and mercury porosimetry (Autoscan-60, Quantachrome). The BET and  $\alpha$ -plot methods were used to evaluate the surface area ( $S_{\text{BET}}$  and  $S_{\text{ext}}$ ) and micropore volume ( $V_{\text{mi}}$ ) from N<sub>2</sub> adsorption data [19,20]. The mesopore and macropore volumes

were deduced from mercury intrusion data. Chemical surface of GAC samples was characterized by analyzing the concentration of SOCs and the PZC by the Boehm and Noh and Schwärz's methods, respectively [21,22].

### 2.2. Adsorption isotherms

Standard stock copper and cobalt solutions (100 mg/L) were prepared by dissolving Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Panreac, reagent grade), respectively, into ultrapure water (Millipore Milli-Q system) acidified to pH 5 with nitric acid. This pH value was chosen as it has been reported as optimum for the adsorption of Cu(II) and Co(II) ions onto GAC prepared from apricot stones [23]. Adsorption isotherms were obtained at 25 °C using the bottle point method. GAC samples weighing from 50 to 800 mg were placed in bottles containing 20 mL of metal stock solution. Each bottle was agitated by means of an orbital shaker (JP Selecta Unitronic-Orbital) at 50 rpm for 24 h to allow the GAC sample to adsorb metal species until equilibrium. Thereafter, GAC particles were decanted and liquid sample was withdrawn, filtered with 0.45  $\mu\text{m}$  membrane and the filtrate analyzed for pH and metal concentration. A Radiometer Copenhagen pH meter was used for pH measurement and a Varian SpectrAA 140 atomic absorption spectrometer for copper and cobalt concentrations. Copper and cobalt atomic absorption standard solutions (Aldrich AA) were used for calibration purposes. The amount of adsorbed metal ( $q_e$ ) was deduced from the mass balance Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where  $C_0$  and  $C_e$  stand for the initial and equilibrium concentrations of metal in the aqueous solution,  $V$  is the solution volume and  $w$  is the weight of the GAC sample.

## 3. Results and discussion

### 3.1. Porous and chemical properties of GAC samples

Some textural and chemical surface properties of the GAC samples used in this work are summarized in Table 1. As it is apparent from the data of the CS carbons, the texture and chemical surface of the samples strongly depend on the method of activation and the further oxidation treatment. The air-activated GAC (A3 sample) had the lowest surface area and pore volume. The activation with CO<sub>2</sub> essentially developed the carbon micro- and macropore structure as the volume of mesopores of the samples C2 and C3 remained rather low (<0.1 cm<sup>3</sup>/g). With this activating agent, the increase in the activation time from 2 (C2 sample) to 3 h (C3 sample) resulted in the build-up of porosity over the whole range of pore size. The GAC sample prepared by carbonization of CS followed by activation of the resulting char in steam for 3 h (S3 sample) produced a well-developed porosity with almost equal surface area and volume of micropores and mesopores than commercial GAC Filtrasorb 400. The sample obtained by direct pyrolysis of CS in steam for 3 h (CS3 sample) showed textural properties in-between the C3 and S3 samples.

All the oxidative treatments performed on the C2 sample led to decreases of the BET surface area and the micropore volume while the external surface area and the volumes of large pores (meso- and macropores) were increased, taking the respective values of the precursor C2 as the base for comparison. These effects can be most likely due to pore widening (micropore destruction) and/or micropore blockage by the formation of SOCs [12,24]. It was observed that the extent of changes in textural properties depended on the type of oxidation treatment. Thus, the effect of the nitric acid

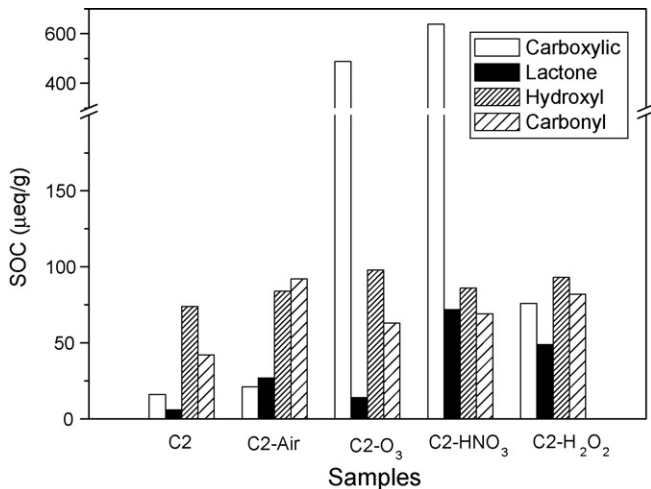


Fig. 1. Distribution of acidic SOC on various GAC samples. Effect of oxidizing agents.

treatment was more severe than the others, the surface area and micropore volume decreasing markedly. Contrary, the ozonation barely affected the textural properties of the non-oxidized C2 sample. A small development of the mesoporosity is the only relevant change produced by ozone from the textural point of view. Owing to the molecular size and geometry of the ozone molecule as well as its high reactivity with carbon, the ozonation process was most likely controlled by diffusion into pores [25]. Hence, ozonation was to be produced mainly on mesopores leaving the GAC micropore structure unaltered.

Concerning chemical surface properties, all the oxidative treatments resulted in the fixation of acidic SOCs and the removal of basic SOCs. As a result, PZC of the oxidized samples came down well below the value corresponding to the precursor C2. From Table 1 it is observed that, at the conditions applied in this work, the nitric acid and ozone treatments produced changes in the surface chemistry of the C2 sample greater than oxidations with air and hydrogen peroxide. Fig. 1 shows the distribution of individual acidic SOCs (i.e., carboxylic, lactone, hydroxyl and carbonyl) on the oxidized GACs. From this figure it is seen that the samples treated with nitric acid and ozone had higher amounts of the strongest acidic functionalities (i.e., carboxylic) than the samples oxidized with air and H<sub>2</sub>O<sub>2</sub>, which had predominance of hydroxyl and carbonyl groups.

### 3.2. Cu(II) uptake on non-oxidized activated carbons

The adsorption isotherms of Cu(II) ions from aqueous solution on A3, C2, C3, S3, CS3 and Filtrasorb 400 samples are shown in Fig. 2. The adsorption data were analyzed according to the Langmuir

Table 1

Some properties of the GAC samples used in this work

GAC	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{ext}}$ (m <sup>2</sup> /g)	$V_{\text{mi}}$ (cm <sup>3</sup> /g)	$V_{\text{me}}$ (cm <sup>3</sup> /g)	$V_{\text{ma}}$ (cm <sup>3</sup> /g)	Acidic SOC (µequiv./g)	Basic SOC (µequiv./g)	PZC
Filtrisorb 400	866	122	0.351	0.166	0.319	207	540	8.9
A3	508	30	0.231	0.038	0.285	171	158	5.7
C2	604	35	0.299	0.055	0.341	138	385	8.8
C3	731	62	0.347	0.075	0.406	156	420	9.1
S3	901	122	0.383	0.134	0.473	92	369	9.8
CS3	771	87	0.336	0.113	0.438	106	225	8.9
C2-air	469	37	0.207	0.062	0.343	224	344	6.7
C2-O <sub>3</sub>	603	46	0.278	0.073	0.356	662	302	4.3
C2-HNO <sub>3</sub>	399	50	0.166	0.097	0.353	866	175	3.5
C2-H <sub>2</sub> O <sub>2</sub>	591	50	0.261	0.084	0.354	300	327	5.3

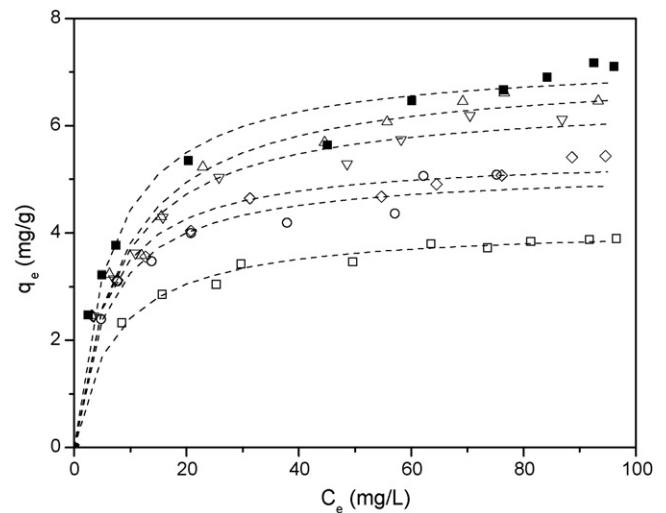


Fig. 2. Adsorption isotherms of Cu(II) on various GACs. Symbols: (■) Filtrasorb 400; (□) A3; (○) C2; (△) C3; (▽) S3; (◇) CS3. Lines: Langmuir model.

Table 2

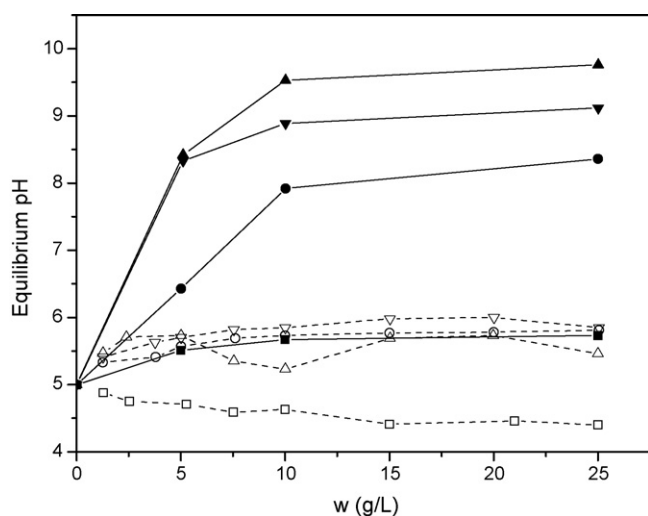
Langmuir isotherm parameters for the adsorption of Cu(II) onto the GAC samples used in this work

GAC	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$
Filtrisorb 400	$7.25 \pm 0.19$	$0.16 \pm 0.02$	0.981
A3	$4.13 \pm 0.06$	$0.14 \pm 0.01$	0.993
C2	$5.17 \pm 0.19$	$0.17 \pm 0.03$	0.978
C3	$7.04 \pm 0.23$	$0.12 \pm 0.02$	0.979
S3	$6.51 \pm 0.18$	$0.13 \pm 0.02$	0.987
CS3	$5.44 \pm 0.15$	$0.18 \pm 0.03$	0.979
C2-air	$16.50 \pm 1.09$	$0.06 \pm 0.01$	0.970
C2-O <sub>3</sub>	$22.21 \pm 1.11$	$0.51 \pm 0.09$	0.965
C2-HNO <sub>3</sub>	$28.12 \pm 1.02$	$0.40 \pm 0.04$	0.988
C2-H <sub>2</sub> O <sub>2</sub>	$14.79 \pm 1.01$	$0.12 \pm 0.03$	0.944

isotherm given in the following Eq. (2).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The parameters of the model,  $q_m$  and  $K_L$ , which are related to the adsorption capacity and the adsorption affinity, respectively, and the coefficient of determination,  $R^2$ , are summarized in Table 2 as determined from the regression analysis of experimental data. The correlation of data ( $R^2 > 0.97$ ) suggests that the Langmuir isotherm provides a good model equation to describe the Cu(II) adsorption equilibrium for over the concentration range studied. Comparing results of Fig. 2 with data from the literature one can conclude that the non-oxidized GACs prepared by physical activation of CS exhibited a capacity to adsorb Cu(II) ions noticeably lower than those of other materials such as ion-exchange resins and oxidized activated



**Fig. 3.** Aqueous equilibrium pH after contact between aqueous solution (pH 5) and GAC samples in the presence (open symbols) and absence (solid symbols) of Cu(II) ions. Symbols: (■), (□) A3; (●), (○) C2; (▼), (▽) C3; (▲), (△) S3.

carbons [7,26]. Nevertheless, their Cu(II) uptake capacity was close to that of the worldwide used Filtrasorb 400 and also to those of other activated carbons prepared from agricultural wastes. Thus, for example, Ferro-García et al. reported  $q_m$  values of 8.3, 9.2 and 7.2 mg/g for the adsorption of copper on GAC samples prepared from almond shells, olive stones and peach stones, respectively [27]. The calculated affinity constants,  $K_L$ , are also in the range of those reported for the adsorption of copper on other non-functionalized activated carbons [27–29]. Comparing the adsorption capacity of the GAC samples prepared from CS, the following order can be established: C3 > CS3 ≈ S3 ≈ C2 > A3. The lowest sorption capacity of the A3 sample, despite of its higher acidity, was likely due to its lower surface area and less developed micro- and mesoporosity. It is interesting to note that all non-oxidized GAC samples had PZC above the actual adsorption pH (i.e., pH 5). Thus, at the adsorption conditions the carbon surface was charged positively and repulsion forces between  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions (i.e., the predominant Cu(II) species at pH 5 according to the speciation diagram [30]) and the carbon surface was expected to prevent adsorption. However, adsorption might occur through interactions between electrons  $\pi$  of the basal planes of the carbon and Cu(II) ions, according to reactions (3) and (4) [11]:

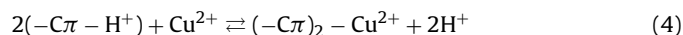
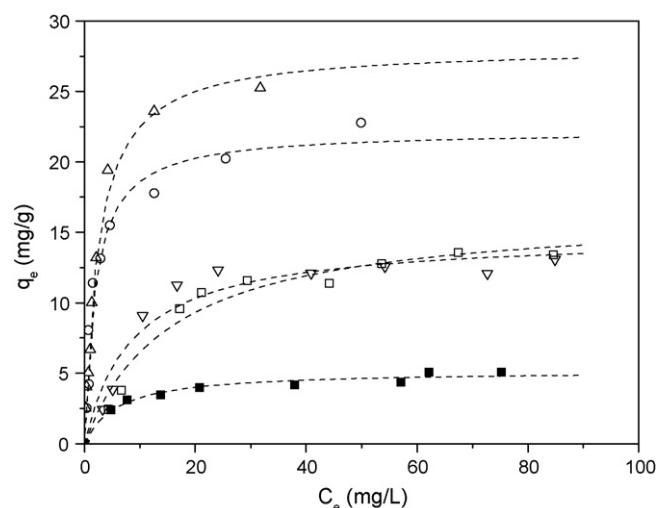


Fig. 3 shows the solution pHs after adsorption of copper onto different amounts of four non-oxidized GAC samples (A3, C2, C3 and S3). Results from blank experiments (i.e., with GAC and without copper) are also presented. In the absence of copper, the aqueous pH increased due to the release of  $\text{OH}^-$  ions according to reaction (3). Final equilibrium pH depended on the amount of GAC sample and on its basicity. Thus, it can be seen that equilibrium pHs were noticeably higher for the C2, C3 and S3 samples (PZC > 8.5) than for the A3 sample (PZC = 5.7). In the presence of Cu(II) ions, the exchange reaction (4) takes place and protons are released to the solution, thus neutralizing  $\text{OH}^-$  ions from reaction (3). Accordingly, small changes of pH were observed in experiments in the presence of copper. Nevertheless, it should be mentioned that small increases of pH in experiments with the C2 and C3 samples led to the appearance of turbidity in the aqueous solution likely due to the precipitation of copper hydroxide.



**Fig. 4.** Adsorption isotherms of Cu(II) on C2 and oxidized GAC samples. Symbols: (■) C2; (□) C2-air; (○) C2-O<sub>3</sub>; (△) C2-HNO<sub>3</sub>; (▽) C2-H<sub>2</sub>O<sub>2</sub>. Lines: Langmuir model.

### 3.3. Cu(II) uptake on oxidized activated carbons

The effect of oxidation treatments of the C2 sample on Cu(II) uptake is shown in Fig. 4. Both, experimental isotherms and the predictions of the Langmuir model are plotted on the figure. It is apparent that all the applied treatments enhanced the adsorption behaviour of the C2 sample, despite the observed decrease in the surface area after some of the oxidation treatments (see Table 1). Particularly, when the oxidation was carried out with ozone and nitric acid, the uptake of Cu(II) ions was strongly increased. This fact is also reflected by the parameters of Langmuir equation shown in Table 2. Thus, the maximum sorption capacity,  $q_m$ , of C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples is about 4 and 6 times higher, respectively, than that of the non-oxidized precursor C2. The affinity constant,  $K_L$ , was also threefolded after the ozone treatment and more than twofolded after the treatment with nitric acid, suggesting a strong affinity of both oxidized carbons toward Cu(II) ions. The air and hydrogen peroxide treatments also gave rise to increases of  $q_m$  but decreases of  $K_L$  with respect to the corresponding values of the unmodified C2 sample.

The enhancement of adsorption as a result of the oxidative treatments can be mainly attributed to the fixation of large amounts of acidic surface oxygen groups on the carbon surface. These groups make the GAC surface more acidic, thus lowering the PZC. In Table 1, it can be seen that the C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples have PZC < 5. At this condition,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions were likely attracted from the solution to the GAC surface by electrostatic forces. Moreover, acidic oxygen complexes might behave as ion-exchange sites retaining  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  species and releasing protons to the aqueous solution and as ligands, giving rise to the formation of metal–ligand surface complexes [5–8]. Fig. 5 illustrates how the overall amount of acidic SOCs was positively correlated to the copper uptake capacity of the used GACs ( $R^2 = 0.93$ ).

To gain understanding on the mechanism of Cu(II) adsorption onto the oxidized GACs, the pH was measured for liquid samples collected at adsorption equilibrium. In Fig. 6 it can be observed that, for all the oxidized GACs, the equilibrium pH decreased with increasing GAC loading. This decrease was greater for C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples than for C2-air and C2-H<sub>2</sub>O<sub>2</sub> samples, suggesting that the change of pH was related to the Cu(II) uptake: the higher the Cu(II) uptake, the higher the pH drop. Eq. (5) was applied to estimate the net amount of protons released to the aqueous solution per



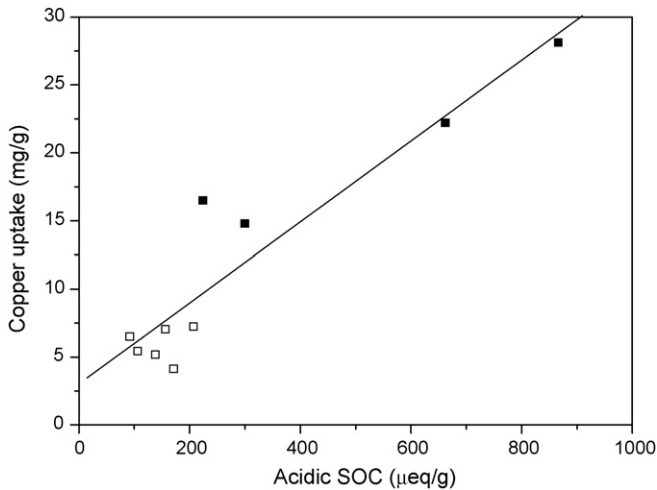


Fig. 5. Relationship between copper uptake and concentration of acidic SOC of GAC. Symbols: ■ oxidized GACs; □ non-oxidized GACs.

mass of GAC sample used:

$$\tau_{H^+} = \frac{(10^{-pH_e} - 10^{-pH_0})V}{w} \quad (5)$$

where  $pH_0$  and  $pH_e$  are the measures of pH of the initial aqueous solution (typically pH 5) and after reaching equilibrium, respectively. Fig. 7 shows the plot of the amount of protons released from the GAC against the copper uptake for the four oxidized GACs. The data in the 0–0.15 mmol/g  $q_e$  range corresponding to C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples are close to the solid line (slope=2), which is consistent with an ion-exchange mechanism (i.e., two hydrogen ions are released from the GAC to the solution by each adsorbed Cu(II) ion). However, data do not follow the ion-exchange guideline for uptakes higher than 0.15 mmol/g but the ratio of hydrogen ions displaced to the amount of Cu(II) ions adsorbed (i.e.,  $\tau_{H^+}/q_e$  ratio) falls down to about 0.6 and 0.8 for C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples, respectively, suggesting an adsorption mechanism other than ion-exchange. In this sense, it has been reported that the adsorption via formation of copper surface complexes usually yields less than two hydrogen ions per each adsorbed Cu(II) ion, the protonation level of the GAC surface and the type of surface functional groups deter-

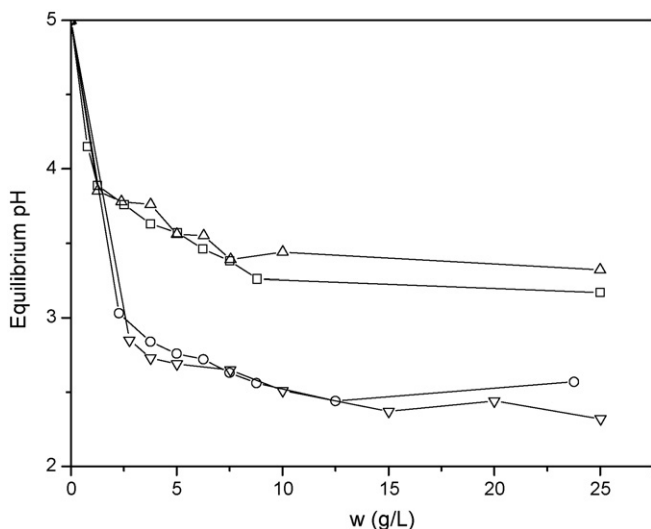
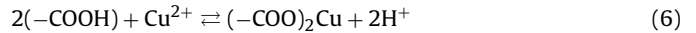


Fig. 6. Aqueous equilibrium pH after Cu(II) adsorption onto oxidized GACs. Symbols: □ C2-air; ○ C2-O<sub>3</sub>; ▽ C2-HNO<sub>3</sub>; △ C2-H<sub>2</sub>O<sub>2</sub>.

mining the particular value of the ratio  $\tau_{H^+}/q_e$  [8,31]. The behaviour of C2-air and C2-H<sub>2</sub>O<sub>2</sub> samples is also in agreement with a surface complexation mechanism rather than with an ion-exchange mechanism as the ratio  $\tau_{H^+}/q_e$  was as low as 0.3–0.4. The role of SOCs in the Cu(II) adsorption process might explain results of Fig. 7. As shown in Fig. 1, C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples contained high amounts of carboxylic groups. At pH 5 some of these weakly acidic groups were likely in their protonated forms and could undergo ion-exchange reactions and thereafter form inner surface complexes with Cu(II) ions:



From results of Fig. 7 it can be deduced that equilibrium (6) is the prevailing adsorption mechanism on C2-O<sub>3</sub> and C2-HNO<sub>3</sub> samples at low copper loading (i.e.,  $q_e < 0.15$  mmol/g). At higher copper loading non-protonated carboxylic groups and other acidic SOCs (e.g., hydroxyl groups) could also bind Cu(II) ions by surface complexation, releasing less than one hydrogen ion by each Cu(II) ion adsorbed [31]. C2-air and C2-H<sub>2</sub>O<sub>2</sub> samples have low concentration of carboxylic groups and therefore the contribution of reaction (6) to the overall Cu(II) adsorption is thought to be rather low. In these samples, copper adsorption is likely to occur mainly through the formation of surface complexes with the participation of hydroxyl groups.

#### 3.4. Comparison between the Cu(II) and Co(II) uptakes on ozonated activated carbon

In the previous section, it has been shown that the treatment of a GAC with ozone improved its sorption capacity for Cu(II). To further investigate whether this effect was also observed on the adsorption of other divalent metal, adsorption isotherms of Co(II) from single-solute system and Co(II)–Cu(II) mixture onto C2 and C2-O<sub>3</sub> GAC samples were obtained. Results are shown in Fig. 8 together with curve fits according to the Langmuir model, whose parameters are listed in Table 3. Note that data of Cu(II) adsorption from single solute solution presented in the previous sections are also reproduced in Fig. 8 and Table 3 for the sake of comparison. From Fig. 8 it is apparent that the ozone treatment of the C2 sample greatly improved the uptake capacity of this GAC for both Cu(II) and Co(II) regardless whether they were in single solute or binary mixture aqueous solution. Thus, for example, the maximum capacity of Co(II) adsorption (i.e.,  $q_m$ ) increased by 3.2 and 4 times upon

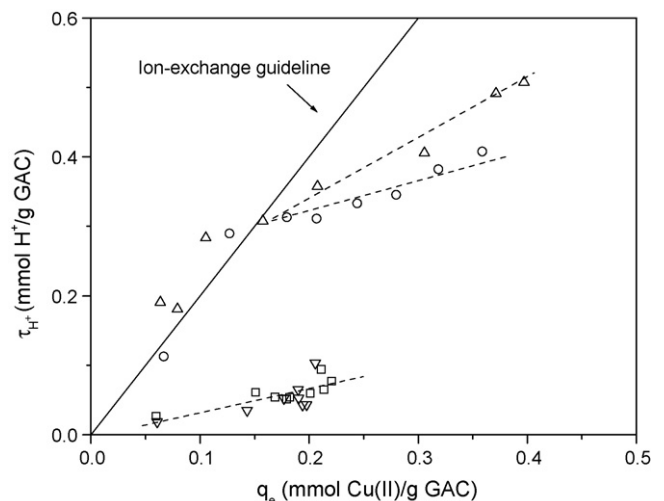
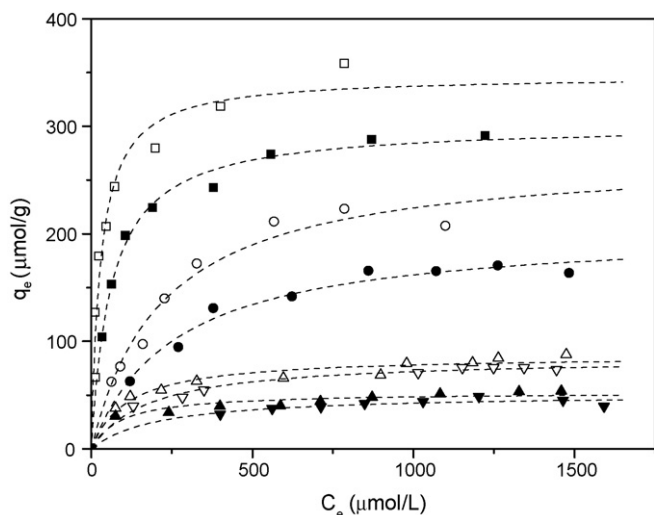


Fig. 7. Amount of hydrogen ions displaced with the amount of Cu(II) ions adsorbed onto oxidized GACs. Symbols: □ C2-air; ○ C2-O<sub>3</sub>; ▽ C2-HNO<sub>3</sub>; △ C2-H<sub>2</sub>O<sub>2</sub>.



**Fig. 8.** Adsorption isotherms of Cu(II) and Co(II) on C2 and C2-O<sub>3</sub> samples. Symbols: (▲), (△) C2, Cu(II); (▼), (▽) C2, Co(II); (■), (□) C2-O<sub>3</sub>, Cu(II); (●), (○) C2-O<sub>3</sub>, Co(II). Open symbols correspond to single solute isotherms and solid symbols correspond to competitive isotherms. Lines: Langmuir model.

C2 ozonation as deduced from single and binary system isotherms, respectively.

In Fig. 8, it was also observed that copper was favourably adsorbed on the C2-O<sub>3</sub> sample over cobalt while on the C2 sample the adsorption capacity of both metals was quite similar. Both Langmuir parameters,  $q_m$  and  $K_L$ , are noticeably higher for the adsorption of copper than for the adsorption of cobalt suggesting not only greater adsorption capacity but also a stronger affinity of the ozonated GAC for Cu(II) species. Strelko and Malik reached similar results with the GAC Filtrasorb 400 treated with nitric acid [7]. They attributed the greater adsorption of Cu(II) to the higher stability of the copper surface complexes in comparison with the cobalt surface complexes. This argument agrees with the proposed mechanism for the metal adsorption through surface complexation.

Another interesting result from Fig. 8 and Table 3 is that simultaneous adsorption of Cu(II) and Co(II) species lowered the uptake of these individual metals, indicating that there was competitive adsorption between Cu(II) and Co(II) species for the GAC active sites. Compared to its adsorption in single solute system, the maximum Cu(II) uptake on C2 and C2-O<sub>3</sub> was decreased by 30% and 20%, respectively. Similarly, the maximum uptake of Co(II) was reduced by 30% and 25%, respectively. These results indicate that the suppression of adsorption of individual metal species because of competition was somewhat higher with the non-oxidized GAC than with the ozonated one. Despite competitive adsorption, the total amount of metal species adsorbed from the binary mixture was higher than Cu(II) adsorption or Co(II) adsorption from single-solute systems.

**Table 3**  
Langmuir isotherm parameters for the adsorption of Cu(II) and Co(II) from single-solute and a binary mixture aqueous solutions

GAC	Solution/metal	$q_m$ ( $\mu\text{mol/g}$ )	$K_L$ (L/mmol)	$R^2$
C2	Single solute/Cu(II)	$86.80 \pm 3.29$	$8.88 \pm 1.66$	0.978
	Single solute/Co(II)	$84.72 \pm 2.12$	$5.58 \pm 0.64$	0.991
	Binary mixture/Cu(II)	$52.79 \pm 2.80$	$10.94 \pm 3.60$	0.937
	Binary mixture/Co(II)	$51.38 \pm 3.84$	$4.80 \pm 0.18$	0.963
C2-O <sub>3</sub>	Single solute/Cu(II)	$347.05 \pm 17.81$	$34.46 \pm 6.77$	0.965
	Single solute/Co(II)	$273.62 \pm 16.92$	$4.52 \pm 0.79$	0.977
	Binary mixture/Cu(II)	$301.76 \pm 5.34$	$16.20 \pm 1.29$	0.994
	Binary mixture/Co(II)	$203.79 \pm 8.59$	$3.86 \pm 0.58$	0.986

## 4. Conclusions

The results of this study show that CS can be used as raw material to produce GACs that can be applied in water and wastewater treatment for the adsorption of metal species. GACs were prepared by conventional physical activation using different activating agents (air, carbon dioxide and steam). They showed reasonably high surface areas (508–901 m<sup>2</sup>/g) but low capacity to adsorb Cu(II) species (4–7 mg/g). The basic character and/or the low mesopore volume of these GACs might be major reasons of the low Cu(II) uptake capacity. Oxidation of a CS-prepared GACs with different agents (air, ozone, nitric acid and hydrogen peroxide) yielded acidic SOCs that made the carbon surface more hydrophilic, thereby improving the adsorption capacity for Cu(II) up to about 15–28 mg/g. Oxidations with ozone and nitric acid led to the fixation of high amounts of carboxylic groups, whereas treatments with air and hydrogen peroxide gave mainly hydroxyl and carbonyl groups. The treatment with ozone, at the conditions applied in this work, did not change appreciably the surface area and micropore volume of the precursor GAC, whereas the treatments with air and nitric acid decreased surface area by 22% and 34%, respectively. Because of the high reactivity of ozone with activated carbons, it is thought that SOCs were fixed on the mesopore structure leaving the non-polar surface of micropores practically unaffected. Therefore, effective bifunctional GACs (micropore surface able to adsorb small non-polar organic molecules and hydrophilic external surface with SOCs able to bind metal species) to be used in water treatment could be obtained by functionalization of GAC with ozone.

The results of this work show the improved ability of a GAC treated with ozone to adsorb Cu(II) and Co(II) species from single-solute and binary mixture aqueous solutions. Ozone treatment was found to be more effective than air and hydrogen peroxide treatments and similar effective that the treatment of the GAC with nitric acid in order to enhance its Cu(II) uptake capacity. Adsorption of Cu(II) species onto highly oxidized GACs (ozone and nitric acid) proceeded through an ion-exchange mechanism at low metal loading and by surface complexation at high metal loading. Further work is to be made to extend these results to systems with other metals and organic compounds.

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## References

- [1] J.W. Patterson, Industrial wastes reduction, *Environ. Sci. Technol.* 23 (1989) 1032–1038.
- [2] G. San Miguel, S.D. Lambert, N.J.D. Graham, A practical review of the performance of organic and inorganic adsorbents for the treatment of contaminated waters, *J. Chem. Technol. Biotechnol.* 81 (2006) 1685–1696.
- [3] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, *Sci. Total Environ.* 366 (2006) 409–426.
- [4] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, 27, Dekker, New York, 2001, pp. 227–405.
- [5] M.A. Ferro-García, J. Rivera-Utrilla, I. Bautista-Toledo, M.D. Mingorance, Removal of lead from water by activated carbons, *Carbon* 28 (1990) 545–552.
- [6] M. Prasad, S. Saxena, Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent, *Ind. Eng. Chem. Res.* 43 (2004) 1512–1522.
- [7] V. Strelko, D.J. Malik, Characterization and metal sorptive properties of oxidized active carbon, *J. Colloid Interf. Sci.* 250 (2002) 213–220.
- [8] S.A. Dastgheib, D.A. Rockstraw, A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells, *Carbon* 40 (2002) 1843–1851.

- [9] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 52 (2007) 403–415.
- [10] M. Sánchez-Polo, J. Rivera-Utrilla, Adsorbent–adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons, *Env. Sci. Technol.* 36 (2002) 3850–3854.
- [11] J. Rivera-Utrilla, M. Sánchez-Polo, Adsorption of Cr(III) on ozonised activated carbon. Importance of C  $\pi$ -cation interactions, *Water Res.* 37 (2003) 3335–3340.
- [12] P.M. Álvarez, J.F. García-Araya, F.J. Beltrán, F.J. Masa, F. Medina, Ozonation of activated carbons: effect on the adsorption of selected phenolic compounds from aqueous solutions, *J. Colloid Interf. Sci.* 283 (2005) 503–512.
- [13] K. Gergova, N. Petrov, V. Minkova, A comparison of adsorption characteristics of various activated carbons, *J. Chem. Technol. Biotechnol.* 56 (1993) 77–82.
- [14] M.G. Lussier, J.C. Shull, D.J. Miller, Activated carbon from cherry stones, *Carbon* 32 (1994) 1493–1498.
- [15] C.J. Durán-Valle, M. Gómez-Corzo, J. Pastor-Villegas, V. Gómez-Serrano, Study of cherry stones as raw material in preparation of carbonaceous adsorbents, *J. Anal. Appl. Pyrol.* 73 (2005) 59–67.
- [16] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Preparation of activated carbon from cherry stones by chemical activation with ZnCl<sub>2</sub>, *Appl. Surf. Sci.* 252 (2006) 5967–5971.
- [17] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Preparation of activated carbon from cherry stones by activation with potassium hydroxide, *Appl. Surf. Sci.* 252 (2006) 5980–5983.
- [18] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Porous structure of activated carbon prepared from cherry stones by chemical activation with phosphoric acid, *Energy Fuels* 21 (2007) 2942–2949.
- [19] S. Brunauer, P. Emmet, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [20] F. Rodríguez-Reinoso, J.M. Martín-Martínez, C. Prado-Burguete, B. McEnaney, Standard adsorption isotherm for the characterization of activated carbons, *J. Phys. Chem.* 91 (1987) 515–516.
- [21] H.P. Boehm, Chemical identification of surface groups, *Adv. Catal.* 16 (1966) 179–274.
- [22] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, *J. Colloid Interf. Sci.* 130 (1989) 157–164.
- [23] M. Kobya, E. Demirbas, E. Senturk, M.A. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, *Biores. Technol.* 96 (2005) 1518–1521.
- [24] A.N.A. El-Hendawy, Influence of HNO<sub>3</sub> oxidation on the structure and adsorptive properties of corncob-based activated carbon, *Carbon* 41 (2003) 713–722.
- [25] H. Valdés, M. Sánchez-Polo, J. Rivera-Utrilla, C.A. Zaror, Effect of ozone treatment on surface properties of activated carbon, *Langmuir* 18 (2002) 2111–2116.
- [26] S. Rengaraj, J.W. Yeon, Y. Kim, Y. Jung, Y.K. Ha, W.H. Kim, Adsorption characteristics of Cu(II) onto ion exchange resins 252H and 1500H: kinetics, isotherms and error analysis, *J. Hazard. Mater.* 143 (2007) 469–477.
- [27] M.A. Ferro-García, J. Rivera-Utrilla, J. Rodríguez-Gordillo, I. Bautista-Toledo, Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products, *Carbon* 26 (1988) 363–373.
- [28] M. Machida, M. Aikawa, H. Tatsumoto, Prediction of simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon by conventional Langmuir type equations, *J. Hazard. Mater.* 120 (2005) 271–275.
- [29] J.P. de Mesquita, P.B. Martelli, H.F. Gourguilho, Characterization of copper adsorption on oxidized activated carbon, *J. Braz. Chem. Soc.* 117 (2006) 1133–1143.
- [30] F. Burriel, F. Lucena, S. Arribas, J. Hernández, *Química Analítica Cualitativa*, Paraninfo, Madrid, 1998.
- [31] A.M. Puziy, O.I. Poddubnaya, V.N. Zaitsev, O.P. Konoplińska, Modeling of heavy metal ion binding by phosphoric acid activated carbon, *Appl. Surf. Sci.* 221 (2004) 421–429.