The adsorption of chromium (VI) from industrial wastewater by acid and base-activated lignocellulosic residues

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Abstract

This study deals with the adsorption of Cr(VI) from synthetic and industrial wastewater, produced by a sewage plant. The activated carbons were prepared from a lignocellulosic raw material by thermal treatment at 450 and 650 °C in the presence of acid ($AlCl_3$, HCl, H_3PO_4 and H_2SO_4) and base (NaOH) agents. To optimize the adsorption of Cr(VI), the chemical modifications caused by each activating agent (related to the capability of Cr(VI) removal), and the optimal experimental conditions of the pH, Cr(VI) concentration, adsorbent dose and residence time, were studied. Thus, treatment with H_3PO_4 gives rise to carbons with a high surface area and high efficiency for Cr(VI) removal at short equilibrium times. In contrast, the generation of active surface sites by means of NaOH requires longer equilibrium times, the adsorption being less effective than in the former case. The adsorption isotherms obey the Langmuir equation only in the first stages of the reaction but fit the Freundlich equations over the whole range studied, so the heat of adsorption can be easily calculated. The results also show that the activated carbons obtained can be recovered by filtration with an efficiency of 30% in the third cycle.
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Keywords: Sawdust; Acidic treatment; Basic treatment; Cr(VI); Adsorption

1. Introduction

Chromium in the hexavalent form Cr(VI) is commonly used in the preparation of a great variety of industrial products, such as pigments for the manufacture of paints, inks, rubber, ceramics, corrosion inhibitors, fungicides [1]. However, hexavalent chromium is known to be a toxic pollutant. Examples of health problems caused by Cr(VI) are the perforation of the nasal septum [2], lung cancer [3], and skin ulceration [4]. More recently, several medical studies have evidenced the capacity of Cr(VI) to produce cancer in workers who manipulate chromates [5]. For this reason, the World Health Organization (WHO) [6] has determined that Cr(VI) is a human carcinogen, and consequently, its presence in daily activities (e.g., wastewaters) must be controlled and limited according to standards defined by international organizations and governmental directives. Thus, adopting the WHO guidelines [7], the Spanish legislation of 2003 limits to $0.05 \, mg \, l^{-1}$ the concentration of Cr(VI) in water destined for domestic consumption [8]. The treatment of wastewater to reduce the presence of Cr(VI) is an inescapable requirement prior to the discharge and reuse of water.

In recent years, many attempts have been made to analyze [9] and to reduce the presence of Cr(VI) in water. Activated carbons have been found to be an effective means of recovering Cr(VI) from wastewater [1]. However, commercial activated carbons are expensive, which has led to the search for new strategies for developing low-cost materials with a good capacity for Cr(VI) removal [10–12]. Thus, rice brand [13], industrial sugar wastes [14], coconut trees [15], wine processing waste sludge [16] or Casurina leaves [17] have been studied as potential precursors for activated carbons because of their mechanical resistance and their facility to generate porous materials. Other lignocellulosic materials, especially residual by-products (e.g., sawdust), might also serve as attractive precursors for obtaining activated carbons. Moreover, the use of sawdust offers the possibility of recycling and increasing the value of a highly abundant by-product generated during the processing of wood (the estimated production of non-reusable sawdust in the Spanish region of Asturias alone amounts to 400,000 t/year).

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The aim of this work is to eliminate the chromium (VI) present in an industrial wastewater supplied by a sewage plant by means of adsorption with activated carbons derived from lignocellulosic residue. The treatment of the sawdust by different reagents (AlCl$_3$, HCl, H$_3$PO$_4$, H$_2$SO$_4$ and NaOH) was studied. The chromium (VI) adsorption capacities of the resultant materials were first optimized using patron solutions and then evaluated in the adsorption of industrial wastewater. The adsorption study was carried out in terms of equilibrium time, pH solution, adsorbent dose, particle size and Cr(VI) concentration.

2. Materials and methods

2.1. Materials used

Before use, sawdust from Scandinavian pine (*Pinus sylvestris*) wood (S) was sieved to obtain a uniform material of <0.2 mm particle size. The proximate analysis (dry basis) gave an ash content of 0.49 wt.%. Extraction of the sawdust with water and acetone [18] yielded a soluble-fraction of 4.4 and 4.6 wt.%, respectively, and the Klason lignin content [19] was 39.5 wt.%.

The wastewater used in this work was supplied by a sewage plant at Oviedo, Spain. Analysis of the sample by ICP-MS showed a Cr(VI) concentration of 110 mg ml^{-1}. The sample also contained K, Fe, Mo and Ag and traces of Sb, Hg and Pb. The pH was found to be 1.3 with 43 mg l^{-1} of suspended solid and 260 mg l^{-1} of total solid residue. The pH of the wastewater was adjusted to 3 by adding HCl.

Synthetic Cr(VI) solutions were prepared by dissolving 25, 50, 100, 200 and 400 mg of K$_2$Cr$_2$O$_7$ in 1 l of distilled H$_2$O. Before they were applied the pH of the Cr(VI) solutions was measured and adjusted to the desired value by adding NaOH or HCl (0.1N).

2.2. Preparation of sawdust-based carbons

Twenty-five grams of sawdust was added to 100 ml of a 1 M aqueous solution of agent and heated at 150 °C for 2 h in order to facilitate the impregnation of the sawdust and removal of the water. The resultant residues were then placed in ceramic crucibles and carbonized under a nitrogen atmosphere at 10 °C min^{-1} up to 450 and 650 °C for 30 min. After cooling, the materials were washed with distilled water until constant pH and dried at 105 °C until constant weight. Finally, all the materials were ground at 350 rpm for 30 min in a ball-mill apparatus and then sieved to <0.075 mm of particle size. The samples were labelled C-AlCl$_3$-450, C-HCl-450, C-H$_3$PO$_4$-450, C-H$_2$SO$_4$-450 and C-NaOH-450; and C-AlCl$_3$-650, C-HCl-650, C-H$_3$PO$_4$-650, C-H$_2$SO$_4$-650 and C-NaOH-650 according to the reagent used (AlCl$_3$, HCl, H$_3$PO$_4$, H$_2$SO$_4$ and NaOH, respectively) and the temperature applied (450 and 650 °C, respectively).

2.3. Characterization of sawdust-based carbons

2.3.1. Proximate analysis

The ash content in the sawdust, before and after treatment, was determined following the UNE32-004 standard (ISO/1171

equivalent standard). A 1–2 g of sample, ground and sieved to <0.2 mm, was heated at 450 °C h^{-1} until 815 °C under air atmosphere. After 1 h at this temperature, the sample was cooled and the ash content was calculated as the percentage of residue quoted as a mean of values from four experiments. The moisture was determined according to the UNE32-002 standard (ISO331 and ISO/5068 equivalent standards). A 1–2 g of sample was placed in an oven preheated at 105 °C for 1 h under nitrogen atmosphere. After cooling, the moisture was calculated from the weight loss as a mean of values from four experiments.

2.3.2. Helium density

The helium density was determined on powdered samples by using a Micromeritics AccuPyc 1330 gas pycnometer.

2.3.3. pH measurements

The pH was measured following the ASTM D3838 standard, using a SevenEasy Mettler Toledo pH-meter equipped with an InLab 421 electrode.

2.3.4. BET surface area

Previous to the isotherm measurement, the samples were outgassed at 250 °C for 12 h. Afterwards, the surface area of the adsorbents was determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 surface area analyzer.

2.4. Adsorption/desorption of Cr(VI)

2.4.1. Adsorption experiment

In a typical procedure, a specific amount of carbon (10, 20, 40, 60 and 80 mg) was added to 10 ml of the Cr(VI) solutions and then stirred in a rotary orbital shaker at room temperature for different periods of time (0–120 min) under different pH media (1.0, 3.0, 5.0, 7.0 and 9.0). Afterwards, the resultant solutions were filtered and the amount of Cr(VI) in solution quantified by UV spectroscopy at a wavelength of 540 nm. A blank test was carried out using filtered wastewater.

2.4.2. Desorption experiments

A test to see if the adsorbents could be regenerated after adsorbing Cr(VI) was carried out on the industrial wastewater containing 110 mg ml^{-1} of Cr(VI) solution and 4 mg ml^{-1} of adsorbent, stirred for 2 h. The Cr(VI) was desorbed by treating the sample with 15 vol.% of H$_2$SO$_4$ 1N overnight. The solid was then separated by filtration and used as a fresh adsorbent in a second and a third experiment under the same conditions as those described above. The regeneration rate of the adsorbent was determined by quantifying the Cr(VI) in the liquid fraction after each cycle.

3. Results and discussion

The main properties of the carbons obtained by treatment with AlCl$_3$, HCl, H$_3$PO$_4$, H$_2$SO$_4$ and NaOH and subsequent carbonization at 450 and 600 °C are summarized in Table 1. The reaction yield ranges between 84 and 93 wt.% when the carbonization is performed at 450 °C and 45–55 wt.% at 650 °C.

Table 1
Characteristics of sawdust-based carbons obtained at 450 and 650 °C

Sample	Y[a]	M[b]	A[c]	dHe[d]	pH	BET[e]
C-Cl$_3$-450	87	2.3	1.3	1.52	4.9	40
C-HCl-450	87	2.2	1.7	1.51	4.7	20
C-H$_3$PO$_4$-450	84	19	0.9	1.57	2.9	450
C-H$_2$SO$_4$-450	89	2.3	1.5	1.51	3.5	30
C-NaOH-450	93	2.7	2.5	1.54	5.3	40
C-AlCl$_3$-650	49	2.1	0.9	1.62	4.9	220
C-HCl-650	53	2.6	1.8	1.69	4.7	218
C-H$_3$PO$_4$-650	45	2.2	0.7	1.89	3.2	1093
C-H$_2$SO$_4$-650	50	2.9	1.1	1.65	3.2	230
C-NaOH-650	55	3.1	2.7	1.66	6.7	45

[a] Reaction yield (wt.%).
[b] Moisture content (wt.%).
[c] Ash content (wt.%).
[d] Helium density (g cm^{-3}).
[e] Nitrogen BET surface area (m^2 g^{-1}).

This is not surprising considering that between 450 and 650 °C the activity of the agent is greater and the sawdust loses a considerable amount of weight [20]. The helium density of the materials is also affected by the carbonization temperature. Higher values of density are obtained in the materials carbonized at 650 °C, an especially noteworthy case being that of C-H$_3$PO$_4$-650 which attains a density of 1.89 g cm^{-3}. The BET area indicates that at the lower temperature only treatment with H$_3$PO$_4$ causes any significant increase in surface area, while at 650 °C the surface area is increased only with acid treatment.

3.1. Adsorption of synthetic Cr(VI) solutions

3.1.1. Effect of pH on Cr(VI) adsorption

The capacity of sawdust-based carbons to adsorb Cr(VI) is strongly dependent upon the pH (Fig. 1). At 450 °C, the carbons obtained by acid treatment exhibit a maximum of Cr(VI) adsorption at a pH of 3 (Fig. 1a). This could be in agreement with the hypothesis that Cr(VI) is adsorbed by means of an ion-exchange mechanism [21]. At a pH of 3, Cr(VI) is mainly in the form of [HCrO$_4$]$^-$ anion, which indicates that this is the active species adsorbed by the carbons. Moreover, the surface of the carbon at this pH may be highly protonated, favouring the uptake of anionic Cr(VI) species [22]. At a lower pH, however, a dra-

matic decrease in Cr(VI) adsorption is observed, which can be attributed to polymerization reactions between the dichromate ions to form [Cr$_3$O$_{10}$]$^{2-}$ and [Cr$_4$O$_{13}$]$^{2-}$ anions. At higher pH values (above 6), [Cr$_2$O$_7$]$^{2-}$ or [CrO$_4$]$^{2-}$ species are commonly present in the solution [23].

Of special interest are the high adsorption values obtained for the C-AlCl$_3$-450 and C-H$_3$PO$_4$-450 carbons. However, their different BET surface areas (450 and 40 m^2 g^{-1} for C-H$_3$PO$_4$-450 and C-AlCl$_3$-450, respectively) suggest that the mechanisms of Cr(VI) adsorption in each case are clearly different. In C-H$_3$PO$_4$-450 physical adsorption seems to play an important role, which could be due to the presence of delaminated structures in the carbon, as observed by other authors [24]. On the other hand, the low BET area value for C-AlCl$_3$-450 seems to indicate that adsorption in this case is controlled mainly by a chemical mechanism.

The adsorption behaviour of C-NaOH-450 differs completely from that observed in the carbons obtained by acid treatment (Fig. 1a) and its adsorption capacity is not as dependent on the pH. This different behaviour may be the result of the basic carbon surface produced during the treatment, as shown in Table 1.

When the treatment temperature is increased to 650 °C, the sawdust-based carbons behave in a similar way, regardless of the treatment applied, showing a pattern of maximum adsorption at a pH of 3 (Fig. 1b). The best adsorption rates were obtained with carbons C-H$_3$PO$_4$-650 (85%) and C-AlCl$_3$-650 (83%). Also interesting is the increase in the adsorption rate of C-HCl-650 and C-H$_2$SO$_4$-650 (~75%). In view of the fact that the BET results obtained for these carbons show a generalized increase in surface area with respect to the carbons obtained at 450 °C (except for NaOH), it may concluded that the degradation reactions between 450 and 650 °C are not very selective, since the chemical active sites generated at 450 °C has been modified.

3.1.2. Effects of residence time on Cr(VI) adsorption and adsorbent concentration

The effect of residence time on the capacity of the carbons to adsorb Cr(VI) was studied at a pH of 3 (predominant specie is HCrO$_4^-$) with a HCrO$_4^-$ solution:adsorbent ratio of 400:4 mg ml^{-1} (Fig. 2). In carbons treated at 450 °C, the highest adsorption rates are for carbons treated with AlCl$_3$ and H$_3$PO$_4$ (75 and 81%, respectively, after 15 min of residence
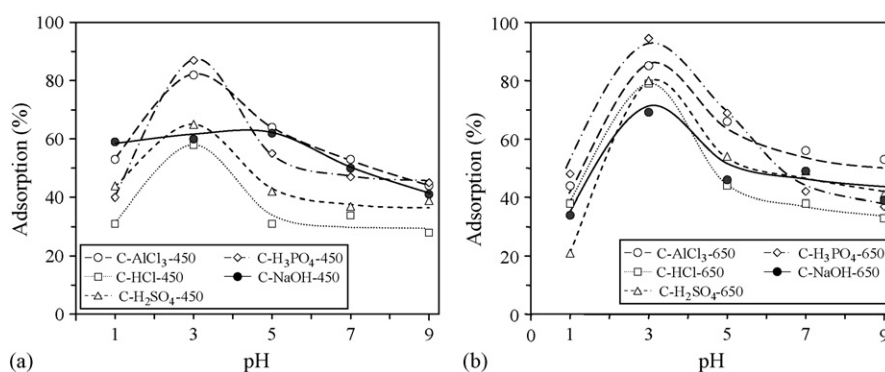

Fig. 1. Variation in Cr(VI) adsorption vs. pH for sawdust-based carbons obtained at (a) 450 and (b) 650 °C. Cr(VI):carbon ratio of 200:4 mg ml^{-1}.
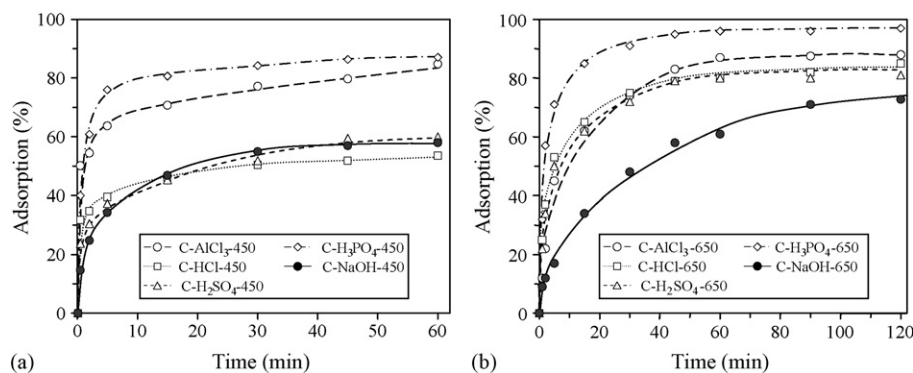
Fig. 2. Variation in Cr(VI) adsorption vs. residence time for sawdust-based carbons obtained at (a) 450 and (b) 650 °C. Cr(VI):carbon ratio of 400:4 mg ml^{-1} and pH 3.

time), while the lowest values are for carbons treated with HCl, NaOH and H_2SO_4 (40–50% for a residence time of 1 h). These results suggest that treatment with $AlCl_3$ and H_3PO_4 at 450 °C causes structural changes in the sawdust, leading to an increase in the active adsorption sites of the material. On the other hand, the lower adsorption rates obtained with C-HCl-450, C-NaOH-450 and C-H_2SO_4-450 could be due to a less effective treatment in the formation of chemically active sites and/or to the coexistence of steric and conformational hindrances that make it more difficult for $HCrO_4^-$ to gain access to the adsorption sites. Carbons obtained at 650 °C show a higher capacity of $HCrO_4^-$ adsorption than carbons at 450 °C (Fig. 2a and b). However, the adsorption equilibrium is reached at longer residence times (except in the case of C-H_3PO_4-650, which behaves in a similar way to C-H_3PO_4-450). This is in agreement with the hypothesis that active sites are removed by the increase in temperature treatment which would seem to indicate that the principal mechanism of $HCrO_4^-$ adsorption in C-H_3PO_4-650 is still physical adsorption, while in the other carbons the adsorption mechanism is changing from chemical to physical.

From the results obtained, the kinetic parameters of adsorption were determined by using the first-order Lagergreen equation $[\log(q_e - q) = (\log q_e - K_{ad}t)/2.303]$. At short adsorption times, linear plots of $\log(q_e - q)$ versus t are obtained, indicating that the reaction follows a pseudo-first order mechanism. Moreover, the rate constants (K_{ad}) shown in Table 2 are in agree-

ment with those previously reported by other authors for aqueous Cr(VI) adsorption [25].

The adsorbent concentration in the solution was also studied (Fig. 3). The general trend is for an increase in adsorption as the carbon concentration increases until saturation is reached. However, the amount of $HCrO_4^-$ adsorbed and the concentration of carbon saturation is dependent upon the agent used and, consequently, on the type and accessibility of the adsorption sites. Thus, C-H_3PO_4-650 adsorbs 90% of $HCrO_4^-$ at a concentration of 4 mg ml^{-1}. On the other hand, C-NaOH-650 requires a con-
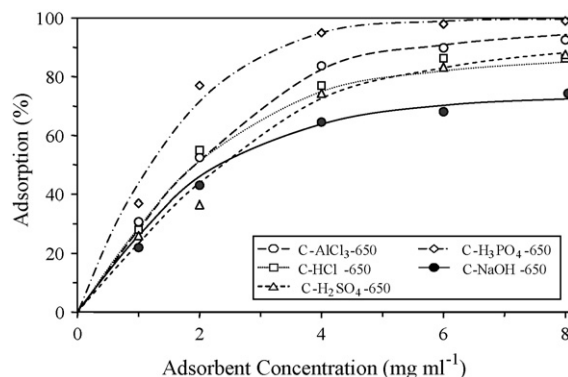

Fig. 3. Variation in Cr(VI) adsorption (400 mg ml^{-1}) vs. adsorbent concentration in sawdust-based carbons obtained at 650 °C. Residence time of 2 h and pH 3.

Table 2
Lagergren, Langmuir and Freundlich adsorption rate constants of sawdust-based carbons

| Sample	Lagergreen, k_{ad} (min^{-1})	Langmuir		Freundlich		
		Q_0 (mg g^{-1})	b (mg l^{-1})	k_f	n	q_m (kcal mol^{-1})
C-$AlCl_3$-450	0.108	0.47	0.40	2.13	2.58	1.48
C-HCl-450	0.020	1.13	1.22	1.00	2.12	1.22
C-H_3PO_4-450	0.166	1.83	0.59	0.66	1.54	0.88
C-H_2SO_4-450	0.042	0.55	0.44	1.94	3.20	1.79
C-NaOH-450	0.038	1.03	0.88	0.83	2.30	1.32
C-$AlCl_3$-650	0.045	0.86	0.81	1.25	2.00	1.15
C-HCl-650	0.050	1.05	0.15	1.03	2.50	1.44
C-H_3PO_4-650	0.080	1.24	0.18	0.80	1.30	0.74
C-H_2SO_4-650	0.061	0.92	0.24	1.16	2.45	1.41
C-NaOH-650	0.019	–	–	1.03	2.70	0.98
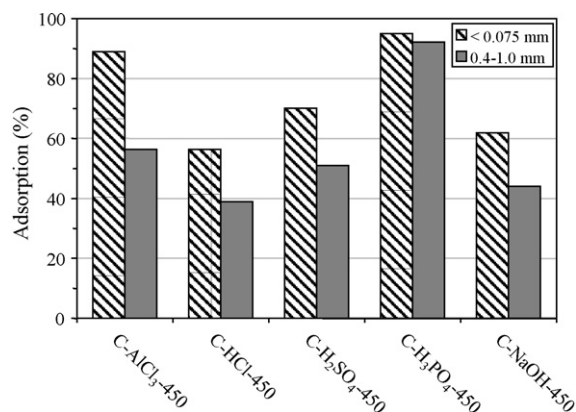
Fig. 4. Effect of the particle size on the adsorption capacity of the sawdust-based carbons obtained at 450 °C. Cr(VI):carbon ratio of 400:4 mg ml^{-1} and pH 3. Residence time of 2 h.

centration of at least 6 mg ml^{-1} to adsorb only 70% of HCrO$_4^-$. C-AlCl$_3$-650, C-HCl-650, C-H$_2$SO$_4$-650 exhibit an intermediate behaviour.

The effect of the carbon particle size (<0.2 and 0.4–1.0 mm) on Cr(VI) adsorption was studied with samples treated at 450 °C (Fig. 4). The general effect obtained is an increase in adsorption rates as the particle size decreases, except for carbon C-H$_3$PO$_4$-450. This peculiar behaviour seems to be related with diffusion effects, which are significantly weaker in delaminated carbons [24].

3.1.3. The adsorption isotherms

The Cr(VI) adsorption isotherms in this work were modelled on the Langmuir and Freundlich equations [25]. The Langmuir model assumes that the uptake of metal ion occurs on a homogeneous surface by monolayer adsorption without any interaction among the adsorbed ions, while the Freundlich model assumes that adsorption occurs on a heterogeneous surface. The results obtained are summarized in Table 2. Carbons treated at 450 °C do not fit the Langmuir equation. Only in the first stages of adsorption, can the Langmuir model be applied and the parameters Q_0 and b be calculated. On the other hand, the use of the Freundlich equation can be applied at all the stages of the adsorption. The Langmuir and Freundlich parameters calculated are in agreement with others obtained for similar adsorbents [25].

According to the statistical treatment of the Freundlich model, the heat of adsorption can be estimated for a coverage of 37% [26]. Of all the carbons treated at 450 °C, C-H$_3$PO$_4$-450 shows the lowest values of adsorption heat (Table 2). On the other hand, the adsorption heat for carbons treated at 650 °C decreases with respect to those obtained at 450 °C. This corroborates the previous remark that at 450 °C adsorption takes place by chemical mechanisms (high values of adsorption heat), while at 650 °C adsorption occurs mainly by physical mechanisms (low values of adsorption heat).

The activation energies were estimated according to the Arrhenius equation [27]. The values obtained are in the 11.3–6.9 kJ mol^{-1} range and are similar to those proposed by other authors for analogous materials [12].

Table 3
Removal efficiency of Cr(VI) exhibited by sawdust-based carbons obtained at 650 °C ([Cr(VI)] = 200 mg ml^{-1}; pH 3; [carbon] = 4 mg ml^{-1})

Sample	1st cycle (%)	2nd cycle (%)	3rd cycle (%)
C-AlCl$_3$-650	82	71	53
C-HCl-650	85	83	68
C-H$_3$PO$_4$-650	100	98	95
C-H$_2$SO$_4$-650	89	83	71
C-NaOH-650	72	69	55

3.2. Application of the adsorption of Cr(VI) present in industrial wastewater

3.2.1. Adsorption of Cr(VI) from wastewater

The carbons prepared at 650 °C were used as adsorbents of Cr(VI) in an industrial wastewater sample (Table 3). According to the preliminary results and with the aim of optimizing the adsorption process, the pH of this wastewater was adjusted to 3 by adding NaOH. The solution was not subjected to further filtration. In agreement with the preliminary studies, the higher adsorption capacity was obtained for C-H$_3$PO$_4$-650 (85 %), C-HCl-650 (75%) and C-H$_2$SO$_4$-650 (70%). The low adsorption rates observed for carbons C-AlCl$_3$-650 and especially C-NaOH-650 could be due to the formation of a white precipitate during the reaction, probably as a result of secondary reactions between the elements present in the wastewater and the functional groups on the surface of the carbon. These values are lower than those obtained for the solution of Cr(VI) previously studied. The presence of other elements (K, Fe, Mo, Ag, etc.) and solid waste in the industrial sample seem to be the cause of the decrease in carbon efficiency.

3.2.2. Regeneration of carbons

Carbon regeneration is usually studied in carbons in the form of pellets [1]. However, for further application, the effect of the presence of solid residue in the industrial wastewater during the recycling of the powdered sawdust-based carbons of the type prepared in this work, using sulphuric acid as the desorption agent, might be an interesting subject of study. After the first cycle, the carbons still retain their capacity for Cr(VI) adsorption virtually unaltered (Table 4), even in the presence of the solid residue, except for C-AlCl$_3$-650 whose efficiency is reduced from 82 (first cycle) to 71% (second cycle). The adsorption capacity of C-AlCl$_3$-650, C-HCl-650, C-H$_2$SO$_4$-650, C-NaOH-650 in a third cycle, is substantially reduced by as much as

Table 4
Efficiency of removal of Cr(VI) from industrial wastewater exhibited by sawdust-based carbons obtained at 650 °C ([Cr(VI)] = 110 mg ml^{-1}; pH 3; [carbon] = 2 mg ml^{-1}; residence time = 2 h)

Activated carbon	Efficiency (%)
C-AlCl$_3$-650	57
C-HCl-650	75
C-H$_3$PO$_4$-650	85
C-H$_2$SO$_4$-650	70
C-NaOH-650	22

~17–19% compared to the first cycle. Once again C-H$_3$PO$_4$-650 shows a completely different behaviour. The regenerability of this carbon goes beyond the third cycle. In fact after three uses, C-H$_3$PO$_4$-650 shows a Cr(VI) adsorption capacity of 95%.

4. Conclusions

The sawdust-based carbons prepared in this work are suitable for the adsorption of aqueous Cr(VI) from industrial wastewater, the adsorption being more effective at acidic pHs (e.g., pH of 3).

The mechanisms of adsorption of the activated carbons prepared were found to be dependent on the agent used and the temperature of the treatment. In carbons obtained at 450 °C, adsorption mainly occurs by physical mechanisms when using H$_3$PO$_4$, while with the other agents physical adsorption competes with chemical adsorption. An increase in the treatment temperature to 650 °C produces significant changes in the mechanisms of adsorption, which become predominantly physical in all cases. This is corroborated by a decrease in the adsorption heats, as confirmed by the application of the Freundlich equations.

Cr(VI) adsorption efficiency is higher in carbons prepared at 650 °C. However, the adsorption kinetics of these carbons are slower than those prepared at 450 °C.

The sawdust-based carbons prepared in this work evidence a good capacity for recycling and they can be used for the removal of Cr(VI) from industrial wastewaters, especially the material obtained by treatment with H$_3$PO$_4$ at 650 °C.

Acknowledgements

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