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Article

New bioadsorbent derived from winemaking waste cluster stalks: application to the removal of toxic Cr(VI) from liquid effluents

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Abstract: A winemaking waste was used as a precursor of activated carbon used in hazardous Cr(VI) removal from solutions. The preparation process consisted of a hydrothermal process, and a chemical activation, of the resulting product, with KOH. The adsorption results showed that the adsorption of Cr(VI) on the obtained activated carbon is strongly dependent on the stirring speed applied to the carbon/solution mixture, pH of the solution, and temperature. The equilibrium isotherm was well fitted to the Langmuir type-II equation, whereas the kinetic can be described by the pseudo-second-order kinetic model. Thermodynamic studies revealed that Cr(VI) adsorption was an exothermic and spontaneous process. Finally, desorption experiments showed that Cr(VI) was effectively desorbed using hydrazine sulfate solutions, and at the same time, the element was reduced to the less hazardous Cr(III) oxidation state.

Keywords: Activated carbon; winemaking waste; wastewater; Cr(VI) removal; adsorption process; Cr(VI) reduction

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1. Introduction

It is known that water is a precious and essential resource, and is a basic requirement for humans and wildlife. Unfortunately, this resource is finite, with no adequate substitute. The great increase in the world population leads to several forms of water pollution, as well as an increase in the global water demand [1]. Nowadays, industrial and urban activities have increased, cause subsequently water pollution, for example with heavy metals. These metals could be introduced by both natural sources (such as weathering of soils and rocks or from volcanic eruptions) and from anthropogenic activities (mining, processing, or use of metals). In this sense, the most common heavy metal pollutants in water are Cd, Cr, Cu, Ni, Pb, and Hg.

The use of chromium in several applications such as electroplating, tanning, pigment manufacture, or biocide among others, leads to great discharges of chromium-containing effluents into the environment [2]. The toxicity of the elements depends on its chemical form [3]. In this sense, chromium ions are present in environmental water principally in two different oxidation states: Cr(III) and Cr(VI). While Cr(III) is the less soluble, low toxicity, and is a required nutrient [2,4], Cr(VI) is toxic and carcinogenic. The continuous exposure of Cr(VI) causes important health problems such as epigastric pain, nausea and vomiting, diarrhea, hemorrhage, and even cancer in the digestive tract and lungs [5]. In addition, according to the International Agency for Research on Cancer [6], Cr(VI) modifies the DNA transcription process causing important chromosomic aberration. Despite of chromium are usually present at low concentrations in environmental water, removal of this metal is an important topic.

Several techniques for chromium removal from wastewaters have been reported including chemical precipitation [7], electrochemical precipitation [8] solvent extraction [9] ion exchange [10], and adsorption process [4,11,12]. Due to its simplicity, effectiveness, and low cost, the adsorption process has been extensively investigated to metal removal from aqueous solutions. However, the great inconvenience in the application of this process by the industries is the cost of adsorbents. Generally, the cost of the commercial adsorbent is very high, which is a barrier for use the adsorption process [5].

In this sense, activated carbons are useful adsorbent materials for the removal of a large variety of pollutants, which have been reported that it is possible to obtain them from renewable sources, as agroindustrial wastes, and new synthesis processes [13]. Among the great variety of waste, winemaking wastes is an attractive option due to the number of grapes were produced worldwide, and the waste generated for winemaking [14]. For this reason, the use of winemaking waste to obtain activated carbon, and their use to heavy metals adsorption is an important aim to the scientific community by both heavy metal removal from wastewater and the re-use and re-cycling of a generated waste.

In the present work, an activated carbon (AC) derived from a waste generated in wine production, cluster stalks, has been described. Cr(VI) removal by adsorption process was assessed. Different parameters that affect the adsorption process such as stirring speed, solution pH, temperature, among others, were evaluated. Adsorption isotherms and kinetic studies were also investigated. Finally, Cr(VI) recovery from Cr(VI)-loaded carbon was addressed in several experimental conditions.

2. Materials and Methods

2.1. Synthesis of the activated carbon

Activated carbon (AC) was obtained from a winemaking waste, cluster stalks, according to the as-previously described procedure [14]. For the sample preparation, an aqueous suspension of 75 g/L of cluster stalks (production of Albariño wine; Denomination of Origin 'RíasBaixas', Galicia, Spain) was introduced into a high-pressure reactor at 30 bars, and 250 ºC for 3 h. After that, the final mixture was filtered obtaining a hydrothermal carbon as a precursor. To obtain the corresponding activated carbon, a mixture of precursor/KOH (1:2) was introduced in a tubular oven under a N_2 flow at 800 ºC for 2 h. Finally, the obtained blackness solid was washed until a neutral pH was reached.

2.2. Adsorption experiments

Cr(VI) adsorption by the obtained activated carbon was performed via batch experiments, using a 250 mL glass reactor provided of mechanical shaking via a four bladed glass impeller of 2.3 cm diameter. Metal concentration in the solution was analyzed by atomic absorption spectroscopy (AAS). The adsorption percentages were calculated by equation (1):

$$\text{Adsorption (\%)} = {[\mathrm{Cr}]_{\mathrm{aq},0} - [\mathrm{Cr}]_{\mathrm{aq},t}}\Big/{[\mathrm{Cr}]_{\mathrm{aq},0}} \cdot 100 \qquad (1)$$

where $[\mathrm{Cr}]_{\mathrm{aq},0}$ and $[\mathrm{Cr}]_{\mathrm{aq},t}$ (mg/L) are the initial and the concentrations of Cr(VI) in solution. The associated analytical error was within ±2%.

Different experiments were carried out to analyze the effect of several parameters which affect the adsorption process. Stirring speed was modified between the range 250-1000 min^{-1} in 200 mL of Cr(VI) solution (10 mg/L concentration), at pH 4, with 10 mg of the activated carbon. The as-described solutions pH was adjusted by adding suitable HCl and NaOH solutions until the desirable pH value was achieved. The temperature of the experiments was modified (each 10 ºC) between 20 ºC and 60 ºC. The effect of the ionic strength was investigated by adding different amounts of lithium chloride to the solutions of Cr(VI) concentration 10 mg/L and 1 mg of the activated carbon. Finally, the adsorption equilibrium isotherms were analyzed varying the activated carbon amount between 0,5 and 100 mg using the type-1 Langmuir (equation (2)), type-2 Langmuir (equation (3)), Freundlich (equation (4)) and Temkin (equation 5)) linear forms:

$$\frac{[\mathrm{Cr}]_{\mathrm{aq,e}}}{[\mathrm{Cr}]_{\mathrm{c,e}}} = \frac{1}{[\mathrm{Cr}]_{\mathrm{c,m}} \cdot K_L} + \frac{1}{[\mathrm{Cr}]_{\mathrm{c,m}}} \cdot [\mathrm{Cr}]_{\mathrm{aq,e}} \qquad (2)$$

$$\frac{1}{[\mathrm{Cr}]_{\mathrm{c,e}}} = \frac{1}{[\mathrm{Cr}]_{\mathrm{c,m}} \cdot \mathrm{K_L}} + \frac{1}{[\mathrm{Cr}]_{\mathrm{c,m}}} \cdot \frac{1}{[\mathrm{Cr}]_{\mathrm{aq,e}}} \qquad (3)$$

$$\ln\,[\mathrm{Cr}]_{\mathrm{c,e}} = \ln \mathrm{K_F} + \frac{1}{\mathrm{n}} \cdot \ln\,[\mathrm{Cr}]_{\mathrm{aq,e}} \qquad (4)$$

$$[\mathrm{Cr}]_{\mathrm{c,e}} = {}^{\mathrm{R}\cdot\mathrm{T}}\!/_{\mathrm{b_T}} \cdot \ln \mathrm{A_T} + {}^{\mathrm{R}\cdot\mathrm{T}}\!/_{\mathrm{b_T}} \cdot \ln[\mathrm{Cr}]_{\mathrm{aq,e}} \qquad (5)$$

where $[\mathrm{Cr}]_{\mathrm{aq,e}}$ (mg/L) is the concentration of the metal in solution at the equilibrium, $[\mathrm{Cr}]_{\mathrm{c,e}}$ (mg/g) is the adsorbed metal amount per gram of activated carbon at the equilibrium, $[\mathrm{Cr}]_{\mathrm{c,m}}$ is the maximum adsorbed metal amount per gram of activated carbon, $\mathrm{K_L}$ (L/mg) and $\mathrm{K_F}$ (L/g) are the corresponding Langmuir constants, 1/n (adimensional) is the adsorption intensity, and $\mathrm{b_T}$ (adimensional) is the Temkin isotherm constant.

The kinetic study was carried out using the following equations (6)-(9):

$$\text{first order } \ln[\mathrm{Cr}]_{\mathrm{aq,t}} = \ln[\mathrm{Cr}]_{\mathrm{aq,0}} - \mathrm{k} \cdot \mathrm{t} \qquad (6)$$

$$\text{second order} \quad \frac{\mathrm{t}}{[\mathrm{Cr}]_{\mathrm{aq,t}}} = \frac{1}{[\mathrm{Cr}]_{\mathrm{aq,0}}} + \mathrm{k} \cdot \mathrm{t} \qquad (7)$$

$$\text{pseudo-first-order} \quad \ln\left([\mathrm{Cr}]_{\mathrm{c,e}} - [\mathrm{Cr}]_{\mathrm{c,t}}\right) = \ln[\mathrm{Cr}]_{\mathrm{c,e}} - \mathrm{k} \cdot \mathrm{t} \qquad (8)$$

$$\text{pseudo-second-order} \frac{\mathrm{t}}{[\mathrm{Cr}]_{\mathrm{c,t}}} = \frac{1}{\mathrm{k} \cdot [\mathrm{Cr}]_{\mathrm{c,e}}^2} + \frac{1}{[\mathrm{Cr}]_{\mathrm{c,e}}} \cdot \mathrm{t} \qquad (9)$$

Also, the rate law which governing the adsorption process onto the adsorbent was analyzed by three possible adsorption mechanisms: film diffusion, equation (10) [15], intraparticle diffusion, equation (11) [16] and moving boundary, equation (12) [17]:

$$\ln(1 - \mathrm{F}) = -\mathrm{k} \cdot \mathrm{t} \qquad (10)$$

$$\ln(1 - \mathrm{F}^2) = -\mathrm{k} \cdot \mathrm{t} \qquad (11)$$

$$3 - 3 \cdot \left(1 - \mathrm{F}^{2/3}\right) - 2 \cdot \mathrm{F} = \mathrm{k} \cdot \mathrm{t} \qquad (12)$$

where k is the corresponding constant and F is the factorial approach to equilibrium, equation (13):

$$\mathrm{F} = {}^{[\mathrm{Cr}]_{\mathrm{ads,t}}}\!/_{[\mathrm{Cr}]_{\mathrm{ads,e}}} \qquad (13)$$

where $[\mathrm{Cr}]_{\mathrm{ads,t}}$, and $[\mathrm{Cr}]_{\mathrm{ads,e}}$ (mg/L) are the concentrations of metal adsorbed onto the carbon after an elapsed time and at equilibrium, respectively.

Finally, the thermodynamic parameters (standard enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0)) were calculated using the following equations (14)-(16) [18,19]:

$$\Delta G^0 = -\mathrm{RT} \ln \mathrm{k_d} \qquad (14)$$

$$\ln \mathrm{k_d} = \frac{\Delta S^0}{\mathrm{R}} - \frac{\Delta H^0}{\mathrm{RT}} \qquad (15)$$

where $\mathrm{k_d}$ is known as the thermodynamic equilibrium constant (equation 16):

$$\mathrm{k_d} = {}^{[\mathrm{Cr}]_{\mathrm{ads,e}}}\!/_{[\mathrm{Cr}]_{\mathrm{aq,e}}} \qquad (16)$$

2.3. Desorption experiments

These experiments were performed also in glass reactors provided with glass impellers as described above. To carried out these desorption experiments, 0.1 g of the Cr(VI)-loaded activated carbon was added to hydrazine sulfate solutions with a concentration of 10 g/L at 20 ºC for 4 h. Different volumes of eluent solution were investigated for a fixed carbon amount. Cr(VI) desorption percentage, as well as chromium concentration in the final solution, were assessed.

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3. Results and discussion

3.1. Cr(VI) adsorption experiments

3.1.1. Stirring speed

The stirring speed applied to the carbon-solution system may have a key role in the adsorption process due to modify the mass gradient of adsorbate from the solution to the adsorbent interface [20]. Thus, different experiments were carried out to study the influence of this variable on the Cr(VI) adsorption process. Activated carbon dosage of 0.5 $g \cdot L^{-1}$ was added into Cr(VI) solutions of 0.01 $g \cdot L^{-1}$ (resulting pH 4) at 20 ºC. Fig. 1 exhibits the adsorption percentage of Cr(VI) after a contact time of 5 h versus the stirring speed. It can be appreciated that the adsorption process was influenced by stirring speed. Cr(VI) adsorption percentage increase with the stirring speed from 250 to 1000 min^{-1}. However, using higher stirring speeds decreased the adsorption percentage. So, these results indicate that the thickness of the aqueous boundary layer at 1000 min^{-1} was lowest and leads to a higher adsorption percentage. The decrease in the adsorption of Cr(VI) at higher stirring speeds could be due to the formation of local equilibria which hinders the adsorption process. According to these results, a stirring speed of 1000 min^{-1} was used in the subsequent experiments.

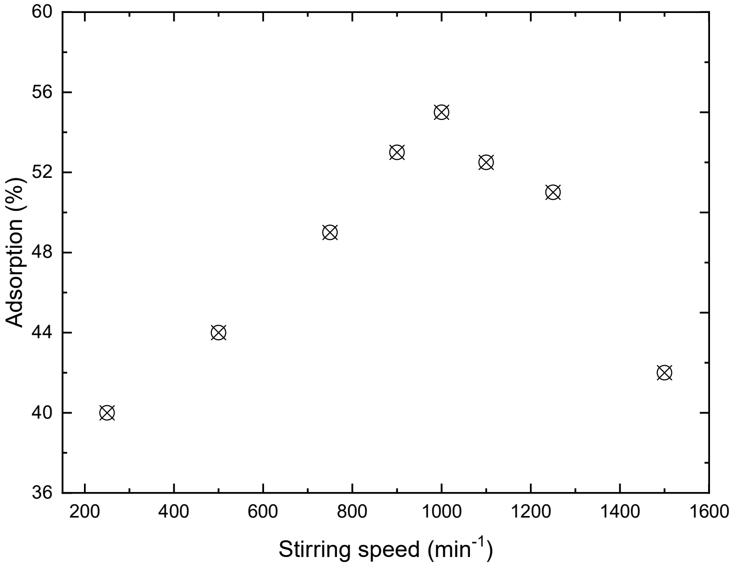

Figure 1. Influence of the stirring speed on the Cr(VI) adsorption.

3.1.2. pH of the solution

As in the case of the stirring speed, the pH of the solution could play a significant role in the adsorption process of heavy metals [21]. In the case of Cr(VI), and as it is shown in Fig.2, the pH value influences the element speciation. In this figure, it can be appreciated that in the 0.01 g/L Cr(VI) concentration range, the same concentration being used in the present investigation, the metals are present as $HCrO_4^-$ and CrO_4^{2-} species, at pH values of 0-6 and 8-14, respectively.

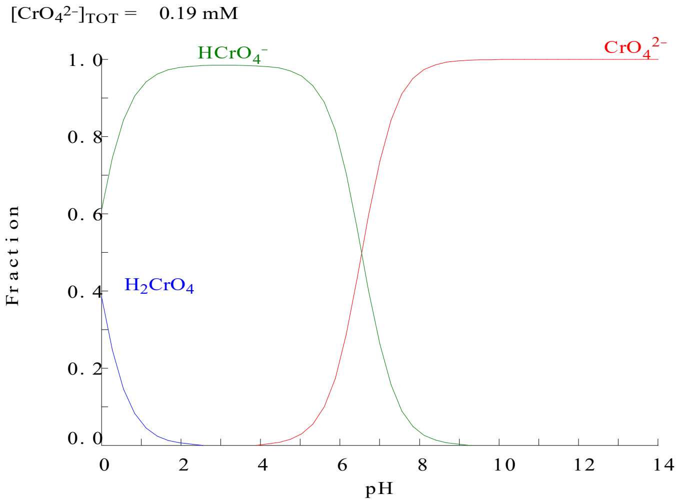

Figure 2. Cr(VI) speciation as pH function [22].

Based on the above, the adsorption of Cr(VI) onto the activated carbon can be represented by the next equilibria:

i) at pH 0-6:

$$\mathrm{HCrO_{4,aq}^{-}} \Leftrightarrow \mathrm{HCrO_{4,c}^{-}} \qquad (17)$$

ii) at pH 8-14:

$$\mathrm{CrO_{4,aq}^{2-}} \Leftrightarrow \mathrm{CrO_{4,c}^{2-}} \qquad (18)$$

and in the 6-8 pH range by both equilibria. In the above equations, the subscripts aq and c represented the equilibrated aqueous and carbon phases, respectively.

Thus, metal uptake onto the carbon was investigated as a function of this variable, and the results of these series of tests are represented in Fig. 3. It can be appreciated that the adsorption percentage dramatically increases from pH 0 to 3, resulting in this value of 3, the pH at which maximum Cr(VI) adsorption percentage (90%) resulted. Thereafter, metal uptake decreased until a constant percentage of 38% resulted at pH values higher than 8. These results can be attributed to that at acid pH values, the carbon surface becomes positively charged [23,24]; thus, when the solution pH increases, the surface losses its positive charge. Accordingly, at pH of 8 and onwards, Cr(VI) adsorption becomes constant, the reason probably due to one (or a combination) of three effects: i) decrease of the positive charge, ii) less adsorption capacity of the carbon to adsorb CrO_4^{2-} species, and iii) a competition of CrO_4^{2-} and OH^- species to be adsorbed onto the carbon. Based on the above, a pH of 3 was used in the subsequent experiments.

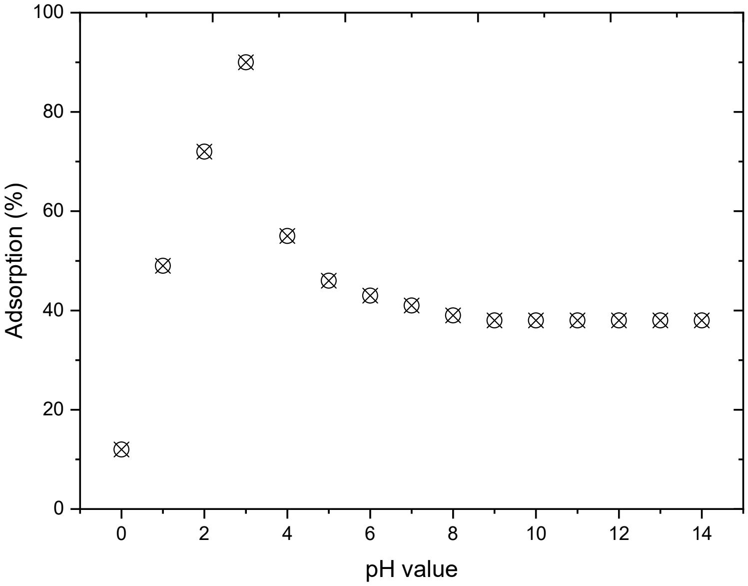

Figure 3. Cr(VI) adsorption percentage as a function of the solution pH. Aqueous phase: 0.01 g/L Cr(VI) at different pH values. Carbon dosage: 0.5 g/L. Temperature: 20º C. Time: 5 h. Stirring speed: 1000 min-1.

3.1.3. Effect of the temperature

The temperature at which the process is carried out could improve or hampers the adsorption process. The adsorption percentage as a function of the different temperatures used is shown in Fig. 4. It can be appreciated that when the experiment temperature increases, the Cr(VI) removal, from the solution drastically decreases. Thus, the calculated adsorption percentages vary between 45 % (at 20 ºC) and 3% (at 60º C). These results revealed that an increase of the temperature hampers the Cr(VI) adsorption process from the solution onto the activated carbon.

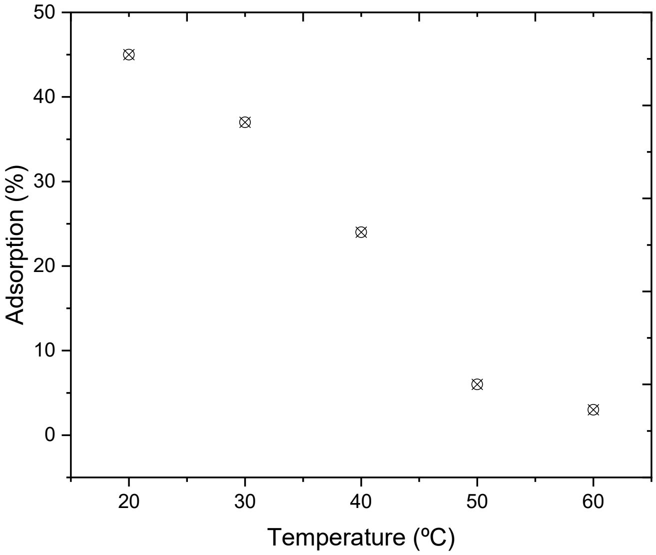

Figure 4. Cr(VI) adsorption at different temperatures. Aqueous phase: 0.01 g/L Cr(VI) at pH 3. Carbon dosage: 0.5 g/L. Time: 5 h. Stirring speed: 1000 min-1.

3.1.4. Effect of the ionic strength

Usually, other metallic and nonmetallic components different to the metal to be removed are present in the liquid solution. These components could affect its ionic strength, so the effect of this parameter on the adsorption process is also interesting to investigate. Fig. 5 exhibits that when the ionic strength increases, dramatically reduced adsorption percentage. The obtained results reveal that the electrostatic forces between the activated carbon surface and Cr(VI) ions are attractive [25].

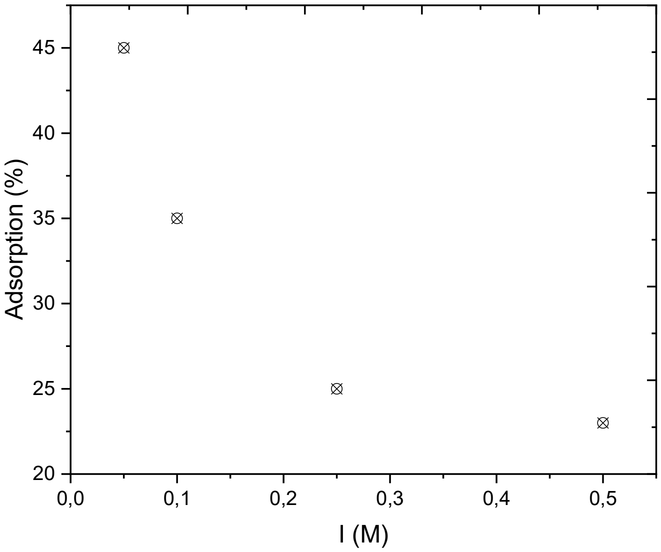

Figure 5. Effect of solution ionic strength on the Cr(VI) adsorption process. Aqueous phase: 0.01 g/L Cr(VI) at pH 3. Carbon dosage: 0.5 g/L. Temperature: 20º C. Time: 5 h. Stirring speed: 1000 min-1.

3.1.5. Influence of the adsorbent dosage

The effect of the adsorbent dosage on the Cr(VI) adsorption process was also evaluated. Table 1 summarized the obtained results from the different experiments carried out. As expected, metal removal increases with the increase of the adsorbent dosage and for a fixed metal concentration. It should be noted that for an extremely low adsorbent dose (i.e. $2.5\cdot10^{-3}$ g/L), an adsorption percentage exceeding 30% was found. Also, for 0.5 g/L adsorbent, the Cr(VI) adsorption was almost.

Table 1. Adsorption percentage as a function of the adsorbent dosage.

Adsorbent dosage (g/L)	$[Cr]_{aq,e}$ (mg/L)	Adsorption (%)
$2.5\cdot10^{-3}$	6.4	36
$5\cdot10^{-3}$	5.5	45
0.025	4.6	54
0.05	3.1	69
0.25	2	80
0.5	1	90

3.2. Adsorption isotherms, kinetic study and rate law

To analyze the adsorption isotherm associated with the metal uptake onto the adsorbent, the results, from subsection 3.1.5., were fitted to various adsorption isotherms using equations (2-5). The results from these fits indicated that the highest correlation coefficient ($R^2 = 0.9667$) was obtained for the Langmuir isotherm type-II, being K_L estimated as 0.01 L/mg. Moreover, being R_L defined as:

$$R_L = \frac{1}{1+K_L \cdot [Cr]_{aq,0}} \qquad (19)$$

it was found that the process is favorable since $R_L<1$.

Adsorption kinetics provides information about the uptake rate of adsorbate onto the adsorbent and controls the residual time during the adsorption process occurs [26]. To analyze the mechanism that controlling the kinetic adsorption process, the obtained data were fitted using equations (6 to 9). The results from the fit indicated that the best correlation coefficient ($R^2 = 0.9976$) was obtained for the pseudo-second-order kinetic model, estimating a calculated kinetic constant of 0.0014 L/mg·min.

To determine the probable rate law governing the Cr(VI) adsorption, the experimental data were fitted to equations 10-12. The best fit ($R^2 = 0.9969$) was found within the film-diffusion model, with a calculated rate constant of 0.0473 min^{-1}.

Finally, from the results of section 3.1.4, the thermodynamic parameters were calculated using Equation 14 and 15. The negative value obtained for the standard enthalpy -71 kJ/mol, was indicative of the exothermic nature of the adsorption process. The negative calculated value for the entropy, -13 J/mol·K, indicates a decrease of the randomness in the Cr(VI) uptake onto the carbon. Despite this, in all cases the calculated Gibbs free energy change was negative, revealing that the adsorption is a spontaneous process.

3.3. Desorption process

Table 2 summarizes the results derived from the different desorption experiments. It can be shown that an increase in the volume of the eluent solution does not influence the percentage of Cr(VI) desorption, reaching values of around 50 %; however, the chromium concentration in the resulted solution increased as the volume of solution/carbon weight relationship decreased. The reduction of Cr(VI) to Cr(III) responded to the next reaction:

$$4HCrO_4^- + 10H^+ + 3N_2H_4 \cdot H_2SO_4 \rightarrow 4Cr^{3+} + 16H_2O + 3N_2 + 3SO_4^{2-} \qquad (19)$$

In the present case, Cr(VI) is reduced to Cr(III), which as described is low toxic [2,4]. In addition, as a result of the low solubility of the Cr(III), it can be precipitated leading to Cr_2O_3 and/or $Cr(OH)_3$, which could be used as a pigment [27–29].

Table 2. Desorption results.

Volume of the solution/carbon weight	$[Cr(III)]_{aq,t}$ (mg/L)	Desorption (%)
2000	4	49
1000	9	50
500	17	49
250	34	50

4. Conclusions

Activated carbon (AC) from winemaking waste has been obtained by a hydrothermal process, followed by a chemical activation of the as-resulted product with KOH. In the experimental procedure, an aqueous suspension of cluster stalks was treated at 30 bars, and 250 ºC for 3 h into a high-pressure reactor. After that, the obtained hydrothermal solid was activated with KOH at 800 ºC for 2 h. The final AC was used to Cr(VI) removal from aqueous solution. Several parameters were investigated. The maximum adsorption percentage was found at 1000 min^{-1} and a pH of the solution of 3. An increase in the adsorbent dosage improves the percentage of the Cr(VI) adsorption process. The effect of the temperature on the process reveals that an increase of the temperature leads to a decrease in the chromium removal. Thus, the adsorption is an exothermic process, with a calculated standard enthalpy of -71 kJ/mol, being the process spontaneous in nature. Also, the negative obtained entropy value (-13 J/mol·K) indicates the decrease of the randomness in the final system. Cr(VI) uptake onto the activated carbon responded well to the Langmuir type-II isotherm model as well as to the pseudo-second-order kinetic model. The rate law associated with the adsorption process resulted to be governed by a film-diffusion process. Cr(VI) can be desorbed by the use of hydrazine sulfate solutions. The desorption process rendered chromium as less toxic and potentially profitable, as a pigment product, Cr(III) oxidation state in the solution.

Author Contributions: FJA and FAL conceived the study. LA and FJA carried out the experiments. LA and FJA wrote the manuscript. All authors contributed to the review, editing, and approval of the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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