

Surface Complexes of Cr(VI) by Eucalyptus Barks

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Abstract: The sorption mechanism of hexavalent chromium sorption on eucalyptus barks was evaluated as a function of solution pH for different adsorbent dosages, surface coverage, and the amount of adsorbent. The chromium retention was evaluated based on the distribution coefficient (D), and this retention is attributed to $HCrO_4^-$ species, which is predominant between pH 1 and 6.5. The biosorption of Cr(VI) ions onto barks achieved at pH 2.0 in the highest sorbet conditions corresponding to $[Cr(VI)] = 10^{-5}$ mol ($V = 100$ mL) is examined for various surface coverage. The surface complexes formed between chromate and eucalyptus barks were found to be $> S (HCrO_4^-)$ and $> S (CrO_4^{2-})$. Logarithmic stability for $\log K_{1-1}$ and the $\log K_{10}$ values of the complexes were measured and found to be -5.93 in acidic medium and -0.76 in alkaline medium, respectively. Pointed out that the adsorption of Cr(VI) on eucalyptus bark was greater than 90% in all cases, Cr(VI) recovery is strongly acidic dependent and shows maximum retention, for various sorbet amounts, at pH around 2, and this retention is attributed to $HCrO_4^-$ species, which is predominant between pH 1 and 6.5, the morphological surface of eucalyptus barks were examined by Scanning Electron Microscope (SEM) connected to a micro analyzer EDS.

Keywords: chromium(VI); eucalyptus barks; surface complexes; adsorption; surface charge

■ INTRODUCTION

Heavy metals (HM) are among the most toxic elements introduced into aquatic systems as a result of natural or industrial processes. The rising use of HM, which are soluble, persistent, and non-biodegradable, is associated with environmental pollution through effluents. Chromium is significantly introduced into the aquatic medium from various industrial activities, including alloying, plating, corrosion inhibition, tanning, and pigments [1-3]. Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the most preponderant in soils and aquatic environments [4-5].

Generally, Cr(III) is reported to be not harmful, insoluble $Cr(OH)_3$ at pH typical of groundwater and complexed by organic matter. On the other hand, Cr(VI)

is more toxic, highly mobile in soil and groundwater, persistent, and non-biodegradable. This species prevails in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) can precipitate with divalent cations. Hexavalent chromium is ranked among the metals of public health concern; hence, it is severely controlled in environmental management. Usually, Cr(VI) anion species are badly sorbed by the negatively charged soil particles and, consequently, can be transferred to the aqueous environments [6-8]. Therefore, total chromium in drinking water with a maximum contamination level of 50 $\mu\text{g/L}$ was taken into account when adjusting Cr(VI) discharged into the environment. Consequently, the presence of this species in drinking water is regulated through the total chromium, whose maximum

contaminant Level is 50 $\mu\text{g/L}$. Cr(VI) recommended maximal permissible limit (MPL) in the surface water is regulated to 2 mg/L and to 0.1 mg/L in drinking water [9-13]. Naturally occurring Cr(VI) is found in ground and surface waters at values above 50 $\mu\text{g/L}$ [6,14]. To meet these environmental standards/regulations, effluents and metal-polluted water must be treated prior to discharge into freshwater. The elimination of Hexavalent chromium ions from wastewater becomes an absolute necessity. The conventional methods used for this purpose are precipitation, coagulation, electroplating, ion exchange, adsorption, liquid-liquid extraction, and ion exchange processes. The adsorption route is an efficient method for hexavalent chromium removal due to its simplicity, availability of various adsorbents, and convenience for lower heavy metals contamination [15-17]. Efficient sorbents such as granular activated carbon show low chromium uptake due to their anionic nature associated with strong hydration.

However, the biosorption process appears as a potential alternative for detoxification and metal recovery from industrial wastewater. This technique achieved by different biosorbents has received considerable interest in water treatment for the uptake of trace metals, in particular, hexavalent chromium. Biosorption has emerged as a potential technique and promising alternative to a conventional method for environmental clean-up using waste biomass. These advantages include availability, regeneration, short operation time, and no chemical sludge [4,18-21]. One can note that more than one process is implicated in the sorption operation, which is performed by combining adsorption, ion exchange, and micro precipitation process. Thus, complex interactions are involved in biosorption, and optimal physicochemical parameters are determined using numerical calculations combining mathematical and statistical models [15,22]. As suggested, understanding the sorption mechanisms requires the distribution of functional groups of binding sites, depending on time and pH suspensions. In this case, global sorptions combining various reactions make the overall kinetic model more complicated to evaluate [23]. To avoid this dilemma, the sorption phenomenon is

studied at even time intervals over the process duration [24].

Biomass materials have strong metal binding power due to various surface functional groups, such as hydroxyl, alkyl, carbonyl, sulfhydryl, amino, and phosphate groups. Bark, as a ligno cellulosic residue, is predominantly utilized in thermal energy production [24]. For this material, uronic acid units with both carbonyl and carboxylic acid functional groups and phenolic groups are the active sites involved in metal sorption, mainly governed by surface complexation [23,25]. Indeed, it is reported that the eucalyptus barks exhibit a caves-like, rough, and irregular surface morphology with active groups that are mainly composed of carboxylic acid ($-\text{COOH}$), followed by Hydroxyl ($-\text{OH}$) and amine groups ($-\text{NH}_2$). The carboxyl and hydroxyl groups are H^+ exchangers, while the other groups are OH^- exchangers [26-28].

Mechanisms of Cr(VI) sorption is rather complex process, including chemisorption and ion exchange. Removal of this metal with various biosorbents is found to be dependent on pH solution. As a result, the sorption of anion species is controlled mainly by surface exchange reactions. Further insertions occurring in the unavailability of active sites are considered to be due to diffusion into the biomass system. In addition, unidentified mechanisms may also be involved in biosorption, and which definition is suggested to require, firstly, the characterization of the functional groups. Generally, the rate of hexavalent chromium sorption is strongly pH-dependent and rises with a decrease in medium acidity. The optimum pH for sorption of Cr(VI) ranges from 1 to 3 [29]. Indeed, the biosorption process of Cr(VI) is strongly dependent on the suspension acidity and is more dependent on pH. Optimal uptake conditions are achieved at pH ranging from 1 to 3. From the distribution diagram of chromium, acid chromate (HCrO_4^-) is the prevailing species in these optimal sorption conditions. As a result, this sorption technique is more convenient for acid effluent clean-up [9,18,30-33].

Nevertheless, some studies report maximum Cr(VI)

biosorption at relatively higher pH ranging from 5.5 to 6.2 [34-35]. The adsorption mechanisms occurring between Cr(VI) anions and biosorbents are due to predominantly the electrostatic interactions and exchange of proton ions with biosorbent surface [9,36]. Several biomasses are used to remove metals from an aqueous solution, including bacteria, algae, fungi, olive waste, cassia, and neem barks. While various kinetic models are successfully used to fit biosorbent sorption, the chemical reaction mechanism is nevertheless required for the whole description of this process [9,20]. For bark sorbents, extensive studies are mainly dealing with the kinetic removals of cationic metals whose maximum uptake is rapidly occurring within the first 5–10 min. For Cr(VI), this maximum is reached at a minimum duration explored of 30 min [4,25]. Assessment of the most suitable sorption equilibrium model needs optimization of the various physicochemical parameters such as initial Cr(VI) concentration, adsorbent dose, contact time, and pH. For this purpose, mathematical and statistical models are developed to evaluate the main influent parameters on this process involving complex interactions [37]. Comparing these models with mass transfer rate is often found to best fit with Freundlich and Langmuir models [38].

The regeneration of biosorbent is a primordial operation for the successful use of biosorption technology. Therefore, total metal elution is more required for biomass reutilization in biosorption cycles. After seven adsorption-desorption cycles, full regeneration is achieved with 0.1 M HCl, and Cr(VI) adsorption capacity remains similar to the initial value. Thus, the main objective of the present study is to investigate the sorption mechanism of Cr(VI) sorption on eucalyptus barks using column mode. For this purpose, Cr(VI) removal is performed to examine the effect of contact time and biomass dosage.

■ EXPERIMENTAL SECTION

Materials

All reagents are of analytical grade obtained from Sigma Aldrich and used without further purification. Stock metal solutions of Cr(VI) (10^{-4} M) were prepared by

dissolving suitable amounts of potassium bichromate ($K_2Cr_2O_7$, 99%). Chemicals used were sodium hydroxide (NaOH, 99%), nitric acid (HNO_3 , 99%), hydrochloric acid (37%), sodium chloride (NaCl, 99%), phosphoric acid solution (H_3PO_4 , 85%), and all chemicals were used without further purification. The acidity of this suspension is adjusted using a 0.1 M solution of HNO_3 or NaOH for all experiments, we used High quality of distilled water.

Instrumentation

Morphological surface features were examined by applying Jeol JSM-IT100 In TouchScope™ Scanning Electron Microscope (SEM) connected to a microanalyzer EDS [39]. Analysis of the dosage of chromium(VI) is carried out in the aqueous phases before and after adsorption by a (EPA 7196A) UV-Visible spectrophotometer.

Procedure

Preparation of biosorbent

The eucalyptus barks are washed, air dried, milled, and then crushed between 40 and 60 mesh. To avoid coloration release, the biosorbent is suspended successively in a 2 M caustic solution and 1.4 M phosphoric acid for 4 h at 80 °C. The adsorption studies are conducted with a fixed-bed process. A given amount of adsorbent is placed in a glass column with an internal diameter of 8 mm and a length of 40 cm. Fig. 1 shows the biosorbent appearance before and after initial preparation.

The effect of pH is investigated in the elute medium for biomass suspension of 1.0, 1.5, and 2.0 g/L. The acidity of this suspension is adjusted using a 0.1 M solution of HNO_3 or NaOH. An aliquot of 5.0 mL of the supernatants is filtered, and the chromium concentration is determined using the 1,5-diphenylcarbazide (EPA 7196A) spectrophotometry method. The distribution coefficient (D), which is the ratio of Cr(VI) concentrations in solid and aqueous phases, is evaluated chromium retention. One can note that the eluted solution is discarded for successive volumes of 10 mL. The Adsorption of Cr(VI) ions by the biosorbent, eucalyptus barks, is examined according to the pH, the contact time,

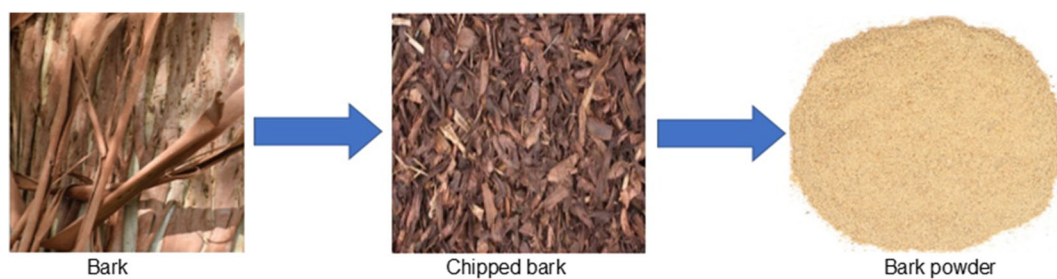


Fig 1. Raw eucalyptus barks material before and after initial preparation

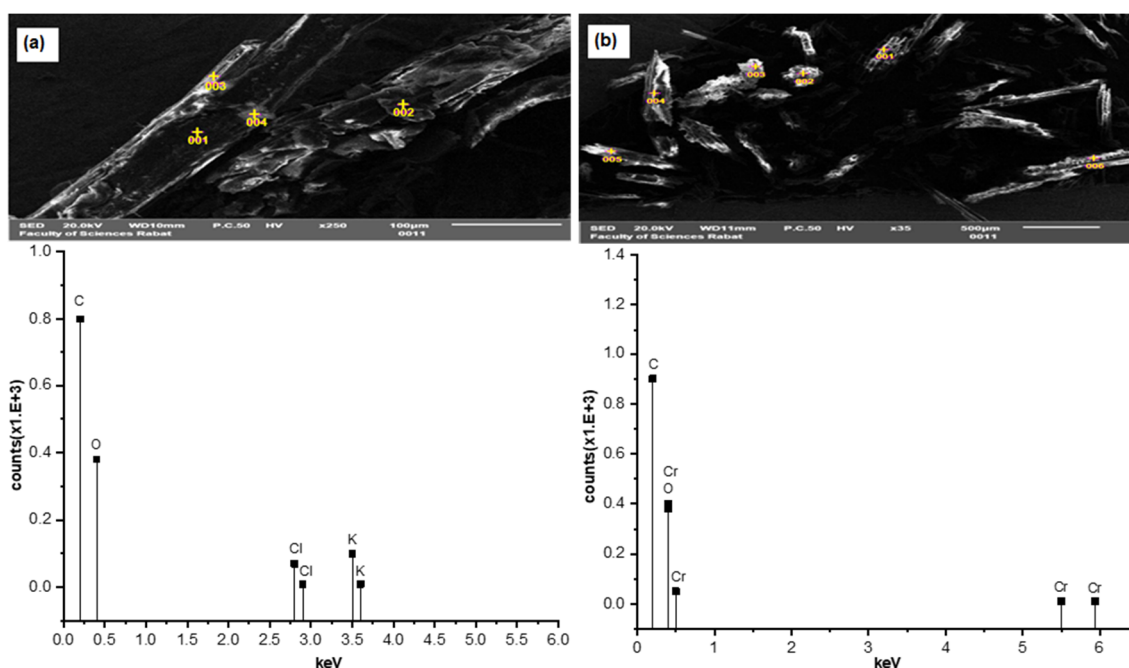


Fig 2. Surface images and EDX analysis of eucalyptus bark obtained by SEM (a) sample extracted with water only (b) eucalyptus bark in the presence of Cr(VI)

the suspension, and the mass of the biosorbent. The effect of pH on the partition of Cr(VI) between the solution and the solid phase is examined for various contact times [40].

Adsorption studies are carried out at room temperature as a function of pH and adsorbent dosage (m). Potassium dichromate solution (1×10^{-4} M) is channeled into the column at a flow rate of 5 mL/min, corresponding to 5×10^{-7} mol/min of Cr(VI).

■ RESULTS AND DISCUSSION

Surface Morphology of Eucalyptus Barks

The surface morphology of eucalyptus bark samples is studied by the scanning electron microscopy (SEM) technique. Fig. 2 shows the SEM micrograph and its

energy-dispersive X-ray spectroscopy (EDX) images obtained with 1000 \times magnification and a scale bar of 20 μ m. SEM images of the eucalyptus barks before and after Cr(VI) sorption are shown in Fig. 2; a comparison of these micrographs before and after Cr(VI) sorption shows that the adsorption of Cr(VI) occurs on the surface of the eucalyptus barks.

To examine the morphology of eucalyptus barks, SEM was applied, and the image is shown in Fig. 2; it is shown that the eucalyptus bark surface is porous and composed of (a), (b).

EDX analysis results of the eucalyptus barks with water only and in the presence of chromium(VI). As evident in Table 1 and Table 2.

Table 1. EDX results of the eucalyptus barks

Elements symbol	Mass%	Atom%
C	51.97	59.98
O	44.85	38.86
Cl	0.97	0.38
K	2.20	0.78

Table 2. EDX results of the eucalyptus barks in the presence of chromium(VI)

Elements symbol	Mass%	Atom%
C	56.19	63.21
O	40.91	34.24
Cr	2.53	0.79

Effect of pH on Chromium Adsorption

The effect of pH on chromium uptake was examined for different adsorbent dosages. As can be seen from Fig. 3 that the logarithmic variations of D decrease with increasing equilibrium pH. As found previously, Cr(VI) recovery is strongly acidic dependent and shows maximum retention, for various sorbent amounts, at pH around 2. As a consequence, this retention is attributed to HCrO_4^-

species that are predominant between pH 1 and 6.5 [40].

As shown, $\log D$ in the function of pH variations are best fitted ($R^2 > 95\%$) with second-order equations that are typical of anionic adsorption behavior, with a decreasing distribution coefficient when the pH is increased. The decrease in anionic adsorption by increasing pH was suggested to be due to competitive $-\text{OH}$ uptake and electrostatic repulsion [41]. Generally, it is assumed that the uptake of the weak acid is optimal at a pH value around its dissociation constant or near the Point of Zero Charge (PZC) of surface sorbent materials. For eucalyptus barks, PZC is found to be equal to 5.5 [42].

Therefore, electrostatic attraction of Cr(VI) to positively charged adsorbent sites prevails in the acidic medium of pH lower than. The variation in the removal efficiency with pH is linked, essentially, to hydrogen chromate (HCrO_4^-) species, predominating in an aqueous medium of pH lower than $\text{pKa}_2 = 6.5$. The value of $y = \frac{\delta \log D}{\delta \text{pH}}$ which ranges between 0.0 and -0.3, means that both electrostatic and chemical sorption mechanisms are occurring.

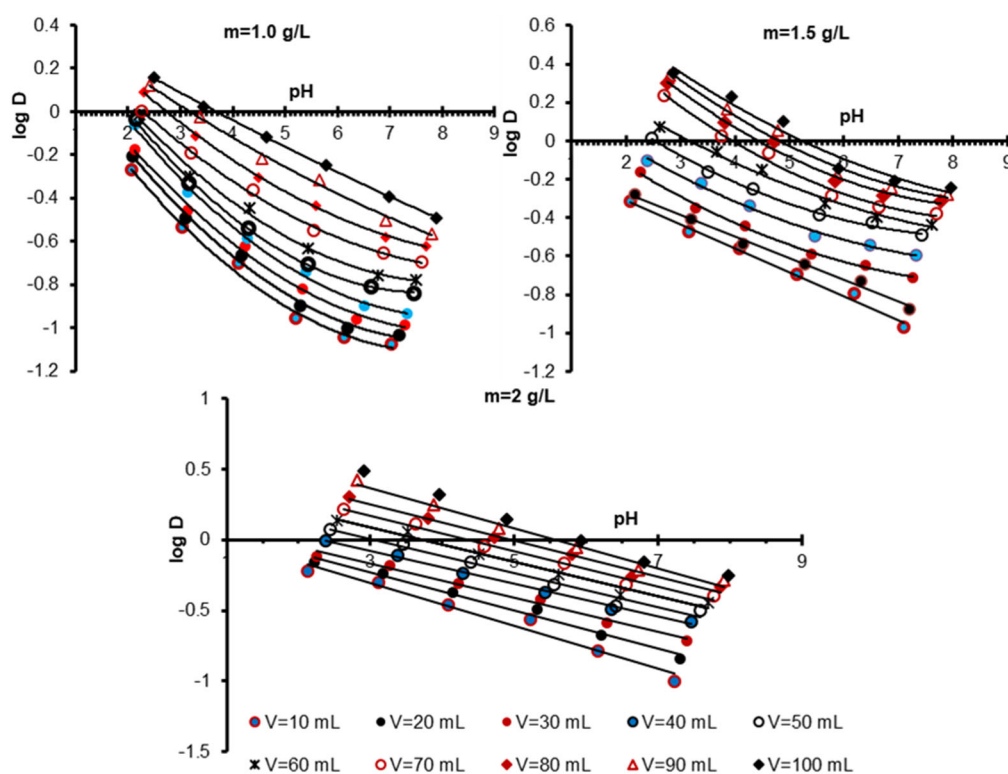


Fig 3. Variations of $\log D$ in the function of pH were obtained for various volumes of 1.0×10^{-4} M Cr(VI) solutions at sorbent $m = 1.0, 1.5,$ and 2.0 g/L. The flow rate is 5×10^{-7} mol/min of Cr(VI), which corresponds to 5 mL/min

The reuse of the biosorbent is tested in optimal conditions by regenerating the barks in 0.1 M NaOH solution. The results obtained show that the recovered adsorbent is reusable over more than seven cycles. Generally, it is assumed not possible to differentiate between these mechanisms [43]. The adsorption is highly dependent on the pH of the aqueous suspension; the Cr(VI) retention is maximal at low pH values. As a result, the eucalyptus barks are more suitable for Cr(VI) removal from acidic mediums such as chromium plating effluent, tannery effluent, and electroplating effluent, whose pH range between 1.0 and 2.2 [44]. Fig. 4 shows $\log D = f(n)$ obtained for various suspension amounts.

Experiment results show that the adsorption increases with the increasing sorbent mass. The lower slope value of about 0.2 of the obtained straight line reveals that the sorption of about 20% of Cr(VI) is carried out through the chemisorptions process. As shown previously, the predominant physical adsorption occurs by strong electrostatic interactions and Van Der Waals forces between the metal anion and the positively charged active sorption sites [46-47].

The slopes $\frac{\delta \log D}{\delta n}$ are varying between 5.8×10^{-8} and 9.3×10^{-8} . At a lower "n" (the mol chromium in eluate) value, adsorption efficiency increases slightly with sorbent amount. As discussed before, the biosorption of the oxyanion depends on the surface coverage (biosorbent dosage or sorbet/sorbent ratio). Indeed, a more pronounced effect of biosorbent dosage is observed at higher chromium coverage [45].

The biosorption of hexavalent chromium ions onto barks was achieved at pH 2.0 in the highest sorbet conditions corresponding to $n = 10^{-5}$ mol ($V = 100$ mL) is examined for various surface coverage. The results are shown in Fig. 5.

Fig. 6 shows the variations of the pH corresponding to 50% ($\text{pH}_{50\%}$) of chromium adsorption carried out with various surface coverage (n/m).

Obtained results show that the slopes of $\text{pH}_{50\%}$ in the function of $\left(\frac{n}{m}\right)$ curves are rising with sorbent amounts. At given "m" (sorbent amount), $\text{pH}_{50\%}$ increases with surface coverage to reach maximal value ($\text{pH}_{50\%}$) max, which decreases as $\left(\frac{n}{m}\right)$ continue to rise. Indeed, ($\text{pH}_{50\%}$) max of

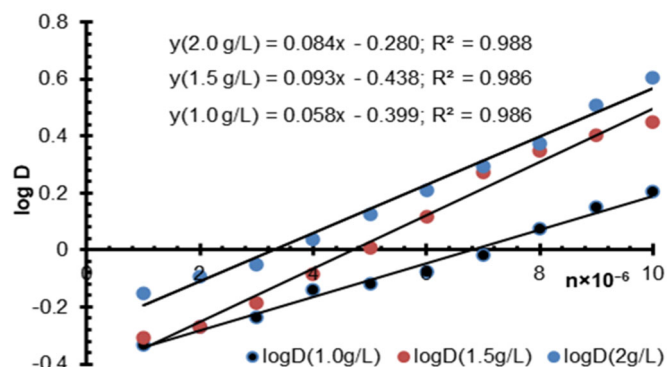


Fig 4. Variations of $\log D$ in the function of n obtained at pH = 2.0 for suspension mass of 1.0, 1.5, and 2.0 g/L at a flow rate of 5×10^{-7} mol/min of Cr(VI), which corresponds to 5 mL/min

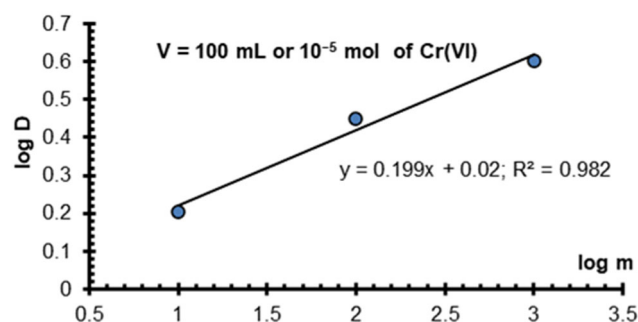


Fig 5. Variations of $\log D$ in the function of $\log m$ obtained at pH 2.0 at a flow rate of 5×10^{-7} mol/min of Cr(VI), which corresponds to 5 mL/min

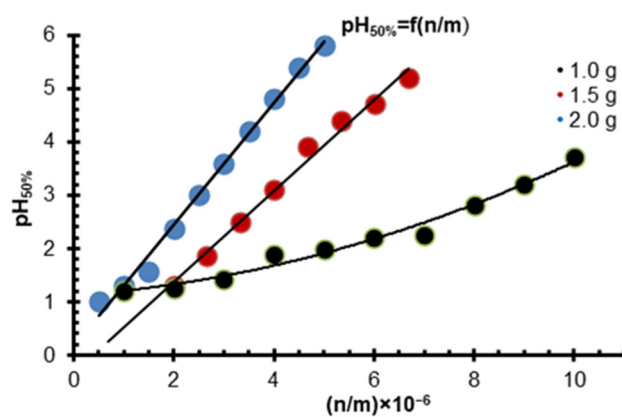


Fig 6. Variations of $\text{pH}_{50\%}$ in the function of $\left(\frac{n}{m}\right)$

about 4, 5, and 6 are reached at surface coverage of 1.0×10^{-5} , 6.7×10^{-6} , and 5.0×10^{-6} , respectively.

Chromium(VI) Adsorption Reactions

The distribution of chromium between sorbate and sorbent phases is expressed as a Cr(VI) biosorption

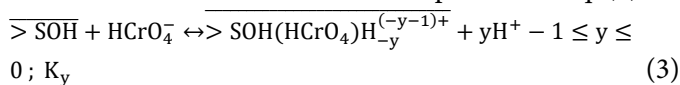
isotherms. These isotherms are often used to define the relationship between the mass of the sorbate and the mass of the sorbent. Several isotherm models are successfully used to analyze data of Cr(VI) biosorption. Nevertheless, the adsorption reactions are slightly, or not described. Recently, it has been shown that these reactions could be quantified from the logarithmic variation of the D, with equilibrium pH [48].

The variation in the sorption efficiency with the pH of the solution is correlated with the protonation and deprotonation reactions of both HCrO_4^- anion and surface groups (>SOH).

These reactions can be expressed in Eq. (1) and (2):



Considering that surface complexes are monodentate and taking into account that $y = \frac{\delta \log D}{\delta \text{pH}}$ was varying between -0.3 and 0, the adsorption reaction of hexavalent chromium on barks is expressed in Eq. (3):



H_{-1} and H_1 designate H^+ and OH^- , respectively.

This notation allows to write:



The surface complexation constant can be expressed in Eq. (5):

$$K_y = \frac{[\text{>SOH}(\text{HCrO}_4)_{\text{H}_{-y}}][\text{H}^+]^y}{[\text{>SOH}][\text{HCrO}_4^-]} \quad (5)$$

To simplify, the surface charge is omitted.

The distribution coefficient is expressed in Eq. (6):

$$D = \frac{[\text{>SOH}(\text{HCrO}_4)_{\text{H}_{-y}}]}{[\text{HCrO}_4^-]} \quad (6)$$

The used sorbent concentration is considered to be $[\text{>SOH}] = m$ (g/L) that it is obtained:

$$\log D = \log K_y + \log m + y\text{pH}; \quad (7)$$

Surface Complexes

The slope analysis method of $\log D = f(\text{pH})$ variations was used to define the nature of the surface complex noted as $C_y \equiv \text{>SOH}(\text{HCrO}_4)_{\text{H}_{-y}}$; Fig. 7 shows $|y| = [(\frac{\delta \log D}{\delta \text{pH}})_m] = f(\text{pH})$ graphs achieved for various sorbent mass and sorbet/sorbent ratio.

As it is indicated in Fig. 7, chromium ions, sorption exhibited differences in shape and surface complexes. Slopes different from zero were achieved at low surface coverage corresponding to $m = 1.0$ and 1.5 g/L, while for

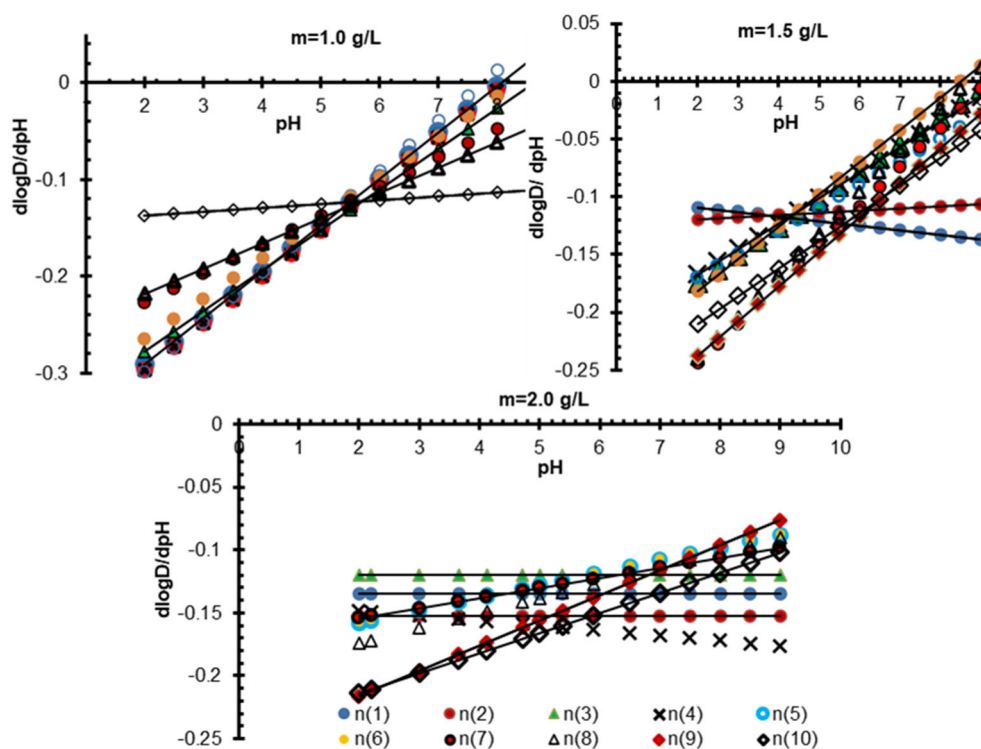


Fig 7. Variations of $y = (\frac{\delta \log D}{\delta \text{pH}})_m$ in the function of pH obtained at various amounts ($n(i)$) of Cr(VI); $n(i) = i \times 10^{-6}$ mol

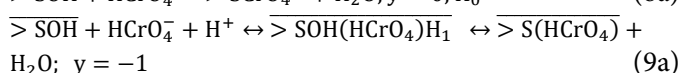
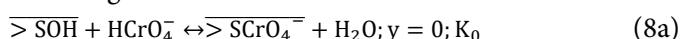
$m = 2.0$ g/L. This result was observed for $n(i)$ greater than 4×10^{-6} mol. The decimal value of H_3O^+ (y) stoichiometry coefficient is due to a partial exchange reaction which is combined with physisorption retention [25].

Indeed, at pH around 2, no more than 25% of chromium uptake is found to be occurring through a chemical exchange process. These results agreed with the previous study, suggesting that adsorption equilibrium associated with eucalyptus barks sorbents was mainly controlled by mass transfer and intraparticle diffusion processes. The common intersection point observed for a low sorbent mass of 1.0 g/L corresponds to the PZC found previously and which is 5.5. For this bark concentration, the retention mechanism of spontaneous nature occurring at pH 5.5 is more convenient for rapid chromium adsorption, as found before [42].

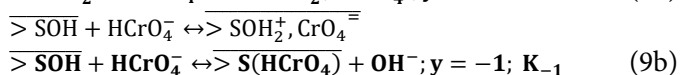
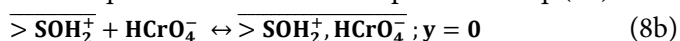
I taking this result into account, $\log D$ can be expressed in general as:

$$\log D = \log K_y + \log m + y pH \quad (7)$$

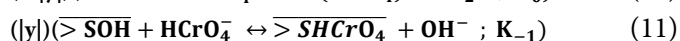
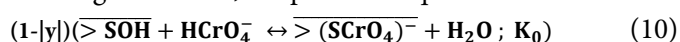
It is important to note that at pH 2, similar values of about 0.2 are obtained for $\left| \left(\frac{\delta \log D}{\delta pH} \right)_m \right|$ and $\left(\frac{\delta \log D}{\delta \log m} \right)_{pH}$. This would suggest that two sorption processes corresponding to $y = 0$ and -1 may contribute to the overall Cr(VI) retention. Therefore, we can conclude that chromium adsorption onto eucalyptus barks consists of physisorption and chemical adsorption due to the prevailing surface complexes described according to the following reactions:



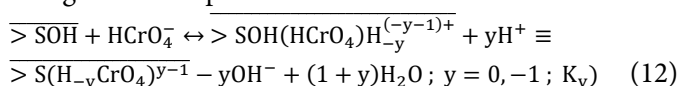
These equilibria could also be expressed in Eq. (8b):



Considering $|y|$ also the fraction 1OH^- (Hydroxyl ion) exchange reactions, the partition equilibrium is:



The global adsorption reaction was:



The apparent constants (K_y) is given by Eq. (13) and (14):

$$K_y = K_0^{(1-x)} K_1^x \quad (13)$$

$$\log K_y = (1-x)\log K_0 + x\log K_1 \quad (14)$$

Equilibrium Constants

The $\log(D)$ in the function of pH variations (Fig. 3) could also be shaped ($R^2 > 95\%$) with straight lines showing, for $m = 1.0$ g/L, slopes ranging from -0.2 to -0.06 . From the obtained results, it can be shown that the plots of $\log K_y$ in the function of y shown in Fig. 8 are linear in all examined conditions. The effect of pH and mass of sorbent on Cr(VI) sorption is described by Eq. (7):

$$\log D = \log K_y + \log m + y pH \quad (7)$$

The apparent constant (K_{ap}) of the overall equilibrium is given in the following equations in Eq. (15) and (16):

$$K_{ap} = (K_0)^{(1-|y|)} (K_{-1})^{|y|} \quad (15)$$

$$\log K_{ap} = (1-|y|)\log K_0 + |y|\log K_{-1} \quad (16)$$

$$\log K_{ap} = \log K_0 + |y|(\log K_{-1} - \log K_0)$$

$$\log K_0 = -0.76; \log K_{-1} - \log K_0 = -5.17; \log K_{-1} = -5.93$$

K_{ap} value could be obtained experimentally and is variable, depending on the pH and the surface charge. As a result, the constants K_0 and K_{-1} are the intercept and the slope of the linear plots of $\log K_{ap}$ in the function of y , respectively. For $y = -1$, which corresponds to OH^- release, Eq. (17) is obtained:

$$\log K_{ap} = \log K_{-1} \quad (17)$$

The constants K_0 and K_{-1} are respectively obtained from the intercept and the gradient of the linear plot of $\log K_{ap}$ versus ' y '. The logarithmic values are $\log K_0 = -0.76 \pm 0.13$ and $\log K_{-1} = -5.93 \pm 0.13$.

The changes of $\log K_{ap}$ in the function of y have to do with the contribution of the electrostatic effect K_{col} , which is related to surface potential [49].

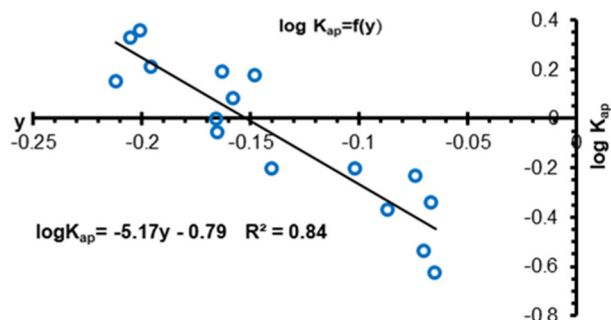


Fig 8. Variations of $\log K_{ap}$ in the function of y obtained at $m = 1.0$ g/L

According to Eq. (18):

$$\ln K_{col} = - \frac{|y| F \Psi_0}{RT} \quad (18)$$

Ψ_0 is the surface potential, and R (8.314), T (273 + 20), and F (96500) are the gas constant, absolute temperature, and Faraday constant, respectively.

The intrinsic adsorption reaction which was predominating in an acidic medium is of electrostatic nature (8b). As a consequence, the coulombic effect is determined by using the following equation obtained for $y = -1$:

$$\begin{aligned} \ln K_{col} = \ln K_0 = - \frac{F \Psi_0}{RT} \rightarrow \Psi_0 = - \frac{RT}{F} \ln K_0 = 0.025165 \times 0.76V \\ = 0.0191V \end{aligned} \quad (19)$$

$$\Psi_0 = 19.1mV$$

Weak Van der Waals forces contribute to physical adsorption, and its activation energy is not higher than the chemical sorption.

$$K_{ap} = K_0 (K_{col})^{-1} \quad (20)$$

For $x = 1$ we obtain:

$$\begin{aligned} K_{-1} = K_{10} (K_{col})^{-1} \rightarrow \log K_{-1} = \log K_0 - \ln K_{col} \rightarrow \ln K_{col} \\ = \log K_0 - \log K_{-1} = -0.76 + 5.93 = 5.17 \end{aligned}$$

Moreover, Cr(VI) removal using modified biomaterials such as activated carbon from tamarind wood and coconut shell, phosphate-treated sawdust, coconut husk, palm pressed fibers, oil palm endocarp, and *Leucaena leucocephala* waste sawdust was documented [35]. However, many of these readily available adsorbents showed a limit of adsorption capacity and could not be reused (Table 3). Therefore, it is always interesting to search for new low-cost adsorbents suitable for practical

application in a large-scale operation.

Response Surface Analysis

The mathematical models for the chrome, Cr(VI), surface complexes with eucalyptus barks were used to build response surfaces and determine the process's optimal conditions. 3D response surfaces plots for the significant interaction.

Fig. 9 presents the For the chrome, Cr(VI), surface complexes with eucalyptus barks, the most significant interactions were the m, pH, V, and log (D). Fig. 9(a) indicates that the chrome number increased with the increase of activation D and m ratio with decreased pH; Fig. 9(b) shows that the chrome number increased with the increase of the impregnation ratio and decrease of activation time when the volume is fixed at 90 mL. The most significant interaction for the V 90 mL index was log D and activation pH. From Fig. 9(b), it can be observed that the chrome index increased with the increase of the activation log D and the pH. The maximal chrome index response was obtained at the volume of 10 mL.

For the V 10 mL index, the same significant interactions are found in the insertion of chrome, including log D and pH. From Fig. 9(c), it can be observed that the chrome insertion increased with the increase of the m and log D. The maximal chrome responses were obtained at a volume of 10 mL. Fig. 9(c) shows that the sodium increased with decreased log D and decreased pH in case the volume is fixed at 10 mL.

Table 3. The adsorption capacity of eucalyptus barks to the other published low-cost adsorbents for Cr(VI) removal

Adsorbent	Maximum Cr(VI) concentration (mg/L)	pH	Adsorption capacity (mg/g)	Reference
Eucalyptus barks	200	2	3.940	This study for Cr(VI)
Mixed waste tea	250	2	94.34	[50]
Coffee ground	250	2	87.72	[50]
Peanut shell	100	4	8.31	[51]
Coconut shell charcoal	25	4	10.38	[51]
Treated waste newspaper	50	3	59.88	[52]
Walnut shell	100	2	40.83	[53]
Fertilizer industry waste	100	4	15.24	[54]
Rice husk	100	2	13.1	[55]
Tamarind hull-based	50	2	81	[56]

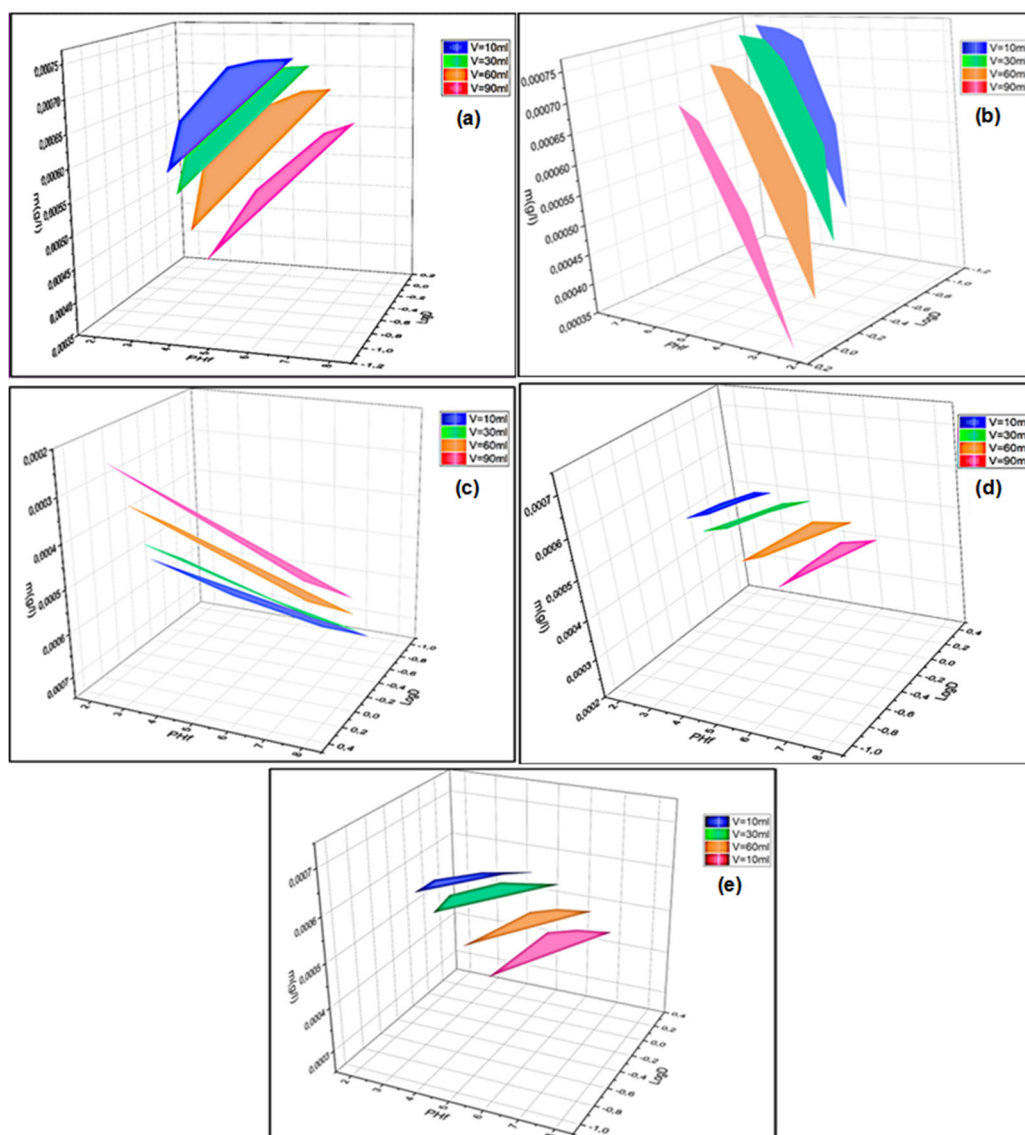


Fig 9. Surface response plots for the chrome, Cr(VI) surface complexes with eucalyptus bark surface response plots

■ CONCLUSION

Thorough research was done on the adsorption of hexavalent chromium Cr(VI) on eucalyptus barks. The sorption mechanism was evaluated as a function of solution pH for different adsorbent dosages, surface coverage, and the amount of adsorbent. The chromium retention is evaluated by the distribution coefficient D . It is obviously seen from obtained variations at a given suspension mass (m) that Cr(VI) adsorption is strongly volume-dependent and increases with an increase in n . The slopes $\frac{\delta \log D}{\delta n}$ are varying between 5.8×10^{-8} and 9.3×10^{-8} . At a lower n value, adsorption efficiency increases

slightly with sorbent amount. As discussed before, the biosorption of the oxyanion is dependent on the surface coverage. The study of $\log D = f(\text{pH})$ experimental data, the Cr(VI) retention is maximal at low pH values. As a consequence, this retention is attributed to HCrO_4^- species which are predominant between pH 1 and 6.5. Therefore, eucalyptus bark exhibited high adsorption capacity for Cr(VI).

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