

# Simulation and optimization of hexavalent chromium adsorption on autohydrolyzed Scots Pine (*Pinus Sylvestris*) sawdust in batch and fixed-bed systems

Dimitrios Sidiras and Dorothea Politi

**Abstract**—In this work, column kinetics of Cr(VI) adsorption on autohydrolyzed (160-240 °C, 0-50 min) Scots pine (*Pinus sylvestris* L.) sawdust were simulated, in order to optimize the potential use of this material for wastewater cleaning. The effect of the autohydrolysis time and temperature on the microstructure and the crystallinity of pine sawdust was investigated by means of SEM, FTIR, XRD and BET. The Modified dose response (MDR) adsorption column capacity  $q_0$  increased from 0.6376 to 23.71 mg.g<sup>-1</sup>, indicating that autohydrolysis treatment at 240 °C for 50 min optimizes the adsorption behavior of the material.

**Keywords**—adsorption, autohydrolysis, chromium, sawdust, column

## I. Introduction

Industrialization has been contaminating water resources by discharging heavy metals and color. Adsorption is widely used for removal of metals and color from wastewater. Activated carbon is a common adsorbent for the reclamation of municipal and industrial wastewater. The high cost of activated carbon has prompted research on suitable low-cost adsorbents, currently focusing on the use of low cost commercially available lignocellulosic materials (wood sawdust and agricultural residues) as viable substitutes for activated carbon [1-5].

Heavy metals in the aquatic environment have been of great concern because of discharges increase, their toxicity, and other adverse effects on the receiving water. Some of them are cumulative poisonous capable of being assimilated, stored, and concentrated by organisms that are exposed to low concentrations of these substances for long periods or repeatedly for short periods. Safe and effective cleaning/disposal of wastewater is always a challenging task due to the fact that cost-effective treatment alternatives are not presently available. The industrial wastewater treatment processes include reduction precipitation, ion exchange,

electrochemical reduction, evaporation, reverse osmosis, direct precipitation. These methods, involve large exposed liquid surface area and long detention periods. Besides, they need high capital cost and recurring expenses such as chemicals, which are not suitable for small-scale industries [6].

Hexavalent chromium exhibits high toxicity. Industrial sources of Cr(VI) include leather tanning, cooling tower blowdown, plating, electroplating, anodizing baths, rinse waters, etc. The sorption capacities of commercial developed carbons and low-cost alternative sorbents for tri- and hexavalent chromium remediation have been studied by numerous researchers [7], and the mechanisms of adsorption on various adsorbents have been established. Chromium's impact on environmental quality, sources of chromium pollution and toxicological / health effects have been, also, investigated.

More specifically, untreated and pretreated lignocellulosic industrial byproducts and agricultural residues have been employed as adsorbents for hexavalent chromium removal from water. These materials include sawdust [4, 8-10], coir pith [10], oil palm fibre [11], olive bagasse [12], wheat straw carbon [13], barley straw carbon [13], pistachio hull [14], leaf mould [15], wheat bran [16], cotton stalk peel [17], walnut shell [18], walnut hull [19], hazelnut shell [18], almond shell [18], rice bran [20], rice husk [10], soybean hulls [21], eucalyptus bark [22], Tamarindus indica seeds [23], short-chain polyaniline synthesized on jute fiber [24], tea factory waste [25], spent mushroom modified by cationic surfactant [26], and olive stone [27].

Furthermore, since lignocellulosic materials are used in the bioethanol industry as source of sugars [28], the process solid residue can be implemented as adsorbent. Autohydrolysis is frequently used to increase the efficiency of lignocellulosics' enzymatic hydrolysis to sugars [29]. Many industrial byproducts and agricultural residues can be autohydrolyzed for the sugars production [30]. The autohydrolysis solid residue can be efficiently used as adsorbent as it has been proved in the case of some basic dyes [31, 32].

In this work, a low cost adsorbent with high capacity is presented, suitable for the efficient removal of hexavalent chromium from water and wastewater. The adsorbent was produced from autohydrolysis of Scots Pine sawdust. The effect of the autohydrolysis conditions on the microstructure and the crystallinity of pine sawdust was determined using SEM, FTIR, XRD and BET surface area techniques. The column adsorption kinetics of Cr(VI) were used to estimate and compare the adsorption capacity of the untreated and pretreated pine sawdust.

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## II. Materials and Methods

### A. Material development

The Scots Pine (*Pinus Sylvestris*) sawdust used was obtained from a local furniture manufacturing company, as a suitable source for full-scale/industrial applications. The moisture content of the material when received was 8.7% w/w; after screening, the fraction with particle sizes between 0.2 and 1 mm was isolated. The composition of the raw material was as follows (expressed in % w/w on a dry weight basis): 40.1% cellulose measured as glucan (with 52.5% XRD degree of crystallinity); 28.5% hemicelluloses (16.0% measured as manan, 8.9% measured as xylan and the rest 3.6% measured as arabinan); 27.7% Klason acid-insoluble lignin, 0.2% ash, and 3.5% extractives and other acid soluble components (e.g. acid soluble lignin).

The autohydrolysis process was performed in a 3.75-L batch reactor PARR 4843. The isothermal hydrolysis times were 0, 10, 20, 30, 40 and 50 min (not including the non-isothermal preheating and the cooling time-periods); the reaction was catalyzed by the organic acids produced by the pine sawdust itself during autohydrolysis at a liquid-to-solid ratio of 10:1; the liquid phase volume (water) was 2000 mL and the solid material dose (pine sawdust) was 200 g; stirring speed 150 rpm. The reaction ending temperature values were 160°C, 200°C and 240°C, reached after 42, 62 and 80 min preheating time values, respectively.

### B. Column studies

Fixed-bed up-flow adsorber studies were conducted in a 15 cm internal height × 2.5 cm internal diameter stainless steel column. The experimental set-up consisted of one column, fed by a multi-channel peristaltic pump at constant flow rates of 10, 20, 30, 40 mL min<sup>-1</sup>. The initial constant Cr(VI) concentration was 75.0 mg L<sup>-1</sup>. Interconnective tubing and fittings were made of polytetrafluoroethylene (PTFE). Effluent samples were analyzed to yield output concentration breakthrough curves.

### C. Analytical techniques

The degree of crystallinity of pine sawdust cellulose was measured by X-ray diffraction, according to the Segal et al. method [33]. The powder X-ray diffraction (XRD) patterns of the untreated and the pretreated samples were measured by a SIEMENS D5005 X-Ray Diffractometer using Ni-filtered CuKα (λ=0.154 nm) radiation at 45 kV and 40 mA and continuous scan mode. The XRD patterns were recorded in the scan range 2θ=5-70, at scan rate step=0.04°, dwell time=3 sec, i.e. total scan time approximately 1 h and 30 min.

The quantitative saccharification of the original and the autohydrolyzed material was carried out according to the Saeman et al. [34] technique. The filtrates from the quantitative saccharification were analyzed for glucose, xylose and arabinose using high-performance liquid chromatography (HPLC, Agilent 1200) with Aminex HPX-87H Column,

refractive index detector and 5 mM H<sub>2</sub>SO<sub>4</sub> in water as the mobile phase in order to estimate the cellulose and hemicelluloses. Finally, the acid-insoluble Klason lignin was determined according to the Tappi T222 om-88 method [34].

The BET (Brunauer, Emmet and Teller) surface area of the original and the pretreated pine sawdust was measured from the N<sub>2</sub> adsorption isotherm with a Nova® Surface Area Analyzer (Quantachrome Instruments) in accordance with DIN 66132 [35].

The scanning electron microscope (SEM) used herein was a JEOL JSM-6700F Field Emission Scanning Electron Microscopy. The SEM tests were carried out on Pt coated (5 nm) samples. The magnifications were 7500 and 50000.

Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (MAGNA-IR 750 Spectrometer, Serrie II, Nicolet). The sampling technique used herein was diffuse reflectance. The powder samples were scanned for wavenumber 650-4000 cm<sup>-1</sup>.

The concentration of Cr(VI) was measured by using a HACH DR4000U UV-visible spectrophotometer, according to the Method 8023 (1,5-Diphenylcarbohydrazide Method) HACH DR/4000 PROCEDURE, CHROMIUM, HEXAVALENT.

## III. Results and Discussion

### A. Autohydrolysis

Cellulose crystallinity, accessible surface area, protection by lignin, and sheathing by hemicelluloses, all contribute to lignocellulosic biomass resistance to autohydrolysis [28-31]. Autohydrolysis of cellulose and hemicelluloses produces glucose, xylose and degradation products as 5-HMF and furfural, respectively. The autohydrolysis is affected by temperature and reaction time. Cellulose fractions are hydrolyzed to water-soluble cellulo-oligosaccharides and glucose, hemicelluloses are hydrolyzed to xylo-oligosaccharides and xylose and acid-insoluble lignin fraction is not affected by autohydrolysis.

The solid residue yield and the composition of the autohydrolyzed pine sawdust (dry weight of product % w/w of the original dry material) are presented in Table I, as a function of autohydrolysis time. The hemicelluloses percentage of the autohydrolyzed pine sawdust was significantly decreased by autohydrolysis intensification.

The cellulose percentage of the pretreated sawdust reached a maximum of 50.3% w/w at 200°C for 50 min. The lignin percentage of the solid residue increased up to 62.4% w/w at 240 °C for 50 min.

### B. Microstructure

The SEM micrographs for untreated autohydrolyzed (at 160, 200 and 240 °C for 40 min) pine sawdust are given in Fig. 1. The magnifications were 7500 for Fig. 1a, c, e, g and 50000 for Fig. 1b, d, f, h. The texture of the pretreated materials was rougher than that of the untreated sawdust.

TABLE I. SOLID RESIDUE YIELD, COMPOSITION AND BET SURFACE AREA OF THE AUTOHYDROLYZED PINE SAWDUST AS A FUNCTION OF THE AUTOHYDROLYSIS TIME AT 160-240 °C.

| Time, $t_{ai}$<br>(min)                           | 160 °C | 200 °C | 240 °C |
|---|--------|--------|--------|
| <b>Solid residue yield (% w/w)</b>                |        |        |        |
| -   | 100.0  | 100.0  | 100.0  |
| 0   | 94.1   | 80.1   | 65.4   |
| 10  | 90.7   | 76.8   | 60.0   |
| 20  | 88.3   | 75.0   | 56.3   |
| 30  | 84.7   | 72.1   | 54.7   |
| 40  | 85.6   | 70.9   | 45.8   |
| 50  | 83.9   | 68.5   | 44.6   |
| <b>Cellulose (% w/w)</b>                          |        |        |        |
| -   | 40.1   | 40.1   | 40.1   |
| 0   | 42.6   | 48.6   | 44.2   |
| 10  | 44.2   | 49.1   | 44.1   |
| 20  | 45.4   | 49.2   | 33.5   |
| 30  | 47.3   | 49.5   | 30.1   |
| 40  | 46.9   | 49.2   | 22.8   |
| 50  | 47.8   | 50.3   | 18.9   |
| <b>Hemicelluloses (% w/w)</b>                     |        |        |        |
| -   | 28.5   | 28.5   | 28.5   |
| 0   | 28.2   | 10.7   | 0      |
| 10  | 23.9   | 5.9    | 0      |
| 20  | 19.1   | 2.3    | 0      |
| 30  | 17.2   | 1.0    | 0      |
| 40  | 15.3   | 0.3    | 0      |
| 50  | 14.6   | 0.2    | 0      |
| <b>Lignin (% w/w)</b>                             |        |        |        |
| -   | 27.7   | 27.7   | 27.7   |
| 0   | 29.9   | 34.9   | 42.4   |
| 10  | 31.4   | 36.6   | 47.0   |
| 20  | 31.9   | 37.8   | 49.6   |
| 30  | 33.1   | 39.1   | 51.4   |
| 40  | 33.0   | 39.8   | 60.8   |
| 50  | 33.2   | 40.6   | 62.4   |
| <b>BET surface area (<math>m^2 g^{-1}</math>)</b> |        |        |        |
| -   | 0.894  | 0.894  | 0.894  |
| 0   | 2.510  | 3.622  | 5.290  |
| 10  | 2.621  | 3.703  | 7.011  |
| 20  | 2.802  | 3.812  | 10.093 |
| 30  | 2.911  | 4.023  | 10.998 |
| 40  | 2.943  | 4.578  | 19.075 |
| 50  | 3.055  | 5.109  | 19.202 |

Roughness was increasing by increasing the autohydrolysis severity (e.g. autohydrolysis temperature) as it can be easily observed at magnification 50000. Moreover, the opening of the lignocellulosic structure and the presence of larger pores

can be, also, observed. These changes of the lignocellulosic matrix seem reasonable, taking into account that the pretreated material has a high lignin percentage (see Table 1) with more open Klason lignin structure. The rough surface, the open structure and the larger pores of the autohydrolyzed pine sawdust explains its enhanced adsorption properties. In Fig. 2 we present the SEM micrographs for untreated pine sawdust before and after Cr(VI) adsorption. The adsorption conditions were 23 °C,  $C_0=75 \text{ mg L}^{-1}$ ,  $m/V=4 \text{ g L}^{-1}$ ,  $pH=2.0$  and agitation speed=300 rpm. The texture of the sawdust after Cr(VI) adsorption seems more rough and shows a higher contrast than before Cr(VI) adsorption. This is more obvious at magnification 50000, and it is obviously due to the adsorption of Cr(VI) on the pine sawdust surface.

### C. Surface Chemistry

The cell walls of pine sawdust consist mainly of cellulose hemicelluloses, lignin and many hydroxyl groups, such as tannins or other phenolic compounds. Lignin is a polymer material that is built up from the phenyl propane nucleus, an aromatic ring with a three-carbon side chain. Tannins are complex polyhydric phenols that are soluble in water and have the property of precipitating protein. The FTIR spectra of the untreated pine sawdust and the autohydrolyzed at 160, 200 and 240 °C for 0 and 40 min pine sawdust are given in Fig. 3a. The FTIR spectra of sawdust show that some peaks were shifted. In the case of the untreated pine sawdust, there is a strong peak at wavenumber  $3471 \text{ cm}^{-1}$  representing the  $-OH$  stretching of phenol group of cellulose and lignin, whereas the peaks at  $2939 \text{ cm}^{-1}$  and  $2146 \text{ cm}^{-1}$  indicate the presence of  $-CH_2$  stretching of aliphatic compound and  $-NH$  stretching, respectively. The appearance of peaks at  $1741 \text{ cm}^{-1}$  and  $1612 \text{ cm}^{-1}$  imply the presence of  $C=O$  stretching of aldehyde group and  $C=C$  stretching of phenol group, respectively. The peaks at  $1516 \text{ cm}^{-1}$  can be due to  $C=C$  of aromatic ring. Peaks at  $1470 \text{ cm}^{-1}$  and  $1437 \text{ cm}^{-1}$  suggest  $-CH_2$  bending and  $-OH$  bending, respectively. The peak at  $1372 \text{ cm}^{-1}$  shows  $C-O-H$  bending. Peaks at  $1286 \text{ cm}^{-1}$  and  $1140 \text{ cm}^{-1}$  can be due to  $C-O$  stretching of phenolic group and six-member cyclic ether group of cellulose, respectively. These wavenumber values are very close to those reported for pine sawdust by Wang et al. [37] and for meranti sawdust by Ahmad *et al.* [38].

In addition, the pretreated with autohydrolysis pine sawdust shows a strong peak shift towards the region  $3354-3412 \text{ cm}^{-1}$  representing the  $-OH$  stretching of phenol group of cellulose and lignin. The peak shift towards the region  $2065-2139 \text{ cm}^{-1}$  indicates the presence of  $-NH$  stretching, whereas the appearance of peak shift towards the region  $1701-1738 \text{ cm}^{-1}$  indicates the presence of  $C=O$  stretching of aldehyde group. The peak shift towards the region  $1425-1450 \text{ cm}^{-1}$  can be attributed to  $-OH$  bending. The peak shift towards the region  $1065-1120 \text{ cm}^{-1}$  can be due to six member cyclic ether group of cellulose. The new peak at  $822 \text{ cm}^{-1}$  suggests the presence of aromatic  $C-H$  deformation. These shifts observed in the FTIR spectrum imply the changes of the respective functional groups on the surface of autohydrolyzed pine sawdust.

As regards the untreated pine sawdust after Cr(VI) adsorption (23 °C,  $C_0=75 \text{ mg L}^{-1}$ ,  $m/V=4 \text{ g L}^{-1}$ ,  $pH=2.0$ ,



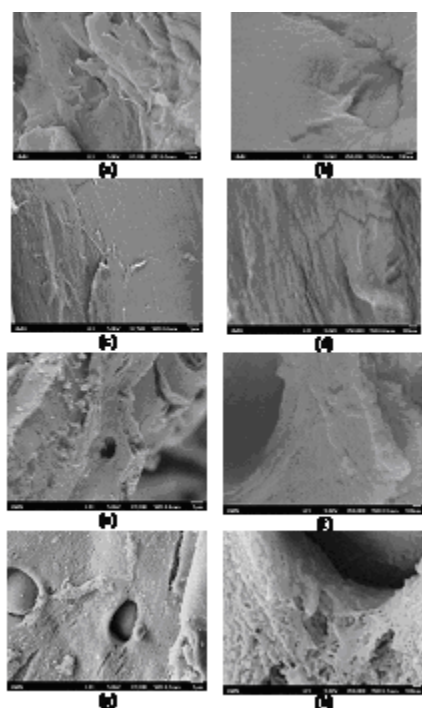


Figure 1. SEM micrographs for untreated (a, b) and autohydrolyzed at 160 °C (c, d) 200 °C (e, f) and 240 °C (g, h) pine sawdust (autohydrolysis isothermal time 40 min).

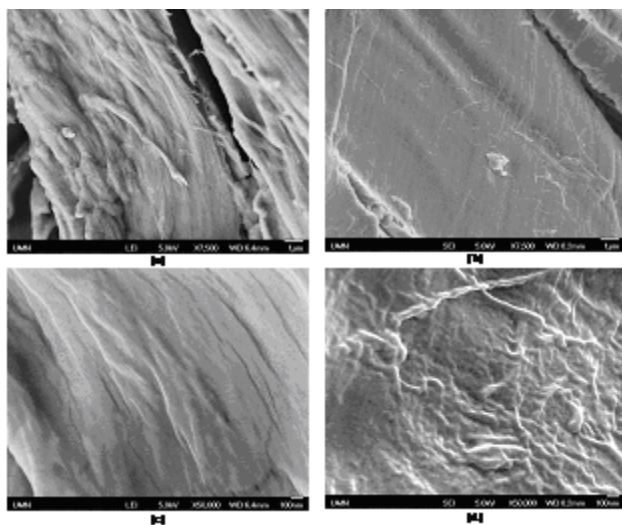


Figure 2. SEM micrographs for untreated pine sawdust before (a, c) and after Cr(VI) adsorption (b, d).

agitation speed=300 rpm), there is a strong peak shift at wavenumber  $3386\text{ cm}^{-1}$  representing the  $-\text{OH}$  stretching of phenol group of cellulose and lignin, and a peak shift at  $2904\text{ cm}^{-1}$  indicating the presence of  $-\text{CH}_2$  stretching of aliphatic compound (Fig. 3b). The peak shift at  $1452\text{ cm}^{-1}$  can be attributed to  $-\text{CH}_2$  bending. Peaks shift at  $1271\text{ cm}^{-1}$  and  $1117\text{ cm}^{-1}$  can be due to  $\text{C}-\text{O}$  stretching of phenolic group and six-member cyclic ether group of cellulose, respectively.

Moreover, a strong peak shift at wavenumber  $3417\text{ cm}^{-1}$  appears in the autohydrolyzed (240 °C, 40 min) pine sawdust

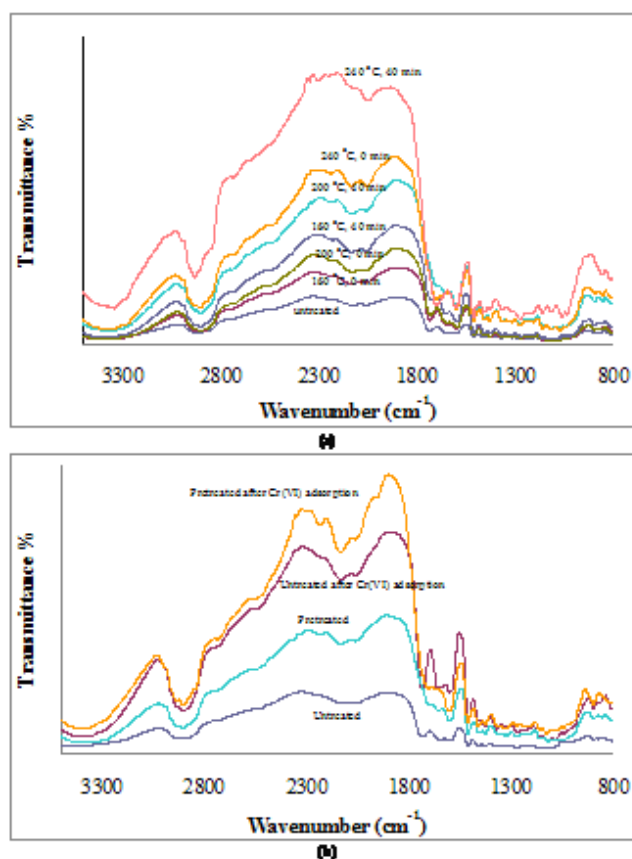


Figure 3. FTIR spectra of (a) untreated and autohydrolyzed at 160, 200 and 240 °C for 0 and 40 min sawdust, and (b) untreated and autohydrolyzed at 200 °C for 40 min sawdust before and after Cr(VI) adsorption.

after Cr(VI) adsorption (Fig. 3b), representing the  $-\text{OH}$  stretching of phenol group of cellulose and lignin, and a peak shifted at  $2906\text{ cm}^{-1}$  indicate the presence of  $-\text{CH}_2$  stretching of aliphatic compound. The peak shift at  $2135\text{ cm}^{-1}$  implies the presence of  $-\text{NH}$  stretching. The appearance of peak shift at  $1593\text{ cm}^{-1}$  shows the presence of  $\text{C}=\text{C}$  stretching of phenol group. The peak shift at  $1427\text{ cm}^{-1}$  can be attributed to  $-\text{OH}$  bending. The peak shift at  $1126\text{ cm}^{-1}$  can be due to six-member cyclic ether group of cellulose.

The peak shifts observed in the FTIR spectra of the untreated and autohydrolyzed sawdust before and after Cr(VI) adsorption suggest some changes of functional groups on the surface of the sawdust that can be attributed to bonding with the adsorbed Cr(VI).

#### D. Crystalline structure

An excellent X-ray diffraction is suitable to analyze the crystallinity of cellulose in wood. Fig. 4 shows the XRD patterns of the untreated pine sawdust and of the autohydrolyzed at 240 °C for 40 min (+80 min preheating period) pine sawdust. Two broad peaks at the  $2\theta$  values of around  $16^\circ$  and  $22^\circ$  for the untreated sawdust were due to the 1 0 1 and 0 0 2 lattice spacing of cellulose in wood [31]. For the autohydrolyzed sawdust, these two peaks became low-height and broad, suggesting structural destruction of crystalline cellulose, in accordance with a sharp weight loss at

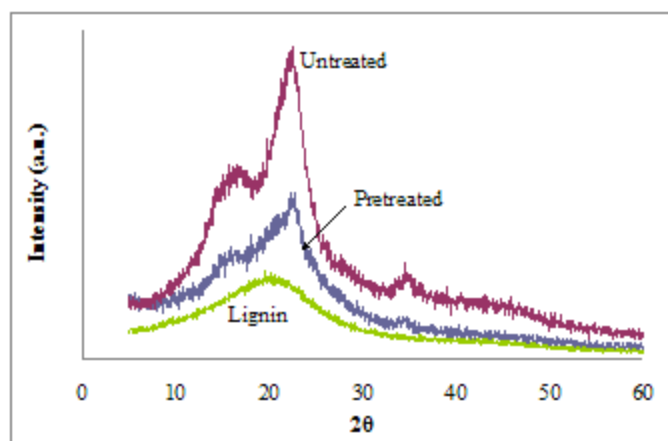


Figure 4. XRD patterns of untreated pine sawdust, autohydrolyzed at 240 °C for 40 min pine sawdust and Klason Lignin produced from untreated sawdust.

these conditions (Table I). The obtained rich-to-lignin material is relatively amorphous. Klason Lignin obtained from the pine sawdust gives a very broad peak at the  $2\theta$  value of around  $20^\circ$ . This  $2\theta$  value is close to that of amorphous cellulose produced by ball milling.

### E. BET surface area as affected by the autohydrolysis conditions

The surface area (in  $\text{m}^2\cdot\text{g}^{-1}$ , measured by the BET method) experimental data are given in Table I as a function of the autohydrolysis time at  $160$ – $240^\circ\text{C}$ . The effect of autohydrolysis is not significant at  $160^\circ\text{C}$  and only moderate at  $200^\circ\text{C}$ . The BET surface area is increasing significantly for autohydrolysis at  $240^\circ\text{C}$ . The efficient removal of the hemicelluloses and the amorphous part of cellulose results in ‘opening’ of the pores of the structure of the lignocellulosic matrix [5, 29]. This phenomenon, and the rough texture (see the SEM micrographs in Fig. 1 and 2), increases the BET surface area of the material, which accounts partly for the advanced adsorption properties of the autohydrolyzed sawdust over the untreated one.

### F. Column studies

For the adsorption column experiments the ‘bed depth service model’ developed by Bohart and Adams [39] is commonly used as follows

$$\ln\left(\frac{C_i}{C} - 1\right) = \frac{K \cdot N \cdot x}{u} - K \cdot C_i \cdot t \quad (1)$$

where  $C$ =effluent concentration ( $\text{mg}\cdot\text{L}^{-1}$ );  $C_i$ =influent concentration ( $\text{mg}\cdot\text{L}^{-1}$ );  $K$ =adsorption rate coefficient ( $\text{L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ );  $N$ =adsorption capacity coefficient ( $\text{mg}\cdot\text{L}^{-1}$ );  $x$ =bed depth (cm);  $u$ =linear velocity ( $\text{cm}\cdot\text{min}^{-1}$ ); and  $t$ =adsorption time (min).

Robert Clark [40] has developed an alternative to the ‘simple logistic function’, called the ‘generalized logistic function’, which incorporates the parameter  $n$  of the Freundlich adsorption isotherm:

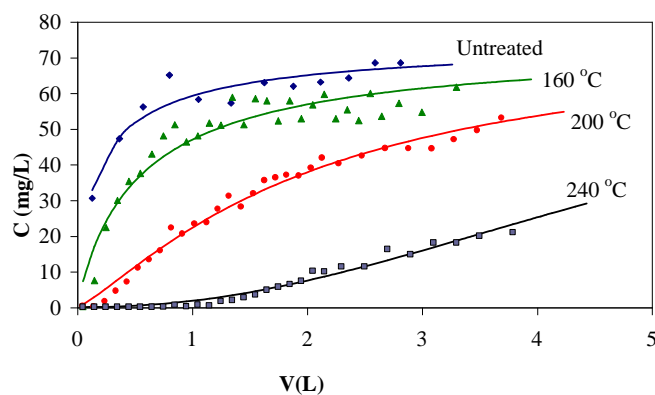


Figure 5. Breakthrough curves for fixed beds of untreated and autohydrolyzed (at  $160$ ,  $200$  and  $240^\circ\text{C}$  for 50 min pine sawdust.)

$$C = \left[ \frac{C_i^{n-1}}{1 + Ae^{-rt}} \right]^{\frac{1}{n-1}} \quad (2)$$

where  $n$  is the Freundlich isotherm parameter;  $A = e^{K \cdot N \cdot x / u}$ ;  $r = K \cdot C_i$ . Transforming and linearizing (2), we obtain:

$$\ln\left[\left(\frac{C_i}{C}\right)^{n-1} - 1\right] = \ln A - r \cdot t \quad (3)$$

For  $n=2$ , we obtain the Bohart–Adams model given by (1), which can be rewritten under the form of the logistic (symmetric sigmoid) model, this expression is reduced to

$$C = \frac{C_i}{1 + Ae^{-rt}} \quad (4)$$

$K$ ,  $N$  can be calculated from the equations  $K = r/C_i$  and  $N = u \ln A / (xK) = C_i u \ln A / (x r)$ , while the values of  $A$  and  $r$  can be estimated by NLRA from the column effluent data ( $C_i = 75 \text{ mg}\cdot\text{L}^{-1}$  for the cases presented in Fig. 5). The effluent Cr(VI) solution volume  $V$  (in L) is  $V = Q \cdot t$ , where  $Q$  is the Cr(VI) solution flow rate, equal to  $20 \text{ mL}\cdot\text{min}^{-1}$ . The theoretical estimations sufficiently simulate the experimental data.  $N$  was found to be  $4744 \text{ mg}\cdot\text{L}^{-1}$  for the autohydrolyzed pine sawdust (at  $240^\circ\text{C}$  for 50 min), i.e., much higher than the  $N = 451 \text{ mg}\cdot\text{L}^{-1}$  for the untreated one. In addition,  $K$  was found to be  $0.000242 \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$  for the autohydrolysis-treated material, i.e., very close to the  $K = 0.000241 \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$  for the untreated one. The  $SEE$ -values are given in Table II. The fitting of the Bohart–Adams model to experimental data was better than the fitting of the Clark model. In general, for autohydrolysis time equal to 50 min,  $N$ -value was found to be given by the following equation

$$N = 331.0e^{0.0158T_{\text{au}} - 100} \quad (5)$$

where  $T_{\text{au}}$  is the autohydrolysis temperature in  $^\circ\text{C}$ . In this case  $R^2 = 0.8218$  and  $K = 0.00031 \pm 0.00013 \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ .

The Thomas [41] model is one of the most widely used models in the column performance theory. The main

TABLE II. PARAMETERS AND VALUES OF SEE, WHEN NLRA IS USED, FOR THE ALTERNATIVE COLUMN MODELS CONSIDERED HEREIN.

| $T_{0a}$  | Bohart-Adams           |                                 |        | Modified Dose-Response   |           |       |
|-----------|------------------------|---------------------------------|--------|--------------------------|-----------|-------|
|           | $N$<br>( $mg L^{-1}$ ) | $K$<br>( $L mg^{-1} min^{-1}$ ) | $SEE$  | $q_0$<br>( $mg g^{-1}$ ) | $a_{mdr}$ | $SEE$ |
| untreated | 451.1                  | 0.00024                         | 13.091 | 0.6376                   | 0.7569    | 2.107 |
| 160       | 616.0                  | 0.00051                         | 7.582  | 2.181                    | 0.9241    | 4.455 |
| 200       | 1055.6                 | 0.00027                         | 7.315  | 7.211                    | 1.249     | 1.968 |
| 240       | 4743.8                 | 0.00024                         | 2.239  | 23.71                    | 2.184     | 1.233 |

difference between the Bohart-Adams and the Thomas model is the form of the sorption isotherm assumed. The latter assumes a Langmuir (favorable) isotherm. It has been shown that, when the sorption isotherm is highly favorable, the actual Thomas model reduces to the Bohart-Adams model. The expression by Thomas for an adsorption column is:

$$\frac{C}{C_i} = \frac{1}{1 + e^{k_{Th} q_e x / Q - k_{Th} C_i t}} \text{ or } \frac{C}{C_i} = \frac{1}{1 + A e^{-bt}} \quad (6)$$

where  $A = k_{Th} q_e x / Q$  and  $b = k_{Th} C_i$ ,  $q_0 = NEx/m$  = maximum solid-phase concentration of the solute (mg/g),  $q_e = EN$ ,  $k_{Th} = K$ ,  $V = Qt$  = volume of metal solution passed into the column (L),  $E$  = cross-section of the column ( $cm^2$ ),  $Q$  = flow-rate ( $L min^{-1}$ ),  $m$  = adsorbent mass (g). It can be seen that the Thomas model equation can be transformed the Bohart-Adams model.

The Yoon–Nelson [42] model is not only more simplified than the other models, but, also, it does not require detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of the adsorption bed. Evidently, the Yoon–Nelson model can be transformed to the Bohart–Adams model. The Yoon–Nelson model equation for a single component system is expressed as:

$$\frac{C}{C_i} = \frac{e^{k_{YN} t - \tau k_{YN}}}{1 + e^{k_{YN} t - \tau k_{YN}}} \text{ or } \frac{C}{C_i} = \frac{1}{1 + A e^{-bt}} \quad (7)$$

where  $k_{YN}$  is the rate constant ( $min^{-1}$ ),  $\tau$  the time required for 50% adsorbate breakthrough (min) and  $t$  is the breakthrough/sampling time (min).  $A = e^{k_{YN} \tau}$  and  $b = k_{YN}$ .

The Modified Dose–Response (MDR) model was proposed by Yan *et al.* [43, 44] because it minimizes the error resulting from the use of the Thomas model, especially at lower and higher time periods of the breakthrough curve. The MDR model is expressed as:

$$\frac{C}{C_i} = 1 - \frac{1}{1 + [C_i V / (q_0 m)]^{a_{mdr}}} \quad (8)$$

where  $b_{mdr} = (q_0 m) / C_i$  and  $a_{mdr}$  are the modified dose–response constants. The experimental data and the simulation results are given in Fig. 5. The fitting of the MDR model was much more

satisfactory compared to the Bohart–Adam model. More specifically, for autohydrolysis time equal to 50 min, it was found that:

$$q_0 = 0.5624 e^{0.0259(T_{0a} - 100)} \quad (9)$$

where  $T_{0a}$  is the autohydrolysis temperature in  $^{\circ}C$  and  $R^2 = 0.9903$ . In this case

$$a_{mdr} = 0.6784 e^{0.0073(T_{0a} - 100)} \quad (10)$$

where  $R^2 = 0.8989$ .

In view of the above the adsorption capacity of autohydrolyzed Scots pine sawdust for Cr(VI) is satisfactory, rendering this low cost material suitable as an alternative to commercial activated carbons for the removal of chromium from water/wastewater effluents. Autohydrolysis may become a cost-effective method, since the pretreatment expenses are covered by the produced fermentable sugars for the bioethanol production industry, which is subsidised in the EU Countries. Furthermore, as sawdust is an industrial waste and no addition of chemicals is required, this process of adsorbent modification may be considered to take place within an ‘Industrial Ecology’ framework, since a solid waste is used to treat an aquatic waste, contributing to pollution abatement without entailing excessive cost [31, 32].

## iv. Conclusions

Column kinetics of Cr(VI) adsorption on autohydrolyzed pine sawdust were successfully simulated, and the autohydrolysis conditions as regards time and temperature were optimized. The MDR adsorption column capacity  $q_0$  increased 37 times, indicating the impressive effectiveness of autohydrolysis pretreatment on Cr(VI) adsorption by sawdust. The optimal autohydrolysis conditions are  $240^{\circ}C$  for 50 min.

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