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ORIGINAL PAPER

Efficient removal of hexavalent chromium from aqueous solutions using autohydrolyzed Scots Pine (*Pinus Sylvestris*) sawdust as adsorbent

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Abstract In this work, a low-cost lignocellulosic adsorbent with high biosorption capacity is proposed, suitable for the efficient removal of hexavalent chromium from water and wastewater media. The adsorbent was produced by autohydrolyzing Scots Pine (*Pinus Sylvestris*) sawdust. The effect of the autohydrolysis conditions, i.e., pretreatment time and temperature, on hexavalent chromium biosorption was investigated using energy-dispersive X-ray spectroscopy (EDS) and UV–visible spectrophotometry. The Freundlich, Langmuir, Sips, Radke-Prausnitz, Modified Radke-Prausnitz, Tóth, UNILAN, Temkin and Dubinin-Radushkevich adsorption capacities and the rate constant values for pseudo-first- and pseudo-second-order kinetics indicated that the autohydrolyzed material exhibits significantly enhanced hexavalent chromium adsorption properties comparing with the untreated sawdust. The Freundlich's adsorption capacity K_F increased from 2.276 to 8.928 (mg g^{-1})(L mg^{-1})$^{1/n}$, and the amount of hexavalent chromium adsorbed at saturation (Langmuir constant q_m) increased from 87.4 to 345.9 mg g^{-1}, indicating that autohydrolysis treatment at 240 °C for 50 min optimizes the adsorption behavior of the lignocellulosic material.

Keywords Biomass · Biosorption · Heavy metals · Lignocellulosic · Modification

Introduction

Adsorption is by far the most versatile and widely used method for wastewater metal removal and decoloration. Activated carbon has been commonly used as an adsorbent for the municipal and industrial wastewater cleaning, but its high cost has prompted research on suitable low-cost substitutes, currently focusing on wasted lignocellulosic materials; in fact, wood sawdust and agricultural residues have been extensively investigated as adsorbents (Bansal et al. 2009; Gupta and Babu 2009; Gupta et al. 2009; Mohan et al. 2011).

The presence of heavy metals in the aquatic environment has been of great concern because discharges increase their toxicity and other adverse effects on the receiving waters. Biomagnification, an increase in trace metal concentration through at least two trophic levels in a food chain, elevates trace metal concentrations in higher trophic group organisms, posing a threat to the organisms themselves or to human consumers (Barwick and Maher 2003). Hexavalent chromium exhibits a well-established toxicity and it is considered a priority pollutant. Especially for Greece, the issue of Cr(VI) water contamination has recently received much attention owing to its impact on Assopos basin, a proclaimed processed industrial waste receiver that is also used for irrigation (Economou-Eliopoulos et al. 2011). 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 adsorbents for tri- and hexavalent chromium remediation have been studied by numerous researchers and the mechanisms of adsorption on various adsorbents have been established (Mohan et al. 2011). Mostly untreated and pretreated lignocellulosic industrial byproducts and agricultural residues have been employed as adsorbents for hexavalent chromium removal

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from water. These materials include sawdust (Baral et al. 2006; Aliabadi et al. 2006; Vinodhini and Das 2010), coir pith (Sumathi et al. 2005), oil palm fiber (Isa et al. 2008), wheat straw carbon (Chand et al. 2009), barley straw carbon (Chand et al. 2009), leaf mould (Sharma and Forster, 1996), wheat bran (Nameni et al., 2008; Singh et al. 2009), cotton stalk peel (Xu et al. 2011), maize tassel (Zvinowanda et al. 2009), walnut shell (Pehlivan and Altun 2008), walnut hull (Wang et al. 2009), hazelnut shell (Pehlivan and Altun 2008), almond shell (Pehlivan and Altun 2008), rice bran (Oliveira et al. 2005), rice husk (Sumathi et al. 2005), soybean hulls (Marshall and Wartelle 2004), eucalyptus bark (Sarin and Pant 2006), *Tamarindus indica* seeds (Agarwal et al. 2006), tea factory waste (Vinodhini and Das 2010), spent mushroom modified by cationic surfactant (Jing et al. 2011), and olive stone (Blázquez et al. 2009). Furthermore, since lignocellulosic materials are used in the bioethanol industry as source of sugars (Mosier et al. 2005), the process solid residue can be, also, implemented as adsorbent.

Autohydrolysis is frequently used to increase the efficiency of lignocellulosics' enzymatic hydrolysis to sugars (Nabarlatz et al. 2007). Many industrial byproducts and agricultural residues can be autohydrolyzed for the production of sugars (Sidiras et al. 2011a), while the autohydrolysis solid residue can be efficiently used as dye adsorbent (Sidiras et al. 2011b).

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 Scots Pine (*Pinus Sylvestris*) sawdust autohydrolysis. In an earlier work (Sidiras et al. 2011b), the effect of pretreatment on the microstructure and the crystallinity of pine sawdust was investigated by means of SEM, FTIR, XRD, and BET; in this work, energy-dispersive X-ray spectroscopy (EDS) was further used to measure the percentage of the chromium at the solid phase of the adsorption system, i.e., at the untreated and pretreated sawdust before and after adsorption. The batch adsorption kinetics of Cr (VI) was used to estimate and compare the adsorption capacity of the untreated and pretreated pine sawdust. The study was done at (i) Laboratory of Simulation of Industrial Processes, Department of Industrial Management and Technology, University of Piraeus and (ii) Institute of Material Science, National Centre for Scientific Research "Demokritos", Athens, Greece from January 2011 to January 2012.

Materials and methods

Material development

The Scots Pine (*Pinus Sylvestris*) sawdust was obtained from a local furniture manufacturing company. The moisture content of the material was 8.7 % w/w; the fraction with particle sizes between 0.2 and 1 mm was used. The composition of the raw material is presented in Table 1. The autohydrolysis pretreatment 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 liquid-to-solid ratio was 10:1; the liquid-phase volume was 2,000 mL, the solid material dose was 200 g, and the stirring speed 150 rpm. The temperature values were 160, 200, and 240 °C, reached after 42, 62, and 80 min preheating period values, respectively.

Table 1 Composition of the autohydrolyzed pine sawdust as a function of the autohydrolysis time at 160–240 °C

Time, t_{ai} (min)	160 °C	200 °C	240 °C
Cellulose (% w/w)			
–	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
Hemicelluloses (% w/w)			
–	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
Lignin (% w/w)			
–	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

Adsorption isotherm studies

Adsorption isotherms were derived from batch experiments. Following the batch procedure, accurately weighed quantities of adsorbent were transferred into 0.8 L bottles, where 0.5 L of adsorbate solution was added. The adsorbent weight varied from 0.5 g to 4 g (i.e. $m/V = 1$–8 g L^{-1}), the temperature was 23 °C, and the initial Cr(VI) concentration varied from 15 mg L^{-1} to 700 mg L^{-1};

$K_2Cr_2O_7$ was used as Cr(VI) source. The pH of the solutions was adjusted to 2.0 using dilute H_2SO_4. The bottles were sealed and mechanically tumbled for a period of 7 days. Isotherms were studied for 4 h to 14 days and the equilibrium achieved at 7 days. The resulting solution concentrations were determined and the equilibrium data from each bottle provided one point on the adsorption isotherm plots.

Kinetic studies

Adsorption rate batch experiments were conducted in a 2 L completely mixed glass reactor fitted with a twisted blade-type stirrer, operating at 600 rpm for keeping the lignocellulosic material in suspension. Stirring speed 100–600 rpm was studied and 600 rpm was chosen to achieve kinetic parameter values, not affected by the stirring speed. This was comparable to the literature findings (Baral et al. 2008). The reactor, containing 1 L aqueous Cr(VI) solution, was placed into a water bath to keep temperature constant at the desired level (23 °C). The sorbent weight varied from 1 g to 8 g sawdust (i.e. $m/V =$ 1–8 g L^{-1}), and the initial Cr(VI) concentration varied from 1.6 to 7.7 mg L^{-1}. The effect of contact time (t in min), adsorbent dose (sawdust in g), and initial concentrations of adsorbate (mg L^{-1} Cr(VI)) on the uptake of Cr(VI) were studied in triplicate batch experiments. The pH effect was also studied in the range of 1.2–3.4; the pH of the solutions was adjusted using H_2SO_4 solution according to the guidelines of numerous researchers (Dean and Tobin 1999; Isa et al. 2008); the H_2SO_4 solution was 3.6 N with maximum volume 5 mL per 1 L of Cr(VI) solution. The predominant species at pH 2 is expected to be $HCrO_4^-$ (Dean and Tobin 1999) while other species of chromium ($Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$) coexist in the acid media (Blázquez et al. 2009). Desorption experiments were carried out using 1 L pure water per 4 g of Cr(VI) saturated sawdust; the pH was 7.8.

Analytical techniques

The Saeman et al. (1945) technique was used for the quantitative saccharification of the original lignocellulosic material and the autohydrolysis reaction solid residues. 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_2SO_4 in water as the mobile phase. Cellulose was estimated as glucan and hemicelluloses were estimated as xylan and arabinan. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi Standards (1997) T222 om-88 method.

The study of pine sawdust samples by scanning electron microscopy (SEM) was conducted at the Institute of Materials Science of the National Center for Scientific Research 'Demokritos' using an FEI INSPECT SEM equipped with an EDAX super ultra thin window analyzer for energy-dispersive X-ray spectroscopy (EDS). EDAX was used for the direct measurement of the percentage of the chromium at the untreated and pretreated sawdust before and after adsorption.

Hexavalent chromium was determined by the 1,5-Diphenylcarbohydrazide method using a single dry powder formulation. This reagent contains an acidic buffer combined with 1,5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present. Test results are measured at 540 nm. A HACH DR4000U UV–visible spectrophotometer was used. The method applied is suggested under the code 8023 in the Procedures Manual by the instrument manufacturer (http://www.hach.com/asset-get.download-en.jsa?id=7639983704). This method is USEPA accepted for reporting for wastewater analysis; it is also equivalent to (i) the Standard Method 3500 Cr B in "Standard Methods for the Examination of Water and Wastewater" suggested by American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), and (ii) to USGS method 1-1230-85 for wastewater. The maximum concentration that can be measured with this method is 0.7 mg L^{-1}; dilution factor was 10–1,000. Each sample was measured in triplicate to eliminate the dilution error. Finally, pH measurements were made using a digital pH meter, MultiLab model 540.

Results and discussion

Autohydrolysis

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 significantly affected by autohydrolysis (Mosier et al. 2005; Sidiras et al. 2011a). The composition of the autohydrolyzed pine sawdust (dry weight of product % w/w of the original dry material) is presented in Table 1, as a function of autohydrolysis time (t_{ai} in min). 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. Maximum lignin % w/w was the desirable property of the autohydrolyzed final product to achieve maximum adsorption capacity q_m. An

Table 2 Estimated parameter values for the alternative isotherm models

	K_L (L mg^{-1})	q_m (mg g^{-1}) or K_F [(mg g^{-1}) (L mg^{-1})$^{1/n}$]	n	SEE
Untreated sawdust				
Freundlich		2.276 (2.024–2.527)	1.945 (1.879–2.024)	2.524
Langmuir	0.00348 (0.00204–0.00592)	87.4 (66.4–108.5)		5.430
Sips	9.9×10^{-8} (7.3×10^{-8}–12.9×10^{-8})	9,132 (7,810–10,458)	1.945 (1.889–1.996)	2.674
Radke-Prausnitz	89,617 (66,210–116,560)	0.00651 (0.00557–0.00745)	2.057 (2.019–2.091)	2.662
Modified Radke-Prausnitz	1.32×10^{-5} (0.671×10^{-5}–2.74×10^{-5})	15,897 (10,288–21,534)	0.0111 (0.0060–0.0247)	6.429
Tóth	0.761 (0.749–0.771)	1.77×10^{8} (1.50×10^{8}–2.05×10^{8})	0.0459 (0.0455–0.0463)	2.850
UNILAN	1.83×10^{-9} (0.906×10^{-9}–2.81×10^{-9})	15,896 (8,015–23,803)	11.507 (10.733–11.977)	8.887
Temkin	0.6529 (0.1072–3.979)	7.579 (4.034–11.124)		10.206
Dubinin-Radushkevich		46.80 (23.85–69.75)	3,408 (73–73,446)	10.651
Autohydrolyzed sawdust (at 200 °C for 50 min)				
Freundlich		9.227 (8.100–10.354)	2.077 (1.995–2.179)	9.618
Langmuir	0.00702 (0.00370–0.0140)	224.1 (175.3–273.0)		17.034
Sips	8.4×10^{-8} (5.8×10^{-8}–11.5×10^{-8})	23,649 (19,878–27,435)	2.077 (2.008–2.140)	10.164
Radke-Prausnitz	351.48 (244.39–479.02)	0.566 (0.476–0.657)	1.919 (1.865–1.967)	10.195
Modified Radke-Prausnitz	3.49×10^{-5} (1.60×10^{-5}–9.55×10^{-5})	23,639 (15,225–32,050)	0.0213 (0.0126–0.0388)	22.344
Tóth	0.850 (0.833–0.864)	3.12×10^{7} (2.60×10^{7}–3.63×10^{7})	0.0513 (0.0507–0.0518)	10.503
UNILAN	4.8×10^{-10} (2.4×10^{-10}–7.7×10^{-10})	23,634 (12,417–35,649)	13.918 (13.171–14.431)	29.914
Temkin	0.8858 (0.1303–6.025)	23.97 (13.10–34.83)		34.235
Dubinin-Radushkevich		152.18 (90.79–213.56)	1,473 (98–46,996)	30.744

increasing of (62.4–27.7)/27.7 = 125 % was achieved for lignin (see Table 1). As a side effect, a decrease of (40.1–18.9)/40.1 = 53.4 % for cellulose and 100 % for hemicelluloses was observed. This resulted also in the improvement of the adsorption capacity q_m (see Table 2).

The effect of the autohydrolysis conditions, i.e., time and temperature, on hexavalent chromium quantity adsorbed by the sawdust was investigated using energy-dispersive X-ray spectroscopy (EDS), and the results are presented in Fig. 1; the adsorbed Cr(VI) was found to be 5 mg g^{-1} for the untreated sawdust and 16 mg g^{-1} for the pretreated material (autohydrolysis 200 °C, 50 min). When measured spectrophotometrically (indirectly by Cr(VI) decline in solution), the adsorbed Cr(VI) was found to be 12 mg g^{-1} for the untreated sawdust and 32 mg g^{-1} for the pretreated material. The higher values given by the spectrophotometer method are due to the presence of Cr(III) in the solution that cannot be discriminated by the Cr(VI) HACH method. Notwithstanding, the sawdust adsorptivity improved approximately three times according to both measurement methods. Furthermore, Park et al. (2005), reported that Cr(VI) removal occurred partly through reduction as well as anionic adsorption. This reduction could only have taken place under strong acidic conditions. Cr(VI) is easily or spontaneously reduced to Cr(III) when Cr(VI) comes in contact with sawdust in acidic medium. Moreover, reduction of Cr(VI) to Cr(III) is dependent on the nature of the adsorbent, the Cr(VI) concentration, and the time.

Adsorption isotherms

Isotherm models' equations

Seven isotherm models were applied to fit the experimental results. The Freundlich (Freundlich 1906) isotherm is given by the following equation:

$$q = K_F \cdot (C_e)^{\frac{1}{n}} \qquad (1)$$

where q is the amount adsorbed per unit mass of the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), and K_F, n are the Freundlich constants related to adsorption capacity and intensity, respectively. Eq. (1) in logarithmic form gives

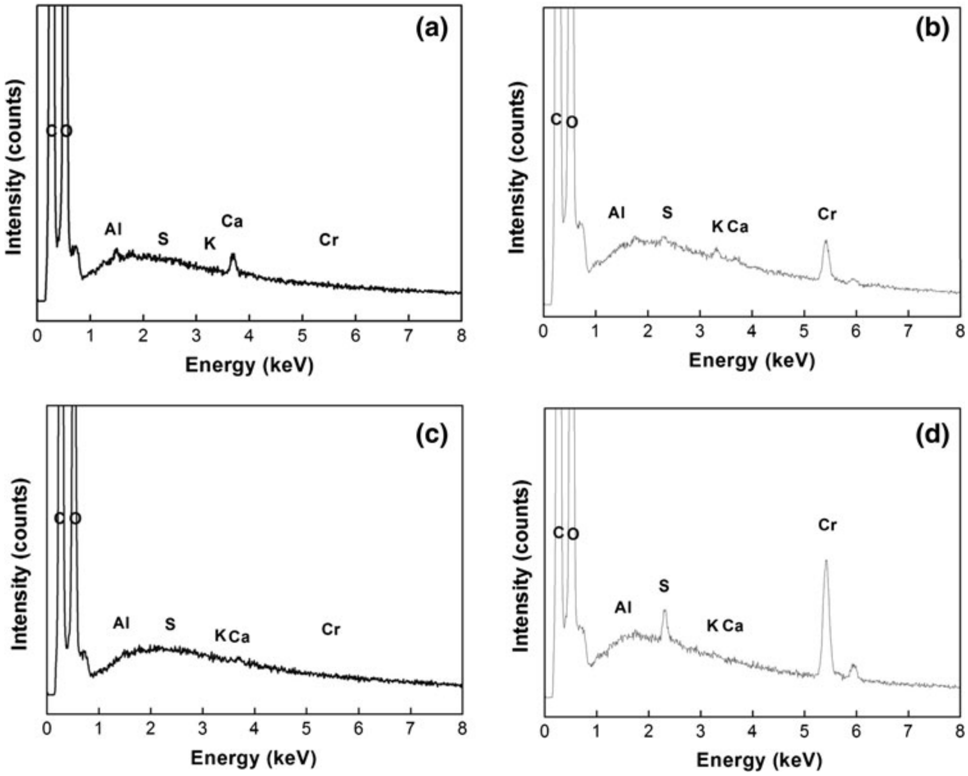

Fig. 1 EDS spectra for untreated (**a**, **b**) and autohydrolyzed at 200 °C for 50 min (**c**, **d**) pine sawdust, before (**a**, **c**) and after (**b**, **d**) Cr(VI) adsorption. Conditions: initial Cr(VI) concentration 700 mg/L, sawdust weight 4 g (i.e. $m/V = 4$ g/L), pH 2, adsorption temperature 23 °C, and adsorption time 190 min

$$\log q = \log K_\mathrm{F} + \frac{1}{n}\log C_\mathrm{e} \tag{2}$$

K_F and n were estimated by non-linear regression analysis (NLRA) from the experimental adsorption data obtained at 23 °C for Cr(VI), while the values of K_F and n estimated by linear least squares regression through Eq. (2) were used as initial values for starting the algorithmic procedure of NLRA. From the environmental point of view, parameter K_F is the most important one representing the adsorption capacity of the materials produced herein for low Cr(VI) concentration $C_\mathrm{e} = 1$ mg L^{-1}.

The Langmuir isotherm (Langmuir 1916) is given by the following equation:

$$q = \frac{K_\mathrm{L} q_\mathrm{m} C_\mathrm{e}}{1 + K_\mathrm{L} C_\mathrm{e}} \tag{3}$$

or

$$\frac{1}{q} = \left(\frac{1}{q_\mathrm{m}}\right) + \left(\frac{1}{K_\mathrm{L} \cdot q_\mathrm{m}}\right) \cdot \left(\frac{1}{C_\mathrm{e}}\right) \tag{4}$$

where K_L is the Langmuir constant related to the energy of adsorption (L mg^{-1}) and q_m the amount of Cr(VI) adsorbed (mg g^{-1}) when saturation is attained. The parameters K_L and q_m can be obtained either by plotting $1/q$ versus $1/C_\mathrm{e}$ or by non-linear regression analysis. From the technical point of view, parameter q_m is the most important parameter representing the maximum adsorption capacity of the materials produced herein.

The characteristics of the Langmuir isotherm can be described by a dimensionless constant, called 'equilibrium parameter' or 'separation factor' R_L:

$$R_\mathrm{L} = \frac{1}{1 + K_\mathrm{L} \cdot C_0} \tag{5}$$

where C_0 is the initial Cr(VI) concentration (mg L^{-1}).

The Sips (Langmuir–Freundlich) (Sips 1948) isotherm equation is

$$q = \frac{q_\mathrm{m} \cdot (K_\mathrm{L} \cdot C_\mathrm{e})^{1/n}}{1 + (K_\mathrm{L} \cdot C_\mathrm{e})^{1/n}} \quad or$$

$$\frac{1}{q} = \left(\frac{1}{q_\mathrm{m}}\right) + \left(\frac{1}{K_\mathrm{L}^{1/n} \cdot q_\mathrm{m}}\right) \cdot \left(\frac{1}{C_\mathrm{e}}\right)^{1/n} \tag{6}$$

where K_L and q_m is the Langmuir constants, and n the Freundlich constant.

The Radke–Prausnitz (Radke and Prausnitz 1972; Chern and Wu 2001) isotherm equation is

$$q = \frac{K_\mathrm{L} \cdot q_\mathrm{m} \cdot C_\mathrm{e}}{1 + K_\mathrm{L} \cdot C_\mathrm{e}^{1/n}} \tag{7}$$

The Modified Radke–Prausnitz (Chern and Wu 2001) isotherm equation is

$$q = \frac{K_L \cdot q_m \cdot C_e}{(1 + K_L \cdot C_e)^{1/n}} \tag{8}$$

The Tóth (Toth 2000) isotherm equation is

$$q = \frac{q_m \cdot C_e}{(1/K_L + C_e^n)^{1/n}} \tag{9}$$

The UNILAN (Chern and Wu 2001) isotherm equation is

$$q = \frac{q_m}{2s} \ln\left(\frac{1 + K_L \cdot C_e \cdot e^s}{1 + K_L \cdot C_e \cdot e^{-s}}\right) \tag{10}$$

where s is a new constant.

The Temkin isotherm model (Temkin and Pyzhev 1940) is

$$q = \frac{RT}{b_T} \ln(A_T C_e) \; or \; q = B_T \ln(A_T C_e) \; or \; q = q_m \ln(K_L C_e) \tag{11}$$

where $R = 0.008314$ kJ mol^{-1} K^{-1}, T is the adsorption temperature in K, $K_L = A_T$ in L mg^{-1} and $q_m = B_T = RT/b_T$ in mg g^{-1}. In linearized form Eq. (11) is as follows:

$$q = a_T + q_m \ln(C_e) \tag{12}$$

where $a_T = q_m \ln(K_L)$.

The Dubinin-Radushkevich (Dubinin and Radushkevich 1947) isotherm model is

$$q = q_D \exp\{-B_D[RT \ln(1 + \frac{1}{C_e})]^2\} \; or$$

$$q = q_D \exp\{-A_D[\ln(1 + \frac{1}{C_e})]^2\} \; or$$

$$q = q_m \exp\{-n[\ln(1 + \frac{1}{C_e})]^2\} \tag{13}$$

where $q_m = q_D$ in mg g^{-1} and $n = A_D = B_D R^2 T^2$ a dimensionless constant for $T =$ constant.

Isotherm results and discussion

Figure 2 presents, as an example, Cr(VI) adsorption isotherms for untreated and pretreated (200 °C, 50 min) pine sawdust following the Freundlich model. The Freundlich parameter values are shown in Table 2; the confidence intervals of the isotherm model coefficients are also presented in this Table, for confidence level 95 %. The K_F values estimated for the autohydrolyzed samples were higher than those of the untreated material, while the n values were similar for both materials. The K_F confidence intervals are not overlapping for confidence level 95 %. For example, $K_F = 2.276$ (mg g^{-1}) (L mg^{-1})$^{1/n}$ with confidence interval 2.024–2.527 (mg g^{-1}) (L mg^{-1})$^{1/n}$ for untreated while 9.227 (mg g^{-1}) (L mg^{-1})$^{1/n}$ with confidence interval 8.100–10.354 (mg g^{-1})(L mg^{-1})$^{1/n}$ for pretreated sawdust. Consequently, $2.527 < 8.100$ (mg g^{-1}) (L mg^{-1})$^{1/n}$. The standard error of estimate (SEE) was calculated in each case by the following expression:

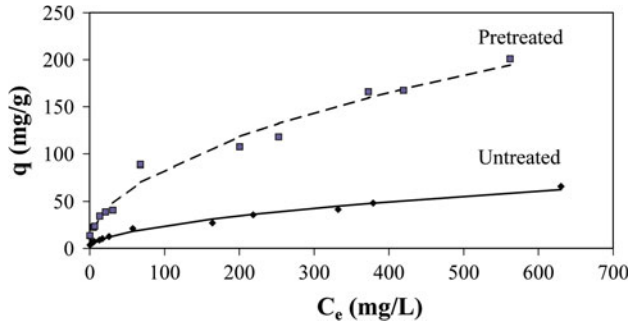

Fig. 2 Isotherms of untreated and autohydrolyzed at 240 °C for 50 min pine sawdust

$$\mathrm{SEE} = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,\mathrm{theor}})^2 / (n' - p')} \tag{14}$$

where y_i is the experimental value of the depended variable, $y_{i,\mathrm{theor}}$ is the theoretical or estimated value of the depended variable, n' is the number of the experimental measurements, and p' the number of parameters (the difference n–p' being the number of the degrees of freedom). The fitting of the Freundlich adsorption model to the experimental data was very satisfactory (see Table 2; Fig. 2). Moreover, the Freundlich constants K_F for the removal of Cr(VI) by adsorption on pine sawdust as affected by the autohydrolysis time t_a was found herein to follow the parabolic relation:

$$K_F = a_2 t_a^2 + a_1 t_a + a_0 \tag{15}$$

where a_0, a_1, and a_2 are empirical parameters, depending on the autohydrolysis temperature, given in Table 3.

Moreover, Table 2 presents the Langmuir NLRA parameter values estimates for the data gathered in the present study. The values of q_m obtained for untreated pine sawdust were lower than the values for the pretreated samples; e.g., $q_m = 87.4$ mg g^{-1} with confidence interval 66.4–108.5 mg g^{-1} for untreated while 224.1 mg g^{-1} with confidence interval 175.3–273.0 mg g^{-1} for pretreated sawdust. It is obvious that $108.5 < 175.3$ mg g^{-1}. The fitting of the Langmuir's adsorption model to the present data was also very satisfactory but to a lesser degree than that using the Freundlich model for both materials, as shown by the corresponding SEE-values given in Table 2. The Langmuir constant q_m was similarly found to follow the same as in Eq. (15) parabolic relation (see Table 2):

$$q_m = a_2 t_a^2 + a_1 t_a + a_0 \tag{16}$$

At the present work, the R_L values were found between 0 and 1 for all Cr(VI) concentrations C_0 and for all adsorbents studied. This fact indicates a favorable

Table 3 Parameters of Eqs. (4) and (7) for the prediction of the Freundlich and Langmuir parameters as affected by the pine sawdust autohydrolysis time and temperature

$T_{\theta a}$ (°C)	a_2	a_1	a_0	R^2
The case of the Freundlich isotherm model				
160	0	0.0257 ± 0.0038	2.2404 ± 0.2427	0.9021
200	−0.00043 ± 0.0009	0.1082 ± 0.0100	2.2943 ± 0.2776	0.9907
240	−0.00072 ± 0.00005	0.1459 ± 0.0065	2.2656 ± 0.2004	0.9964
The case of the Langmuir isotherm model				
160	0.0184 ± 0.0029	−0.7905 ± 0.2778	87.5047 ± 6.4788	0.9727
200	0.0030 ± 0.0022	0.9091 ± 0.2664	86.8949 ± 6.8402	0.9852
240	0.0102 ± 0.0040	0.6964 ± 0.5142	87.4997 ± 15.7820	0.9780

adsorption, while $R_L > 1$ represents an unfavorable adsorption and $R_L = 1$ represents the linear adsorption. Moreover, the adsorption operation is irreversible if $R_L = 0$ (Gupta and Babu 2009).

The parameters of the other seven presented isotherm models were estimated by NLRA. The fitting of these models to the present data was less satisfactory than the fitting of the Freundlich model for both treated and untreated materials (Table 2).

Kinetics of adsorption

Kinetic models' equations

The kinetics of adsorption of Cr(VI) on various materials has been extensively studied using four kinetic equations. The widely used Lagergren equation (Lagergren 1898) is shown below:

$$q - q_t = q \cdot e^{-k \cdot t} \tag{17}$$

where q and q_t are the amounts of Cr(VI) adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium time ($t \rightarrow \infty$) and adsorption time t, respectively, while k is the pseudo-first order rate constant for the adsorption process (in min^{-1}). Furthermore, $q = (C_0 - C_e)V/m$ and $q_t = (C_0 - C)V/m$ (18)where C, C_0, C_e are the concentrations of Cr(VI) in the bulk solution at time t, 0, and ∞, respectively, while m is the weight of the adsorbent used (in g), and V is the solution volume (in mL). Further modification of Eq. (18) in logarithmic form gives

$$\ln(q - q_t) = \ln q - k \cdot t \tag{19}$$

The κ-order kinetic model is

$$dq/dt = k_\kappa (q - q_t)^\kappa \tag{20}$$

Solving this differential Eq. for $\kappa \neq 1$, we obtain:

$$q_t = q - \left[q^{1-\kappa} + (\kappa - 1)k_\kappa t\right]^{1/(1-\kappa)} \tag{21}$$

The commonly used second-order kinetic model (Ho et al. 2000) is as follows:

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \quad or \quad q_t = q - \frac{1}{\frac{1}{q} + k_2 t} \tag{22}$$

The possibility of intra-particle diffusion was explored using the intra-particle diffusion model (Weber and Morris 1963):

$$q_t = c + k_p \cdot \sqrt{t} \tag{23}$$

where q_t is the amount of Cr(VI) adsorbed at time t, c is a constant (mg g^{-1}), and k_p is the intra-particle diffusion rate constant in mg g^{-1} min$^{-0.5}$.

Kinetic results and discussion

The plots of $\ln(q - q_t)$ vs. t for all Cr(VI) adsorbent systems were found to be linear, indicating the possibility of first-order nature of the adsorption process.

The Lagergren plots, as affected by the Cr(VI) initial concentration C_0 (mg L^{-1}), are shown in Fig. 3a. The maximum adsorbed amount of Cr(VI) q (in mg g^{-1}) vs. the initial concentration C_0 (in mg L^{-1}) was found herein to follow the equation given below:

$$q = 0.0973C_0 + 0.1588 \tag{24}$$

with $R^2 = 0.9593$. The adsorption temperature was 23 °C, the pH = 2.0, and the solid to liquid ratio $m/V = 4$ g sawdust per L of solution. The k-values, as affected by C_0, were 0.013 ± 0.002 min^{-1}.

The Lagergren plots as affected by the solid/liquid ratio m/V (in g L^{-1}) are shown in Fig. 3b. The % removal of Cr(VI) $r = q/(C_0 \cdot V)$ vs. solid/liquid ratio was equal to

$$r = q/(C_0 \cdot V) = -0.0833(m/V) + 0.1558 \tag{25}$$

with $R^2 = 0.9663$. The adsorption temperature was 23 °C, the Cr(VI) initial concentration $C_0 = 5.0$ mg L^{-1}, and the pH = 2.0. In this case, the k-values were found to follow the equation given below:

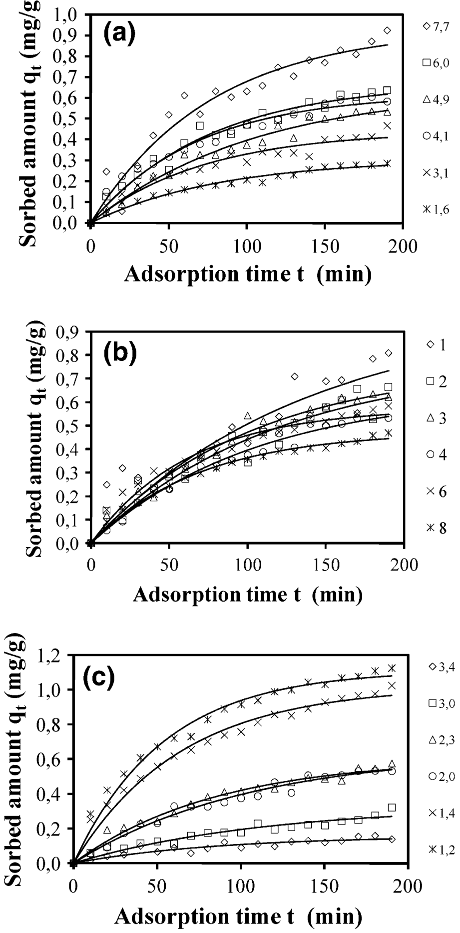

Fig. 3 Lagergren curves of Cr(VI) adsorption on pine sawdust as affected by **a** Cr(VI) initial concentration, **b** solid/liquid ratio *m*/*V* and **c** pH

$$k = 0.0012(m/V) + 0.0061 \quad (26)$$

with coefficient of determination $R^2 = 0.8232$. The *k*-value range was 0.011 ± 0.003 min^{-1}.

The effect of the pH of the Cr(VI) solution on the amount of Cr(VI) adsorbed was studied by varying the initial pH under constant process parameters. The adsorption was negligible for pH = 7.8 or higher. In Fig. 3c the adsorption of Cr(VI) as affected by pH is presented. The % removal of Cr(VI) *r* was according to the following equation:

$$r = q/(C_0 \cdot V) = -0.3617pH + 1.3418 \quad (27)$$

with $R^2 = 0.9787$. The adsorption temperature was 23 °C, the Cr(VI) initial concentration $C_0 = 5.0\ \text{mg L}^{-1}$, the solid to liquid ratio $m/V = 4$ g sawdust/L solution, and pH = 1.2–3.4. The *k*-value range was 0.013 ±0.004 min^{-1}.

The first-order adsorption kinetics for untreated and pretreated sawdust is presented in Fig. 4a as regards the effect of the preheating time periods (i.e., zero isothermal autohydrolysis time periods) and in Fig. 5a for 50 min

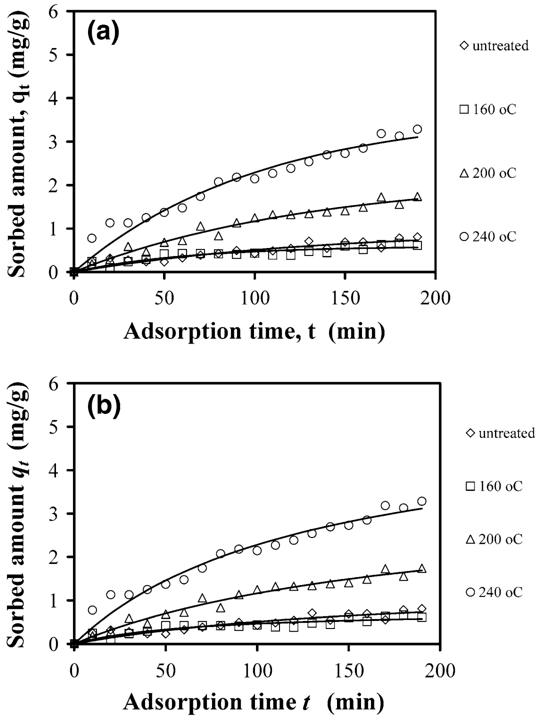

Fig. 4 **a** Lagergren curves and **b** second-order curves of Cr(VI) adsorption on untreated and autohydrolyzed (at 160, 200 and 240 °C for 0 min) pine sawdust, showing the effect of preheating

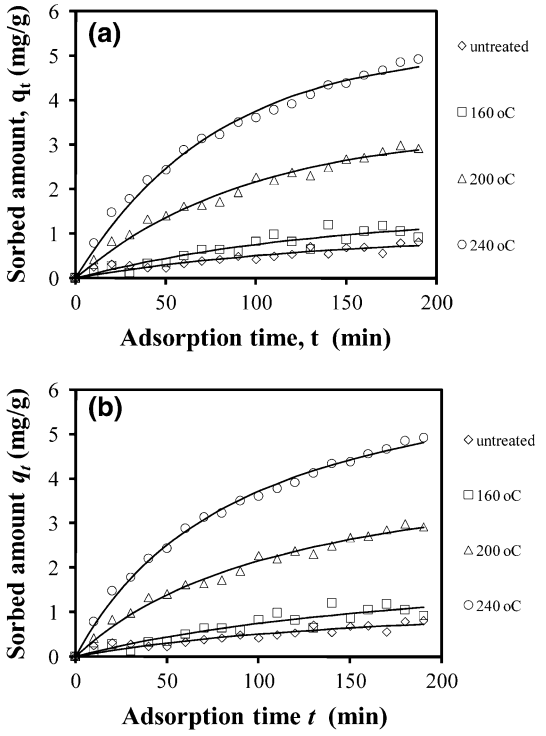

Fig. 5 **a** Lagergren curves and **b** second-order curves of Cr(VI) adsorption on untreated and autohydrolyzed (at 160, 200 and 240 °C for 50 min) pine sawdust

isothermal autohydrolysis time periods. The preheating periods were 42, 62, and 80 min for autohydrolysis temperatures 160, 200, and 240 °C, respectively. Adsorption was significantly enhanced for preheating at 200 and 240 °C while the effect of preheating at 160 °C was negligible (Fig. 4a). The NLRA estimates of the first-order rate constants k were 0.0074–0.0129 min^{-1} (0.0074 min^{-1} for the untreated sawdust and 0.0129 min^{-1} for the most severe pretreated sawdust) and the SEE-values were 0.089–0.133. All SEE-values were found low, indicating the high applicability of this kinetic equation to the adsorption of Cr(VI) on pine sawdust.

The second-order kinetics is presented in Figs. 4b and 5b for Cr(VI) for untreated and pretreated pine sawdust. The NLRA-estimated values of the second-order rate constants k_2 were 0.00151–0.00387 min^{-1} and the SEE-values were 0.088–0.127. All SEE-values were found to be somewhat lower than those of the first-order kinetic model, indicating the marginally higher applicability of the second-order kinetic equation to the adsorption of Cr(VI) on pine sawdust.

The k-values of the first-order kinetic model were significantly increased by the autohydrolysis pretreatment of pine sawdust, whereas the k-values of the second-order kinetic model were not significantly increased by autohydrolysis. However, the adsorption rate $\mathrm{d}q/\mathrm{d}t$ is significantly enhanced for both kinetic models due to the increase of the $(q - q_t)$ difference (Figs. 4, 5).

On the other hand, the order of the kinetic model was found to be $\kappa = 2.11$ for the untreated and $\kappa = 1.98 - 2.01$for the pretreated pine sawdust at various conditions.

Finally, the NLRA-estimated values of the intra-particle diffusion model rate constants k_p were 0.0511–0.3596 mg g^{-1} $\mathrm{min}^{-0.5}$ (0.0511 for the untreated and 0.3596 for the most severe pretreated sawdust) and the SEE values were 0.079–0.148.

Desorption and reusability

The Cr(VI) saturated adsorbent is not safe for the disposal due to stringent environmental constraints. The regeneration and reuse of adsorbent is important so as to reduce the

Table 4 Freundlich and Langmuir isotherms parameters of Cr(VI) adsorption on various adsorbents

Materials	Freundlich		Langmuir		pH	T (°C)	Reference
	K_F [(mg g^{-1})(L $\mathrm{mg}^{-1})^{1/n}$]	n	q_m (mg g^{-1})	K_L (L mg^{-1})			
Almond shell	0.153	2.86	0.046	0.580	3.5	25	Pehlivan and Altun (2008)
Almond shell	0.6134	1.661	22.05	0.053	4	–	Agarwal et al. (2006)
Coir pith	0.159	1.84	–	–	3	–	Sumathi et al. (2005)
Cotton stalk peel	2.9	2.99	13.8	0.014	5.12	20	Xu et al. (2011)
Cotton stalk peel (amine-cross linked)	0.36	3.74	117.9	0.024	5.12	20	Xu et al. (2011)
Ground nut shell	0.3239	1.146	5.88	0.057	4	–	Agarwal et al. (2006)
Hazelnut shell	0.386	2.83	0.086	4.423	3.5	25	Pehlivan and Altun (2008)
Mushroom (spent, modified by cationic surfactant)	4.017	2.168	43.86	0.03176	3	25	Jing et al. (2011)
Oak bark chars	1.332	2.32	7.515	0.149	2	25	Mohan et al. (2011)
Oil palm fibre	71.285	34.542	22.73	0.1807	1.5	28	Isa et al. (2008)
Rice husk	0.056	1.566	–	–	3	–	Sumathi et al. (2005)
Rice husk carbon	21.61	5.36	48.31	0.27	2	25	Bansal et al. (2009)
Sawdust	1.481	26.74	–	–	3	–	Sumathi et al. (2005)
Sawdust	16.66	0.209	41.52	0.438	1	30	Gupta and Babu (2009)
Sawdust (carbonized)	0.96	7.75	53.48	0.56	2	25	Bansal et al. (2009)
Sawdust	2.276	1.945	87.4	0.00348	2	23	In this work
Sawdust (autohydrolyzed, 240 °C, 50 min)	8.928	4.776	345.9	0.00696	2	23	In this work
Tamarindus indica seeds	49.910	4.162	98.04	1.29	2	–	Agarwal et al. (2006)
Tea residue	7.0129	1.845	29.76	0.27	–	25	Dizadji and Abootalebi Anaraki (2011)
Walnut hull	45.60	6.87	98.13	0.1795	1	30	Wang et al. (2009)
Walnut shell	0.244	3.36	0.076	2.982	3.5	25	Pehlivan and Altun (2008)
Walnut shell	0.9866	2.277	2.28	1.286	4	–	Agarwal et al. (2006)
Wheat bran	0.272	3.246	282.54	0.604	2	20	Singh et al. (2009)

load on environment in terms of disposal of polluted adsorbent (Gupta and Babu 2009). Cr(VI) desorption from saturated untreated and pretreated sawdust using pure water was studied in the present work. Desorption efficiency was calculated using following equation:

$$\text{Desorption\_efficiency} = \frac{\text{amount\_of\_Cr(VI)\_desorbed}}{\text{amount\_of\_Cr(VI)\_sorbed}} \times 100 \tag{28}$$

The results were 23.3–48.8 % Cr(VI) desorption for untreated pine sawdust and 5.8–17.6 % Cr(VI) desorption for autohydrolyzed pine sawdust batch experiments at $\mathrm{pH} = 7.8$. These findings are comparable to some literature data (Jing et al. 2011). These desorption efficiency values limit the reusability of the pretreated material. On the other hand, it is reported that desorption of Cr(VI) is facilitated by increasing the solution pH (Singh et al. 2009). Moreover, desorption of Cr(VI) from sawdust using acid and base treatment exhibits higher desorption efficiency by more than 95 % (Gupta and Babu 2009). In this case the material has high reusability.

Comparison with other biobased materials

Comparing the Cr(VI) adsorption capacities K_F and q_m of the autohydrolyzed and untreated pine sawdust with other agricultural or waste lignocellulosic-based adsorbents in literature (Table 4), the autohydrolyzed (240 °C, 50 min) pine sawdust exhibits the higher $q_m = 345.9\ \mathrm{mg\ g^{-1}}$.

Adsorption using activated carbon is considered to be one of the most efficient commercial methods for removing heavy metals from water/wastewater which is a major environmental problem. The process could be extremely expensive due to the high cost of activated carbon, especially when treating large amounts of water/wastewater containing heavy metals in low concentrations from small scale industries (Wang and Chen 2009).

Thereby, the Cr(VI) adsorption capacity of autohydrolyzed pine sawdust is quite satisfactory, rendering this low-cost material a suitable alternative of commercial activated carbons for the removal of chromium from water/wastewater effluents. Moreover, the pretreatment expenses can be covered by the produced sugars, raw materials for the bioethanol production industry. Evidently, this process of adsorbent modification, where a wasted material is used in the management of another waste, may be considered to take place within an ‘Industrial Ecology’ framework (Sidiras et al. 2011b).

The proposed herein material can be used at pilot or large-scale either in batch tanks or in packed bed columns for removing Cr(VI) from water and industrial wastewater.

Conclusion

The results presented herein indicate that the batch kinetics of Cr(VI) adsorption on autohydrolyzed pine sawdust was significantly enhanced, compared with those of the untreated material. The severity of autohydrolysis had a positive effect on the adsorptivity of the pine sawdust as determined using the EDS technique. The Freundlich and Langmuir adsorption capacity values of the autohydrolyzed sawdust were significantly increased by autohydrolysis pretreatment temperature and time. The material autohydrolyzed at 240 °C for 50 min exhibited the higher adsorption capacity as compared with other autohydrolysis conditions and materials presented in literature.

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Nomenclature

A_D	Dubinin-Radushkevich isotherm dimensionless constant
a_i	Empirical parameters of Eqs. (15) and (16) $i = 0, 1, 2$
A_T	Temkin isotherm constant ($\mathrm{L\ g^{-1}}$)
B_T	Temkin isotherm constant ($\mathrm{mg\ g^{-1}}$)
B_D	Dubinin-Radushkevich isotherm constant
b_T	Temkin isotherm constant related to heat of sorption ($\mathrm{J\ mol^{-1}}$)
C	Concentrations of Cr(VI) in the bulk solution at time t
c	Intercept of the intra-particle diffusion equation ($\mathrm{mg\ g^{-1}}$)
C_0	Initial Cr(VI) concentration ($\mathrm{mg\ L^{-1}}$)
C_e	Equilibrium concentration of the adsorbate ($\mathrm{mg\ L^{-1}}$) for $t \to \infty$
k	First-order rate constant for the batch adsorption process ($\mathrm{min^{-1}}$)
k_2	Second-order rate constant for the batch adsorption process ($\mathrm{min^{-1}}$)
k_κ	κ-order rate constant for the batch adsorption process ($\mathrm{min^{-1}}$)
K_F	Freundlich constant related to adsorption capacity ($\mathrm{mg\ g^{-1}}$) ($\mathrm{L\ mg^{-1}}$)$^{1/n}$
K_L	Langmuir constant related to the energy of adsorption ($\mathrm{L\ mg^{-1}}$)
k_p	Intra-particle diffusion rate constant ($\mathrm{mg\ g^{-1}\ min^{-0.5}}$)

m	Adsorbent mass (g)
n	Inverse of the slope of the linearized (logarithmic) Freundlich isotherm, is related to adsorption intensity
NLRA	Non-linear regression analysis
q	Amount adsorbed per unit mass of the adsorbent for $t \to \infty$ (mg g^{-1})
q_{D}	Dubinin-Radushkevich isotherm constant (mg g^{-1})
q_{m}	Langmuir constant related to the amount of Cr(VI) adsorbed (mg g^{-1}) when saturation is attained
q_{t}	Amount of Cr(VI) adsorbed per unit mass of the adsorbent (mg g^{-1}) at time t
r	The % removal of Cr(VI)
R	The gas constant (0.008314 kJ mol^{-1} K^{-1})
R^2	Coefficient of determination
R_{L}	Dimensionless constant called 'equilibrium parameter' or 'separation factor' expressing the essential characteristics of the Langmuir isotherm
s	Constant of the UNILAN isotherm model
SEE	Standard error of estimate
t	Adsorption time (min)
T	Adsorption temperature (K)
t_{a}	Autohydrolysis time (min), $t_{\mathrm{a}} = t_{\mathrm{p}} + t_{\mathrm{ai}}$
T_{a}	Autohydrolysis temperature (K)
t_{ai}	Autohydrolysis isothermal time (min)
t_{p}	Autohydrolysis preheating time (min)
T_{θ}	Adsorption temperature ($^{\mathrm{o}}$C)
$T_{\theta\mathrm{a}}$	Autohydrolysis temperature ($^{\mathrm{o}}$C)
V	Volume of Cr(VI) solution (L)
κ	Order of the adsorption kinetic model
λ	Spectrophotometer wavelength (nm)

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