



Modeling of kinetics of Cr(VI) sorption onto grape stalk waste in a stirred batch reactor

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ABSTRACT

Recently, Cr(VI) removal by grape stalks has been postulated to follow two mechanisms, adsorption and reduction to trivalent chromium. Nevertheless, the rate at which both processes take place and the possible simultaneity of both processes has not been investigated. In this work, kinetics of Cr(VI) sorption onto grape stalk waste has been studied. Experiments were carried out at different temperatures but at a constant pH (3 ± 0.1) in a stirred batch reactor. Results showed that three steps take place in the process of Cr(VI) sorption onto grape stalk waste: Cr(VI) sorption, Cr(VI) reduction to Cr(III) and the adsorption of the formed Cr(III). Taking into account the evidences above mentioned, a model has been developed to predict Cr(VI) sorption on grape stalks on the basis of (i) irreversible reduction of Cr(VI) to Cr(III) reaction, whose reaction rate is assumed to be proportional to the Cr(VI) concentration in solution and (ii) adsorption and desorption of Cr(VI) and formed Cr(III) assuming that all the processes follow Langmuir type kinetics. The proposed model fits successfully the kinetic data obtained at different temperatures and describes the kinetics profile of total, hexavalent and trivalent chromium.

The proposed model would be helpful for researchers in the field of Cr(VI) biosorption to design and predict the performance of sorption processes.

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1. Introduction

The chromium present in industrial wastewaters is mainly in the hexavalent form as chromate and dichromate. Cr(VI) is much more toxic than Cr(III) and its discharge to surface water is regulated to below 0.05 mg L^{-1} by the US EPA [1]. Dechromisation is the first step in the pre-treatment of effluents from plating industry. The chromic acid effluents are treated in the dechromisation reactor with sodium bisulfite and sulfuric acid under mechanical agitation to reduce Cr(VI) to Cr(III). Alternative reagents to sodium bisulfite include SO_2 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_4$, $\text{Na}_2\text{S}_2\text{O}_3$ and it can also be undertaken with the help of ferrous salts, as FeSO_4 . The reduced form Cr(III) is lately precipitated as insoluble chromium hydroxides by addition of CaO or soda [2]. The overall process is costly due to the high consumption of the reagents, which must be present in the reactor in excess, and the need of the disposal of the significant amount of sludge produced as a consequence of the added reagents and metal hydroxides precipitation. In addition to this, the removal by these conventional methods is limited to a certain extent; low concentrations of hexavalent chromium still remain in the solution

after chromium reduction–precipitation processes [3]. Therefore, additional effluent treatments like ion exchange, membrane separation, adsorption on activated carbon, etc. which are quite expensive must be carried out in order to meet regulatory standards.

All the above mentioned problems have led to the development of alternative low-cost and cleaner technologies for the removal of Cr(VI) and other metals from industrial effluents. Biosorbents are available and abundant in the nature; they contain proteins, polysaccharides, enzymes, etc. that are associated with functional groups with reductive and adsorptive properties. As mentioned before, reduction to trivalent chromium is the first step of the generalized methods for hexavalent chromium removal. For Cr(VI) reduction to occur, a suitable redox couple having a compatible electron symmetry to allow electron exchange must be present [4]. Biosorbents are potential electron donors and Cr(VI) has the potential of electron acceptor [5].

Grape stalks waste has been reported to be an efficient biosorbent for Cr(VI) removal [6] and in a recent work, it has been postulated that Cr(VI) removal by this sorbent is due to two different mechanisms, adsorption and reduction to trivalent chromium [7]. Nevertheless, the rate at which both processes take place, and the possible simultaneity of both processes, have not yet been investigated.

Hundreds of works have been published in international journals devoted to Cr(VI) biosorption but only in a few number of them

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the mechanism of Cr(VI) sorption onto the biomaterials has been investigated [8–12]. Therefore, the aim of the present work is to investigate kinetics of Cr(VI) sorption onto grape stalk waste and to develop a model that includes hexavalent chromium adsorption and reduction and sorption of the formed trivalent chromium which can be useful to predict the overall process of Cr(VI) removal onto grape stalks.

2. Materials and methods

2.1. Materials

Grape stalk waste was kindly supplied by a wine producer from the Catalonia region, Spain. Grape stalks were rinsed three times with abundant cold water and then dried in an oven at 105 °C until constant weight. The wastes were cut and ground to get a particle size of 0.25–0.56 mm. Hexavalent chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate ($K_2Cr_2O_7$) in deionized water. A 1 M solution of HCl was used to adjust the initial pH to 3.0. Solutions of 1.5% of HCl and NaOH were used for the automatic control of pH by a programmable logic control (PLC). All reagents were analytical grade and were purchased from Panreac (Barcelona, Spain). Chromium standard solution (1000 mg L^{-1}) purchased also from Panreac was used for flame atomic absorption (FAAS) calibrations.

2.2. Experimental set-up

Experiments were performed in a 5 L volume, jacketed glass reactor depicted in Fig. 1. The double wall allows temperature regulation by water recirculation from a bath with thermostatic control. Temperature fluctuations in the reactor were within $\pm 0.1\text{ }^\circ\text{C}$. The reactor is closed by a detachable glass cap with different openings that enable the introduction of the sorbent, the paddle agitator, the

addition of acid and base solutions; and the introduction of pH and temperature sensors.

The reactor was operated in batch mode and continuously stirred at 250 rpm. Constant pH (3.0 ± 0.1) was assured by means of a programmable logic control (PLC), which was in charge of comparing the pH measured by means of a pH sensor inside the reactor and adjusting the pH by pumping either NaOH or HCl into the reactor to reach the fixed set point.

2.3. Sorption studies

For all experiments, a volume of 4 L of Cr(VI) solutions at pH 3.0 ± 0.1 was introduced into the reactor under constant agitation. As soon as the liquid attained the desired pH and temperature, both parameters controlled by a PLC and a thermostatic water bath, respectively, 10 g of grape stalk waste was added. The operation time (time required for the system sorbate–sorbent to reach equilibrium) was maintained within the range 120–180 min. For preliminary experiments three different initial concentrations of Cr(VI) within the range $5\text{--}20\text{ mg L}^{-1}$ were used. For the study of sorption kinetics at different temperatures Cr(VI) initial concentration was 10 mg L^{-1} and temperature was varied within the range $5\text{--}60\text{ }^\circ\text{C}$. The experiments were carried out in duplicate and the average results are presented in this work.

2.4. Sampling

During the first hour, sampling was performed manually by taking 5 mL samples every 2 min in order to get as much as possible information about the rate sorption at the beginning of the process. After this time, a peristaltic pump (Gilson, Minipuls 3, USA) pumped 0.85 L h^{-1} solution from the reactor to a fractions collector (Gilson, FC203B, USA) where fixed volumes (7 mL) of the solution were collected. A recirculation system was adapted to return the excess of sampled solution or when the auto sampler was inactive.

2.5. Analytical methods

The total concentration of chromium, i.e., Cr(VI)+Cr(III), was determined by flame atomic emission spectroscopy (FAES) (Varian SpectrAA 220FS). Hexavalent chromium was analyzed by the standard colorimetric 1,5-diphenylcarbazide method [13], in a spectrophotometer (Cecil, CE2021). The concentration of trivalent chromium was determined as the difference between total chromium and hexavalent chromium concentration. The Cr(VI) standard solution used for obtaining the calibration curve in the diphenylcarbazide method was analyzed by FAES. Analytical measurements made by the two techniques were comparable within 5%.

3. Results and discussion

3.1. Preliminary experiments

Results of kinetics of Cr(VI) sorption at three different initial concentrations are presented in Fig. 2 in which kinetic profiles of total, hexavalent and trivalent chromium have been plotted separately. As seen, total chromium concentration decreases with time until it reaches a plateau at 0.9 , 2.5 and 4.2 mg L^{-1} for the tested Cr(VI) initial concentrations of 5.4 , 10.7 and 19.7 mg L^{-1} , respectively (Fig. 2a). Fig. 2b shows the fast decrease of Cr(VI) concentration until its total disappearance and Fig. 2c the simultaneous appearance of Cr(III) in solution and its further sorption up to a constant concentration value that coincides with the observed one in Fig. 2a. These observations are in part, in accordance with the ones observed in a previous work where experiments were carried

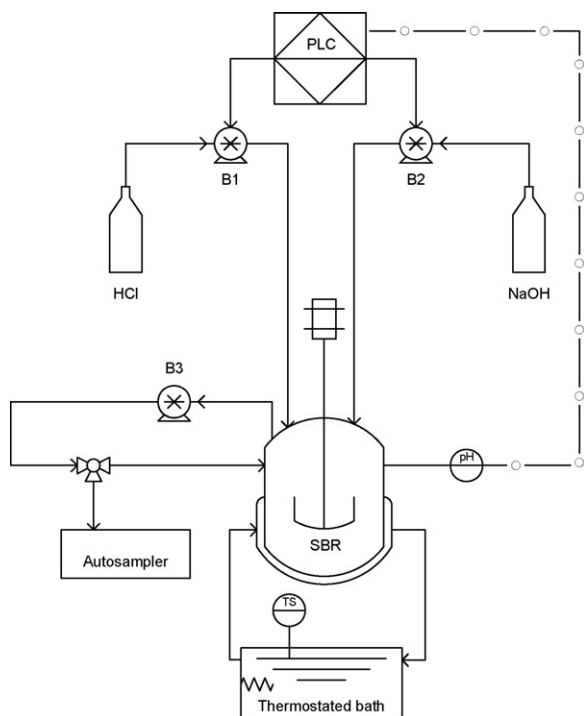


Fig. 1. Experimental set-up for Cr(VI) sorption onto grape stalk waste. SBR: stirred batch reactor, PLC: programmable logic controller, B1 and B2: peristaltic pumps for the addition of HCl and NaOH, B3: peristaltic pump for sampling and recirculating, and pH: pH sensor.

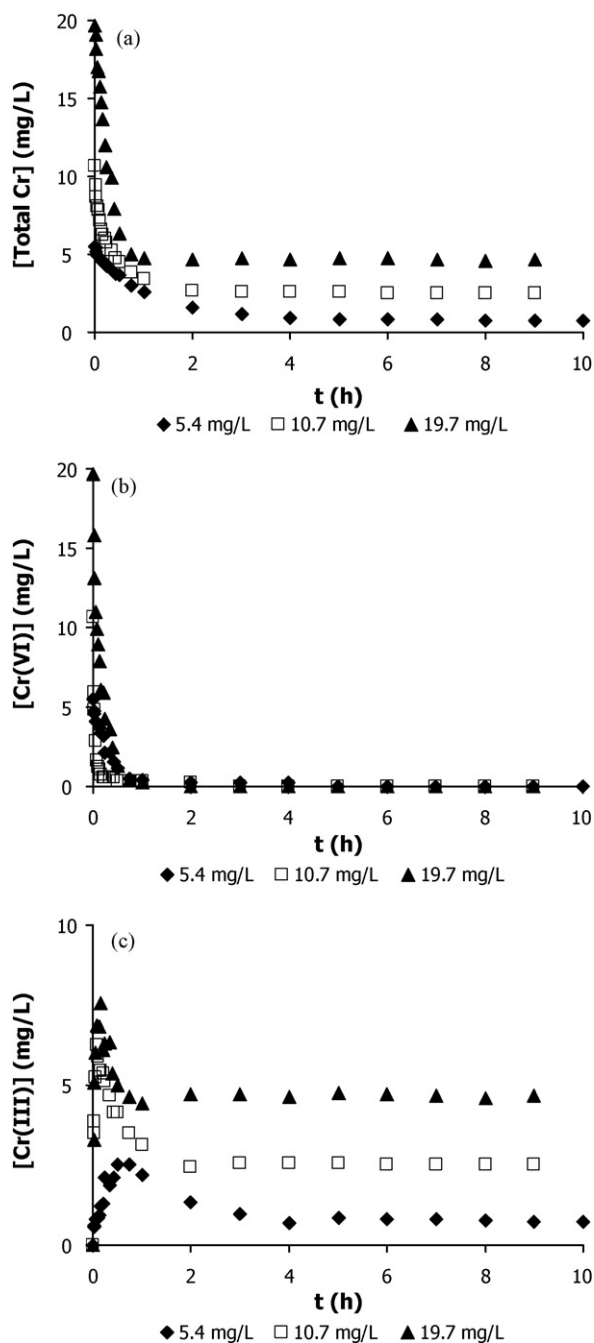


Fig. 2. Kinetics profile of total chromium, Cr(VI) and Cr(III) at different Cr(VI) initial concentrations. Sorbent dose: 2.5 g L^{-1} , particle size: $0.25\text{--}0.56 \text{ mm}$ and temperature: 20°C .

out in batch mode at laboratory bench scale [7]. In that work, it was observed the total disappearance of hexavalent chromium and also that chromium in the remaining solution was exclusively in its reduced oxidation state but it was not possible to observe that the formed Cr(III) was further partially adsorbed. In the present work, the use of a reactor confirmed the evidence of partial sorption of the formed Cr(III). In the literature, the partial sorption of the formed trivalent chromium onto a lignocellulosic substrate was also observed by Dupont and Guillon [14]. Conversely, other authors who studied the ability of different materials to reduce Cr(VI) to Cr(III) reported that the formed trivalent chromium is not sorbed on seaweed *Sargassum siliquosum* [15] and coal [16] or it is poorly adsorbed on Sphagnum moss peat [17].

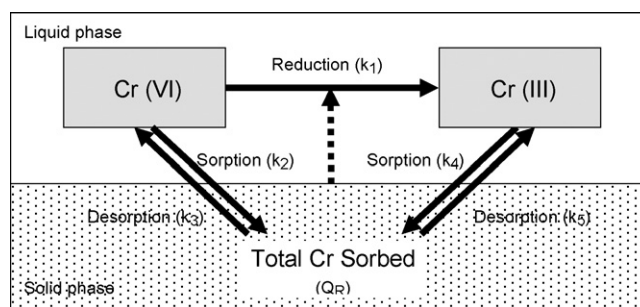


Fig. 3. Reactions scheme of Cr(VI) sorption onto grape stalk waste. $Q_R = q_{\text{Cr(VI)}}/q_{\text{Tot}}$.

From the results obtained in the present work (Fig. 2), it is clear that the decrease of Cr(VI) from solution is mainly due to its reduction to Cr(III). It is also evident that part of the formed Cr(III) is sorbed onto grape stalk waste. Nevertheless, it is important to take into account that a part of chromium might be sorbed as Cr(VI) before the reduction reaction starts. Indeed, X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of chromium in both oxidation states Cr(VI) and Cr(III) on grape stalk waste surface in our previous work [7].

3.2. Modelling

Taking into account the evidences above mentioned, a model has been developed in basis to (i) irreversible reduction of Cr(VI) to Cr(III) reaction, whose reaction rate is assumed to be proportional to the Cr(VI) concentration in solution and (ii) adsorption and desorption of Cr(VI) and formed Cr(III) assuming that all the processes follow Langmuir type kinetics [18]. A scheme of the different steps is depicted in Fig. 3. The different phenomena can be included in a series of dimensionless equations, leading to the system:

$$\frac{du_{\text{Cr(VI)}}}{dt} = -k_1 u_{\text{Cr(VI)}} - k_2 u_{\text{Cr(VI)}}(1 - Q_R u_{q_t}) + k_3 Q_R u_{q_t} \quad (1)$$

$$\frac{du_{\text{Cr(III)}}}{dt} = k_1 u_{\text{Cr(VI)}} - k_4 u_{\text{Cr(III)}}(1 - (1 - Q_R)u_{q_t}) + k_5(1 - Q_R)u_{q_t} \quad (2)$$

$$\frac{du_{q_t}}{dt} = k_2 u_{\text{Cr(VI)}}(1 - Q_R u_{q_t}) - k_3 Q_R u_{q_t} + k_4 u_{\text{Cr(III)}}(1 - (1 - Q_R)u_{q_t}) - k_5(1 - Q_R)u_{q_t} \quad (3)$$

where $u_{\text{Cr(VI)}}$ is defined as the ratio between Cr(VI) concentration in solution at time t and initial Cr(VI) concentration ($C_{\text{Cr(VI)}}/C_{\text{Cr(VI)0}}$) and $u_{\text{Cr(III)}}$ as the ratio between Cr(III) concentration at time t and initial Cr(VI) concentration ($C_{\text{Cr(III)}}/C_{\text{Cr(VI)0}}$); u_{q_t} is defined as q_t/q_e where q_t and q_e are the amount of total chromium sorbed at time t and at equilibrium, respectively.

Concerning the constants, k_1 is the rate constant for the irreversible reaction of Cr(VI) reduction to Cr(III); k_2 and k_4 ; k_3 and k_5 are the sorption and desorption rate constants respectively, for Cr(VI) and Cr(III). In the differential equations system, Q_R has been defined as the ratio of the amount of hexavalent chromium ($q_{\text{Cr(VI)}}$) to total chromium sorbed at equilibrium (q_{Tot}) ($Q_R = q_{\text{Cr(VI)}}/q_{\text{Tot}}$).

Results of sorption experiments corresponding to 10 mg L^{-1} Cr(VI) initial concentration performed at different temperatures are plotted in Fig. 4. In this figure, total chromium, Cr(VI) and Cr(III) concentrations change with time have been plotted separately to better visualize kinetics profile of the different chromium species. It is important to remark that in all the cases chromium in the remaining solution was always in its trivalent oxidation state with a final concentration of around 3 mg L^{-1} ($C/C_0 = 0.3$). These results indicate that for a given concentration, temperature does not affect equilibrium. Nevertheless, it affects the kinetics of the overall pro-

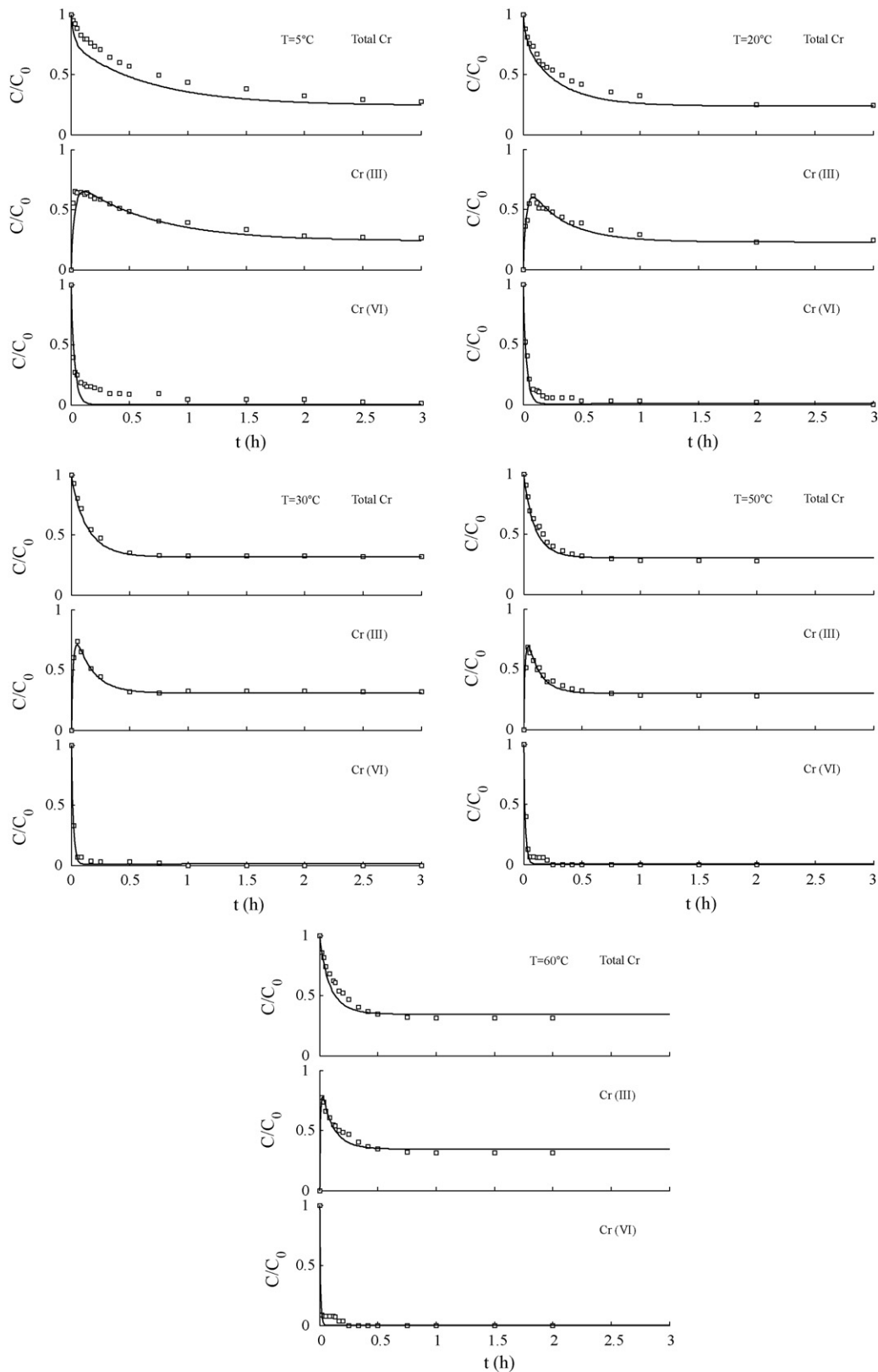


Fig. 4. Kinetics of Cr(VI) sorption onto grape stalk waste at different temperatures. Solid lines represent predicted data by the proposed model. Cr(VI) initial concentration: 10 mg L^{-1} ; sorbent dose: 2.5 mg L^{-1} ; particle size: $0.25\text{--}0.56 \text{ mm}$.

cess as attainment of equilibrium is faster with the increase of the temperature.

Experimental results have been submitted to the above proposed model. Results have been obtained by integration of the dif-

ferential equations system by means of the function Ode 45 of Matlab v. 7.1 (R-14), which applies Runge–Kutta method of 4–5 order.

The overall process constants ($k_1\text{--}k_5$) and Q_R were determined by minimizing the sum of squared error (SSE) (see Eq. (4)). The

Table 1

Model constants for the different processes: reduction of Cr(VI), and Cr(VI) and Cr(III) sorption/desorption processes of Cr(VI) sorption onto grape stalk waste at different temperatures. Initial Cr(VI) concentration: 10 mg L⁻¹; sorbent dose: 2.5 g L⁻¹; sorbent particle size: 0.25–0.56 mm.

T (°C)	k ₁ (h ⁻¹)	k ₂ (h ⁻¹)	k ₃ (h ⁻¹)	k ₄ (h ⁻¹)	k ₅ (h ⁻¹)	Q _R	SSE
5	23.75	9.84	0.21	1.23	0.91	0.80	0.30
20	25.77	9.79	0.57	3.23	0.65	0.45	0.07
30	50.57	6.49	1.42	5.33	2.33	0.60	0.02
50	60.73	6.18	1.49	8.83	2.14	0.30	0.03
60	110.33	6.10	1.51	8.90	1.98	0.10	0.05

k₁, reduction reaction; k₂, Cr(VI) sorption; k₃, Cr(VI) desorption; k₄, Cr(III) sorption; k₅, Cr(III) desorption; Q_R, q_{Cr(VI)}/q_{Tot}; SSE, sum of square error.

function is described as the sum of the relative square errors for Cr(VI) and Cr(III):

$$SSE = \sum_{i=1}^n \left(\frac{C_{Cr(VI)_{exp}}(t_i) - C_{Cr(VI)_{calc}}(t_i)}{C_0} \right)^2 + \left(\frac{C_{Cr(III)_{exp}}(t_i) - C_{Cr(III)_{calc}}(t_i)}{C_0} \right)^2 \quad (4)$$

Minimization of the function was carried out by using the method of Generalized Reduced Gradient (GRG).

In Table 1, the constants obtained with the model are presented: k₁ (Cr(VI) to Cr(III) reduction), k₂ and k₃ (Cr(VI) sorption and desorption), k₄ and k₅ (Cr(III) sorption and desorption as well as Q_R (sorbed Cr(VI)/total Cr ratio). It can be seen in the table that k₁ values are very high compared to the sorption and desorption constants rates. It can also be observed that this constant is strongly dependent on temperature, varying from 23.75 at 5 °C to 110.33 at 60 °C following an equation of Arrhenius type. The acceleration of the reaction with increasing temperature is explained by lowering the energy barrier to the redox reaction. The decrease of k₂ and the increase of k₄ with temperature are related to k₁ values. The higher the k₁ value the lower Cr(VI) concentration in solution and the subsequent higher Cr(III) concentration as a consequence of chromium reduction. Therefore, Cr(VI) adsorption rate decreases, Q_R also decreases and Cr(III) adsorption increases with temperature.

Calculated values obtained from the model have been superimposed on the kinetics experimental data in Fig. 4. It can be observed that the model describes quite well the kinetics profile of total chromium, Cr(VI) and Cr(III). The goodness of the fit can be confirmed by plotting calculated values versus experimental values. As an example, calculated and experimental values corresponding to experiments performed at 30 °C have been plotted in Fig. 5. It can be seen that all the data are distributed on the bisecting first quadrant confirming the goodness of the fitting. Similar results were obtained with the rest of calculated and observed data.

Several equations to model kinetics of Cr(VI) adsorption, apart from the pseudo-first and pseudo-second order equation models, have been reported in the literature to predict the rate of Cr(VI) removal. Most of them are focused on describing Cr(VI) kinetics profile [19–21]. Recently, some authors have proposed models based on the reduction rate to predict kinetics of Cr(VI) and the assumption that the reduced Cr(III) sorption follows Langmuir to calculate the amount of chromium sorbed in this oxidation state [9,22]. Nevertheless, any of the models found in the literature takes into account the three different reactions that take place, Cr(VI) reduction, Cr(VI) adsorption/desorption and adsorption/desorption of the formed Cr(III).

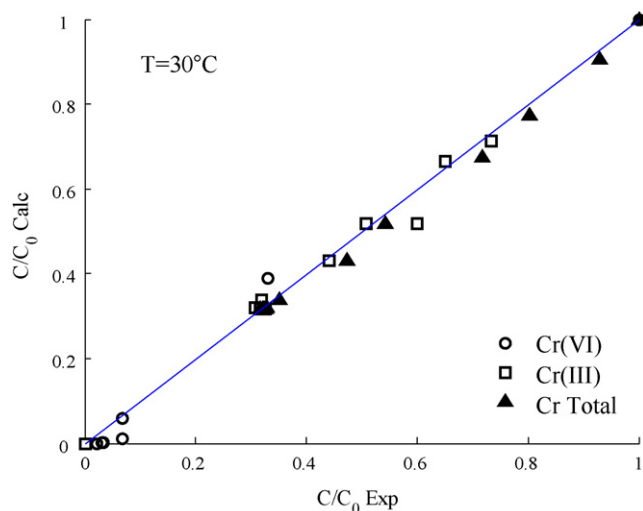


Fig. 5. Experimental versus calculated values by the model corresponding to Cr(VI) sorption onto grape stalk waste at 30 °C. Cr(VI) initial concentration: 10 mg L⁻¹; sorbent dose: 2.5 mg L⁻¹; particle size: 0.25–0.56 mm.

4. Conclusions

The use of a stirred reactor allowed to observe that the Cr(III) formed due to reduction is partially adsorbed onto grape stalk waste. Therefore reversible reaction adsorption–desorption of Cr(III) was introduced in the model formulation. The rate constants values put into evidence that reduction is the main reaction, Cr(VI) is rapidly reduced to Cr(III) and the rest of the processes are affected by this fact. The proposed model fits adequately the obtained experimental data for total chromium, Cr(VI) and the calculated Cr(III). Furthermore, this model would be helpful for researchers in the field of Cr(VI) biosorption to design and predict the performance of biosorption processes, specially when chromium sorption is in part totally based on the sorbent capacity of reducing hexavalent chromium.

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References

- [1] A. Baral, R.D. Engelken, Chromium-based regulation and greening in metal finishing industries in the USA, *Environ. Sci. Policy* 5 (2002) 121–133.
- [2] INASMET Tecnalia, in: M. Cox, P. Negré, L. Yurramendi (Eds.), *A Guide Book on the Treatment of Effluents from the Mining/Metallurgy, Paper, Plating and Textile Industries*, London, 2006, pp. 181 and 184.
- [3] J.W. Patterson, *Industrial Waste Water Treatment Technology*, Science Publishers, New York, 1997.
- [4] R.R. Patterson, S. Fendorf, M. Fendorf, Reduction of hexavalent chromium by amorphous iron sulfide, *Environ. Sci. Technol.* 31 (1997) 2039–2044.
- [5] L.H. Bopp, H.L. Ehrlich, Chromate resistance and reduction in *Pseudomonas fluorescens* strain LB300, *Arch. Microbiol.* 150 (1988) 426–431.
- [6] N. Fiol, I. Villaescusa, M. Martínez, N. Miralles, J. Poch, J. Serarols, Biosorption of Cr(VI) using low cost sorbents, *Environ. Chem. Lett.* 1 (2003) 135–139.
- [7] N. Fiol, C. Escudero, I. Villaescusa, Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark, *Bioresour. Technol.* 99 (2008) 5030–5036.
- [8] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake, *J. Hazard. Mater. B* 94 (2002) 49–61.
- [9] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weeds: kinetics and mechanics studies, *J. Hazard. Mater.* 152 (2008) 100–112.
- [10] D. Park, S.-R. Lim, Y.-S. Yun, M.J. Park, Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction, *Chemosphere* 70 (2007) 298–305.

- [11] D. Park, Y.-S. Yun, C.K. Ahn, J.M. Park, Kinetics of the reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass, *Chemosphere* 66 (2007) 939–946.
- [12] R.S. Laxman, S. More, Reduction of hexavalent chromium by *Streptomyces griseus*, *Miner. Eng.* 15 (2002) 831–837.
- [13] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, *Standard Methods for the determination of water and wastewater*, 20th ed., United Book Press, Inc., Baltimore, USA, 1998, pp. 3–65.
- [14] L. Dupont, E. Guillon, Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, *Environ. Sci. Technol.* 94 (2003) 49–61.
- [15] L.K. Cabatingan, R.C. Agapay, J.L.L. Rakels, M. Ottens, L.A.M. van der Wielen, Potential of biosorption for the recovery of chromate in industrial wastewaters, *Ind. Eng. Chem. Res.* 40 (2001) 2302–2309.
- [16] J. Lakatos, S.D. Brown, C.E. Snape, Coals as sorbents for the removal and reduction of hexavalent chromium from aqueous waste streams, *Fuel* 81 (2002) 691–698.
- [17] D.C. Sharma, C.F. Forster, Column studies into the adsorption of chromium (VI) using Sphagnum moss peat, *Bioresour. Technol.* 52 (1995) 261–267.
- [18] S.-Y. Suen, A Comparison of Isotherm and Kinetics Models for Binary-solute Adsorption to Affinity Membranes, *J. Chem. Technol. Biotechnol.* 65 (1996) 249–257.
- [19] A.M. Ferro Orozco, E.M. Contreras, N.E. Zritzky, Modelling Cr(VI) removal by a combined carbon-activated sludge system, *J. Hazard. Mater.* 150 (2008) 46–52.
- [20] D. Park, Y.-S. Yun, H.W. Lee, J.M. Park, Advanced kinetic model of the Cr(VI) removal by biomaterials at various pHs and temperatures, *Bioresour. Technol.* 99 (2008) 1141–1147.
- [21] D. Park, S.-R. Lim, H.W. Lee, J.M. Park, Mechanism and kinetics of Cr(VI) reduction by waste slag generated from ion making industry, *Hydrometallurgy* 93 (2008) 72–75.
- [22] D. Park, Y.-S. Yun, J.Y. Kim, J.M. Park, How to study Cr(VI) biosorption: use of fermentation waste for detoxifying Cr(VI) in aqueous solution, *Chem. Eng. J.* 136 (2008) 173–179.