A model to describe Cr(VI) kinetics biosorption

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ABSTRACT

In this work, the effect of pH control on kinetics of Cr(VI) sorption onto grape stalks has been studied. A set of experiments were performed at a constant pH 3 ± 0.1 which was assured by means of a Programmable Logic Controller (PLC). In a second set of experiments the initial pH was adjusted to pH 3 and then pH was allowed to freely evolve during the sorption process. Both sets of experiments were carried out at different temperatures within the range 5–50 °C. Constant temperature was assured by water recirculation from a thermostatic bath. Results demonstrated that pH has high influence on kinetics only at the lowest temperatures studied. A model based on a complex reaction sequence which takes into account Cr(VI) sorption, reduction of Cr(VI) to Cr(III), sorption of the formed Cr(III) which includes the pH variation during the sorption process has been proposed to model Cr(VI) kinetics sorption onto grape stalk waste. Furthermore, the robustness of the model has been tested.

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1. Introduction

The extensive use of chromium compounds in various industries (e.g. metal electroplating, leather tanning, wood preservatives) lead to huge amounts of chromium discharged into the environment due to inefficient removal treatments of Cr-bearing wastewaters or improper disposal of sludge contaminated with chromium with the risk of leakage.

During the last decades, a lot of studies on Cr(VI) biosorption by various biomaterials such as bacteria [1], algae [2], fungi [3], industrial wastes [4] and agricultural wastes [5] have been undertaken in order to find out an alternative to the costly additional effluents treatments like ion exchange, membrane separation and adsorption on activated carbons, commonly used to remove the low concentrations of hexavalent chromium that still remain in the solution after the traditional chromium reduction–precipitation processes. Nevertheless, only in few reported studies mechanism of Cr(VI) sorption has been investigated. Recently, the capacity of some of biomasses to reduce Cr(VI) to Cr(III) has been evaluated and it has been confirmed that Cr(VI) removal by these biomaterials is due to an "adsorption-coupled reduction" mechanism. Chromium reduction by bacteria [6], by algae [7] by fungi [8], by industrial wastes [9–11] and by agricultural wastes [12] has been

recently reported. Therefore, in those cases, two different steps can be considered in the overall process, Cr(VI) reduction and Cr(VI) sorption.

The knowledge of the mechanism that governs metal adsorption is of great importance to propose a model that explains the experimental data and predicts the effect of the variation of some parameters on the sorption process efficiency. Among the authors who have investigated the mechanism of Cr(VI) onto different biomasses, a very few of them have proposed a model that takes into account the above mentioned steps of Cr(VI) reduction and Cr(VI) adsorption. Park et al. found an empirical model able to describe the pH dependence on hexavalent chromium sorption with the brown seaweed *Ecklonia biomass* [13], with pine needle [14] and with different biomaterials [10,15] nevertheless they did not succeed in expressing the dependence of pH in a mechanistic manner.

It is well recognised that metal biosorption processes are pH dependent as proton concentration influences on the sorbent ionization and the chemical speciation of metal in solution. Additionally, in the case of Cr(VI) sorption proton concentration influences on the rate of Cr(VI) to Cr(III) reduction. Therefore, models including a term that takes into account pH variation during the sorption process are necessary to predict the rate at which the process will take place.

The aim of the present work is to propose a kinetics model for Cr(VI) sorption onto grape stalk waste which takes into account the rates at which Cr(VI) is reduced and Cr(VI) and Cr(III) are

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adsorbed and desorbed; and also, the variation of pH during Cr(VI) sorption.

2. Materials and methods

2.1. Materials

Grape stalks 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 distilled water. A 1 M solution of HCl was used to adjust the initial pH to pH 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 used in a previous work [17]. The double wall allows temperature regulation by water recirculation from a bath with thermostatic control. Temperature fluctuations in the reactor were within ± 0.1 °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 was maintained continuously stirred at 250 rpm. Constant pH was assured by means of a Programmable Logic Controller (PLC) (Eutech Instrument, αlpha-pH2000W), 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

A set of experiments were performed at constant pH 3 and at four different temperatures 5, 20, 30 and 50 °C. For these experiments, a volume of 4 L of $10\,mg\,L^{-1}$ Cr(VI) solutions was introduced in the reactor under constant agitation. As soon as the liquid attained the desired pH and temperature, 10 g of grape stalks wastes was added. The pH was kept constant at pH 3.0 ± 0.1 by the PLC. The corresponding results have already been published in a previous work [17].

For comparison sake, in this work, experiments in the same conditions were carried out without pH control so as to ascertain the effect of pH variation during the sorption process on Cr(VI) sorption. In this case the initial pH was adjusted at 3.0 ± 0.1 and then it was allowed to freely evolve until equilibrium was reached. Each experiment was carried out in duplicate.

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 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
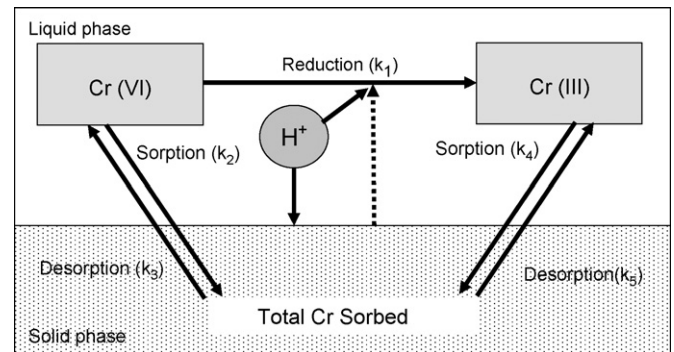

Fig. 1. Reactions scheme of Cr(VI) sorption onto grape stalk waste.

return the excess of sampled solution or when the autosampler 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 analysed by the standard colorimetric 1,5-diphenylcarbazide method [16], 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 used for obtaining the calibration curves in the diphenylcarbazide method was analysed by FAES. Analytical measurements made by the two techniques were comparable within 5%.

2.6. Kinetics modelling

The model proposed in this work has been developed on the basis of our recently developed kinetics model [17]. In that model the different processes taking place in Cr(VI) sorption onto grape stalks waste were taken into account: (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. A scheme of the different steps is depicted in Fig. 1.

In this work, a new term has been introduced into the model: the variation of the pH during Cr(VI) sorption due to both chromium reduction and sorbent protonation. The different processes taking place in Cr(VI) sorption onto grape stalks have been formulated with the following series of dimensionless equations leading to the system:

$$\frac{du_{Cr(VI)}}{dt} = -k_1 u_{Cr(VI)} u_H^n - k_2 u_{Cr(VI)}(1 - p u_{qt}) + k_3 p u_{qt} \quad (1)$$

$$\frac{du_{Cr(III)}}{dt} = k_1 u_{Cr(VI)} u_H^n - k_4 u_{Cr(III)}(1 - (1-p)u_{qt}) + k_5(1-p)u_{qt} \quad (2)$$

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

$$\frac{du_{H^+}}{dt} = -k_1 u_{Cr(VI)} u_H^n - g(t, u_H) \quad (4)$$

where $u_{Cr(VI)}$ is defined as the ratio between Cr(VI) in solution at time t and initial Cr(VI) concentration ($C_{Cr(VI)t}/C_{Cr(VI)0}$) and $u_{Cr(III)}$ as the ratio between Cr(III) concentration at time t and initial Cr(VI)
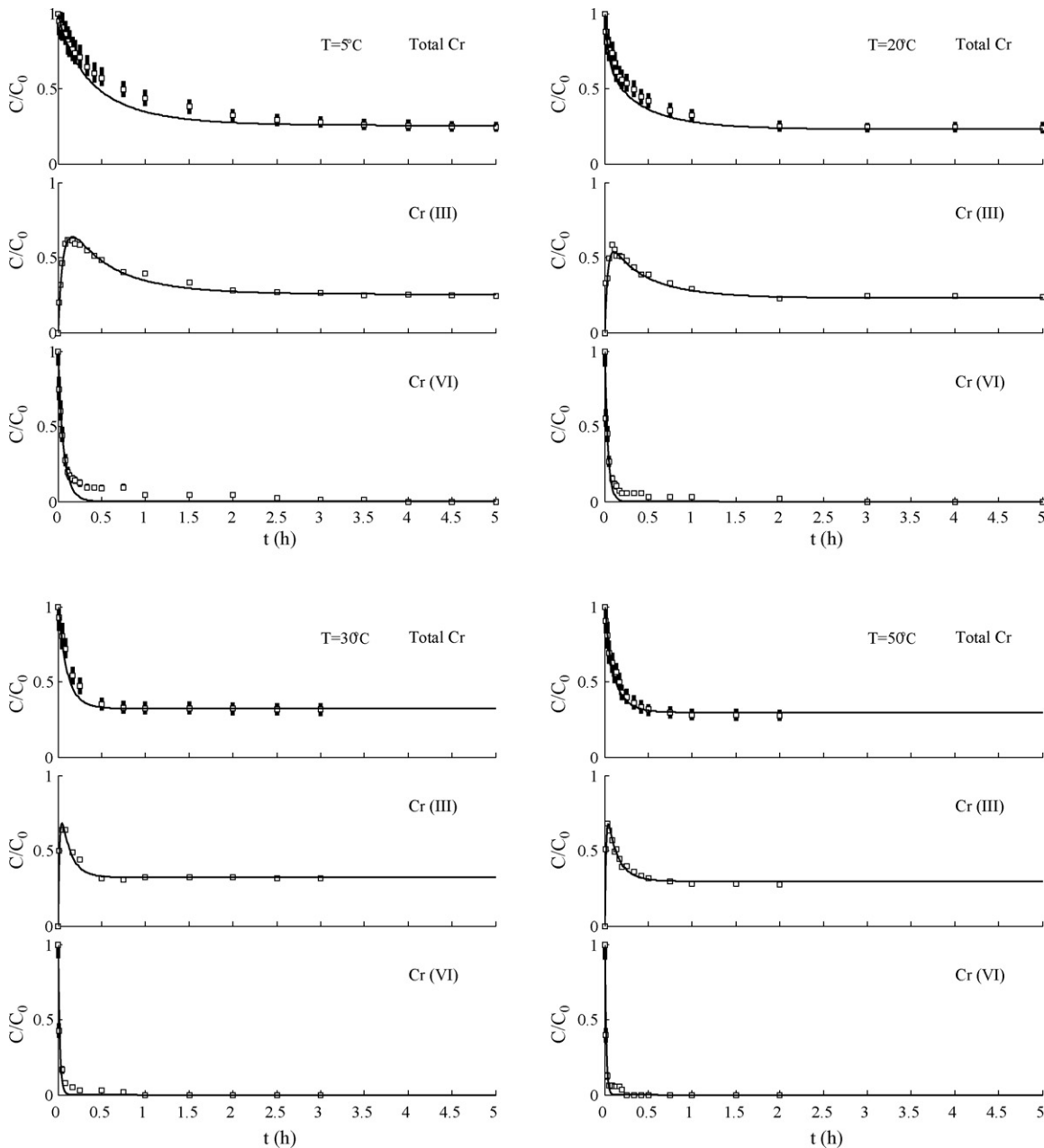
Fig. 2. Kinetics of Cr(VI) sorption onto grape stalk waste at different temperatures and pH 3.0. Solid lines represent predicted data by the proposed model, dotted symbols the simulated data and open symbols the experimental data. Cr(VI) initial concentration: 10 mg L^{-1}; sorbent dose: 2.5 mg L^{-1}; particle size: 0.25–0.56 mm.

concentration ($C_{Cr(III)t}/C_{Cr(VI)0}$); u_H as the ratio of protons in solution at time t; and protons initial concentration ([H$^+$]$_t$/[H$^+$]$_0$) and n is the reaction order with respect to H$^+$ that was estimated by the model to be 2.64; u_{qt} 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; p as the ratio between Cr(VI) and total chromium (Cr(VI)+Cr(III)) in solution; and $g(t,u_H)$ the rate of protons consumption due to sorbent protonation, has been modelled with the expression $g(t, u_H) = au_H^b$.

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; and k_3 and k_5 are the sorption and desorption rate constants, respectively, for Cr(VI) and Cr(III).

The results of the model have been calculated by integration of the differential equations system by means of the function ode15s of Matlab v. 7.1 (R-14), based on Numerical Differentiation Formulas.

The constants of the model were determined by minimizing the Sum of Squared Residuals (SSR) (see Eq. (5)). The function is described as the sum of the relative square errors for Cr(VI) and Cr(III).

$$SSE = \sum_{i=1}^{N} \left(\frac{C_{Cr(VI)_{exp}}(t_i) - C_{Cr(VI)_{calc}}(t_i)}{C_0} \right)^2$$
$$+ \left(\frac{C_{Cr(III)_{exp}}(t_i) - C_{Cr(III)_{calc}}(t_i)}{C_0} \right)^2 \qquad (5)$$

Minimization of the function was carried out by using the method of Generalized Reduced Gradient (GRG).
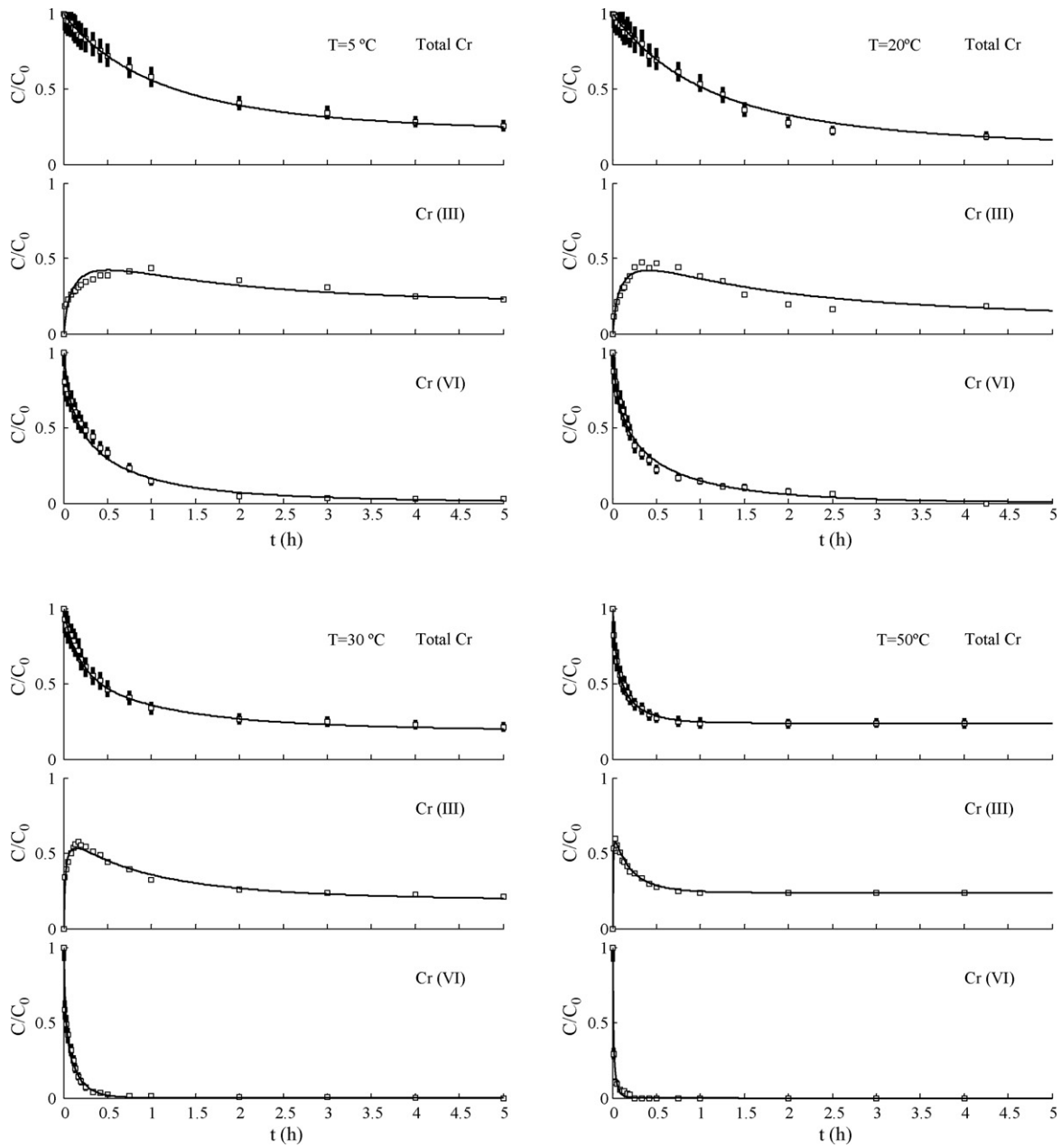
Fig. 3. Kinetics of Cr(VI) sorption onto grape stalk waste at different temperatures and initial pH 3.0. Solid lines represent predicted data by the proposed model, dotted symbols the simulated data and open symbols the experimental data. Cr(VI) initial concentration: $10\,mg\,L^{-1}$; sorbent dose: $2.5\,mg\,L^{-1}$; particle size: 0.25–0.56 mm.

Table 1
Model constants for the processes: reduction of Cr(VI), and Cr(VI) and Cr(III) sorption/desorption processes of Cr(VI) sorption onto grape stalks 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})	SSR
Constant pH = 3.0 ± 0.1						
5	12.72 ± 0.98	2.13 ± 1.83	1.55 ± 4.43	2.42 ± 0.45	0.21 ± 0.07	0.085
20	18.88 ± 1.50	7.57 ± 2.58	2.06 ± 6.92	3.63 ± 0.68	0.28 ± 0.07	0.059
30	42.31 ± 6.06	3.98 ± 6.13	1.57 ± 7.38	7.39 ± 1.84	1.09 ± 0.32	0.023
50	52.02 ± 4.52	6.65 ± 6.27	0.53 ± 4.44	8.73 ± 1.42	1.05 ± 0.26	0.024
Initial pH = 3.0 let free to evolve						
5	6.02 ± 0.75	0.79 ± 0.26	0.18 ± 0.22	0.60 ± 0.14	0.036 ± 0.015	0.070
20	7.81 ± 0.86	0.85 ± 0.20	0.12 ± 0.07	0.87 ± 0.12	0.008 ± 0.004	0.056
30	44.65 ± 5.59	3.82 ± 0.77	0.00 ± 0.00	1.42 ± 0.23	0.065 ± 0.009	0.023
50	284.94 ± 70.02	16.46 ± 4.46	0.89 ± 5.03	6.86 ± 0.95	0.505 ± 0.071	0.012

k_1, reduction reaction; k_2, Cr(VI) sorption; k_3, Cr(VI) desorption; k_4, Cr(III) sorption; k_5, Cr(III) desorption; SSR, sum of square residuals.
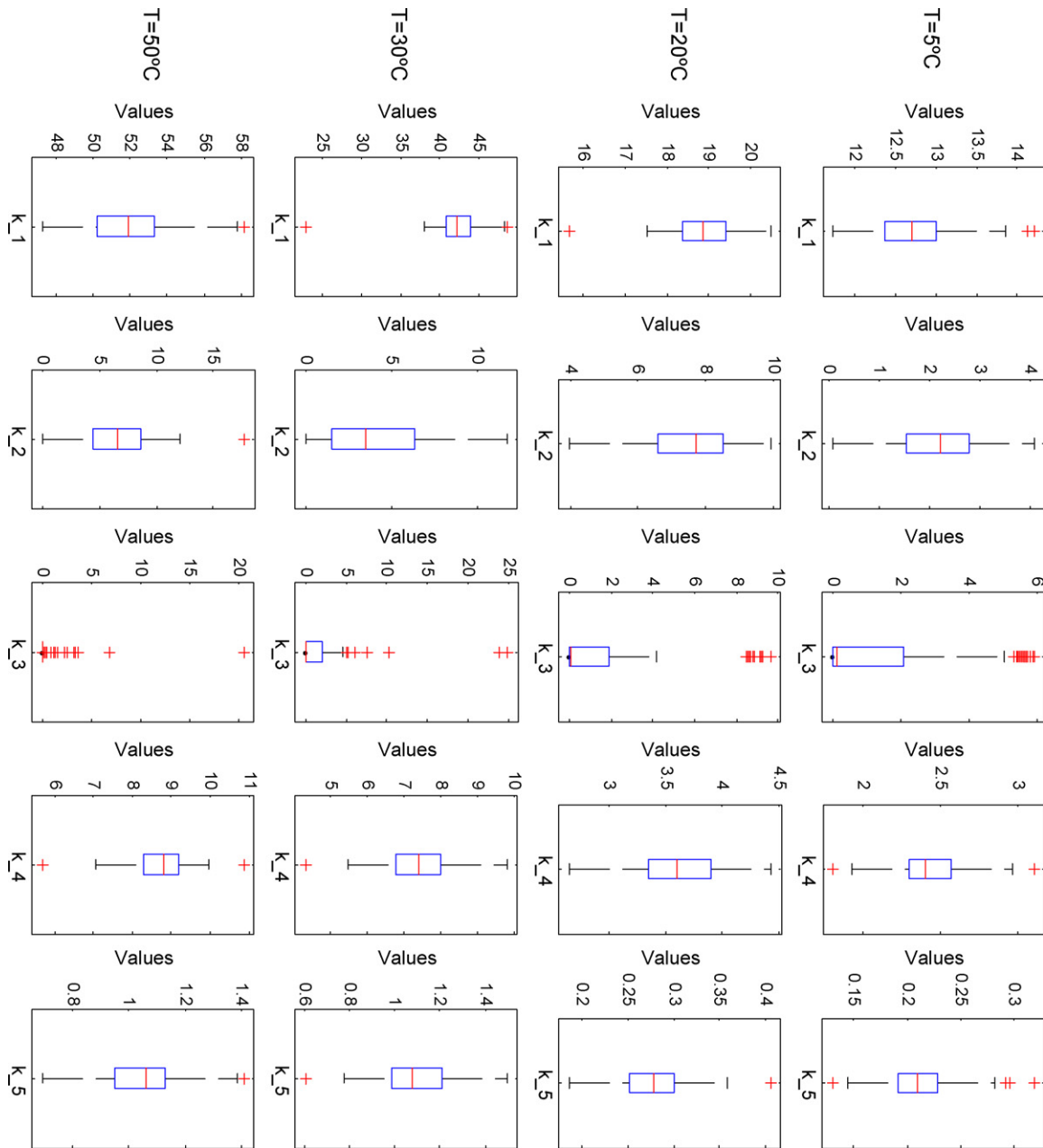
Fig. 4. Box plots for k_1, k_2, k_3, k_4 and k_5 values at different temperatures and pH 3.0.

Constants a and b of expression $g(t, u_H) = a u_H^b$ were determined by minimizing the Sum of Square Errors (Eq. (6)):

$$SSE = \sum_{i=1}^{N} (u_{H_{exp}}(t_i) - u_{H_{calc}}(t_i))^2 \tag{6}$$

where $u_{H_{calc}}(t_i)$ is the solution of equation $\frac{du_H}{dt} = -g(t, u_H)$ for $t = t_i$ with the initial condition $u_H(0)=1$

In order to analyse the sensitivity of the different constants toward experimental data, a certain error ($\pm 5\%$), following a uniform distribution, was introduced in each of the experimental data points. A total of 100 simulations were considered and the corresponding parameters were calculated by following the procedure indicated above.

3. Results and discussion

Experimental data and the 100 simulations of each sorption experimental data point obtained from kinetics carried out at different temperatures of total chromium, trivalent and hexavalent chromium at constant pH 3 and at initial pH 3 are plotted in Figs. 2 and 3, respectively. When looking at results presented on both figures, two analogies can be stated with independence of temperature and pH: (a) when equilibrium is attained, Cr(VI) is totally removed and chromium in the remaining solution is in its trivalent form (around 30% of the initial Cr(VI) concentration); (b) Cr(VI) reduction process is very fast and the formed Cr(III) is progressively adsorbed until equilibrium is reached. For all the sets of experiments, Cr(VI) and Cr(III) concentrations values at equilibrium were quite similar, nevertheless, differences in kinetics rate due to the effect of temperature and pH were observed.
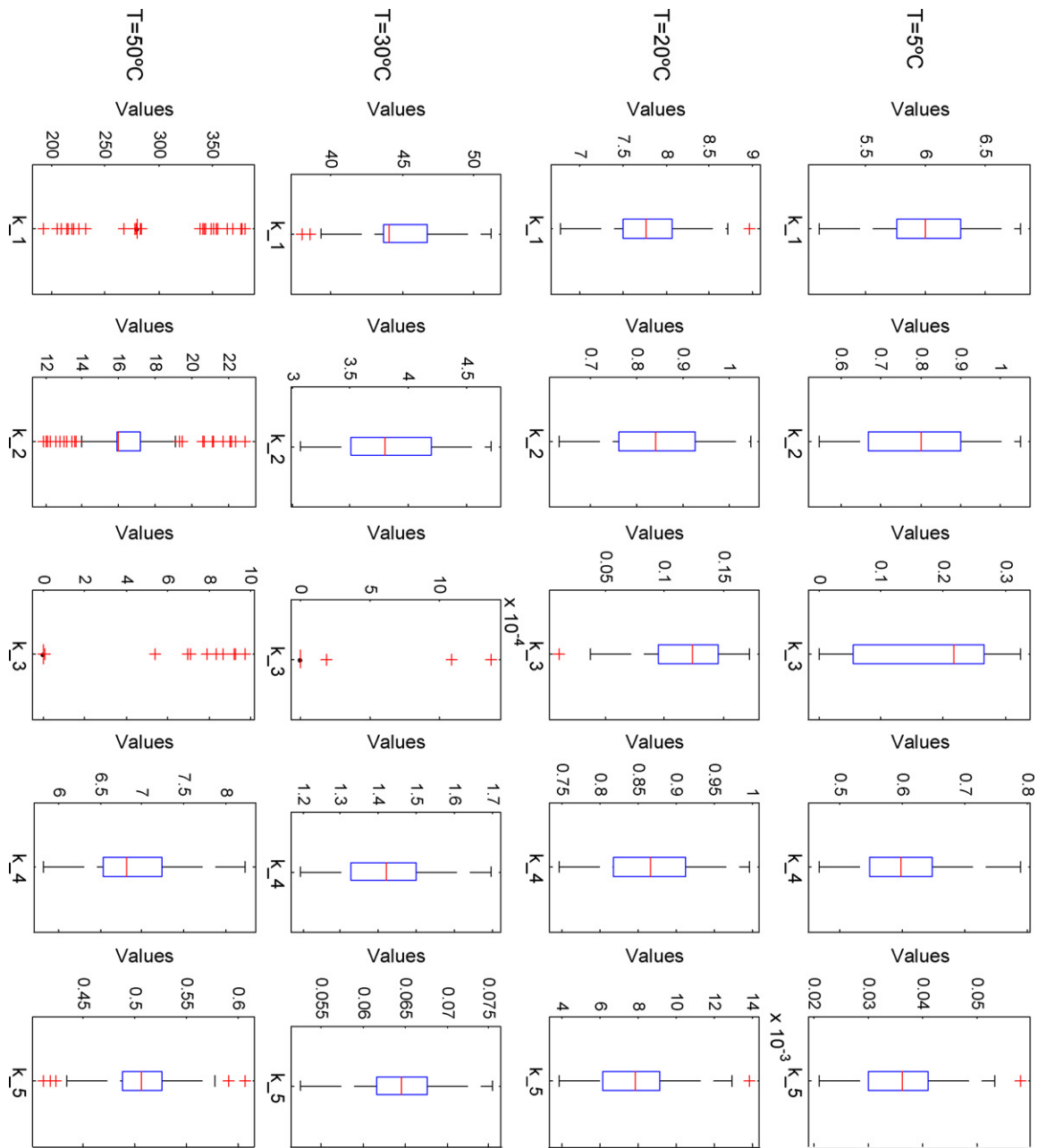
Fig. 5. Box plots for k_1, k_2, k_3, k_4 and k_5 values at different temperatures and initial pH 3.0.

When looking at Figs. 2 and 3 separately, it can be observed that in general, the increase of temperature seems to exert a favourable effect on the rate of Cr(VI) reduction and adsorption. The effect of temperature on the reduction of Cr(VI) has been reported [18].

When comparing results presented in Fig. 2 (constant pH 3.0) and in Fig. 3 (initial pH 3.0), some evident differences in kinetics of total chromium, Cr(VI) and Cr(III) rates can be noticed. Similar observation can be done when comparing results obtained at different temperatures. Cr(VI) disappearance and Cr(III) appearance rates are significantly slower when pH is allowed to freely evolve. This fact indicates that the continuously adjustment of pH to keep it at its optimum value (pH 3) favours the overall process as a fixed concentration of protons is assured for the reduction reaction taking place. Cr(VI) sorption dependence on solution pH is well known and the decrease of reduction rates with time due to the protons consumed by the redox reaction has been reported [14,18].

At this point it must be said that in the experiments performed at initial pH 3, final pH was 3.8 ± 0.1. The increase of pH is not only due to protons consumption for the reduction reaction taking place but is also due to the protonation of the sorbent. Indeed, the final pH of a blank performed in the same conditions but in the absence of Cr(VI) resulted to be 3.5.

It must to be pointed out that pH effect appears to be less important when temperature is 50 °C, surely because the activation of the reduction reaction due to the increase of temperature compensates the decrease of protons disposal for the same reaction to be accomplished.

Park et al. [14], observed that at a fixed temperature, the removal of Cr(VI) by different biomaterials decreased with increasing pH. The same authors found that Cr(VI) could be completely removed in all experiments, even at a relatively high pH (pH 4.0) when sufficient contact time had been given.
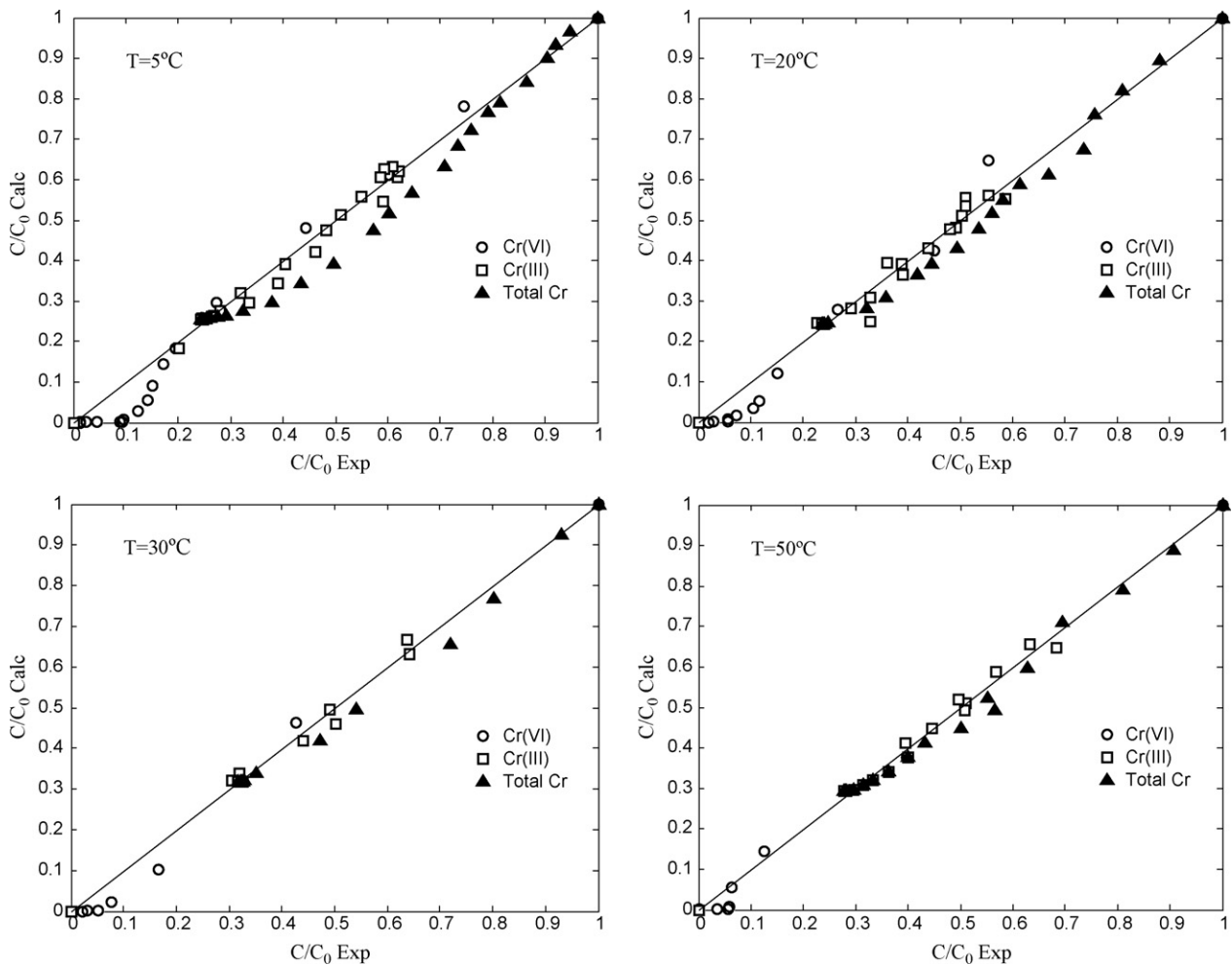
Fig. 6. Experimental versus calculated values by the model corresponding to Cr(VI) sorption onto grape stalk waste at different temperatures and pH 3.0. Cr(VI) initial concentration: $10\,mg\,L^{-1}$; sorbent dose: $2.5\,mg\,L^{-1}$; particle size: 0.25–$0.56\,mm$.

In Table 1, the mean value and estimated error (95% confidence interval) of the constants of Cr(VI) to Cr(III) reduction (k_1), Cr(VI) sorption (k_2) and desorption (k_3), Cr(III) sorption (k_4) and desorption (k_5) obtained from 100 simulations, as well as the corresponding SSR are presented.

As seen in the table, the constants corresponding to the experiments conducted at constant pH 3 are in general higher than the ones obtained at initial pH 3 with freely evolution of pH. This observation indicates that the rates of the processes that take place are dependent on the H^+ concentration. Also, it can be observed that in general, constants values increase with the increase of temperature. Nevertheless, this trend is not observed for k_1 and k_2 in some of the studied experimental conditions. pH seems not to have any effect on k_1 and k_2 when the temperature is 30 °C. An increase of the temperature to 50 °C seems to have a favourable effect on the reduction reaction and Cr(VI) sorption with a spectacular increase of k_1 and k_2 values when the pH is not maintained constant.

The obtained results from the model by using the constants values presented in Table 1 are superimposed to the experimental data and the simulated perturbations in Figs. 2 and 3. It can be observed that the model describes quite well the kinetics profile of total chromium, Cr(VI) and Cr(III).

To describe the distribution of the data obtained from the studies performed, box plots have been used (Figs. 4 and 5). A box plot provides an excellent visual summary of many important aspects of a values distribution. The line across the box represents the median, whereas the bottom and top of the box show the location of the

first and third quartiles (Q_1 and Q_3). The whiskers are the lines that extend from the bottom and top of the box to the lowest and highest observations inside the region defined by $Q_1 - 1.5(Q_3 - Q_1)$ and $Q_3 + 1.5(Q_3 - Q_1)$ [19]. Individual points with values outside these limits, called outliers, are plotted with crosses. The box itself contains the middle 50% of the data. If the median is not equidistant from the top and the bottom of the box, then the data are skewed. In the literature, box plots were applied to represent and compare elemental composition in relation to environmental and occupational health [20] and to assess of the seasonal and polluting effects on the quality of river water [19].

In general, the values presented in Fig. 4 are distributed around the median with an acceptable inter-quartile range. In the case of k_3, the median is practically zero and the values distribution is skewed toward zero. Moreover, when increasing the temperature, values tend to accumulate around zero. That implies that at the highest temperature (50 °C), when the median is zero, only the outlier values are observed in the corresponding box plot.

In Fig. 5, it can be observed that k_1 values at 5 and 20 °C, k_2 values in the range of temperatures 5–30 °C, and k_4 and k_5 in the entire range of temperatures studied are distributed around the median with an acceptable inter-quartile range. k_1 values at 30 °C are skewed toward lowest values. At 50 °C, most k_1 values are accumulated around the median value ($280\,h^{-1}$) with a very narrow inter-quartile range ($0.02\,h^{-1}$), nevertheless it appears that 42% of the values are outliers with a great variation range ($189\,h^{-1}$). k_2 values at 50 °C are also skewed to the lowest values, the median
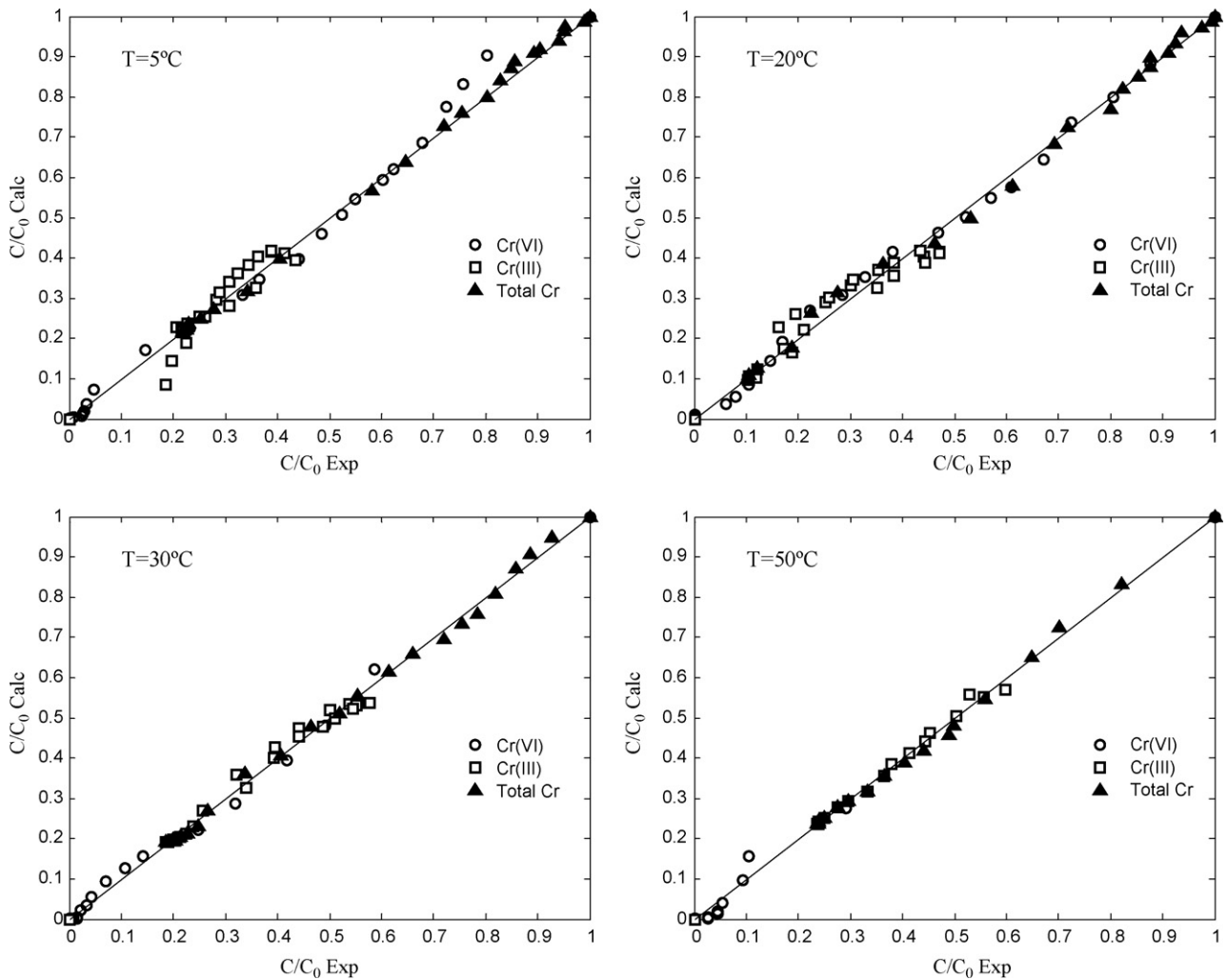
Fig. 7. Experimental versus calculated values by the model corresponding to Cr(VI) sorption onto grape stalk waste at different temperatures and initial pH 3.0. Cr(VI) initial concentration: 10 mg L^{-1}; sorbent dose: 2.5 mg L^{-1}; particle size: 0.25–0.56 mm.

is 16.0 h^{-1}, the inter-quartile range 1.3 h^{-1} and 23% are outliers. In the case of k_3, a different values distribution is found for each of the studied temperatures. At 5 °C the values are skewed toward highest values and at 20 °C, the values are distributed around the median. It must be pointed out that in those cases (5 and 20 °C) k_3 is not zero like it occurred when the pH was kept constant at pH 3.0 (Fig. 4). The median of k_3 values is zero at the two highest temperatures with most of the values around the median and a low percentage of outliers.

Box plots corresponding to k_3 values distribution when pH is kept constant to pH 3 (Fig. 4) put into evidence that desorption of Cr(VI) does not take place taking into account the value of the median that is practically zero for all the temperatures. Confidence intervals for k_3 (Table 1) clearly include the zero value.

When pH is kept constant to pH 3, Cr(VI) desorption for all temperatures is negligible as can be deduced from the great dispersion of k_3 values observed in Table 1 and also in the corresponding box plots (Fig. 4) with median values practically zero. When the initial pH 3 is allowed to freely evolve, Cr(VI) desorption is only negligible at the highest temperatures. At 5 and 20 °C, the average value (Table 1) and the median are different from zero and the values dispersion is low (Fig. 5). Therefore, Cr(VI) desorption must be taken into account when pH is free and the temperature is low.

The values of k_1 and k_2 obtained at 50 °C and free pH show a great variability (Table 1). This fact can be explained by taking into account that a little perturbation of some of the experimental data (specifically values corresponding to the kinetics 20 first minutes data) implies a great variation of the constant value so as the model can fit the new set of data (Fig. 3). This effect is evidenced by the great number of outliers 42% and 23% for k_1 and k_2, respectively, as shown in Fig. 5. Conversely, a little perturbation of the rest of experimental data does not have such a great effect and values are grouped around the median with a narrow inter-quartile range.

The goodness of the model fit can be seen in Figs. 6 and 7 where calculated values versus experimental values were plotted. As seen in the figures, all the data are distributed on the bisecting first quadrant (slope range (0.968–0.982) and R^2 range (0.983–0.993) (Fig. 6) and slope range (1.01–0.994) and R^2 range (0.993–0.997) (Fig. 7)).

4. Conclusions

The proposed model which includes, a part from the Cr(VI) reduction reaction, Cr(VI) and Cr(III) sorption/desorption, the variation of pH during Cr(VI) sorption onto grape stalks, fits satisfactorily the experimental data obtained at different temperatures and at fixed pH 3.0 and at initial pH 3.0 which was allowed to freely evolve

during the process. The robustness of the model is confirmed by the fitting of the model to the 100 simulated data.

The obtained results evidenced that:

- Both parameters, pH and temperature influence on the rate of Cr(VI) sorption onto grape stalk waste. The control of pH is of great importance at low temperatures. High temperatures favour the reduction reaction.
- The constants k_1 (Cr(VI) reduction) and k_2 (Cr(VI) sorption) resulted to be very sensitive to the variation of the original experimental data points.
- Cr(VI) desorption (k_3) must be taken into account when formulating the model. This constant only resulted to be negligible at high temperatures and when pH is free to evolve during the sorption process.

The inclusion in the model formulation of the term of pH variation constitutes an importance advance on the modelling of biosorption processes in which most of the processes are pH dependent.

Acknowledgements

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