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Short communication

Novel comparison of kinetic models for the adsorption-coupled reduction of Cr(VI) using untreated date pit biomaterial

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ABSTRACT

Biosorption of Cr(VI) onto date pit biomass has been investigated via kinetic studies as functions of initial Cr(VI) concentration, solution temperature and date pit particle size. Kinetic experiments indicated that chromate ions accumulate onto the date pits and then reduce to less toxic Cr(III) compounds. The López-García, Escudero and Park Cr(VI) biosorption kinetic models, which take into consideration the direct reduction, the passivation process and the follow-on decrease of the active surface area of reaction, were applied to the kinetic data. The models represented the experimental data accurately at low Cr(VI) concentration (0.480 mM) and small particle size (0.11–0.22 mm) at which the Cr(VI) was completely removed from the aqueous solution and completely reduced to Cr(III) after 420 min. Date pit biomass thus offers a green chemical process for the remediation of chromium from wastewater. This investigation will help researchers employ the adsorption-coupled reduction of Cr(VI) models and simplify their application to kinetic experimental data.

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1. Introduction

Chromium in its hexavalent and trivalent oxidation states are a main species of environmental significance (Albadarin et al., 2012; Marta López-García et al., 2013). Cr(VI) is the toxic form of Cr; approximately 1000 times more toxic than Cr(III) when consumed by the acute oral route (Dayan and Paine, 2001; Ullah et al., 2013), presumably owing to the stronger oxidizing potential and membrane transport of Cr(VI) (Hawley et al., 2004). The rate of toxic Cr(VI) reduction to Cr(III) is of great interest because of the dramatic differences in physical and chemical properties of the two chromium types and the benign character of Cr(III) (Deng and Stone, 1996). The most widely-used approach for detoxifing chromium containing solutions is to reduce it to the less toxic and less mobile Cr(III) and its immobilization as an amorphous hydroxide, which is either adsorbed or precipitated at acidic pH (Erkan Sahinkaya et al., 2012). Such methods are only applicable for concentrated industrial wastewater and produce large amounts of chemical sludge (Cabatingan et al., 2001). Bioremediation is a treatment methodology which can overcome the limitations of conventional techniques and is mainly based on the biomaterial–metal ion interaction (Irem et al., 2013; Kiran and Kaushik, 2012). Date pits are described as one of the best candidates among the agricultural wastes because they are cheap and quite abundant, especially in Mediterranean countries (Ahmed and Theydan, 2012). In a previous study, it was found that raw date pits (DP) are alternative and effective biosorbents for the reduction and elimination of toxic Cr(VI) to non-toxic Cr(III) ions in aqueous solutions (Albadarin et al., 2013). It has been proven that Cr(VI) removal by biomass is never a simple adsorption reaction of anionic Cr(VI) onto cationic functional groups of biomaterial (Albadarin et al., 2011, 2013). Four models for Cr(VI) biosorption are reported: (i) anionic adsorption; (ii) adsorption-coupled reduction; (iii) anionic and cationic adsorption; (iv) reduction and anionic adsorption (Albadarin et al., 2011; Saha and Orvig, 2010). The adsorption-coupled reduction mechanism of Cr(VI) to Cr(III) was first proposed by Huang and co-workers. Huang proposed significant kinetic equations to obtain the individual rates of removal due to reduction and adsorption (Huang, 1979). Since then, attempts

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have been made to develop a model which is able to describe the overall mechanism of Cr(VI) removal (Escudero et al., 2009; López-García et al., 2013; Park et al., 2008; Poch and Villaescusa, 2010). Therefore, researchers cannot continue to apply the known first- and second-order kinetic adsorption models to fit the data of Cr(VI) reduction by biomaterials. To the best of our knowledge, nobody has ever considered simultaneously applying these models and carrying out a comparison of kinetic models for the adsorption-coupled reduction of Cr(VI) using a biomaterial. The purpose of the present study, therefore, was to examine the influence of altering the kinetic experimental conditions and comparing the various proposed adsorption–reduction models. This study will hopefully encourage researchers to use the adsorption-coupled reduction of Cr(VI) models and simplify their fitting to kinetic experimental data.

2. Experimental procedure

2.1. Date pit biomass and reagents

The date pit (DP) bio-waste was oven-dried and crushed in an electric mixer. The dried product was then sieved to obtain different particle sizes corresponding to 0.11–0.22, 0.22–0.85, 0.85–2.00 and >2.00 British Standard Sieve (BSS) mesh, and stored without any chemical treatment in glass jars until its use. The physical and chemical characteristics of date pits can be found in (Albadarin et al., 2013). However, main properties are: surface area = 78.89 $m^2\,g^{-1}$, total pore volume = 0.0716 $cc\,g^{-1}$ and point of zero charge = 4. Chemical analysis: C: 83.03%; Si: 0.91%; S: 0.35%; Ca: 0.28% and O: 15.43%. The reagents used in this work were HNO_3 and NaOH from Merck, 1,5-diphenylcarbazide, and $K_2Cr_2O_7$ from Aldrich (Sigma–Aldrich, UK). All solutions were prepared with deionised water (Millipore apparatus, water resistivity = 18.0 Ω).

2.2. Kinetic experiment

For kinetic studies, 0.50 g of date pits (DP) was agitated with 250 cm^3 of Cr(VI) ion solutions at various experimental conditions on hot plate stirrers to adjust the temperature if necessary. The effect of initial Cr(V) concentration (0.480–2.884 mM), solution temperature (22–60 °C) and date pit particle size (0.11–2.00 mm) was examined. The pH of the experimental solutions was adjusted by adding 1 M NaOH or HNO_3 using a micro-pipette as required. At time intervals, samples (1 cm^3) were withdrawn over a total period of 420 min. Different time intervals were chosen: 0, 1, 3, 5, 10, 15, 20, 30, 40, 60, 90, 120, 150, 180, 240, 300, 360 and 420 min. In all experimental series, the common biosorption conditions were 2 g dm^{-3} of date pits, stirring speed 180 rpm, and pH equal to 2.0. A standard colorimetric method was used to measure the concentrations of Cr(VI) (Albadarin et al., 2013). The total Cr (Cr(VI) and Cr(III)) concentrations were analyzed by a Perkin-Elmer 2100 atomic absorption spectrophotometer (ICP-AES) at a wavelength of 357.9 nm.

3. Kinetic modelling

3.1. López-García model

The rate expression derived for the reduction of Cr(VI) includes the concentration of organic matter present in the biosorbent (López-García et al., 2013):

$$\frac{d[\mathrm{Cr(VI)}]}{dt} = k_1 \cdot [\mathrm{OM}] \cdot [\mathrm{Cr(VI)}] \quad (1)$$

where k_1 ($dm^{-3}\,mg^{-1}\,s^{-1}$) is the rate constant for the reaction, [OM] is the amount of oxidizable organic matter ($mg\,dm^{-3}$). Assuming a 1:1 stoichiometry between OM and Cr(VI), the following equation can be obtained:

$$\frac{d[\mathrm{Cr}(VI)]}{dt} = k_1 \cdot [\mathrm{Cr(VI)}] \cdot ([\mathrm{OM}]_o - [\mathrm{Cr(VI)}]_o - [\mathrm{Cr(VI)}]) \quad (2)$$

$[OM]_o$ is proportional to the mass of the biosorbent in the experiment: $[OM]_o = f_1 . [\mathrm{sorbent}]$. where f_1 ($mg\,g^{-1}$) represents the amount of organic groups capable of reducing Cr(VI) per gram of biomass and it is considered as a fitting parameter. The rate equation for Cr(III) adsorption onto the biomaterial is:

$$\frac{d[\mathrm{Cr(III)}]}{dt} = -\frac{d[\mathrm{Cr(VI)}]}{dt} - k_2 \cdot [\mathrm{Cr(III)}] \cdot (Q_{max} - q) + k_3 \cdot q \quad (3)$$

$$q = \frac{[\mathrm{Cr(VI)}]_o - [\mathrm{Cr(VI)}] - [\mathrm{Cr(III)}]}{[\mathrm{sorbent}]} \quad (4)$$

where k_2 and k_3 represent the rate constants for the adsorption and desorption of Cr(III) respectively and Q_{max} is the binding capacity of the biosorbent obtained by the Langmuir isotherm (Albadarin et al., 2013); q ($mg\,g^{-1}$) is the amount of Cr(III) bound.

3.2. Escudero model

Escudero and co-worker (Escudero et al., 2009) developed a model describing the different phenomena in a series of dimensionless equations, leading to the system:

$$\frac{du_{\mathrm{Cr(VI)}}}{dt} = -k_1 u_{\mathrm{Cr(VI)}} - k_2 u_{\mathrm{Cr(VI)}}(1 - Q_R u_{qt}) + k_3 Q_R u_{qt} \quad (5)$$

$$\frac{du_{\mathrm{Cr(III)}}}{dt} = -k_1 u_{\mathrm{Cr(VI)}} - k_4 u_{\mathrm{Cr(III)}}(1 - (1 - Q_R u_{qt})) + k_5(1 - Q_R) u_{qt} \quad (6)$$

$$\frac{du_{qt}}{dt} = -k_2 u_{\mathrm{Cr(VI)}}(1 - Q_R u_{qt}) + k_3 Q_R u_{qt} + k_4 u_{\mathrm{Cr(III)}}(1 - (1 - Q_R) u_{qt}) - k_5(1 - Q_R) u_{qt} \quad (7)$$

where $u_{\mathrm{Cr(VI)}}$ is defined as the ratio between Cr(VI) concentration in the solution at time t and initial Cr(VI) concentration ($C_{\mathrm{Cr(VI)}t}/C_{\mathrm{Cr(VI)o}}$) and $u_{\mathrm{Cr(III)}}$ as the ratio between Cr(III) concentration at time t and initial Cr(VI) concentration ($C_{\mathrm{Cr(III)}t}/C_{\mathrm{Cr(VI)o}}$); 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. k_1 is the rate constant for the irreversible reaction of Cr(VI) reduction to Cr(III); k_2 and k_4 are the sorption and desorption rate constants for Cr(VI) and k_3 and k_5 are the sorption and desorption rate constants for Cr(III). In the differential equations system, Q_R has been defined as the ratio of the amount of hexavalent chromium ($q_{\mathrm{Cr(VI)}}$) to total chromium sorbed at equilibrium (q_{Tot}); ($Q_R = q_{\mathrm{Cr(VI)}}/q_{\mathrm{Tot}}$).

3.3. Park redox model

Park developed a model equation in the general form, as follows (Park et al., 2008):

$$[\mathrm{Cr(VI)}] = \frac{C^*_{OC}[B][\mathrm{Cr(VI)}]_o - [\mathrm{Cr(VI)}]_o^2}{C^*_{OC}[B]\exp(k_{redox}(C^*_{OC}[B] - [\mathrm{Cr(VI)}]_o)t) - [\mathrm{Cr(VI)}]_o} (\mathrm{mM}) \quad (8)$$

where k_{redox} is the rate coefficient, B is the biomass, and C^*_{OC} indicates the content of the equivalent organic compound per unit gram of biomass, $mmol\,g^{-1}$.

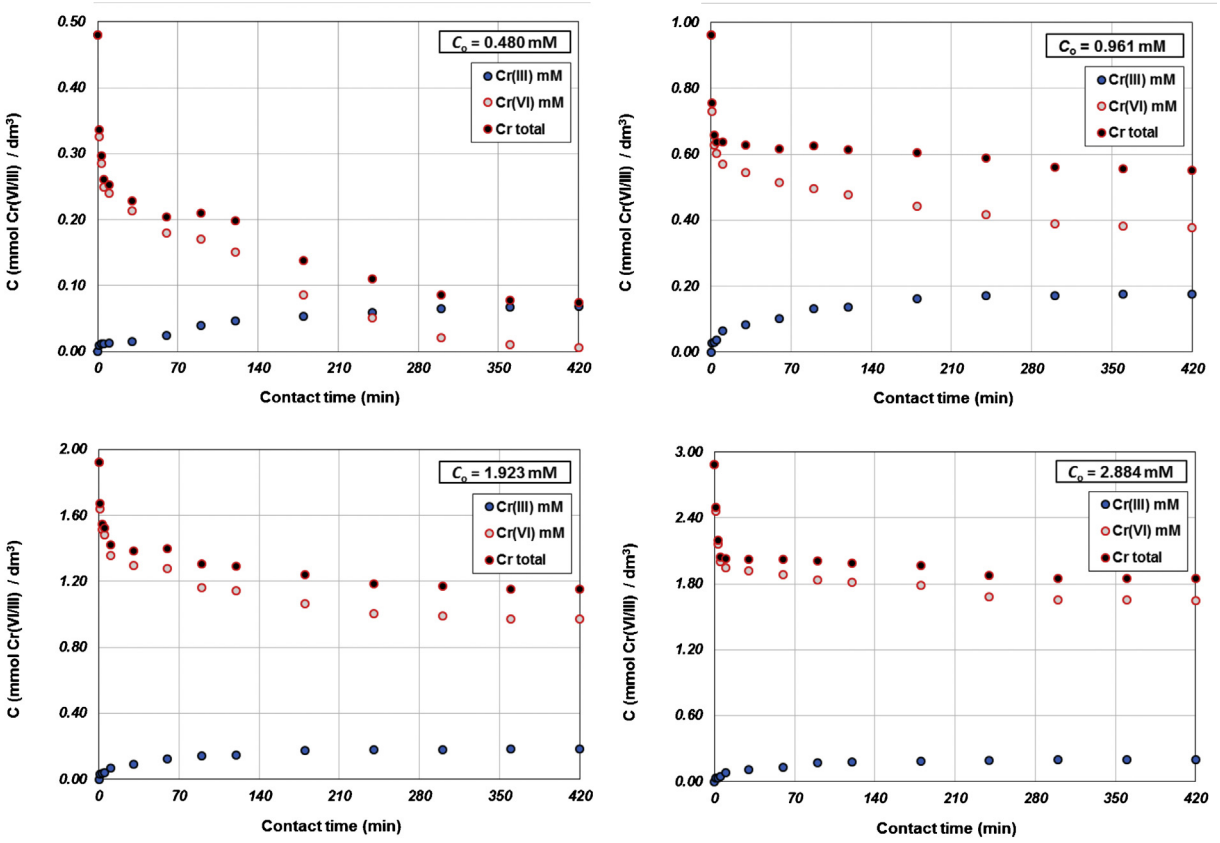

Fig. 1. Time-dependent concentrations of different chromium species during Cr(VI) biosorption by date pits at various initial Cr(VI) concentrations. Experimental conditions: solution pH 2; DP dose 2 g dm^{-3}; contact time 420 min; temperature 22 °C; stirring rate 180 rpm.

4. Results and discussion

4.1. Effects of various parameters on Cr(VI) biosorption

These experiments were carried out to estimate the influence of initial Cr(VI) concentration, solution temperature and particle size on the adsorption–reduction of Cr(VI) by date pit biomass using low biosorbent dosages.

4.1.1. Initial Cr(VI) concentration

The concentration of Cr(VI) versus time was studied at various initial Cr(VI) concentrations in the range of 0.480–2.884 mM. As can be seen from Fig. 1, initial Cr(VI) concentration considerably affected both Cr(VI) and total Cr removals. At low Cr(VI) concentration, C_o = 0.480 mM, Cr(VI) was totally removed from the solution after 420 min and the chromium remaining in the solution is in its trivalent form (around 15% of the initial Cr(VI) concentration), which is adsorbed up to a constant concentration value. At concentrations higher than 0.480 mM, Cr(VI) was not totally removed and there was no significant difference in the removal percentage for total Cr. As the initial Cr(VI) concentration increased, the Cr(III) remaining in the aqueous solution increased. For all of the studied concentrations, the removal percentage showed a value around 40%. These observations are to some extent in compliance with the results obtained in previous works (Dupont and Guillon, 2003; Silva et al., 2009).

4.1.2. Solution temperature

The solution temperature effect was examined and it was found that the removal rate of Cr(VI) increased with an increase in solution temperature from 20 °C to 60 °C (results not shown). The increase in temperature enhanced the removal rate of Cr(VI). It appears that biosorption is accelerated as the temperature of the solution rises, suggesting that Cr(VI) biosorption onto DP is a kinetically controlled process (Tazrouti and Amrani, 2009). The rate of diffusion of the Cr(VI) ions across the external boundary layer into the interior pores of DP increases with an increase in temperature due to the decrease in the viscosity of the Cr(VI) ions (Li et al., 2010). This might also be attributed to the enlargement of the pore size of the adsorbent (Anandkumar and Mandal, 2011). When the solution temperature increased from 22 °C to 60 °C, the equilibrium concentration decreased from 0.379 mM to 0.248 mM. High temperature exerts a favourable effect on the rate of Cr(VI) reduction and adsorption and the Cr(III), which was not initially present, appeared in the aqueous phase, and increased proportionately with the Cr(VI) reduction (Barrera-Díaz et al., 2012). At solution temperature 60 °C, about 75% of Cr(VI) is removed and the chromium in the remaining solution is in both its hexavalent and trivalent form.

4.1.3. Date pits particle size

The reduction-adsorption process is found to be dependent on particle size (results not shown). It was found that a reduction in the particle size of DP resulted in an increase in the external surface area of particles, yielding more reduction and adsorption sites for Cr(VI) and Cr(III) ions, and hence, more efficient biosorption. Particle size 0.11–0.22 mm gives the maximum reduction and adsorption capacity with a complete Cr(VI) removal and 87.5% Cr total percentage removal. As the particle size increased, the equilibrium concentration of Cr(VI) and Cr(III) increased. However, this small particle size was not used for the other sets of experiments. The powdered DP is difficult to use in these applications because of its disadvantages and the difficulty in the separation

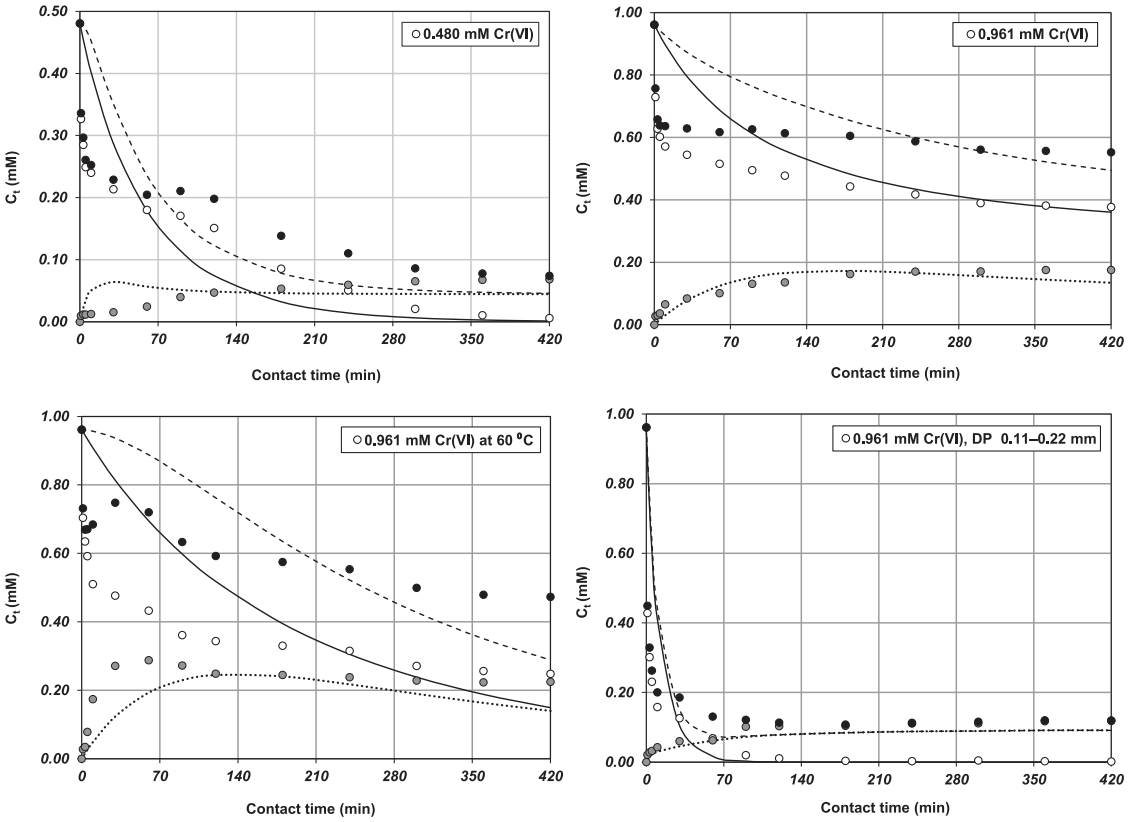

Fig. 2. The López-García model plots of the Cr concentrations as a function of time.

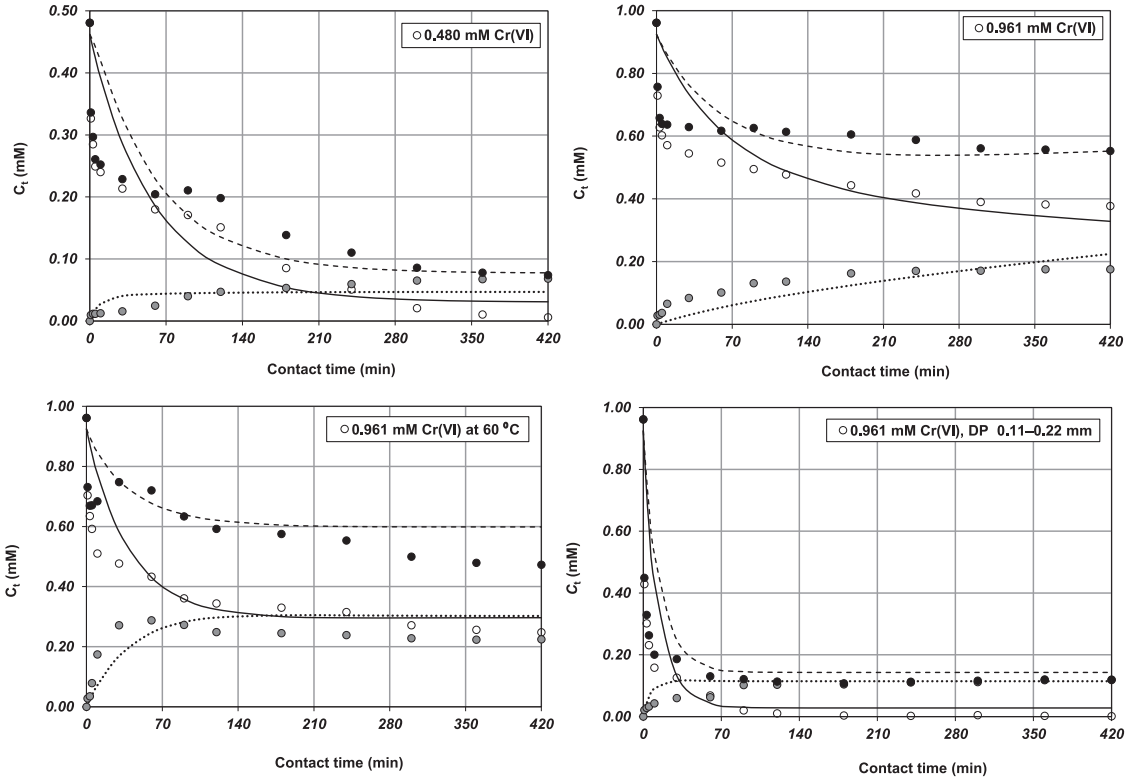

Fig. 3. The Escudero model plots of the Cr concentrations as a function of time.

of the biomass after biosorption and considerable mass loss after regeneration.

4.2. Kinetic modelling of Cr(VI) biosorption

The biosorption kinetic was modelled as the López-García, Escudero and Park reduction-adsorption process. These models are developed in basis to (i) irreversible reduction of Cr(VI) to Cr(III) reaction, where the reaction rate is assumed to be proportional to the Cr(VI) concentration in the solution and (ii) adsorption and desorption of Cr(VI) and formed Cr(III) assuming that all of the processes follow Langmuir type kinetics (Escudero et al., 2009). Results have been obtained by integration of the differential equation system by means of the function Ode 45 of Matlab (R2013a). The model constants were determined by minimizing the sum of squared error (SSE) using SigmaPlot 11. The SSE function is described as the sum of the relative square errors for Cr(VI) and Cr(III):

$$\mathrm{SSE} = \sum_{i=1}^{n} \left[\frac{C_{\mathrm{Cr(VI)\,exp}}(t_i) - C_{\mathrm{Cr(VI)cal}}(t_i)}{C_o} \right]^2 + \left[\frac{C_{\mathrm{Cr(III)\,exp}}(t_i) + C_{\mathrm{Cr(III)cal}}(t_i)}{C_o} \right] \quad (9)$$

The Park model was used to describe the Cr(VI) biosorption only and the sum of square errors was calculated using the above equation while ignoring the Cr(III) term in Eq. (9). Fig. 2 illustrates the López-García model for the Cr(VI) biosorption onto DP at four selected experimental conditions: $C_o = 0.480$ and $C_o = 0.961$ at 22 °C; $C_o = 0.961$ at 60 °C and $C_o = 0.961$ at DP particle size 0.11–0.22 mm and 22 °C. It can be observed in Fig. 2 that, to a certain extent, the López-García model was able to describe the Cr(VI) biosorption process. The model fitted the experimental data very well at low Cr(VI) concentrations and small particle size where the Cr(VI) was totally removed from the aqueous solution and completely reduced to Cr(III). These finding are in agreement with the model assumptions i.e. Cr(VI) is irreversibly reduced to Cr(III), which is adsorbed onto the biomaterial. The López-García model constants (k_1–k_3) and f_1 were determined (Table 1). The value of f_1, which represent the amount of organic groups capable of reducing Cr(VI) per gram of DP biomass, was found to be approximately 1 mg g^{-1}. The f_1 slightly increased with an increase in the Cr(VI) initial concentration. This may be attributed to a higher chance of collision between Cr(VI) ions and the adsorbent surface and hence a better driving force (Hodaifa et al., 2013). The rate of Cr(VI) reduction k_1, k_2 and k_3 values decreased by increasing the initial concentration, indicating that the biosorption process requires more contact time and a higher biomass dose for complete removal. The k_1 and k_2 values increased with an increase in the solution temperature, while the value of desorption rate k_3 decreased. These trends indicate an increase in the total Cr removed. The reduction-adsorption rates were high at small particle sizes, as expected. The Cr(VI) biosorption data were also fitted to the Escudero model (Escudero et al., 2009) and the model constants are given in Table 1 (Fig. 3). The model describes the biosorption data well for the total chromium, Cr(VI) and Cr(III) kinetic profiles. For the sake of model simplicity, it was decided to consider Q_R as a fitting parameter in the model calculations and values below 1 were used to minimize the relative square errors. The constants, k_1, the rate constant for the irreversible reactions of Cr(VI) reduction to Cr(III); k_2 and k_4; k_3 and k_5, the sorption and desorption rate constants for Cr(VI) and Cr(III) respectively are tabulated in Table 1. The reaction constant k_1 values decreased by increasing the initial Cr(VI) concentration and DP particle size, indicating a lower Cr(VI) reduction rate. On

Table 1
López-García, Escudero and Park model constants at various experimental conditions.

	Effect	López-García model constants					Escudero model constants						Park model constants		
		f_1	k_1	k_2	k_3	SSE	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})	k_5 (min^{-1})	SSE	k_{redox} (mmol min^{-1})	C^*_{OC} (mmol g^{-1})	SSE
C_o (mM)	0.480	0.913	1.00×10^2	5.19×10^2	1.73×10^2	0.600	9.70×10^3	7.01×10^3	2.19×10^3	9.90×10^2	1.29×10^2	0.179	0.043	0.194	0.943
	0.961	0.916	1.65×10^3	3.24×10^3	3.17×10^3	0.523	1.20×10^3	7.74×10^3	4.60×10^3	1.30×10^4	2.00×10^3	0.370	0.061	0.199	0.983
	1.923	1.160	8.57×10^4	4.20×10^3	5.51×10^4	0.363	1.07×10^3	9.91×10^3	5.00×10^3	7.50×10^5	2.99×10^3	0.102	0.199	0.221	0.612
	2.884	1.190	4.57×10^4	3.78×10^4	5.04×10^4	0.471	1.02×10^3	9.92×10^3	5.47×10^3	1.05×10^5	3.38×10^3	0.154	2.785	0.227	1.178
T (°C)	22 °C	0.916	1.65×10^3	3.24×10^3	3.17×10^3	0.260	1.20×10^3	7.74×10^3	4.60×10^3	1.30×10^4	2.00×10^3	0.140	0.059	0.191	6.278
	30 °C	0.977	2.05×10^3	2.95×10^3	1.41×10^3	0.488	2.40×10^3	9.73×10^3	8.37×10^3	2.18×10^3	1.82×10^3	0.182	0.067	0.202	1.019
	40 °C	0.994	2.18×10^3	3.99×10^3	1.24×10^3	0.636	3.93×10^3	9.89×10^3	9.56×10^3	4.80×10^3	1.92×10^3	0.233	0.074	0.227	1.115
	60 °C	0.972	2.37×10^3	4.19×10^3	1.03×10^3	0.854	8.76×10^3	9.89×10^3	9.99×10^3	7.20×10^3	2.07×10^3	0.331	0.078	0.241	0.678
Particle size (mm)	0.11–0.22	0.979	4.02×10^3	4.15×10^2	1.90×10^3	0.646	2.00×10^2	6.40×10^2	4.16×10^3	0.123	2.00×10^2	0.121	0.276	0.625	0.175
	0.22–0.85	1.030	2.94×10^3	8.46×10^3	2.45×10^3	0.391	1.70×10^3	6.74×10^3	4.46×10^3	1.24×10^4	2.00×10^3	0.309	0.073	0.250	0.937
	0.85–2.0	0.971	1.80×10^3	9.39×10^3	5.74×10^3	0.378	1.10×10^3	7.74×10^3	4.60×10^3	1.35×10^4	2.00×10^3	0.164	0.065	0.216	1.290
	>2.0	0.975	1.20×10^3	9.92×10^3	7.25×10^3	0.285	9.30×10^4	9.30×10^4	2.50×10^3	8.00×10^5	2.00×10^3	0.199	0.056	0.203	1.398

the other hand, k_1 increased with an increase in the solution temperature. The increase in temperature increases the removal rate of Cr(VI) due to the endothermic nature of the redox reaction (Park et al., 2008). The Cr(III) sorption rate, k_2, and desorption constant, k_3, values increase with an increase in both initial concentration and the solution temperature. These trends are in good agreement with the study on which the model was developed (Escudero et al., 2009). k_4 and k_5 decreased as the initial Cr(VI) concentration increased and increased as the DP particle size increased. At DP particle size 0.11–0.22, it can be seen that the adsorption rates were high and decreased as the particle size increased. Finally, the Cr(VI) data were fitted to the Park redox model (Park et al., 2005, 2008) to compare the reaction rate constants, the results are illustrated in Table 1. The rate coefficient k for the Park model was found to increase with an increase in the initial Cr(VI) and solution temperature and decrease with an increase in the particle size of the date pit biomass. The models used to describe the Cr(VI) biosorption are all based on the same assumptions and, to a certain extent, the models should be able to fit the experimental data with the same degree of accuracy. The López-García model and the Escudero model satisfactorily fitted the experimental data. The SSE values for the Escudero model were lower than those for the López-García model at all experimental conditions. The Park redox model curves were always underestimated with relatively high SSE values. The Park model predicted a complete removal of Cr(VI) at equilibrium. This was expected as the model is developed on the basis that the Cr(VI) will be totally removed when in contact with the biomass if sufficient contact time is given. Still, from a practical viewpoint, even if the biomass is able to completely remove Cr(VI) from the aqueous solution, there exists an optimum condition attributable to the limitations of cost, space and operational time. When comparing our current results with those reported by Park and co-workers (Park et al., 2005), it was found that the experimental conditions at which studies were carried out were very different. The model was developed to describe the redox reaction of Cr(VI) over long periods of time i.e. 500 h, where low levels or no Cr(VI) ions were left in the aqueous solution. In this study, the contact time of the kinetic experiments was 420 min which could be insufficient. Also the biomass mass to solution volume ratio was lower in this study.

5. Concluding points/remarks

Kinetics studies revealed that the biosorption of Cr(VI) onto date pits follows a two-phase process involving rapid reduction of chromate ions to less toxic trivalent chromium followed by adsorption. The results indicated that the Cr(VI) was totally reduced to Cr(III) when put into contact with the date pit biomass at Cr(VI) initial concentration 0.480 mM and particle size 0.11–0.22 mm only. The biosorption kinetic data was modelled as the López-García, Escudero and Park reduction-adsorption process. The models used were derived from the same assumptions, and fitted the experimental data very well at low Cr(VI) concentration and small particle size.

References

Ahmed, M.J., Theydan, S.K., 2012. Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated date stones and its ability to adsorb organics. Powder Technol. 229, 237–245.

Albadarin, A.B., Al-Muhtaseb, A.H., Al-laqtah, N.A., Walker, G.M., Allen, S.J., Ahmad, M.N.M., 2011. Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. Chem. Eng. J. 169, 20–30.

Albadarin, A.B., Mangwandi, C., Walker, G.M., Allen, S.J., Ahmad, M.M.N., Khraisheh, N., 2013. Influence of solution chemistry on Cr(VI) reduction and complexation onto date-pits/tea-waste biomaterials. J. Environ. Manag. 114, 190–201.

Albadarin, A.B., Mangwandia, C., Al-Muhtaseb, A.H., Walker, G.M., Allen, S.J., Ahmad, M.N.M., 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. Chem. Eng. J. 179, 193–202.

Anandkumar, J., Mandal, B., 2011. Adsorption of chromium(VI) and rhodamine B by surface modified tannery waste: kinetic, mechanistic and thermodynamic studies. J. Hazard. Mater. 186, 1088–1096.

Barrera-Díaz, C.E., Lugo-Lugo, V., Bilyeu, B., 2012. A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction. J. Hazard. Mater. 223–224, 1–12.

Cabatingan, L.K., Agapay, R.C., Rakels, J.L.L., Ottens, M., van der Wielen, L.A.M., 2001. Potential of biosorption for the recovery of chromate in industrial wastewaters. Ind. Eng. Chem. Res. 40, 2302–2309.

Dayan, A.D., Paine, A.J., 2001. Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. Hum. Exp. Toxicol. 20, 439–451.

Deng, B., Stone, A.T., 1996. Surface-catalyzed chromium(VI) reduction: reactivity comparison of different organic reductants and different oxide surfaces. Environ. Sci. Technol. 30, 2484–2494.

Dupont, L., Guillon, E., 2003. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. Environ. Sci. Technol. 94, 49–61.

Erkan Sahinkaya, E., Kilic, A., Altunc, M., Komnitsasd, K., Lense, P.N.L., 2012. Hexavalent chromium reduction in a sulfur reducing packed-bed bioreactor. J. Hazard. Mater. 219-220, 253–259.

Escudero, C., Fiol, N., Poch, J., Villaescusa, I., 2009. Modeling of kinetics of Cr(VI) sorption onto grape stalk waste in a stirred batch reactor. J. Hazard. Mater. 170 (1), 286–291.

Hawley, E.L., Deeb, R.A., Kavanaugh, M.C., James Jacobs, R.G., 2004. Treatment Technologies for Chromium(VI). CRC Press LLC.

Hodaifa, G., Ochando-Pulido, J.M., Driss Alami, S.B., Rodriguez-Vives, S., Martinez-Ferez, A., 2013. Kinetic and thermodynamic parameters of iron adsorption onto olive stones. Ind. Crops Prod. 49, 526–534.

Huang, C.P., 1979. Activated Carbon Process for the Treatment of Wastewater Containing Hexavalent Chromium. U.S. Environmental Protection Agency.

Irem, S., Mahmood Khan, Q., Islam, E., Jamal Hashmat, A., Anwar ul Haq, M., Afzal, M., Mustafa, T., 2013. Enhanced removal of reactive navy blue dye using powdered orange waste. Ecol. Eng. 58 (0), 399–405.

Kiran, B., Kaushik, A., 2012. Equilibrium sorption study of Cr (VI) from multimetal systems in aqueous solutions by Lyngbya putealis. Ecol. Eng. 38 (1), 93–96.

Li, L., Liu, S., Zhu, T., 2010. Application of activated carbon derived from scrap tires for adsorption of rhodamine B. J. Environ. Sci. 22, 1273–1280.

López-García, M., Lodeiro, P., Herrero, R., Barriada, J.L., Rey-Castro, C., David, C., Sastre de Vicente, M.E., 2013. Experimental evidences for a new model in the description of the adsorption-coupled reduction of Cr(VI) by protonated banana skin. Bioresour. Technol. 139, 181–189.

Marta López-García, Pablo Lodeiro, Roberto Herrero, Barriada, José L., Carlos Rey-Castro, Calin David, Vicente, M.E.S.d., 2013. Experimental evidences for a new model in the description of the adsorption-coupled reduction of Cr(VI) by protonated banana skin. Bioresour. Technol. 139, 181–189.

Park, D., Lim, S.-R., Yun, Y.-S., Park, J.M., 2008. Development of a new Cr(VI)-biosorbent from agricultural biowaste. Bioresour. Technol. 99 (18), 8810–8818.

Park, D., Yun, Y.-S., Park, J.M., 2005. Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics. Process Biochem. 40 (7), 2559–2565.

Poch, J., Villaescusa, I., 2010. A model to describe Cr(VI) kinetics biosorption. J. Hazard. Mater. 175 (1–3), 770–778.

Saha, B., Orvig, C., 2010. Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. Coord. Chem. Rev. 254 (23–24), 2959–2972.

Silva, B., Figueiredo, H., Neves, I.C., Tavares, T., 2009. The role of pH on Cr(VI) reduction and removal by arthrobacter viscosus. Int. J. Chem. Biol. Eng. 2, 100–103.

Tazrouti, N., Amrani, M., 2009. Chromium(VI) adsorption onto activated kraft lignin produced from alf grass (*Stipa tenacissima*). BioResources 4, 740–755.

Ullah, I., Nadeem, R., Iqbal, M., Manzoor, Q., 2013. Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass. Ecol. Eng. 60 (0), 99–107.