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Spray-dried calcined clays in water filtration columns used for chromium removal

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Abstract Well-rounded grains are normally used as filtration media, because the spherical shape seems to be most suitable to get rapid and efficient removal operations. In this sense, the direct use of natural clays as filtration media is problematic, due to the plate-type shape of the particles. In this work, rounded grains of two natural clays processed by spray-drying are tested as filtration media. The settling regime of the grains in a filtration column was determined and the chromium removal from water was also tested. Sieved fractions now used (355–1680 μm) show settling behavior according to the transition regime. Preliminary results of chromium removal by the selected 355–420 μm sieved fraction bed show interesting capabilities for the Cr^{3+} species, while chromate (VI) retention is extremely low.

Key words Spray-dried grains – settling – chromium removal

Introduction

Traditionally, the sand is used as the granular media for treating potable water, due to its abundance, cheapness, and absence of any special treatment of the natural material before use as filter media [1]. However, the increasing amount of pollutants and continuous requirements for faster cleaning operations lead to a decreasing efficiency of the slow sand filters [2]. Several alternatives have been suggested, involving different designs and/or filter media [3–5]. Among these, granular activated carbon has become the most common, but some other alternatives had been tried.

The use of higher flow rates as an alternative to improve the speed of the filtration process leads to a faster accumulation of deposits on the filter grains, causing a continuous decrease in the permeability and an increasing head loss through the filter [1]. By this reason, a regular backwashing step is necessary in rapid filters, and is normally achieved by flow reversal of water with or without air scour [6–8]. The resistance of filter grains to attrition during this cleaning operation is a vital property, and the use of angular particles having some prominent surfaces easily broken is not recommended [4]. Once stopped the application of the reversal flow through the filter, the settling velocity of individual grains is an interesting characteristic, because it will control the stratification behavior of the particles and the relevant geometrical parameters (porosity and packing density) of the bed for further filtration steps [4]. Moreover, the interpretation of the settling velocity, using fluid mechanical theory (often in the transitional, or non-Stokesian regime) can give the equivalent hydraulic diameter of a sphere (d_h in cm) and leads to the calculation of hydraulic shape (also called sphericity – Ψ).

Sedimentation regimes

The equivalent hydraulic diameter and sphericity are related by the following equation:

$$\Psi = d_h/d_m \; , \qquad (1)$$

where d_m is the average diameter of a sieved fraction (cm). On the other hand d_h is obtained by

$$d_h = \mu\, Re/\rho U_q \,, \tag{2}$$

where μ and ρ represent, respectively, the viscosity and density of the water (at known temperature), Re is the Reynolds number and U_q is the average settling velocity of an individual grain (m/s). The Reynolds number of a fluid is a good indication of the settling regime and its dependence on drag coefficient of the grain (C_D) is usually given by Camp curves [9]. C_D gives the fluid resistance to the movement of the particle on settling. Figure 1 shows the direct dependence of C_D on the Reynolds number, for spherical and cylindrical particles. Three different settling regimes are normally assumed [10]: (a) Stokes, (b) transition, and (c) Newton. In the Stokes regime ($C_D < 1$) the grain follows a linear trajectory and the settling velocity is constant. By the gravity action the larger particles will settle more rapidly than the smaller ones and serious changes on the bed structure can occur after each cleaning operation. In the Newton regime the trajectory of the grains continuously change and the settling velocity is less dependent on the grain size.

For spherical discrete particles, the general balance between gravitational and viscous forces gives the settling velocity [11]

$$U_q = [4g(S_S - 1)d_m/3C_D]^{1/2} \,, \tag{3}$$

where $S_S = \rho_S/\rho$ is the specific gravity of the particle (being ρ_S the density of solid grains).

Removal tests

Despite the well-known characteristics of natural clays, such as high adsorbent power, cheapness and abundance, their use as filtration media for the removal of the heavy metals or organic substances from water is not well documented [12, 13]. More frequent in the literature are descriptions of adsorption tests involving clay-type media [14–16]. Generally, promising adsorption capabilities were observed, due to the high surface areas and cationic exchange properties of the clay materials.

The typical small size of raw clay grains and their flaky shapes impart their direct use as filtration beds. Generally, very packed structures are formed and attrition resistance of the grains is very low. In previous works [17(a), (b)] we tested the use of spray-dried clays as filtration media for lead removal from water. The use of spray-drying techniques to process natural clays proved to be an efficient way to produce large amounts of rounded grains having suitable mechanical strength. In the present paper, spray-dried clays are tested as filtration beds to remove chromium species from water. Chromium is commonly contained in a variety of industrial wastewater, including those from textile, electroplating and metal finishing industries. In those effluents the chromium species might assume either hexavalent, chromate (VI), or trivalent Cr (III), forms [18]. The toxicity of chromate (VI) is well documented and it is considered a health hazard to man and animals [19]. The removal process of chromium from aqueous media is rather complex and seems to be dependent on the dominant stable species in the solution, which is strongly dependent on pH values [20].

Materials and methods

Two natural Portuguese ball-clays named Taveiro (from Coimbra) and ZA-4 (from Pombal) were selected and then processed by spray-drying, as described elsewhere [17(b)]. The rounded grains were then calcined at 600 °C for 2 h and sieved by using the following series: 1680–1000–500–420–355–210 μm. The sieved fraction between 420–355 μm

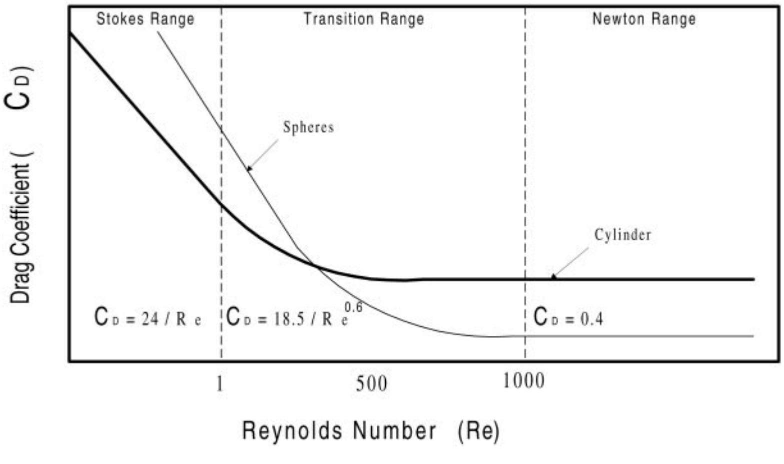
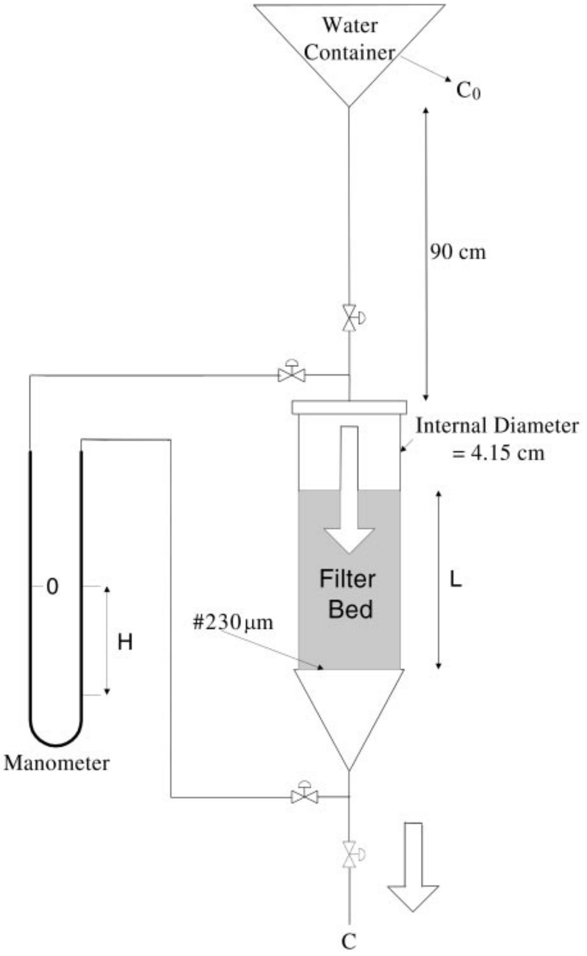


Fig. 1 Settling regimes of spherical and cylindrical discrete particles, represented as drag coefficient versus Reynolds number, as suggested by Weber [9]

was the only one used in filtration tests, because it gives the best compromise between well-controlled experimental conditions (high and constant filtration rates, suitable head loss through the filter, see Fig. 2) and higher removal efficiencies. Initial (C_0) and final (C) chromium concentrations in aqueous solution were estimated by ICP (Jobin Yvon 70 Plus).

The true powder density (ρ_S) was measured with a liquid picnometer using water ($\rho_S = 2.66$ and $2.75\ \mathrm{g/cm^3}$ for Taveiro and ZA-4 clays, respectively). Other relevant parameters of the filter grains like settling velocity and sphericity were estimated as described by Ives [4]. The settling velocity was estimated by timing the fall of 20 individual grains through a 1 m column of water. A 41.5 mm-diameter glass tube, 1.5 m long, with two marks 1 m apart, the upper one about 200 mm below the top, was found adequate. The grains were always pre-wetted by immersion in water, and insertion with tweezers allows their release approximately on the column axis. Any grains falling in the proximity of the wall should be discounted. The sphericity of the grains was obtained by combining Eqs. (1)–(3) and using the results from Fig. 1.

Fig. 2 Schematic representation of filtration apparatus used in water purification. H = pressure head loss; L = depth (4.8 cm); C_0, C = initial and final concentration of contaminant



Results and discussion

Shape of the grains and settling regime

As indicated above, the fall velocity can be used to derive the hydraulic shape, or sphericity, of the grains. For a sphere $\Psi = 1$, and for non-spherical grains $\Psi < 1$ (Ψ decreases with decreasing sphericity of the grains). The method of calculation is well described elsewhere [4]. The fall velocities of different sieved fractions for the two clays are given in Table 1. As expected, the settling speed tends to decrease for smaller particles. Differences between both clays are not very sensitive, but Taveiro tends to present higher fall rates. Further comments about the implications of these values on the settling/stratification behavior will be discussed later.

Table 2 gives the estimated values of sphericity, hydraulic size, and C_D/Re dimensionless parameter for different sieved fractions of both clays. ZA-4 grains are slightly less spherical than Taveiro ones, excepting for the larger sieved fraction. However, these larger particles were obtained by the agglomeration of individual grains (see Fig. 3), and their behavior does not correspond to the intrinsic properties of each material. By this reason, results obtained with coarser particles are not directly comparable. The enlargement of particles promoted by agglomeration during processing (spray-drying) also explains the decreasing sphericity of the larger sieved fractions. The flaky-type shape of these large particles might create some weakness problems on the attrition resistance, as confirmed elsewhere [17(a)]. Assuming the sphericity limit of 0.6 suggested by Ives [21], it is easy to conclude that only the sieved fraction 420–355 μm is nearly to satisfy this requirement. In fact, backwashing tests [17(a)] confirmed that only smaller sieved particles (<420 μm) have suitable mechanical properties (hardness) to continuously support

Table 1 Settling velocity for different sieved particles of both clays

Sieved fraction [μm]	Fall velocity [cm/s]	
	Taveiro	ZA-4
1680–1000	7.41	7.81
1000–500	5.76	5.32
500–420	4.12	4.13
420–355	3.54	3.46

Table 2 Estimated values for C_D/Re coefficient, Reynolds number (Re), hydraulic size (d_h), and sphericity (Ψ), of different sieved fractions of both clays

Sieved fraction [μm]	Taveiro				ZA-4			
	C_D/Re	Re	d_h [mm]	Ψ	C_D/Re	Re	d_h [mm]	Ψ
1680–1000	0.049	31.0	0.3823	0.285	0.044	34.0	0.3978	0.297
1000–500	0.105	19.0	0.3014	0.402	0.139	16.0	0.2748	0.366
500–420	0.285	11.0	0.2439	0.530	0.298	10.5	0.2323	0.505
420–355	0.449	8.5	0.2194	0.566	0.507	7.7	0.2030	0.525

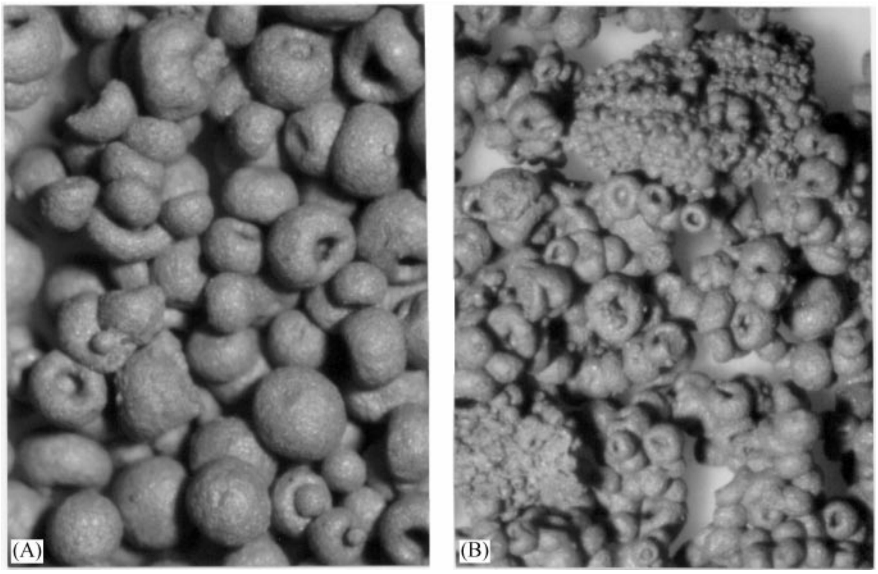


Fig. 3 Morphology of different sieved spray-dried Taveiro particles calcined at 600 °C: (A) 355–420 μm (44 ×); (B) 1000–1680 μm (33 ×)

this cleaning operation. However, the use of particles under 355 μm tends to form very packed beds, creating serious constrains in the maximum filtration rate (typically under the rapid filtration limit).

The direct comparison with a standard filtration material like sand [21] – grains of 0.557 mm and 0.85 for hydraulic diameter and sphericity, respectively – clearly shows that spray-dried particles now used are much less spherical. This result is related to the intrinsic sheet-type nature of clay materials (phyllosilicates), while sand particles are less angular. Moreover, the spray-drying technique always produces a central cavity on the grains (see Fig. 3A) that contributes to a decreasing sphericity.

As previously mentioned the settling regime of grains after each backwashing step might effect the further structural arrangement of particles and the consequent morphology of the filtration bed. In order to determine the predicted settling regime, experimental fall speed of Taveiro grains was measured and theoretical velocities were also calculated for the three different regimes.

The settling of non-spherical grains in the Stokes regime corresponds to $Re < 1$ (see Fig. 1) and results [9, 11]:

$$C_D \cong 24/Re = 24\mu_c/(U_q d_m) \; , \tag{4}$$

where μ_c is the kinematics viscosity of the liquid ($\mu_c = \mu/\rho$ in cm^2/s). By rearranging Eqs. (4) and (3), the well-known expression of Stokes law is obtained

$$U_q = g d_m^2 (S_S - 1)/(18\mu_c) \; . \tag{5}$$

Substituting the known characteristics of Taveiro clay ($\rho_S = 2.66$) in the last equation, one obtains the fall velocity of discrete particles in this regime:

$$U_q = 8967.1 d_m^2 \; . \tag{6}$$

Assuming now the settling of particles in the transition regime, drag coefficient is given by (see Fig. 1)

$$C_D = 18.5/Re^{0.6} = 18.5/[(U_q d_m/\mu_c)]^{0.6} \tag{7}$$

and substituting this parameter in Eq. (3) gives

$$U_q = 4g(S_S - 1)d_m\,U_q^{0.6}d_m^{0.6}/(55.5\,\mu_c^{0.6}) \tag{8}$$

or

$$U_q = 215.41\,d_m^{8/7} \tag{9}$$

for Taveiro clay.

Finally, for the Newton regime C_D is constant (Fig. 1) and not dependent on Reynolds number: $C_D = 0.4$ for $10^3 < Re < 10^6$ [11]. Substituting again this value in Eq. (3) one obtains

$$U_q = [4g(S_S - 1)\,d_m/1.2]^{1/2} \tag{10}$$

or

$$U_q = 73.716\,d_m^{1/2} \tag{11}$$

for Taveiro clay.

Experimental values of fall velocity as a function of the average grain size (sieved fraction) of Taveiro clay are represented in Fig. 4. Simultaneously, predicted fall velocities according to different settling regimes (Eqs. (6), (9), and (11)) are also represented. The two smaller sieved fractions (grains under 500 μm) clearly fall according to the transition regime, without any significant (visible) change in the trajectory. Particles larger than 500 μm will also fall in the transition regime, but their settling behavior is closer to the Newton regime (see slopes in Fig. 4). This approach was detected during tests by stronger changes in the trajectory and/or velocity of the grains. In general, a similar trend was observed for ZA-4 clay, with slightly differences in the fall velocity when compared with Taveiro one.

The predicted behavior for granular clays agrees with the results obtained by other authors [10] assuming different values for the density of filter media (Fig. 5). According to this work, particles with density (ρ_S) around 2.5 and average size between 0.015 and 0.55 cm will settle in the transition regime. Particles under 0.015 cm will settle in the Stokes regime, while grains coarser than 0.55 cm will fall according to the Newton regime. These limits were also extrapolated from the results in Fig. 4, by determining the grain size corresponding to the intersection of curves (describing the different regimes) and assuming that the controlling one corresponds to the smallest velocity. Remarkably, the lower limit of the transition regime is coincident (0.015 cm) in the two analyses, but a slight discrepancy is observed in the upper limit. In our extrapolation (see Fig. 4), particles above 0.20 cm will fall in the Newton regime. This disagreement arises from the use of unequal *Re* values, assumed in our study to predict the effects of using non-spherical grains.

The slight dependence of the fall velocity of each individual grain on its size (transition regime) suggests that selected granular clay media now used (355–1680 μm) do not tend to segregate on settling in water due to size differences. In consequence, particle stratification behavior is constant and final morphology of the filter bed remains almost unchanged after each backwashing operation.

Chromium removal

Preliminary tests of chromium removal from aqueous solutions were performed with sieved filtration media that assure an easy control and reasonable values of the flow rate (355–420 μm). The flow rate was kept constant, in order to compare the performance of different materials. Respecting the initial concentration of contaminant (C_0), different solutions were tested from 0.5 to about 10 ppm (for chromate anions) and from 10 to about 1000 ppm

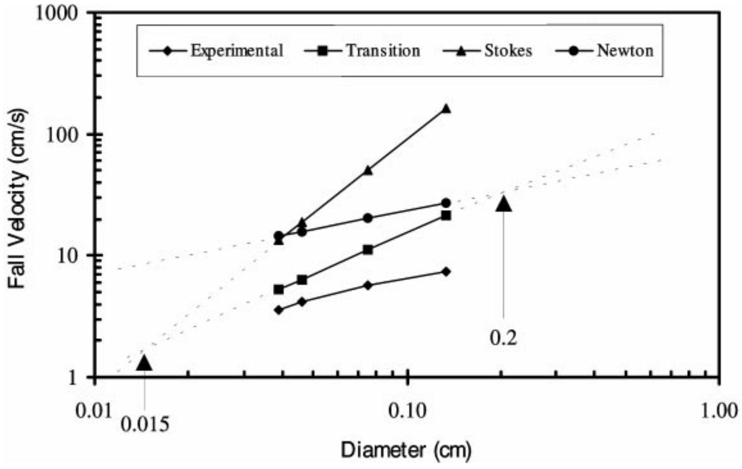


Fig. 4 Experimental and calculated fall velocities of discrete particles as a function of their average size for the three settling regimes

(Cr^{3+}). Table 3 resumes the relevant features obtained after a single passage of the starting polluted solution through the filter. Results of removal efficiency are expressed in two different ways: (a) ratio of chromium concentrations of the final and initial solution (C/C_0%); (b) amount of chromium removed per weight of filtration media and per minute. This later representation is common in filtration tests. It is obvious that spray-dried clay grains are able to remove significant amounts of Cr^{3+} species, while chromate (VI) removal efficiency is very poor. By using low-concentraion solutions ($C_0 \leq$ 10 ppm), the removal efficiency for trivalent species is almost complete (nearly 100%), irrespective of the nature of the clay. This observation might be related to the actual working conditions, very far from the saturation limit of the filter. At the same time, these results suggest the interesting capabilities of clay filter media for cleaning treatments of potable waters, where the amount of pollutants are obviously low. The removal performance tends to decrease for highly concentrated solutions, but total amounts of chromium retention are still very interesting (>700 μg/g min). In general, ZA-4 clay shows better performances than Taveiro, as observed and explained elsewhere [17(b)] for the removal of different species.

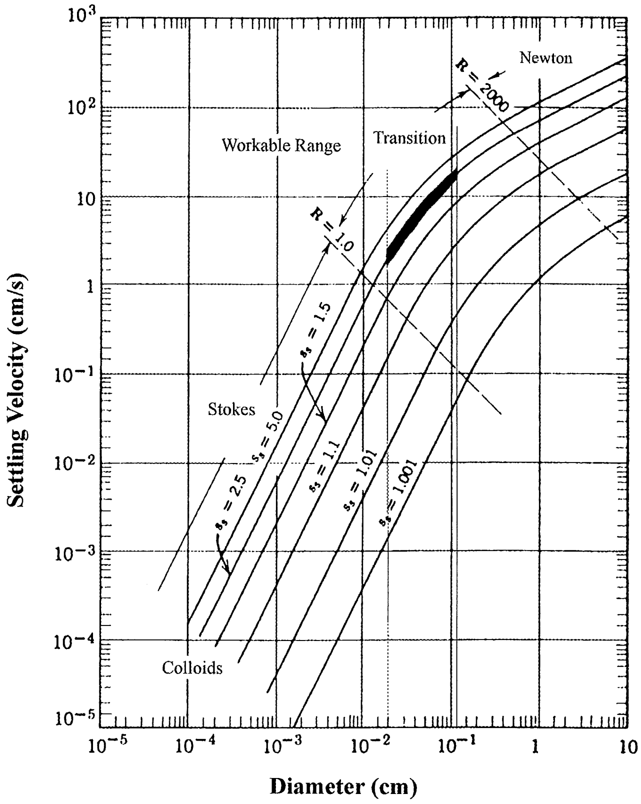


Fig. 5 Settling velocities of discrete spherical particles in quiescent water at 10 °C, as calculated by Fair et al. [10]. The marked region in the curve corresponds to the actual working conditions

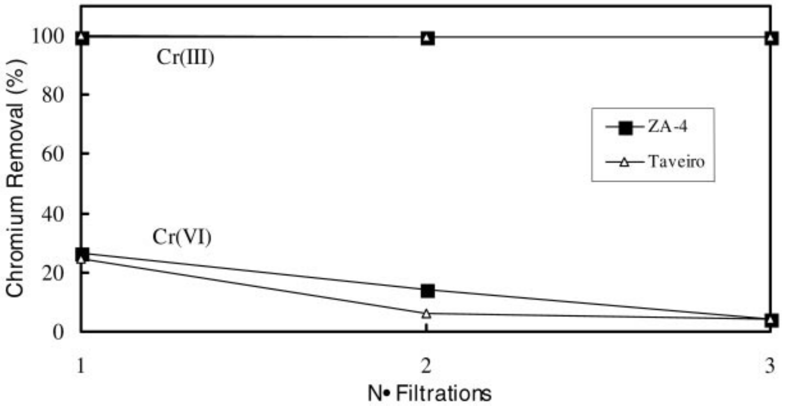
As previously mentioned the removal efficiency for hexavalent species is very poor ($\leq 25\%$). At pH ≈ 6 (corresponding to the solutions now tested), negatively charged complexes are present and their removal by clay particles (electrokinetically negative by nature) is not electrostatically favorable. The removal capabilities of clay particles are clearly improved for positively charged contaminants, as suggested from results of Cr^{3+} and Pb^{2+} retention [17(a)].

As an attempt to determine the filter performance in continuous operation, the removal efficiency was evaluated after second and third passages of the same initial solution through the clay bed. Figure 6 clearly confirms the good performance of both clays on Cr^{3+} removal consecutive operations, by using an initial solution of $C_0 \approx 10$ ppm. By contrast, the efficiency for chromate (VI) removal (low from the beginning) strongly diminishes with increasing number of operations, suggesting that current clay-based filters are unsuitable for continuous filtration of hexavalent species.

Table 3 Results of chromium removal from water by using different clay beds made with the sieved fraction (355–420 μm) and unequal concentrations for the initial solution (C_0)

Clay	C_0 [ppm]	Chromium removal			
		Chromate (VI)		Cr (III)	
		[%]	[μg/g min]	[%]	[μg/g min]
ZA-4	0.5	26.5	0.20	–	–
Taveiro	0.5	24.5	0.19	–	–
ZA-4	9.5	24.2	3.59	–	–
Taveiro	9.5	18.9	2.81	–	–
ZA-4	9.4	–	–	99.8	14.7
Taveiro	9.4	–	–	99.8	14.7
ZA-4	985	–	–	54.5	839.1
Taveiro	1013	–	–	44.4	703.1

Fig. 6 Chromium removal efficiency of the clay beds after consecutive filtration operations. Initial concentration of contaminants (C_0) was kept constant and equal to 9.5 and 0.5 ppm for Cr (III) and chromate (VI) solutions, respectively



Conclusions

Spray-drying technique proved to be an interesting way to produce large amounts of clay rounded grains. However, the formation of a central cavity on clay particles decreases the sphericity and effects the settling velocity through the water. All the sieved fractions tested showed a settling behavior belonging to the transition regime. By this reason, the occurrence of morphological changes on clay beds (packing density and porosity) after each backwashing step is improbable. The observed deviations to the theoretical predictions arise from the use of non-uniform-sized particles in each batch. In the current experimental conditions the following predictions were obtained: (a) grains under 150 μm will sediment according to the Stokes regime, causing serious alterations on the morphological structure of the filtration bed after each backwashing process that might change the subsequent experimental filtration conditions; (b) particles larger than 2 mm follow the Newton settling regime and the forming beds have constant morphological structures. However, the high porosity of these beds strongly reduces the overall removal efficiency and induces experimental problems in fixing and controlling the filtration process.

Preliminary results of chromium removal from water suggest interesting capabilities for the Cr^{3+} species, while chromate (VI) retention is extremely poor.

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