

Cadmium and Zinc Adsorption Kinetics onto Activated Carbon in Single and Binary Systems

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In this paper, we are presenting a study aimed to understand the adsorption kinetics of a binary system with zinc and cadmium. Firstly, the zinc adsorption kinetic study as single compound was carried out in terms of initial concentration and carbon particle size. Then the adsorption kinetics of the Zn/Cd binary system was accomplished in different experimental configurations. For a thorough comprehension of the multicomponent adsorption, a specific preloaded test was also carried out by adding a zinc solution to a single-compound cadmium-carbon suspension at equilibrium. The experiments showed that the zinc adsorption rate decreases with the increase of its initial concentration, while remaining almost constant with the carbon particle size. The preloaded test revealed that the cadmium desorbed once the zinc was added and the system reached suddenly the equilibrium condition of the binary system. The experimental data were interpreted by several kinetic models and it turned out that the Elovich model described adequately most of the adsorption data. In conclusion, the activated carbon presents a higher affinity toward zinc with respect to cadmium, and the binary tests showed a competition toward the same active sites between the two compounds, being zinc ions always preferred.

1. Introduction

The presence of heavy metals in wastewater is one of the main concerns for environmental protection, due to the intrinsic toxicity and long lifetime of these compounds. Therefore, there is a pressing need to remove them from polluted water, using efficient and cost-effective remediation techniques that at the same time do not produce toxic residues. Many different technologies have been developed to remove heavy metals from contaminated natural water and wastewater. Among these, adsorption has emerged as a highly effective technology applicable to both wastewater treatment and to groundwater remediation. Despite the high number of papers in the literature dealing with heavy metal adsorption, most of the studies have been focused on the assessment of single-compound adsorption equilibrium and its dependence on the main process parameters. Similarly, the kinetic aspects of the process have been far less studied.

However, the design of either industrial devices (e.g. adsorption reactors) or in-situ intervention for groundwater restoration (e.g. permeable adsorbing barrier) requires the knowledge of adsorption dynamics in experimental conditions near to real case-studies, which are often characterized by the simultaneous presence of different heavy metals.

Water solutions containing cadmium and zinc are typical examples of such systems. Cadmium is unanimously recognized as very dangerous; it is extremely toxic and classified as carcinogenic. Its high toxicity is enhanced by the ability to bioaccumulate in the aquatic ecosystem, reaching humans through the food chain. Differently, zinc is an essential element for human beings but it can become toxic at high concentrations. Cadmium and zinc are often associated; for example, the main sources of the simultaneous cadmium and zinc releases in water include metal plating plants, metallurgic industries, battery production and disposal, mine drainage and the leaching from natural rocks. Therefore, the removal of cadmium by adsorption should often be carried out in presence of zinc. Despite of single adsorption of cadmium (Ali, 2013) and zinc ions (Leyva Ramos et al., 2002) onto activated carbon have been extensively investigated, very few studies have been dealt with

experimental evaluation of adsorption equilibrium and kinetics in solution containing both heavy metal ions (Mohan and Singh, 2002).

Erto et al. (2015) showed that cadmium adsorption capacity is affected by the presence of zinc in solution, while zinc adsorption is almost independent on cadmium presence. Moreover, cadmium adsorption capacity seems to depend monotonically on the $C_{Zn}^0: C_{Cd}^0$ molar ratio, and it increases with the cadmium initial concentration (i.e. $C_{Zn}^0: C_{Cd}^0 = 1:2$).

Concerning the kinetic studies, the literature works are focused mainly on cadmium adsorption and, among them, Di Natale et al. (2014) showed that cadmium adsorption rate presents different control mechanisms, depending on a critical uptake value. Based on this former study, in the present work the adsorption kinetics of zinc as single-compound and cadmium-zinc binary systems were experimentally investigated, in different experimental configurations.

The effect of initial zinc concentration and carbon particle size were studied, as they represent important operating parameters. Simultaneous adsorption tests were carried out in different reactor configurations, so to investigate the influence of cadmium on zinc dynamics and vice versa, the kinetic parameters and the rate-determining step for both the compounds. Finally, a modelling analysis and a thorough comparison of single-compound and binary systems were carried out.

2. Material and methods

Aquacarb 207EATM is a commercially available non-impregnated granular activated carbon (GAC), produced by Sutcliffe Carbon starting from a bituminous coal. This material has a BET surface area of 950 m²/g and an average pore diameter around 26 Å. Two different sorbent particle size distribution 0.85 - 1.18 mm and 1.18 - 1.4 mm were used. The sorbent is slightly basic (pH_{PZC} = 8) and its surface functional groups, obtained by Boehm's titration analysis, are mainly represented by basic active sites and by lactones and phenols acid sites. Morphological and chemical properties of the GAC are reported in Di Natale et al. (2008). Before each experimental run, the sorbents were carefully rinsed with distilled water and oven dried for 48 h at 80°C. Solutions of the two analyses were prepared by dissolving Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O in double distilled water to obtain the desired total metal ions concentration, ranged from 0.08 to 0.8 mmol/L. Solution pH was monitored but not controlled over time. The adsorption tests were carried out in two different configurations: stirred tank and fixed bed column. Test apparatus to simulate stirred tank process consisted in a 100 mL glass bottles with Teflon cups that were kept in agitation on an orbital shaker at 200 rpm. The fixed-bed apparatus consisted in a glass column with internal diameter of 0.9 cm and height of 60 cm, loaded with 10 g of activated carbon. The column was connected in a closed loop circuit, which included a stirred vessel, containing the solution, and a gear pump, which allowed the solution circulation. At different times, a little amount of solution in the stirred vessel was sampled for analysis. The fixed bed column was designed as a differential reactor, thanks to which it was possible to study the adsorption rate. Single-compound zinc adsorption tests were performed in a fixed-bed column, at a constant temperature of 20 °C, by varying the initial concentration and the sorbent particle size. Cadmium-zinc binary adsorption tests were carried out at 20 °C in the two different reactor configurations, using equimolar solutions of the two metals (i.e. $C_{Zn}^0: C_{Cd}^0 = 1:1$). A specific test was performed in the stirred tank, where a preloaded activated carbon with cadmium solution at the equilibrium condition was altered by adding the zinc solution with the same initial cadmium concentration, respecting the equimolar ratio ("preloaded multi" test). This was done in order to check whether the experimental results obtained in the canonical binary test depend on the different adsorption rates of the two compounds. In both the stirred tank and fixed bed column, the analyte adsorption capacity at the temporal step t_i was calculated starting from the adsorption capacity q (mmol/g), at the previous step t_{i-1} , and the difference of the liquid concentration, C (mmol/L), between two consecutive temporal steps, through the mass balance written as:

$$q(t_i) = \frac{V_i}{m} \cdot (C_{i-1} - C_i) + q(t_{i-1}) \quad (1)$$

where V_i is the adsorption solution volume taking count the alteration by the sampling, and m is the sorbent mass. When saturation was achieved, the adsorption capacity (q_{eq}) and the liquid concentration (C_{eq}) corresponded to the equilibrium conditions. At the end of each kinetic test, once equilibrium conditions were reached, both the cadmium and zinc concentrations in solution and on the carbon surface were measured. In the stirred tank test, the solution was filtered in a Hirsch funnel ceramic filter by a vacuum pump. The filtered solution was then analysed for pH and total concentrations. The exhaust carbon in the fixed bed and in the stirred tank was leached with 1 M HNO₃ to obtain the complete analyte desorption, allowing a direct measure of the uptake on the solid surface. The accuracy of the experimental runs was checked by allowing a maximum error of 5 % in the material balances and repeating the tests in triplicates. Analytical concentrations

were measured by air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer.

3. Experimental results

The effect of the initial zinc concentration in the range 0.08-0.8 (mmol/L) and the effect of two different GAC particle size ranges, 0.85 - 1.18 and 1.18 - 1.40 mm, were investigated in the fixed bed column. The corresponding kinetic adsorption data are reported in terms of zinc uptake, q (mmol/g), as a function of the time, as shown in Figure 1.

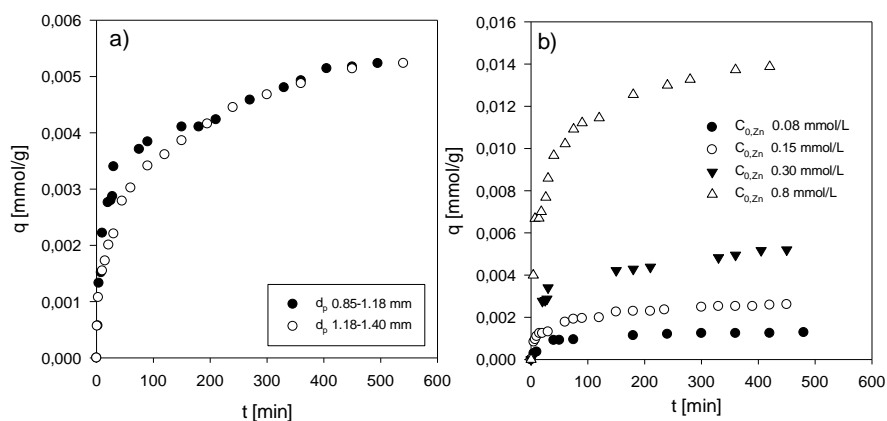


Figure 1: Zinc adsorption kinetic plots in fixed bed at different particle size ranges (a) and initial concentrations (b); $m/V = 40$ g/L $T = 20$ °C; a) $C_0 = 0.3$ mmol/L, b) $d_p = 0.85 - 1.18$ mm

Figure 1(a) shows that the two particle size ranges investigated gave rise to negligible variation in the adsorption dynamics. Differently, Figure 1(b) shows that adsorption rate was faster for smaller values of the initial concentration. The pH solution reached suddenly a constant value roughly 7.3 for all the tests out of the test with $C_0 = 0.3$ mmol/L and $d_p = 1.18 - 1.40$ mm that reached the value of 7.5.

The binary kinetic adsorption tests with a solution $C_{Zn}^0 : C_{Cd}^0$ ratio equal to 1 were carried out in two different configurations: stirred tank and fixed bed. As the single adsorption tests, the experimental data are reported in terms of zinc uptake, q , as function of the time, as shown in the Figure 2.

The process reached the equilibrium in the fixed bed, Figure 2(a), after 600 min while in the stirred tank, Figure 2(b) it required 150 h. This result highlights that the adsorption rate in the fixed bed was faster than in the stirred tank. The equilibrium uptake was slightly different in the two configurations due to the different final pH, respectively 6.89 and 7.28. In fact, the equilibrium adsorption capacity of these compounds is greatly affected by pH (Erto et al., 2015), which unfortunately evolves out of our control.

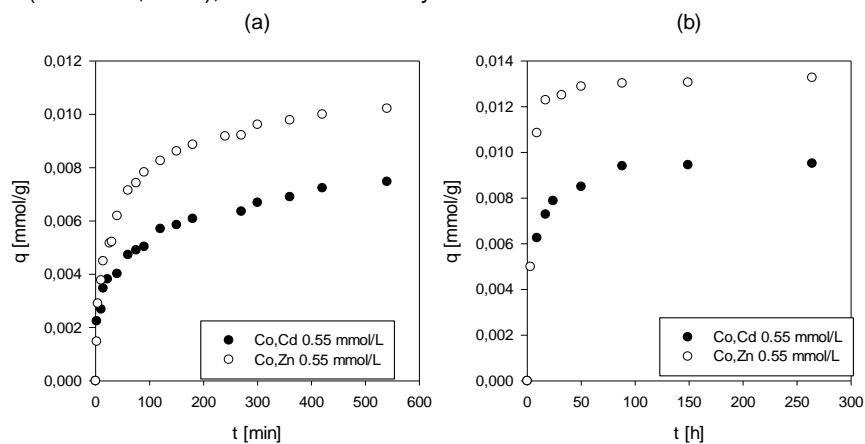


Figure 2: Binary adsorption kinetic plots in fixed bed (a) and stirred tank (b) $m/V = 40$ g/L $T = 20$ °C; $d_p = 0.85 - 1.18$ mm, $C_{0,Zn} = C_{0,Cd} = 0.55$ mmol/L

Figure 3 shows the results of the “cadmium preloaded binary tests” run in the stirred tank, comparing the experimental results with those of cadmium adsorption in a corresponding binary adsorption test. To allow a better comparison, the experiments were reported in terms of $q(t_i)/q_{\max}$, where $q(t_i)$ is cadmium adsorption capacity at the temporal step t_i and q_{\max} is the equilibrium adsorption capacity achieved in single-compound Cd adsorption test.

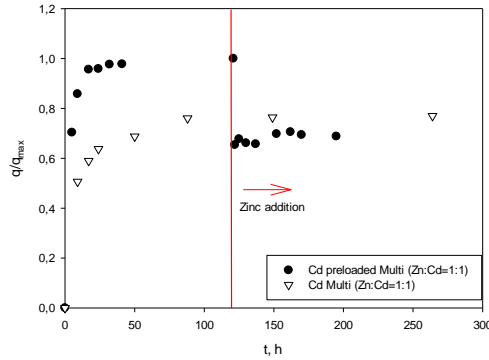


Figure. 3-Cd kinetic plots in the cadmium preloaded test and in the corresponding binary test; $m/V = 40$ g/L $T = 20$ °C; $d_p = 0.85 - 1.18$ mm, $C_{0,Cd} = 0.55$ mmol/L, $C_{0,Zn}|_{t=120h} = 0.55$ mmol/L

As showed in Figure 3, the preloaded test pointed out that the Cd underwent through a desorption process once the Zn solution was added. Subsequently, cadmium reached a new equilibrium with a fast kinetic and the whole system reached the equilibrium conditions of the binary system with the same final pH. Once the zinc was added, its kinetic evolved in the same way of the corresponding multicomponent system (data not reported).

This result confirms that the zinc has a higher affinity towards activated carbon with respect to cadmium. Moreover, the higher affinity does not depend on kinetic factors, which would favor zinc that has a faster adsorption kinetics, likely due to a higher diffusivity in carbon pores. In fact, the preloaded test showed that zinc substituted cadmium on the preloaded carbon after its addition, hence due to thermodynamic factors. These results are consistent with those of former equilibrium studies reported in a recently published work (Erto et al., 2015).

4. Discussion

For a thorough comprehension of the adsorption kinetic data, several adsorption rate models such as external mass transfer rate, first order, pseudo-second order, diffusional models (Reichemberg, Vermulen) and Elovich model were tested (Plazinski et al. 2009). To this aim, the q/q_{eq} ratio as function of the time was evaluated, where q_{eq} is the maximum uptake capacity reached for each test. The best fitting of data was achieved by the Elovich model applied in its analytical form (Eq(2)):

$$\frac{q}{q_{eq}}(t) = \frac{1}{b} \cdot \ln(1 + A \cdot b \cdot t) \quad (2)$$

where A is the initial adsorption rate, min^{-1} , and b is the desorption constant. Experiments were interpreted considering that the parameter b , which is a function of specific solute-sorbent interactions, should be the same for all the tests, while the parameter A is related to the initial adsorption rate, and, consequently, it is expected to be a function of the operating conditions. The zinc single-compound experimental data fitted by Elovich model are reported in Figure 4. The fitting parameters of Elovich model are listed in Table 1, together with the corresponding coefficient of determination (R^2).

Table 1: Kinetic parameters obtained by Elovich model for zinc adsorption

Operating condition		A [min^{-1}]	b [-]	R^2
C_0 [mmol/L]	D_p [mm]			
0.08	0.85 - 1.18	0.15 ± 0.01		0.96
0.15	0.85 - 1.18	0.13 ± 0.01		0.99
0.30	0.85 - 1.18	0.11 ± 0.01	5.83 ± 0.14	0.99
0.80	0.85 - 1.18	0.19 ± 0.02		0.98
0.30	1.18 - 1.40	0.09 ± 0.01		0.99

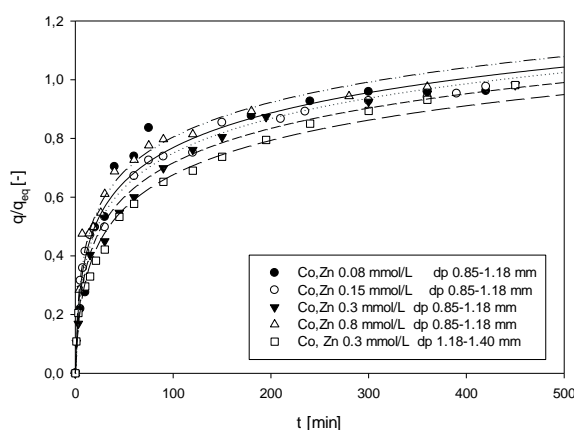


Figure 4: Interpretation of zinc adsorption experimental data by Elovich model (parameters in Table 1)

From Table 1 it can be confirmed the good data interpretation provided by Elovich model hypothesizing the same b and a different A for the different experimental conditions, as suggested by the theory. The Elovich model data of binary system are showed in the Figure 5 and the corresponding fitting parameters are reported in the Table 2. In Figure 5, the adsorption patterns of the binary system were compared with the corresponding plot of single-compound adsorption, reported in this work and in Di Natale et al. (2014) for zinc and cadmium, respectively.

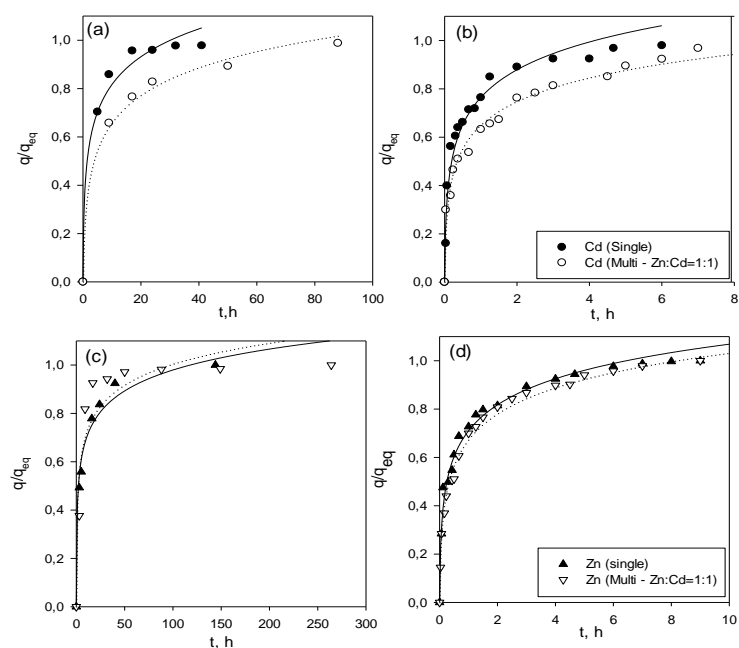


Figure 5: Cadmium and zinc kinetic plots by Elovich model in binary and single-compound systems, in stirred tank (a, c) and in fixed bed (b, d)

Table 2: Kinetic parameters obtained by Elovich model for cadmium and zinc adsorption in binary system, in stirred tank and fixed bed configurations

	$C_{Zn}^0 : C_{Cd}^0$	Configuration	A [min^{-1}]	b [-]	R^2
Zn	1	Stirred tank	0.02 ± 0.003	5.83 ± 0.14	0.94
		Fixed bed	0.14 ± 0.01		0.99
Cd	1	Stirred tank	1.92 ± 0.61	7.48 ± 0.39	0.98
		Fixed bed	18.12 ± 4.42		0.98

As shown in Figure 5, in both configurations, cadmium adsorption rate was lower in the presence of zinc, likely due to internal diffusion effects, while zinc rate is almost constant.

Table 2 shows that all the tests were well described by Elovich model, using, for each compound, the same b and a different A , as suggested by the basic hypotheses of the model. Furthermore, for zinc, the parameter b was the same of the single-compound adsorption, confirming that zinc adsorption occurred without any influence exerted by cadmium co-presence in solution. Di Natale et al (2014) showed that cadmium adsorption rate, in single-compound system, depended on a critic value of cadmium uptake (at 0.004 mmol/g), at which an external mass transfer control was replaced by an internal one, well described by Elovich. The parameter b for cadmium adsorption in single-compound system resulted to be 6.84, slightly lower than that one retrieved for the binary system. This result revealed that in the binary system the cadmium was adsorbed by activated sites characterized by a higher potential energy. On the contrary, in the binary system, the cadmium adsorption rate was well described by Elovich model in all the time and any control mechanism change was identified.

5. Conclusions

This work reports the results of a study of zinc and cadmium adsorption dynamics, in both single-compound and binary system, on a commercial non-impregnated granular activated carbon. The experiments were performed in different contact systems (fixed bed column and stirred tank), carbon particle sizes and metal concentrations.

Experimental results indicated that the zinc adsorption rate in the single-compound system was controlled by an internal mass transfer mechanism independently of particle size and concentration. The applicability of Elovich's model suggests the existence of active sites with a wide distribution of adsorption energies. These may be related either to surface reactions and surface electric potential or to progressive activation of active sites in deeper micropores.

For binary adsorption data, the zinc adsorption dynamics was not influenced by the cadmium presence as it evolved in the same way of single-compound case. On the other hand, the cadmium adsorption rate was highly dependent on zinc concentration and more specifically, to reach the 50% of the equilibrium condition, it took 60 min in the binary system compared with the 10 min necessary in the single compound adsorption. This evidence can be explained by considering the lower diffusion of cadmium inside carbon pores. In the binary system, the cadmium data were well described by Elovich model for all time, confirming the presence of an energy distribution of the active site.

Besides, as shown by equilibrium tests, the interaction of zinc and cadmium also rely on the specific affinity potential of the two metals toward the active sites. In fact, it was shown that simultaneous adsorption of zinc and cadmium also provided a reduction of cadmium adsorption compared with the single-compound case, while zinc adsorption magnitude remained unchanged. This result is further confirmed by the preloaded test which showed that, even if the cadmium is preliminary adsorbed on the activated carbon, in the presence of zinc it experienced a desorption process and was replaced by the zinc ions, reaching the same equilibrium results of normal binary test.

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