

Optimization of an Activated Carbon Adsorber for Cadmium Removal in Wastewater

Francesco Di Natale^{*a}, Francesco La Motta^a, Alessandro Erto^b,
Amedeo Lancia^a

^a Università di Napoli "Federico II", Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, P.le Tecchio 80, 80125 Napoli, Italy

^b Seconda università di Napoli, Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, via Roma 29, 81031, Aversa, Caserta, Italy

francesco.dinatale@unina.it

In this paper, we are presenting preliminary results of tests aimed at exploiting cadmium adsorption kinetics in different kind of ideal reactors (stirred tank, fixed bed column and fluidised bed) at lab scale. Based on a dedicated experimental analysis, the present work sought to compare the performance of the different adsorber configurations investigated, and to clarify the rate controlling mechanisms of cadmium adsorption. Experiments revealed that cadmium adsorption is controlled by external mass transfer only if the activated carbon is loaded below a critical value q_{cr} , which for the investigated conditions corresponds to 0.21 mg/g. For higher loading, the adsorption rate is controlled by an internal mechanisms well described by the Elovich model. The final objective of the study is to suggest appropriate guidelines to select optimal adsorber design.

1. Introduction

Cadmium is a highly toxic inorganic pollutant whose emission sources are widely diffused, giving rise to a large scale environmental pollution. For these reasons, environmental regulations define severe limitations on the maximum cadmium concentration in natural water bodies as well as on the maximum allowed concentration for wastewater discharge.

To assure the compliance with these limits, appropriate depuration technologies are required. Cadmium ions can be suitably removed by chemical-physical process as precipitation, ionic exchange, adsorption, electrochemical deposition and so forth (AWWA, 1999). Adsorption on granular activated carbon is a well-known method largely used for the removal of organic pollutants. Its application to metallic ions removal from polluted waters is undeniably diffused, although the removal efficiencies for these substances are usually lower than those typical for the organic compounds (Erto et al., 2009).

However, activated carbons can be profitably used due to their ability to remove different substances at the same time. Indeed, they are less selective than ion-exchange resins and usually more cost-effective (Benjamin, 2002). For this reason, in order to minimize the amount of required sorbent, the knowledge of the optimal working conditions to maximize the sorbent capture capacity and the kinetic rate is required.

Equilibrium and kinetics are two essential aspects of the adsorption process. As a general rule, it is highly desirable to find out activated carbons with both higher removal capacities and kinetic rates, since they exert a major influence on the overall removal efficiency of the process and play a crucial role in the industrial scale up of adsorption units. Main process parameters such as solute concentration, pH, salinity, temperature, solution composition, severely affect the equilibrium adsorption capacity of a given sorbent and together with fluid dynamic parameters, such as the mixing intensity of adsorbent particles and liquid solution, they determine the adsorption rates.

In this sense, it is worth noticing that almost all the adsorption studies in literature are focused on model aqueous solutions rather than on pilot plant applications (see, for example the review of Mohan and

Pittman, 2006). Even if this condition can be considered as too restrictive for the industrial scale-up, the high variability of natural and industrial waters is a severe limitation to the extension of pilot plant results to different working conditions. For this reason, the study of adsorption in model aqueous solutions allows a more interesting and reliable analysis of adsorption phenomena and a more meaningful method for the comparison of sorbents adsorption capacity.

In previous studies (Di Natale et al., 2008a) we analysed cadmium adsorption at equilibrium conditions onto a granular activated carbon, namely the Aquacarb 207EA, also addressing values of the Gibbs free energy of adsorption for cadmium ions in solutions using a multicomponent Langmuir model based on a robust set of experiments. The application of the same approach to other solutes on the same carbon confirms the correctness of the equilibrium modelling approach although it was clear that Langmuir-like approach also provide information on the average Gibbs free energy for the adsorption of a given solute on different active sites on the activated carbon (Di Natale et al., 2009). Comparison with other sorbents (Molino et al, 2013) also revealed that this activated carbon has good adsorption properties and wide field of application in water treatment.

In this paper, we are presenting preliminary results of tests aimed to exploit cadmium adsorption kinetics in different kind of ideal reactors (stirred tank, fixed bed column and fluidised bed) at lab scale. The work sought to compare the performance of the different adsorber configurations investigated, and to clarify the rate controlling mechanisms of cadmium adsorption. The final objective of the study is to suggest guidelines to select optimal adsorber design.

2. Materials and methods

2.1 Sorbents characteristics

Aquacarb 207EATM is a commercially available non impregnated granular activated carbon, 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. Selected sorbent particles with mean Sauter diameter of 752 µm were used in this work.

The sorbent is slightly basic (pH_{PZC} = 8) and its surface functional groups, obtained with the Boehm's titration analysis, are mainly represented by basic activated sites and by lactones and phenols acid sites. Morphological and chemical properties of the GAC are reported in Di Natale et al. (2008b). Before each experimental run, the sorbents were carefully rinsed with distilled water and oven dried for 48 h at 80 °C.

2.2 Sorption procedure

Cadmium solutions were prepared by dissolving Cd(NO₃)₂ in double distilled water to obtain the desired total cadmium concentration. Solution pH was monitored but not controlled over time. The experimental tests were carried out at room temperature that was almost constant and equal to about 25 °C.

The fixed bed consists in a glass column with internal diameter of 0.9 cm and height of 60 cm, whereas the fluidized bed consists in a glass column with internal diameter of 6 cm and height of 72 cm. Both columns were implemented in a closed loop circuit which includes a stirred vessel and a pump. A Verder Gear "micropump" with a magnetic coupling head is used to feed the run solution to the columns. Cadmium concentration were measured at different times in the stirred vessel. Preliminary calculations indicated that the fixed bed and the fluidised beds can be approximated as differential reactors and this result was confirmed by the experiments.

Tests in stirred tank were carried out using 100 mL glass bottles with Teflon cups that were kept in agitation on an orbital shaker at 200 rpm.

All the experiments were carried out with an initial Cadmium concentration of 20 mg/L and with an adsorbent mass/volume solution ratio of 50 g/L, keeping constant temperature, pH and salinity.

At the end of each kinetic test, once equilibrium conditions are reached, both the cadmium concentrations in solution and on the carbon surface were measured. The solution was filtered in a Hirsch funnel ceramic filter by a vacuum pump. The filtered solution was then analysed for pH and total cadmium concentrations while the carbon was leached with 1 M HNO₃ to obtain the complete cadmium desorption allowing for a direct measure of the uptake of cadmium on the solid surface. The accuracy of the experimental runs was checked by allowing a maximum error of 5 % in the cadmium material balance.

2.3 Analytical methods

The total cadmium concentration in solution was measured by means of air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer, with cadmium standard solution provided by Sigma Aldrich. Dilutions, where required, are carried out with 1M HNO₃ water solution.

To establish the accuracy, reliability, and reproducibility of the collected data, all batch isotherm tests were recorded in triplicate and average values only were reported. Blank tests were carried out in parallel. All the labware used in the study was previously soaked in 1M HNO_3 , triply rinsed with distilled water and oven dried. All the chemicals are AR grade supplied by Sigma Aldrich.

3. Experimental results

The kinetic adsorption data were reported in terms of cadmium concentration, c , cadmium uptake, q , and pH temporal trend for the three different configurations, as shown in the Figure 1.

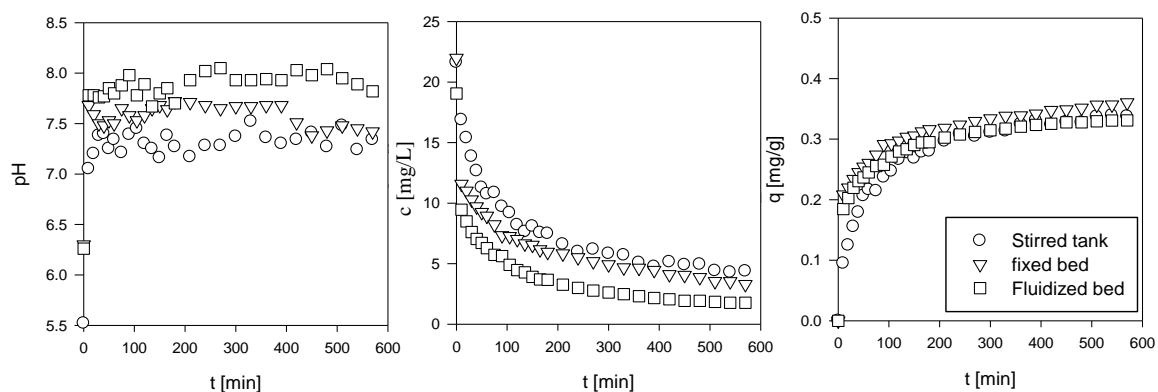


Figure 1: Kinetic plots in stirred tank fixed bed and fluidized bed

Figure 1 shows that both concentration and uptake trends are similar for the three configurations. As expected, the concentration and the uptake present opposite trends, as the former decreases and the latter increases with time. However, in both the cases the curves changes significantly in the first 100 min and then reach gradually the equilibrium. The pH trend allows to assume it as almost constant.

In order to further investigate the adsorption kinetic, the experimental data were analysed by plotting the adsorption rate dq/dt , calculated from experimental runs, versus the dimensionless loading q/q_{eq} , where q_{eq} is the asymptotic, equilibrium, point of the kinetic test.

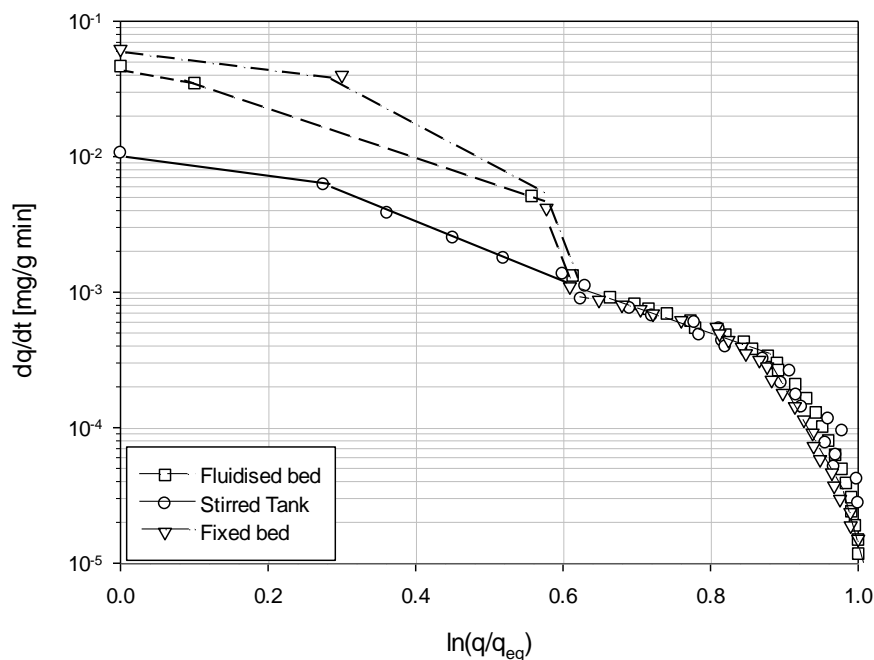


Figure 2: Kinetic plots in batch mode, in fixed bed and fluidized bed with initial metal ion concentration of 20 mg/L and $d_p=0.4-0.6$ mm as particle size

According to Figure 2, it is possible to identify two different controlling mechanisms, characterized by two different plot slopes switching at $q/q_{eq}=0.6$.

In the first part, i.e. below $q/q_{eq}=0.6$, the three configurations showed different slopes, thus suggesting that the adsorption phenomena is controlled by a fluid dynamic driven mass transfer mechanism, i.e. the fluid-solid mass transfer rate. Above $q/q_{eq}=0.6$ the plots converged onto the same parallel line, suggesting that an internal mass transfer rate become the controlling mechanism. Thus, the value of q corresponding to $q/q_{eq}=0.6$ can be identified as a critical sorbent loading, q_{cr} .

To investigate the validity of this assumption, the experimental data were interpreted in light of several adsorption rate models as: external mass transfer rate; first order; pseudo-second order; diffusional models (Reichemberg, Vermulen) and Elovich model. It was found that experimental data can be properly interpreted in light of the external mass transfer rate model for $q < q_{cr}$:

$$\frac{d\bar{q}}{dt} = \frac{k_f a}{\rho_p} \cdot (c - c^*) \quad (1)$$

Where c^* is the cadmium concentration in solution in equilibrium with the actual sorbent loading q , which is determined from cadmium adsorption isotherm (Di Natale et al, 2009), k_f is the mass transfer coefficient between a carbon particle and the solution, a is the total interfacial area of carbon particles calculated as

$$a = \frac{6}{\rho_p \cdot d_p} \quad (2)$$

and ρ_p is the apparent density of carbon (1100 kg/m^3) and d_p the mean Sauter diameter of particles.

Plots of dq/dt against $(c-c^*)$ are shown in Figure 3, which reveals the correctness of the assumptions. The values of k_f can be calculated from the plot slopes. The values for stirred tank ($k_f = 1.39 \cdot 10^{-6} \text{ m/s}$, $R^2=0.97$), fixed bed ($k_f = 6.94 \cdot 10^{-6} \text{ m/s}$, $R^2=0.93$) and fluidised bed ($k_f = 5.56 \cdot 10^{-6} \text{ m/s}$, $R^2=0.92$) are consistent with former literature predictions ($k_f = 1.91 \div 5.24 \cdot 10^{-6} \text{ m/s}$ for stirred tank, $k_f = 2.02 \div 34 \cdot 10^{-6} \text{ m/s}$ for fixed bed, $k_f = 6.25 \div 22 \cdot 10^{-6} \text{ m/s}$ for fluidised beds) taken from Table 5.26-27 of Perry's Chemical Engineering Handbook (Perry and Green, 2007). Some discrepancies can be related to the specific experimental conditions of this study but, especially for the stirred tank and the fluidised bed, to the occurrence of complex fluid dynamic and porous solid-fluid interface conditions in a multiphase flow. Some reference can be found, for example, Carotenuto et al. (2011a,b) reviewed the main models and provide a description of the fluid dynamic field close to a porous layer.

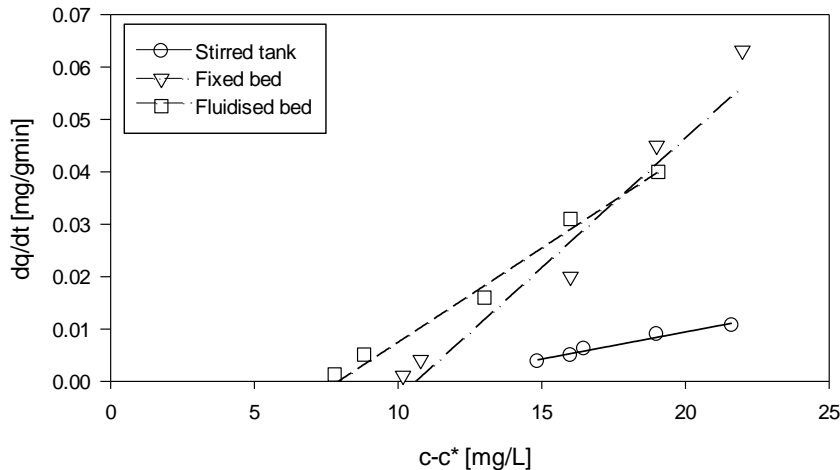


Figure 3: Regression accomplished by means external mass transfer model plotting $\frac{d\bar{q}}{dt}$ vs $(c - c^*)$

The fixed and fluidized bed present a similar mass transfer coefficient. As expected, the stirred tank presents the lowest mass transfer coefficient since in this configuration liquid and solid have a lower mixing grade with respect to the other two configurations.

Data for $q > q_{cr}$ were found to be well described only by the Elovich model, generally expressed as:

$$\frac{d\left(\frac{q}{q^*}\right)}{dt} = A \cdot \exp\left(-b \cdot \frac{q}{q^*}\right) \quad (3)$$

where q^* is the cadmium uptake capacity in equilibrium with solution concentration c at each time, A is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and b is the desorption constant ($\text{g} \cdot \text{mg}^{-1}$). Experiments were interpreted considering that the parameter b , which is a function of specific solute-sorbent interactions, should be the same for all tests while the parameter A is related to the adsorption rate when the system approached q_{cr} , and, consequently, it is a function of the system configuration, mirroring the different external mass transfer rates at $q < q_{\text{cr}}$. Data fitting by Elovich model is reported in Figure 4, which shows the good matching between model and experimental results. The same fitting extrapolated for $q < q_{\text{cr}}$, gives a fair description of data. The fitting parameters are listed in Table 1.

Table 2: Kinetic parameters obtained by Elovich model for cadmium adsorption

Configuration	A [min^{-1}]	b [-]	R ²
Stirred tank	64.37±10		0.98
Fixed bed	75.01±1	1.77±0.01	0.94
Fluidized bed	70.21±11		0.98

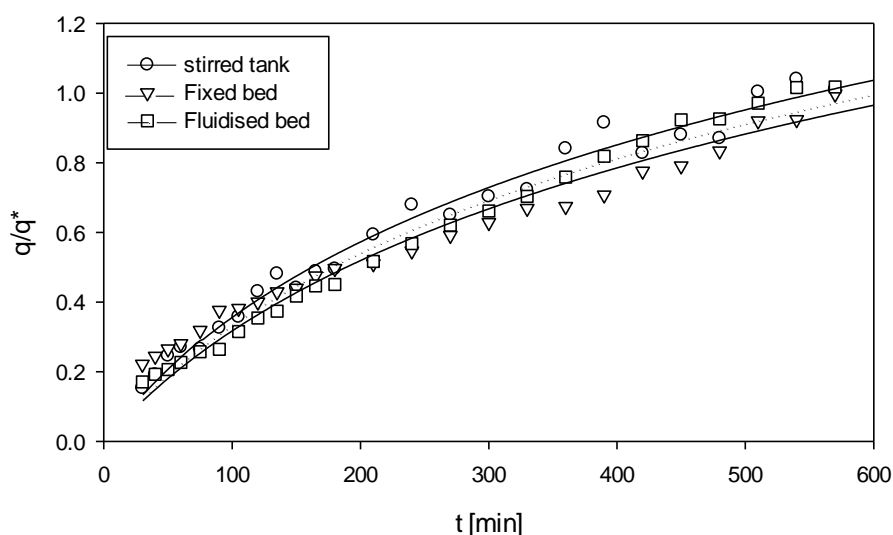


Figure 4: Interpretation of experimental data with Elovich model (parameters in Tab.1) at $q > q_{\text{cr}}$

4. Conclusion and final remarks

This paper reports preliminary results of an ongoing study on cadmium adsorption rate on a conventional non-impregnated granular activated carbon, aimed at exploiting and estimating the rate controlling mechanisms. Data were supported by equilibrium results available from former studies. Experimental results indicated that adsorption rate is controlled by fluid-solid mass transfer rate for $q < q_{\text{cr}}$, where $q_{\text{cr}} = 0.21 \text{ mg/g}$ for the given particle size. Differently, for $q > q_{\text{cr}}$, adsorption rate is controlled by an internal mass transfer mechanism. It is expected that q_{cr} decreases with particle size being representative of the high reactivity of external surface sites. The applicability of Elovich's model suggests the existence of active sites with a widely distribution adsorption energy. These may be related either to surface reactions and surface electric potential or to progressive activation of active sites in deeper micropores. Further investigations are required to clarify the nature of this phenomenon.

Experimental results are extremely useful for adsorber design. In fact, they indicate that the use of adsorbers with high fluid-solid mass transfer rate can be relevant only if the sorbent is used with an uptake lower than q_{cr} .

If the sorbent loading is higher than this level, adsorber with a lower quality of solid fluid contact (i.e. mild stirred tanks) can be used without significant reduction of the actual adsorber performances. This results is valuable because the behaviour of fixed bed column strongly depends on the internal transfer rate dynamics and, besides, if the system is operated at higher interstitial velocities or if higher concentration of cadmium are involved, the relevance of internal mass transfer rate is emphasized. Further studies are, however, required to finally address the effects of cadmium concentration, pH and solution salinity upon adsorption kinetic.

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