Cd(II) removal from aqueous solutions by adsorption onto activated carbon

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This paper documents the results of an experimental study on cadmium removal from model aqueous solutions by adsorption onto a granular activated carbon (GAC). Adsorption isotherms have been carried out at different pH, salinity and temperature levels. Cadmium adsorption is the highest at neutral pH levels while it strongly decreases by decreasing pH. Due to $Cd(OH)_2$ precipitation, the adsorption becomes irrelevant in alkaline systems. On the contrary temperature and salinity have more limited effects on cadmium capture by the GAC.

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 usually required. Cadmium ions can be removed by chemical precipitation, ionic exchange, adsorption, electrochemical deposition, etc (Letterman, 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 is undeniably diffused, although the removal efficiency for these substances is usually lower than for the organic ones.

However, activated carbon can be profitably used due to their ability to contemporary remove different substances. Indeed they are less selective than ion-exchange resins and usually more cost-effective. For this reason, in order to minimize the amount of sorbent required, the knowledge of the optimal working conditions to maximize the sorbent capture capacity is required (Letterman, 1999; Mohan and Pittman, 2006).

The values of process parameters (solute concentration, pH, salinity, temperature, solution composition) severely affect the equilibrium adsorption capacity of a given sorbent determining a strong variation of the overall removal efficiency of the process and playing a crucial role in the industrial scale up of adsorption units. In this sense, it is worth noticing that almost all the adsorption studies in literature are focused on model

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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.

This work concerns the uptake of cadmium ions in aqueous solutions by a non-impregnated activated carbon (Aquacarb 207EA™ commercialised by Sutcliffe Carbon). In order to give a complete description of adsorption phenomena, experimental runs have been carried out at different cadmium concentration, pH, salinity and temperature levels.

2. Materials and methods

2.1 Sorbents characteristics

Aquacarb 207EA^{TM} 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 m^2/g and an average pore diameter around 26 Å. Sorbent particles with averaged diameter between 1 and 1.2 mm has been used in this work.

The sorbent is slightly alkaline ($pH_{PZC} = 8$) 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. (2006). Before each experimental run, the sorbents have been carefully rinsed with distilled water and oven dried for 48 h at 80°C.

2.2 Sorption procedure

The stock solutions of test reagent are prepared by dissolving $Cd(NO_3)_2$ in double distilled water to obtain total cadmium concentration levels ranging from 5 to 50 mg/l. The pH values of the initial solutions are adjusted by adding HNO_3 (0.1 M) or KOH (0.1 M) but they are not further altered during the experimental runs. Solution salinity has been modified by adding either $NaNO_3$ or NaCl. The experimental runs have been carried out in batch mode at constant temperature in a P.I.D. controlled thermostatic oven. Each sample consists of a 200 ml aqueous solution at the desired cadmium concentration, put in contact with a mass of sorbent ranging between 0.5 and 2 g.

Preliminary tests show that a contact time of 60 hours is required to reach equilibrium conditions without additional stirring. At equilibrium conditions, both the cadmium concentrations in solution and on the carbon surface have been measured. The solution is filtered in a Hirsch funnel ceramic filter with the aid of a vacuum pump. The filtered solution is then analysed for pH and total cadmium concentrations while the carbon is leached with 1 M HNO_3 to obtain the complete desorption allowing a direct measure of the uptake of cadmium on the solid surface. The accuracy of the experimental runs is checked by allowing a maximum error of 5% in the cadmium material balance.

2.3 Analytical methods

The total cadmium concentration in solution is 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 HNO_3 water solution.

The amount of adsorbed cadmium is measured by leaching the solid material with 100 ml nitric acid aqueous solution (HNO_3, 1M) for 24 h, which assures a complete desorption of cadmium from carbon surface. Then, the solution is analysed by means of AAS-F.

To establish the accuracy, reliability, and reproducibility of the collected data, all batch isotherm tests are recorded in triplicate and average values only are reported. Blank tests are carried out in parallel. All the labware used in the study is 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

3.1 Effect of cadmium concentration and pH

The typical adsorption isotherms for cadmium capture on the GAC are reported in Figure 1 for experimental runs carried out at 20°C and equilibrium pH levels between 2 and 7.5.

Experimental results show that the adsorption capacity increases with cadmium concentration until it reaches an almost asymptotic value which strongly depends on the working conditions. The typical shape of adsorption isotherm is characteristic of a Langmuir-like behaviour. Furthermore, adsorption isotherms clearly show that adsorption capacity monotonically increases by increasing pH.

The effect of solution pH on cadmium capture is further analyzed by considering eight solutions with the same cadmium concentration, c°, and carbon dosage, m/V, and different initial pH values. Experimental results (reported in Figure 2 in terms of adsorption capacity as a function of the equilibrium pH) reveal that the GAC has a maximum value of adsorption capacity for pH 7.5 *circa*. At higher pH, due to the precipitation of cadmium hydroxide, the determination of significative adsorption isotherms is not allowed.

The effect of solution pH can be related to the well known competition phenomena among cadmium ions (mainly represented by Cd^{++} and $CdOH^+$ cations) and H^+, as described, for example, by Benjamin (2002).

3.3 Effect of solution salinity

The assessment of solution salinity dependence on cadmium adsorption capacity has a great relevance for the estimation of carbon effectiveness in real waters. Experiments have been carried out by using either $NaNO_3$ or NaCl to modify the salinity level (Figure 3). Experimental results point out that the adsorption capacity constantly decreases by increasing sodium nitrate concentration. The reduction of adsorption capacity at increasing solution salinity may be directly related to the competitive effect of Na^+ ions with cadmium cations.

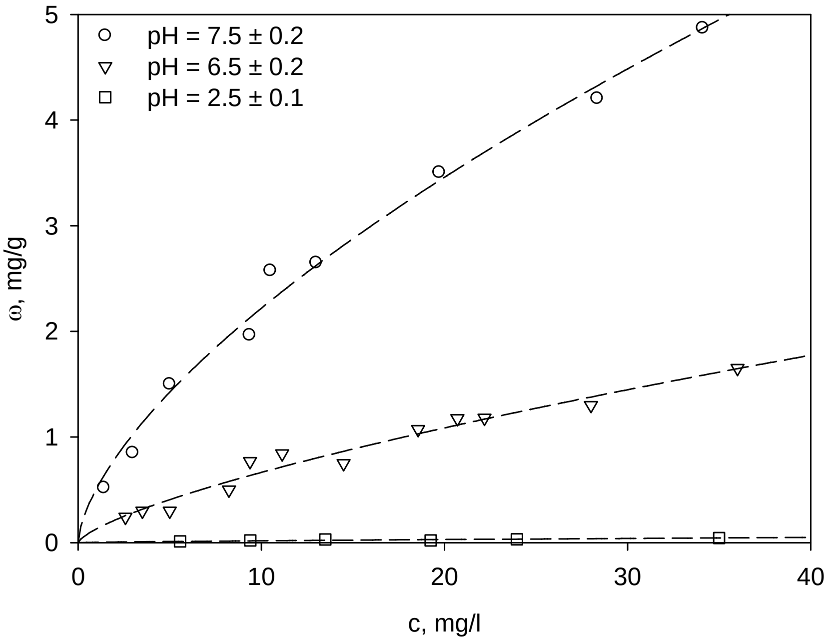

Figure 1 – Cadmium adsorption isotherms in distilled water at different pH. T= 20°C,

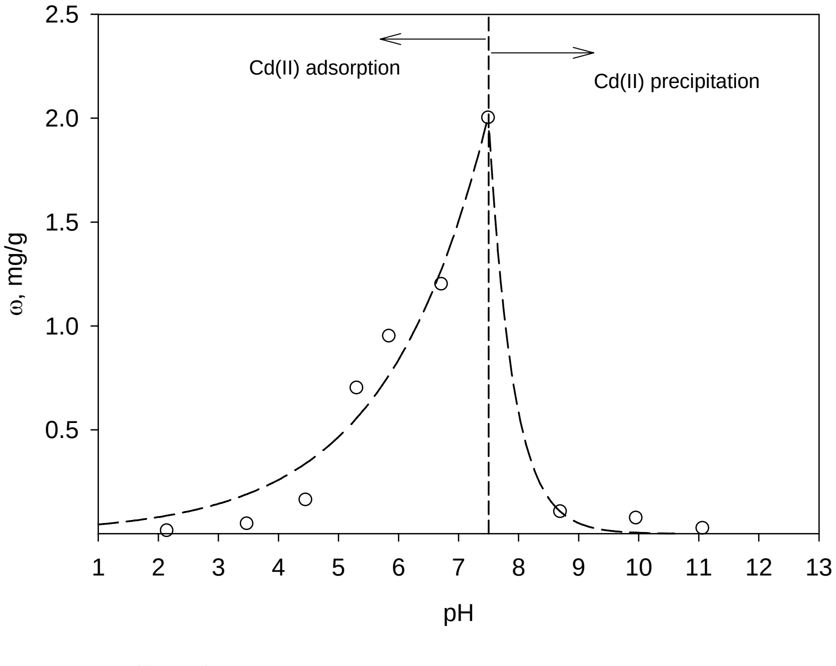

Figure 2 – Effect of solution pH on cadmium adsorption. T= 20°C, c° = 25 mg/l, m/V = 7.5 g/l,

When solution salinity is varied by using NaCl the adsorption capacity presents a slight minimum at I= 0.05 M while for higher values it appears to be almost equal to the value obtained in distilled water. The increase of solution salinity alters the cadmium speciation by inducing the formation of nitrate or chloride cadmium ions (Stumm and Morgan, 1996). Experimental results reveal that the formation of cadmium chlorides compensates for the competitive effect of increasing concentration of Na^+ ions, determining a less variation of adsorption capacity. Similar results have been previously obtained for Hg(II) ions (Di Natale, 2004).

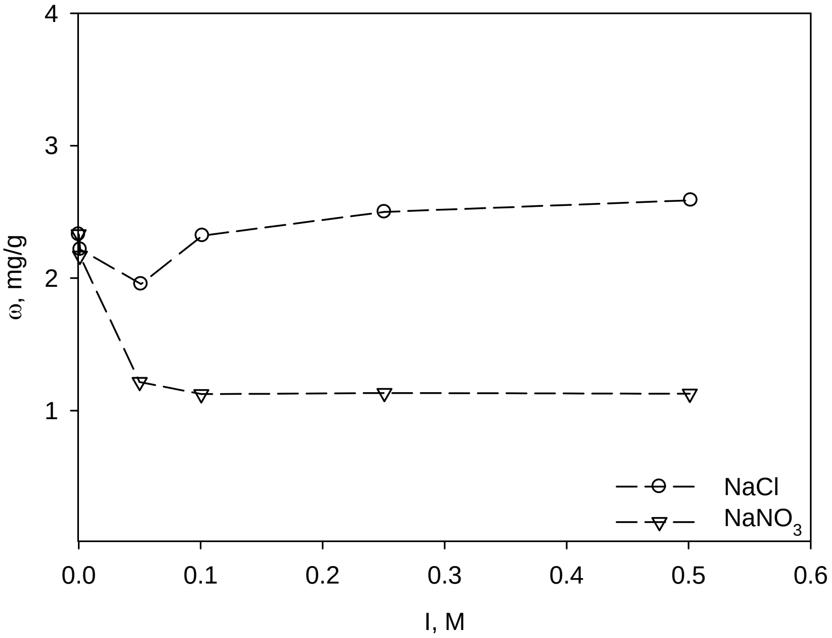

Figure 3 – Effect of solution salinity on cadmium adsorption. T= 20°C, pH = 7,3± 0.2, c° = 25 mg/l, m/V = 5 g/l

3.4 Effect of temperature

Adsorption isotherms of cadmium solutions have been carried out at neutral pH and at 10, 20 and 40°C. The values of the adsorption capacity at three cadmium concentration levels are reported in Figure 4 in function of temperature, showing a slightly reduction of the adsorption capacity at higher temperature according to the exothermicity of the adsorption process.

4. Conclusions

Cadmium adsorption has been investigated in different working conditions including solution pH, salinity temperature and cadmium concentration. Adsorption isotherms show that the maximum cadmium removal is obtained at neutral pH, low salinity levels and low temperatures.

The adsorption capacity increases by increasing pH, although adsorption isotherms at alkaline pH are not available due to cadmium hydroxide precipitation. Cadmium adsorption mechanisms can be easily explained considering the cadmium speciation and the competitive effects of H^+ and Na^+ ions, according to previous studies (e.g. Benjamin, 2002). The presence of cadmium chloride compounds (e.g. Stumm and Morgan, 1996) can be considered responsible for the very limited variation of adsorption capacity in NaCl containing model solutions. Finally, the effect of temperature is coherent with the exothermicity of adsorption processes.

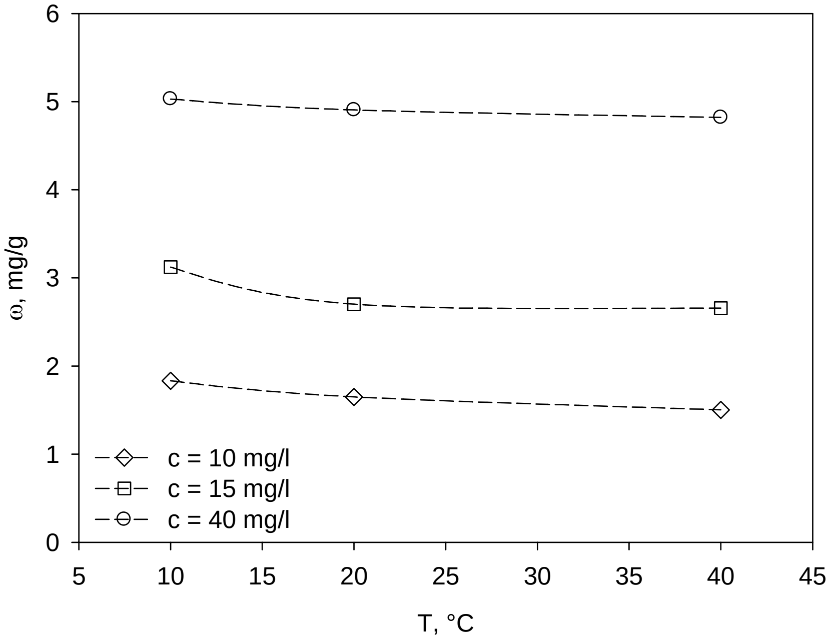

Figure 4 – Effect of temperature on cadmium adsorption. pH = 7.3 ± 0.2.

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