Coal combustion ash sorbents for Cd and Zn capture in single-compound and binary systems

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Abstract

The work deals with the adsorption of cadmium and zinc on coal combustion ash (CCA) sorbents, in both single-compound and binary systems. Three CCA sorbents were tested; two of them deriving from the gasification of a raw sample carried out with either steam (SG) or carbon dioxide (DG). Experimental adsorption runs showed a significantly higher adsorption capacity of zinc with respect to cadmium, for all the investigated sorbents. This was ascribed to a higher affinity of sorbent active sites toward Zn and, secondarily, to the smaller dimension of zinc cations (Zn^{2+}) which result less affected by steric hindrance.. Moreover, for both the analytes, a ranking DG>SG>CCA of adsorption capacity can be recognized. This is likely due to the increase in inorganic fraction of SG and DG sorbent with respect to CCA, due to the gasification treatments. Moreover, for DG sorbent, further improvement of the performances could be ascribed to an increase in the concentration of carbonyl surface functional groups, which are considered to be the more active fractions for zinc and cadmium adsorption on the investigated sorbents. Binary adsorption data showed the same ranking among sorbents retrieved in single-compound tests and a higher zinc adsorption capacity. Different competitive effects arose between the adsorbates, likely ascribable to a different affinity towards the sorbents.

Keywords: coal combustion ash; competitive adsorption; cadmium; zinc; gasification.

1. Introduction

The removal of heavy metals from groundwater and wastewater, to conform their residual concentrations to the effluent regulatory standards, represents a pressing need due to their proven toxicity and resistance to biodegradation. Cadmium is unanimously recognized as one of the most dangerous heavy metals (IARC, 1993). Zinc is an essential element for human being, but it can become toxic at high concentration (ATSDR, 2005). Adsorption is generally considered as a reliable water treatment, due to high versatility and efficiency in a wide range of process parameters. The most popular sorbents for Cd and Zn capture are by far activated carbons, having also the highest adsorption capacity (Babić *et al*., 2002). However, acquisition, regeneration and disposal of the spent sorbent are generally characterized by high costs. Coal combustion ash (CCA), one of the most abundant waste materials deriving from the combustion of powdered coal, are considered as a valid precursor for the production of sorbents both as raw (Wang and Wu, 2006; Balsamo *et al*., 2011) or after beneficiation treatments (Wang and Wu, 2006; Balsamo *et al*., 2011). In this paper, the attention was focused on the gasification of a CCA, carried out with either steam or carbon dioxide. In general, these treatments involve the conversion of the unburnt carbon fraction of the CCA into gaseous products, simultaneously determining the development of ash porosity and chemical modification of surface as reported in the literature (Balsamo *et al*., 2012). Most of the works reported in literature on the adsorption of heavy metals on CCA or beneficiated CCA considered only single metal ions, whereas industrial effluents generally contain several metals. Thus it is important to investigate the simultaneous removal of two or more metals, also taking into account the possible occurrence of interference or competition phenomena during adsorption. The aim of the present work is to explore the possibility of utilizing a CCA deriving from a plant for energy production by coal combustion for the adsorptive removal of cadmium and zinc from aqueous solution. In this study, the experimental runs were performed on both raw CCA and after activation by either steam or CO_2 gasification. Experimental tests were carried out on both single-compound and cadmium/zinc binary systems, in order to verifying the occurrence of competition effects. The influence of sorbent properties on adsorption performances is critically discussed.

2. Materials and methods

2.1. Sorbent properties and activation

The raw coal combustion fly ash utilized in this work came from an Italian power plant operated by Enel, in which a bituminous coal is used as fuel. Laser granulometric

Table 1. Main physical and chemical properties of coal combustion ashes (raw: CCA; steam gasified: SG; CO_2 gasified: DG)

Property	CCA	SG	DG
Sauter particle diameter (µm)	10	6	6
B.E.T. surface area (m^2 g^{-1})	19	31	28
Cumulative pore volume (mm^3 g^{-1})	30.0	63.0	49.0
Fixed carbon (% db)	22.3	14.4	15.1
Ash content (% db)	74.0	85.5	84.8
pH$_{PZC}$	9	9	9

analysis was performed by a Malvern Instrument Master Sizer 2000 granulometer, operating down to a minimum particle size of 0.02 µm. Surface area measurement was derived from N_2 porosimetry (@ 77 K) carried out by a CE Instruments Sorptomatic 1990 analyzer, and pore size distribution (pore radius range of 3.7–500 nm) was obtained by operating a Thermo Finnigan Pascal 240/140 porosimeter. CCA chemical characterization was obtained by X-ray diffraction (XRD, Bruker D2 Phaser diffractometer) and proximate analysis by means of a Leco CHN-2000 analyzer. Finally the evaluation of the pH of point zero charge (pH$_{PZC}$) was made according the Noh and Schwartz (1990) method, which showed that the CCA has a marked basic nature (pH$_{PZC}$=9). In Table 1, CCA chemical/physical properties are reported. Proximate analysis is provided on dry basis (db). CCA is mainly macroporous with a limited pore volume (30 mm^3 g^{-1}) and B.E.T. surface area (19 m^2 g^{-1}), and a high (74%) ash content. Proximate analysis showed a moderate (22%) fixed carbon content, due to short mean residence times (and, therefore, limited degree of carbon conversion) into the combustor. Mean (Sauter) particle diameter for CCA resulted equal to 10 µm. A complete characterization of the raw CCA is reported in Balsamo *et al.* (2011). In order to increase the adsorption performances, CCA was subjected to two different gasification treatments carried out by either steam or CO_2. Gasification treatments were performed in an electrically-heated tubular reactor (Nabertherm R60/750/13, i.d.=60 mm). In both the cases, the reactor was kept at the temperature of 850°C. Samples (1 g) of CCA were charged into the reactor and kept in contact with a stream of either steam or CO_2: steam was generated by feeding liquid water (flow-rate at room temperature equal to 60 mL h^{-1}) through a pump (Stepdos 03RC) to the reactor, while CO_2 was fed as pure at a flow-rate of 80 L h^{-1} (at room temperature). It is highlighted that both steam and CO_2 flow-rates at the operating temperature (850°C) assume the value of about 300 L h^{-1}. Steam gasification (SG) and carbon dioxide (so-called 'dry') gasification (DG) were carried out for times equal to 10 min, as in a previous work it was demonstrated that the best adsorption properties are obtained for short gasification times (Balsamo *et al.*, 2013). Experimental data on sorbent characterization by XRD showed that the inorganic crystalline structure of the raw ash was fully

retained upon gasication, thus confirming that the only chemical process that took place is either steam or dry gasification of the carbon content. The main SG and DG chemical and physical properties are reported in Table 1, while a complete sorbent characterization is reported in Balsamo *et al.* (2013). In summary, both the gasification treatments ended up into: (i) an increase in porosity, more pronounced for SG; (ii) a decrease in the mean particle size; (iii) an obvious consumption of C with the related increase in the ash content.

2.2. Sorption tests

Thermodynamic tests, addressing at the evaluation of CCA, SG and DG adsorption capacity, were carried out in batch stirred glass reactors kept in a PID controlled thermostatic oven. All the tests were conducted in model aqueous solutions; stock solutions of cadmium and zinc were prepared by dissolving a given quantity of $Cd(NO_3)_2 \cdot 4H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich, 99.9%), respectively, in distilled water. For single-compound tests, each sample consisted of 0.1 L of metal (Zn or Cd) solution at different initial concentration put in contact with a constant mass of adsorbent (1 g). Similarly, for the binary tests, 0.1 L of Zn/Cd solution were used with same sorbent dosage (1 g) and initial concentration ratio of the two analytes ($C_{Zn}^0 : C_{Cd}^0$ =1:1, on molar basis).

Each experimental point corresponded to different zinc and cadmium initial concentrations, in order to describe two complete adsorption isotherms in the range of concentrations typically found in polluted waters. All the experimental tests were carried out at 20°C and neutral equilibrium pH. To this aim, a pH adjustment of the initial solution was always necessary by adding HNO_3 (1 M). Analytical concentrations of both zinc and cadmium were measured by air/acetylene flame atomic absorption spectrophotometry (AAS-F) by using a Varian SpectrAA-220 spectrophotometer.

3. Result and discussion

Experimental tests of Cd and Zn adsorption on CCA, SG and DG sorbents in single-compound systems at a constant temperature (20°C) and equilibrium pH (around neutrality) are reported in Figure 1, where ω represents the molar specific adsorption capacity of the metal under investigation.
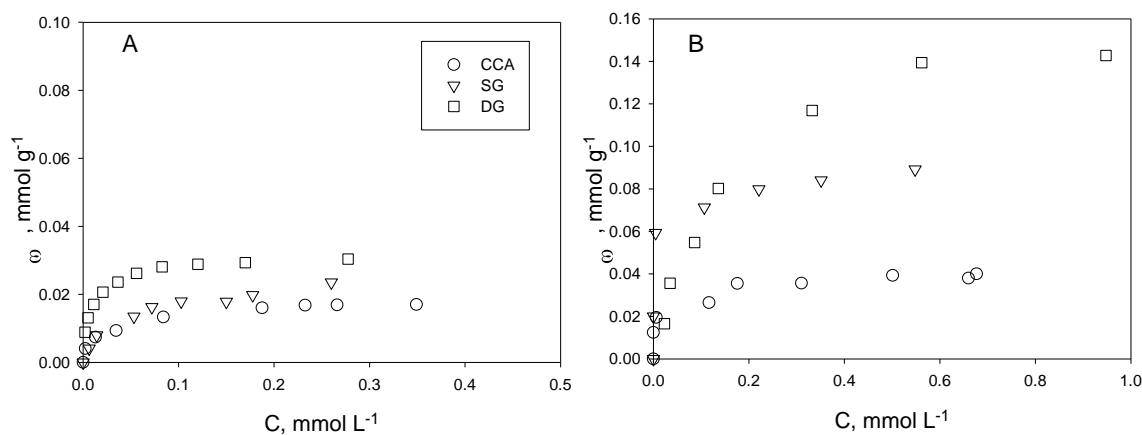
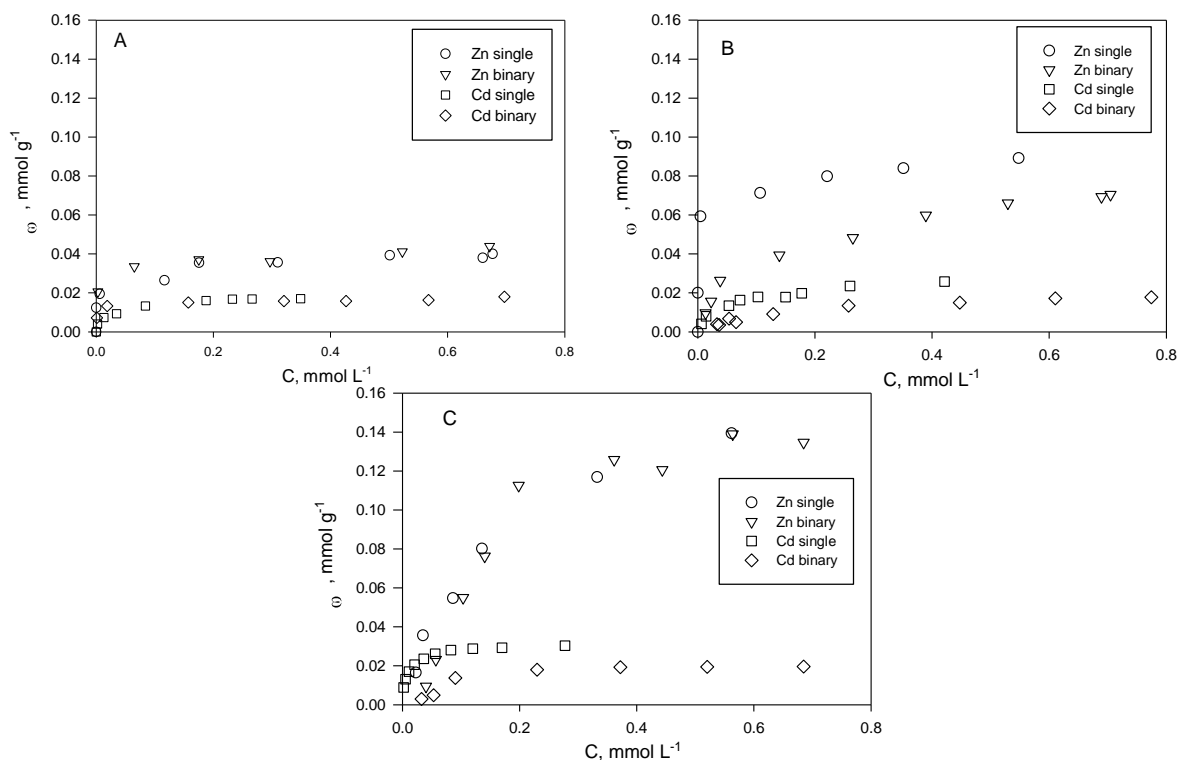**Figure 1.** Cadmium (A) and zinc (B) adsorption isotherms on CCA, SG and DG sorbents.
T=20°C; equilibrium pH=7.0±0.3

The first evident result is the significantly higher adsorption capacity of Zn with respect to Cd for all the investigated sorbents, likely due to a higher affinity of active sites toward zinc and, secondarily, to the smaller dimension of zinc cations (Zn^{2+}) which are less affected by steric hindrance and cation–cation repulsions than cadmium cations (Cd^{2+}) (El-Eswed *et al.*, 2012). Indeed it is worth observing that, in the experimental conditions adopted, Cd^{2+} and Zn^{2+} are largely the predominant ions present in solution among Cd and Zn species, respectively (Erto *et al.*, 2013). For both the analytes, a ranking DG>SG>CCA of adsorption capacity can be recognized. For cadmium, the removal efficiency increased by more than 50% for DG and SG with respect to that of raw CCA. For zinc, the differences are much more evident and a 3-times and 6-times average increasing of adsorption capacity was observed for SG and DG, respectively. Both the gasification treatments determined an increase in particle porosity, even if a competition between porosity development and sintering was recorded. A decrease in particle size was recorded as well: these aspects concur in explaining the better adsorption performance offered by SG and DG with respect to the raw ash. However, the ranking of sorbent porosity (Table 1) did not reflect the one corresponding to the Cd (or Zn) adsorption capacity. Form a chemical point of view the gasification treatments determined also a significant reduction in the carbon content and, consequently, an increase in the inorganic ash content with respect to CCA, while no significant differences were observed between SG and DG sorbents concerning these parameters. It can be inferred that the inorganic fraction is the main active part for Cd and Zn adsorption, as already demonstrated in a previous work dealing with Cd adsorption on demineralized CCA (Balsamo *et al.*, 2011). Moreover, the gasification carried out with carbon dioxide likely determined a higher concentration of carbonyl functional groups by reaction of the organic matrix with CO_2 at high temperature. These oxidized functional groups are commonly believed to be active sites for heavy metals adsorption and they can play a parallel role in determining the highest adsorption capacity showed by DG sorbents towards both Cd and Zn (Gao *et al.*, 2009). Moreover they are likely responsible of the

peculiar shape of the DG adsorption isotherms, for both Cd and (more evidently) Zn. In fact both the DG adsorption isotherms show an asymptote in correspondence of the highest investigated equilibrium concentrations, likely associated with the contribution of the oxidized surface functional groups. These groups are activated at higher concentration with respect to the inorganic fraction sites and, particularly for Zn, they determine a significant increase in adsorption capacity at higher equilibrium concentrations. These results are corroborated by the acid/base behavior of the sorbents (both CCA and the gasified samples), which also gives important indications about the adsorption mechanisms. In fact it was previously referred that the addition to the cadmium/zinc adsorption solution of a defined amount of HNO_3 was necessary, in order to obtain an equilibrium pH near to neutrality. Indeed the basic character of the investigated ashes (Table 1) is related to the presence of CaO in the sorbent matrices which is completely hydrated in aqueous solution, giving rise to $Ca(OH)_2$. In turn the $Ca(OH)_2$ concentration achieves a value 0.56 g L^{-1}, well below the solubility limit at room temperature; $Ca(OH)_2$ is thus completely dissociated into Ca^{2+} and OH^-. Moreover, the HNO_3 added quantity was optimized for each experimental run and resulted proportional to the concentration of analyte in solution, i.e. a higher quantity of HNO_3 was necessary for tests conducted at higher cadmium/zinc concentration. These results suggest an ion exchange mechanism for the adsorption of both cadmium/zinc on CCA and gasified samples, likely due to a substitution of cations originally present on ash surface and released in water (mainly represented by Ca^{2+}) with Cd^{2+} or Zn^{2+} ions. For a deeper analysis of cadmium/zinc adsorption on CCA, SG and DG sorbents, further tests in binary system ($C_{Zn}^0 : C_{Cd}^0 = 1:1$) were carried out to verify the applicability of the proposed sorbents to multicomponent systems and to assess the possible occurrence of competition phenomena during simultaneous adsorption. Figure 2 reports the experimental results for Cd/Zn binary adsorption on CCA, SG and DG at 20°C and neutral pH; the corresponding single-compound adsorption isotherms at the same temperature were also included, so to allow for a direct comparison.

Figure 2. Cadmium and zinc adsorption isotherms in binary system ($C_{Zn}^0 : C_{Cd}^0$ =1:1) on CCA (A), SG (B) and DG (C) sorbents. Comparison with single-compound data. T=20°C; equilibrium pH=7.0±0.3

In the range of equilibrium concentration investigated, the three sorbents showed an evidently different behavior although in all the cases they were able to capture at a significant extent both the analytes. The ranking among sorbents retrieved in single-compound tests was kept for the binary system and all the sorbents showed a Zn adsorption capacity higher than that corresponding to Cd, the differences becoming more marked for the gasified samples. It is important stating that a speciation analysis carried out for the binary system provided the same qualitative results observed for the single-compound systems and Zn^{2+} and Cd^{2+} ions confirmed to be largely predominant in solution (Erto *et al.*, 2015). For CCA, experimental data show that no significant differences can be observed between the performances in single-compound and binary systems for both the analytes. This can be likely ascribed to the nature of the active sites hypothesized for Cd and Zn. Indeed, for CCA, Zn and Cd are expected to adsorb on the inorganic fraction likely by an adsorption/ion exchange mechanism which is not selective for any of the analytes (Figure 2A). For gasified samples, the layout of binary tests appears different than the one observed for CCA and dependent on the gasifier agent. Experimental data on SG sorbent showed that both Zn and Cd adsorption capacity is reduced in binary system, the extent of reduction with respect to the corresponding single-compound data being in percentage similar (Figure 2B). This result clearly testifies the rise of a competition between analytes, greater at low equilibrium concentration where Zn appears to be energetically favored. Differently, the experimental data for DG sorbent show that the zinc

adsorption isotherms almost overlap in single-compound and binary systems. Hence, the zinc adsorption capacity does not depend on the presence of cadmium in the range of equilibrium concentration tested (Figure 2C). Conversely, cadmium adsorption capacity in binary system is lower than in single-compound system even for a very low concentration range. This competitive effect is likely due to a higher affinity of DG active sites (mainly based on carboxylic and oxidized carbon groups) toward zinc.

4.   Conclusions

The adsorption of cadmium and zinc from aqueous solution onto three different coal combustion ashes, both in single-compound and binary systems, was studied. The coal combustion ashes were used as raw (CCA) and after a beneficiation treatment based on either steam (SG sample) or CO_2 (DG sample) gasification. The gasification treatments determined a significant reduction in the carbon content, similar for SG and DG sorbents, and a consequent increase in the inorganic fraction. Adsorption experimental results in single-compound systems showed a ranking DG>SG>CCA of adsorption capacity for both zinc and cadmium. The increase in inorganic content and the formation of oxidized functional groups, for which metallic cations have great affinity, are likely responsible for the observed experimental results. The experimental data on binary system showed that zinc is more adsorbed than cadmium, mirroring the same behavior of the corresponding single-compound systems. However, the three sorbents showed evidently different behaviors. For CCA, experimental data showed that any significant

differences can be observed between the performances in single-compound and binary systems for both the analytes. For gasified samples, the experimental data on SG sorbent showed that both Zn and Cd adsorption capacity is reduced in binary system with respect to the corresponding of single-compound systems, while the experimental data for DG sorbent indicated that zinc adsorption capacity does not depend on the presence of cadmium which, conversely, is significantly affected by the presence of zinc. The competitive effects were ascribed to the nature of adsorption active sites for SG and to a higher affinity toward zinc in the case of DG active sites (mainly based on carboxylic and oxidized carbon groups).

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