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

M. Balsamo[a], F. Di Natale[a], A. Erto[a,*], F. Montagnaro[b]

[a]*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy, Tel. +39 081 7682236; Fax +39 081 5936936; email: aleserto@unina.it (A. Erto)*
[b]*Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Complesso Universitario di Monte Sant'Angelo, 80126 Napoli, Italy*

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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 sorbents were tested; one is CCA as received, the other two derived from the gasification of raw CCA carried out with either steam (SG sample) or carbon dioxide (DG sample). 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 towards Zn(II) and, secondarily, to the smaller dimension of zinc cations (Zn^{2+}), which resulted to be 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 oxidized surface functional groups, which are considered the preeminent active sites 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.

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 [1]. In nature, it occurs either as cadmium sulphide (CdS) or cadmium carbonate ($CdCO_3$) but more often as a minor component or substitute in zinc ores [2]. Zinc is an essential element for human being, but it can become toxic at high concentrations [3]. The main sources of cadmium and zinc release in water bodies include plating plants, metallurgic industries, batteries production and disposal, mine drainage and natural rocks leaching, where often these two metals are simultaneously present.

Considering the worldwide diffusion of water contamination by heavy metals, suitable depuration methods should be characterized by good efficiency, high simplicity, low-cost and possibility to make use of local and easily accessible materials. Several methods (e.g. physicochemical, biological and thermal processes) have been proposed for water treatment and to decrease the impact of heavy metals on the environment. Among these, adsorption is generally considered as a reliable water treatment, due to high versatility and efficiency in a wide range of operating conditions.

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* Corresponding author.

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The most popular sorbents for Cd and Zn capture are by far activated carbons, which show high adsorption capacities [4–7]. However, acquisition, regeneration and disposal of the spent sorbent are generally characterized by high costs. Moreover, the regeneration techniques specifically applied to heavy metal recovery are still far to be optimized and the possible loss of adsorption efficiency has limited this saving operation [8–10].

In the recent years, this has prompted a growing research interest into the production of low-cost alternative sorbents from a range of carbonaceous and mineral precursors. Indeed, the development of new materials is of paramount importance in order to reach a worldwide diffusion of effective technologies for the depuration of heavy metal polluted waters. Many different low-cost materials can be potentially used as sorbents for wastewater treatment and critical reviews have been presented in the last years [11–13]. Moreover, the reutilization of waste materials represents a stimulating challenge as an effective alternative to their disposal.

Coal combustion ash (CCA) is one of the most abundant waste materials deriving from the combustion of coal. It is considered as a valid precursor for the production of sorbents both as raw [13–16] or after beneficiation treatments, such as acid/basic attack [14,16–19], mechanical sieving [16], sonochemical treatment [18], alkali activation for zeolite production [20] or thermal oxidation/gasification [21–23].

The effect of a given activation treatment is strictly dependent on the raw sorbent properties and on the pollutant target to be adsorbed. For example, acid treatments of a raw CCA resulted detrimental for cadmium adsorption [16] and positive for arsenic [19]. In both the cases, it was demonstrated that the exposed contact surface, porosity and mineral content of the ash particles have significant effects on the adsorption of these pollutants from model aqueous solutions [16,19].

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 [21–23].

Most of the published works reported on the adsorption of heavy metals on CCA or beneficiated CCA, as among which those of our research group [16,19,23], 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 association of cadmium and zinc in the environment and their chemical similarity, in fact, can lead to mutual interactions. Moreover, the adsorption behaviour is strictly influenced by the specific adsorbent adopted, so that the literature indications about adsorption on CCA of such binary system are apparently not consistent. For example, Mohan and Gandhimathi [15] stated that zinc adsorption is affected by cadmium presence, while Cho et al. [24] found a synergistic effect that leads to an increase in zinc adsorption capacity. Indeed, competitive effects are the most experienced for other multicomponent systems, for both cadmium [14,20] and zinc [25,26] and, in any case, the experimental results show that single-compounds data are hardly extendible to multicomponent systems analysis.

The aim of this work is to explore the possibility of utilizing a CCA derived from a coal-fired power plant 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 of CCA by either steam or CO_2 gasification. Experimental tests were carried out on both single-compound and cadmium/zinc binary systems, in order to verify the occurrence of competition effects. The influence of sorbent properties on adsorption performances was critically discussed. Finally, a modelling analysis of experimental data was presented.

2. Materials and methods

2.1. Sorbents properties and activation treatments

The raw coal combustion fly ash (CCA) utilized in this work came from an Italian power plant operated by Enel, in which a bituminous coal is used as fuel. Laser granulometric analysis was performed by a Malvern Instrument Mastersizer 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 analyser, 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 analyser. Finally, the evaluation of the pH of point zero charge (pH_{PZC}) was made according to the Noh and Schwartz [27] method, which showed that the CCA has a marked basic nature (pH_{PZC} = 9). In Tables 1 and 2, the CCA chemical composition and main chemical/physical properties are reported, respectively. Data concerning proximate analysis are provided on dry basis (db).

The raw CCA has a mean Sauter particle diameter around 10 μm; it 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

Table 1
Raw CCA chemical composition

Chemical composition	%wt
CaO	4.25
SO_3	n.d.
Al_2O_3	21.80
SiO_2	34.20
MgO	1.03
Na_2O	0.55
K_2O	0.96
TiO_2	1.49
Fe_2O_3	7.24
Loss on ignition	26.70
Total	98.22

Table 2
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

a moderate to high (74%) ash content. In detail, XRD analysis showed the presence of a significant silico-aluminous fraction, mainly represented by quartz (SiO_2) and mullite ($3Al_2O_3{\cdot}2SiO_2$) crystalline phases. Moreover, calcium and iron oxide are also present. Proximate analysis showed a high (22%) fixed carbon content, possibly related to a short mean residence time (and, therefore, limited degree of carbon conversion) into the combustor.

The raw CCA was subjected to a batch leaching test to determine the metallic ions release, for a complete evaluation of its suitability for the proposed water treatment. To this end, 1 g of raw ash was put into contact, for 72 h and under stirring, with 100 mL of distilled water, and thereafter the liquid solution was analysed by ICP spectrophotometry (employing an Agilent 7500ce apparatus). The results are reported in Table 3, where concentration represents the milligram of element released per gram of CCA.

The results show a consistent Ca release and a moderate Si, Al, Na and K release, while neither Cd nor Zn (negligible) were found in appreciable concentration in the leaching solution.

Table 3
Release of metals from raw ash in distilled water

Element	Concentration (mg g^{-1})
Ca	6.720
Al	0.671
K	0.60
Ba	0.49
Si	0.320
Na	0.240
Sr	0.129
Mo	0.065
V	0.021
Cr	0.0062
As	0.0017
Fe	0.0002
Zn	0.0002
Cd	—
Co	—
Hg	—
Mg	—
Mn	—
Ni	—
Pb	—

A complete characterization of the raw CCA is reported in Balsamo et al. [16].

The CCA was subjected to two different gasification treatments carried out by either steam or CO_2 (so-called 'dry' gasification) according to the following endothermic reactions, respectively:

$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)} \tag{1}$$

$$C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)} \tag{2}$$

The derived activated sorbents were named SG and DG for steam- and dry-gasification, respectively. Their properties (such as carbon content, porosimetric, diffractometric, chemical and granulometric properties) were determined with the same techniques previously cited.

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 and carbon dioxide gasification 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 [28].

XRD patterns of both raw and gasified samples are reported in Fig. 1:

The patterns showed that the inorganic crystalline structure of the raw ash was fully retained upon gasification, thus confirming that the only chemical process that took

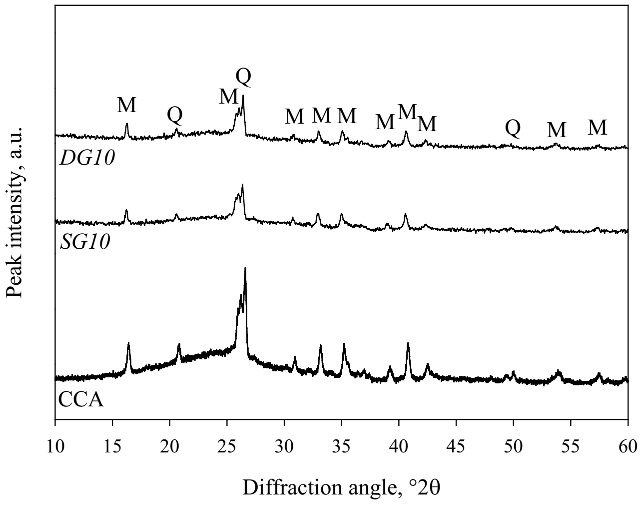

Fig. 1. XRD patterns for gasified ashes (*SG10* and *DG10*, treated at 850°C for 10 min using steam and carbon dioxide, respectively) and (for comparison) raw CCA. M = mullite, $3Al_2O_3{\cdot}2SiO_2$; Q = quartz, SiO_2.

place is either steam or dry gasification of the carbon content, as indicated in Eqs (1) and (2).

The main SG and DG chemical and physical properties are reported in Table 2, while a complete sorbent characterization is reported in Balsamo et al. [28]. In summary, both the gasification treatments ended up into: (1) an increase in porosity, more pronounced for SG; (2) a decrease in the mean particle size; (3) an obvious consumption of C with the related increase in the ash content.

2.2. Sorption tests

Adsorption equilibrium tests, addressing at the evaluation of CCA, SG and DG adsorption capacity, were carried out in batch stirred glass reactors kept in a Proportional, Integrative, Derivative-controlled thermostatic oven. All the tests were performed with 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, Milan, Italy, 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). For the binary tests, 0.1 L of Zn/Cd solution were used with same sorbent dosage (1 g) and with initial concentration ratio of the two analytes equal to $C^0_{Zn} : C^0_{Cd} = 1 : 1$ 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. Indeed, preliminary tests indicated that, in presence of raw CCA, SG and DG sorbents, the equilibrium pH for both cadmium and zinc solutions was 12. This strong alkaline character is likely related to calcium ions leaching from CCA, as reported in Balsamo et al. [16]. These operating conditions would strongly affect cadmium/zinc adsorption, since species such as $Cd(OH)_2$ or $Zn(OH)_2$ would likely precipitate, leading to unreliable adsorption data. For this reason, the initial cadmium/zinc solution pH was adjusted with HNO_3 (1 M), and was not further altered during the tests.

The time necessary for reaching equilibrium conditions was 6 and 12 d, for single-compound and binary systems, respectively. At equilibrium, the systems were sampled and the metal concentration in the solution and on the sorbent was measured. To this purpose, the solution was filtered with a Millipore filter (0.45 μm) and analysed for pH and metal concentration, while the sorbent was leached with 0.1 L of nitric acid (1 M) to extract all the adsorbed metals. Finally, the extractive solution was analysed to measure the metal uptake on the sorbent surface and was compared with the same quantity calculated through a metal mass balance, allowing for a maximum error of 6%. To assure the accuracy, reliability and reproducibility of the data collected, all the isotherm tests were repeated in triplicate and only average values were reported. All the lab-ware used in the study was previously soaked in nitric acid (1 M), triply rinsed with distilled water and oven dried.

Analytical concentrations of both zinc and cadmium were measured by air/acetylene flame atomic absorption spectrophotometry by using a Varian SpectrAA-220 spectrophotometer.

3. Results and discussion

Adsorption experiments of Cd(II) and Zn(II) ions were carried out in both single-compound and binary systems, testing alternatively the three sorbents (CCA, SG and DG), in order to compare the performances of the raw and the gasified sorbents.

The results of experimental tests of Cd(II) and Zn(II) 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 Fig. 2. The term ω represents the molar specific adsorption capacity of the metal under investigation, which was determined as follows:

$$\omega = \frac{\left(C_0 - C\right)V}{m} \tag{3}$$

where C_0 and C (mmol L^{-1}) are the initial and equilibrium metal concentrations in liquid; V is the volume of the solution (L); and m is the amount of the adsorbent (g).

The first evident result is the significantly higher adsorption capacity of Zn(II) with respect to Cd(II), for all the investigated sorbents. This is likely due to a higher affinity of active sites towards zinc and, secondarily, to the smaller dimension of zinc cations (Zn^{2+}) which are less affected by steric hindrance than cadmium cations (Cd^{2+}) [29]. Indeed, it is worth observing that, under the experimental conditions adopted, a speciation analysis of Cd(II) and Zn(II) ions indicated Cd^{2+} and Zn^{2+} as the predominant ions present in solution, respectively. This condition was assessed by a dedicated speciation analysis of cadmium/zinc solution at equilibrium carried by using mass and electric charge balance equations in a system including the equations representative of chemical equilibria [30,31].

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 three times and six times average increasing of adsorption capacity was observed for SG and DG, respectively, with respect to CCA.

A comparison with literature data concerning the use of similar or alternative low-cost sorbents confirmed the good performances of the investigated ashes, in particular of the gasified samples. Srivastava et al. [32] investigated the use of a bagasse fly ash for the removal of cadmium from aqueous solution obtaining a maximum adsorption capacity around 0.046 mmol g^{-1} (against 0.0304 mmol g^{-1} obtained in the present work) in correspondence of a higher equilibrium concentration (about 0.44 mmol L^{-1}) with respect to the maximum value investigated in this work. Similarly, Anwar et al. [33] worked on banana peel obtaining a maximum Cd adsorption capacity of 0.051 mmol g^{-1}, comparable with our results. Finally, Cho et al. [24] used a fly ash for Cd removal and a maximum adsorption capacity of 0.028 mmol g^{-1} was retrieved, which is higher than the value obtained with the raw fly ash investigated in this work but lower than the corresponding obtained on dry-gasified sample.

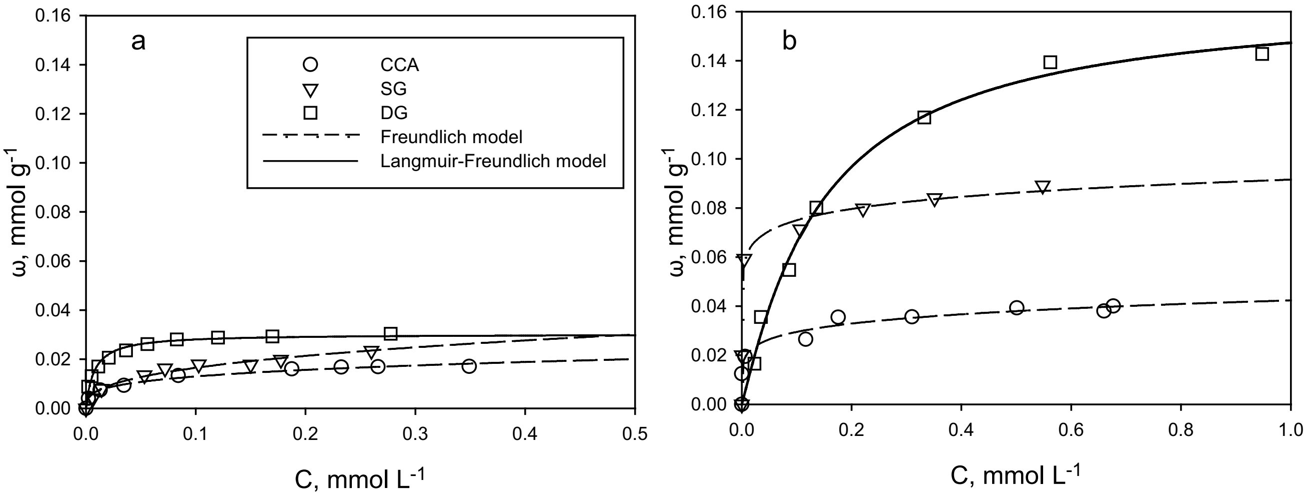

Fig. 2. Cadmium (a) and zinc (b) adsorption isotherms on CCA, SG and DG sorbents. Comparison between experimental data and Freundlich (CCA, SG) and Langmuir–Freundlich (DG) model. *T* = 20°C; equilibrium pH = 7.0 ± 0.3.

The comparison for zinc capture is even more encouraging. Velazquez-Jimenez et al. [34] used an Agave bagasse obtaining a maximum adsorption capacity of 0.12 mmol g^{-1} (against a maximum value of 0.14 mmol g^{-1} obtained in this work for the dry gasified sample). Similarly, López-Delgado et al. [35] tested a blast furnace slag and obtained a maximum adsorption capacity of 0.14 mmol g^{-1}. The results of the present work are even more interesting if compared with those of sorbents of similar nature (i.e. a fly ash deriving from coal combustion [36]), for which a maximum adsorption capacity of 0.049 mmol g^{-1} was achieved.

For a deeper analysis of the retrieved experimental results, it is interesting observing that both the gasification treatments determined an increase in particle porosity and a decrease in the mean particle size (cf. Table 2). However, the ranking of sorbent porosity (Table 2) did not reflect the one corresponding to the Cd(II) (or Zn(II)) adsorption capacity. From a chemical point of view, the gasification treatments also determined 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. From a qualitative point of view, the inorganic crystalline structure of the raw ash (mainly silico-aluminous and based on quartz and mullite) was fully retained upon gasification, thus underlining that the only chemical process to take into consideration is, for practical purposes, the steam (or dry) gasification of the carbon content [28]. It can be inferred that the inorganic fraction is the main active part for Cd(II) and Zn(II) adsorption, as already demonstrated in a previous work dealing with Cd adsorption on demineralized CCA [16]. Moreover, the gasification carried out with carbon dioxide likely determined a higher concentration of oxidized 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 [31,37,38]. 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 superior adsorption performances with respect to those obtained for CCA and SG samples, in particular for higher investigated equilibrium concentrations, likely associated with the contribution of the oxidized surface functional groups. These groups are likely activated at high equilibrium concentration and, particularly for Zn, they determine a significant increase in adsorption capacity, accordingly. On the contrary, the higher Zn(II) adsorption capacity of SG sorbent at low equilibrium concentrations (cf. Fig. 2(b)) could be ascribed to a higher accessibility of Zn^{2+} to the sorbent active sites and reduced cation–cation repulsive interactions due to larger porosity and surface area with respect to DG sorbent. These results are corroborated by the acid/base behaviour of all the sorbents, 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 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, that is, 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 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. This evidence is also in line with the hypothesis of the predominant contribution of the inorganic part in adsorption phenomena.

The hypothesized adsorption mechanisms for the sorbents tested appear to be compatible with the base hypotheses of Freundlich and Langmuir–Freundlich models (i.e. a defined adsorption energy distribution due to their heterogeneous nature). In particular, the latter model accounts for both the hetero-energetic adsorption and the existence of an upper limit of adsorption capacity, as verified in the experimental data, which is not predictable by the Freundlich model. The results of regression analysis are reported in Table 4, together with the standard error of each parameter.

As can be observed, the Freundlich model provides better fitting results for CCA and SG sorbents, as also confirmed by the comparison with experimental data (Fig. 2). The accuracy of the experimental data and the model appropriateness are testified by the low value of the standard errors, always an order of magnitude lower than the corresponding parameter.

Conversely, for DG sorbent a different functionality can be inferred by the significant contributions of both the inorganic fraction and the oxidized superficial functional groups. In this case, the Langmuir–Freundlich model showed more accurate regression results, also describing the asymptotic value of the Cd/Zn adsorption capacity (Fig. 2), which is more evident for this sorbent in the range of investigated equilibrium concentrations. It is added that, for all the experimental conditions, the Langmuir model also provided good fitting results, probably due to the relatively low values of equilibrium concentration investigated in this work. However, the fitting results were poorer than those obtained with the proposed models, hence they were not reported.

Adsorption of binary mixture ($C^0_{\mathrm{Zn}} : C^0_{\mathrm{Cd}} = 1:1$) on CCA, SG and DG sorbents was 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. Eventually, for all the adsorption systems, a comparative analysis of single-compound and binary systems was carried out. As discussed earlier, cadmium and zinc are expected to be adsorbed according to the same mechanism, but the adsorption phenomena strictly depend on the analyte concentrations, hence the behaviour of the binary system cannot be easily predicted.

Fig. 3 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.

In the range of equilibrium concentration investigated, the three sorbents showed an evidently different behaviour 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 to state 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 [39].

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 be adsorbed on the inorganic fraction, likely by an adsorption/ion exchange mechanism. The experimental results suggest that they are adsorbed on a different subfraction when compared with each other, as no mutual competitive effects are present (Fig. 3(a)).

For gasified samples, the differences between single-compound and binary tests are remarkable and depend on the gasifying agent. Experimental data on SG sorbent

Table 4
Freundlich and Langmuir–Freundlich parameters and their standard errors for regressions of cadmium/zinc adsorption isotherms at $T = 20°\mathrm{C}$ (single-compound adsorption)

		CCA	SG	DG
Cd				
Freundlich	K (mmol^{1-n} L^n g^{-1})	$2.557 \times 10^{-2} \pm 8.0 \times 10^{-4}$	$3.894 \times 10^{-2} \pm 4.40 \times 10^{-3}$	$4.348 \times 10^{-2} \pm 2.9 \times 10^{-3}$
$\omega = K \cdot C^n$	n (–)	$2.888 \times 10^{-1} \pm 1.44 \times 10^{-2}$	$3.728 \times 10^{-1} \pm 4.64 \times 10^{-2}$	$2.068 \times 10^{-1} \pm 2.38 \times 10^{-2}$
	R^2	0.995	0.979	0.927
Langmuir-Freundlich	w_{max} (mmol g^{-1})	$2.778 \times 10^{-2} \pm 5.91 \times 10^{-3}$	$3.885 \times 10^{-2} \pm 9.13 \times 10^{-3}$	$3.42 \times 10^{-2} \pm 9.28 \times 10^{-4}$
$\omega = \frac{\omega_{max}(K \cdot C)^n}{1+(K \cdot C)^n}$	K (L mmol^{-1})	$2.895 \times 10^{0} \pm 1.831 \times 10^{0}$	$3.259 \times 10^{0} \pm 2.32 \times 10^{0}$	$9.49 \times 10^{1} \pm 9.62 \times 10^{1}$
	n (–)	$4.814 \times 10^{-1} \pm 8.24 \times 10^{-2}$	$6.161 \times 10^{-1} \pm 1.17 \times 10^{-2}$	$6.75 \times 10^{-1} \pm 4.01 \times 10^{-2}$
	R^2	0.995	0.983	0.997
Zn				
Freundlich	K (mmol^{1-n} L^n g^{-1})	$4.216 \times 10^{-2} \pm 2.5 \times 10^{-3}$	$9.155 \times 10^{-2} \pm 7.8 \times 10^{-3}$	$1.519 \times 10^{-1} \pm 8.91 \times 10^{-3}$
$\omega = K \cdot C^n$	n (–)	$1.544 \times 10^{-1} \pm 4.23 \times 10^{-2}$	$8.686 \times 10^{-2} \pm 3.82 \times 10^{-2}$	$3.775 \times 10^{-1} \pm 5.43 \times 10^{-2}$
	R^2	0.906	0.940	0.931
Langmuir-Freundlich	w_{max} (mmol g^{-1})	$1.96 \times 10^{-1} \pm 2.64 \times 10^{0}$	$2.05 \times 10^{-1} \pm 2.15 \times 10^{0}$	$1.65 \times 10^{-1} \pm 8.65 \times 10^{-3}$
$\omega = \frac{\omega_{max}(K \cdot C)^n}{1+(K \cdot C)^n}$	K (L mmol^{-1})	$2.72 \times 10^{-1} \pm 4.61 \times 10^{0}$	$7.82 \times 10^{-1} \pm 1.44 \times 10^{1}$	$6.86 \times 10^{0} \pm 9.94 \times 10^{-1}$
	n (–)	$1.851 \times 10^{-1} \pm 4.50 \times 10^{-1}$	$1.309 \times 10^{-1} \pm 7.33 \times 10^{-1}$	$1.09 \times 10^{0} \pm 1.19 \times 10^{-1}$
	R^2	0.884	0.939	0.994

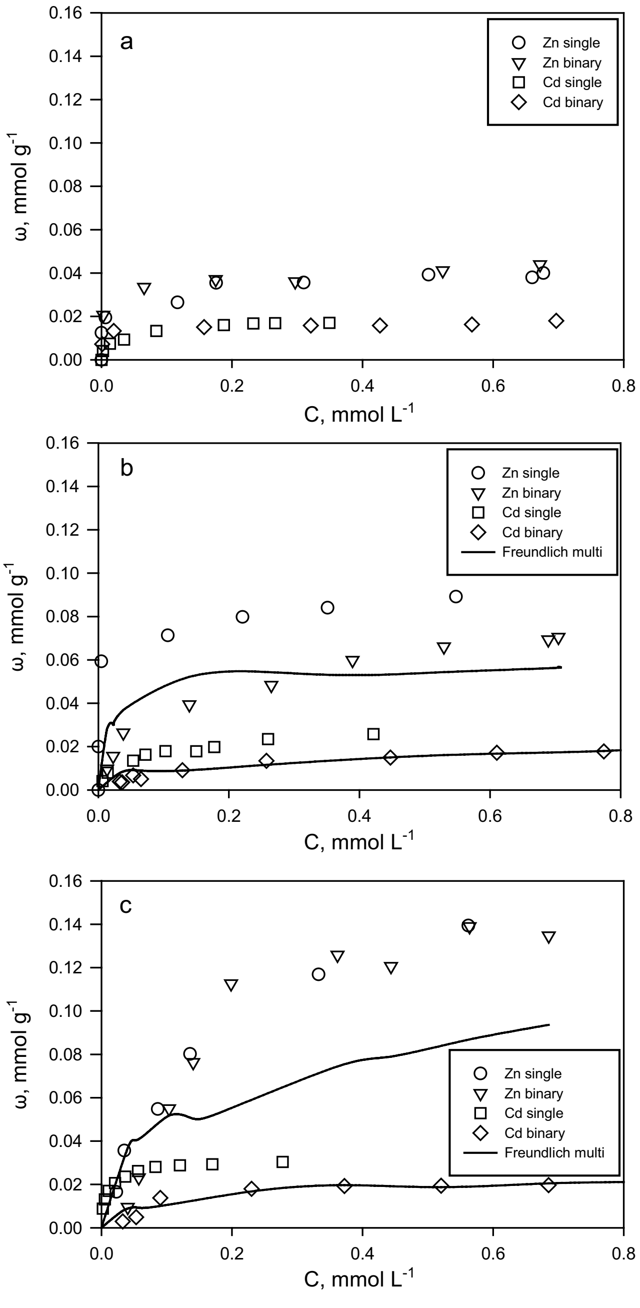

Fig. 3. Cadmium and zinc adsorption isotherms in binary system ($C^0_{Zn}:C^0_{Cd}=1:1$) on CCA (a), SG (b) and DG (c) sorbents. Comparison with single-compound data and Freundlich multicomponent model. T = 20°C; equilibrium pH = 7.0 ± 0.3.

showed that both Zn and Cd adsorption capacity is reduced in binary systems, the extent of reduction with respect to the corresponding single-compound data being in percentage similar (Fig. 3(b)). This result clearly testifies the rise of a competition between analytes, this effect being more marked at low equilibrium concentration where Zn appears to be energetically favoured.

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 onto the dry gasified adsorbent does not depend on the presence of cadmium, at least in the range of equilibrium concentration tested (Fig. 3(c)). Conversely, cadmium adsorption capacity in binary system is lower than the one in single-compound system, even for a very low concentration range (i.e. Henry region). This competitive effect is likely due to a higher affinity of DG active sites (mainly based on oxidized carbon groups) towards zinc with respect to cadmium.

The experimental data for which a competitive effect was observed (i.e. binary adsorption on SG and DG sorbents) were modelled with several multicomponent models retrievable in the literature, such as Langmuir multicomponent [39], Extended Langmuir multicomponent [40], Langmuir–Freundlich multicomponent [41] and Freundlich multicomponent [42] model.

For both SG and DG sorbents, the best fitting results were obtained by application of the Freundlich multicomponent model; the model equation is reported as follows:

$$\omega_i = K_i c_i \left(\sum_{j=1}^{N} a_{ij} c_i \right)^{n_i - 1} \qquad (4)$$

in which K_i and n_i are the Freundlich parameters obtainable from single-compound data and a_{ij} is defined as a competition coefficient, which can be determined by regression of multicomponent experimental data. For a binary system as the one under analysis:

$$a_{ij} = \frac{1}{a_{ji}} \qquad (5)$$

and the determination might be done in the same modelling framework, hence performing a simultaneous regression for both Cd and Zn binary experimental data, assuming the constraint expressed by Eq. (5). In particular, for DG sorbent the obtained constants are a_{ij} = 0.484 and a_{ji} = 2.065, while for SG sorbent a_{ij} = 0.577 and a_{ji} = 1.731 (assuming i = zinc; j = cadmium).

In Fig. 3, the regression results obtained by application of the Freundlich multicomponent model are reported. As it can be observed, for both SG and DG, a very good interpretation of Cd binary adsorption data can be obtained, while the results for Zn binary adsorption data are variable. For SG sorbent, Zn data were acceptably predicted, while for DG sorbent appreciable results were obtained only in a narrow range of equilibrium concentration (i.e. $C < 0.1$ mmol L^{-1}) after which the model is roughly inadequate. However, this result was expected because the hypotheses of Freundlich multicomponent model include a mutual competition between the adsorbates, which was not verified for Zn adsorption in binary system on DG sorbent. A similar result was obtained working on the same binary system (i.e. Cd/Zn) but using a granular activated carbon [24].

Finally, all the multicomponent models tested resulted inadequate for the description of CCA binary adsorption data. For this sorbent, the absence of significant competition effects for both the adsorbates allows adopting the corresponding single-compound model parameters for the prediction of binary adsorption data, at least in the range of equilibrium concentration investigated.

4. Conclusions

The adsorption of cadmium and zinc from aqueous solution onto three different CCAs, both in single-compound and binary systems, was studied. The CCAs were tested 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. Moreover, the inorganic crystalline structure of the raw ash (mainly silico-aluminous and based on quartz and mullite) was fully retained upon gasification. From a chemical point of view, 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.

Adsorption experimental results in single-compound systems showed a ranking DG > SG > CCA of adsorption capacity for both zinc and cadmium. 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 three times and six times average increasing of adsorption capacity was observed for SG and DG, respectively, with respect to CCA. The increase in inorganic content and the formation of oxidized functional groups, for which metallic cations have 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 behaviour of the corresponding single-compound systems. However, the three sorbents showed different behaviours. For CCA, experimental data showed that negligible 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 capacities are reduced in binary system with respect to the corresponding of single-compound systems, while the experimental data for DG sorbent indicated that the 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 towards zinc in the case of DG active sites (mainly based on oxidized carbon groups).

Finally, a modelling analysis carried out for both single-compound and binary systems showed that the Freundlich model correctly describes the experimental results for which a competitive effect was observed.

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