Reuse of coal combustion ashes as dyes and heavy metal adsorbents: Effect of sieving and demineralization on waste properties and adsorption capacity

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A B S T R A C T

Among the possibilities of limiting the disposal of coal combustion ashes (CCA), their reutilization as adsorbent materials is worthy of consideration. To this end, proper ashes beneficiation techniques can be put into practice. The adsorption of toxic compounds from industrial wastewaters is an effective method for both treating these effluents and recycling CCA. The aim of this paper is to give a contribution for understanding the relationships among beneficiation treatments, adsorbent properties and adsorption mechanism/efficiency. In this context, as-received CCA together with mechanically sieved and demineralized ashes were employed as adsorbents of methylene blue and cadmium from aqueous solutions. The maximum values of the specific adsorbate quantity captured by the adsorbent were fairly good, ranging from 23 to 110 mg/g, with removal efficiency close to 1 for a pollutant/solid initial ratio ranging from 10 to 20 mg/g. Moreover the influence of the beneficiation treatments on the adsorbent physico-chemical/microstructural properties was thoroughly discussed. These properties, in turn, affect the adsorption mechanism (either cooperative/multilayer or high-affinity monolayer) and the capture efficiency. In this respect, when the operating conditions are those of greater practical interest, the different adsorbents can be ranked in the order demineralized ashes > mechanically sieved ashes > CCA, in excellent agreement with previsions based on materials characterization.

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1. Introduction

In the last decades particular attention has been paid to landfill disposal of coal combustion ashes (CCA), with the issuing of specific regulations aimed at limiting this management option. On the contrary, addressing CCA reuse in sectors such as, *e.g.*, building materials manufacture is much more environmentally sound and should be preferred. In this framework, any novel proposal aimed at employing this industrial residue (thus retarding its final disposal) should be carefully considered [1–8]. A very interesting possibility of CCA reutilization is as adsorbent material with respect to both organic and inorganic compounds either in liquid or in gaseous phase. The research on this topic is nowadays driven by the increasing investment and regeneration costs of traditionally employed activated carbons. In this context, many carbon-containing wastes (besides CCA) have also been proposed for reuse as adsorbents, such as heavy oil fly ashes [9], tyre wastes [10], municipal residues [11], forest and agricultural wastes [12]. To this end, proper beneficiation techniques aimed at obtaining "activated carbons" by improving the carbon content and/or the

porosimetric characteristics of the residues can be advantageously implemented. Among these techniques, mechanical sieving of CCA particles is very simple and cheap, and allows to take advantage from the (unavoidable) physico-chemical differences of the various size ranges. Then, adsorption processes can only make use of the waste particles belonging to particular size ranges of more favourable properties. Moreover, demineralization by acid attack appears to be another promising CCA beneficiation method, since it makes the waste carbon content increase by removing its mineral fraction. Furthermore, other beneficiation methods have been also proposed, such as CO_2/steam gasification or pyrolysis [12–14].

The presence of dyes in liquid effluents generated by, *e.g.*, textile, tanning, paper, alimentary, ceramic, printing and plastic industries is undesired and harmful, and thus must be reduced; in particular, Methylene blue (MB) is a common dye of difficult biodegradability with various toxic effects [15–17]. Possible dye separation methods are coagulation, filtration, sedimentation, flocculation, ionic exchange, advanced oxidation processes and biotechnological treatments. Another valid alternative is represented by adsorption, which has shown to be very effective in significantly lowering the dye concentration in wastewaters [18–29]. In this respect, MB is generally employed as a reference compound to evaluate the adsorption capacity of a sample of activated carbon (the "MB number" is also defined, as the mg of MB adsorbed by 1 g of activated

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carbon in equilibrium with an 1 mg/dm^3 MB solution [30]). In addition, heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are dangerous for both human health and the environment, and can be present in unacceptable amounts into industrial waste streams [31–33] such as those generated by metal extraction, mine drainage and paint/ink formulation processes [34]. In particular, cadmium is very harmful [34,35] and its removal from effluents is an issue of great environmental relevance. Heavy metals separation methods relying on precipitation/filtration are commonly employed, but they will result in low effectiveness and/or high process cost when wastewaters with small heavy metals concentrations have to be treated; in these cases, adsorption can represent an interesting removal mean [6,33–36].

Although many papers can be found in the literature on the possibility of removing dyes and heavy metals from wastewaters by adsorption on low-cost activated carbons, the intertwining among waste properties, beneficiation treatments, properties of the beneficiated materials, adsorption mechanisms and efficiencies has only been partly elucidated [37,38]. The aim of this paper is to give a contribution in this direction, by beneficiating CCA in two different ways (mechanical sieving and demineralization) and by carrying out adsorption tests with MB and cadmium. The physico-chemical/microstructural characterization of the solid materials was thoroughly carried out by a number of methods (plasma chemical analysis, X-ray diffraction (XRD), thermogravimetry, porosimetry, laser granulometry).

2. Materials and methods

2.1. Physico-chemical/microstructural characterization of the solid materials

The adsorbent materials employed in this study were characterized by means of: (i) plasma chemical analysis (performed by the ash supplier); (ii) XRD analysis (carried out by a Philips PW1830 diffractometer operating at diffraction angles ranging from 5°2θ to 60°2θ with a 0.025°2θ/s rate and using Cu Kα radiation); (iii) thermo gravimetric (TG) analysis (performed in air by a TA Instruments SDT 2960 apparatus from 105 °C up to 900 °C at a heating rate of 5 °C/min); (iv) porosimetric analysis (pore size distributions were obtained with a nitrogen porosimeter working in a pore radius range of 0.85–125 nm; pore specific surface areas were measured by a CE Instruments Sorptomatic 1990 analyzer working in a P/P_0 range = 0.03–0.4); (v) laser granulometric analysis (carried out by a Malvern Instruments Master Sizer 2000 granulometer operating with water as dispersion solvent down to a minimum particle size of 0.02 μm).

2.2. Coal combustion ashes properties

The coal combustion fly ashes employed in this work came from an Italian power plant operated by Enel. As expected, CCA elemental chemical analysis showed the presence of significant fractions of silicon and aluminium (contents of Si > 18% and Al > 12% as reported in Table 1). The silico-aluminous nature of the ashes was confirmed by XRD. Fig. 1 clearly shows the peaks of quartz and mullite (crystalline phases of SiO$_2$ and 3Al$_2$O$_3$·2SiO$_2$, respectively). TG data for CCA are shown in Fig. 2: as a general value, a loss on ignition = 27% was recorded; moreover, this weight loss was homogeneously distributed over a quite wide temperature range, indicating that it was much likely related to the unburnt C in fly ash. This hypothesis was supported by the observation that Fig. 1 shows no evidence of the presence of phases (such as CaCO$_3$) able to give loss on ignition in the operating temperature range. Table 1 also reports the porosimetric data for the waste employed: the cumulative specific

Table 1
Si and Al elemental chemical analysis, porosimetric characteristics and Langmuir parameters (in the case of MB adsorption) of the adsorbents investigated.
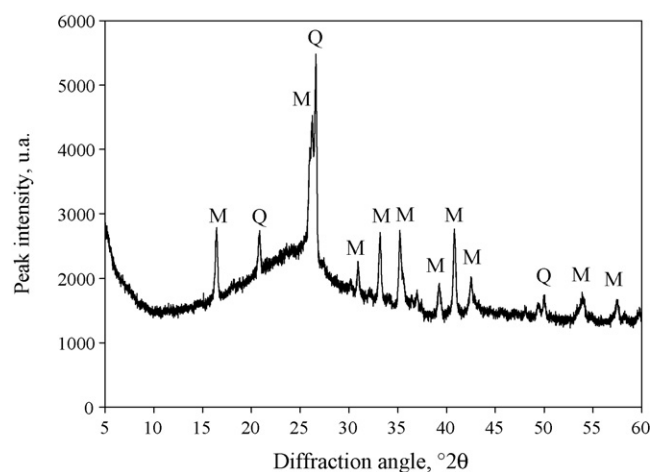
	CCA	F100	DEM
Si [wt%]	18.34	10.88	n.d.[c]
Al [wt%]	12.38	7.02	2.04
Specific mesoporosity[a] [mm^3/g]	11.0	17.4	40.0
Specific porosity[b] [mm^3/g]	18.1	31.0	103.0
Specific surface area [m^2/g]	19	32	68
q_m [mg/g]	n.a.[d]	27.7	22.8
K [dm^3/mg]	n.a.	0.021	0.327
r [–]	n.a.	0.045	0.003

[a] Reference pore radius range = 0.85–10 nm.
[b] Reference pore radius range = 0.85–125 nm.
[c] Not detected.
[d] Not applicable.

Fig. 1. XRD analysis for CCA (Q = quartz, SiO$_2$, ASTM#33-1161; M = mullite, 3Al$_2$O$_3$·2SiO$_2$, ASTM#15-776).

mesopore volume (a mesopore radius range = 0.85–10 nm was considered) was 11.0 mm^3/g, the overall value (in the pore size range investigated) was 18.1 mm^3/g, the pore specific surface area was 19 m^2/g. Laser granulometric analysis results for CCA were reported both as absolute (Fig. 3a) and cumulative (Fig. 3b) volumetric distributions. From the former, a bimodal distribution with a significant peak at 70 μm and a minor peak at 500 μm was observed. From the latter, a d_{50}-value of 35 μm was obtained together with the
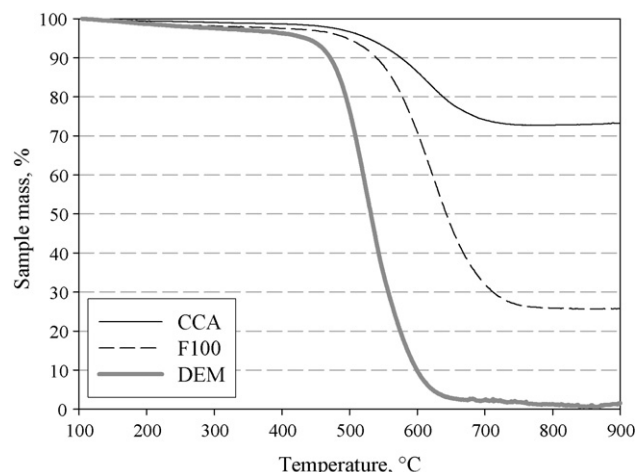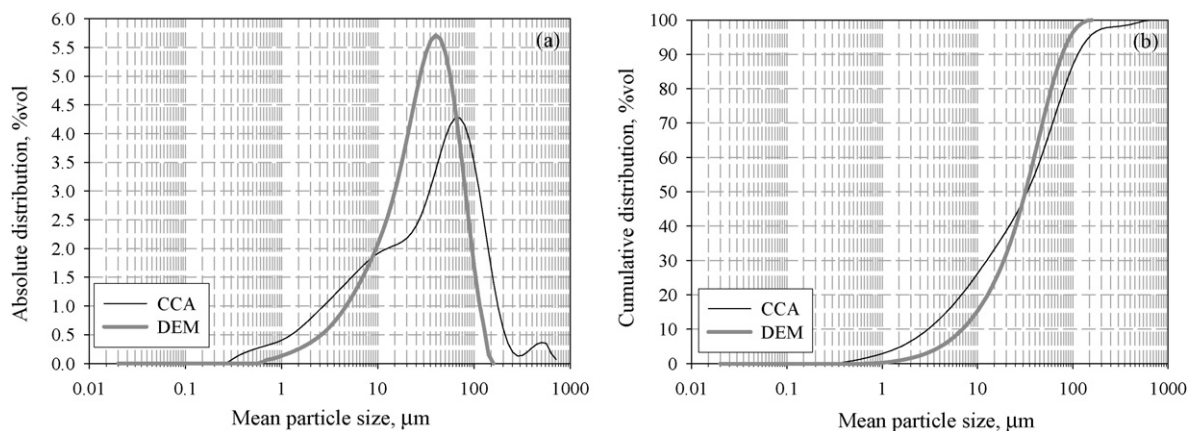

Fig. 2. TG analysis for CCA, F100 and DEM.

Fig. 3. Laser granulometric analysis for CCA and DEM: (a) absolute distribution, and (b) cumulative distribution.

information that 87% of CCA particles had mean size smaller than 100 μm and 97% were finer than 200 μm.

2.3. Beneficiation treatments

Mechanical sieving of CCA was performed with the aim of obtaining a particle size range in which unburnt C was significantly increased. Loss on ignition analyses carried out on samples retrieved on sieves of different sizes have shown that the >100-μm fraction (though of minor importance in the CCA particle size distribution, *cf.* Fig. 3) had quite high carbon percentage (*vide infra*): therefore, this sample (termed F100) was employed for further characterization. CCA sample demineralization was obtained by treating the ash with an HCl solution (18 wt%, liquid/solid ratio = 0.007 dm^3/g) at 60 °C for 24 h. After filtering and washing, the solid was treated with an HF solution (40 wt%, liquid/solid ratio = 0.006 dm^3/g) at 60 °C for 1 h. The conceptual basis for adopting this demineralization procedure can be found in Ciambelli et al. [39]: it is recalled here, anyway, that Al- and Si-based compounds are essentially removed by HCl and HF solutions, respectively. After a further treatment of filtering and washing, followed by dehydration at 105 °C, the beneficiated ashes (termed DEM) appeared much darker than the parent ones, phenomenon mainly ascribable to the increased C-content of the waste.

2.4. Adsorption tests

MB (reagent grade) adsorption tests were conducted using CCA, F100 and DEM as adsorbents. Adsorbent amounts (*m*) from 0.5 to 3 g were contacted with MB aqueous solutions in a 0.3-dm^3 stirred glass beaker. The volume (*V*) of the solution ranged from 0.02 to 0.25 dm^3, and its initial concentration was C_0 = 1000 mg/dm^3. Cadmium (as reagent grade Cd(NO$_3$)$_2$·4H$_2$O) adsorption tests were conducted using CCA as adsorbent. In these tests, *m* varied from 1 to 3 g and the volume of the aqueous solution ranged from 0.06 to 0.125 dm^3 with cadmium initial concentration C_0 = 1000 mg/dm^3; the contactor was a 0.25-dm^3 stirred polyethylene vessel, previously washed with HNO$_3$ to avoid cadmium adsorption on the walls. Each adsorption test was carried out at room temperature and lasted 24 h, a time long enough to reach equilibrium conditions. After filtration, the liquid solutions were analyzed by either UV spectrophotometry (in the case of MB adsorption tests, employing a UV/VIS Jasco V-550 apparatus) or atomic absorption spectrophotometry (in the case of Cd adsorption tests, employing a Varian SpectrAA 220 apparatus), in order to obtain the equilibrium pollutant concentration C_e. In this way the adsorption isotherms could be obtained in terms of specific adsorbate quantity captured by the adsorbent:

$$q = \frac{(C_0 - C_e)V}{m} \left[\frac{\text{mg adsorbate}}{\text{g adsorbent}} \right] \tag{1}$$

as a function of C_e. Moreover, efficiency curves were also obtained, by relating the removal efficiency:

$$\eta\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

to the pollutant/solid (*P/S*) initial ratio:

$$\frac{P}{S} = \frac{C_0 V}{m} \left[\frac{\text{mg initial pollutant}}{\text{g adsorbent}} \right] \tag{3}$$

3. Results

3.1. Effects of the CCA beneficiation treatments

As already pointed out in Section 2.3, the >100-μm ash particle size range was characterized by the greatest loss on ignition among the fractions studied in this work. Fig. 2 shows TG data for F100, where a carbon content of 74% can be observed. Table 1 reports F100 Si and Al elemental chemical analysis, together with its porosimetric characteristics: it is highlighted the decrease of both silicon (≅11%) and aluminium (≅7%) contents with respect to CCA. Moreover, the cumulative specific mesopore volume was 17.4 mm^3/g, the overall value was 31.0 mm^3/g, the pore specific surface area was 32 m^2/g. Therefore, the mechanical sieving of CCA allowed to obtain a sample (F100) with a greater (2.7-times) content of carbonaceous fraction which, in turn, improves the porosimetric characteristics (all the three pertinent parameters increased by a >1.5-factor).

Table 1 reports DEM Si and Al elemental chemical analysis, and Fig. 2 its TG characterization. From these data, it appears that the demineralization treatment was very effective in depleting the ash of its inorganic fraction, giving a C-content as high as 98%. Table 1 also shows DEM porosimetric data: the mesoporosity was 40.0 mm^3/g (3.6-times that of CCA), the overall porosity was 103.0 mm^3/g (5.7-times that of CCA) and the surface area was 68 m^2/g (3.6-times that of CCA). Thus the CCA demineralization allowed to obtain a material (DEM) with improved characteristics, sometimes even better than those of samples more extensively beneficiated [10]. Laser granulometry results reported in Figs. 3a and b showed: (i) a unimodal distribution peaked at 40 μm; (ii) a d_{50}-value of 32 μm; (iii) that 96% of DEM particles were finer than 100 μm; (iv) that no particles greater than 160 μm were observed. Thus the CCA demineralization treatment induced a decrease of both the particle size dispersion and the mean diameter, even if it is believed that these particle size distribution differences are
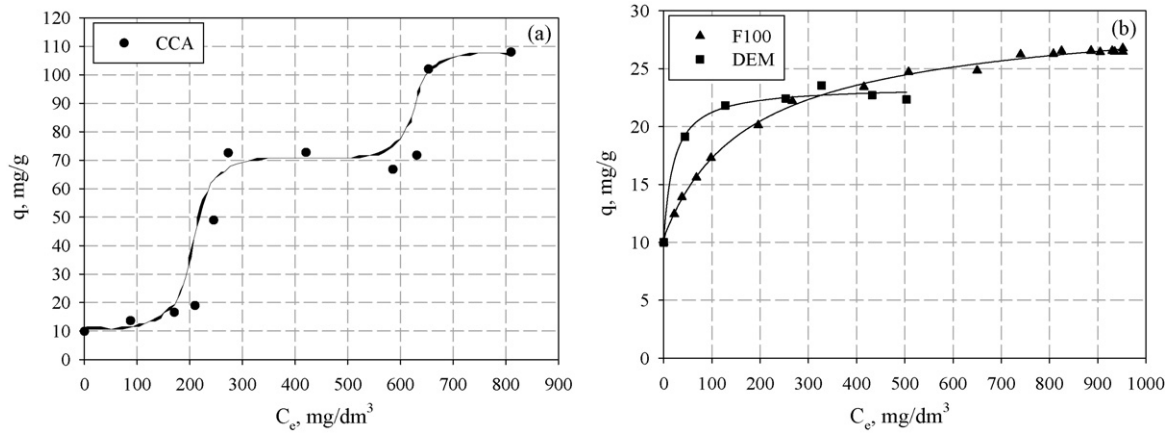
Fig. 4. Adsorption isotherms of methylene blue on: (a) CCA, and (b) F100 and DEM.

not able to justify the marked increase in the porosimetric characteristics observed after the demineralization. Instead, this should be mainly related to the chemical modifications induced by this beneficiation treatment, specifically the increase of carbonaceous fraction content.

3.2. Adsorption tests of MB on CCA, F100 and DEM

The adsorption isotherm of MB on CCA is reported in Fig. 4a: it shows two plateaux and, according to Giles et al. [40,41], is classified as an S4-isotherm (where "S" stands for S-shaped and "4" is related to the existence of a double plateau). Therefore, adsorption in this case has a cooperative nature, in the sense that at C_e values in the range 200–300 mg/dm^3 the specific adsorbed quantity q strongly increases: this should be related to the cooperation of the MB already captured that makes the adsorbent–adsorbate interactions increase as the loading increases. The first plateau (around $q = 70$ mg/g) indicates a monolayer condition, with the saturation of all the CCA active sites. At $C_e > 600$ mg/dm^3, the q-values increase again, by virtue of a so-called "multiple layer adsorption" possibly given by an asymmetric distribution of the adsorbent pore sizes. This phenomenon is active up to around $C_e = 700$ mg/dm^3, where the second plateau ($q \cong 110$ mg/g) is observed. Fig. 5 shows the removal efficiency curve: η (obviously decreasing as P/S increases) is 100% for $P/S = 10$ mg/g and 91% for $P/S = 15$ mg/g. Moreover, for P/S as high as 126 mg/g, more than half of MB is still captured. Altogether, as-received CCA sample shows a satisfying MB adsorp-

tion capacity, ascribable to its fairly good values of carbon content, porosity and pore specific surface area.

The adsorption isotherms of MB on F100 and DEM are reported in Fig. 4b: they can be classified as "Langmuir-type" curves H2 (where "H" stands for adsorbent/adsorbate high-affinity at very low C_e, and "2" is related to the existence of a single plateau). The saturation conditions (monolayer) are observed at C_e of about 800 mg/dm^3 (correspondingly, the monolayer value of q was $q_m \cong 27$ mg/g) for F100, and at C_e of about 150 mg/dm^3 ($q_m \cong 23$ mg/g) for DEM adsorbent.

These adsorption isotherms can be described by the well-known Langmuir equation:

$$q = \frac{Kq_mC_e}{1 + KC_e} \tag{4}$$

where K (here expressed in dm^3/mg) is the adsorption equilibrium constant. Eq. (4) can be linearized in the form:

$$\frac{C_e}{q} = \frac{C_e}{q_m} + \frac{1}{Kq_m} \tag{5}$$

Fig. 6 shows C_e/q from Eq. (5) vs. C_e for both F100 and DEM adsorbents: the straight lines fitting the experimental data give the slope $= 1/q_m$ and the ordinate-intercept $= 1/(Kq_m)$, from which the values of q_m (27.7 mg/g for F100, 22.8 mg/g for DEM, in excellent agreement with experimental data) and K (0.021 dm^3/mg for F100 and 0.327 dm^3/mg for DEM) are obtained. These parameters are
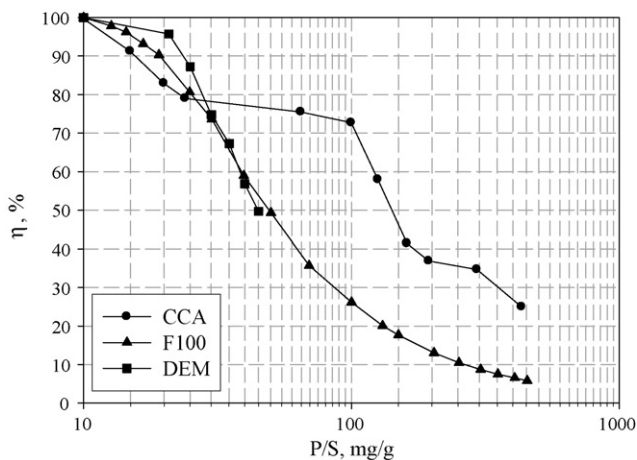

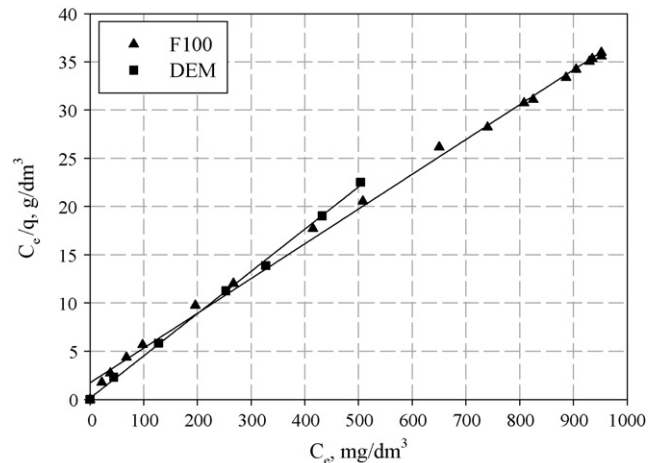**Fig. 5.** Removal efficiency curves for adsorption of methylene blue on CCA, F100 and DEM.

Fig. 6. Linearization of the Langmuir adsorption isotherms of methylene blue on F100 and DEM.
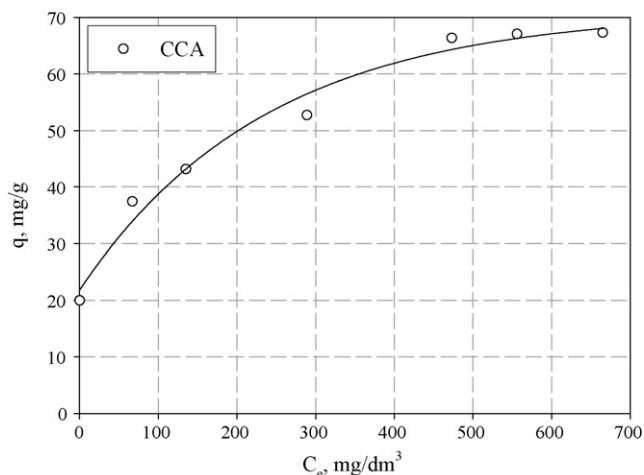
Fig. 7. Adsorption isotherm of cadmium on CCA.

reported in Table 1, together with the value of the separation factor:

$$r = \frac{1}{1 + KC_0} \tag{6}$$

which is known to characterize a favourable adsorption if smaller than 1 ($r = 0.045 \ll 1$ for MB/F100 system; $r = 0.003 \ll 1$ for MB/DEM system) [15,16,20,30].

Fig. 5 reports the removal efficiency curves: η is 100% for $P/S = 10$ mg/g (for both F100 and DEM), and 98% for $P/S = 13$ mg/g (F100) or 96% for $P/S = 21$ mg/g (DEM). Furthermore, for $P/S = 50$ mg/g (F100) or for $P/S = 45$ mg/g (DEM), nearly half of MB is still retained on the adsorbent surface.

3.3. Adsorption tests of Cd on CCA

The H2-type adsorption isotherm of Cd on CCA is reported in Fig. 7 (monolayer at C_e of about 550 mg/dm^3 and $q_m \cong 67$ mg/g), while the Cd removal efficiency curve is reported in Fig. 8 (η is 100% for $P/S = 20$ mg/g and 93% for $P/S = 40$ mg/g; furthermore, for $P/S = 126$ mg/g more than half of Cd is adsorbed). Thus, the physico-chemical CCA properties make this waste a good adsorbent with respect to this dangerous metal, even without submitting the ash to any beneficiation treatment.

As a general comment, when the q-values obtained in this work are compared with those published in the literature [7,19,28,37,42], it can be observed that the materials employed here behave in
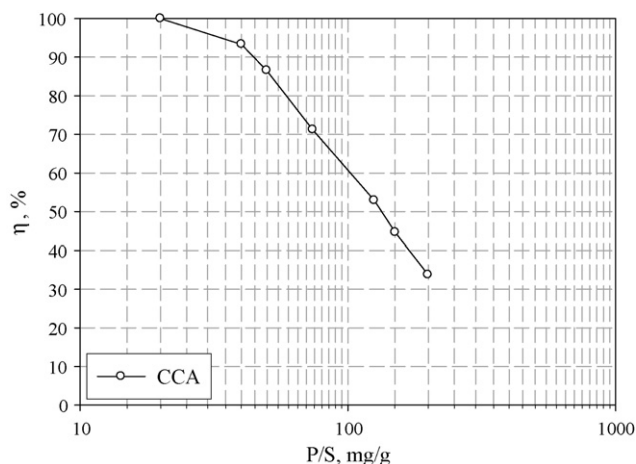

Fig. 8. Removal efficiency curve for adsorption of cadmium on CCA.

a comparable way, or even better, with respect to other wastes employed as adsorbents for both MB and Cd. Moreover, when the adsorption isotherms shown in this paper (Figs. 4 and 7) are considered and compared with those obtained in the pertaining literature, a strong influence of both the adsorbent and the adsorbate nature on the adsorption mechanism can be recognized.

4. Discussion

The coal combustion ashes employed in this work interact with MB following a cooperative adsorption path, while the two beneficiated materials obtained from CCA adsorb MB following a Langmuir monolayer mechanism. Since one of the main differences between the raw ash (CCA) and the two beneficiated materials (F100 and DEM) consists in the significantly higher inorganic (silico-aluminous) fraction content of the former (Table 1), it is likely that Si- and Al-containing compounds could play a significant role in adsorbing MB molecules according to a cooperative/multilayer pattern. Moreover, DEM shows a higher MB affinity than F100, as witnessed by the slope of the isotherm at low values of C_e: consistently, the equilibrium constant K turned out to be 15-times greater and the separation factor r 15-times smaller for DEM (Table 1). In this context, differences in particle mean sizes do not seem to play a leading role.

In order to better compare the behaviour of the three adsorbents, it would be more useful to refer to both their physico-chemical properties and removal efficiency curves. From the data reported in Table 1, the ranking DEM > F100 > CCA is observed. When the efficiency curves are considered, it should be kept in mind that: (i) low C_e values in the adsorption isotherms (conditions far from saturation) correspond to low P/S values in the efficiency curves, and *vice versa*; (ii) practical systems characterized by a low P/S value are those of prevailing interest, because they refer to the purification of wastewaters with low concentration of the pollutant to be removed (for example, $P/S = 10$ mg/g could mean 1 dm^3 of solution with $C_0 = 100$ mg/dm^3 in contact with 10 g of ash). If the attention is focused on the η vs. P/S curves for P/S up to 25 mg/g (Fig. 5), an actual ranking DEM > F100 > CCA is observed, in agreement with that predicted on the basis of the relevant physico-chemical properties. This highlights the main role that C-content and porosimetric characteristics should have in the adsorbent performances in conditions far from saturation, and is bound up with the adsorption mechanisms observed in Fig. 4. The change from an S-shaped curve (CCA) to H2 curves (F100 and DEM, with higher MB affinity for DEM) makes DEM adsorbent more effective than F100 and CCA at low C_e- (i.e., at low P/S-) values. On the contrary, at higher P/S values (systems closer to saturation), while the efficiency curves for F100 and DEM are very similar to each other, that for CCA decreases much more slowly: again, this is likely to be related to the shape of the adsorption isotherms in the sense that, at high C_e- (i.e., at high P/S-) values, when the monolayer is fully formed on CCA surface other adsorbate molecules are easily attracted, and this phenomenon may well promote adsorption on a material (CCA) whose physico-chemical properties are less favourable.

Altogether the results show that, for a specific adsorbent/adsorbate system, the choice of beneficiating or not the solid material may not be straightforward since it should depend on the specific operating conditions. In this study, both waste beneficiations induce a change in the adsorption mechanism (from cooperative/multilayer to monolayer) and an improvement in the physico-chemical properties with respect to the as-received ashes. Which effect is more important cannot be established on an absolute basis: the adsorbent physico-chemical properties appear to regulate the MB capture efficiency in conditions far from saturation, while η is regulated by the adsorption mechanism in conditions closer to saturation. Anyway, under these last conditions the role

of carbon content and porosity [37] should not be ruled out, since they are likely to regulate the adsorbent behaviour also close to saturation when the beneficiation treatments do not induce any change in the adsorption mechanism. However, since the operating conditions far from saturation appear to be those of major practical interest, the improvement in carbon content and porosimetric characteristics caused by beneficiation turns out to result very important in ameliorating the adsorption efficiency of the waste material employed. Finally, the complex effect of different operating conditions should be taken into consideration: in this respect, further work is needed to investigate the influence of mechanical sieving and demineralization conditions, adsorbent amount, solution volume and initial concentration on both the adsorbent properties and the adsorption mechanism/efficiency.

5. Concluding remarks

In this study, an industrial waste (coal combustion ashes) was employed, both as-received and beneficiated by either mechanical sieving or demineralization, as adsorbent material toward a dye (methylene blue) and a heavy metal (cadmium) in aqueous solutions. The solids physico-chemical/microstructural characterization showed that mechanical sieving and, to a greater extent, demineralization were both able to beneficiate the ash, by significantly improving carbon content and porosimetric characteristics. A strong influence of both the adsorbent and adsorbate nature on the adsorption mechanism was recognized: in particular, the as-received ashes adsorbed methylene blue following a cooperative/multilayer pattern while the two beneficiated materials showed a high-affinity/monolayer mechanism. The maximum values of the specific adsorbate quantity captured by the adsorbent ranged from 23 to 110 mg/g. These values highlighted that the behaviour of the materials employed in this study was comparable to, or even better than, that of other wastes utilized as adsorbents for methylene blue or cadmium. Moreover, pollutant capture efficiencies were close to 100% for a pollutant/solid initial ratio ranging from 10 to 20 mg/g, and nearly 50% when this ratio was as high as 45–126 mg/g depending on the system. Finally, it was underlined that the relative behaviour of the different adsorbents was strongly dependent on the operating conditions (far from or close to saturation) adopted.

Acknowledgements

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