

On the Effect of the Coal Ash Pre-treatment as a Mean to Improve their Sorptive Behaviour toward Heavy Metals in Wastewaters

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The use of raw coal combustion ash (CCA) and of suitable pre-treatments to enhance its adsorption capacity towards specific pollutants (namely cadmium and arsenic) were considered in this work. Pre-treatments included mechanical sieving, acidification, demineralization and gasification (either with steam or CO₂ as gasifying agents). After each pre-treatment, ash characteristics were determined and both equilibrium and kinetic adsorption experiments were carried out under fixed operating conditions. Results were expressed in terms of adsorption isotherms and kinetic curves, which confirmed that specific pre-treatments allow achieving substantial improvements of CCA adsorption capacity towards heavy metals. Post-processing of experimental data allowed the estimation of relevant parameters such as the equilibrium and the kinetic constants, the separation factor, the initial adsorption rate and the characteristic adsorption time. Besides, a correlation between the properties of raw or pre-treated CCA samples and the magnitude of heavy metals adsorption was carried out to assess the optimal pre-treatment for each of the investigated pollutant.

1. Introduction

The coal combustion ashes are solid by-products of combustion processes; usually, landfill disposal is the most adopted solution to discard this material. A large and economic use of coal ash is in cement and concrete industry (Ondova et al., 2011), even if it can be usefully employed as sorbent for water treatment. Indeed, the same properties of CCA justify the great interest for their use in this field. CCA, in fact, have both a silico-aluminous and a carbonaceous fraction and a certain porosity; furthermore, their origin led to the presence of oxygenated groups and hetero-atomic bonds on their surface, which may have a role in the adsorption of heavy metals from water streams. This process is usually accomplished by activated carbons, either powdered or granular, or ion exchange resins. The unit price of the activated carbons is, however, around 1-2 Euro/kg, while that of resin is usually over 8 EUR/kg. In this sense, there are research efforts aimed to improve the performance of low cost alternative sorbents for water treatment (e.g. Bailey et al., 1999, Crini, 2006, Russo et al., 2010). Examples in the pertinent literature on the use of CCAs for heavy metal removal are reported (e.g. Balsamo et al., 2010, 2011, 2012a,b, 2013, Wang et al., 2008, Zhang et al., 2003). Although results are encouraging, the CCAs can be better used as raw materials for the production of sorbent with enhanced adsorption capacity towards specific target pollutants. However, a cost benefit analysis is still needed to assess the optimal beneficiation treatment. In this work, equilibrium and kinetic adsorption experiments on the use of a raw CCA and of several CCA-based sorbents are described. Two different case studies are considered, i.e. As(V) and Cd (II) removal from contaminated natural water. These results are mandatory to understand potentialities of the CCA based sorbent for water treatment and to support cost benefit analysis.

2. Materials and methods

2.1 Properties of the coal combustion ashes

The 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 analysis was performed by a Malvern Instrument Master Sizer 2000 granulometer, operating down to a minimum particle size of 0.02 μm . From this characterization, a mean Sauter diameter of 10 μm can be inferred. Pore size distribution was obtained by operating a Thermo Finnigan Pascal 240/140 porosimeter, in a pore radius range of 3.7-1000 nm. While the surface area and cumulative pore volume resulted equal to 19 m^2/g and 30 mm^3/g , respectively, pore size distribution analysis revealed a broad distribution with a large peak in the radius range of 1.5-4.5 μm . The CCA chemical characterization was obtained by performing X-Ray Diffraction (XRD, Philips PW1830) and proximate analysis. Table 1 resumes the chemical composition and proximate analysis of the CCA.

Table 1. CCA chemical composition and proximate analysis (dry basis), %wt

Chemical composition	%wt	Proximate analysis (dry basis)	%wt
CaO	4.25	Volatiles	3.68
SO ₃	n.d.	fixed carbon	22.26
Al ₂ O ₃	21.80	Ashes	74.06
SiO ₂	34.20	Total	100.00
MgO	1.03		
Na ₂ O	0.55		
K ₂ O	0.96		
TiO ₂	1.49		
Fe ₂ O ₃	7.24		
loss on ignition	26.70		
total	98.22		

The XRD analysis showed the presence of a significant silico-aluminous fraction, mainly represented by quartz (SiO₂) and mullite (3Al₂O₃·2SiO₂) crystalline phases. Proximate analysis showed a moderate fixed carbon content, around 22 %, due to short mean residence times (and, therefore, limited carbon conversion degree) into the combustor. The evaluation of the pH of point zero charge shows that the CCA has a marked basic nature, with a pH_{PZC} around 9.

The CCA sample was subjected to a batch leaching tests to determine the release of ionic metals, for a preliminary 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 0.1 L of distilled water, and thereafter the liquid solution was analyzed by ICP spectrophotometry (employing an Agilent 7500CE apparatus). Significant amounts of different metallic ions are released by CCA, mainly consisting of Ca, Al, K, Ba, Si, Sr, but also including minor quantities of Cr, Mo and As (Balsamo et al., 2010). By considering the existing limitations of specific elements content for solids disposal in the soils, As, Cr and Mo are the most critical substances to be accounted for, if the sorbent is proposed for groundwater remediation.

2.2 Beneficiation treatments of Coal Combustion Ashes

2.2.1 CCA treatments

Different CCA treatments were considered in this study: 1. Sieving; 2. Demineralization; 3. Acidification; 4. Wet gasification, 5. Dry gasification.

Among them, only acidification was used for As(V) adsorption, while, the other were applied to Cd(II) adsorption.

The first sorbent (termed F25) was obtained by sieving raw CCA through a 25 μm -size sieve. Indeed, almost 50 % of CCA particles is finer than 25 μm , and this less-than-25 μm fraction was chosen in order to have a material with a smaller mean diameter than raw CCA. The second one (termed DEM) derived from raw CCA demineralization by HCl/HF attack followed by a neutralizing treatment with NaOH, as described elsewhere (Balsamo et al, 2011).

Sorbent acidification was proposed to remove arsenic, chromium and molybdenum from the raw CCA in order to allow its use for groundwater or even drinking water treatments, which are the main target for arsenic removal. Preliminary tests indicated HCl solutions as the most promising acid treatment as predicted by Wang et al. (2008), Montagnaro and Santoro, (2009) and other authors. The optimal acidification conditions were obtained by immersing 1 g of raw CCA in 0.1 L of 1 M HCl solution, for 72 h

under continuous stirring; the sample was then filtered and oven dried for 12 h at 105 °C, washed with distilled water and dried again.

Gasification involves the conversion of the ash unburnt carbon into gaseous products by using either steam or carbon dioxide (e.g. Zhang et al., 2003). The CCA was gasified in an electrically-heated tubular reactor (Nabertherm R60/750/13, i.d.=60 mm) kept at 850 °C. Samples (1 g) of CCA were charged into the reactor and kept in contact with a stream of steam or CO₂. Both steam and CO₂ flow-rates at the operating temperature (850 °C) are about 300 L h⁻¹. Steam gasification (SG) or carbon dioxide (so-called 'dry') gasification (DG) were carried out for times equal to 10, 30 and 60 min. In both the cases (i.e. DG and SG), the most promising sorbents for cadmium adsorption resulted those produced after 10 min of gasification, which are named DG10 and SG10 (Balsamo et al., 2012a,b, 2013).

2.2.2 Adsorption tests

Equilibrium and kinetic tests for As(V) and Cd(II) were performed similarly, but specific details are reported in former works, among which, Di Natale et al. (2008) and Balsamo et al. (2010) for As(V) adsorption and Balsamo et al. (2011) for Cd(II) adsorption.

Equilibrium tests were carried out at constant temperature in batch stirred reactors using model aqueous solutions. Each sample consisted of a volume, V, of aqueous solution at different concentration, c°, put in contact with a constant amount of sorbent, m. Initial solution pH was adjusted by addition of nitric acid (1 M) or sodium hydroxide (1 M) to the stock solutions and it was not further altered during the experimental run. When equilibrium was established, the solution was filtered and then analysed for pH and heavy metals concentration. Simultaneously, the CCA was leached to obtain the complete extraction of the adsorbed species, thus providing for a direct measure of its uptake on the solid surface. Atomic absorption spectrophotometry was used to measure As(V) and Cd(II) concentrations.

Kinetic tests on Cd(II) were performed with 1 g of CCA sorbent and 0.1 L of aqueous solution for times ranging from 15 minutes to 7 days and using cadmium initial concentration of 50 mg/L. All the experimental tests were carried out at an equilibrium pH around 7.5 achieved by suitably adjusting initial solution pH with HNO₃ (0.1 M) and NaOH (0.025 M) solutions.

2.2.3 Methods for data analysis

Starting from the determination of solute concentration in the liquid phase, the following parameters can be inferred:

The adsorption capacity can be determined by means of the material balance:

$$q(t) = \frac{[(c_0 + q_0 m/V) - c(t)] V}{m} \quad (1)$$

which accounts for both the solute captured from solutions and for that originally present on the sorbent (q_0), previously determined through leaching tests. In eq. (1), c_0 is the initial solute concentration in solution, $c(t)$ and $q(t)$ are its liquid and solid concentration at time t , m is the CCA mass and V the solution volume. The corresponding equilibrium conditions are denoted as q_{eq} and c_{eq} .

The well-known Langmuir equation:

$$q_{eq} = \frac{q_{max} K c_{eq}}{1 + K c_{eq}} \quad (2)$$

was used to interpret the adsorption isotherms. In this equation q_{max} is the maximum adsorption capacity and K is the equilibrium constant, which can be expressed as:

$$K = \exp\left[\frac{-\Delta G^\circ}{RT}\right] \quad (3)$$

where ΔG° is the standard Gibbs free energy of adsorption and T is the actual temperature.

The Langmuir equation provides a simple expression of the separation factor σ , commonly adopted to characterize a favorable adsorption if smaller than 1:

$$\sigma = \frac{1}{1 + K c_0} \quad (4)$$

The adsorption kinetic curves can be characterized by the initial adsorption rate, θ :

$$\theta = \left. \frac{dq(t)}{dt} \right|_{t=0} \quad (5)$$

which is the initial slope of the kinetic curve, and by a characteristic adsorption time, τ , which can be estimated as:

$$\tau = \frac{d_s^2}{16 \cdot D} \quad (6)$$

where d_s is the mean Sauter particle diameter and D is an effective diffusivity. Indications on the values of the effective diffusivity were based on the application of the Reichenberg model to the interpretation of the kinetic tests and were presented in Balsamo et al. (2011).

3. Results

3.1 Arsenic adsorption

In Figure 1, arsenic adsorption isotherms on raw (CCA) and acidified CCA (Ac-CCA) were reported. The CCA isotherm shows an almost linear trend under the operating conditions explored in this work, thus the availability of the sites remains constant at all concentrations. Differently, the Ac-CCA sample shows an isotherm that follows a “Langmuir-like” behaviour, and it is characterized by a higher adsorption capacity. This result is of great importance, as the Ac-CCA sample shows a good arsenic adsorption capacity also for low contamination levels, where generally sorbents show scarce adsorption properties. This result can be attributed to a surface oxidation, due to the HCl treatment, that enhances arsenic adsorption, as extensively reported in the literature (e.g. Wang et al., 2008). Moreover, these physical-chemical changes can be responsible for the different shape of the isotherms observed for Ac-CCA with respect to raw CCA. Further experimental data (not reported) showed that arsenic adsorption capacity is almost the same both in distilled and mineral water. As a general consideration, the presence of anions in solution (i.e. in mineral water) can determine the occurrence of competition phenomena towards the adsorption of arsenates (Di Natale et al., 2008) but, in this case, CCA anions release in distilled water and anions concentrations in mineral water are of the same order of magnitude, so that there are limited effects on CCA adsorption. However, this result suggests that the CCA can be used as a sorbent for the depuration of groundwater.

3.2 Cadmium adsorption

Figure 2 describes the cadmium adsorption isotherms at 25 °C and pH 7.5 on different sorbents deriving from activation treatments. As can be observed, all the isotherms exploit a Langmuir-like pattern. Experimental results show that the mechanical sieving and the dry gasification produced a sorbent with an adsorption capacity towards cadmium almost double than that pertaining to the raw material (CCA).

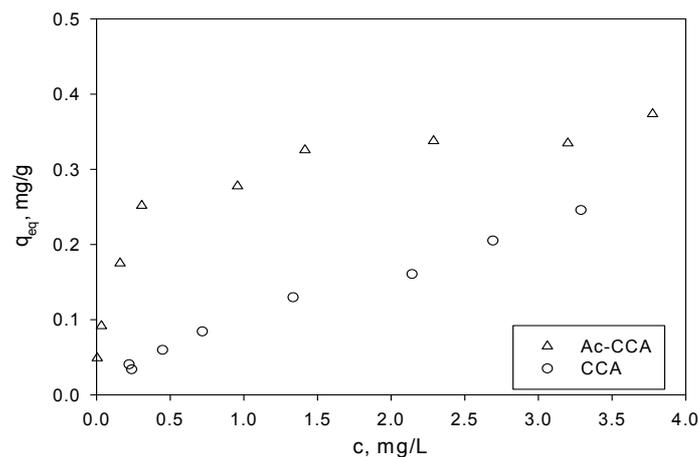


Figure 1. Arsenic adsorption isotherms on raw CCA and acidified CCA at 25°C and pH 7.5.

The wet-gasification leads to a slight improvement of cadmium adsorption capacity while the demineralization reduced it by a factor more than two thirds. The effects of sorbent beneficiations can be resumed in terms of maximum adsorption capacity, q_{max} , and thermodynamic affinity between the cadmium and sorbents, expressed by the Langmuir constant K .

Figure 3 reports the kinetic tests on cadmium adsorption on the different sorbents. The kinetic tests must be carefully considered: the plots are different due to the differences in both sorbents equilibrium capacity and kinetic properties. All the beneficiated sorbents are characterized by a higher initial adsorption rate than the CCA, although for the DEM sample this seems related to the lowest equilibrium capacity (see Figure 2). Notwithstanding this, the dynamics of F25, SG10 and DG10 are comparable in terms of characteristic time, which is of the order of 5000 of minutes.

All the main thermodynamic and kinetic parameters of cadmium adsorption are resumed in Table 2.

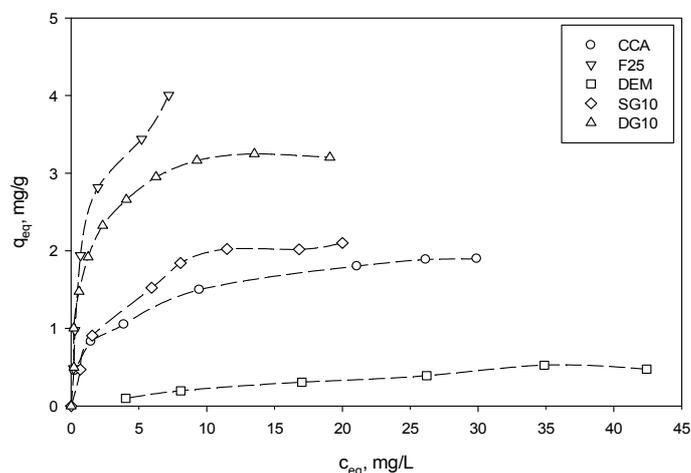


Figure 2. Cadmium adsorption isotherms on raw and pre-treated CCA. $T=25^{\circ}\text{C}$, $\text{pH}=7.5$

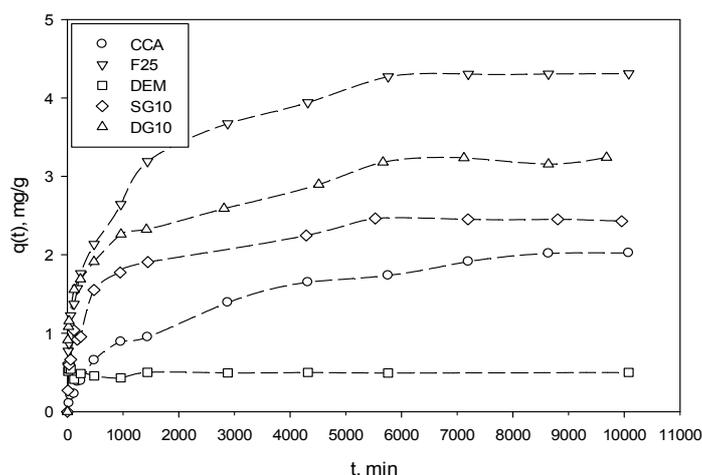


Figure 3: Cadmium adsorption kinetics on raw and pre-treated CCA. $T=25^{\circ}\text{C}$, $\text{pH}=7.5$, $c_0=50\text{ mg/L}$, $m/V=10\text{ g/L}$.

Table 2: Main chemical-physical, morphological and Cd(II) adsorption properties of the CCAs sorbents.

Sorbent	Fixed C [%]	d_p [μm]	Cum. pore distr. [mm^3/g]	pH_{PZC}	q_{max} [mg/g]	K [L/mg]	ΔG° [kJ/mol]	σ ($c_0=50$ mg/L) [-]	Θ [mg/(g·min)]	τ [days]
CCA	22	10	30	9	2.0	0.41	-26.6	0.047	$1.4 \cdot 10^{-3}$	6
F25	22	3	148.8	9	4.3	0.87	-28.5	0.022	$4.3 \cdot 10^{-3}$	4
DEM	93	15	62.4	6.7	0.5	0.04	-26.6	0.333	-	-
DG10	15	6	49	9	3.2	1.09	-28.5	0.018	$15 \cdot 10^{-3}$	4
SG10	14	6	63	9	2.41	0.31	-20.8	0.061	$10 \cdot 10^{-3}$	4

From this comparison, sieving and the dry gasification resulted to be the most useful beneficiation treatments for cadmium adsorption. In the first case, the chemical-physical characteristics of the sorbent

are the same of the raw material, although the morphological properties (in particular, the particle-size) of the sorbent are changed. Notwithstanding this, the higher external surface area and porosity of the F25 leads to a higher adsorption capacity and a fastest adsorption rate. The dry gasification, instead, leads to the formation of a new chemical-physical structure with a more kindred surface for cadmium adsorption coupled with an increase in the sample porosity. This is mirrored both by the higher values of the initial adsorption rate and of the Langmuir equilibrium constant.

4. Conclusion

This work describes the effects of several type of beneficiation treatments on a coal combustion fly ash aimed at improving its adsorption capacity towards heavy metals. At the moment, only the cases of arsenic and cadmium ions were considered. The experimental results showed that specific CCA treatments lead to adsorption capacities smaller but almost comparable with those observed by granular activated carbons, conventionally used in wastewater treatments. Furthermore, a simple acidification treatment can allow the use of CCAs also for groundwater remediation, reducing any potential unwanted CCAs release of heavy metals below detection limits. The CCAs and its derived sorbents are powdered materials that should be used in stirred reactors, rather than in fixed bed columns. To this end, also the separation of particles from clean water at the end of the adsorption should be accounted for. With reference to cadmium adsorption, the most useful beneficiation treatments are the sieving and the dry gasification. The second process, although more expensive, had the advantage of producing a sorbent with a surface structure more affine to cadmium adsorption, preserving the particle size at the same time. This aspect allows the use of less expensive particle-water separators, that may have a significant impact on the overall process costs. With the support of the results on cadmium adsorption reported in this work, a cost benefit analysis on the use of DG10 and F25 and a suitable comparison with GAC adsorption is now possible and will be among the next steps of our work.

References

- Balsamo M., Di Natale F., Erto A., Lancia A., Montagnaro F., Santoro L., 2010, Arsenate removal from synthetic wastewater by adsorption onto fly ash, *Desalination* 263, 58-63.
- Balsamo M., Di Natale F., Erto A., Lancia A., Montagnaro F., Santoro L., 2011, Cadmium adsorption by coal combustion ashes-based sorbents – Relationship between sorbent properties and adsorption capacity, *J. Hazard. Mater.* 187, 371-378.
- Balsamo M., Di Natale F., Erto A., Lancia A., Montagnaro F., Santoro L., 2012a, Steam- and carbon dioxide-gasification of coal combustion ash for liquid phase cadmium removal by adsorption, *Chem. Eng. J.* 207-208, 66-71.
- Balsamo M., Di Natale F., Erto A., Lancia A., Montagnaro F., Santoro L., 2012b, Reuse of coal combustion ash as sorbent: The effect of gasification treatments, *Comb. Sci. Techn.* 184(7-8), 956-965.
- Balsamo M., Di Natale F., Erto A., Lancia A., Montagnaro F., Santoro L., 2013, Gasification of coal combustion ash for its reuse as adsorbent, *Fuel* 106, 147-151.
- Bailey S.E., Olin T.J., Bricka R.M., Adrian D.D., 1999, A review of potentially low-cost sorbents for heavy metals, *Water Research* 33(11), 2469-2479.
- Crini G., Non-conventional low-cost adsorbents for dye removal: A review, 2006, *Biores. Technol* 97(9), 1061-1085.
- Di Natale F., Erto A., Lancia A., Musmarra D., 2008, Experimental and modelling analysis of As(V) ions adsorption on granular activated carbon, *Water Res.* 42 (8-9), 2007-2016.
- Montagnaro F., Santoro L., 2009, Reuse of coal combustion ashes as dyes and heavy metal adsorbents: effect of sieving and demineralization on waste properties and adsorption capacity, *Chem. Eng. J.* 150, 174-180.
- Ondova M., Stevulova N., Zelenakova E., 2011, Energy savings and environmental benefits of fly ash utilization as partial cement of pavement building, *Chem. Eng. Trans.* 25, 297-302.
- Russo M.E., Di Natale F., Prigione V., Tigini V., Marzocchella A., Varese G.C., 2010, Adsorption of acid dyes on fungal biomass: Equilibrium and kinetics characterization, *Chem. Eng. J.* 162(2), 537-545.
- Wang J., Wang T., Burken J.G., Chusuei C.C., Ban H., Ladwig K., Huang C.P., 2008, Adsorption of arsenic (V) onto fly ash: A speciation-based approach, *Chemosphere* 72, 381-388.
- Zhang Y., Lu Z., Maroto-Valer M.M., Andrésen J.M., Schobert H.H., 2003, Comparison of high-unburned-carbon fly ashes from different combustor types and their steam activated products, *Energy Fuel.* 17, 369-377.