

## Adsorption of chlorophenol, chloroaniline and methylene blue on fuel oil fly ash

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### Abstract

Fuel oil fly ash has been tested as low-cost carbon-based adsorbent of 2-chlorophenol (CP), 2-chloroaniline (CA) and methylene blue (MB) from aqueous solutions. In all the cases the adsorption was found to be of cooperative type. Different adsorption capacities were found for the three organics. Specifically, it was highest for 2-chlorophenol, reaching about  $70 \text{ mg g}^{-1}$ , and quite lower in the other two cases, that is about 47 and  $36 \text{ mg g}^{-1}$  for methylene blue and 2-chloroaniline, respectively. Varying the initial pH and adding KCl were found to have different effects on the adsorption of the three organics. In particular, the presence of other ions had no effect on the adsorption of methylene blue, adverse effect in the case of 2-chlorophenol and enhancing effect in the case of 2-chloroaniline.

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### 1. Introduction

Activated carbon is widely employed in water treatment, due to its broad spectrum of adsorption capacity. An extraordinary wide range of chemicals, including harmful pollutants such as organochlorides and heavy metals, are easily retained on its surface [1–10]. Molecules that are slightly polar, generating taste and smell, and molecules with a relatively high molecular weight are well adsorbed on activated carbon. On the other hand, the hardest to retain are the most polar molecules and the linear ones with a very low molecular weight such as simple alcohols and primary organic acids.

Activated carbon can be effectively employed in the tertiary treatment of municipal and industrial wastewaters. In fact, it is able to retain dissolved organic pollutants, such as phenols, aromatic amines and synthetic dyes, which are resistant to upstream physico-chemical and biological treatments, and thus removes a large part of the residual COD. In addition, activated carbon also exhibits the property to act as a bacteria support capable

of breaking down a fraction of the adsorbed phase. Thus, a part of the support can be continuously regenerated allowing new molecules to be retained.

The attraction towards solid–liquid adsorption processes for wastewaters treatment largely relies on their simplicity and can be further increased if, instead of expensive activated carbon, use is made of cheaper sorbents. To this scope, many high-carbon materials have been recently tested deriving from either available bio-resources or industrial wastes [11–24]. These sorbents comprise pyrolyzed agricultural wastes and wastes from combustion processes which can be directly employed without any prior beneficiation treatment. Obviously, this is a key point to achieve low-cost operation in actual treatment processes.

Whenever a solid or liquid fossil fuel is used in a combustion process, fly ash is generated, and, among the different types, that produced by coal combustion is the most well known from the points of view of characteristics, properties and uses. Although coal fly ash may contain harmful heavy metal oxides, it finds satisfactory recycling in different fields of civil engineering. However, due to the great availability of this waste material, new ways of recycling have been searched for. For this reason, some recent studies can be found in the literature on the use of coal fly ash as adsorbent cheaper than activated carbon [16,21,22,24].

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This application mainly relies on the content of unburned carbon particles, in which, coal fly ash is in general not particularly high. This was evidenced in a study on the hydraulic properties of five samples of this type of ash produced in Italy from the combustion of coals of different origin [25].

As well as coal, fuel oil is widely employed in thermal power plants, and its combustion generates an equally large amount of ash. However, when compared to coal fly ash, that from fuel oil shows significantly different chemical composition and properties that make it unsuitable for recycling in civil engineering applications. To this regard, it is to be pointed out that a further reason that hampers fuel oil ash from being addressed towards matter recovery is its classification as hazardous waste. This can be checked in the European waste catalogue where this material is given the code 10.01.04\* (the asterisk denotes a hazardous waste). On the other hand, fuel oil fly ash is much more attractive as potential substitutes of activated carbon because it usually has a quite high content of unburned particles.

In this paper, fuel oil fly ash has been tested for the adsorption of selected organic contaminants of common occurrence in wastewaters: 2-chlorophenol (CP), 2-chloroaniline (CA) and methylene blue (MB). Of these three organics, CP is formed, among other chloro-organics, in chlorination processes. It is of great concern among the environmentalists, due to its high toxicity against living organisms. For this reason, many papers are found in the literature on the removal of chlorophenols by adsorption on several different sorbents [26–29]. CA has been selected because chloroanilines are frequently employed as raw materials in organic syntheses and then are common contaminants of industrial wastewaters. Furthermore, CA is a secondary product in drinking water disinfection by sodium hypochlorite and its presence in the final product must not exceed a specific limit. Finally, MB is one of the dyes commonly employed in textile industries and contributes to the pollution of water discharges [30]. Even dyes are of environmental concern, as it is well known that many of them are toxic and, in some cases, carcinogen. Also for anilines and synthetic dyes, many papers can be found in the literature on their removal by adsorption [11,16,31–38].

## 2. Materials and methods

The fuel oil fly ash was supplied by the main Italian electrical company (ENEL). It was generated in a large plant located in Brindisi (Southern Italy). Its quantitative characterization was carried out by means of chemical analysis, while differential thermal analysis, X-ray diffraction analysis and FT-IR spectrophotometric analysis were used for qualitative characterization. The chemical analysis was carried out by means of commonly accepted methods for this type of material, starting from firing at 1050 °C followed by alkaline melting in a muffle furnace and HCl dissolution. Then, silica content is determined gravimetrically, while metal oxides contents by atomic absorption spectroscopy and sulphate content by ionic chromatography. Thermal, X-ray diffraction and FT-IR spectrophotometric analyses were carried out by means of a Netzsch STA 409 thermoanalyzer, a Philips PW1830 diffractometer and

a Nicolet Nexus spectrometer, respectively. Finally, fly ash was characterized for pore size distribution using a Carlo Erba 1990 Sorptomatic apparatus.

The chemicals used in the adsorption experiments were reagent grade CP, CA and MB supplied by Fluka. Of each of these chemicals, stock solutions were prepared and 50 mL aliquots were sampled and contacted with different amounts of solid adsorbent. The concentration of these stock solutions was 1 g L<sup>-1</sup> for CA and MB and 1.8 g L<sup>-1</sup> for CP. The 50 mL samples were contacted with variable amounts of ash within the ranges 0.81–200 g L<sup>-1</sup> for CA, 0.81–160 g L<sup>-1</sup> for MB and 0.8–200 g L<sup>-1</sup> for CP. Solid–liquid contact was ensured in a beaker glass and the system was thoroughly mixed by means of a mechanical stirrer driven at 200 rpm. The adsorbate solution and the adsorbent were kept in contact for 24 h at 25 °C. It was checked that this contacting time was sufficient for equilibrium to be reached. The adsorption isotherms were obtained by filtering a portion of the liquid phase through a 45 µm Millipore filter and analysing it by means of a UV spectrometer. These measurements were carried out at the maximum absorption wavelength, that is 275, 289 and 664 nm for CP, CA and MB, respectively. The specimens were diluted 1:10, 1:50 or 1:100, depending on the adsorbate nature and concentration. In some adsorption experiments the initial pH was changed between 2 and 12 by adding proper quantities of HCl or KOH. In these cases 7 g of fly ash were contacted with 50 mL of 1 g L<sup>-1</sup> adsorbate solution. Furthermore, a final test was carried out adding KCl to the adsorbate solutions in such amount to have a 10<sup>-2</sup> M concentration. In all these additional adsorption tests, the contact time and temperature as well as the technique of liquid sampling and analysing were the same as before.

## 3. Results and discussion

The fly ash was entirely made of particles passing a 180-µm sieve. The results of chemical analysis are shown in Table 1 in terms of content of the main components. It is clearly seen that, from this point of view, fuel oil fly ash strongly differs from coal fly ash. In particular, the loss on ignition (LOI), mostly given by unburned particles, is much higher than that usually found for coal fly ash, while the silica content is considerably lower. In fact, when submitted to chemical analysis, five samples of coal fly

Table 1  
Chemical composition of fly ash

Component	wt%
LOI <sup>a</sup>	54.4
Na <sub>2</sub> O	1.0
K <sub>2</sub> O	0.8
CaO	3.4
Al <sub>2</sub> O <sub>3</sub>	16.2
MgO	1.0
Fe <sub>2</sub> O <sub>3</sub>	3.9
SiO <sub>2</sub>	15.0
SO <sub>4</sub> <sup>2-</sup>	4.0
Total	99.7

<sup>a</sup> Loss on ignition at 1050 °C.

ash from Italian power plants were found to have silica content ranging from 42.74 to 50.23% and LOI ranging from 3.92 to 12.94% [25]. Both these properties are favourable for recycling this waste as an adsorbent. Obviously, this comes directly from the higher content of unburned particles and indirectly from the lower silica content. This property makes fuel oil fly ash unsuitable for recycling in the field of building materials as its pozzolanic activity cannot be as high as that of coal fly ash. On the contrary, testing fuel oil fly ash for its adsorptive property can well be worthy of consideration.

The results of thermal, X-ray diffraction and FT-IR analyses (not shown) allow to draw the following conclusions. A wide exothermic peak is seen in the result of differential thermal analysis between 400 and 650 °C, obviously due to air-oxidation of the unburned fraction. No other significant peak is seen. The simultaneous thermogravimetric analysis shows that almost all the weight loss up to 1050 °C occurs in the above temperature range. Then, the LOI resulting from chemical analysis is almost completely given by the unburned fraction in the ash. X-ray diffraction analysis shows an almost amorphous material, differently from coal fly ash that usually contains some crystalline phases such as mullite. Finally, the results of FT-IR analysis only show significant absorption in a wavenumber range around 1100  $\text{cm}^{-1}$  where resonances relative to silicates and silico-aluminates lay.

The results of pore size distribution measurement are reported in Fig. 1 and Table 2. It is seen that almost all accessible porosity is in the field of mesopores. In fact, according to the classification given by Anderson and Pratt [39], micro-, meso- and macropores belong to the size ranges below 2 nm, between 2 and 50 nm and above 50 nm, respectively. This characteristic of fuel oil fly ash is surely attractive for enhancing adsorptive capacity.

It has already been pointed out that fuel oil fly ash is classified as hazardous waste because it may contain harmful heavy metal oxides, those of Ni and V being the most abundant [40]. Then, if such a waste is used for water treatment in an adsorption process, secondary water pollution may occur. However, the Italian clean water acts pose a limit of 4  $\text{mg L}^{-1}$  for Ni and no one for V. Then, only possible pollution from Ni release should be taken into account. For this reason the fuel oil ash was submitted to the Italian standard leaching test for waste recycling [41]. This test gave the result of 172  $\text{mg L}^{-1}$  of Ni released, which highly

Table 2  
Differential pore size distribution of fly ash

Size range (nm)	vol.%
1.5–1.7	7.3
1.7–1.9	8.0
1.9–2.1	4.7
2.1–2.4	9.4
2.4–2.7	8.8
2.7–3.0	7.3
3.0–3.4	6.7
3.4–3.8	6.6
3.8–4.2	4.5
4.2–4.7	5.6
4.7–5.3	6.4
5.3–6.0	5.7
6.0–6.7	5.7
6.7–7.5	6.5
7.5–8.4	6.8
Total	100.0

exceeds the limit for this metal. However, the liquid to solid ratio employed in the leaching test (static with 24 h contact time) is 10  $\text{L kg}^{-1}$ , while in a real adsorption application (continuous flow process with much lower contact time) the solid is usually contacted by, at least, a two to three orders of magnitude greater amount of liquid [42]. The result is that Ni concentration in the treated water can decrease well below the law limit.

The results of the adsorption experiments carried out on all the three organics are reported in Fig. 2 in terms of adsorption isotherms. In all cases the isotherms are of class S, sub-group 4, according to the classification by Giles et al. [43] based on the initial slope and the shape of the upper part of the curves. Such isotherms occur when the adsorbent–adsorbate interactions increase as the loading increases. They are characterized by low adsorption at low concentration, due to weak adsorbent–adsorbate interactions. However, once a molecule is adsorbed, adsorbent–adsorbate forces increase and promote the adsorption in a cooperative fashion. At high concentration, multilayer adsorption can take place too.

Despite the similarities described above, significant differences can be seen from case to case. First of all, the ash maximum

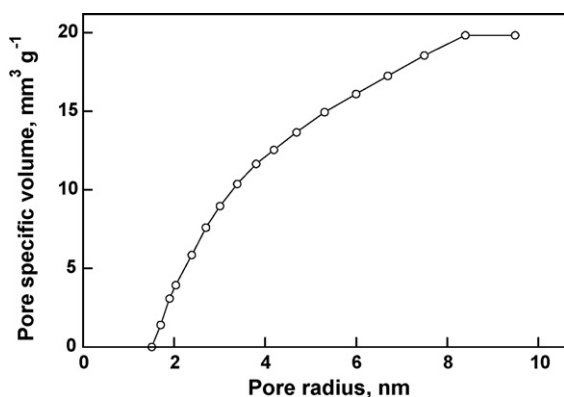


Fig. 1. Cumulative pore size distribution of ash.

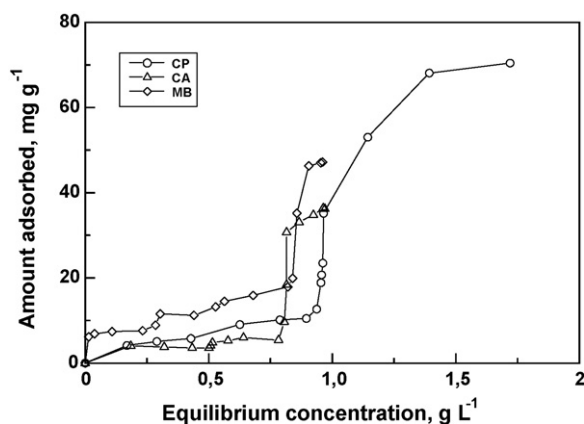


Fig. 2. Adsorption isotherms of 2-chlorophenol, 2-chloroaniline and methylene blue.

adsorption capacity is highest for CP, reaching the value of about  $70 \text{ mg g}^{-1}$ , while quite lower values are observed in the other two cases, that is about 47 and  $36 \text{ mg g}^{-1}$  for MB and CA, respectively. Furthermore, the equilibrium concentration at which the isotherms attain their highest steepness is about  $0.95 \text{ g L}^{-1}$  (highest value) for CP and about  $0.82\text{--}0.86 \text{ g L}^{-1}$  for CA and MB. Finally, one more significant difference is the quite higher adsorption capacity observed for MB at low equilibrium concentration in respect to the other two organics. This characteristic is of value when MB is to be removed from diluted solutions.

The above differences are given to the different adsorbent–adsorbate interactions that occur from case to case. At low equilibrium concentration, these interactions are highest for MB, giving rise to the observed highest adsorbed amount. On the other hand, the lowest adsorbent–adsorbate interactions occur in the case of CA and, consequently, the adsorbed amount is the lowest for this organic. Despite the significant difference in adsorbent–adsorbate interactions described above for MB and CA, the steep increase in adsorption capacity (and in adsorbent–adsorbate interactions) occurs at almost the same equilibrium concentration for these two organics. Beyond these values, the adsorbent–adsorbate interactions show the same ranking and an ultimate amount of MB adsorbed higher than that of CA is reached.

The behaviour of CP is not very different from that of CA at low equilibrium concentration, the adsorbent–adsorbate interactions being slightly higher. However, the equilibrium concentration at which these interactions steeply grow is significantly higher than that for the other two organics, reaching the value of about  $0.95 \text{ g L}^{-1}$ . Beyond this concentration, the adsorbent–adsorbate interactions increase even more giving an ultimate value of maximum adsorption capacity as high as about  $70 \text{ mg g}^{-1}$ .

The differences in adsorption behaviour among the three organics can also be seen on the graph of Fig. 3, where the removal efficiency is reported against the loading ratio. The removal efficiency is defined as the percentage ratio between the amount of adsorbate removed and the one initially present in the solution, while the loading ratio is the initial adsorbate

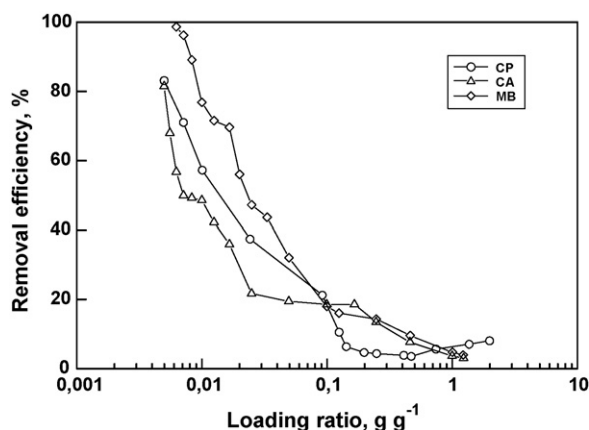


Fig. 3. Removal capacity of ash against 2-chlorophenol, 2-chloroaniline and methylene blue.

amount divided by the adsorbent mass. In all cases the removal efficiency decreases as the loading ratio increases, but great differences can be seen in the initial part of the curves. Specifically, the adsorption of the three organics studied can be ranked in the order  $\text{MB} > \text{CP} > \text{CA}$ . The observed differences are important from the applicative point of view because the higher the removal efficiency, the lower the adsorbent amount required for effectively carrying out an adsorption process.

In this paper the adsorption experiments were carried out with the waste material “as received”, that is with no beneficiation treatment. The results are to be compared to those that can be found in the literature on similar systems in order to rank the fuel oil fly ash among other waste-derived adsorbents. In many cases, however, this comparison is made difficult by the different operative conditions chosen by other authors. This is the case of CP and MB, as in most papers the isotherms refer to an equilibrium concentration range much lower than that studied in this paper. In such cases the cooperative character of the adsorption is not evidenced and the isotherms appear of the Langmuir type.

Kao et al. [26] and Namasivayam and Kavitha [28] studied CP adsorption on coal fly ash and coir pith carbon, respectively. The adsorption capacity was found to be  $0.8\text{--}1 \text{ mg g}^{-1}$  at temperature between  $10$  and  $30^\circ\text{C}$  in the former case, and  $17.6 \text{ mg g}^{-1}$  in the latter one. The adsorption of MB was studied by Janoš et al. on coal fly ash [16], Wang et al. on coal fly ash and red mud [38] and Woolard et al. on coal fly ash [44]. The following adsorption capacities were found:  $1.02 \text{ mg g}^{-1}$  in the first case,  $4.16 \text{ mg g}^{-1}$  (coal fly ash) and  $2 \text{ mg g}^{-1}$  (red mud) in the second one and  $1 \text{ mg g}^{-1}$  in the third one. These results prove that fuel oil fly ash compares favourably with other waste-derived adsorbents.

In the case of CA the lack of adsorption data for this specific aniline does not allow any comparison to other adsorbents.

Wang and co-workers made extensive use of carbon-enriched wastes to obtain more effective adsorbents for dyes removal [45–47]. Starting from coal fly ash, an adsorbent enriched in unburned carbon content from 5 to 85% was obtained with adsorption capacity of  $80 \text{ mg g}^{-1}$  for MB [45] and  $31\text{--}48 \text{ mg g}^{-1}$  at  $30\text{--}50^\circ\text{C}$  for Rhodamine B [46]. Furthermore, a coal fly ash-derived adsorbent with unburned carbon content of 36.7% was found to have adsorption capacity of about 38 and  $33 \text{ mg g}^{-1}$  against MB and crystal violet, respectively [47]. The results obtained in this study are in good agreement with those by Wang and co-workers.

Table 3 and Fig. 4 show the results of the adsorption experiments carried out at different pH values. Fig. 4 also shows the results obtained when  $10^{-2} \text{ M}$  KCl is added to the solution (solid

Table 3  
Initial and equilibrium pH of adsorption experiments

CP	Initial pH	2.26	4.16	5.62 <sup>a</sup>	8.24	10.08	11.56
	Equilibrium pH	6.65	7.44	7.45	7.52	7.66	7.70
CA	Initial pH	2.09	4.29	6.20 <sup>a</sup>	8.06	10.24	11.83
	Equilibrium pH	7.00	7.45	6.77	7.49	7.54	7.77
MB	Initial pH	2.26	4.17	6.77 <sup>a</sup>	8.40	10.27	11.83
	Equilibrium pH	7.60	7.98	7.44	7.94	7.85	7.84

<sup>a</sup> With no HCl or KOH addition.

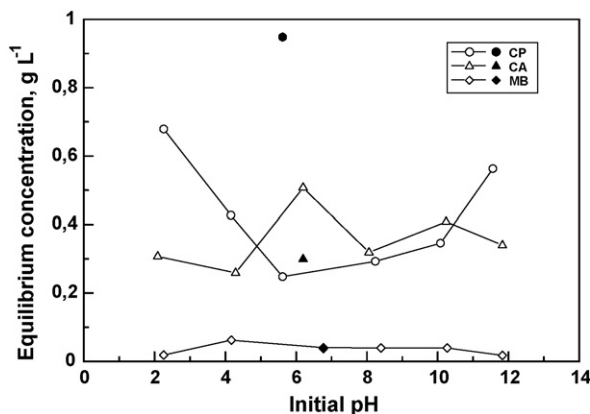


Fig. 4. Effect of initial pH and KCl addition on ash adsorption capacity. Open symbols: no KCl added; solid symbols: KCl added. For MB open and solid symbols overlap at pH 6.77.

symbols). As already pointed out, these experiments were all carried out by contacting 7 g of fly ash with 50 mL of an adsorbate solution of  $1 \text{ g L}^{-1}$  initial concentration. First of all, the data of Table 3 shows that, whatever the initial pH, a value close to neutrality is reached at equilibrium. Then, the ash revealed to have strong buffering capability, being able to adsorb both hydrogen ions and hydroxyl ions. This also means that the nature of the adsorbent surface changes, as acid or basic sites are alternatively neutralized.

The data of Fig. 4 relative to CP show that when HCl or KOH are added to the initial solution, CP adsorption is depressed, as both  $\text{H}^+$  and  $\text{OH}^-$  compete favourably with this organic. Furthermore, when KCl is added to the initial solution, the presence of both cations and anions has a synergistic effect and CP adsorption takes place to a very low extent. The reason for this behaviour may be the fact that, at equilibrium, CP is present in molecular form ( $\text{p}K_{\text{a}} = 8.94$ ) and its adsorption is unfavoured with regard to ionic species.

The addition of both HCl and KOH favours the adsorption of CA, and the same happens when KCl is present in the solution (Fig. 4). At equilibrium, as for CP, CA is present in molecular form, but its behaviour may be different from that of CP because the presence of an electronic doublet on nitrogen makes CA a Lewis base with nucleophilic character. This may favour its adsorption on the partially neutralized adsorbent sites.

The adsorption of MB is not affected by the addition of any of the chemicals HCl, KOH and KCl. This may be due to the fact that the MB molecule has both hydrophilic and hydrophobic character; then, its adsorption is favoured on any type of adsorbent site.

#### 4. Conclusions

The results of this study have shown that 2-chlorophenol, 2-chloroaniline and methylene blue can be effectively adsorbed onto fuel oil fly ash. This waste can be employed without any expensive pre-treatment, due to the high fraction of unburned particles. The adsorption capacity against 2-chlorophenol and methylene blue has been found similar to that of other carbon-

rich waste-based adsorbents. Due to the lack of literature data, such comparison was not possible for 2-chloroaniline.

Experiments carried out at variable initial pH revealed that fuel oil fly ash has high-buffering capacity, due to the presence of surface sites able to bind both anions and cations. In these cases, as well as when KCl is added, the change of the nature of the adsorbent surface modifies the adsorption capacity against 2-chlorophenol and 2-chloroaniline. It was depressed for the former, and enhanced for the latter. No such effect was found for methylene blue.

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