Valorisation of coal fly-ash residue as adsorbent for the removal of dyes from aqueous media

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Abstract

The disposal of dye contaminated water, from textile, leather, printing and food processing industries poses a serious environmental problem due to its poor biodegradability, carcinogenicity and toxicity. Fly-ashes are a particle waste resulting from high temperature combustion of coal and wood exhibiting a complex organic and inorganic composition. This by-product holds good sorption properties, low-toxicity level and hydrophilicity. Due to the large amounts produced, huge costs are involved in storage and disposal of fly-ashes, especially the ones with high content in un-burnt carbon. In this work, two types of coal fly-ashes with distinct un-burnt content, were tested as adsorbent of two dyes, the Mordant Orange 1 and Rhodamine B. Isothermal kinetic studies were performed at a temperature of 30ºC and the amount of soluble dye were quantitatively determined by spectroscopy. The Langmuir isotherm was used to model the dye adsorption phenomena by the coal fly-ash powder. Experimental data showed independence of the fly-ash carbon content in the adsorption efficiency to the same substrate (MO 1 and RB). However, the adsorption capacity is highly dependent on the adsorbate chemical nature being roughly 40x higher for the MO 1 (126 ± 17 mg/g) than for the RB (5.91 ± 0.36 mg/g).

1. Introduction

Valorisation routes of coal fly-ashes generated in thermal power-plants are widely recognized as a relevant environmental topic. Several uses of this by-product can be listed, such as in construction (production of cement and concrete products, material additives, brick manufacture, etc.), in agriculture (soil amelioration), or even in pollutant abatement (as adsorbents, zeolites, etc.) [1, 2]. Although, the accepted usages for the residue are closely linked with the coal type and the fly-ash characteristics, namely their chemical composition and unburned carbon content [3, 4]. At present massive amounts of fly-ash material are landfilled which rises economic and environmental concerns. The pursuit of improved usages for all waste materials alleviates both the treatment and storage problems, providing an added value product that can be marketed. New upcoming applications of coal fly-ash residues are the synthesis of geopolymers (alternative to cement), silica aerogels (insulating materials), carbon nanotubes (carbon allotropes) for electronic devices, and the separation of radioactive isotopes as well as rare earth elements [5]. However, the immediate use of the raw material is still attractive due to the low processing costs and straightforward.

Dyes are colored substances, present as contaminants in the effluents from industries such as pulp and paper, textiles, leather, dyeing, etc., causing severe environmental pollution problems. They produce intense coloration in water even in extremely low concentrations, affecting the light penetration through water and the photosynthetic activity. Among the most common dyes are the azoic and the heteropolyaromatic dyes which are complex molecules having a potential environmental harsh effect. The cleavage of the chemical azo linkage in molecules is responsible for the formation of amines, which are toxic and carcinogenic materials [6]. When absorbed in soil, the azo dyes remain for a long period affecting the population of useful microorganisms, leading to the reduction in agricultural productivity and destruction of flora [7]. The removal of these contaminants from aqueous system using simple and low-cost process is an actual challenge. Several techniques have been tested for the elimination of dyes from the effluents such as flotation [8], chemical degradation [9], membrane filtration [10] biological degradation [11, 12], and physical adsorption [13]. Among them adsorption technology is still an appealing path in special due to their simple design and easy operation [14]. Recent research has focus in the development of inexpensive residues, like coal fly-ash, to work as adsorbents for the removal of pollutants, like dyes, from wastewaters [4, 15].

The work presented here intends to give a contribution to the valorisation route of coal fly-ash residue as an adsorbent material to the dye removal from wastewaters. Two distinct organic dye molecules were tested, the Mordant Orange 1 and Rhodamine B, over two fly-ash types (F-A1 and F-A2) with different unburn content. The adsorption experiments were held at a constant temperature of 30ºC.

2. Materials and Methods

2.1 Raw materials

Two different coal fly-ashes types were studied. One type (F-A1) is a selected fly-ash portion, collected in the electrostatic precipitators, that is a marketable commodity to the cement industry, the other type (F-A2) is a mixed fly-ash material of different origins in the coal power-plant process which is sent to landfill deposition.

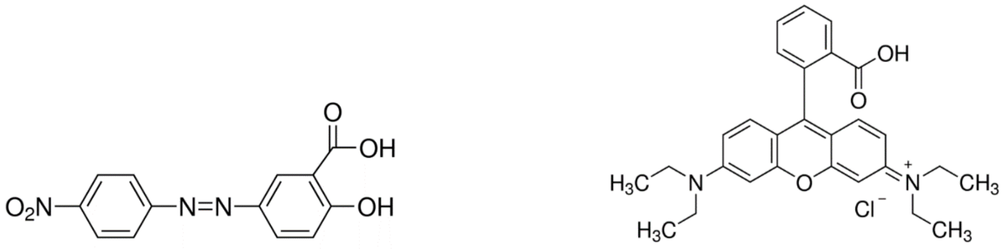
2.2 Characterization of the fly-ashes

The surface chemistry and textural properties of coal fly-ash types F-A1 and F-A2 were determined. The surface chemistry characterization was assessed by the determination of the point of zero charge (pH_{PZC}). In these studies, 0.5 g of the raw fly-ash material was added to 10 mL of ultra-pure deionized water (previously boiled for about 1 h to remove CO_2 and then cooled to room temperature). The slurries were remains under stirring for about 1 h then the pH was measured using a glass electrode (Crison, GLP22 pH meter). The textural parameters of the materials were determined by performing low temperature nitrogen (N_2) adsorption isotherms using a tailor-made glassware vacuum apparatus equipped with a rotatory (RV5) and a diffusion pump (Difftak MK2), from Edwards as well as pressure sensors (Barocell 600 AB) and Penning (AIM-S-NW25), also from Edwards. Prior to the adsorption essays the fly-ash samples were outgassed under vacuum at 300ºC for 2 h. After cooling, the sample container cell was immersed in liquid nitrogen and the admission of gas (N_2) to the cell were made at successive higher pressures until reaching a relative pressure higher than 0.95. The surface morphology of the materials was observed by Scanning Electron Microscopy (SEM) using a Hitachi S400 microscope.

Further characterization of coal fly-ash materials such as elemental analysis, X-ray diffraction to search the presence of crystalline phases and the identification of functional groups by infrared spectroscopy (FTIR) are currently in progress.

2.3 Dyes

Two dyes were study, the Mordant Orange 1 (MO I) and Rhodamine B (RB), obtained from Sigma-Aldrich with respectively 70% and 95% (w/w) purity. The selection of these dyes, whose molecular structures are presented in **Fig. 1**, was based on their wide use in industrial processes of printing and dyeing of textiles and leather. Additionally, the choice was based on their significantly different molecular size and functional groups, establishing a distinct interaction with the fly-ash adsorbent.



(a) MO 1: Mordant Orange 1 (b) RB: Rhodamine B

Fig. 1 Molecular structures of the tested dyes: (a) MO 1, $C_{13}H_9N_3O_5$; (b) RB, $C_{28}H_{31}ClN_2O_3$

2.4 Adsorption experiments

For the adsorption experiments about 100 mg of raw fly-ash powder were weighted and placed in stoppered flasks where 40 mL of dye solutions were added. The flasks were immersed on a thermoestatic bath (Julabo MP) at 30ºC which is placed on a multi-position magnetic stirrer (Multimatic 9-S, Selecta) for 15 min in the case of F-A1 and 45 min for F-A2 samples. These equilibration times for each dye were previously assessed by kinetic studies. Upon equilibrium, the fly-ash powder was separated from the dye solution using membrane filters (Milipore Durapore 0.45 µm HV). Aliquots of each solution were taken and their correspondent absorbances were measured by a double beam UV/vis spectrometer (Jasco V530) using standard quartz cells of 2 mm and 10 mm optical length. Each data point resulted from an average of at least three independent scans, assuring a relative standard deviation below 5% [16]. For each dye solution, the absorbance calibration curves were previously made using dye concentrations up to 35.0 mg/L for MO-1 and up to 10.0 mg/L for the RB. Different absorbance wavelength was selected for each dye, 372 nm for the MO-1 and 552 nm for the RB, correspondent to the absorbance bandhead of each dye.

3. Results and discussion

Table 1 shows the pH_{PZC} values and the textural parameters of the tested coal fly-ashes obtained experimentally. For the quantification of the specific surface area (S_{BET}), the Brunauer, Emmet and Teller method was applied in its linearized form, using the amounts of gas adsorbed and respective pressures until a maximum relative pressure of 0.4, obeying the validity of the model. The total porous volume (V_{Total}) was determined by the Gurvich rule, that consists on the determination of the volume of nitrogen gas adsorbed by the fly-ash sample at a relative pressure of 0.95 [17].

Table 1 Coal fly-ashes characterization

Sample	pH_{PZC}	S_{BET} [m^2/g]	V_{Total} [cm^3/g]
F-A1	10.88	13.1	0.017
F-A2	9.45	9.4	0.013

The F-A1 exhibit a higher basic nature than F-A2, which can influence differently the interaction between the dye molecules and the solid surface of the fly-ash. Concerning the textural parameters, the fly-ashes specific surface area is quite low when compared with traditional adsorbent materials such activated carbons, which typically have S_{BET} values above 200 m^2/g. The F-A1 exhibit both S_{BET} and V_{Total} higher than F-A2 which indicates that there are differences on the textural properties of these materials.

The SEM micrograph images of F-A1 and F-A2, depicted on **Fig. 2** gives detailed information that may explain the differences observed on textural parameters. Both materials are made of tiny spherical particles (microspheres), which are shaped by the high temperatures and venting out process from the furnace of the boiler [18]. Along with these spherical particles it is possible to identify spongiform particles of unburn material (carbon). The F-A1 sample (**Fig. 2a**), have a greater homogeneity when compared with sample F-A2 (**Fig. 2c**) that is more heterogeneous either in particle size and shape. For both coal fly-ash types some particles are covered with a darker unburn material (**Fig. 2b** and **Fig. 2d**).

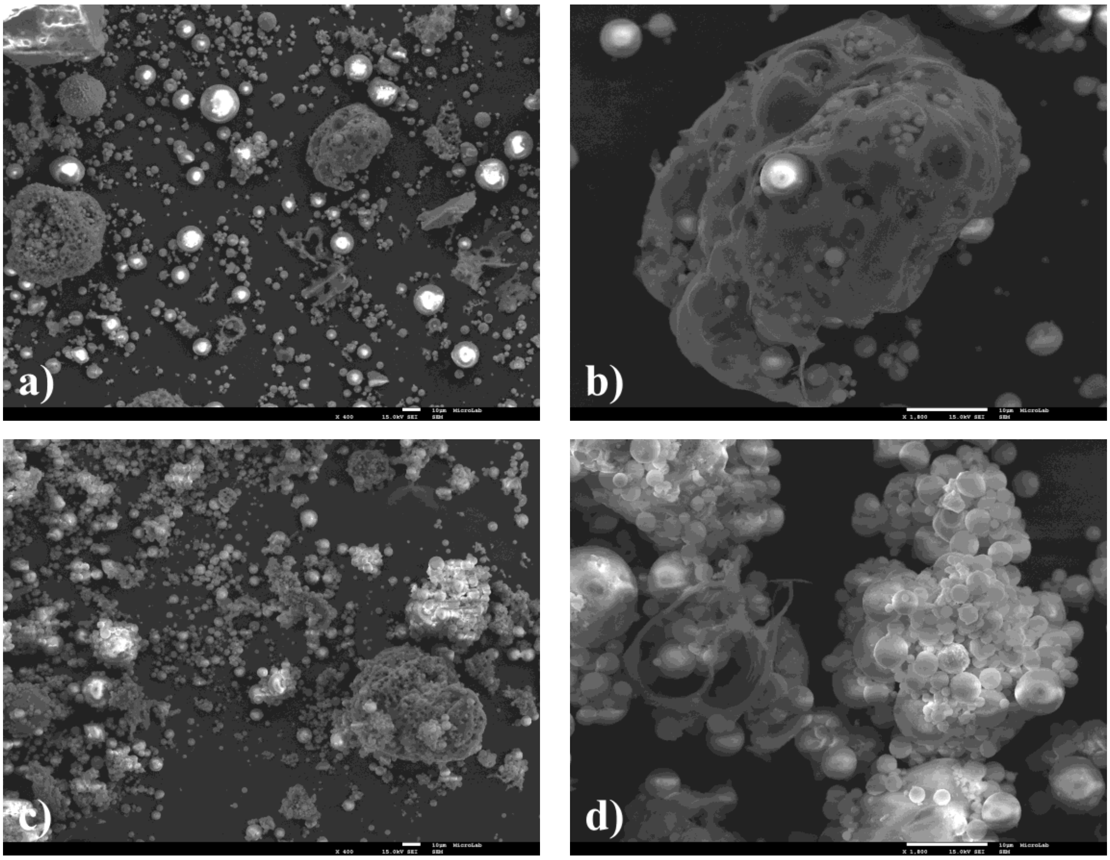
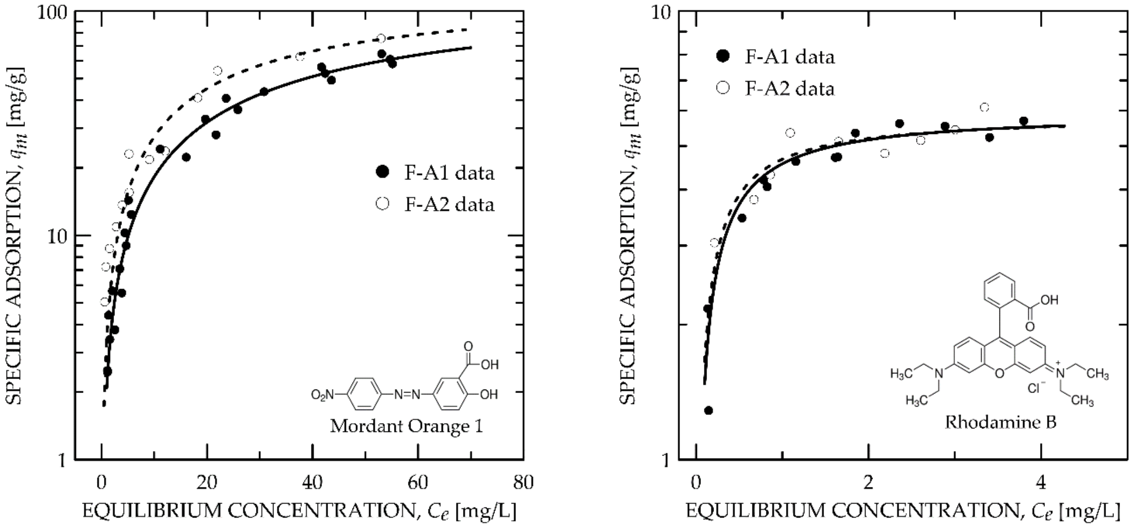


Fig. 2 SEM micrograph images of coal fly-ash samples. F-A1: (a) and (b); F-A2: (c) and (d). Magnification: ×400 (a) and (c), ×1800 (b) and (d)

In **Fig. 3** is shown the adsorption isotherms of F-A1 and F-A2 fly-ashes corresponding to the adsorption of the dyes MO 1 (**Fig. 3a**) and RB (**Fig. 3b**).



(a) Mordant Orange 1

(b) Rhodamine B

Fig. 3 Adsorption isotherms at 30ºC of MO 1 (a) and RB (b) on coal fly-ashes F-A1 and F-A2. Symbols: experiments; Lines: data fit according to Langmuir relation (**Eq. 2**).

The experimental data of specific dye adsorption q_e [mg/g] represented in the adsorption isotherm plots (**Fig. 3)**, is calculated according to **Eq. 1**,

$$q_e = \frac{V}{w} (C_0 - C_e) \tag{1}$$

where (C_0 - C_e) is the difference between, respectively the initial and equilibrium concentration of the dye in solution [mg/L], w is the mass of the fly-ash [g] and V is the volume of the dye solution [L].

The experimental data were modelled according with the Langmuir relation (**Eq. 2**) where q_m is the adsorption capacity [mg/g] and K_L is the Langmuir constant [L/mg].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

The adsorption experimental data, processed by Langmuir isotherm model, is presented in **Fig. 3** through the depicted curves. The numerical results of the application of this model are presented in **Table 2**.

Table 2 Langmuir isotherm coefficients (at 30ºC) for the adsorption of Mordant Orange 1 and Rhodamine B on coal fly-ashes F-A1 and F-A2

Adsorbate	Adsorbent	q_m [mg/g]	K_L [dm^3/mg]
MO 1	F-A1	127 ± 18	0.016 ± 0.003
	F-A2	125 ± 16	0.028 ± 0.006
RB	F-A1	5.95 ± 0.33	3.30 ± 0.88
	F-A2	5.86 ± 0.39	3.93 ± 1.47

From the magnitude of the Langmuir coefficients presented in **Table 2** it is possible to predict a significantly different performance of the fly-ashes in the adsorption of the dyes tested. At 30ºC, data indicates an adsorption of MO 1 dye markedly higher than the one of RB dye. This notorious difference, almost 20× higher, is related with different nature and chemical behaviour of the dye molecules. Rhodamine B is a basic cationic dye and mordant orange 1 is an acid anionic dye. Performing the adsorption at a pH value below the pH_{PZC} the adsorbent acquires positive charge interacting preferentially with the anionic dye [19].

Minimal differences were obtained in the adsorption capacities of the two adsorbent types (F-A1 and F-A2). Although, for MO 1 the deviation detected in the q_m values associated to F-A1 and F-A2 samples, may be attributed to the differences in fly-ash composition, namely the carbon content and textural characteristics.

4. Conclusions

Two types of coal fly-ashes residues (F-A1 and F-A2) were tested as adsorbent of two distinct dye molecules (MO 1 and RB) in aqueous solutions. The F-A1 is a marketable material to the cement industry while the F-A2 is not a commodity being deemed as a landfill residue. The Langmuir isotherm model was used to describe the adsorption phenomena of dyes by the fly-ash powder. Experimental data demonstrate an identical behaviour of F-A1 and F-A2 as adsorbent to the same substrate (MO 1 and RB). The fly-ash adsorption capacity is highly dependent on the adsorbate chemical nature (type of interaction). Further work should be performed on characterization of the fly-ashes types and evaluating different parameters affecting the process.

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