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Mechanochemical Processing of Blast Furnace Slag for its Reuse as Adsorbent

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Mechanochemistry is a very interesting branch of chemistry for its potentiality in processes of environmental relevance. In this work, an innovative application has been proposed, namely to mechanochemically treat a blast furnace slag to be reused as a low-cost adsorbent. In particular, the adsorptive properties of this industrial waste towards methylene blue present in aqueous solutions have been considered. To this end, the slag has been treated in a planetary mill at different charge ratios, rotational speeds and milling times, and then characterized by laser granulometry, porosimetric and XRD analyses. These investigations allowed to shed light on the interrelationships between milling conditions and slag physico-chemical characteristics, and to choose the most interesting samples to submit to the following adsorption equilibrium and kinetic tests. These runs have been conducted at different dye initial concentration and adsorption times, and results have been interpreted according to the previously-analyzed slag characteristics. Furthermore, adsorption data have been post-processed to give values for the equilibrium and kinetic constants, the removal efficiency and the characteristic adsorption times.

1. Overview

Mechanochemistry makes use of mechanical energy to promote chemical reactions and is often referred to as high-energy milling. Although used since time immemorial, mechanochemistry only became of scientific interest in the early years of the 20th century (Suryanarayana, 2001). The applications of mechanochemistry, initially in the fields of mineral processing and mechanical alloying, nowadays extend to the production of advanced materials characterized by mechanochemically-induced highly far-from-equilibrium state and metal oxides of spinel structure type. In the last twenty years, mechanochemistry has earned renewed interest due to its potential use in waste transformation processes in environmental engineering. Indeed, materials containing asbestos can be mechanochemically treated to convert toxic asbestos fibres into a non-toxic amorphous form (Plescia et al., 2003). Furthermore, mechanochemistry has proved to be effective in the detoxification of materials containing polycyclic aromatic hydrocarbons, organohalide compounds (Zhang et al., 2010), aliphatic hydrocarbons (Cioffi et al., 2008) and expired pharmaceuticals (Andini et al., 2012). In all the above-cited cases, mechanochemical treatment is a relatively cheap process that can be carried out at ambient temperature and pressure and more importantly, yields non-toxic end products. On the contrary, alternative processes may require much more sophisticated equipment and dangerous operating conditions or may lead to a large mass and volume increase in the treated waste, such as in the case of applications concerning MSWI ash (Cioffi et al., 2011; Colangelo et al., 2012) and FBC ash (Montagnaro et al., 2008, 2009). In addition to promoting chemical reactions, high-energy milling has the potentiality to modify the properties of certain materials thus making them more suitable for specific applications. To this regard, it has been proved that high-energy milling activation significantly improves the performance of cement-based materials (Sobolev, 2005), enhancing both the adsorption capacity (Stellacci et al., 2009a) and the pozzolanic reactivity (Stellacci et al., 2009b) of coal fly ash and offers at the same time, innovative options for the management of wastes. Furthermore, the adsorption capacity of basic oxygen furnace slag, the final waste product in the steel making process,

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against three synthetic textile dyes was enhanced after grinding with a high-energy vertical planet ball mill and subsequent activation with hydrochloric acid (Xue et al., 2009). The interest towards the adsorption properties of waste materials and the use of high-energy milling as an improvement tool has increased recently since low-cost adsorbents can be obtained in this way. In the literature, the need for alternative sorbents rather than activated carbons has been widely highlighted, as in the case of clinoptilolite (Dizadji et al., 2012) and bauxite (Lavecchia et al., 2012). In this context, blast furnace slag (BFS) has received a good deal of attention, for example studying the adsorptive properties of BFS against some water pollutants such as phosphates, heavy metals and organic dyes. Among these, methylene blue (MB) is one of the synthetic dyes most commonly used by textile industries that can easily be found in water discharges. MB can have several harmful effects when ingested or inhaled. For this reason, many papers can be found in the literature on the removal of MB using low-cost adsorbents such as fuel oil fly ash (Andini et al., 2008) and coal combustion ash (Montagnaro and Santoro, 2009). In this work, the following innovative application has been studied, namely to use high-energy milling to enhance the adsorptive properties of BFS towards MB. Specifically, the effects of milling time and speed as well as charge ratio (milling bodies to sample weight ratio) are investigated.

2. Experimental

An Italian cement company located in the Tuscany area supplied the BFS used in this study. The chemical characterization of the raw material, obtained by X-ray fluorescence analysis, shows significant presence of both the silico-aluminous (SiO_2+Al_2O_3) fraction (fuel-derived, 45 %) and the dolomitic (CaO+MgO) fraction (fluxing agent-derived, 51 %). Solid materials were characterized by: laser granulometric analysis, performed by a Malvern Instruments Master Sizer 2000 granulometer (operated down to a minimum particle size of 0.02 μm); porosimetric analysis, carried out by a Sorptomatic 1990 apparatus (operated in the pore size range 0.25–1500 nm); X-ray diffraction (XRD), performed by a Bruker D2 Phaser diffractometer (operated at diffraction angles ranging between 10 and 60 °2θ with a scan velocity equal to 0.02 $°2\theta\ s^{-1}$). Liquid solutions after adsorption tests were analyzed by UV spectrophotometry, by means of a UV/VIS Jasco V-550 apparatus, to obtain the MB concentration. The BFS was mechanochemically activated via room-temperature treatment in a Fritsch Pulverisette 6 planetary mill, equipped with a tungsten carbide (WC) grinding set. Operational parameters were: the charge ratio C_R (defined as the weight ratio milling balls/BFS) was set at either 50 or 100; the rotational speed v was set at either 300 or 600 rpm; the milling time t_M ranged between 15 and 120 min. MB adsorption thermodynamic and kinetic tests were conducted at room temperature. A sorbent amount of 1 g was contacted in a stirred beaker with an aqueous solution having a volume of 0.1 L and MB initial concentration ranging from 10 to 1000 mg L^{-1} (thermodynamic tests) or equal to 1000 mg L^{-1} (kinetic tests). Preliminary investigations indicated that an adsorption time (t) of 48 h was needed to reach equilibrium conditions, while times ranging from 15 min to 48 h were used for kinetic runs. After each test, liquid solutions were filtered and analyzed to determine the MB concentration and, therefore, the specific adsorption capacity, expressed as mg of MB captured per 1 g of sorbent. The adsorption isotherm and kinetic curves were obtained and then described by the linearized forms of the Langmuir and pseudo-first order Lagergren equations, respectively (see Balsamo et al., 2011, 2012, for details). Moreover, after thermodynamic tests the efficiency curves were evaluated and expressed the MB removal efficiency vs. the pollutant-to-sorbent mass ratio.

3. Mechanochemical activation treatments: results and discussion

The raw BFS was characterized by an absolute particle size distribution showing a mean Sauter diameter (d_S) of 4.0 μm and that particles finer than 0.2 μm and coarser than 130 μm were absent. From the cumulative particle size distribution, a d_{50}-value (the particle diameter for which 50 wt% of the material is finer) of 13.4 μm could be observed. Results concerning d_S and d_{50} are reported, for BFS and for all the milled materials, in Table 1. For treatments carried out at v=600 rpm, it can be argued that: (i) each mechanochemical treatment determined a reduction in both d_S and d_{50}, down to 2.5 and 7.1 μm, respectively; (ii) the agglomeration phenomena induced by the BFS residence for t_M longer than 60 min (at fixed C_R) led to a renewed increase of the mean particle sizes; (iii) similar reasons could be invoked in explaining the similar trend observed for greater C_R-values (at fixed t_M). Moreover, the same effect was also observed when increasing either v (by holding C_R) or vice versa for treatments carried out at fixed t_M (60 min). In the last case, d_S and d_{50} as low as 1.8 and 3.8 μm were obtained, respectively. Therefore, the smaller C_R-value (50) and v-value (300 rpm) seemed to give rise to a treated BFS characterized by the finer particle sizes. To optimize the mechanochemical treatment, further characterization was carried out by milling the BFS sample (by holding C_R and v at their lowest values) for different t_M.

Table 1: Values of d_S and d_{50} (μm) for raw BFS and for BFS milled under different operating conditions.

	raw BFS			
d_S	4.0			
d_{50}	13.4			
	by holding v=600 rpm			
	C_R=50; t_M=60 min[a]	C_R=50; t_M=120 min	C_R=100; t_M=60 min[b]	C_R=100; t_M=120 min (BFS/χ)
d_S	2.5	2.7	3.2	3.1
d_{50}	7.1	8.0	10.0	11.2
	by holding t_M=60 min			
	C_R=50; v=300 rpm[c]	C_R=50; v=600 rpm[a]	C_R=100; v=300 rpm	C_R=100; v=600 rpm[b]
d_S	1.8	2.5	2.2	3.2
d_{50}	3.8	7.1	4.8	10.0
	by holding C_R=50 and v=300 rpm			
	t_M=15 min (BFS/α)	t_M=60 min[c]	t_M=120 min	
d_S	1.8	1.8	2.0	
d_{50}	3.3	3.8	4.4	

[a, b, c] Denote 'same sample'.

Results in Table 1 did confirm that the shorter t_M the finer the milled particles. Two samples characterized by the two extreme operating conditions can be identified: the first (BFS/α) treated under the mildest conditions (C_R=50, v=300 rpm, t_M=15 min) and having d_S=1.8 μm and d_{50}=3.3 μm; the second (BFS/χ) treated under the strongest conditions (C_R=100, v=600 rpm, t_M=120 min) and having d_S=3.1 μm and d_{50}=11.2 μm (values quite close to those of the untreated raw sample). The former (BFS/α) has the best-exposed contact surface, a relevant feature when considering BFS as a possible sorbent; the worst behavior characterizes BFS/χ. To investigate the increase in solid porosity related to the milling treatment, the porosimetric analysis results are here discussed. While the untreated material showed a total specific porosity of 23.9 mm^3 g^{-1}, this value slightly increased (64.2 mm^3 g^{-1}) for BFS/χ and was strongly enhanced (596.3 mm^3 g^{-1}) for BFS/α. The increase in the specific porosity appeared to be particularly relevant in the mesoporosity (2–50 nm) region: values of 14.9, 29.8 and 188.5 mm^3 g^{-1} were obtained for BFS, BFS/χ and BFS/α, respectively. The specific surface area for raw BFS (7.0 m^2 g^{-1}) was barely affected by the strongest activation treatment (8.0 m^2 g^{-1}), but significantly by the mildest one (15.5 m^2 g^{-1}). These results show that the strongest mechanochemical operating conditions led to agglomeration phenomena not only detectable on the particle scale (as revealed by particle size analysis), but also at a microstructural level. Again, experimental results reinforce the consideration that BFS/α is the most promising material to be used as a sorbent. The XRD spectra for raw BFS, BFS/α and BFS/χ showed that the untreated material was characterized by a highly amorphous structure (only a calcite peak was detected, related to the presence of limestone as a fluxing agent in the parent reactor) and that the mechanochemical treatment increased the solid amorphous content: for BFS/α, the calcite peak had a smaller intensity, and it was no more detectable in BFS/χ. This last sample also showed the unwanted presence of WC-contaminations (Zhang et al., 1991), due to the prolonged contact of the waste with the milling bodies. This adds to the case for opting for BFS/α as a potential sorbent.

4. Adsorption tests: results and discussion

Figure 1 reports the results of the equilibrium tests concerning MB adsorption on raw BFS and BFS/α. Both isotherms were Langmuir-like, thus suggesting a monolayer-type MB adsorption on solid surfaces. It is observed that, at fixed C_e-values (where C_e is the MB equilibrium concentration), the equilibrium specific adsorption capacity q_e was greatly higher for BFS/α. This could be particularly relevant in more dilute solutions to be treated since, for BFS/α, q_e assumed satisfactory values even at low C_e, as opposed to what happened for the raw blast furnace slag. Linearization of the adsorption isotherms according to the Langmuir model (R^2 was as high as 0.98) allowed to estimate the values of the adsorption equilibrium constant: it was increased about 7-times (from 0.037 to 0.258 L mg^{-1}) by the activation treatment. This again underlines a more favourable MB adsorption for the treated waste thanks to the greater exposed contact surface and specific mesoporosity, together with the absence of evident agglomeration phenomena, induced by the mildest mechanochemical treatment.

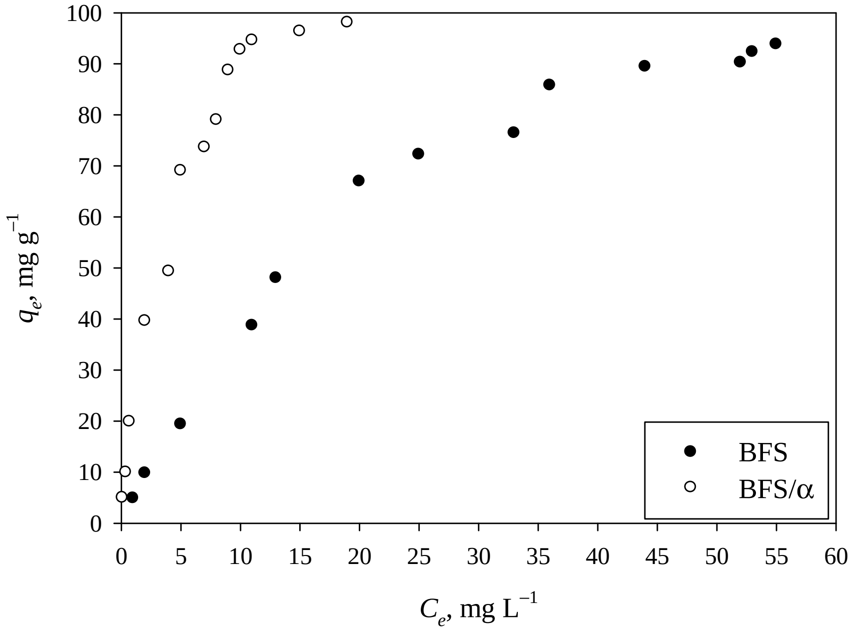

Figure 1: Isotherms for methylene blue adsorption under equilibrium conditions on raw BFS and BFS/α.

Figure 2 (Up) shows the removal efficiency (η) curves: η-values were in all cases very high, and decreased as P/S (the pollutant-to-sorbent mass ratio) increased from 98.0 % (P/S=5 mg g^{-1}) to 94.5 % (P/S=100 mg g^{-1}) for BFS, from 99.8 % (P/S=5 mg g^{-1}) to 98.1 % (P/S=100 mg g^{-1}) for BFS/α. This confirmed, on the one hand, the better sorptive behaviour of BFS/α and, on the other hand, that this waste is a very interesting low-cost sorbent with very high MB removal efficiency especially for systems characterized by low pollutant concentrations (i.e., low P/S values). Kinetic results are reported in Figure 2 (Down). After each adsorption time, values of the specific adsorption capacity (q) were higher for BFS/α, and this is particularly evident for shorter t-values. Linearization of the adsorption kinetic curves according to the Lagergren model (R^2 as high as 0.98) allowed the evaluation of the specific kinetic constant, equal to 1.3×10^{-3} and 1.7×10^{-3} min^{-1} for BFS and BFS/α, respectively. An analysis of the characteristic times for the adsorption process now follows, according to the path drawn in previous papers (Balsamo et al., 2011, 2012). The time for external fluid-to-particle mass transfer and that for MB macropore diffusion can be expressed as a function of d_S, the Sherwood number (set equal to 2), the MB diffusivity in water (on the order of 10^{-9} m^2 s^{-1}) and the MB diffusivity in macropores (known once fixed the particle porosity and mean pore radius from the porosimetric analysis results): both times assume negligible values with respect to the times experienced by the systems under investigations. The time for micropore diffusion, τ, can be estimated as:

$$\tau = \frac{(d_S/4)^2}{D_{micro}} \tag{1}$$

where D_{micro}, the MB effective diffusivity in micropores, is obtained through the Reichenberg equation:

$$\ln\left[1-\left(\frac{q(t)}{q_{max}}\right)^2\right] = -\frac{4\pi D_{micro}}{d_S^2}t \tag{2}$$

In Eq. (2), q_{max} is the maximum specific adsorption capacity. If the LHS of Eq. (2), derived from kinetic runs, is plotted against t, it is possible to estimate the effective diffusivity in micropores (on the order of 10^{-17}–10^{-18} m^2 s^{-1}) and, therefore, τ (on the order of tens of hours), a value fully comparable with the time experimentally needed to reach equilibrium conditions. This should underline the building-up of a micropore diffusion-controlled regime for the systems under investigation.

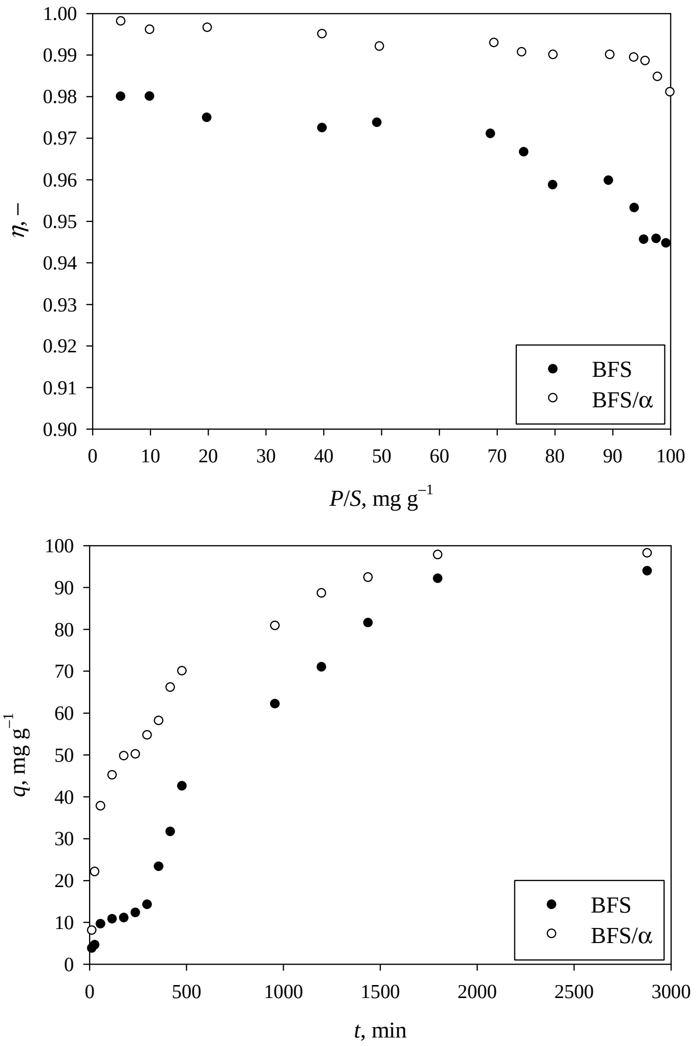

Figure 2: Up: removal efficiency vs. pollutant-to-sorbent ratio for methylene blue adsorption under equilibrium conditions on raw BFS and BFS/α. Down: kinetic curves for methylene blue adsorption on raw BFS and BFS/α.

5. Conclusions

Mechanochemical activation treatments results for the blast furnace slag under investigation showed that the sample milled under the mildest conditions, with respect to that milled under the strongest conditions, was characterized by: (i) best exposed contact surface; (ii) greater specific mesoporosity and surface area; (iii) absence of contamination and agglomeration phenomena. This means that the more extreme milling conditions were able to induce agglomeration (‘cold-sintering’) phenomena detectable both on the particle scale and at a microstructural level. These results were very significant in suggesting the best milling operating conditions for the slag reuse as a low-cost adsorbent towards methylene blue present in aqueous solutions. The mechanochemical activation treatment appeared useful in enhancing the dye sorption behaviour of the raw slag: (i) specific adsorption capacities for the activated waste were greater than for the parent material, especially for dilute solutions and shorter adsorption times; (ii) pollutant removal efficiencies under equilibrium conditions were always greater than 94 %; (iii) the adsorption equilibrium and kinetic constants were increased by a factor of nearly 7 and 1.3, respectively, when comparing the treated and raw slag. Furthermore, an analysis of the characteristic times for the adsorption processes revealed the building-up of a micropore diffusion-controlled regime for the systems under investigation.

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