Short Term Mobility CNR Bando 2017

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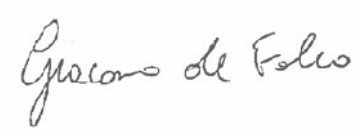
Relazione Finale

Abstract

Il dr Giacomo de Falco, vincitore della Short Term Mobility 2017 (protocollo numero 0080842/2017 del 07/12/2017- CUP B53C17001430005), ha svolto un soggiorno di ricerca nel mese di Febbraio 2018 presso il City College of New York a New York City (USA) nel gruppo di ricerca guidato dalla professoressa Teresa J. Bandosz, dedicandosi ad attività sperimentale nel campo dello sviluppo di sorbenti altamente porosi funzionalizzati per la rimozione di formaldeide, composto inquinante presente in aria indoor. Nello specifico, è stata condotta la sintesi di nuovi sorbenti quali carboni attivi funzionalizzati con gruppi contenti azoto e zolfo e sono stati svolti test d'adsorbimento di formaldeide su tessuti di carbone ingegnerizzati.

Parte dell'attività di ricerca svolta al City college of New York risulta in via di pubblicazione in un contributo su rivista internazionale del settore, e si prevede di proseguire l'attività di collaborazione scientifica con il gruppo operante all'IRC-CNR di Napoli.

Napoli, il 22/03/2018



1. Introduction

Formaldehyde, HCHO, is one of the most common toxic pollutants found in indoor air. Formaldehyde has been classified as a human carcinogen, as it causes nasopharyngeal cancer, pulmonary damage and probably leukaemia[1]. As a consequence, the World Health Organization (WHO) has fixed the exposure limit to formaldehyde at 0.08 ppm for 30 min[2]. The removal of HCHO from air via adsorption offers numerous advantages related to the operating flexibility of this purification technology coupled with generally low costs. In particular, activated carbons (AC) are extensively used as adsorbent for removing HCHO from air because of their properties, such as high surface area and surface chemistry that play an important role. There are only few reports addressing adsorption of formaldehyde on activated carbons, AC[3]. To increase the formaldehyde adsorption on carbons, modifications with amides have been explored[4]. As an example, Lee et al. studied the adsorbent behavior of seven different activated carbon[5]. The measured adsorption capacities were in the range of 0.01 to 0.478 mmol g^{-1}. These different adsorption capacities were attributed to the surface functionalization groups in particular to high presence of nitrogen groups. My objective of the short term mobility was to investigate in details the effects of surface heterogeneity, chemical and textural, on the formaldehyde retention on the highly porous sorbent. In particular, the STM was focused on i) HCHO adsorption tests on carbon textiles. ii) synthesis of different sorbents, functionalized activated carbon and poly-derived carbon. Only a partial investigation was possible: textural proprieties of fresh sorbents and HCHO adsorption in dry condition. Future tests were carried out in order to fully characterized the adsorption properties of these sorbent.

2. Materials and methods

2.1. Materials

2.1.1 Carbon textile

The carbon textile was received from the U.S. Army Natick Soldier Research, Development & Engineering Center. It is composed of an inner porous carbon layer and outer nylon layer, after the removing of nylon is referred to this sorbent as CC. Four different functionalized sorbents were studied for HCHO adsorption obtained from dicyandiamide (D), penicillin G (P), thiourea (T), or urea (U), respectively.The obtained samples are referred to as CC-D, CC-P, CC-T and CC-U, where last letter represents the modifier. A CC thermally treated at 800°C under inert flow is referred as CC-HT.

2.1.2 Activated carbons

Different sorbents were prepared for HCHO adsorption tests: two commercial activated carbons BAX-1500 (wood based carbons-Westvaco, indicates as BAX AC) and S208 (coconut shell based carbon-Waterlink Barnabey and Sutcliffe, indicates as S208 AC), a polymer-derived carbon and two functionalized activated carbons. To obtain the polymer derived carbon was used as precursor Poly(sodium 4-styrene sulfonate), it was carbonized at 800 °C, heating rate was 10 °C min^{-1}, for 40 min under nitrogen flow (100 mL min^{-1}), in a horizontal furnace. The carbon was extensively washed after the synthesis to remove the excess of sodium. This polymer-derived carbon is referred to as C2. In order to realize the two functionalized carbons, thiourea and melamine were dispersed on BAX AC. BAX AC was soaked by a thiourea suspension (mass ratio=1:1) in water overnight or a melamine suspension (mass ratio=1.5:1) in ethanol for 5h, both suspensions were under stirring at room temperature. The mixtures were then boiled until the evaporation of the water or alcohol and dried at 120 °C. The following step, for both sorbents, was heated at 950 °C in inert atmosphere (nitrogen). The heating rate was set to 10 °C min^{-1} and maintained at 950 °C for 30 min. Then the samples were washed in a Soxhlet apparatus to remove the excess of the oxidizing agent and water-soluble

compounds (10 days). The last step was to dry the sorbents in an oven at 100 °C. The samples were referred as BAX-T AC and BAX-M AC for thiourea and melamine precursors, respectively.

2.2 Methods

2.2.1 HCHO adsorption tests

Adsorption of HCHO at dynamic conditions was carried out at ambient pressure and *T*=25 °C. A glass column of an internal diameter 9 mm was filled with approximately 0.130 g of carbon textiles cut in little pieces and with about 1 cc of activated carbons (mass sorbents are around 0.3 g for activated carbon and 0.130 g for C2). The bed height was 2.7 cm. Formaldehyde was generated by a calibrated formaldehyde permeation tube (Metronics, Inc.) using a Dynacalibrator® (Model 150, Metronics, Inc.) operated at 80 °C with 100 mL min^{-1} nitrogen as a carrier gas. The outlet flow from the generator, before reaching the testing column, was mixed with 400 mL min^{-1} of air, dry (passing through $CaSO_4$ to totally remove any humidity) or moist of 70% humidity (passing through a water bed). The inlet flow rate of a challenge gas was set to 500 mL min^{-1}, the inlet concentration of formaldehyde (C_{HCHO}^{in}) was set to approximately 1 ppmv. Before running experiments in the moist conditions (only for the carbon textile), the adsorbent bed was prehumidified for 1 hour with moist air (500 mL min^{-1}). The samples after exposure to moist air were weighted and the weight difference represents the amount of water adsorbed. Gas analysis was performed with a continuous analyzer equipped with an electrochemical sensor (RM 16 Interscan Corporation) with accuracy of 2% of the reading value (working range of analyzer 0–2 ppmv of formaldehyde). The specific adsorption capacity of HCHO at saturation, ω_{ads} [mg g^{-1}], was determined through the integration of the area above the breakthrough curve using the flow rate, concentration of HCHO, time and mass of the adsorbent material.

2.2.2 Sorption of Nitrogen

The textural proprieties of the activated carbon samples and C2 were determined by N_2 adsorption measured on an ASAP 2020 (Micromeritics) at 196 °C. All the samples were degassed at 120 °C to a constant vacuum (10^{-4} Torr). BET method was used to determine the specific surface area (S_{BET}), while the total pore volume, V_{tot}, was calculated from the Gurvitsch's rule using the last point of the isotherms and the micropore volume, V_{μ}, and pore size distribution were calculated using nonlinear density functional theory, 2D-NLDFT, which assumes the heterogeneity of the pore sizes.

3. Results

3.1 HCHO adsorption tests on carbon textiles

The formaldehyde (HCHO) breakthrough curves measured in the dry conditions on the carbon textiles are collected in Figure 1A. From the breakthrough curves, the dynamic data and corresponding adsorption capacities at saturation were determined and the results are summarized in Table 1, in which t_{br} [min] is the breakthrough point time (assumed as the time for which the ratio of the HCHO concentration at the bed outlet relative to that in the feed is 0.05), ω_{ads} [mg g^{-1}] is the HCHO breakthrough capacity and C_{HCHO}^{in} [ppmv] is the inlet concentration of HCHO in the fixed bed reactor. Since in some cases, even after a very long experimental time, the bed saturation was not reached, the HCHO capacity at $\frac{C}{C^{in}} = 0.95$ was arbitrary chosen for the performance comparison. CC and CC-HT revealed similar dynamic behaviors, even though the breakpoint time for CC-HT is longer than that for CC. They show relatively fast kinetics of the adsorption process and similar saturation capacity (ω_{ads}=0.56 and 0.53 mg g^{-1} for CC and CC-HT, respectively). The heat treatment, which was expected to remove even traces of the residual nylon and/or modify fibers, did not affect the adsorption capacity.

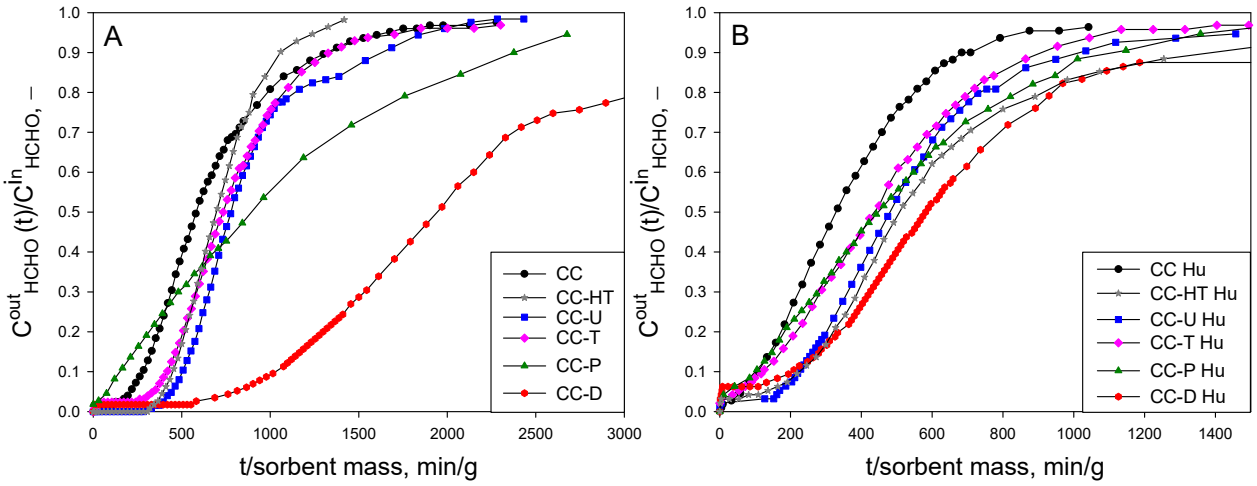


Figure 1. HCHO breakthrough curves measured in dry (A) and moist (B) conditions (designed with the symbol Hu).

All chemically modified carbon textiles exhibit better performance as HCHO adsorbents than their unmodified counterparts (CC and CC-HT). Interestingly the breakthrough curve of CC-P differs markedly from those of the other textiles, which suggests different mechanisms of HCHO adsorption. The saturation capacities ω_{ads} of CC-T, CC-U, CC-P and CC-D are 20, 30, 44 and 170% greater, respectively, than that for CC. The best adsorbent is CC-D whose t_{br} value equals to 109 min, and the saturation capacity reaches 1.56 mg g^{-1}. CC-P is characterized by the shortest breakpoint time with respect to the others functionalized samples (12 min) but its saturation adsorption capacity is bigger than those of CC-U and CC-T.

Figure 1B shows the HCHO breakthrough curves measured in the moist conditions (samples are denoted with "Hu") for the modified carbon textiles; the corresponding adsorption capacities and t_{br} values are listed in Table 1. As seen, the presence of moisture on the surface and in the challenge gas markedly decreased the performance of the materials tested as HCHO adsorbents.

Table 1. The parameters of the HCHO adsorption performance of the carbon textiles studied.

Sorbent	C^{in}_{HCHO} [ppmv] Dry	ω_{ads} [mg g^{-1}] Dry	t_{br} [min] Dry	C^{in}_{HCHO} [ppmv] Moist	Water adsorbed [mg g^{-1}]	ω_{ads} [mg g^{-1}] Moist	t_{br} [min] Moist
CC	1.25	0.56	29	1.10	311	0.27	7
CC-HT	1.12	0.53	50	0.95	325	0.34	13
CC-U	1.25	0.73	55	0.94	303	0.33	18
CC-T	1.28	0.68	47	0.95	244	0.29	6
CC-P	1.10	0.80	12	0.96	252	0.34	3
CC-D	1.15	1.56	109	0.95	252	0.53	3

The effect of water is visualized in Figure 2. Even though its presence worsens the performance, the extent of the decrease differs. Thus, the most pronounced effect was found for the best performing sample CC-D and the least- for CC-HT. It is likely caused by 1) occupation of HCHO adsorption centers by water during the

prehumidification and/or 2) competition between water and HCHO for these centers[6]. All functionalized sorbents adsorbed considerable amounts of water (Table 1) that can block the micropores which would be otherwise accessible to HCHO, limit the diffusion of the pollutant gas inside the pore structure, and in this way decreasing the adsorption capacity. This decrease occurs even though some amount of HCHO is expected to be dissolved in the adsorbed water film. Nevertheless, no direct dependence between the amount of water adsorbed and the decrease in the saturation capacity was found.

3.2 First investigations on activated carbon

Figure 2 reports breakthrough curves for formaldehyde (HCHO) adsorption tests carried out at room temperature in dry conditions on the activated carbons, functionalized and not, and the polymer (C2). From the breakthrough curves, the dynamic data and corresponding adsorption capacities at saturation were determined and the results are listed in Table 1. Since the bed saturation was not reached, even after a very long experimental time, the HCHO capacity at $C_{HCHO}^{OUT}(t)/C_{HCHO}^{IN} = 0.8$ was arbitrary chosen for the comparison of the data.

Fig. 2 shows the outlet HCHO concentration profiles, in dry condition, of raw BAX AC and S208 AC have steeps slopes corresponding to a rapid saturation of the sorbents. Moreover, both raw activated carbons are characterized by almost the same breakpoint time (t_{br}), 8 and 9 min for BAX AC and S208 AC respectively, but S208 AC exhibits a greater adsorption capacity. In particular, ω_{ads} is greater of 25% comparing to BAX AC. C2 shows similar adsorption capacity of S208 AC but it is characterized by a longer t_{br} about 55% greater compared to the t_{br} of S208 AC. The functionalization treatment by thiourea and melamine of BAX AC resulted into a significant increase in both the quantitative parameters of adsorption with respect to BAX AC, the breakpoint time increase from 9 min to 25 and 59 min and the adsorption capacity reach values equal to 0.4 and 0.66 mg g^{-1} for BAX-T AC and BAX-M AC respectively. In Table 3 is listed the structural parameters of the fresh samples derived by sorption on nitrogen.

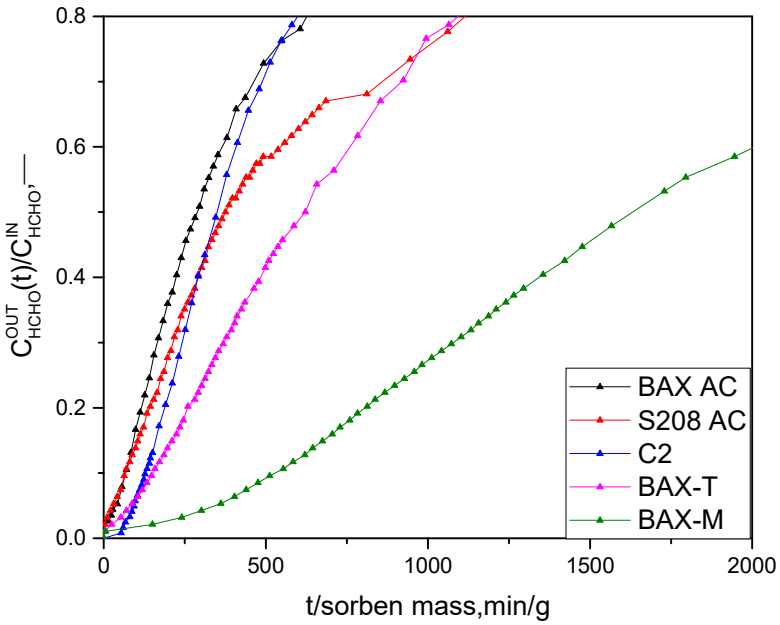


Figure 2. Breakthrough curves of HCHO obtained in dry condition for the activated carbons.

Table 2. HCHO adsorbents performances in dry and moist conditions of the carbons studied.

Sorbent	C_{HCHO}^{IN} [ppmv] Dry	ω_{ads} [mg g^{-1}] Dry	t_{br} [min] Dry
BAX AC	1.14	0.25	8
S208 AC	0.94	0.31	9
C2	1.22	0.31	14
BAX-T AC	0.94	0.40	25
BAX-M AC	0.94	0.66	59

Table 3. Textural proprieties of initial carbons studied.

Sorbent	S_{BET} [m^2 g^{-1}]	V_{TOT} [cm^3 g^{-1}]	$V\mu$[cm^3 g^{-1}]	$V\mu_{<7\,Å}$[cm^3 g^{-1}]	$V\mu_{<10\,Å}$ [cm^3 g^{-1}]
Fresh sorbents					
BAX AC	2175	1.32	0.73	0.10	0.26
S208 AC	1042	0.50	0.47	0.24	0.34
C2	433	0.40	0.17	0.08	0.14
BAX-T AC	1288	0.72	0.50	0.17	0.29
BAX-M AC	1558	0.90	0.58	0.19	0.32

BAX AC show a high BET surface area equal to 2175 m^2 g^{-1} and it is characterized by the presence of micropores ($\frac{V\mu}{V_{TOT}}$=55%) and mesopores with characteristic peaks at 0.65, 1.1,1.9 and 3.6 nm. After the functionalized treatment with thiourea and melamine the sorbents show a decrease in their surface area down to 1288 and 1588 m^2 g^{-1} (BAX-T AC and BAX-M AC, respectively), but an increase of $V\mu_{<7\,Å}$ probably related to the thermal treatment after the deposition of the active phase. Moreover, we observe the disappear of the peak at 1.1 nm for both functionalized sorbents and in general the surface and pore volume decrease (Table 2), for the deposition of the active phase that determines the pore blocking. In the case of C2, it has a BET surface area of 455 m^2 g^{-1} and it is characterized by the presence of microporous and mesoporous. Finally, S208 is predominantly microporous ($\frac{V\mu}{V_{TOT}}$=94%) and it shows a BET surface area of 1042 m^2 g^{-1}.

References

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