

TEXTURAL AND ADSORPTION PROPERTIES OF A CARBON- SILICA COMPOSITE ADSORBENT FOR AIR FILTRATION

Ebenezer Twumasi, Mikael Forslund, Peter Norberg and Christer Sjöström

Materials Technology, KTH Research School, Centre for Built Environment, University of Gävle, Sweden

Introduction

Air pollution in cities and urban areas has been a recognised problem since the beginning of the nineteenth century [1]. Molecular filtration is the term used to describe filtration (in air) of non particle species. The key to most static molecular filtration devices is the adsorbent. Typical adsorbents for air filtration include activated carbon, activated alumina, molecular sieves and silica gel [2,3]. Precipitated silicas are distinguished from silica gels by way of synthesis, BET surface area and pore size distribution [4]. A simplified preparation route [5] has been employed to make unimpregnated [6] and impregnated precipitated silica structure (PSS) pellets for adsorption of air pollutants. A characterisation of the unimpregnated pellets revealed a wide pore distribution (1-35 nm) with two maximum pore diameters of around 1.4 nm and of around 5.5 nm, a pore volume of 0.63 cm³/g and a BET surface area of 372 cm²/g [6]. In order to broaden possible applications of the material e.g. into physical adsorption of volatile organic compounds, the micropore volume could be enhanced by preparation of a PSS-carbon composite. Comprehensive studies on carbon-mineral composites by using different methods of preparation have been reported by several groups [7,8,9]. To avoid surface area reduction and to take advantage from a ready-made micropore structure, the present work has been concentrated on direct incorporation of coconut based activated carbon into different process steps of the preparation of the PSS.

The aims of this work were: i) to synthesize the carbon-silica composites by the simplified precipitation using three different routes to incorporate the carbon ii) to characterise the pore systems of the sample obtained in these three routes in comparison with the pore systems of the pure components and iii) to estimate the adsorption properties by subjecting the different composites to an air stream containing toluene.

Experimental

Materials

PSS: The basic preparation involves the following steps: 1. preparation of salt and water glass solutions, 2. mixing & coagulation, 3. washing, 4. filtration, 5. additives e.g. carbon, 6. casting and 7. drying [5]. The detailed recipe has been described elsewhere [6].

PSC: A coconut based activated carbon with a CTC value of 50 was grinded and sieved to a size < 500 micron. Three probable routes I-III for the composite formation was tested: (I) Activated carbon were added to step 5 and vigorously mixed for 30 minutes. At that time the carbon appeared to be fully dispersed. Activated carbon was mixed with (II) the salt solution or (III) with the water glass solution in step 1. In route II and III the carbon is present even before coagulation. The Precipitated Silica Carbon composites obtained were designated by an abbreviation; e.g. a composite made by method I containing 8 wt% carbon will be called PSC(I)-8

Surface and pore structure characterization

The nitrogen adsorption/desorption isotherms were measured by Micromeritics ASAP 2000 volumetric adsorption analyser. The

samples were degassed at 250°C in vacuum for 4 hrs. The BET (Brunauer-Emmet-Teller) standard equation was used to calculate the surface area (S_{BET}) from adsorption data obtained in the relative pressure (p/p_0) range of 0.03 to 0.3. The micropore surface area S_{mic} and micropore volume V_{mic} were obtained via t-plots [10]. The total pore volume (V_{tot}) was calculated from the amount of gas adsorbed at $p/p_0 = 0.99$ for PSS and PSC samples and $p/p_0 = 0.86$ for carbon. Pore size distribution were derived using (DFT) the density functional theory method assuming cylindrical pores-oxide surface model and cylindrical pore geometry. These were performed with the software of the apparatus.

Dynamical challenge test of toluene uptake

Adsorbent media may be tested by a challenge gas stream where the concentration is monitored upstream and downstream of the bed. One standardised test specifies a 25.4 mm high bed of 50 mm diameter subjected to a 100 ppm gas stream at a flow giving 0.1 s contact time in the bed [11]. The bed should be enclosed in a chamber capable of keeping the temperature at 23 ± 2 and the relative humidity (RH) at 50 ± 5 [11]. Here samples of ~30 g were formed into 52mm high beds and challenged with 3–8 ppm of toluene at 0.41s contact time during 46 hours at RH 50 ± 5 % and 22 ± 1 °C. Upstream and downstream concentrations were recorded and removal efficiency (%) and uptake (mg toluene) were calculated. Samples with 16 wt% carbon and pure PSS were tested.

Results and Discussion

Nitrogen physisorption

Nitrogen adsorption isotherms and pore size distribution for pure PSS, carbon and various PSC-16 series samples are presented in Fig.1 and the corresponding physicochemical parameters are summarized in Table 1. For all the PSC-16 samples and PSS the isotherms are of Type IIb with high nitrogen uptake in the p/p_0 range 0.03-0.3, typical of microstructure. This same pattern was observed in the case of PSC-8 sample series. The pure carbon exhibits type I isotherm [11]. The steep increase in nitrogen uptake was more pronounced in PSC(I)-16. All the composite materials obtained show an increase in BET area, micropore surface area and exhibit a higher micropore volume than pure PSS. The increase in micropore surface area was 3-46% in PSC(I), 29-48% in PSC(II) and 3-32% in PSC(III). It was observed that the total pore volumes are similar in PSC I and II irrespective of carbon content. In contrast to PSC(I) and PSC(II), the total pore volume of PSC(III)-8 was higher than PSC(III)-16. For PSC(I) and PSC(III) samples, the pore size distribution (Fig. 2) was wide (1-35nm) as in pure PSS, whereas PSC(II) samples exhibit narrow pore size distribution (1-4nm).The pore size distribution is narrow (1-2nm) for carbon. Therefore it appears that in PSC(I) and PSC(III) samples the pore systems was apparently subjected to silica pore structure whereas in PSC(II) the pore structure was dominated by carbon pore system. It can be observed (Fig.2c) that the PSC(II) maximum pore size (2.4nm) is located at an almost average position between higher

Table 1. Surface area and pore properties of pure PSS, carbon and composites synthesized

Samples	S _{BET} (m ² /g)	S _{mic} (m ² /g)	S _{mes} (m ² /g)	V _{tot} (m ³ /g)	V _{mic} (m ³ /g)	V _{mes} (m ³ /g)	d _{mic} (nm)	d _{mes} (nm)
PSS pure	372	44.5	327.5	0.63	0.021	0.609	1.41	8.3
Carbon	1020	829	193	0.50	0.423	0.077	1.54	0
PSC(I)-8	489	46	423	0.67	0.021	0.649	1.39	5.4
PSC(II)-8	512	82.5	429.5	0.70	0.042	0.658	1.39	5.4
PSC(III)-8	394	63.2	330.8	0.59	0.034	0.556	1.41	2.4
PSC(I)-16	391	86.3	304.7	0.55	0.049	0.501	1.41	2.4
PSC(II)-8	365	46.4	318.7	0.70	0.023	0.677	1.40	5.3
PSC(III)-16	408	65	277.4	0.58	0.033	0.547	1.41	5.4

S_{BET} - BET specific surface area, S_{mic} - t-plot micropore surface area, S_{mes} - mesopore surface area, V_{tot} - total pore volume, V_{mic} - micropores pore volume, V_{mes} - mesopores pore volume, d_{mic}, d_{mes} - micro-and mesopore size obtained as maxima peaks in NDFT pore size distribution

pore size 2nm for carbon and 6nm for pure PSS.

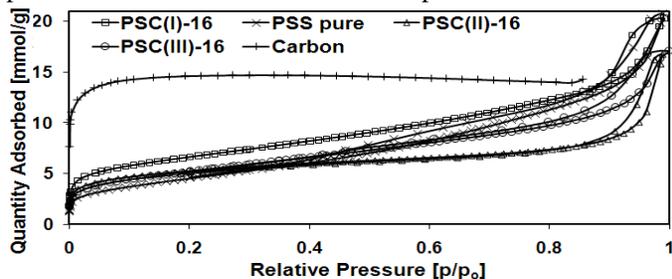


Fig 1: Nitrogen physisorption isotherms of carbon, PSS pure and PSC-16 composite samples.

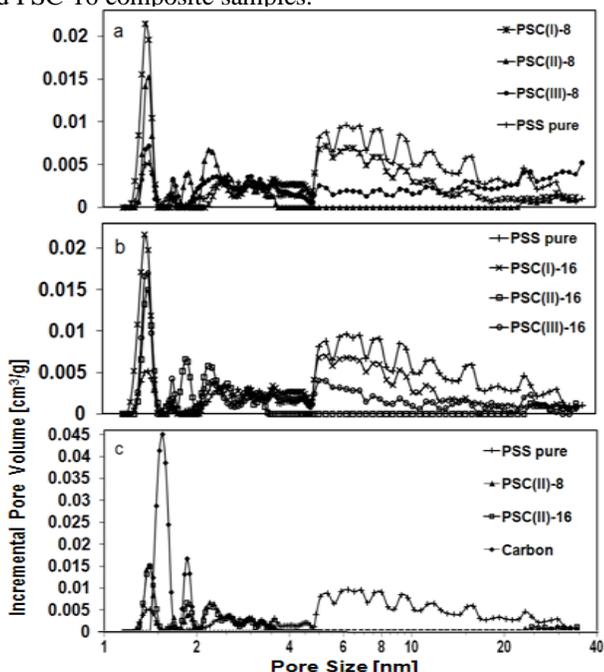


Fig. 2: DFT pore size distribution of (a) Pure PSS, PSC(I)-8, PSC(II)-8, PSC(III)-8 (b) Pure PSS, PSC(I)-16, PSC(II)-16 and PSC(III)-16 (c) Pure carbon, PSS, PSC(II)-8 PSC(II)-16

Toluene adsorption:

Upstream and downstream concentrations for PSS pure, PSC(I)-16, PSC(II)-16 and PSC(III)-16 together with RH data are shown in Fig 3a. Fig 3b shows efficiency vs. adsorbed amount in (wt %) of the sample bed. The downstream concentration of pure PSS traces the upstream concentration i.e. no adsorption occurs at 3-9 ppm. This is also evident from Fig 3b where the PSS pure data immediately drops toward zero adsorbed amount. When comparing this to the PSC samples all three exhibit a much lower downstream concentration with low variability despite the variation in upstream concentration and humidity that depend on experimental errors (Fig.3a). The toluene adsorption performance increase in the order PSC(II)-16 < PSC(III)-16 < PSC(I)-16 (Fig.3b). If the adsorbed amounts are compared at 65% efficiency and by this avoiding the

concentration and humidity variation after 36 hours the uptake in (wt %) of the carbon content are for II: 4.4(wt %), III: 4.5(wt %) and I: 8.9(wt %). If the sample would have consisted of 100% carbon the uptake at 65% efficiency would have been in the range of 16-18(wt %) depending on the granule size 2-7 mm. [12]. This indicates that the carbon pore system is accessible to a great extent even if the composite composition may be further improved.

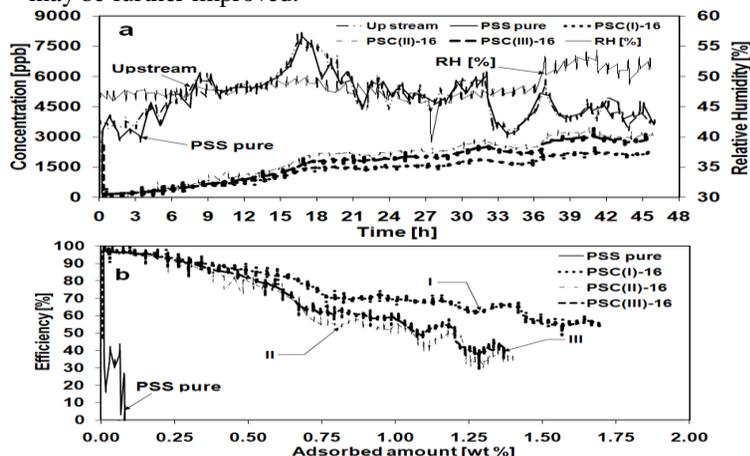


Fig. 3: (a) Concentration vs time and (b) removal efficiency vs adsorbed amount (wt %) for pure PSS, PSC(I)-16, PSC(II)-16 and PSC(III)-16

Conclusions

Composites with up to 16 (wt %) carbon were successfully prepared. These exhibited better micropore volume, BET and micropore surface area than pure PSS. The composites in route I and III exhibit a wide pore size distribution (1-35nm) whereas in route II shows narrow pore size range (1-4nm). All composites were able to adsorb toluene while pure PSS did not, indicating that the carbon pore system was accessible to the surrounding air. PSC(I)-16 exhibited best properties (surface area and pore volume) and higher toluene adsorption than in route II and III.

References

1. B.J. Finlayson-Pitts, J.N. Pitts. Atmospheric chemistry: Fundamentals and experimental techniques, John Wiley & Sons, New York (1986)
2. S. Brunauer, The adsorption of gases and vapors, Volume I Physical Adsorption. Princeton University Press 1943
3. J.L.Kovach. Handbook of separation techniques for chemical engineers James Peter Associates Inc.
4. H.E Bergna, W.O. Roberts. Colloidal silica fundamentals and applications; Surfactant science series v.131 CRC Press 2006
5. Swedish patent SE 529160 C2
6. E.Twumasi, M.Forslund, P.Norberg, C.Sjöström. Preparation and characterization of novel precipitated silica (to be publish)
7. R. Lebeda. Carbon-mineral adsorbents-new type of sorbents? Part I the methods of preparation. Materials Chemistry and Physics, 31 (1992) 243-255
8. Liu C., Komarneni S. Carbon-silica xerogel and aerogel composite J. Porous Materials, 1,75-84(1995)
9. P.J.M. Carrott, K.S.W. Sing. The adsorption of nitrogen and water vapour by carbon-coated precipitated silica Colloids and Surfaces, 21 (1986) 9-15
10. F.Rouquerol, J. Rouquerol, K.Sing. Adsorption by powders & porous solids principles, methodology and applications, Academic press, 1996, p.174
11. Ashrae Standard I45.I Laboratory test method for assessing the performance of gas-phase air-cleaning systems: Loose Granular Media, 2008
12. C. Lindahl, Camfil AB, personal communication