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Tailored Precipitated Silica Adsorbents for the Built Environment

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ABSTRACT

The paper provides a review of the synthesis and adsorptive properties of a novel class of precipitated silica materials. To enhance or tailor the adsorption efficiency, various trapping chemicals (potassium hydroxide, potassium permanganate) or co-adsorbents (coconut activated carbon) are incorporated in the structure of the substrate material. Further, it discusses the applicability and performance over time of the material as adsorbents for removal of hydrogen sulphide, sulphur dioxide and toluene contaminants which are potentially hazardous to sensitive equipment and more importantly, human health. Chemical substances in the air are an unavoidable by-product of most human endeavours within industry and transportation. The need for adsorbents to combat Airborne Molecular Contamination (AMC) follows from the continued intensification of the global environmental movement as well as the rapid industrialisation of developing countries. The removal performance of modified precipitated silica adsorbent shows that the new adsorbent can be tailored to remove low concentrations of sulphur dioxide, hydrogen sulphide and toluene contaminants at indoor environment conditions. The results further shows that the new precipitated silica adsorbent impregnated with 8 wt% KOH shows better performance than commercial alumina impregnated with 8 wt% $KMnO_4$.The adsorbent material may find interesting and efficient uses as passive sinks for pollutants incorporated into more traditional building products such as acoustic baffles or as ingredients in various coatings. The filter material is environmentally friendly and consists of benign chemicals that are abundant worldwide. Performance over time aspects, re-use and recycling of exhausted filter materials are key issues.

KEYWORDS

Precipitated silica, Adsorbents, Molecular filtration, Indoor air quality, Performance over time.

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1 INTRODUCTION

The lifestyles (work and leisure activities) of people living in industrialized nations mean they spend more than 90 percent of their time indoors [CPSC Document #455 1994]. The necessary ventilation of buildings means we are increasingly exposed to gas contaminants in the external air. Exposure to air contaminants in the indoor environment have been associated with health symptoms such headaches, itchy eyes, reduced work efficiency, and others that have generally been referred to as Sick Building Syndrome (SBS). Whether in museums or microelectronics production units even trace levels of pollutant gases can do irreversible damage [Sucha *et al*.1991 and Muller 2002]. Therefore it may be more economical to clean the indoor air and recycle a certain portion of it as compared to heating (or cooling) and eventually humidify or dehumidify the fresh air from the outside [John 2000]. The methods used to remove contaminating gas in the built environment are known but only adsorption has found widespread use [Schweitzer 1979]. The performance of the adsorption process depends on the quality of the adsorbent. The most generic adsorbents used commercially are activated carbon, activated alumina, molecular sieve and silica gel [Yang 2003]. Considering the global environmental movement for clean air as well as rapid growth of developing countries, the development of new and better sorbents will not only make major advances in gas adsorption technology, but also help meet the new challenges that cannot be met with the currently commercially available sorbents. Herein we present the synthesis of a new sorbent material that can be used as filter medium to remove contaminating gases. The adsorptive property of the prepared sorbent has been studied by the use of nitrogen gas adsorption. To enhance it adsorption performance various impregnate chemicals (KOH and $KMnO_4$) or co-adsorbents (coconut activated carbon) were incorporated in the structure of this sorbent material. The dynamic adsorption performance over time of the modified sorbents was tested by subjecting them to an air stream containing sulphur dioxide, hydrogen sulphide or toluene contaminants. These contaminating gases have been chosen because they are commonly found in the built environment at low concentration levels.

2 EXPERIMENTAL

2.1 Adsorbent Synthesis

The synthesis was based on the method published by Norberg et al., 2006. In this specific laboratory preparation 30g (22ml) of waterglass (SiO_2:Na_2O = 3.35) as silica source was diluted with 78ml of deionised water. A salt solution was prepared from 60g of $MgCl_2 \cdot 6H_2O$; 20g of $CaCl_2 \cdot 2H_2O$ and 930ml of deionised water. The salt solution (500ml) was added to the silicate solution (500ml) while being under vigorous stirring at room temperature. The resulting white precipitated silica slurry was allowed to settle. The slurry was then washed to remove soluble salts. Finally the slurry was dewatered by vacuum filtering until a coagulum holding 85% of water was obtained. From here activated coconut carbon and different impregnate chemicals were added to the coagulum. The detailed synthesis procedure has been described elsewhere [Twumasi *et al*. 2010]. The adsorbent with 16 wt% activated carbon added is denoted PSC(I)-16, with 8 wt% KOH addition named PSS-KOH whereas 8 wt% and 13 wt % $KMnO_4$ is denoted as PSS(I)-8 and PSS(I)-13 respectively.

2.2 Nitrogen Physisorption

The nitrogen adsorption/desorption isotherms were measured by a Micromeritics ASAP 2010 volumetric adsorption analyser. The samples were degassed at 150°C in vacuum for 20 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_o) range of 0.03 to 0.3. The micropore surface area S_{mic} and micropore volume V_{mic} were obtained via thickness method (t-method) [Rouquerol *et al*. 1996]. The total pore volume (V_{tot}) was calculated from the amount of gas adsorbed at $p/p^o \approx 0.99$. Pore size distribution (PSD) was derived using the density functional theory method (DFT) assuming cylindrical pores, oxide surface model and cylindrical pore geometry. These were performed with the software provided with the Micromeritics apparatus.

2.3 Dynamic Adsorption of H_2S, SO_2 and Toluene

The most common concentration range for pollutant gases emitted in the indoor environment are very low and by far the principles of dynamic adsorption has been employed for removal of these contaminant gases [John 2000]. Therefore the performance of tailored silica adsorbents for purification of contaminated gases has been done using a dynamic challenge test at indoor conditions in other to mimic a real life scenario.

The analysis was performed in a system similar to the setup described in ASHRAE 145.1 [Ashrae 2008] but with four parallel columns. Air with controlled temperature and humidity is fed from a large supply chamber and the selected challenge gas (i.e. H_2S; SO_2; toluene) is injected from a pressurised gas cylinder by means of a computer controlled mass flow valve. The H_2S is measured by a Thermo Environmental 43 C UV fluorescence instrument with a TE 340 H_2S converter. Four parallel samples of ~50 g each were loaded into the four columns forming 52 mm high beds. The flow was 0.9 m^3/h and 0.4 s contact time. The challenge upstream concentrations were ~12000 ppb H_2S and 3100 ppb SO_2 at 23 °C and 50% RH. In adsorption of SO_2, flow rate was 1.8 m^3/h, contact time of 0.1s and bed height of 26mm. The downstream concentrations with time as well as removal efficiency [%] in relation to adsorbed amount in grams were recorded.

3 RESULTS AND DISCUSSIONS

3.1 Surface Area and Pore Structure

Nitrogen adsorption isotherms and pore size distribution for pure PSS, PSC-16 and impregnated PSS samples are presented in Fig.1 and the corresponding physicochemical parameters are summarized in Table 1. Pure PSS substrate exhibits type IIb isotherm. The incorporation of impregnate chemicals or carbon into the PSS substrate did not change the shape of the isotherm. However, in the PSC (I)-16 isotherm a high nitrogen uptake in the p/p^o range of 0.003-0.3 was observed which is typical of micropore structure. The PSC (I)-16 shows an increase in S_{BET} area, micropore surface area and exhibits a higher micropore volume than pure PSS. When compared with pure PSS a 46% increase in micropore surface area was observed in PSC(I)-16. The presence of micropores in the samples prepared is confirmed by the fact that the linear region of the *t*-plot intercepts the y-axis in these plots (Fig.1B).

Table 1. Textural properties of new silica sorbent with various impregnates or activated carbon.

Samples	S_{BET} (m^2/g)	S_{mic} (m^2/g)	Smes (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	dmic (nm)	dmes (nm)
PSS pure	373	45	328	0.65	0.021	0.625	1.41	5.4
PSC(1)-16	511	82	429	0.70	0.042	0.658	1.39	5.4
PSS-KOH	312	30	282	0.59	0.012	0.578	1.41	5.4
PSS(I)-8	320	10	310	0.493	0.003	0.490	1.41	5.4
PSS(I)-13	260	8.4	252	0.399	0.002	0.397	1.41	5.4

SBET - BET specific surface area, Smic – t-plot micropore surface area, Smes – mesopore surface area, Vtot – total pore volume, Vmic – micropores volume, Vmes – mesopores volume, dmic, dmes – micro-and mesopore maxima peaks in DFT pore size distribution

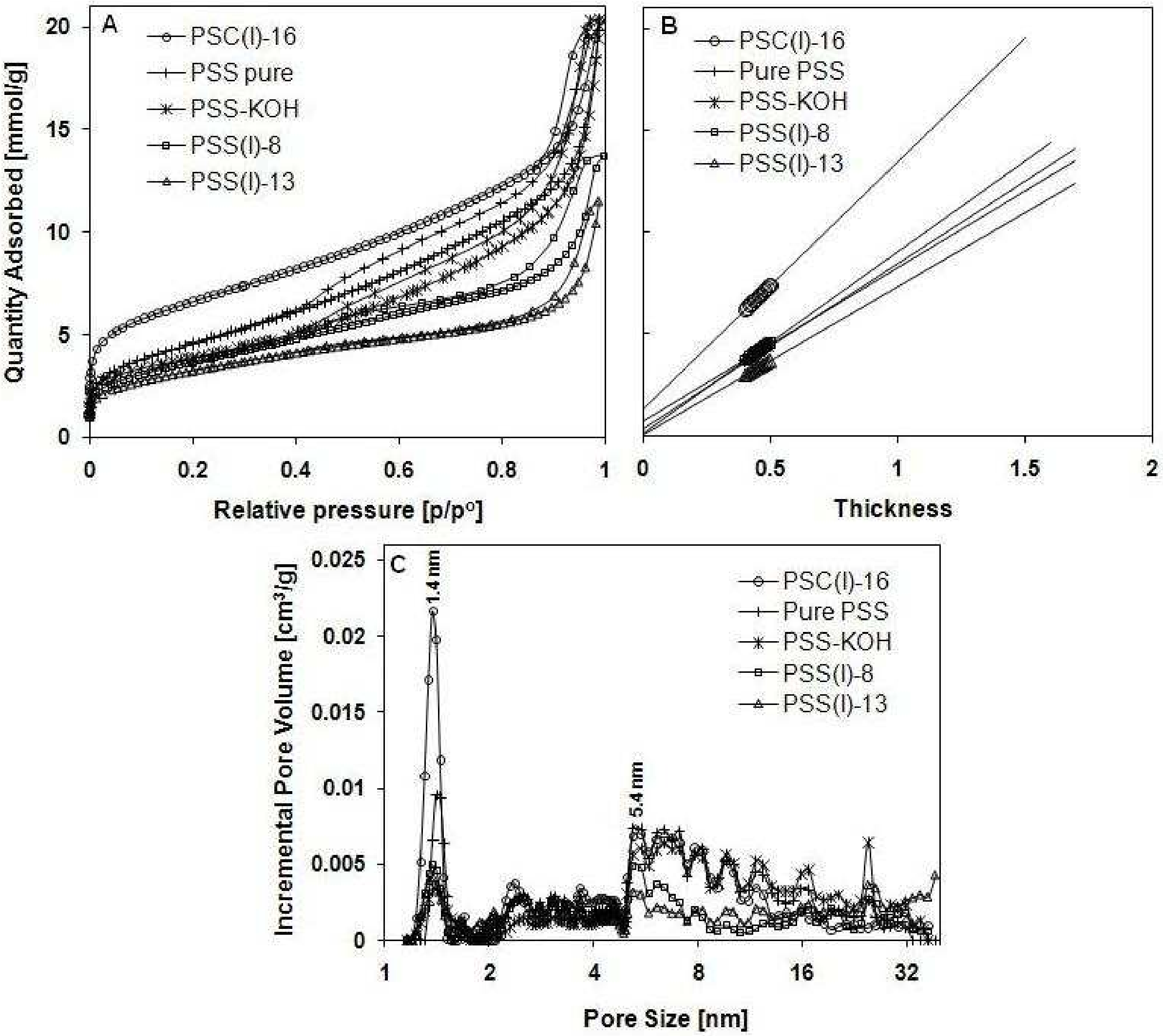

Figure 1. (A) Nitrogen adsorption isotherm, (B) t-plot and (C) pore size distribution of pure PSS and samples (PSS(I)-8,PSS(I)-13 and PSS-KOH) modified with doped chemicals and PSC(I)-16 with activated carbon.

A decrease in total pore volume and S_{BET} surface area were however observed for all impregnated materials in comparison to the corresponding pure PSS and PSC (I)-16, indicating the location of the impregnates into the pore systems of the PSS. The total pore volume, micro- and mesopore volumes and areas also decrease with increasing impregnate amount (Table 1).

The decrease of micro porosity with impregnation indicates that some deposition took place in the micropores; however when comparing the difference in micropore volume and mesopore volume reduction it turns out that the amount of e.g. permanganate deposited in mesopores pores was higher than that deposited in the micropores. This was further proven by the large reduction in incremental pore volume in the mesopore region of pore size distribution (Fig. 1C). The decrease was more pronounced for material (PSS (I) -13) obtained by 13 wt % $KMnO_4$ impregnation.

The maximum peaks from the PSDs of all the samples are identified in Fig. 1b and were about 1.4 nm in the micropore region and 5.4 nm in the mesopore region. Regardless of the impregnate chemical or activated carbon incorporated in the structure of the pure PSS, the complete pore size distribution (PSD) remained even if the incremental pore volume was changed. In the case of PSC (I)-16, an increase in incremental pore volume was observed in the micropore size region which confirmed also an increase in micropore volume. The samples treated with impregnate chemicals however show a decrease in peak height of the distribution. This can be explained by that fact that the impregnated chemicals did not block pore entrance but rather are sited within and on the surface of the pore walls and volume of the silica substrate. The isotherms (Fig.1A) and pore size distribution (Fig.1C) for samples incorporating impregnation chemicals did not show any significant changes when compared to the starting substrate. These findings indicate that the porous structure of the new silica adsorbent do not significantly change when a chemical impregnant is added.

3.2 Dynamic Adsorption Performance of H_2S, SO_2 and Toluene

3.2.1 Toluene adsorption performance of pure PSS and PSC (I)-16

The uptake performance together with RH data of pure PSS substrate versus PSS incorporating 16 wt% activated carbon (PSC(I)-16) is shown in Fig.2A. The downstream concentration of pure PSS traces the upstream concentration thus no adsorption occurs at 3-9 ppm level of toluene. The plot of efficiency versus adsorbed amount (grams of toluene/grams of PSC (I)-16) as shown in Fig.2B, further confirms the poor performance of pure PSS by a sudden drop of its efficiency towards zero adsorbed amounts. In comparison, The PSC(I)-16 sample exhibits a much lower downstream concentration despite the variation in upstream concentration and humidity that depend on experimental errors. 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 is 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 [Lindahl, 2010]. This indicates that the carbon pore system is accessible to a great extent even if the composite composition may be further improved.

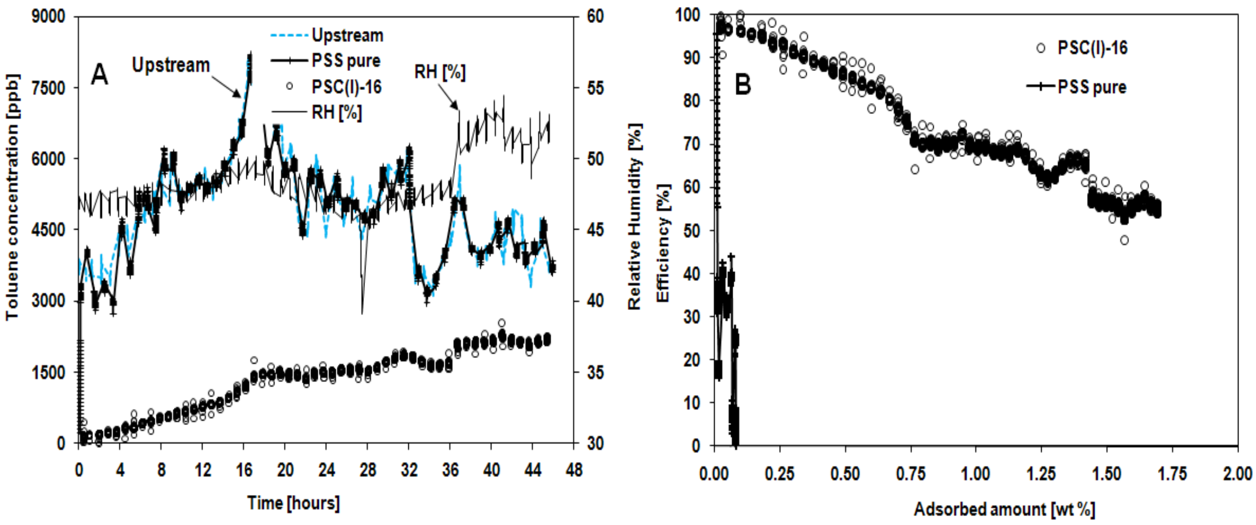

Figure 2. (A) Decrease of toluene inlet concentration with time and (B) efficiency vs. adsorbed amount (grams of toluene /grams of samples).

3.2.2 Desulfurization performance of the impregnate PSS

Figure 3 shows the desulphurization performance of the PSS doped with 8 wt % $KMnO_4$ (PSS (I)-8) versus PSS doped with 13 wt % $KMnO_4$, (PSS(I)-13). Table 1 shows the hydrogen sulphide uptake capacity (grams of sulphur/grams of doped PSS). The adsorbed amounts of hydrogen sulphide were compared at the time of 50% breakthrough (i.e. at 50% efficiency). The PSS(I)-13 shows a better performance over the PSS(I)-8 sample. This is evident from Fig.3A where downstream concentration of PSS(I)-8 traces the upstream concentration thus no adsorption occurs after ~60 hours while even lower downstream concentration was observed for materials impregnated with 13 wt% $KMnO_4$ after 120 hours. Fig.3A also indicate the immediate drop of PSS(I)-8 efficiency towards zero adsorbed amount while that of PSS(I)-13 shows gradual decline of performance over a wide period of time. It can be concluded that H_2S uptake performance occurred via chemical adsorption and relates to the amount of $KMnO_4$ in the PSS substrate. Nevertheless, the use of $KMnO_4$ poses health hazards for human and environmental challenges when it comes to reuse or recycle of the worn out doped materials. In line with this, an alternative effective and yet environmental friendly impregnate chemical, potassium hydroxide (KOH), has been used as option for SO_2 removal.

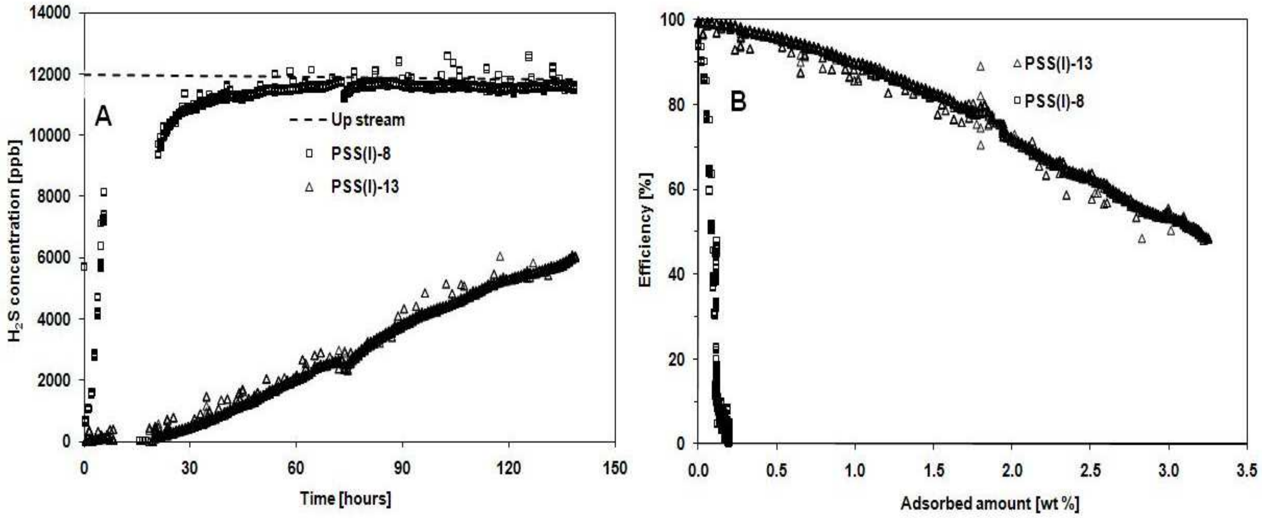

Figure 3. (A) Decrease of H_2S upstream concentration with time and (B) efficiency vs. adsorbed amount (grams of H_2S /grams of samples).

Figure 4 shows the performance of PSS substrate impregnated with 8 wt% KOH versus commercially available alumina impregnated with 8 wt% $KMnO_4$. The PSS-KOH sorbent has shown a better performance over commercial alumina-$KMnO_4$ material. This is evident from Fig.4A where downstream concentration of alumina impregnated with $KMnO_4$ traces the upstream concentration while lower downstream concentration was observed for PSS-KOH even after 250 hours. From Fig.4A if the sulphur dioxide uptake capacity (wt %, grams of SO_2/grams of sorbent) is compared at the 50% breakthrough (i.e. at 50% efficiency), the uptake in (wt %) are for PSS-KOH: 1.7 (wt %) and 0.49 (wt %) for alumina-$KMnO_4$. This indicates that the KOH impregnate in the PSS pore system is accessible to a great extent and possess high reactivity.

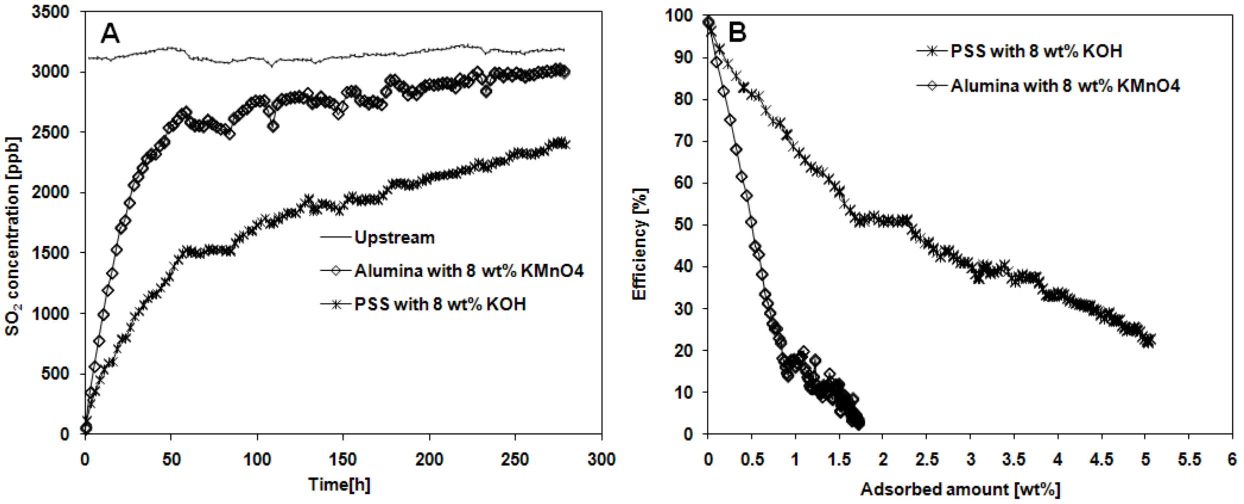

Figure 4. Comparative performance of PSS impregnate with 8wt% KOH vs. commercial alumina impregnated with 8 wt% $KMnO_4$.

3.3 Service Life and Re-use of the Tailored Silica Adsorbent

The assessment of the acceptable performance of adsorbents used in e.g. cleaning of air in the process industry may be performed by sampling of filter media from the filter cassettes. However, the most common approach is based on experience, i.e. with knowledge of the contaminant loading over time the filter media is exchanged well before the filter bed is completely used. Surveillance of filters by use of sensor technologies is less common. The used filter media is normally deposited, and reuse or recycling of filter media is today largely unusual. The environmental burden of this approach is evident, especially if considering that a significant amount of the deposited filter media may still contain active impregnate chemicals.

For cleaning of air also in indoor built environment applications, the service life of adsorbents will depend on the concentration of contaminants. Given the variability in the concentration of contaminants, the temperature and humidity, it will always be challenging to estimate the service life of an adsorbent material in a specific built environment condition. There are several complicating factors in determining the service life. The performance and prediction of lifetime of the tailored silica adsorbents have been determined and compared under carefully controlled conditions of flow velocity, temperature, relative humidity, challenge gas composition and concentration, among other factors. A performance standard ASHRAE 145.1 has been used to test the performance and estimate the service life of the tailored silica adsorbent under controlled conditions. Expressed generically, the time that the tailored silica adsorbent can remain in service depends on the amount of impregnate chemical or, as in the case of the silica/carbon composite, the composition of carbon in the adsorbent. Therefore the performance can be improved by altering the composition of impregnate chemicals or carbon with due concern at the same time not to negatively affect the porous system.

There is in general a pronounced need to further develop the reuse and recycling properties of filter media. Re-use means in this context that a used filter medium is gassed off under controlled conditions and then again may serve as a filter. This normally implies that the filtering process is predominantly physical adsorption in the porous system of the filter media. When the contaminants are chemisorbed within the adsorbents, and when no longer posing any risk, the used silica filter media may effectively serve as an ingredient material in other material matrixes. Examples may be based on using the effective porous system for insulation purposes, or just simply as a fertilizer together with e.g. other compounds rich in phosphor and/or nitrogen.

4 CONCLUSIONS

A new silica adsorbent has been prepared using sodium silicate and precipitated with magnesium and calcium salts. Their adsorptive properties; specific surface area, total pore volume and pore size distribution have been determined by nitrogen gas adsorption/desorption. The removal performance of sulphur dioxide, hydrogen sulphide and toluene has been tested by dynamic adsorption.

The adsorptive properties of a PSS adsorbent incorporating the co-adsorbent activated carbon shows an increase in surface area and total porous volume, whereas chemical impregnate incorporation results in a relative decrease in surface area and pore volume. However, the porous structure of the modified sorbent does not significantly change when carbon or chemical impregnate is added.

The removal performance of the precipitated silica adsorbent shows that the new sorbent can be tailored to remove low concentrations of sulphur dioxide, hydrogen sulphide and toluene contaminants at indoor environment conditions. The results further show that the new precipitated silica adsorbent impregnated with 8 wt% KOH provides better performance than commercially available alumina impregnated with 8 wt% $KMnO_4$.

Besides the use of KOH as an impregnate chemical, a search for other environmentally friendly and yet effective impregnate chemicals compatible with this new silica adsorbent is ongoing. In cases where contaminates are chemisorbed on the adsorbent and does not pose any risk, the material can be used in insulation panels or as fertilizer with other compounds rich in phosphorus and nitrogen.

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