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Polymer-derived ceramic aerogels as sorbent materials for the removal of organic dyes from aqueous solutions

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Abstract

Polymer-derived SiC and SiOC aerogels have been synthesized and characterized both from the microstructural point of view and as sorbent materials for removing organic dyes (Methylene Blue, MB, and Rhodamine B, RB) from water solutions. Their adsorbent behavior has been compared with a polymer-derived SiC foam and a commercial mesoporous silica. The aerogels can efficiently remove MB and RB from water solution and their capacity is higher compared to the SiC foams due to the higher surface area. The SiOC aerogel remains monolithic after the water treatment (allowing for an easy removal without the need of a filtration step) and its maximum capacity for removing MB is 42.2 mg/g, which is higher compared to the studied mesoporous silica and many C-based porous adsorbents reported in the literature. The reason for this high adsorption capacity has been related to the unique structure of the polymer-derived SiOC, which consists of an amorphous silicon oxycarbide network and a free carbon phase.

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1. Introduction

Ceramics obtained through polymer pyrolysis, generally known as Polymer-Derived Ceramics (PDCs), are a novel class of multifunctional nanostructured materials [1]. The PDC family derived from Si-based preceramic polymers is by far the most studied one and comprises ceramics of the Si-C (silicon carbide), Si-O-C (silicon oxycarbides) and Si-C-N (silicon carbonitrides) systems [2]. The PDC route allows the synthesis of unusual ceramic structures, which cannot be obtained with any other method. The PDC structure consists of an amorphous network built-up from mixed silicon units, $\text{SiC}_x\text{O}_{4-x}$ or $\text{SiN}_x\text{C}_{4-x}$, $0 < x < 4$, in which Si atoms are bonded simultaneously with oxygen, nitrogen and carbon atoms [3]. Often, a free carbon phase made of sp^2 C layers organized to give amorphous carbon, turbostratic or nanocrystalline graphite is also present [4]. Accordingly, PDCs can be properly defined as nano-composite materials.

The chemical composition and the phase assemblage of the PDCs can be controlled by the chemistry [2] and the architecture [5, 6] of the pre-ceramic polymers and by the pyrolysis atmosphere: for example phase pure silicon oxycarbides without the free carbon phase, are obtained through pyrolysis in H_2 flow [7, 8]. The unique properties of PDCs, such as the extremely low creep rate [9, 10], the excellent chemical durability and oxidation resistance [11, 12], semiconducting and gas sensing behavior [13, 14] and the high Li-storage capacity [15, 16, 17] have all been related to the distinctive nanostructure described above.

The polymer pyrolysis method offers another important advantage compared to the traditional powder processing of ceramic materials: a wide range of forming techniques are available to shape the components in the polymeric state which is then retained in the final ceramic state. Consequently, PDCs fibers, films, ceramic matrix composites, MEMS and a variety of macro-, meso- and micro-porous ceramics (even with lotus-type porosity [18]) have been obtained via the PDC route and several comprehensive reviews are available on this topic [19, 20, 21]. Concerning the processing of porous materials, the synthesis of PDC aerogels has been

recently proposed by some of us [22] and SiC, SiOC and SiCN aerogels have been obtained and characterized [23, 24, 25].

The treatment of industrial wastewater deriving from textile sector is an important issue for the quality of wastewater generated. In fact, about 30% of the dye used in the textile process is deactivated, thus causing the discharge of dyes in wastewater at amounts of tens of mg/L [26]. These concentrations must be considered significant since, according to the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), levels of dye higher than 0.1-1 mg/L originate visual pollution [27].

The removal of colour from wastewater of textile districts through different treatment techniques, i.e. coagulation/flocculation, ultrafiltration, biological degradation, adsorption, oxidation and advanced oxidation processes, has been the object of numerous papers and specific reviews [28, 29, 30].

Within adsorption methods, the widest employed adsorbent is activated carbon [31] where adsorption of dyes is controlled not only by adsorbent microstructure such as surface area and porosity, but also by the surface functional groups (types and areal density). However other substrates like mesoporous silica-based materials have been proposed for dyes removal [32], due to their high surface area, large and uniform pore size, and tuneable pore structure. These sorbents can be either used as such [33] or after grafting functional groups selective towards special pollutants [34, 35].

The study of porous PDCs as sorbent materials for water purification has been rarely reported in the literature. Riedel's group described the use of mesoporous SiOC loaded with TiO₂ or ZnO nanopowders for the adsorption and photodegradation of organic contaminants [36, 37]. Mesoporous SiOC obtained via a liquid-liquid phase separation at the preceramic stage followed by pyrolysis, showed a good adsorption capacity toward organic dyes (Rhodamine B) [38]. Porous PDCs obtained from polysiloxane and sewage sludge have been studied as

adsorbents for pharmaceutical from aqueous solutions [39]. A recent paper reported very high adsorption capacity of methyl-blue for a porous Si-C-N [40]. Our group has recently reported the adsorption behaviour of macroporous silicon carbide foams made from preceramic polymers toward non steroidal anti-inflammatory drugs (NSAIDs) and their metabolites [41].

In general, the most important features that a material should display in order to be successfully used as a sorbent are: (i) high specific surface area (SSA) and porosity and (ii) the surface should contain specific functional groups for bonding the target compounds. From this point of view, PDCs seem the ideal sorbent candidates: indeed PDCs with SSA up to 600 -700 m²/g can be easily obtained and their structure displays, at the same time, a variety of different functional groups which could make this material able to adsorb, with high efficiency, different molecules or metals. Accordingly, porous PDCs could lead to the development of novel multi-target adsorbents in contrast to the commercial ones, which are designed to efficiently remove only one, or few, types of pollutant.

In our laboratory, porous PDCs aerogels showing hierarchical porosity ranging from some microns to few nanometers and with high SSA in the range 100 - 700 m²/g have been recently synthesized [42]. Moreover, their structure contains different types of chemical bonds (Si-O, Si-N, Si-C, C=C, C=O) and functional groups (OH, NH, COOH) depending on the composition and pyrolysis atmosphere [23, 24, 43]. This unique combination of hierarchical porosity, high SSA and broad range of surface chemical functionalities makes the PDC aerogels ideal candidates as sorbent materials for water purification. In this work, we proposed to use SiC, SiOC aerogels and a PDC SiC foam as adsorbents for organic dyes to purify contaminated water and we compared their behavior with a commercial mesoporous silica. The rationale for testing SiC foams, even if they display much lower SSA compared to the PDCs aerogels and therefore will probably show lower adsorption capacity, is related to

the possibility of easily removing the adsorbent for regeneration without requiring any additional filtration step. This could be an important advantage compared to many other commercial adsorbents such as active carbons and could open the way to the fabrication of integrated filtering cartridges.

The dyes tested in this study are two model basic dyes, namely Methylene Blue, MB, and Rhodamine B, RB, and were chosen for their water-soluble properties and for their widespread use in textile industry [44].

2. Experimental procedures

2.1 Synthesis of the PDCs aerogels and foam

The preceramic aerogels were prepared crosslinking two Si-based preceramic polymers bearing Si-H moieties with divinylbenzene (*DVB, technical grade, 80%, CAS: 1321-74-0, Sigma-Aldrich, St. Louis, MO, USA*) in the presence of a platinum catalyst (*Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution, in xylene, Pt ~2 %, CAS: 68478-92-2, Sigma-Aldrich, St. Louis, MO, USA*) and using cyclohexane (90 vol%) or acetone (80 vol%) as solvent. The SiC aerogels were prepared from a liquid allylhydridopolycarbosilane (SMP-10, Starfire Systems, Schenectady, USA) while for the SiOC aerogel a linear poly(methylhydridosiloxane) (*PMHS, MW~1900, CAS: 63148-57-2, Alfa Aesar, Ward Hill, MA, USA*) was used. Details of the synthesis of the preceramic aerogels can be found in the literature [23, 25]. The preceramic samples were converted in the corresponding PDCs by a pyrolysis process in controlled atmosphere (Ar, 100 cm³/min). An alumina tubular furnace (Lindberg Blue) was used for the pyrolysis: the furnace was purged for 5 h at room temperature and then heated at 5°C/min up to 900 °C with 1 h holding at the maximum temperature before free cooling at room temperature.

SiC foams were prepared from polyurethane foams following a replica method recently developed in our laboratory [45]. SMP-10 was dissolved in cyclohexane together with the Pt catalyst and used to impregnate the PU foam (60 PPI, from A.R.E. s. r. l., Rosate, Milano) with a weight ratio SMP-10/PU = 3. Details of the impregnation process have been published elsewhere [41]. The impregnated PU foams were then pyrolyzed at 1200 °C for 1 hour in Ar flow into the corresponding SiC foams.

For comparison purposes the adsorption studies have also been performed on a commercial mesoporous silica SBA-15 (ACS Material LLC, CAS: 7631-86-9, Pasadena, CA, USA).

2.2 PDCs characterization

Chemical bonds present in the structure of the ceramic aerogels were characterized by infrared spectroscopy (FT-IR). FT-IR spectra were collected on aerogels powders using a Nicolet Avatar 330 spectrometer (Thermo Electron Corporation, Waltham, MA, USA) in transmission mode using KBr. Spectra were recorded in the 4000 – 500 cm^{-1} range collecting an average of 64 scans with 2 cm^{-1} resolution.

Microstructural characterization designed to evaluate the specific surface area, SSA, the total pore volume, TPV, and the pore size of the PDCs aerogels was performed by N_2 physisorption at -196 °C with a Micromeritics ASAP 2010 instrument. Samples were degassed at 150 °C and the SSA was calculated in the relative pressure (p/p_0) range between 0.05 and 0.30, by applying the Brunauer-Emmett-Teller (BET) multi-point method. Pore size distribution was evaluated by Barrett-Joyner-Halenda (BJH) method from desorption branch of the isotherm.

FE-SEM images of the fracture surface of PDC aerogels were acquired with a Zeiss supra 60 equipment (Carl Zeiss NTS GmbH, Germany) operating in high-vacuum mode at 2.00 kV and after sputtering the samples with a thin gold film.

The bulk density of the aerogels was calculated on regular cylindrical samples while the skeleton density was measured with a Micromeritics 1305 He picnometer (Micromeritics Norcross, GA, USA). Thermogravimetric analysis (TGA) was recorded with a Netzsch STA 409 equipment (Netzsch Geraetebau GmbH, Selb, Germany) at 5 °C/min in air flow (30 cc/min) up to 1300 °C. Microstructural characterization of the SiC foam was already performed in a previous work and the details are available in the literature [41, 45].

2.3 Adsorption studies

2.3.1 Chemical and standard solution

Solutions of MB and RB (both from Sigma-Aldrich) were prepared by dilution of stock solutions (1000 mg/L). For eluent preparation, HCOONa and HPLC grade CH₃CN from Sigma-Aldrich were used. High-purity water (18.2 MΩ cm⁻¹ resistivity at 25 °C) was produced by an Elix-Milli Q Academic system (Millipore, Vimodrone, MI, Italy).

2.3.2 Instrumentation

Dyes were quantified by reversed-phase liquid chromatography (RPLC) using a Varian 9012 HPLC Gradient Pump, equipped with a 25µL loop, a reversed-phase C-18 analytical column (LiChroCart PuroSphere RP-18, 125 mm x 3.0 mm, 5 µm, Merck). Dyes were eluted by 46% of 50 mM sodium formate buffer (pH 3), and 54% CH₃CN (eluent flow rate 0.5 mL/min). Dyes were detected by spectrophotometric detection (at 660 nm and 550 nm for Methylene blue and Rhodamine B, respectively) by a 4000i UV-Vis absorbance system (Dionex, Thermo Fisher). Limits of detection (LODs) and limits of quantification (LOQs) were calculated as: $LOD = 3x SD_{xy} / b$ and $LOQ = 10x SD_{xy} / b$ (where SD_{xy} is the standard deviation and b is the slope of the calibration curve) [46] and were 34 µg/L and 104 µg/L for MB, 28 µg/L and 86 µg/L for RB.

2.3.3 Adsorption procedure

Adsorption of MB and RB was assessed by batch experiments. In detail, 0.1 g of SiC foam, SiC and SiOC aerogels and SBA-15 were put in contact with 17.5 mL of dye solutions (1 mg/L, pH 5.0) and stirred on a rotary shaker. Samples were withdrawn at 48 h, centrifuged (10000 rpm, 5 min) diluted 1:1 and analyzed by RPLC.

For the system MB-SiOC aerogel only, adsorption studies at high concentrations (100 mg/L) were also performed. All the experiments were performed in triplicate.

The percentage of dye adsorbed (R_{ads}) was calculated as follows:

$$R_{ads} = (C_0 - C) / C_0 * 100$$

where C_0 (mg/L) and C (mg/L) are respectively the initial and the remaining concentrations of dyes in solution after adsorption. Finally, for the SiOC aerogel (and for comparison, for the mesoporous silica, SBA-15) the adsorbent capacity was also evaluated following a similar procedure at 800mg/L MB after 172 h of contact time.

3 Results and discussion

3.1 Characterization of the ceramic aerogels and foam

Figure 1 shows digital photo images and FE-SEM pictures of the studied aerogels. After pyrolysis at 900 °C in Ar flow monolithic aerogels samples were obtained having a colloidal nanometer-sized microstructure. Particles forming the SiC aerogels are larger compared to those observed for the SiOC system. In both samples, large pores in the hundreds nm range can also be noticed.

INSERT FIGURE 1

Figure 1. Digital photo images of typical aerogel samples: (a) SiOC pre-ceramic aerogels; (b) SiOC ceramic aerogel after pyrolysis in Ar at 900 °C and FE-SEM pictures showing the microstructure of (c) SiC and (d) SiOC ceramic aerogels.

Microstructural information derived from the N₂ physisorption analysis (see **Fig. S1**) and He pycnometry are reported in **Table 1**. The combined FE-SEM and N₂ physisorption studies verified the expected formation of highly porous PDC aerogels having hierarchical porosity ranging from ten to hundreds nm and high SSA values [25]. At a first inspection the values of skeleton density of the SiOC and SiC aerogels may seem low compared to the typical values reported in the literature for silicon oxycarbide glasses (2 – 2.4 g/cm³) and polymer-derived SiC (2.5 – 3.05 g/cm³) [1, 2]. However, we must consider that the studied materials have been pyrolyzed at low temperature (900 °C) and, as will be shown later on, contain an important amount of free C. Finally very close density values have been reported for SiOC [47] and SiC [48] PDCs pyrolyzed in the 800 – 1000 °C temperature range.

Insert Table 1

The chemical bonds present in the aerogel structure have been investigated with FT-IR measurements (**Figure 2**).

INSERT FIGURE 2

Figure 2. FT-IR spectra recorded on the SiC, SiOC aerogels and on the SiOC aerogels after MB adsorption test using a starting MB concentration of 800 ppm, as described later on.

The FT-IR spectrum of the SiC aerogel shows a main adsorption at 780 cm^{-1} related to the Si-C bonds of the amorphous silicon carbide network and a band at 1580 cm^{-1} assigned to the C=C bonds of the free carbon phase [49, 50]. A shoulder at 1010 cm^{-1} suggests the presence of few Si-O bonds, arising from the reaction of the aerogel with O_2 and/or H_2O , which is known that may occur at any stage of the aerogel processing, i.e. before, during or after pyrolysis [51].

The IR spectrum of the SiOC aerogel has a main band at 1020 cm^{-1} and a less intense one at 800 cm^{-1} related to the Si-O bonds of the amorphous silicon oxycarbide phase. Similarly to the SiC aerogel, the presence of the free carbon phase leads to the band at 1600 cm^{-1} (C=C bonds), however, in the SiOC spectrum an adsorption at 1700 cm^{-1} is also visible indicating the existence of C=O groups [49, 50, 52]. C=O moieties could have been formed during pyrolysis or after exposing the pyrolyzed aerogel to the laboratory atmosphere [51]. Finally, for the SiOC aerogel a broad band around 3400 cm^{-1} and a shoulder at 3635 cm^{-1} reveal the presence of O-H and Si-OH moieties, respectively. The IR investigation of the SiC foam was already reported in a previous work and showed similar bonding related to Si-C, Si-O, C=C and surface OH groups [41].

In order to have a quantitative estimation of the amount of the free carbon phase existing in the SiC and SiOC aerogels a TGA in air flow has been recorded on the two SiC and SiOC aerogels. The amount of free carbon can be easily estimated from the weight loss observed in the TGA analysis according to the oxidation reaction: $\text{C}_{(\text{solid})} + \text{O}_{2(\text{gas})} \rightarrow \text{CO}_{2(\text{gas})}$. The TGA patterns are shown in **Figure 3**. Both curves display similar features: a small weight loss below 150°C associated to the evolution of adsorbed water, a minor weight increase step, which spans from 200 up to $\sim 300^\circ\text{C}$ for the SiOC and from 200 up to $\sim 400^\circ\text{C}$ for the SiC aerogel, and a large weight loss step in the range $400 - 650^\circ\text{C}$. The slight weight increase at low-temperature is due to the oxidation of C atoms bonded to Si atoms with the formation of new Si-O/Si-OH bonds leading to a corresponding net

weight increase [53] while the large weight loss between 400 and 650 °C is directly associated to the amount of free carbon present in the samples [54]. Accordingly, the SiC and SiOC aerogel contains ~ 61.5 wt% and 42.4 wt% of free carbon, respectively.

INSERT FIGURE 3

Figure 3. TGA curves recorded in air flow for the SiC and SiOC aerogel. The weight losses between 400 and 650 °C are due to the oxidation of C_{free} present in the aerogel microstructure.

The microstructure of the SiC foam is shown in **Figure 4**. It is a typical reticulated open cell foam with cell, window and strut sizes of 490, 170 and 55 μm respectively. Interestingly, unlike the foams obtained through the replica method using ceramic slurries, which have hollow struts, in the present case the struts are dense. The SiC foams have bulk and skeletal density of 0.16 and 2.41 g/cm^3 respectively resulting in 93 % open porosity (see Table 1) and they are X-ray amorphous [45].

INSERT FIGURE 4

Figure 4. SEM image of the SiC foam pyrolyzed for 1 h at 1200 °C in N_2 flow.

3.2 Adsorption studies

The adsorption studies of MB and RB were carried out according to the batch analytical procedure detailed in the “*Experimental*” section. Adsorption experiments were conducted at pH 5, i.e. in conditions where MB is positively charged, while RB is mainly present in the zwitterionic form (85%) and positively charged for 15% [55], as reported in **Figure 5**.

INSERT FIGURE 5

Figure 5. The molecular structures of representative dyes: **(a)** methylene blue (MB); **(b)** rhodamine B (RB) (zwitterionic form).

The two organic dyes have both a molecular structure based on polyaromatic-conjugated structure, but RB has a more complicated bulky structure with a greater steric hindrance. The results of the adsorption tests are reported in **Table 2**.

Insert Table 2

Considering the tests performed with an initial concentration of 1 ppm, after 48 h of contact time the SiC and SiOC aerogels and the mesoporous silica remove 100 % of both MB and RB while the SiC foam removes 65.3% and 35.5% of MB and RB respectively. The lower adsorption of the SiC foam compared to the aerogels could be related to the SSA of this sample which is approximately 3 orders of magnitude lower compared to the aerogel (SSA SiC foam 0.1 – 0.3 m²/g) [41]. On the other hand, to discuss the different adsorption of the MB and RB on the SiC foam it is useful to analyze the adsorption mechanism. The interaction dyes-substrate can be attributed either to: (i) Van der Waals forces between the aromatic structure of the dyes and the sp² free carbon phase which is generally present in the Si-based PDCs as a result of the pyrolysis process and to (ii) the electrostatic interaction between the carbon-oxygen complex (C-O/C-OH) or Si-OH moieties present at the silicon-carbide surface [41] and the positive charge of the organic dyes. Between the two mechanisms the most likely to occur is probably the latter one since the amount of free carbon in silicon carbide-based ceramics obtained from self crosslinked SMP-10 is of the order of 2-4 wt% [56]. Accordingly, the organic dyes are adsorbed onto the SiC foam surface via electrostatic interactions and the lower RB adsorption of the SiC foam compared to MB could be simply due to the lower positive charge ($\approx 15\%$) of RB in the adsorption experimental conditions (pH 5).

It is worth noting that SiOC aerogel maintains a monolithic structure at the end of the experiment while the SiC aerogel breaks up into fine particles. Although the reason for this difference is not clear at the moment and needs to be further investigated, this result can certainly be considered an advantage of the SiOC system compared to the SiC aerogel since will lead to an easy removal after wastewater treatment without requiring a further filtering step. Consequently, we decided to investigate the MB adsorption behaviour of the SiOC aerogel using solutions with higher initial concentration of MB of 100 mg/L. Accordingly, after 48 h of contact time of the SiOC aerogel with the 100 mg/L MB solution the 87.4 % was removed which corresponds to 14.8 mg/g of MB adsorbed by the SiOC aerogel (**Table 2**).

In order to estimate the maximum adsorption capacity of the SiOC aerogels we increased the initial concentration up to 800 mg/L, and we measured the equilibrium concentration of MB in the solution after 172 h of contact time. For comparison purposes, the same experiment has been performed with the mesoporous silica, SBA-15. SBA-15 was chosen since there is a growing interest in using this adsorbent for the removal of various pollutants due to its high surface area, pore volume and tunable pore size [57, 58]. The results of the adsorption experiments with the highest initial dye concentration are reported in **Table 3** and compared with similar results published in the literature for different types of active carbons.

Insert Table 3

Accordingly the maximum adsorption capacity measured for the SiOC aerogel was 44.2 mg/g while, for the same experimental conditions SBA-15, in spite of the fact that it has roughly 3 times the SSA that has the SiOC aerogel (490 m²/g for SBA-15 [57] vs 163 m²/g for the SiOC aerogel), shows a lower capacity of 41.2 mg/g. The presence of the adsorbed MB on the surface of the SiOC aerogel after 172 h of contact with the 800 ppm solution of MB has been confirmed by FT-IR (**Figure 2**): MB leads to two new bands in the FT-IR spectrum in the range 1600 – 1300 cm⁻¹. The absorption capacity of the SiOC aerogels is also higher than the capacity reported in the

literature for different types of porous carbons (**Table 3**). The higher adsorption capacity we measured for the SiOC aerogel compared to other adsorbents, SBA-15 and C-based porous adsorbents, could be related to the multifunctionality of the SiOC aerogels surface which can adsorb MB either via a strong adsorbate-adsorbent ionic interactions with the amorphous SiOC network as well as via Van der Waals interactions with the free carbon phase. The MB adsorbance capacity of the SiOC aerogel can be estimated knowing the cross-sectional area of the MB molecule and the SSA of the adsorbent. Thus, based on the minimum and maximum projection radius values reported in the literature for MB (4.12 – 8.35 Å) [55] and considering a SSA of 163 m²/g for the SiOC aerogel (**Table 1**) we estimate (assuming a monolayer formation) the following range for the adsorption capacity: 40 – 160 mg/g. Accordingly, the measured capacity value (44.2 mg/g) seems to fit well in the estimated range.

4. Conclusion

In this work three different porous silicon carbide-based polymer derived ceramics have been synthesized and tested as adsorbent for organic dyes removal from water solution. In details, one SiC foam, one SiC and one SiOC aerogels have been synthesized and characterized. While the SiC foam displays high porosity but low surface area the PDC aerogels are more than 70vol% porous and have SSA in the range 100-160 m²/g.

All the tested samples adsorb the organic dyes (MB and RB), however the SiC foam display lower capacity due to its lower surface area compared to the SiC and SiOC aerogels. Between the two aerogels samples only the SiOC remains monolithic after the water treatment allowing for an easy removal from the solution without the need of a further filtration step. The SiOC aerogels has been studied in more in details and revealed a maximum capacity for MB removal of 44.2 mg/g, which is higher than many C-based adsorbent reported in the literature. A commercial mesoporous silica, SBA-15, shows, in the same experimental conditions, a lower absorption capacity of 41.2 mg/g in

spite of having approximately 3 times the SSA of the SiOC aerogel (490 m²/g for SBA-15 vs 163 m²/g for the SiOC aerogel) This higher capacity observed for the SiOC aerogel may be due to the simultaneous presence, in the aerogel structure, of free carbon which interacts with the organic dye via Van der Waals interaction and of the inorganic SiOC network which may develop stronger ionic interactions. Taken all together these data suggest that Si-based PDC aerogels can efficiently adsorb organic dyes and further studies on this topic are worth to be pursued.

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References

- 1 Colombo P, Riedel R, Soraru GD, Kleebe H-J, Editors. *Polymer derived ceramics. From nanostructure to applications*, DEStech Publications, Lancaster, Pennsylvania, USA (2010).
- 2 Colombo P, Mera G, Riedel R, Soraru GD. Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics. *J Am Ceram Soc.* 2010; 93:1805-1837.
- 3 Mera G, Navrotsky A, Sen S, Kleebe H-J, Riedel R. Polymer-derived SiCN and SiOC ceramics – structure and energetics at the nanoscale. *J Mater Chem A.* 2013;1:3826-3836.
- 4 Trassl S, Motz G, Rossler E, Ziegler G. Characterisation of the free-carbon phase in precursor-derived SiCN ceramics. *J Non-Cryst Sol.* 2001;293:261–267.
- 5 Laine RM, Babonneau F, Blowhowiak KY, Kennish RA, Rahn JA, Exarhos GJ, Waldner K. The Evolutionary Process During Pyrolytic Transformation Of Poly(N-Methylsilazane) From a Preceramic Polymer Into an Amorphous-Silicon Nitride Carbon Composite. *J Am Ceram Soc.* 1995;78:137-145.
- 6 Dibandjo P, Diré S, Babonneau F, Soraru GD. Influence of the Polymer Architecture on the High Temperature Behaviour of SiCO glasses: a Comparison between Linear- and Cyclic-derived Precursors. *J Non-Cryst Sol.* 2010;356:132–140.
- 7 Narisawa M, Watase S, Matsukawa K, Dohmaru T. White Si-O-C(-H) Particles with Photoluminescence synthesized by Decarbonization Reaction on Polymer Precursor in a Hydrogen Atmosphere. *Bull Chem Soc Jpn.* 2012;85:724-726.
- 8 Diré S, Borovin E, Narisawa M, Soraru GD. Synthesis and Characterization of the First Transparent Silicon Oxycarbide Aerogel Obtained Through H₂ Decarbonization. *J Mater Chem A.* 2015;3:24405-24413.
- 9 An L, Riedel R, Konetschny C, Kleebe H-J, Raj R. Newtonian Viscosity of Amorphous Silicon Carbonitride at High Temperature. *J Am Ceram Soc.* 1998;81:1349–52.

- 10 Rouxel T, Massouras G, Sorarù GD. High Temperature Behavior of an SiOC Oxycarbide Glass: Elasticity and Viscosity. *J Sol-Gel Sci Technol*. 1999;14:83-94.
- 11 Soraru GD, Modena S, Guadagnino E, Colombo P, Egan J, Pantano C. Chemical Durability of Silicon-Oxycarbide Glasses. *J Am Ceram Soc*. 2002;85:1529-36.
- 12 Chollon G. Oxidation behavior of ceramic fibers from the Si-C-N-O system and related sub-systems. *J Am Ceram Soc*. 2000;20:1959-74.
- 13 Zhang LG, Wang YS, Wei Y, Xu WX, Fang DJ, Zhai L, Lin KC, An L. A silicon carbonitride ceramic with anomalously high piezoresistivity. *J Am Ceram Soc*. 2008;91:1346–1349.
- 14 Karakuscu A, Ponzoni A, Aravind PR, Sberveglieri G, Soraru, Gas sensing behavior of mesoporous SiOC glasses,. *J Am Ceram Soc*. 2013;96:2366–2369.
- 15 Sanchez-Jimenez PE, Raj R. Lithium Insertion in Polymer-Derived Silicon Oxycarbide Ceramics. . *J Am Ceram Soc*. 2010;93:1127–1135.
- 16 Fukui H, Harimoto Y, Akasaka M, Eguchi K. Lithium Species in Electrochemically Lithiated and Delithiated Silicon Oxycarbides. *ACS Appl Mater Interfaces*. 2014;6:12827–12836.
- 17 Pradeep VS, Graczyk-Zajac M, Riedel R, Soraru GD, New Insights in to the Lithium Storage Mechanism in Polymer Derived SiOC Anode Materials. *Electroch Acta*. 2014;119:78– 85.
- 18 Vakifahmetoglu C, Zeydanli D, Innocentini MDM, dos Santos Ribeiro F, Orlandi Lasso PR, Soraru GD. Gradient-Hierarchic-Aligned Porosity SiOC Ceramics. *Sci Rep*. 2017;7: 41049.
- 19 Riedel R, Mera G, Hauser R, Kloneczynski A. Silicon-based polymer-derived ceramics: Synthesis properties and applications - A review. *J Ceram Soc Jap*. 2006;114:425-444.
- 20 Bernardo E, Fiocco L, Parciannello G, Storti E, Colombo P. Advanced Ceramics from Preceramic Polymers Modified at the Nano-Scale: A Review. *Materials*. 2014;7:1927-56.
- 21 Vakifahmetoglu C, Zeydanli D, Colombo P. Porous polymer derived ceramics. *Mater. Sci. Eng. R-Reports*. 2016;106: 1-30.
- 22 Sorarù GD, Dalcanale F, Campostrini R, Gaston A, Blum Y, Carturan S, Aravind PR. Novel Polysiloxane and Polycarbosilane Aerogels via Hydrosilylation of Preceramic Polymers. *J Mater Chem*. 2012;22:7676-7680.
- 23 Zera E, Campostrini R, Aravind PR, Blum Y, Sorarù GD. Novel SiC/CAerogels through Pyrolysis of Polycarbosilane Precursors. *Adv Eng Mater*. 2014;16: 814-819.
- 24 Nguyen VL, Zera E, Perolo A, Campostrini R, Li W, Sorarù GD, Synthesis and characterization of polymer-derived SiCN aerogel. *J Europ Ceram Soc*. 2015;35:3295-3302.
- 25 Pradeep VS, Zera E, Graczyk-Zajac M, Riedel R, Soraru GD, Structural Design of Polymer Derived SiOC Ceramic Aerogels for High-rate Li-ion Storage Applications. *J Am Ceram Soc*. 2016;99:2977–2983.
- 26 Goyal R, Sreekrishnan TR, Khare M, Yadav S, Chaturvedi M. Experimental Study on Color Removal from Textile Industry Wastewater Using the Rotating Biological Contactor. *Prac Period Hazard Toxic Radioact Waste Management*. 2010;14:240-245.
- 27 Chemical Safety: International Reference Manual. Edited by Richardson M. 1994; VCH Publishers. Germany.

- 28 Verma AK, Dash RR, Bhunia P. A review on chemical coagulation/flocculation technologies for removal of colour. *J Environ Management*. 2012;93:154-168.
- 29 Singh K, Arora S. Removal of Synthetic Textile Dyes From Wastewaters: A Critical Review on Present Treatment Technologies. *Critical Rev Environ Sci Technol*. 2011;41:807-878.
- 30 Gupta VK, Suhas. Application of low-cost adsorbents for dye removal – A review. *J Environ Manag*. 2009;90:2313-2342.
- 31 Al-Degs Y, Khraisheh MAM, Allen SJ, Ahmad MNA. Sorption behaviour of cationic and anionic dyes from aqueous solution on different types of activated carbons. *Sep Sci Technol*. 2001;36:91-102.
- 32 Tian Y, Cui G, Liu Y, Li H, Sun Z, Yan S. Self-assembly synthesis of hollow double silica @ mesoporous magnesium silicate magnetic hierarchical nanotubes with excellent performance for fast removal of cationic dyes. *App Surf Sci*. 2016;387:631-641.
- 33 Bruzzoniti MC, De Carlo RM, Rivoira L, Del Bubba M, Pavani M, Riatti M, Onida B. Adsorption of bentazone herbicide onto mesoporous silica: application to environmental water purification. *Environ Sci Pollution Res*. 2016;23:5399-5409.
- 34 Bruzzoniti MC, De Carlo RM, Fiorilli S, Onida B, Sarzanini C. Functionalized SBA-15 mesoporous silica in ion chromatography of alkali, alkaline earths, ammonium and transition metal ions. *J Chromatogr A*. 2009;1216:5540-5547.
- 35 Caldarola D, Mitev DP, Marlin L, Nesterenko EP, Paull B, Onida B, Bruzzoniti MC, De Carlo RM, Sarzanini C, Nesterenko, PN. Functionalisation of mesoporous silica gel with 2-[(phosphonomethyl)-amino] acetic acid functional groups. Characterisation and application. *Appl Surf Sci*. 2014;288:373-380.
- 36 Hojamberdiev M, Prasad RM, Morita K, Schiavon MA, Riedel R. Polymer-derived mesoporous SiOC/ZnO nanocomposite for the purification of water contaminated with organic dyes. *Microp Mesopor Mater*. 2012;151:330-338.
- 37 Hojamberdiev M, Prasada RM, Morita K, Zhu Y, Schiavon MA, Gurlo A, Riedel R. Template-free synthesis of polymer-derived mesoporous SiOC/TiO₂ and SiOC/N-doped TiO₂ ceramic composites for application in the removal of organic dyes from contaminated water. *Appl Catalysis B: Environ*. 2012;115-116: 303-313.
- 38 Yua Z, Feng Y, Li S, Pei Y. Influence of the polymer-polymer miscibility on the formation of mesoporous SiC(O) ceramics for highly efficient adsorption of organic dyes. *J Europ Ceram Soc*. 2016;36:3627-3635.
- 39 Simões dos Reisa G., Hoffmann Sampaio Ca, Lima EC, Wilhelm M. Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions. *Coll Surf A: Physicochem Eng Aspects*. 2016;497:304-315.
- 40 Meng L, Zhang X, Tang Y, Su K, Konget J. Hierarchically porous silicon-carbon-nitrogen hybrid materials towards highly efficient and selective adsorption of organic dyes. *Sci Rep*. 2015;5:7910.
- 41 Jana P, Bruzzoniti MC, Appendini M, Rivoira L, Del Bubba M, Rossini D, Ciofi L, Sorarù GD. Processing of polymer-derived SiC foam and its adsorption capacity for nonsteroidal anti-inflammatory drugs. *Ceram Intern*. 2016;42:18937-18943.

- 42 Aerogels from Preceramic Polymers, G. D. Sorarù, E. Zera, R. Campostrini, in Handbook of Sol-Gel Science and Technology, L. Klein et al. (eds.), Springer International Publishing Switzerland 2016, DOI 10.1007/978-3-319-19454-7_121-1.
- 43 Nguyen VL, Laidani NB, Soraru GD. N-doped polymer-derived Si(N)OC: the role of the N-containing precursor. *J Mater Research*. 2015;30:770-781.
- 44 El-Ashtoukhy E-S, Fouad Y. Liquid-liquid extraction of methylene blue dye from aqueous solutions using sodium dodecylbenzenesulfonate as an extractant. *Alexandria Eng J*. 2015;54:77-81.
- 45 Jana P, Zera E, Sorarù GD. Processing of preceramic polymer to low density silicon carbide foam. *Mater Design*. 2017;116:278-286.
- 46 Shrivastava A. Gupta VB. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron Young Sci*. 2011;2:21-25.
- 47 Bois L, Maquet J, Babonneau F, Mutin H, Bahloul D. Structural Characterization of Sol-Gel Derived Oxycarbide Glasses. 1. Study of the Pyrolysis Process. *Chem Mater*. 1994;6:796-802.
- 48 Hasegawa Y, Iimura M, Yajima S. Synthesis of continuous silicon carbide fibre. Part2 Conversion of polycarbosilane fibre into silicon carbide fibres. *J Mater Sci*. 1980;15:720-728.
- 49 G. Socrates, Infrared and Raman Characteristic Group Frequencies: Tables and Charts, John Wiley & Sons, 2004.
- 50 Kolár F, Machovic V, Svitilová J, Borecká L. Structural characterization and thermal oxidation resistance of silicon oxycarbides produced by polysiloxane pyrolysis. *Mater Chem Phys*. 2004;86:88-98.
- 51 Zera E, Nickel W, Kaskel S, Sorarù GD. Out-of-furnace oxidation of SiCN polymer-derived ceramic aerogel pyrolyzed at intermediate temperature (600 – 800°C). *J Europ Ceram Soc*. 2016;36:423-428.
- 52 Assefa D, Zera E, Campostrini R, Soraru GD, Vakifahmetoglu C. Polymer-derived SiOC aerogel with hierarchical porosity through HF etching. *Ceram Intern*. 2016;42:11805-11809.
- 53 Narisawa M, Terauds K, Raj R, Kawamoto Y, Matsui T, Iwase A. Oxidation process of white Si-O-C(-H) ceramics with various hydrogen contents. *Scripta Materialia*. 2013;69: 602-605.
- 54 Brewer CM, Bujalski DR, Parent VE, Su K, Zank GA. Insights into the Oxidation Chemistry of SiOC Ceramics Derived from Silsesquioxanes. *J Sol-Gel Sci Technol*. 1999;14: 49-68.
- 55 Chemicalize. 2016; Available from: www.chemicalize.org.
- 56 Sreeja R, Swaminathan B, Painuly A, Sebastian TV, Packirisamy S. Allylhydridopolycarbosilane (AHPCS) as matrix resin for C/SiC ceramic matrix composites. *Mater Sci Eng B*. 2010;168:204-207.
- 57 Rivoira L, Appendini M, Fiorilli S, Onida B, Del Bubba M, Bruzzoniti MC. Functionalized iron oxide/SBA-15 sorbent: investigation of adsorption performance towards glyphosate herbicide. *Environ Sci Pollut Res*. 2016;23:21682-21691.
- 58 Nesic AR, Kokunesoski MJ, Volkov-Husovic TD, Velickovic SJ. New method for quantification of dye sorption using SBA mesoporous silica as a target sorbent. *Environ Monitor. Assessm*. 2016;188: art. 160.
- 59 Banerjee S, Dastidar MG. Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics, *Bioresource Technol*. 2005;96:1919-1928.

- 60 Tsai WT, Yang JM, Lai CW, Cheng YH, Lin CC, Yeh CW. Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresource Technol.* 2006;97:488-493.
- 61 Bulut Y, Aydın H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination.* 2006;194:259-267.
- 62 Bhattacharyya KG, Sharma A. Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. *Dyes and Pigments.* 2005;65: 51-59.
- 63 Yener J, Kopaca T, Dogu G, Dogu T. Dynamic analysis of sorption of methylene blue dye on granular and powdered activated carbon. *Chem Eng J.* 2008;144:400-406.

Figure Captions

Figure 1. Digital photo images of typical aerogel samples: (a) SiOC pre-ceramic aerogels; (b) SiOC ceramic aerogel after pyrolysis in Ar at 900 °C and FE-SEM pictures showing the microstructure of (c) SiC and (d) SiOC ceramic aerogels.

Figure 2. FT-IR spectra recorded on the SiC, SiOC aerogels and on the SiOC aerogels after MB adsorption test using a starting MB concentration of 800 ppm, as described later in Table 3.

Figure 3. TGA curves recorded in air flow for the SiC and SiOC aerogel. The weight losses between 400 and 650 °C are due to the oxidation of C_{free} present in the aerogel microstructure.

Figure 4. SEM image of the SiC foam pyrolyzed for 1 h at 1200 °C in N_2 flow.

Figure 5. The molecular structures of representative dyes: (a) methylene blue (MB); (b) rhodamine B (RB) (zwitterionic form).

Tables

Table 1. Properties of the studied PDCs aerogels and SiC foam

PDC aerogel sample	Bulk Density (g/cm³)	Skeleton Density (g/cm³)	Porosity Vol/Vol (%)	SSA (m²/g)	TPV_{BET} (cm³/g)	Pore size range (nm)
SiOC	0.47	1.66	72	163	0.723	10 -70
SiC	0.23	1.80	86	102	0.394	20-90
SiC foam	0.16	2.41	93	0.1 – 0.3 [Ref. 41]	--	--

Table 2. Results of the adsorption tests: percentage of dye adsorbed (R_{ads}) after 48 h of contact time for the SiC foam, SiC/SiOC aerogels and SBA-15 mesoporous silica as a function of the initial dye concentration. Test conditions: mg of sorbent/ml of solution at pH 5/time, h = 0.1/17.5/48.

Sample	Initial Concentration	R_{ads} (%)	
		MB	RB
SiC foam	1 mg/L	65.3±□□□	35.5±□□□
SiC aerogel	1mg/L	100	100
SiOC aerogel	1mg/L	100	100
SBA-15	1 mg/L	100	100
SiOC aerogel	100 mg/L	87.4±□□□	--

Table 3. MB adsorption capacity for different sorbents and corresponding references.

Adsorbent	Capacity (mg/g)	Ref.
SiOC aerogel	44.2	This work
SBA-15	41.2	This work
Jute	22.4	[59]
Eggshell	0.80-0.24	[60]
Wheat shell	16.6-21.5	[61]
Neem leaf	8.8-19.6	[62]
Granular activated carbon	21.5	[63]