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Application And Synthesis Of Silica-Based Aerogels For The Removal Of Persistent Organic Pollutants From Water: A Review

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Abstract:
Background: *Water contamination is a major global issue that necessitates the development of new and sustainable purification technologies. Aerogels, ultra-light porous materials with a large surface area and unique properties, have emerged as promising candidates for water treatment, particularly in removing organic contaminants. These materials are highly porous and low-density foams with a microstructure consisting of nano-sized pores and interconnected primary particles.*
Materials and Methods: *The sol-gel synthesis of silica aerogels involves hydrolyzing a silica precursor such as tetraethyl orthosilicate (TEOS) in the presence of a catalyst to form a sol, which undergoes condensation reactions to create a three-dimensional siloxane (Si–O–Si) network. This sol gradually transitions into a wet gel, which is then aged to strengthen the structure. The solvent within the gel is carefully replaced with a low surface tension liquid, often ethanol, to minimize damage during drying. Various methods are used to dry the gel while preventing collapse of the delicate network.*
Results: *Silica aerogels are excellent adsorbents for removing organic pollutants like PCBs because of their high surface area, ultra-high porosity and tunable pore sizes, which enhance contact and diffusion of pollutants.*
Conclusion: *Their elemental composition and structural properties can be precisely tailored using the sol-gel method, enabling the efficient adsorption and degradation of organic pollutants from water sources*

Key Word: *Persistent; Organic; Pollutants; Aerogel; Sol-gel; Oxidation; Activated; Carbon; Water*

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I. Introduction

Sustainable Development Goal 6 demands universal and equitable access to safe and cheap drinking water [1]. Water demand is increasing as a result of fast population expansion, urbanisation and increased water requirements in agriculture, industry and the energy sector. However, inadequate management of urban, industrial and agricultural wastewater means that hundreds of millions of people's drinking water is contaminated. The natural presence of chemicals, such as arsenic and fluoride, particularly in groundwater, can be harmful to health. Compounds such as lead, may be raised in drinking water due to leaching from water supply components in contact with drinking water [1]. Persistent organic pollutants (POPs) are synthetic organic chemical substances, either intentionally produced or accidentally generated, that have raised widespread public concern in recent years. These substances are hazardous and pose a significant environmental risk due to their persistence, long-distance transportability, bioaccumulation and possibly harmful impacts on living species. Uncontrolled inputs paired with poor environmental management frequently, cause high levels of persistent organic pollutants in affected estuaries [2]. POPs are largely man-made chemicals designed to be employed in various applications such as agriculture and industry, or unintended byproducts of industrial operations or garbage incineration. Organochlorinated pesticides (OCP), polychlorinated biphenyls (PCBs), perfluorinated compounds (PFCs), brominated compounds (BFR), dioxins and furans are among the several types of POPs. The majority of these chemicals are of anthropogenic origin [2]. However, substances such as dioxins and furans may have natural origins such as volcanic activities and vegetation fires [3].

Types of POPs

Many POPS have proved to be beneficial in pest and disease control, but they have unforeseen effects on human health and the environment [4]. Figure 1 shows categories of Persistent organic pollutants (POPs) that have been introduced into the environment

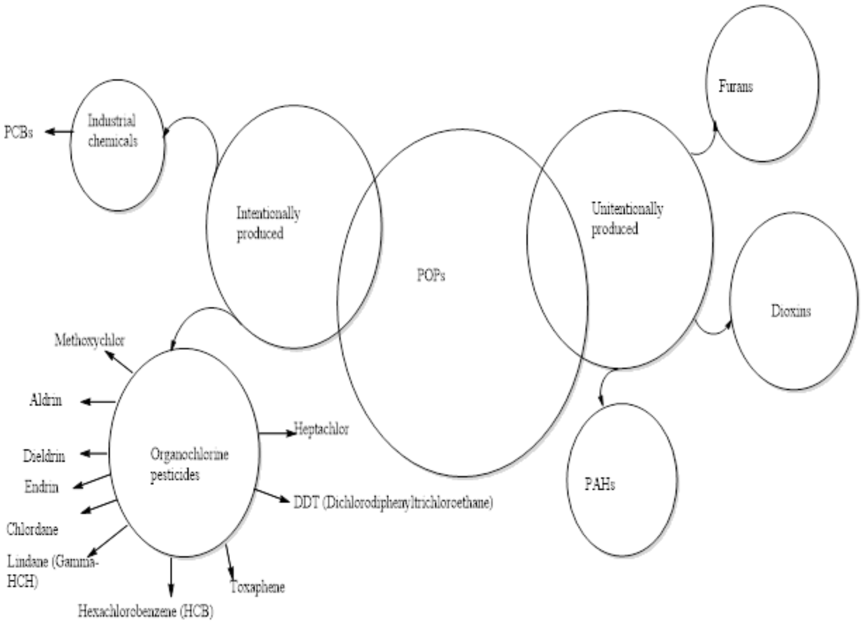

Figure 1: Categories of persistent organic pollutant

Intentional persistent organic pollutants

Intentional persistent organic pollutants are chemicals that are or were purposefully generated and utilised in manufacturing, industrial operations, agriculture, or disease prevention [5] . These deliberate POP compounds were created as desired byproducts of various chemical processes involving chlorine [6]. They are known as organochlorine compounds and are organic molecules with linked chlorine atoms, high lipophilicity and typically high neurotoxicity [2]. Some of the well-known examples of organochlorine chemicals are the chlorinated insecticides, such as dichlorodiphenyltrichloroethane and polychlorinated biphenyls [2]. There are two categories of intentional persistent organic pollutants: industrial chemicals and organochlorine insecticides [7].

Industrial chemicals

PCBs are a class of synthetic organic compounds comprised of atoms of carbon, hydrogen and chlorine. Many of the physical and chemical characteristics of a PCB molecule are determined by the quantity and placement of chlorine atoms. PCBs differ in viscosity from an oil to a waxy solid and are known to have no taste or smell [8]. From 1929 until their production was outlawed in 1979, PCBs were made in the United States. Their viscosity ranges from thin, light-coloured liquids to waxy solids that are either yellow or black and their toxicity varies as well. PCBs were utilised in hundreds of commercial and industrial applications because of their electrical insulating qualities, high boiling point, chemical stability and non-flammability. These applications included electrical, heat transfer and hydraulic equipment, plasticizers in paints, plastics and rubber products, pigments, dyes and carbonless copy paper [9]. Many industrial applications, such as fire-resistant transformers and insulating condensers, relied heavily on PCBs [2]. Figure 2 shows some intentionally produced PBCs in the industries.

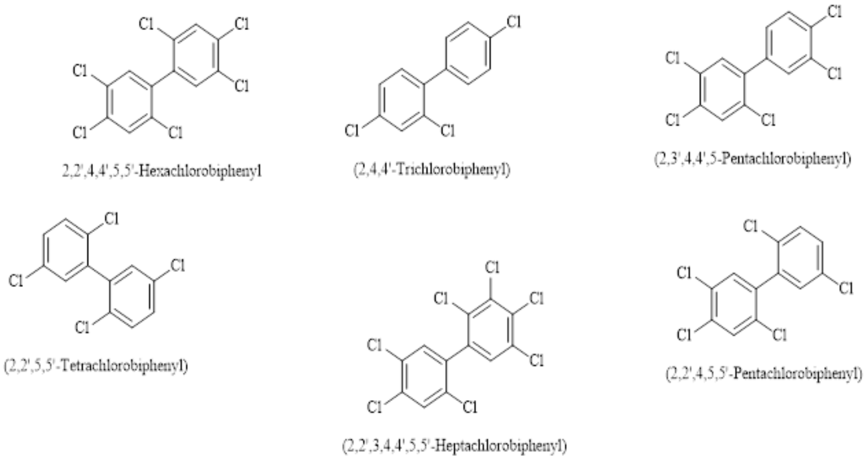

Figure 2: Examples of Polychlorinated Biphenyls

Organochlorine insecticides

Organochlorine pesticides (OCPs) or insecticides are synthetic chlorinated hydrocarbons, which are used to kill insects (e.g., mosquitoes, termites, head lice, fire ants) [10]. They belong to the group of chlorinated hydrocarbon derivatives [2]. Despite the benefits of pesticides in agricultural production and disease management, pesticides pose considerable risks to the environment and public health. Pesticide components are now persisted in our atmosphere, contaminating water, food and soil, posing health risks ranging from acute to chronic toxicities [11]. Pesticides (e.g., DDT and derivatives, hexachlorocyclohexane (HCH), aldrin, dieldrin, heptachlor and endosulfan) are examples of chlorinated hydrocarbon substances (ClHCs). These compounds, which are lipophilic and have low volatility and water solubility, have been used in both developed and developing countries for many decades [12]. In order to manage malaria, numerous countries continue to use DDT against mosquitoes [2]. This is because of DDT durability, persistence and extensive use [2]. DDT traces can be found anywhere, including the Arctic [2]. However, prior to 1975, certain pesticides, including DDT and other chlorinated hydrocarbons were banned [13].

Unintentionally POPs

Unintentionally generated chemicals are the outcome of medical waste combustion, incarnation and certain industrial activities. They are classified into three categories: polycyclic aromatic hydrocarbons (PAHs), dioxins and furan compounds [2].

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds made up of two or more fused benzene rings arranged in a linear, angular, or cluster pattern [14]. Polycyclic aromatic carbons (PACs), contain both unsubstituted hydrocarbons (PAHs) and substituted PAHs (nitro-PAH, oxygenated PAH). PAHs are the most stable type of hydrocarbons, with a low hydrogen-to-carbon ratio and are typically found in complex mixtures rather than single compounds. They are typically formed under poor combustion conditions [14]. The principal pathway of exposure to PAHs in the general population is from inhaling ambient indoor air, eating food containing PAHs, smoking cigarettes, or breathing smoke from open fireplaces and from the fossil fuels that are used to run cars and cook food [15]. For the majority of PAHs, the carcinogenic and genotoxic potential is a crucial component in hazard and risk assessment. In assessments of PAHs in food, the Scientific Committee on Food (SCF) considered the evaluations conducted by numerous international expert organisations and prioritised compounds based on the health risk rather than their presence in food [16].

Dioxins and dibenzofurans

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are classes of compounds characterized by two benzene rings connected by oxygen atoms, with varying numbers and positions of chlorine atoms attached. The general structures of these compounds are depicted in **Figure 3.**

Octachlorodibenzo-p-dioxin   1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin

2,3,7,8-Tetrachlorodibenzo-p-dioxin   1,2,3,4,7,8-Hexachlorodibenzofuran

2,3,4,7,8-Pentachlorodibenzofuran   2,3,7,8-Tetrachlorodibenzofuran

Figure 3: Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF)

Waste water treatments methods

Advanced oxidation processes (AOPs), uses hydroxyl radical ($^{\cdot}OH$) for oxidation, have gained attention in wastewater treatment research in recent decades [17]. AOPs are effective methods for degrading organic pollutants in wastewater [17]. One prominent AOP is Fenton's Reagent, which combines ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) to generate highly reactive hydroxyl radicals ($^{\bullet}OH$). These radicals efficiently oxidize a wide range of organic contaminants, leading to their breakdown into less harmful substances [17].

Another method is Electrochemical Oxidation technologies, which utilizes an electric current to produce reactive species at the anode. Electrochemical oxidation appears as a potential process for eliminating contaminants from wastewater, which has recently been an important topic of research. Its key advantages include environmental compatibility, adaptability, energy efficiency and cost-effectiveness [18]. The efficiency of electrochemical treatment as well as the potential generation of harmful byproducts is heavily dependent on the choice of electrode materials and the oxidation mechanism [19]. In the anodic oxidation (AO) the pollutants are oxidized by $^{\bullet}OH$ radicals generated at the anode surface during water discharge [19].

Photolysis and Photocatalysis is a method that can be used to treat water. Photolysis of water using UV radiation with a wavelength less than 190 nm produces strong oxidising species ($\cdot OH$; quantum yield ~OH = 0.42 at 172 nm) and reducing species ($\cdot H$; ~H <0.05 at 172 nm) that can destroy contaminants in water [20,21]. The combination of ozone with UV results in a net enhancement of organic matter degradation due to the direct and indirect generation of OH radicals during ozone decomposition and H_2O_2 formation [22]. Ozone reacts with organic molecules either directly or indirectly, via electrophilic assault or radical chain reactions. The sluggish reactivity of molecular ozone with organic molecules relative to $^{\cdot}OH$ suggests that $^{\cdot}OH$ is the primary mechanism in the UV/O_3 system [23]. Among all semiconductor photocatalysts, TiO_2 is garnering overwhelming interest as a prospective photocatalyst due to its outstanding properties, such as nontoxicity, chemical stability, high photocatalytic activity, ability to be coated as a thin film on a substrate and environmental friendliness [24–26]. This is because the macroporous channels could act as light-transfer pathways for distributing photon energy onto the broad surface of inner photoactive mesoporous frameworks. As a result, the light utilization efficiency of heterogeneous photocatalytic systems, including photooxidation reactors could be enhanced [27]. TiO_2 nanoparticles (<10 nm) are commonly used to enhance photocatalytic activity. Several approaches have been developed, including doping TiO_2 with metals (e.g., V, Cr, Mn, Fe, Co, Ni, Cu and W) and nonmetals (e.g., carbon, nitrogen, fluorine, phosphorus and sulphur); doping with semiconductors (e.g., WO_3, MnO_2 and ZnO); and using nanomaterials as TiO_2 support [27].

Activated carbon (AC) materials having specific surface areas of ~103 m^2/g are widely employed as adsorbent. Aside from ozonation, AC adsorption is now the most widely used and recommended process for upgrading wastewater treatment plants [28]. Carbonization and activation are the most important steps in activated carbon synthesis since they control the adsorbent's surface characteristics and porous structure. Carbonization removes both non-carbon and volatile carbon species. An elementary pore structure with a constant carbon mass is formed. The carbonized material produced will be an elementary graphitic crystallite with a disordered and poorly developed porosity structure. The procedure is normally carried out at temperatures below 800°C in a gaseous atmosphere with no existing oxidants. The criteria that determine the quality and yield of the carbonised product include the rate of heating, final temperature, processing time at the final temperature and the physical state of the carbonaceous precursor. The activation process increases the pore volume of the material, widens the holes generated during carbonization and creates new pores in carbonized materials. As a result, the adsorbent's properties will improve following the activation process [29]. The surface of activated carbon helps in effective removal or adsorption of organic compounds [29].Similarly, aerogel is a type of material that uses gas as a dispersion medium and has a continuous 3D porous network. It was successfully created by Kistler in 1931 [30]. In contrast, nanocellulose-based aerogels combine great features such as green repeatability, good biocompatibility and rapid breakdown [31]. Nanocellulose-based aerogels can compensate for the drawbacks of brittleness and sophisticated equipment of typical aerogel materials such as silica (SiO_2), carbon and tin dioxide**.**

II. Material And Methods

Synthesis of Aerogel by Sol-Gel Process

Silica aerogels are extensively used to remove VOCs, including monocyclic aromatic hydrocarbons (MAHs), PAHs, textile dyes and heavy metals from wastewater. Some VOCs were eliminated from waste gas streams. Silica aerogels can be functionalised or combined with other materials [32]. Sol-gel processing refers to the synthesis of an inorganic network via a chemical reaction in solution at low temperatures, or the production of an amorphous network in opposition to crystallization from the solution. The most visible aspect of this reaction is the change from a colloidal solution (liquid) to a multiphase gel (solid), hence the term "sol-gel process"[33].

Sol can be created using two techniques: particle dispersion and condensation. Sol-gel processing has advanced due to its controllable nanoarchitecture throughout the synthesis phase. Tailoring the structure of nanosystems from early processing stages promotes the creation of pure materials with superior qualities. Compounds with advanced characteristics can be used in a variety of applications, including fibres, films, fine powders and monoliths. Sol-gel processing can also be used to make aerogels [34]**.** Sol-gel processing typically involves four phases namely sol formation, gelation process, aging and drying) with extra operations used to improve mechanical qualities and gel characteristics [34].

Sol formation and gelation processes

Silica gel is created using the sol-gel process, which involves adding a catalyst to a silica source to create a gel. Gels are classified based on the dispersion media employed, such as hydrogel, aqua gel, alcogel and aerogel for water, alcohol and air, respectively [35]. To accomplish this, a system must move from a liquid "sol" phase to a solid "gel" phase. The sol-gel method involves three stages: sol formation, gelation and gel ageing. In contrast to crystallisation from solution or the synthesis of an inorganic network by a chemical reaction in solution at low temperature, sol-gel processing produces an amorphous network [36].

Precursors are soluble beginning materials in the sol-gel process that must be reactive enough to participate in gel formation [37]. Alkoxides are the most popular sol-gel precursor due to their widespread availability. Ebelmen [38] invented the use of tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) as precursors for aerogel production. Table 1 summarizes some of the commonly used precursors in aerogel synthesis.

Table 1: Precursors used in the synthesis of aerogels

S/N	Precursor	References
1	Tetraethyl orthosilicate (TEOS)	[39]
3	Tetra-methoxysilane (TMOS)	[40]
4	Methyltrimethoxysilane (MTMS)	[41]
5	Polymethylsilsesquioxane	[40]
6	Methyltriethoxysilane (MTES)	[42]
7	Sodium silicate (Na_2SiO_3)	[43]

The hydrolysis and condensation processes can be influenced by a range of parameters including the activity of the metal alkoxide, water/alkoxide ratio, pH, temperature, solvent used and additives used [33]. In the process of gel formation, hydrolysis and condensation are the two reactions that take place [43].

In the hydrolysis step, water or hydroxide ions (nucleophiles) attack the silicon atom, forming a tetrahedral intermediate, followed by the elimination of ethanol, resulting in silanol (-Si-OH) groups. In the condensation step, two silanol groups react, leading to the formation of a siloxane (Si-O-Si) bond with the loss of water, or a silanol reacts with an alkoxysilane (Si-OR), releasing alcohol. These reactions repeat , forming an extended three-dimensional silica network, ultimately yielding silica gel. Hydrophobic aerogels are formed without surface chemical modification from hydrophobic precursors, while hydrophilic aerogels are formed from hydrophilic precursors [43].

Aging of the gel

In this stage, the gel produced is soaked (aged) in the mother liquor for some days. The aging helps to strengthen the gel to prevent shrinkage during drying [43]**.** Two independent mechanisms might operate during aging that modify the properties of the gel is neck growth between particles caused by the precipitation of silica dissolved from their surfaces or dissolution of small particles and precipitation onto larger ones [43]. Aging leads in a porous solid in which solvent is trapped [43]. Research has shown that the composition, pH and ageing period of an aerogel can impact its interior structure, including the surface area, strength and stiffness. Washing has been reported to increase the permeability of the gel. Several aging solutions have been used, for instance, tetraethyorthosilicate (TEOS)-water-ethanol solutions have been used to age sodium silicate gels [44]. The gels were washed with 20% water and ethanol solution for 24 hours at 60˚C, then the aging solution (70% TEOS: ethanol, v/v) was used for 6–72 hrs at 70˚C, followed by washing with ethanol and heptane. The use of solvents with low vapour pressure has been proposed [45]. During the aging of gel, it is customary that the solvent evaporation could make the network slightly shrink before completing the aging process. Nevertheless, this little shrinkage can be avoided by using the solvents with low vapor pressure. Besides, ionic liquids can also be used for this purpose (because they have extremely low vapor pressure and a variety of solvent properties [45] ,[46].

Drying of Gel

Aerogel preparation relies heavily on drying the gel. Different drying processes have been developed including supercritical drying, ambient pressure drying (subcritical drying), evaporation and lyophilisation or freeze-drying [34]. Drying removes moisture from the solid structure's pores, preventing the silica framework from collapsing [35]. Capillary pressure (P_c) controls the drying process, affecting crucial parameters such as surface tension ($-\gamma lv$), pore volume (V_p), surface area (S_p) and surface adsorbed layer thickness (θ) [47],[34].

$$Pc = \frac{-\gamma lv}{2(Vp/Sp - \theta)} \tag{1}$$

Capillary pressure and surface tension are proportional to each other. Using a solvent with high surface tension during drying increases capillary pressure within gel pores. When the liquid is removed, the pores collapse and the gel shrinks, creating a low surface area material [34].

In supercritical drying gels are dried to a critical point to minimise capillary forces in supercritical drying processes. Surface tension causes concave menisci in the gel's pores as soon as the liquid begins to evaporate. As the liquid continues to evaporate, compressive forces build up along the pore's perimeter, causing it to constrict. Surface tension eventually leads to the collapse of the gel body [48]. To prevent surface tension buildup, the gel is dried supercritically in an autoclave. When the autoclave temperature and pressure exceed a critical point (243°C and 7.9 MPa for methanol, respectively), the liquid becomes a "supercritical" fluid, allowing molecules to move freely and eliminating surface tension. Menisci cannot develop in the absence of surface tension. The vapours are then gradually discharged from the autoclave until the pressure within reaches atmospheric levels. The autoclave is flushed with dry nitrogen (~3 bar) to remove trapped solvent molecules from the dry gel [33].

Ambient pressure or subcritical method is becoming more popular because of its lower cost compared to supercritical drying. Rather than employing temperature and pressure to evaporate the pore liquid, ambient pressure drying utilises surface modification to dry the gel at ambient pressure. The gel's pores exchange liquid for a low-surface tension solvent appropriate for evaporative drying. Diffusion of a low-surface tension solvent alters the gel's surface, replacing polar groups with non-polar ones. At ambient temperature, the solvent is evaporated from the gel's pores. Gels dried at ambient pressure can have densities as low as 0.150 g/cm^3 and increased pore volume [34].

In the alkoxide sol-gel technique, the solid phase consists of connected nanometre-sized spherical particles with unreacted silanol groups on the surface. Two groups successfully manufactured silica aerogels at ambient pressure after altering the gel surface [49]. Einarsrud and colleagues aged wet gels in two solutions: water/alcohol and alkoxide/alcohol. This procedure reduces surface area and strengthens the gel's microstructure by filling in the necks between connected particles [50]. Wet gels that have a greater Young's modulus can sustain capillary pressures caused by surface tension when the liquid meniscus recedes into the gel. Aerogels with densities as low as 240 kg m^{-3} have been made [49]. Smith and Brinker took another approach since evaporation of pore liquid can cause sterically favoured condensation processes between two surface silanol groups, resulting in irreversible syneresis [49]. Recognising this, they methylated the gel surface by proton abstraction of the surface hydroxyl groups [49] as shown in equation 2;

$$Si - OH + Si(CH_3)_3Cl \longrightarrow Si - O - Si(CH_3)_3 + HCl \tag{2}$$

The reaction involves surface silanol (-Si-OH) groups reacting with trimethylchlorosilane ($Si(CH_3)_3Cl$). The hydroxyl (-OH) groups on the silica surface are deprotonated. The chlorine from trimethylchlorosilane ($Si(CH_3)_3Cl$) reacts with these hydroxyl groups, replacing them with $Si\text{-}(CH_3)_3$ groups. The substitution makes the silica surface more hydrophobic, reducing the likelihood of further condensation reactions and syneresis.

Freeze-drying is a method that eliminates the need for a phase boundary between the liquid and gas phases. The solvent is exchanged with a low expansion coefficient and high sublimation pressure and the pore liquid is frozen and sublimed under vacuum conditions [33].

III. Result

Properties of silica aerogels

Pore structure

The IUPAC taxonomy of porous materials categorises pores as "micropores" (less than 2 nm), "mesopores" (2-50 nm) and "macropores" (more than 50 nm). Silica aerogels have pores of three sizes. However, most pores are in the mesopore range, with few micropores [51]. Therefore, the pore size ranges from 5 to 100 nm, with an average diameter of 20-40 nm and a BET surface area of 600–1000m^2. Porosity can reach up to 99% [35]. The interconnectedness and "open" nature of the aerogel pore network is crucial. Fluids in open-pore formations can freely flow from pore to pore, eventually travelling through the entire material [35]. Silica aerogels' pore structures make them suitable for use as filters, absorption media for desiccation and waste containment [52].

When reporting porosity data, it is critical to specify the type of measurement employed. Aerogels are difficult to characterise due to their high porosity and tiny pore size, making mercury intrusion (MIP), thermoporometry (TPM) and nitrogen adsorption/desorption (NAD) challenging [35]. These approaches use capillary pressures to compress the aerogel network, which can result in inaccurate pore size and volume measurements [53].

Aerogel microstructure can be studied using high resolution SEM and TEM techniques. These approaches provide challenges, particularly in sample preparation. During the experiment, the fine aerogel powder may become electrostatically loaded, altering its properties. These approaches allow for direct examination of the aerogel structure, estimating particle and pore sizes [35].

Optical properties

Silica aerogels are transparent, a rare property for a porous material. This is due to the microstructure of the aerogel having a small scale compared to the wavelength of light. The scattered light has a relatively isotropic angular distribution with little multiple scattering, resulting in transparency [54–57].

Rayleigh scattering theory describes the isotropic scattering of vertically polarised incident light, the intensity of which varies with scattering angle as cos θ for horizontally polarised incident light and the wavelength dependence of scattered light as 1/~4. However, aerogels differ from Rayleigh scatterers in that they also exhibit a wavelength independent component of scattering, which may not be isotropic [55]. Efforts have been made to improve the transparency of silica aerogels, including investigating the impact of the drying process, water adsorbed to Si-OH groups and absorbed organic components. Heating the aerogels improves transparency by desorbing water and burning organic components [58]. The optical characteristics of aerogel are significantly influenced by the sol-gel process parameters and silation agent used [59]. New aerogels with refractive index greater than 1.03 were synthesised using di-methyl formamide (DMF) as a solvent in the sol-gel technique [60].

Thermal conductivity

Aerogels have extraordinarily low effective heat conductivity, making them a promising new thermal insulation material. Aerogels' nanoporous structure prevents gas molecules from moving, while the nano-skeleton system limits heat transfer due to size. Numerous studies and models have been conducted to anticipate heat transport [61]. Therefore, silica aerogel has extremely low thermal conductivity, 12–20 mW/(m·K) at room temperature, which is much lower than conventional thermal insulation materials [61].

Hydrophobicity

The synthesis conditions determine whether silica aerogels are hydrophilic or hydrophobic. The aerogel structure's hydrophilicity stems from the presence of silanol polar groups (Si-OH), which enhance water sorption. Aerogels made via unaltered hydrolysis and condensation of alkyl orthosilicates and dried at high temperatures are often hydrophobic [62], while those dried with CO_2 are typically hydrophilic. The supercritical drying (SCD) process creates distinct surface groups, resulting in this disparity [62].

Low temperature supercritical drying (LTSCD) adds hydroxyl groups (-OH) to the surface, creating hydrophilic aerogels. High temperature supercritical drying (HTSCD) converts surface hydroxyl groups into methoxy groups ($-OCH_3$) X, resulting in hydrophobic aerogels [35]. Fourier transform infrared spectroscopy (FTIR) and Carbon-13 Nuclear Magnetic Resonance (13C NMR) were used to study the chemical bonding status of aerogels [63]. There are two ways to increase the hydrophobicity character of aerogels by adding a silylating chemical during the sol-gel phase, another method for improving hydrophobicity is by modify the aerogel surface after drying [35].

Hydrophilic aerogels can have their surface modified by reacting with gaseous methanol [64]. In another report the monolithic silica aerogel surfaces were made hydrophobic by treating them with hexamethyldisilane (HMDS) using $scCO_2$ as a solvent. The procedure produced hydrophobic silica aerogels that were as transparent as untreated aerogels [65]. The FTIR spectra revealed a reduction in hydrophilic surface silanol groups and the appearance of hydrophobic CH_3 groups. The bubble point pressures of the HMDS-CO_2 system were measured at temperatures of 298.2 K, 313.2 K, 327.7 K and 342 K, at varied concentrations. At a constant temperature, the bubble point pressure fell as the concentration of HMDS rose. At a fixed composition, bubble point pressure increased with temperature [65].

Thermogravimetric and differential thermal analyses (TGA-DTA) can be used to determine the thermal stability of aerogels in terms of hydrophobicity retention. Samples can also be heated in the furnace and placed on the water surface. Aerogels' retention of hydrophobicity (water-repelling property) can be assessed by their ability to absorb water. Hydrophobic gels are hydrophobic for a limited amount of time. Long-term exposure to air causes adsorption of water, which is not normal for hydrophobic materials [35].

IV. Discussion

Application of silica-based aerogel to remove organic pollutants from water

Silica aerogels, both modified and synthesised can be successfully used in environmental applications. Modifying silica aerogel results in an 18-fold increase in adsorption capacity (from 14 mg/g to 214 mg/g) [66]. Somaklı & Şengel [66] synthesised silica aerogels and nano/microparticle-embedded silica aerogels using SiO_2 and carbon particles (CP) using a hydrothermal-supported sol-gel synthesis method in a short time. New functional groups were introduced to improve application performance. The synthesised structures were used as adsorbent to remove organic contaminants such as phenols and textile colours from water.

A hydrothermal technique and heated reflux reaction approach was used to create tin dioxide microspheres modified with methyltrimethoxysilane (MTMS). The characterisation results show that the alteration of MTMS caused the creation of a hydrophobic network inside the composites while retaining an abundance of adsorbed oxygen species. The MTMS/SnO_2 microspheres were then utilised as a solid-phase microextraction (SPME) coating to extract and detect trace polychlorinated biphenyls (PCBs) in aqueous solutions using gas chromatography-mass spectrometry. Because of the hydrophobic crosslinking and adsorbed oxygen-enhanced hydrogen bonding, the MTMS/SnO_2 coating outperformed commercial SPME and pure SnO_2 microspheres coatings in terms of PCB extraction [67].

Dyeing is a textile industry procedure that adds colour to fabrics. Untreated wastewater from this procedure diminishes light penetration in the receiving environment, significantly impacting photosynthetic activity [68]. The accumulation of waste dyestuffs in aquatic species poses a risk of harmful and carcinogenic effects. It is not recommended to release dye-containing effluent into the receiving environment without treatment [68]. Table 2 shows the application of silica aerogels monoliths adsorbents in the removal of organic pollutants in water.

Table 2: Application of silica-based aerogel in removal of persistent organic water pollutants

S/No.	Material	Preparation Technique	Persistent organic pollutant	Reference
1	MTMS/SnO_2	Sol-gel process+ supercritical drying	PCBs	[67]
2	Titania– silica–sepiolite nanocomposite	Sol–gel process followed by unidirectional immersion into liquid nitrogen	p-nitrophenol (PNP) and methylene blue (MB)	[69].
3	Silica aerogel	Sol-gel process + ambient drying and then 130 °C	Naphthalene	[70]
4	Silica aerogel	Sol-gel process + supercritical drying	VOCs	[71]
5	Hexagonal Mesoporous Silica	Sol-gel process+ ambient temperature	organochlorine pesticides like 1,1,1-trichloro-2,2′ bis(p-chlorophenyl) ethane)	[72]
6	Aluminosilica monolith disk-like membranes	Sol–gel + dried at room temperature	N, N′-disalicylidene-4,5-diamino-6-hydroxy-2-mercaptopyrimidine (H2DSPy) dye,Organic pollutants: p-nitroanilin, o-aminophenol, p-choroaniline and aniline	[73] [73]
7	Hydrophobic silica monolith aerogel	Sol–gel + Supercritical drying: supercritical CO_2 at 40 °C and 100 bars	Organic solvents: toluene, benzene, ethylbenzene, xylene, cholrobenzene, chloroform, 1,2 dichloroethane, trichloroethylene in water	[71]

V. Conclusion

Silica aerogels represent a cutting-edge solution for water purification, offering high efficiency in pollutant removal. Their unique properties, including high porosity and surface tunability, make them superior to traditional adsorbents. Continued advancements in material engineering and large-scale deployment strategies will enhance their role in sustainable water treatment technologies.

Declaration of conflict of interest

The authors hereby declare no conflict of interest in publishing this paper

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