NÖHÜ Müh. Bilim. Derg. / NOHU J. Eng. Sci., 2023; 12(3), 872-882

Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi
Niğde Ömer Halisdemir University Journal of Engineering Sciences

Araştırma makalesi / Research article

www.dergipark.org.tr/tr/pub/ngumuh / www.dergipark.org.tr/en/pub/ngumuh

Synthesis and modification of hydro(solvo) thermal-supported silica aerogels and their use in adsorption studies

Hidro(solvo)termal destekli silika aerojellerin sentezi, modifikasyonu ve onların adsorpsiyon çalışmalarında kullanımı

Sultan Bütün Şengel[1,*], **Şeyda Somaklı**[2]

[1] *Eskisehir Osmangazi University, Department of Biomedical Engineering, 26480, Eskisehir, Türkiye*
[2] *Eskisehir Osmangazi University, Polymer Science and Technology, 26480, Eskisehir, Türkiye*

Abstract

The hydro(solvo)thermal synthesis method was used to successfully synthesize bare silica aerogels and nano- and microparticle-embedded silica aerogels containing SiO_2 and carbon microparticles in this study. New groups were added to these structures through modification. In the study, first, the effect of the variables was systematically examined to determine the optimum conditions. The most suitable recipe for silica aerogel was created. SiO_2 and CP particles were synthesized, and modified silica aerogels were prepared with these particles and agents containing amine. For the characterization of synthesized silica aerogel, particles (SiO_2, CP) and particle-embedded silica aerogels, TGA, SEM, DLS and BET-BJH techniques were used. These structures were used as adsorbent in environmental applications such as removing organic pollutants like 4-nitro phenol, methylene blue, Victoria blue, bromophenol blue etc. from aqueous media. In this environmental application, the adsorption capacity (mg/g) was determined by using UV-vis spectroscopy. The prepared structures are good adsorbents, and the adsorption capacity can be increased 18-fold with modification.

Keywords: Hydro(solvo)thermal synthesis, Silica aerogel, CP/SiO_2- silica aerogel, Adsorption

Öz

Hidro(solvo)termal sentez yöntemi, bu çalışmada SiO_2 ve karbon mikropartikülleri gibi nano- ve mikropartikül katkılı silika aerojelleri ile boş silika aerojellerini başarılı bir şekilde sentezlemek için kullanılmıştır. Hazırlanan bu yapılara modifikasyon yoluyla yeni gruplar eklenmiştir. Çalışmada öncelikle optimum koşulların belirlenmesi için değişkenlerin etkisi sistematik olarak incelenmiştir. Silika aerojel için en uygun reçete oluşturulmuştur. SiO_2, CP partikülleri sentezlenmiş ve bu partiküller ile ve amin içeren ajanlar ile modifiye silika aerojeller hazırlanmıştır. Sentezlenen silika aerojel, partiküller (SiO_2, CP) ve partiküller gömülü silika aerojellerin karakterizasyonu için; TGA, SEM, DLS ve BET-BJH teknikleri kullanıldı. Hazırlanan bu yapılar 4-nitro fenol, metilen mavisi, victoria mavisi, bromofenol mavisi vb. organik kirleticilerin sulu ortamdan uzaklaştırılması gibi çevresel uygulamada adsorban olarak kullanılmıştır. Bu çevresel uygulamada adsorpsiyon kapasitesi (mg/g) UV-vis spektroskopisi ile belirlenmiştir. Hazırlanan yapıların iyi bir adsorban olduğu ve modifikasyon ile adsorpsiyon kapasitesinin 18 kat arttırılabileceği ortaya konulmuştur.

Anahtar kelimeler: Hidro(solvo)termal sentez, Silika aerojel, CP/SiO_2-silika aerojel, Adsorpsiyon

1 Introduction

Aerogels are nanoporous solids composed of 99.8% air, with complex interconnections and a branched structure several nanometers in size [1-3]. Aerogels generally have low bulk density, thermal conductivity, refractive index, and sound velocity, with high surface area and optical transmittance [4-7]. These superior properties allow aerogels to be used in many applications as chemical sensors, catalyst barriers, particle detectors, acoustics, thermal insulation, adsorbents, and in electronics [8-14]. Silica aerogels are one of the most researched aerogels among aerogel classes. In general, they are prepared by solution-gelation (sol-gel) chemistry, which involves the formation of a wet gel and drying of the wet gel with an intermediate aging process. Silica aerogels are highly porous, open-cell, low-density materials. Since the microstructure consists of nano-sized pores and connected primary particles, they have properties such as low thermal conductivity, good sound absorption, good refractive index, speed of sound and dielectric constant. Silica aerogels are used in many different sectors such as health, chemistry, and electronics due to these properties. In the production of silica aerogels, chemical precursors such as methyltriethoxysilane (MTES), tetraethoxysilane (TEOS), polyethoxydisilane (PEDS), and tetramethoxysilane (TMOS) can be used, and organic materials such as rice husk ash can be used as cheap silicon sources [15-18]. Due to their properties, silica aerogels are used as thermal and acoustic insulation material in the field of construction, as carrier material in the field of agriculture, as sensor and insulator material in the field of electrical-electronics, and as adsorbent and catalyst in the field of chemistry. Silica aerogels allow the production of ideal dielectric materials such as capacitors, integrated circuits, and vacuum screen separators due to their very low dielectric constant [19].

---

* Sorumlu yazar / Corresponding author, e-posta / e-mail: sultanbutun.sengel@ogu.edu.tr (S. Butun Sengel)
Geliş / Recieved: 09.03.2023 Kabul / Accepted: 13.06.2023 Yayımlanma / Published: 15.07.2023
doi: 10.28948/ngmuh.1262687

Hydro(solvo)thermal synthesis is a synthesis method that occurs through chemical reactions in a solution in a closed container (sealed vessel or high-pressure autoclave) at high pressure (1-100 MPa) heated above the boiling point (100-1000 °C) of the solvent [20]. The hydro(solvo)thermal reaction is advantageous compared to other synthetic techniques. Even at low reaction temperatures, many unique materials and various crystals with superior physical and chemical properties can be synthesized by this method. In addition, metastable phases can be produced and materials with high vapor pressure, low melting point, low thermal stability and controllable morphology can be obtained.

Silica aerogels have unique properties due to their nanoporous structure, but their applicability is limited. To expand their applicability, disadvantages such as brittleness, dust release, hydrophilicity, volumetric shrinkage, processing time and high cost need to be overcome. To overcome these disadvantages, reinforcement strategies such as the addition of organic-inorganic substances before the gelation step or before drying and fine-tuning of synthesis conditions are used [21]. In the preparation of polymer / sol-gel composites, the polymer can be added directly to the solution and the polymer can be added at the gelation stage by initiating polymerization with the use of suitable catalysts. In the aging stage after gelation for silica aerogel polymer composites, the problem of polymer leaching from the pores can be encountered. There are studies in the literature that report an increase in density with improved mechanical properties in mixtures prepared in the form of polymer/silica aerogel. There are literature studies examining the effect of crosslinking on the mechanical properties and density of polymers when polyurea, polyurethane, polyacrylonitrile, poly(methyl methacrylate), and polystyrene are used as crosslinkers. It was stated that the polymers used in these studies strengthen the silica aerogel [22,23].

Based on the chemical relationship between the polymer and the surrounding silica network, polymer/sol-gel composites are divided into two categories. The first is two independent networks in which the polymer and the inorganic framework are completely independent of each other; in other words, there are no covalent bonds between them, but instead van der Waals bonds, electrostatic forces or hydrogen bonds. These are called interpenetrating networks. The second category is those with covalent bonds between the polymeric and inorganic components. The materials in this category are not limited to silica but also include other metal oxide-polymer composites such as tin oxide and aluminum oxide, etc. They eliminate the possibility of polymer leaching during the solvent exchange step and benefit by maintaining low density while improving mechanical properties [24].

Recently, the use of silica aerogel as filler in polymer matrix composites has attracted the attention of researchers because it is more advantageous than the use of silica nanoparticles. Silica nanoparticles can be easily used as a filler that preserves the properties of polymer composites without encountering problems such as precipitation and interfacial adhesion with the presence of agents such as surfactant, binder, and co-solvent. Silica aerogels are a preferred and advantageous material for the production of polymer composites due to high thermal stability and porosity as well as low density value. The loose binding of the aerogel to each other during the formation phase (hydrolysis and condensation) ensures homogeneous distribution during composite formation [25]. The use of silica aerogels for the removal of undesirable substances in wastewater has been the subject of different studies [26-28].

In this study, silica aerogels and nano/microparticle-embedded silica aerogels containing SiO_2 and carbon particles (CP) were successfully synthesized by the hydro(solvo)thermal-supported sol-gel synthesis method in a short time. New functional groups were added to these structures to increase application performance. The synthesized structures were tested for their use as an adsorbent in environmental applications such as removing organic pollutants (phenols, textile dyes) from aqueous media.

2 Material and methods

2.1 Material

For the synthesis of silica aerogel and preparation of composite structures, triethoxyorthosilicate (TEOS, 98%, Sigma-Aldrich), methanol (C_2H_5OH, 99.9%, Merck), and ammonium hydroxide (NH_4OH, 26%, Sigma-Aldrich) were used. For the modification of silica aerogel, (3-aminopropyl) triethoxysilane (APTES, ≥98%, Sigma-Aldrich), HCl (37%, Honeywell), tetraethylene pentaamine (TEPA, 95%, Merck), ethylenediamine (EDA, ≥99.5%, Sigma-Aldrich), epichlorohydrin (ECH, 99%, Sigma-Aldrich), dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), and glutaraldehyde (GA, 25% aqueous solution, Sigma-Aldrich) were used. For carbon particle (CP) synthesis, hydroxy ethyl cellulose (HEC, Yegenler Chemistry) was used as carbon source and phytic acid (PA, 50% aqueous solution, Sigma-Aldrich) as catalyst. In the environmental applications of the prepared silica aerogels, 4-nitrophenol (4-NP, 99%, ABCR Gmbh&Co.), methylene blue (MB, Sigma-Aldrich), bromophenol blue (BPB, AFC), and Victoria blue (VB, Acròs) dyes were used as model organic pollutants. An autoclave was used for hydro(solvo)thermal synthesis of silica aerogels. The autoclave was a hydro(solvo) thermal synthesis reactor with 50 mL and 100 mL inner volume consisting of a stainless-steel outer chamber and PPL inner chamber.

2.2 Synthesis of silica aerogel

As an alternative synthesis method, silica aerogel (SA), SiO_2 nanoparticle-embedded silica aerogel, and carbon microparticle-embedded silica aerogels were synthesized via hydro(solvo)thermal-supported sol-gel synthesis method. To determine the optimum conditions and to obtain bare silica aerogel with the desired properties, optimization studies were carried out by changing factors such as component amounts, temperature, and reaction time. Pre-reactions as hydrolysis-condensation and the synthesis scheme for the silica aerogel are given in Figure 1.

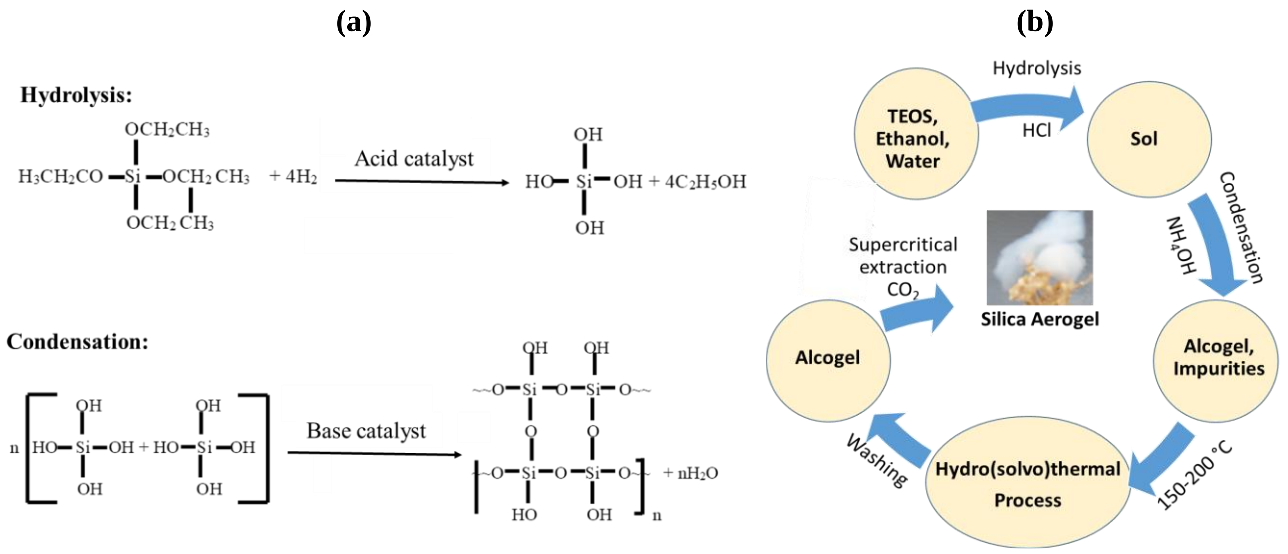

Figure 1. Reactions in hydrolysis and condensation steps (a), schematic representation of hydro(solvo)thermal-supported silica aerogel synthesis (b).

For the synthesis of silica aerogel using the typical sol-gel method, the first step is the hydrolysis reaction and the second step is the condensation reaction (Figure 1a). In this study, pre-reactions for gelation were carried out in a PPL container (autoclave inner chamber) in open air for a short time (from a few minutes to an hour). Then, the PPL containing the mixture was placed in a stainless-steel autoclave and kept at the relevant temperature to complete the gelation process by hydro(solvo)thermal treatment, with the lid tightly closed. When the gelling process was finished, the gel was washed with solvent medium (reaction medium) to remove impurities and dried with the supercritical carbon dioxide drying method.

2.2.1 Synthesis of SiO_2 particle-embedded silica aerogel

For the synthesis of silica aerogels with SiO_2 particles embedded, first SiO_2 particles were synthesized by the Stober method and then nano-silica particles were used in the synthesis of SiO_2-embedded silica aerogel and the product obtained was named SiO_2-SA.

<u>SiO_2 particle synthesis with the Stober method:</u> Three experiments were performed for SiO_2 particle synthesis with the Stober method [29, 30]. All syntheses were realized in 15 mL ethanol stirring at 800 rpm for 2 h by using TEOS: NH_4OH ratio (i) SiO_2_1 (1.0:1.25), (ii) SiO_2_2 (1.5:1.75), and (iii) SiO_2_3 (2.0:2.25). Synthesized SiO_2 particles were cleaned with an ethanol/water mixture after centrifugation at 15000 rpm several times. After the last centrifugation, SiO_2 particles were separated by decantation and then the precipitate was dried with a freeze dryer.

<u>Synthesis of SiO_2 particle-embedded silica aerogel:</u> For this, 50 mg SiO_2 nanoparticles was dispersed in ethanol:water mixture (20:10, v: v) by vortexing and sonication. Then 0.9 mL TEOS was transferred into the mixture and the mixture was stirred at 600 rpm for 15 min for hydrolysis. After that time, the base catalyst (NH_4OH, 0.3 mL) was added and stirring continued for 15 min for the condensation reaction. The mixture was transferred into the PPL chamber of the autoclave. Lastly, gelling was supported by the hydro(solvo)thermal process at 180 ºC for 18 h. The obtained gel was cleaned/washed with ethanol/water mix. The cleaned gels were dried by freeze drying and supercritical CO_2 drying methods. SiO_2 particle-embedded silica aerogel was denoted as SiO_2-SA.

2.2.2 Synthesis and characterization of CP-embedded silica aerogel

For the synthesis of silica aerogels with CP microparticles embedded, first CP microparticles were synthesized via hydrothermal methods and then microparticles were used in the synthesis of CP-embedded silica aerogel and the product obtained was named CP-SA.

<u>CP microparticle synthesis:</u> Carbon particles were synthesized via hydrothermal/dewatering process by using hydroxyethyl cellulose (HEC) as carbon source. The synthesis was prepared in the same way as the carbon sphere prepared as a catalyst in our previous study [31].

<u>Synthesis of CP-embedded silica aerogel:</u> To synthesize carbon particle-embedded silica aerogel, CP-SA, 50 mg CP micro nanoparticle was dispersed in ethanol:water mixture (20:10, v: v) by vortexing and sonication. Then, 0.9 mL TEOS was transferred into the mixture and the mixture was stirred at 600 rpm for 15 min for hydrolysis. After that time, the base catalyst (NH_4OH, 0.3 mL) was added and stirring continued for 15 min for the condensation reaction. The mixture was transferred into the PPL chamber of the autoclave. Lastly, gelling was supported by the hydro(solvo)thermal process at 180 ºC for 18 h. The obtained gel was cleaned/washed with ethanol/water mix. The cleaned gels were dried by freeze drying and supercritical CO_2 drying methods. CP-particle embedded silica aerogel was denoted as CP-SA.

2.2.3 Modification of silica aerogels (SA, SiO_2-SA, CP-SA)

Modification of SA, SiO_2-SA, and CP-SA was applied following the procedure in the literature [32-34]. To increase the application performance of aerogels, the structure was modified by adding new amine groups. For this purpose, APTES, EDA, and TEPA were used as amine sources.

APTES modification of silica aerogels: The modification was performed for SA and SiO_2-SA as reported literature [34]. The same method and same amounts were used to modify CP-SA. APTES-modified SAs were not protonated in this study. The use of acid-treated (protonation by HCl) modified forms as catalysts is the subject of another ongoing study.

EDA and TEPA modification of silica aerogels: For modification with EDA/TEPA directly on aerogel, 3.0 g aerogel (SA, SiO_2-SA, CP-SA) was activated by mixing with 100 mL 0.3 M NaOH for 30 minutes. After mixing, it was washed three times with distilled water and the solid obtained after centrifugation or decantation was dried in an oven or with a heating gun. The activated silica aerogel/particle-embedded silica aerogel was dispersed in a 100 mL flask with 50 mL DMF. The flask was sealed with a septum and placed in an oil bath at 90 ºC. After the system reached equilibrium, 6.0 mL of ECH was added to the mixture and stirred at 500 rpm for 60 minutes. Thenn13 mL of EDA/TEPA was added dropwise to the mixture and the reaction was terminated after stirring for another 60 minutes. The mixture was washed three times with ethanol/water mix and dried in a freeze dryer. EDA and TEPA binding to silica aerogel by modification is shown in Figure 2**.**

Silica aerogel and nano-microparticle-embedded silica aerogels were modified after aerogel formation as shown in Figure 2. As an alternative to this modification, first the particles can be modified (SiO_2, CP) with EDA/TEPA and then these modified particles can be embedded in SA.

2.2.4 Characterization of SA, SiO_2-SA, CP-SA, and modified forms

A Hitachi Regulus 8230 scanning electron microscope (SEM) was used to determine the surface morphology and size of the synthesized and modified particles. Silica aerogels, SiO_2- and CP-embedded silica aerogels were coated with gold-palladium under vacuum with a thickness of 3-5 nm directly on carbon tape after supercritical drying and then imaged at different magnifications. The dried SiO_2 samples (prepared with Stober) were dispersed in ethanol with the help of a vortex and 1-2 drops were dropped on carbon tape and left to dry in an oven. The dried samples were coated with gold-palladium under vacuum.

A Seiko SII EXSTAR600 model thermal gravimetric analysis (TGA) device was used to investigate the mass loss of the synthesized and modified silica aerogels and composite structures with temperature.

The analysis was carried out in the range of 50-1000 °C with a temperature increase rate of 10 °C/min using N_2 at a flow rate of 200 cm^3/min.

An ALV/CGS model dynamic light scattering (DLS) device was used to determine the hydrodynamic diameter of SiO_2 particles synthesized by the Stober method. Before the measurement, the particles were degassed in an ultrasonic bath. Measurements were performed with 3 repetitions at 25 °C and the results are given as average radius.

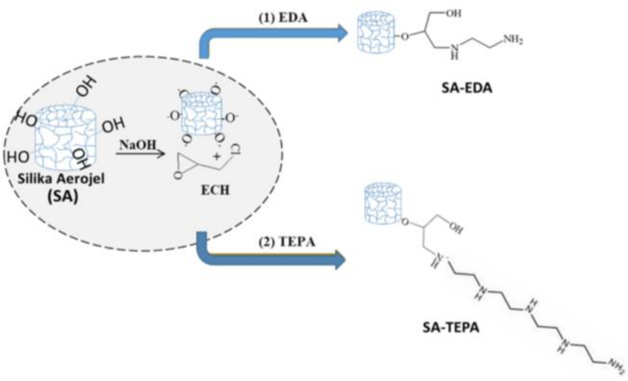

Figure 2. Schematic representation of silica aerogel modification with EDA and TEPA.

A Quantachrome brand device was used to determine the specific surface areas, pore sizes, and pore volumes of the synthesized aerogels. The surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore size and pore volume were determined by the Barret-Joyner-Halenda (BJH) method. The samples were degassed with N_2 gas for 18 h at 80 °C before measurement.

The cleaned gels and modified particles were dried by lyophilization at -60 °C under vacuum using a Christ Alpha 2-4 LSC brand freeze dryer. The particles were placed in the device after freezing in deep freezer and left to dry for 24 hours.

A Perkin Elmer UV-Vis Lambda 35 ultra-violet visible region spectrophotometer (UV-Vis) device was used in environmental applications to determine the amount of organic pollutants absorbed as mg/g.

2.2.5 Environmental Applications

In the textile industry, dyeing is a process applied to give color to the fabric. When the wastewater generated because of this process is discharged without treatment, it reduces light transmittance in the receiving environment due to this color and negatively affects photosynthetic activity. At the same time, increased waste dyestuffs increase the risk of toxic and carcinogenic products as they accumulate in aquatic organisms. In this context, it is not desirable to discharge wastewater containing dyes to the receiving environment without treatment. For the removal of organic pollutants from aqueous medium, 4-nitrophenol (4-NP), methylene blue (MB), bromophenol blue (BPB), and Victorian blue (VB) dyes were used as organic pollutants.

The synthesized and modified silica aerogels were used as adsorbents for the removal of organic pollutants from aqueous medium. For this purpose, 20 mg adsorbent and 20, 20, 10, and 5 mL of dye solutions at concentrations of 4-NP (1000 ppm), MB (300 ppm), BPB (30 ppm), VB (30 ppm) were taken respectively and mixed at 600 rpm at room temperature overnight.

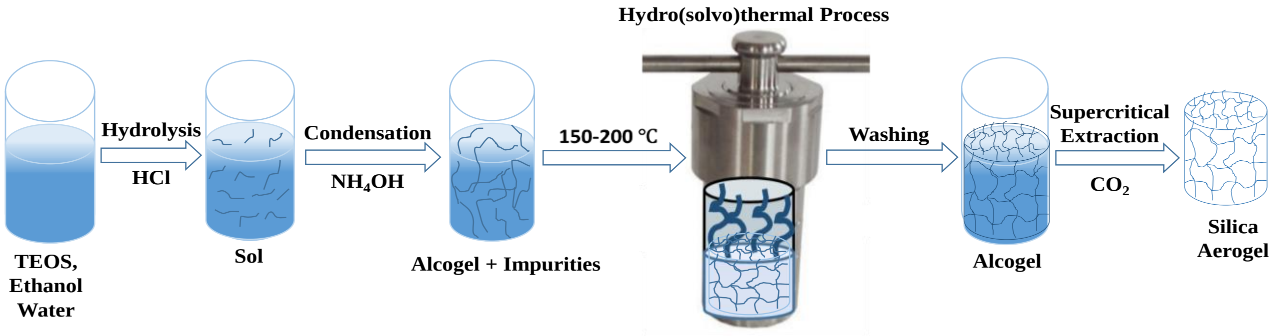

Figure 3. Silica aerogel synthesis schema with hydro(solvo)thermal-supported sol-gel process.

At the end of this period, the mixture was centrifuged and the adsorption values of the liquid remaining on top were measured by UV-Vis spectrophotometer. During the measurement, the amount of pollutant adsorbed per gram of gel was calculated in mg for 4-NP, MB, BPB, and VB at the maximum wavelengths of 317, 664, 590, and 616 nm, respectively, using previously-prepared calibration curves. The adsorption amounts of the dyes were calculated using the following Equation (1);

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Here q_e (mg/g) are the amount of dye adsorbed at equilibrium time. C_0, C_e (mg/L) are the initial and equilibrium concentration of the aqueous dye solutions, respectively. V (L) is the volume of the aqueous dye solution and W (g) is the dry mass of the aerogel.

3 Results and discussion

3.1 *Silica aerogel synthesis and optimization studies*

Initially, the sol-gel method was used for the synthesis of bare silica aerogels. As a result of the experiments, the method was changed because the gelation time was very long, and the strength of the gels was poor. The hydro(solvo) thermally-assisted sol-gel method was preferred due to its shorter gel formation time and controllability. Schematic representation of silica aerogel synthesis by the hydro(solvo)thermal-supported synthesis method is given in Figure 3. Optimization studies were carried out to obtain the optimum conditions for silica aerogel synthesis with the hydro(solvo)thermal method. As a result of the study, the effects of factors such as the components used and their amounts, working pH, working temperature, and hydrothermal treatment time on gel formation were observed. After examining the effect of the variables, the optimum conditions were found to be water/ethanol volume ratio used in the reaction medium 1:2, base/TEOS volume ratio 1:3, hydro(solvo)thermal reaction time 18 h, and the hydro(solvo)thermal reaction temperature 180 ºC.

3.2 *SiO_2 nanoparticle synthesis via Stober method*

In order to prepare SiO_2 particle-doped silica aerogel, SiO_2 nano/micro particles to be embedded in the gel were first synthesized. The synthesis of SiO_2 nanoparticles was carried out by the Stober method. Three different sizes of nanoparticles were synthesized. The hydrodynamic diameters of the synthesized SiO_2 particles were measured by DLS and the results are given in Figure 4.

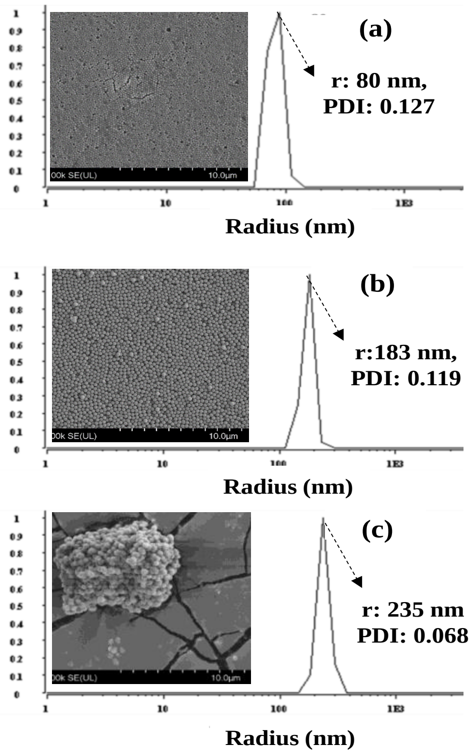

Figure 4. SEM images and DLS measurement results for SiO_2 particles synthesized by the Stober method, (a) SiO_2_1, (b) SiO_2_2, (c) SiO_2_3.

The hydrodynamic diameter of the synthesized SiO_2 particles were measured as 2x80 nm, 2x183 nm and 2x235 nm for SiO_2_1, SiO_2_2, and SiO_2_3, respectively. To examine the surface morphology of these three samples, SEM images of the dry samples were taken, and SEM images taken at different magnifications are given in the same figure. SiO_2 particles close to monodispersed with very low PDI values were successfully synthesized.

3.3 CP microparticle synthesis via hydrothermal process

New functional groups can be added to the structure with various modifications to increase the performance in applications. The desire may be to provide features such as reducing the application time, ensuring the reusability of the material, long shelf life, increasing conductivity and mechanical strength, and adjusting the pore size. Nano-micro sized fillers are important in this sense. They are used as a direct addition of metal-containing filler such as SiO_2, TiO_2, ZnO, Fe_3O_4, MnO_2, HNT or to form composite structures in situ. The increasing interest in carbon-based materials in recent years is remarkable. These can be listed as types with or without metals, with different morphology and dimensions of 0D, 1D, 2D and 3D, such as fullerenes, carbon fiber, carbon nanotube, carbon black, porous carbon, carbon spheres/particles, graphite-graphene, biochar, and carbon dots.

In this study, carbon particles were used as filler agent for silica aerogel. The carbon particles were synthesized using HEC as carbon source via a hydrothermal/dewatering process, which is a cheap and easy method. Synthesis schema and SEM images for CP is shown in Figure 5.

3.4 SiO_2 and CP particle-embedded silica aerogels

SiO_2_2 was selected from the synthesized SiO_2 particles, mass produced and used in the synthesis of SiO_2-embedded silica aerogels. CP particles prepared from HEC were also embedded in aerogels like SiO_2.

Figure 5. CP microparticle synthesis schema and SEM images of prepared particle.

The particles (SiO_2/CP) were placed into the mixture (alcohol/water/TEOS/catalyst) before the gelling step and dispersed well. Then hydro(solvo)thermal-supported gelling process was completed. Digital camera images of the synthesized bare silica aerogel, SiO_2-embedded silica aerogel, and CP-embedded silica aerogel sol form, before hydro(solvo)thermal treatment, in wet state and digital camera images of their dried state after supercritical drying method and SEM images are given in Figure 6.

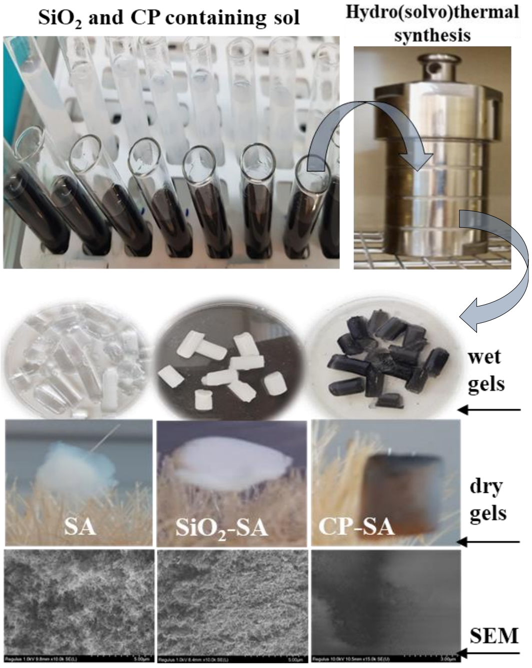

Figure 6. Digital camera images of particle-containing sol (before hydro(solvo)thermal process), wet state of silica gels (after hydro(solvo)thermal process), silica aerogels dried by supercritical drying method and SEM images.

The SEM image of the synthesized silica aerogel is given in Figure 6. It appears to be a highly porous structure with almost homogeneous distribution. The SEM image of SiO_2-embedded silica aerogel is given in the same figure. When the image is examined, there are 250-300 nm SiO_2 particles prepared by Stober method and particles settled in the slit.

3.5 Modification of silica aerogels (SA, SiO_2-SA, CP-SA)

To thermally characterize the synthesized silica aerogel and its modified forms, thermogravimetric analyses were carried out in the range of 50-1000 °C (Figure 7). At the beginning of heating, weight loss due to dehydration was observed in the bare and SiO_2-embedded silica aerogel.

As shown in Figure 7, degradation of CP-embedded silica aerogel was observed in the 400-500 °C range due to the carbon microparticle. Looking at the % remaining at 900 °C, values were 88%, 85% and 73% for bare, SiO_2- and CP-doped silica aerogel, respectively.

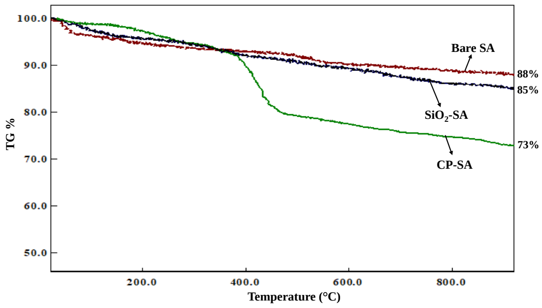

Figure 7. TGA thermogram for bare SA, SiO_2-embedded SA and CP-embedded SA.

The measured specific surface area, pore size and pore volume for SA, SiO_2-SA and CP-SA were summarized in Table 1.

Table 1. Specific surface area, pore size and pore volume parameters for SA, SiO_2-SA and CP-SA.

Samples	Surface area (m^2/g)	Pore size (nm)	Pore volume (cc/g)
SA	297	5.62	1.02
SiO_2-SA	85	8.67	0.59
CP-SA	199	5.58	0.64

Surface area was measured by the BET method and found to be 297 m^2/g, 85 m^2/g, and 199 m^2/g for bare silica aerogel, SiO_2-embedded silica aerogel and CP-embedded silica aerogel, respectively. While the surface area of the bare aerogel is the highest, surface area decrease with embedding of SiO_2 and CP in the silica aerogel. Pore volumes measured by the BJH method were 1.02 cc/g, 0.59 cc/g, and 0.64 cc/g. It was observed that the pore volume decreased less after the process, and the bare silica aerogel pore had the largest pore volume since it was empty. Calculated pore radii were 5.62 nm, 8.67 nm, and 5.58 nm. Since the pore diameter is in the range of 2–50 nm, the aerogels have mesoporous structure.

3.6 Removal of organic pollutants from aqueous media

Since organic pollutants in aqueous media can pose a threat to the environment and human health, in this application, synthesized silica aerogels and modified forms of silica aerogels were used as adsorbents for organic pollutants (4-NP, MB, VB, BPB,) and the potential of the synthesized adsorbent in environmental applications was investigated. To determine the amount adsorbed from the dyestuff solution by the adsorbents, calibration equations were obtained by UV-Vis calibration for each dye solution. For 4-NP, MB, VB, and BPB, respectively, the difference between the initial dyestuff concentrations and the concentration after adsorption was determined with the help of UV-Vis. The amount of pollutant/dye adsorbed per gram of gel weight calculated from the prepared calibration curves is given in mg/g in Table 2.

When the silica aerogels are compared before and after APTES modification, the adsorption capacity increased by increasing the amount of adsorbed dye per unit weight after modification with APTES. While the highest removal for 4-NP was obtained for the TEPA modification of SiO_2-particle embedded aerogel, the best result for methyl blue removal was obtained when the TEPA modified form of CP-embedded silica aerogel was used as adsorbent. For the removal of Victorian blue, the best removal was achieved with use of the APTES modification of SiO_2-embedded silica aerogel as adsorbent. For bromophenol blue removal, the best results were obtained from the modification with APTES of CP-embedded silica aerogel. It was observed that the adsorption capacity of gels for the relevant pollutants can be increased by various modifications.

The maximum adsorption capacity results obtained by using SA and its modified forms as adsorbents were compared with the literature and the values are given in Table 3. In the comparison, silica aerogel-based adsorbent was considered but no silica aerogel-based adsorbent was found for VB and BPB adsorption. Silica-based adsorbents for NP and MB are available in the literature. Based on this table, we can say that the adsorption capacity of SA and its modified forms is quite high and these adsorbents have a good application potential.

Table 2. Adsorption capacity (mg/g) of aerogels for 4-NP, MB, VB and BPB contaminants.

Adsorbent	4-NP (mg/g)	MB (mg/g)	VB (mg/g)	BPB (mg/g)
***Bare SA**	41.05	14.09	91.66	5.93
***SiO_2 - SA**	51.76	6.70	84.09	3.39
CP - SA	39.00	5.92	126.32	6.76
***Bare SA + APTES**	137.34	60.14	137.82	10.34
***SiO_2 - SA + APTES**	140.89	44.09	138.26	17.10
CP - SA + APTES	170.64	58.45	136.84	30.23
Bare SA + TEPA	154.19	121.35	-	-
SiO_2- SA + TEPA	34.98	111.71	89.75	5.97
SiO_2 - SA + EDA	164.53	114.75	128.39	19.50
CP - SA + TEPA	80.79	214.99	-	-

*Adsorbed amounts taken from ref [34].

Table 3. Comparison of the maximum adsorption capacity of various silica aerogel based adsorbents for 4-NP, MB, VB and BPB contaminants

Adsorbent	4-NP (mg/g)	MB (mg/g)	VB (mg/g)	BPB (mg/g)	Ref.
SAE-HS	-	35.94	-	-	[35]
Phenyl-modified SA	-	49.20	-	-	[36]
Hydrophobic-SA (MSA) Hydrophilic-SA (HAS)	-	65.74 47.21	-	-	[37]
SA fibers (SAFs)	-	139.1	-	-	[38]
SA45	-	218.82	-	-	[39]
Calix[6]arene-tethered silica (C[6]TS)	2.30	-	-	-	[40]
β-cyclodextrin grafted silica gel (CD@Si)	41.50	-	-	-	[41]
CD-HMS	50.08	-	-	-	[42]
PF/silica hybrid aerogel	97.09	-	-	-	[43]
SA functionalized by β-cyclodextrin (A-50M50T)	117.8**	-	-	-	[44]
Granular silica aerogel	142*	-	-	-	[45]
Low cost natural sand	-	-	2.37	-	[46]
Nanoporous MCM-41 silicate	-	-	192.3	-	[47]
Polymeric gels	-	-	-	2.98	[48]
MApe-Mt	-	-	-	8.12	[49]
Mesoporous hybrid gel	-	-	-	17.67	[50]
Supported ionic liquid	-	-	-	217.39	[51]

*Phenol, **4-Chloro-phenol.

4 Conclusions

Initially, the sol-gel method was used for the synthesis of bare silica aerogels. As a result of the experiments, the method was changed because the gelation time was very long, and the strength of the gels was not good. The hydro(solvo) thermally-assisted sol-gel method was preferred due to its shorter gel formation time and controllability. The optimum conditions were successfully determined by examining the synthesis parameters. SiO_2 and CP were embedded in silica aerogel and SiO_2-SA and CP-SA were prepared. These particles were characterized by SEM and DLS methods. To increase the efficiency of the synthesized silica aerogels, SiO_2-silica aerogels, and CP-silica aerogels in application, amine groups were added to the structures by using APTES, EDA, and TEPA. The synthesized silica aerogels and their modified forms were successfully used in environmental applications. It was shown that they can be used as adsorbents in organic pollutant removal for environmental applications. The results show that adsorption capacity can be increased 18-fold (from 14 mg/g to 214 mg/g) by modification of SA.

Acknowledgement

Eskisehir Osmangazi University (ESOGU) is thanked for financial support. This work was supported by Eskisehir Osmangazi University Scientific Research Projects Coordination Unit under grant number 2021/15A104.

Conflict of interest

The authors state that there are no conflicts of interest regarding the publication of this article.

Similarity rate (iThenticate): 13%

References

[1] Iswar S, Galmarini S, Bonanomi L, Wernery J, Roumeli E, Nimalshantha S, et al. Dense and strong, but superinsulating silica aerogel. Acta Materials, 213, 116959, 2021. https://doi.org/10.1016/j.actamat .2021. 116959

[2] Sandeep Ahankari, Pradyumn Paliwal, Aditya Subhedar, and Hanieh Kargarzadeh. Recent Developments in Nanocellulose-Based Aerogels in Thermal Applications: A Review. ACS Nano, 15 (3), 3849-3874, 2021. https://doi.org/10.1021/acsnano. 0c09678

[3] Gupta, P., Verma, C., & Maji, P. K. Flame retardant and thermally insulating clay based aerogel facilitated by cellulose nanofibers. The Journal of Supercritical Fluids, 152, 104537, 2019. https://doi.org/10.1016/j .supflu.2019.05.005

[4] Tafreshi, O. A., Mosanenzadeh, S. G., Karamikamkar, S., Saadatnia, Z., Park, C. B., & Naguib, H. E. A review on multifunctional aerogel fibers: processing, fabrication, functionalization, and applications. Materials Today Chemistry, 23, 100736, 2022. https://doi.org/10.1016/j.mtchem.2021.100736

[5] Smirnova I, Gurikov P. Aerogels in Chemical Engineering: Strategies Toward Tailor-Made Aerogels. Annual Review of Chemical and Biomolecular Engineering, 8, 307–34, 2017. https://doi.org/10.1146/annurev-chembioeng-060816-101458

[6] Peng, H., Xiong, W., Yang, Z., Xu, Z., Cao, J., Jia, M., & Xiang, Y. Advanced MOFs@ aerogel composites: construction and application towards environmental remediation. Journal of Hazardous Materials, 432, 128684, 2022. https://doi.org/10.1016/j.jhazmat.2022.128684

[7] Carroll, M.K.; Anderson, A.M.; Mangu, S.T.; Hajjaj, Z.; Capron, M. Aesthetic Aerogel Window Design for Sustainable Buildings. Sustainability, 14 (5), 2887, 2022. https://doi.org/10.3390/su14052887

[8] Nabipour, H., Nie, S., Wang, X., Song, L., & Hu, Y. Zeolitic imidazolate framework-8/polyvinyl alcohol hybrid aerogels with excellent flame retardancy. Composites Part A: Applied Science and Manufacturing, 129, 105720, 2020. https://doi.org/10.1016/j.compositesa.2019.105720

[9] Ghaffari-Mosanenzadeh, S., Tafreshi, O. A., Karamikamkar, S., Saadatnia, Z., Rad, E., Meysami, M., & Naguib, H. E. Recent advances in tailoring and improving the properties of polyimide aerogels and their application. Advances in Colloid and Interface Science, 304, 102646, 2022. https://doi.org/10.1016/j.cis.2022.102646

[10] Wilson, S. M., Gabriel, V. A., & Tezel, F. H. Adsorption of components from air on silica aerogels. Microporous and Mesoporous Materials, 305, 110297, 2020. https://doi.org/10.1016/j.micromeso.2020.110297

[11] McNeil, S. J., & Gupta, H. Emerging applications of aerogels in textiles. Polymer Testing, 106, 107426, 2022. https://doi.org/10.1016/j.polymertesting.2021.107426

[12] Güzel Kaya G, Deveci H. Morphological, textural, and thermal properties of low-cost silica aerogel composites. Konya Journal of Engineering Sciences, 814–23, 2021. https://doi.org/10.36306/konjes.969489

[13] Xia, Y., Man, J., Wu, X., Huang, S., Lu, A., Shen, X., ... & Fu, G. Oxygen-vacancy-assisted construction of Ce–TiO2 aerogel for efficiently boosting photocatalytic CO2 reduction without any sacrifice agent. Ceramics International, 49(4), 6100-6112, 2023. https://doi.org/10.1016/j.ceramint.2022.10.118

[14] Amonette, J. E., & Matyáš, J. Functionalized silica aerogels for gas-phase purification, sensing, and catalysis: A review. Microporous and Mesoporous Materials, 250, 100-119, 2017. https://doi.org/10.1016/j.micromeso.2017.04.055

[15] Shrestha, D., Nayaju, T., Kandel, M. R., Pradhananga, R. R., Park, C. H., & Kim, C. S. Rice husk-derived mesoporous biogenic silica nanoparticles for gravity chromatography. Heliyon, 9(4), 2023. https://doi.org/10.1016/j.heliyon.2023.e15142

[16] Rao, A. V., & Kulkarni, M. M. Hydrophobic properties of TMOS/TMES-based silica aerogels. Materials Research Bulletin, 37(9), 1667-1677, 2002. https://doi.org/10.1016/S0025-5408(02)00795-X

[17] Chao, X., Jun, S., & Bin, Z. Ultralow density silica aerogels prepared with PEDS. Journal of non-crystalline solids, 355(8), 492-495, 2009. https://doi.org/10.1016/j.jnoncrysol.2008.12.010

[18] Nadargi, D. Y., Latthe, S. S., Hirashima, H., & Rao, A. V. Studies on rheological properties of methyltriethoxysilane (MTES) based flexible superhydrophobic silica aerogels. Microporous and Mesoporous Materials, 117(3), 617-626, 2009. https://doi.org/10.1016/j.micromeso.2008.08.025

[19] Wang, Q., Meti, P., Gong, Y. D., Kim, T., Lee, K. Y., Mahadik, D. B., & Park, H. H. Ultralow dielectric constant trifluorophenylvinyl-functionalized silica aerogels with excellent hydrophobicity and enhanced mechanical properties. Ceramics International, 48(23), 34855-34863, 2022. https://doi.org/10.1016/j.ceramit.2022.08.075

[20] Suvaci, E. & Ozel E. Hydrothermal Synthesis. Encyclopedia of Materials: Technical Ceramics and Glasses, Elsevier, 1, 58-69, 2021. https://doi.org/10.1016/B978-0-12-803581-8.12096-X

[21] Linhares, T., de Amorim, M. T. P., & Durães, L. (2019). Silica aerogel composites with embedded fibres: a review on their preparation, properties, and applications. Journal of Materials Chemistry A, 7(40), 22768-22802. https://doi.org/10.1039/C9TA04811A

[22] Diascorn, N., Calas, S., Sallée, H., Achard, P., & Rigacci, A. Polyurethane aerogels synthesis for thermal insulation–textural, thermal, and mechanical properties. The Journal of Supercritical Fluids, 106, 76-84, 2015. https://doi.org/10.1016/j.supflu.2015.05.012

[23] Luo, Y., Zhou, Y., Bai, X., Cai, X., Luo, X., Deng, X., & Wu, D. Preparation and characterization of toughened polyurea aerogels incorporating linear long-chain in the structure. Polymer Engineering & Science, 2023. https://doi.org/10.1002/pen.26260

[24] Lee, J. H., & Park, S. J. Recent advances in preparations and applications of carbon aerogels: A review. Carbon, 163, 1-18, 2020. https://doi.org/10.1016/j.carbon.2020.02.073

[25] Lee, K. Y., Mahadik, D. B., Parale, V. G., & Park, H. H. Composites of silica aerogels with organics: A review of synthesis and mechanical properties. Journal of the Korean Ceramic Society, 57, 1-23, 2020. https://doi.org/10.1007/s43207-019-00002-2

[26] Hasanpour, M., & Hatami, M. Application of three-dimensional porous aerogels as adsorbent for removal of heavy metal ions from water/wastewater: A review study. Advances in Colloid and Interface Science, 284,

102247, 2020. https://doi.org/10.1016/j.cis.2020.102247

[27] Yang, J., Chen, Y., Xu, P., Li, Y., Jia, X., & Song, H. Fabrication of compressible and underwater superoleophobic carbon/g-C_3N_4 aerogel for wastewater purification. Materials Letters, 254, 210-213, 2019. https://doi.org/10.1016/j.matlet.2019.07.069

[28] Rong, N., Chen, C., Ouyang, K., Zhang, K., Wang, X., & Xu, Z. Adsorption characteristics of directional cellulose nanofiber/chitosan/montmorillonite aerogel as adsorbent for wastewater treatment. Separation and Purification Technology, 274, 119120, 2021. https://doi.org/10.1016/j.seppur.2021.119120

[29] Qi D, Lin C, Zhao H, Liu H, Lü T. Size regulation and prediction of the SiO_2 nanoparticles prepared via Stober process. J Dispersion Sci Technol, 38, 70-74, 2017. https://doi.org/10.1080/01932691.2016.1143373

[30] Ashour, M. M., Mabrouk, M., Soliman, I. E., Beherei, H. H., & Tohamy, K. M. Mesoporous silica nanoparticles prepared by different methods for biomedical applications: Comparative study. IET nanobiotechnology, 15(3), 291-300, 2021. https://doi.org/10.1049/nbt2.12023

[31] Deveci H., Bas H., Sengel S. B. & Butun V. Carbon Spheres as Catalyst for Hydrogen Generation from Sodium Borohydride Methanolysis. 10th International Fiber and Polymer Research Symposium, 3, 73-76, Istanbul, Turkey, 2022.

[32] Sahiner, N., & Sengel, S. B. Various amine functionalized halloysite nanotube as efficient metal free catalysts for H_2 generation from sodium borohydride methanolysis. Applied Clay Science, 146, 517-525, 2017. https://doi.org/10.1016/j.clay.2017.07.008

[33] Sahiner, N., & Sengel, S. B. Environmentally benign halloysite clay nanotubes as alternative catalyst to metal nanoparticles in H_2 production from methanolysis of sodium borohydride. Fuel Processing Technology, 158, 1-8, 2017. https://doi.org/10.1016/j.fuproc.2016.12.009

[34] Sengel, S.B., Somakli, S., & Butun, Vural (2021). SiO_2 Particle Embedded Silica Aerogels: Environmental and Energy Applications. Eskisehir Technical University Journal of Science and Technology A-Applied Sciences and Engineering, 22(8th ULPAS-Special Issue 2021), 120-128. https://doi.org/10.18038/estubtda.985092

[35] Güler, Ö., Selen, V., Başgöz, Ö., Safa, H., & Yahia, I. S. Adsorption properties and synthesis of silica aerogel-hollow silica microsphere hybrid (sandwich) structure. Journal of Sol-Gel Science and Technology, 100(1), 74-88, 2021. https://doi.org/10.1007/s10971-021-05622-x

[36] N. Saad, M. Al-Mawla, E. Moubarak, M. Al-Ghoul, H. El-Rassy. Surface-functionalized silica aerogels and alcogels for methylene blue adsorption, RSC Adv. 5 (8), 6111–6122, 2015. https://doi.org/10.1039/C4RA15504A

[37] Han, H., Wei, W., Jiang, Z., Lu, J., Zhu, J., & Xie, J. Removal of cationic dyes from aqueous solution by adsorption onto hydrophobic/hydrophilic silica aerogel. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 509, 539-549, 2016. https://doi.org/10.1016/j.colsurfa.2016.09.056

[38] Meng, S., Zhang, J., Xu, W., Chen, W., Zhu, L., Zhou, Z., & Zhu, M. Structural control of silica aerogel fibers for methylene blue removal. Science China Technological Sciences, 62, 958-964, 2019. https://doi.org/10.1007/s11431-018-9389-7

[39] Liu, G., Yang, R., & Li, M. Liquid adsorption of basic dye using silica aerogels with different textural properties. Journal of non-crystalline solids, 356(4-5), 250-257, 2010. https://doi.org/10.1016/j.jnoncrysol.2009.11.019

[40] Dogan, M., Temel, F., & Tabakci, M. (2020). High-performance adsorption of 4-nitrophenol onto calix [6] arene-tethered silica from aqueous solutions. Journal of Inorganic and Organometallic Polymers and Materials, 30, 4191-4202. https://doi.org/10.1007/s10904-020-01571-0

[41] Shen, H. M., Zhu, G. Y., Yu, W. B., Wu, H. K., Ji, H. B., Shi, H. X., ... & Zheng, Y. F. Fast adsorption of p-nitrophenol from aqueous solution using β-cyclodextrin grafted silica gel. Applied Surface Science, 356, 1155-1167, 2015. https://doi.org/10.1016/j.apsusc.2015.08.203

[42] Bibby A, Mercier L. Adsorption and separation of water-soluble aromatic molecules by cyclodextrin-functionalized mesoporous silica. Green Chem 5:15–19, 2003. https://doi.org/10.1039/B209251B

[43] Seraji, M. M., Soleimankhani, S., Afkhami Abadani, H., & Davarpanah, J. (2017). Adsorption of phenol by super hydrophobic phenol-formaldehyde/silica hybrid aerogel. Journal of Nanoanalysis, 4(3), 214-222. https://doi.org/10.22034/JNA.2017.541096.1011

[44] Matias, T., Marques, J., Quina, M. J., Gando-Ferreira, L., Valente, A. J., Portugal, A., & Durães, L. Silica-based aerogels as adsorbents for phenol-derivative compounds. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 480, 260-269, 2015. https://doi.org/10.1016/j.colsurfa.2015.01.074

[45] Qin, G., Yao, Y., Wei, W., & Zhang, T. (2013). Preparation of hydrophobic granular silica aerogels and adsorption of phenol from water. Applied Surface Science, 280, 806-811. https://doi.org/10.1016/j.apsusc.2013.05.066

[46] Kant, A., & Datta, M. (2014). Adsorption characteristics of Victoria blue on low-cost natural sand and its removal from aqueous media. Eur. Chem. Bull, 3, 752-759.

[47] Mirzajani, R., Pourreza, N., Zayadi, A., Malakooti, R., & Mahmoodi, H. Nanoporous calcined MCM-41 silica for adsorption and removal of Victoria blue dye from different natural water samples. Desalination and Water Treatment, 57(13), 5903-5913, 2016. https://doi.org/10.1080/19443994.2015.1005690

[48] Malana, M. A., Ijaz, S., & Ashiq, M. N. (2010). Removal of various dyes from aqueous media onto polymeric gels by adsorption process: their kinetics and thermodynamics. Desalination, 263(1-3), 249-257. https://doi.org/10.1016/j.desal.2010.06.066

[49] Akpomie, K. G., & Conradie, J. (2020). Efficient synthesis of magnetic nanoparticle-Musa acuminata peel composite for the adsorption of anionic dye. Arabian Journal of Chemistry, 13(9), 7115-7131. https://doi.org/10.1016/j.arabjc.2020.07.017

[50] You, L., Wu, Z., Kim, T., & Lee, K. (2006). Kinetics and thermodynamics of bromophenol blue adsorption by a mesoporous hybrid gel derived from tetraethoxysilane and bis (trimethoxysilyl) hexane. Journal of colloid and interface science, 300(2), 526-535. https://doi.org/10.1016/j.jcis.2006.04.039

[51] Liu, J., Yao, S., Wang, L., Zhu, W., Xu, J., & Song, H. (2014). Adsorption of bromophenol blue from aqueous samples by novel supported ionic liquids. Journal of Chemical Technology & Biotechnology, 89(2), 230-238. https://doi.org/10.1002/jctb.4106