Mohammed A. Anaz [1]
Israa F. Al-sharuee [2]

[1] *Department of Physics, College of Science, Al-Anbar University, Al-Anbar, IRAQ*
[2] *Department of Physics, College of Science, Mustansiriyah University, Baghdad, IRAQ*

Spectroscopic and Compositional Analysis of Hydrophobic Silica Aerogels and Their Applications in Crude Oil Adsorption

The experiments studied the oil adsorption and doping effects of silica aerogels; doped with small percentages of silver and copper chloride, coumarin, and fluorescein dyes, were produced using a two-step acid-base catalyzed via sol-gel procedure. Tetraethoxysilicat (TEOS), methanol (MeOH), acid catalysis (0.1M), base catalysis $NH_4OH:NH_4F$ (1:4), and modified solution trimethylchlorosilane (TMCS): n-hexane (1:10). Raman spectroscopy and Fourier transform infrared spectroscopy are utilized to indicate the molecular bonds and their regions, and field emission scanning electron microscopy to investigate the morphological properties. The hydrophobic aerogel particles showed a very high uptake capacity. The desorption of oil by keeping the liquid-absorbed aerogel. From FTIR examination, the aerogel structure was not significantly altered by the solvent absorption but shrank as a consequence of the oil absorption; the homogenous structure is dominant. The doping gives a strongly skeleton network that gives a bearing to the produced samples to re-use in the mentioned application.

Keywords: Laser dyes; Doped aerogel; Oil adsorption; Hydrophobicity
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1. Introduction

Silica aerogel, as a result of its high porosity and large specific surface area, is a new porous material that has been used and put to good use. Silica aerogels, on the other hand, don't have very good mechanical properties. Because of the drying steps involved in their manufacture, aerogels are notoriously weak, inflexible, and brittle [1]. This severely restricts silica aerogels' potential uses. Two of the most common ways to produce silica aerogels are through sol-gel and hydrothermal processes. Removing the solvent from a solution containing hydrolyzed inorganic compounds leaves behind a gel with a spatial network structure, which can be used to create porous structural materials. This process is known as the sol-gel technique [2]. There are several potential uses for silica aerogels, including thermal insulation, optics, medicine, power, and more. Silica aerogel is often utilized in environmental applications, including wastewater treatment, air purification, and more, because of its high porosity and vast surface area. Aerogels are the most buoyant solids known, with a density lower than water and a surface area higher than that of any other solid. These benefits have led to much research on the sorption of oil and other organics from water using various hydrophobic aerogels [3,4]. Hydrophobic silica aerogels were discovered to adsorb miscible and immiscible organic contaminants, including ethanol, toluene, chlorobenzene, and trichloroethylene. The tiny particles that make up silica aerogel provide the material its unique properties, including a low density that allows it to float on water [5]. Several conventional separation techniques have their limits when it comes to treating offshore crude oil leakages: Oil tanker treatment recycles a huge quantity of oil, but its treatment range is restricted by volume limitations and the spread area of oil slicks, the recovered oil includes a high amount of water, and the separation efficiency is poor. The silica aerogel is very soft had been researched for this project is a good way to solve this problem because it is cheap, good at separating oil and water, easy to use, good for the environment, and has many other benefits [6]. When dealing with offshore crude oil leaks, using aerogel eliminates the drawbacks of secondary separation on oil tankers as well as the drawbacks the combustion treatment and treatment with chemical reagents, all of which contribute to environmental contamination. It effectively separates oil from water and has zero environmental impact. It is distinguished by its low energy use and concern for the environment [7,8]. In this work the parameters that influence the efficiency with which aerogels separate oil and water was investigated. the superhydrophobic aerogels are a potential sorbent for cleaning up crude oil spills [9]. Zhang et al. have proposed that excellent adsorption capacity and high repeated utilization rate of RGO/REMO aerogels indicated the composite adsorbent's prospective application in the remediation of RhB-containing effluent [10]. Liu et al. have shown that the SGA beads exhibited excellent elasticity (rebounding at 70% strain) and oil/water selectivity. A continuous absorption-combustion process could be used to recover the adsorbed organic solvents. Therefore, because of the simplicity of their fabrication and their superior properties, SGA beads have great potential for use in oil spill and organic waste cleaning [11]. Parale et al. have shown that both the absorption capacity and the uptake rate of the hydrophobic aerogel granules were very high. Aerogel granules soaked in liquid were weighed at set intervals until all the absorbed liquid had been completely desorbed in order to study the desorption of solvents and oils. Examination Fourier transform infrared spectroscopy indicated that solvent absorption did not substantially change the aerogel structure, but oil absorption caused the shrinkage that ultimately resulted in a thick structure following desorption [12]. Reynold et al. suggested that powdered CF3-functionalized aerogel may be able to efficiently separate oil from oil-water mixtures up to 14 times the aerogel's weight [13]. The findings of Nguyen et al. verified the superior efficacy of the modified silica aerogel nanoparticles over water in cleaning up the oil spill [14].

In the present study, the prepared hydrophobic aerogel was doped with metal ions and laser dyes. The doping gives a strong skeleton network, which gives a bearing of the produced samples to re-use in the application. The motivation for the prepared hydrophobic silica aerogel was utilized for oil adsorption to contribute to water environmental cleanup; spilled oil poses a danger to living organisms and humans in particular, and to protect fish health and living organisms from water pollution caused by crude oil spills.

2. Experimental Part

The chemicals used in this work includes tetraethylorthosilicat (TEOS, 98%) from Sigma-Aldrich (Germany), trimethylchlorosilane (TMCS, >98%) from TCI (Japan), hexane (>98%) from CHem-LAB (Belgium), ethanol (>99%) from Schariau (Spain), hydrochloric acid (35-38% strength) from Thomas Baker (India), ammonia solution from CDH (India), and silver chloride (AgCl) and copper chloride (CuCl). Both fluorescein ($C_20H_{12}O_5$) laser dye (146.145 g/ml molecular weight), and Coumarin ($C_6H_6O_2$) laser dye (332.31 g/ml molecular weight) were used as doping materials.

Metal ions and laser dyes doping of silica at a concentration of 10^{-2} g/cm^3, yields a variety of silica aerogel. Amounts of 0.71 of AgCl and 0.85 g of CuCl were dissolved in 50 ml ethanol. Fluorescein and Coumarin should be mixed into 50 ml of ethanol, respectively. A 2:40 molar ratio of ethanol was used to dilute TEOS (a precursor). By stirring on a magnetic stirrer for 10 minutes as well as incorporating 2 ml of 0.1M HCL as an acidic catalyst, condensed silica (CS) was successfully produced. First, the dopant materials (10 ml) were mixed with the concentrated and then stirred for 15 minutes using a magnetic stirrer. Finally, a 0.5M NH_4OH base catalyst was added to accelerate the transformation of the sol into a gel. After being prepared for 15 minutes, this gel is aged for 2 hours before being soaked three times every 24 hours, immerse in ethanol. The gel's surface was treated with TMCS (7.5ml) in 30 ml hexane drop by drop, and after baking it for 24 hours at 60°C, it was let to settle at room temperature for 24 hours before being replaced in the oven with pure hexane for 4 hours to modify the surface. After being washed in hexane, the holders were coated with salophen that had tiny holes drilled into it, and the whole thing was let dry at room temperature. Remove moisture from the gel by gradually raising the oven temperature from 80 to 180° degrees with a step of 20°. The application was surveyed via spraying a known quantity of aerogel on the surface of water onto which a quantity of crude oil of known weight was spilled, and after a while an isolated layer was formed on the surface. The layer was scraped off, weighed, and the weight of the aerogel was subtracted from the total weight. This quantity represents what was adsorbed from the crude oil spilled on the surface of the water.

Raman spectroscopy is a kind of spectroscopy used for structural analysis and the observation of rotational, vibrational, and other low-frequency modes. Photoluminescence is an extremely potent, contactless, and nondestructive optical phenomenon that is used to probe the electronic structure of materials. The external source was used to excite the electronic state. Fourier-transform infrared (FTIR) spectroscopy with a scanning wavenumber range of 4000-400 cm^{-1} confirmed the hydrophobicity and surface modification. Field-emission scanning electron microscopy (FE-SEM) analysis validated the porous morphology of silica aerogels, which has drawn a lot of interest due to its unusual features, such as its low density was examined depended on the ratio between mass to volume. To evaluate the practical crude oil adsorption performance by the aerogel. The oil absorption capacity (Q_a) of the aerogels can calculate by weighted it before (M_w) and after (M_d) adsorbed, using the following formula [15]

$$Q_a = \frac{M_w - M_d}{M_d} \qquad (1)$$

3. Results and Discussion

Figures (1) and (2), the Raman spectra, demonstrate the presence of the metal ions copper chloride and silver chloride; the highest intensity of silver chloride is seen at a wavelength of 183.255nm in the case of the aerogel generated via surface modification using TMCS/hexane, the weakest peaks emerged at wavelengths 3630.433 and 4330.878nm; the highest peaks appeared at the wavelengths 666.097 and 2113.214 nm in the copper chloride, where the symmetric stretching vibration constituted the sole form of vibration [16]. The vibration of two symmetrical expansion distinct kinds of atoms is responsible for the formation of these lower-amplitude peaks. The vibration of two symmetrical expansion distinct kinds of atoms is responsible for the formation of these lower-amplitude peaks.

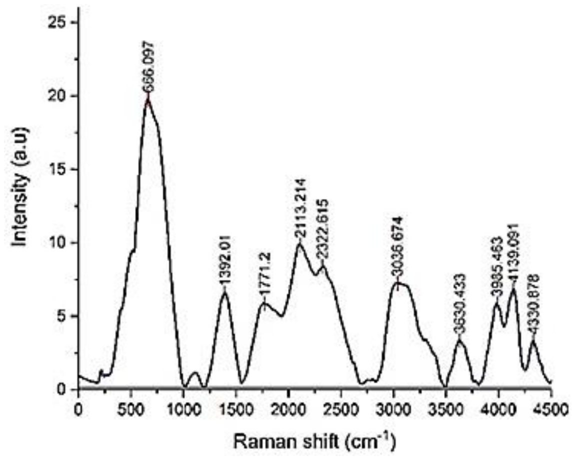


Fig. (1) Raman spectrum of silica aerogel doped with copper chloride (CuCl)

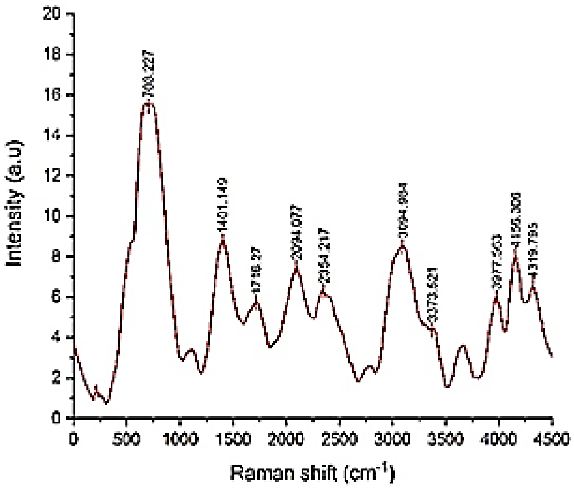


Fig. (2) Raman spectrum of silica aerogel doped with silver chloride (AgCl)

Figures (3) and (4) show the Raman spectra of silica aerogel doped with laser dyes (Coumarin and fluorescein, respectively). They show a shift and regarding the aerogel generated via surface modification utilizing TMCS/hexane, the highest intensity of coumarin emerged at wavelengths of 85.324 and 595.598 nm, while the maximum intensity of fluorescein appeared at wavelengths of 479.627 and 1415.129 nm. This is because one sort of vibration, denoted by the symmetrical stretching vibration, is responsible for the phenomenon, while it manifested itself at the next wavelength for the less powerful peaks at 3630.433 and 4330.878 nm. It is because of the similar stretching vibration that two different kinds of atoms produce that these peaks may be seen with a lesser intensity [17,18]. There are many peaks appeared in Raman spectrum for all produced samples signified in table (1).

Figures (5) and (6) refer to the presence of the metal ions copper chloride and silver chloride. The surface groups react during drying to form Si-O-Si bonds by condensation at ambient pressure. As a result of the increased capillary pressures caused by the creation of Si-O-Si bonds, the wet gel's pore network collapses. A total of 38 Si-O-Si stretching vibrations are reflected in the bands at 1096 cm^{-1}, whereas Si-O vibrations produce the characteristics around 798 cm^{-1}. Bands of adsorption at 3435 cm^{-1} have been identified as belonging to hydroxyls, -H, and CH_3 bands, the primary source of hydrophobicity, peaked at roughly 2981-2900 cm^{-1}.

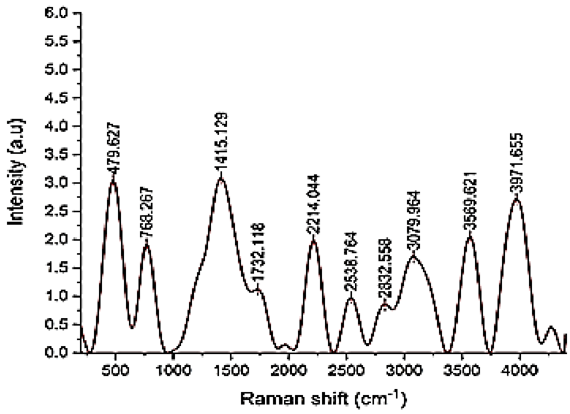


Fig. (3) Raman spectrum of silica aerogel doped with Fluorescein

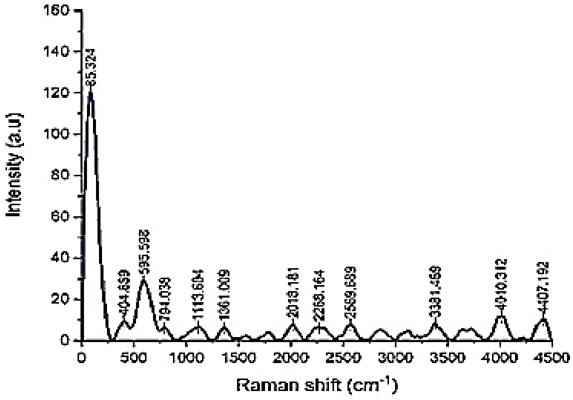


Fig. (4) Raman spectrum of silica aerogel doped with Coumarin

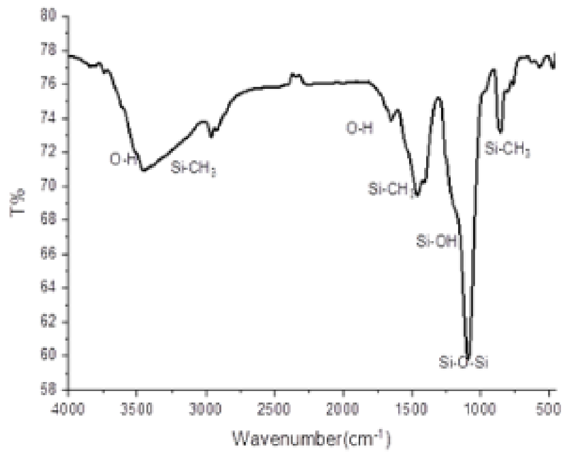


Fig. (5) FTIR spectrum of doped silica aerogel with CuCl

The infrared spectra of modified SiO_2 aerogel show the H-OH peaks at 3425 and 1633 cm^{-1}, which is CO insistent with the aerogel's altered structure. After TMCS modification, hydroxyl groups are replaced by -CH_3 groups, enhancing the compound's hydrophobicity. Diffusion via the wet gel's porous structure ensures that surface reactions take place uniformly throughout the material. The thermogram analysis confirmed that the aerogel's surface hydroxyl (-OH) and alkoxy (-OR) groups were converted to the more stable Si-R group [12].

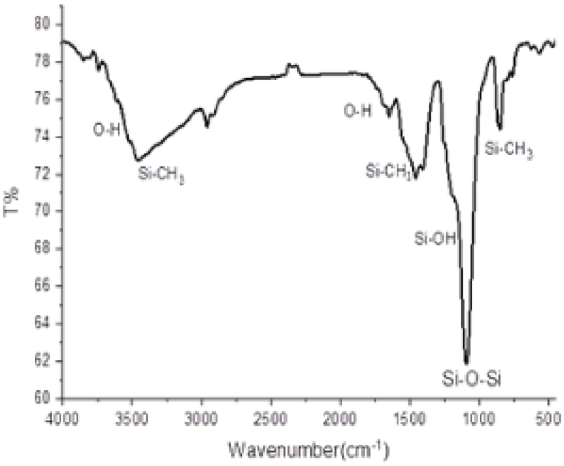


Fig. (6) FTIR spectrum of doped silica aerogel with AgCl

In figures (7) and (8) for Coumarin and fluorescein dyes, the FTIR bands were used to study the chemical bonds of the (SA) changed by TMCS. At 3480 and 1610 cm^{-1}, vigorous absorption peaks are observed are caused by the stretching vibration of hydroxyl (-OH). This shows that these hybrid aerogels can take in water from the air and have strong hydrophilicity. In contrast, Weak absorption peaks for Si-OH at 980 cm^{-1} were observed in the hydrophobic sample (TMCS).

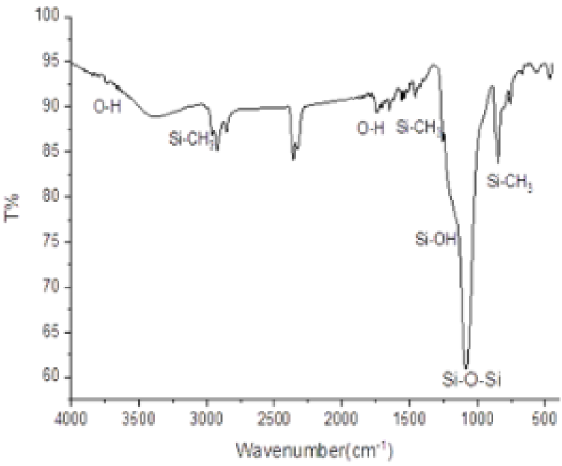


Fig. (7) FTIR spectrum of doped silica aerogel with Coumarin

They appeared Si-O-Si bonds in the silica network exhibit prominent absorption peaks at approximately 1100 cm^{-1}, which meant in which TEOS was effectively hydrolyzed and cross-links were formed, which are attributes characteristic of (SA). At 2990 cm^{-1}, the sample had an absorption peak related to the terminal $-CH_3$ group. At 1280, 840, and 766 cm^{-1}, vibration peaks of Si-C were seen, which were caused by the TMCS surface modification. Furthermore, the TMCS-based hybrid aerogel showed good hydrophobicity and a lowlight weight [19,20].

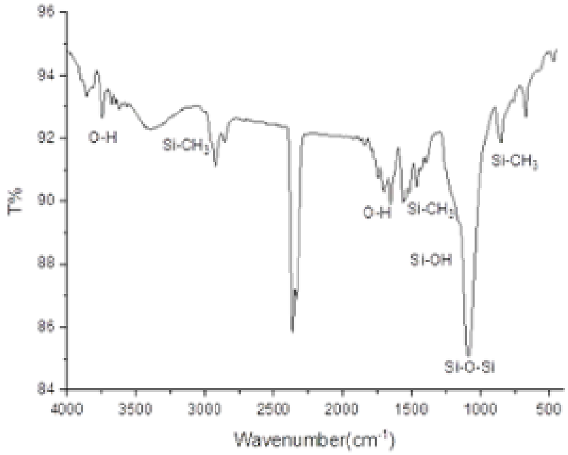
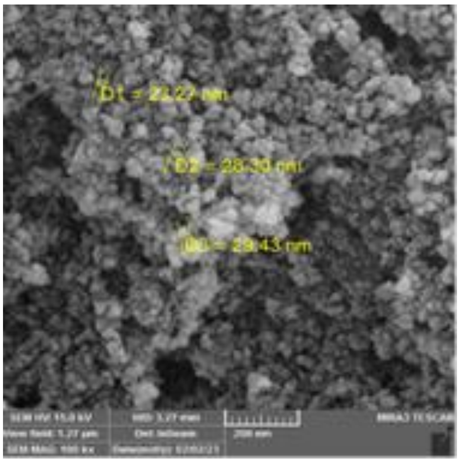
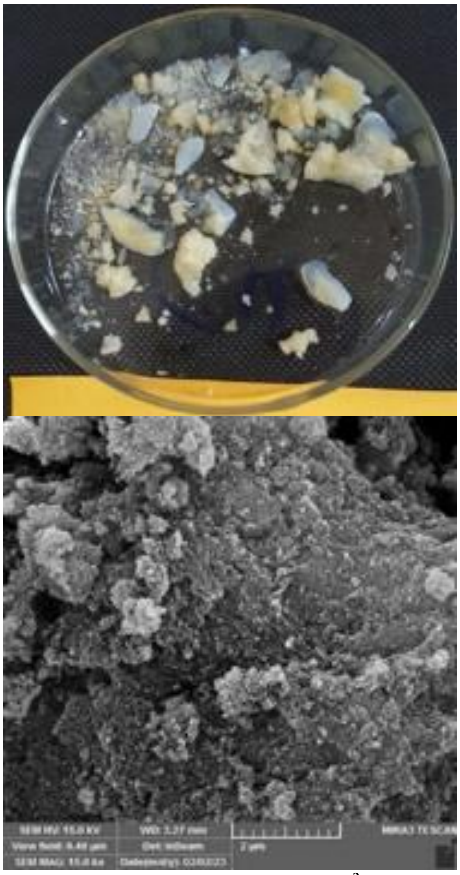


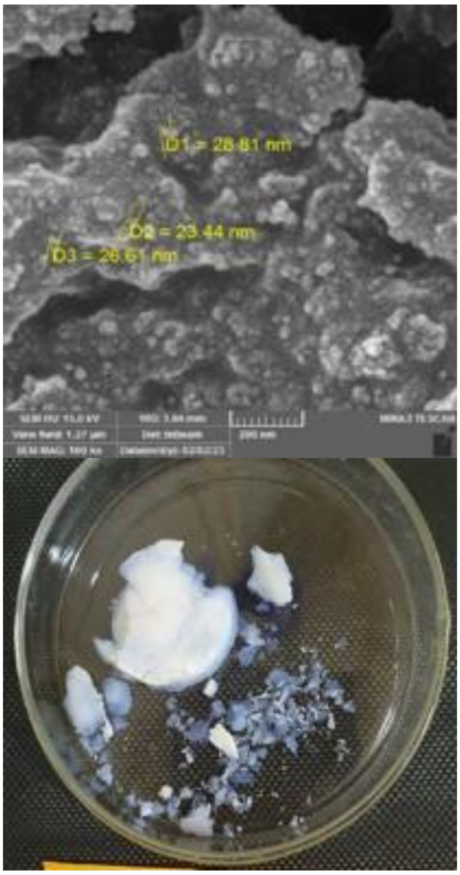
Fig. (8) FTIR spectrum of doped silica aerogel with fluorescein

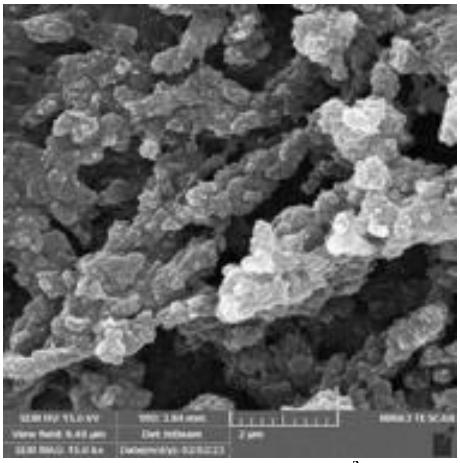
Figure (9) shows FE-SEM results for copper chloride and silver chloride ions. The aerogel had a porous morphology, with pores of varying sizes spread out randomly throughout the material. Previous research has shown that the pore size of aerogels used in oil/water separation applications should be below 200 m [21] and employed to make the nanocomposite aerogels in this research. Various magnification photos of the created aerogel composite aerogel should be shown. Aerogel pores ranged in size 29.43 nm as determined by an image analysis program (ImageJ). Pores in the aerogels have a rough appearance in the high-resolution SEM picture. The creation of an internal phase transition is responsible for the aerogel's enlarged pores. From figures it cleared the morphological study of the as-prepared aerogels for Coumarin and fluorescein dyes was done using FE-SEM analysis, and images were analyzed for their quality.



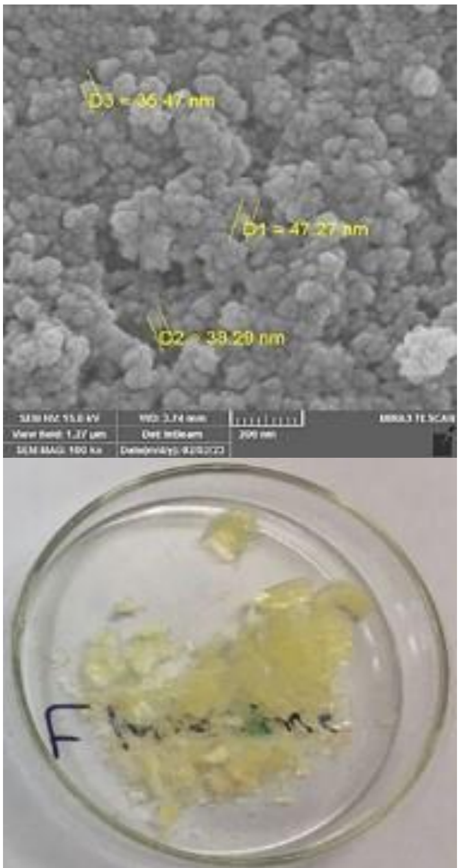


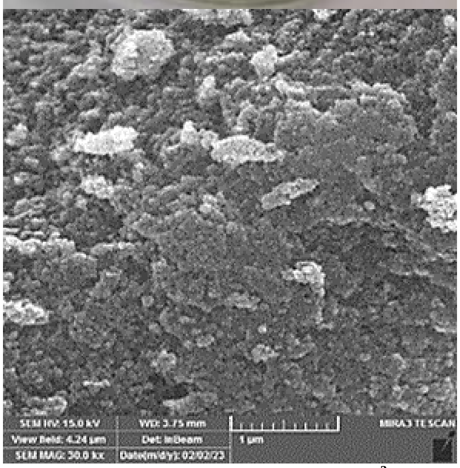
(a) CuCl density 0.219 g/cm^3





(b) AgCl density 0.230 g/cm^3





(c) Fluorescein density 0.221 g/cm^3

(d) Coumarin density 0.20 g/cm^3

Fig. (9) FE-SEM images of doped silica aerogel with (a) copper chloride, (b) silver chloride, (c) fluorescein, and (d) Coumarin with different magnifications

All aerogels seen in the photographs, regardless of magnification, have a porous 3D structure that is well linked. Aerogels are of particular interest due to their unusual features, such as their low density, which results from the tight packing of primary particles in the agglomerates, which is themselves porous. Because of the aerogel's porous, networked interior, it is possible to use gravity to drive a high-flux oil/water separation process using aerogels with superoleophobicity characteristics [22,23].

Figure (10) illustrates the mechanism of absorption during the first few minutes. The aerogel rapidly assimilated the crude oil on the surface of the mixture in about 30 minutes. A 0.053 g of aerogel powder were sprayed over the surface of the oil. The aerogel powder absorbed 4.75 g of oil after 30 minutes. The absorption capacity may be quantified using Eq. (1):

$$Q_a = \frac{4.75 - 0.053}{0.053} = 88.623\%$$

Fig. (10) Photographs before and after the absorption of crude oil by the hydrophobic aerogel

4. Conclusion

Hydroxyl groups are replaced by -CH_3 groups, enhancing the compound's hydrophobicity, in the Raman spectrum, more peaks are different because of the vibration that two different kinds of atoms were produced. These peaks may be seen with a lesser intensity. The aerogel had a porous morphology and a porous 3D structure, with pores of varying sizes spread out randomly throughout the material. The FTIR spectrum shows that the TMCS silylating agents were effective in making the surface of the aerogel hydrophobic by replacing the polar bond -OH with nonpolar bonds like Si-C and C-H. Aerogel materials are gaining a lot of interest because of their peculiar properties, such as their low density. Because of the assumed packing of primary particles in agglomerates, they are very porous. The homogenous structure is dominate for all samples. Using aerogel as an adsorbent medium for oil gave good results through the adsorption of 88% of the oil spilled on the water's surface. The doping gives a strong skeleton network, which gives a bearing of the produced samples to re-use in the mentioned application.

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Table (1) The main peaks of Raman CuCl spectrum

Aerogel doped with CuCl				Aerogel doped with AgCl			
Wavenumber (cm^{-1})	Intensity (a.u)	Wavenumber (cm^{-1})	Intensity (a.u)	Wavenumber (cm^{-1})	Intensity (a.u)	Wavenumber (cm^{-1})	Intensity (a.u)
666.097	20.001	3036.674	7.11	703.227	15.501	3094.984	8.5298
1392.01	6.531	3630.433	3.197	1401.149	8.800	3373.521	4.3790
1771.2	6.12	3985.463	6.10	1716.27	6.77	3977.563	6.130
2113.214	10.002	4139.091	7.009	2094.077	7.09	4156.306	8.2001
2322.615	8.50	4330.878	3.21	2354.217	5.999	4319.795	6.5.1
Aerogel doped with fluorescein				Aerogel doped with Coumarin			
479.627	3.0469	2538.764	1.002	85.324	120.24	2018.181	8.110
768.267	2.109	2832.558	0.988	404.889	9.4384	2268.164	5.449
1415.129	3.0850	3079.964	1.7009	595.598	28.944	2569.689	8.110
1732.118	1.132	3569.621	2.0511	794.038	6.1615	3381.489	8.009
2214.044	1.980	3971.655	2.7151	1113.604	6.42	4010.312	12.220
				1361.009	6.2368	4407.192	10.249

