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Preparation of Silica Aerogel and Study Its Performance for Adsorption of Iron Ions from Aqueous Solution

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Abstract

Silica aerogel was prepared from cheap waterglass precursors via surface modification of wet gels, ambient pressure drying (APD) route and calcination treatment. Xerogel was also synthesized as a comparison to test the influence of microstructure on the adsorption behaviors. (Ethanol (EtOH)/chlorotrimethylsilane (TMCS)/hexane) solution was employed to replace the surface silanol groups (Si-OH) with alkyl, and to prevent the condensation and shrinkage of the gel structure during the (APD) process. The synthesized silica aerogels, characterized by using Fourier transform infrared spectra (FT-IR), nitrogen adsorption/desorption measurement, etc., are porous solids with surface area (879 m^2/g). The transition temperature from hydrophobic to hydrophilic was tested around 395◦C, which corresponds to the disappearance temperature of the $-CH_3$ peaks in FT-IR.These samples were used as absorbent for iron ions. The value of the absorbed percentage in silica aerogel after 4 hours was very close to the value of the absorption percentage after 24 hours, while in silica xerogel the adsorption process continued after 4 hours to be very close to the value of the absorption percentage which was obtained after 4 hours in silica aerogel.

Keywords: Xerogel, Aerogel, Silicon oxide, Sol-gel, Silica gel.

1. Introduction

Aerogels are advanced materials almost like solid smoke, they consist of more than 96 percent air. The remaining four percent is a wispy matrix of silicon dioxide [1]. simply they are gels in which the liquid has been replaced by air, with very moderate shrinkage of the solid network [2]. Aerogels were first discovered by an American scientist Samuel Stephens Kistler in the 1930s [3] It consisted of a simple oxide, namely thoria [4]. While wet gels were previously dried by evaporation, Kistler applied a new supercritical drying technique, according to which the liquid that impregnated the gels was evacuated after being transformed to a supercritical fluid. In practice, supercritical drying consisted in heating a gel in an autoclave, until the pressure and temperature exceeded the critical temperature Tc and pressure Pc of the liquid entrapped in the gel pores. This procedure prevented the formation of liquid–vapor meniscuses at the exit of the gel pores, responsible for a mechanical tension in the liquid and a pressure on the pore walls, which induced gel shrinkage [2]. For silica gels, a first important precursor is sodium metasilicate Na_2SiO_3, also termed waterglass which was previously used by Kistler to produce the first silica aerogels This precursor reacts with an acid such as HCl according to the reactions of the type shown in equation (1):

$$Na_2SiO_3 + 2HCl + (x\text{-}1)\ H_2O \longrightarrow SiO_2.XH_2O + 2NaCl \qquad \text{equation (1)}$$

A salt is produced, which must be eliminated by tedious dialysis or by exchange for H^+ through an acidic ion exchange column [5].

It took nearly three decades for the aerogel to become scientifically and industrially an interesting material. This is because of the tedious synthesis procedures followed by Kistler which used to take several weeks to wash out the salts generated in hydrogel during the process and supercritical drying of the wet-gel to get an aerogel [6]. The rapid development of sol-gel techniques during the past two decades has led to fast progress in the deliberate synthesis of porous materials [7]. The process can be divided into the following general stages:

a) Hydrolysis of precursors-sol formation
b) Polycondensation of hydrolyzed precursors-gelation
c) Aging
d) Drying
e) Calcination

Sols can be prepared from both organic and inorganic compounds [8]. This mixture is a liquid at the creation of the reaction, and becomes more and more viscous as the reaction proceeds. When the reaction is completed, the solution loses its fluidity and the whole reacting mixture turns into a gel [1]. The key issue in the production of aerogels concerns the removal of entrapped solvents from the wet gel while maintaining the integrity and high porosity of the gel. Many efforts have been directed toward the development of aerogel production with ambient pressure drying [9]. Dai and et al successfully synthesized monolithic silica aerogels at ambient pressures by using room-temperature ionic liquids as the solvent. This development, however, requires the removal of the entrapped ionic liquid with acetonitrile, a highly toxic chemical [10]. Another approach is to modify the surface characteristics of the wet gel from hydrophilic to hydrophobic with reagents carrying hydrophobic functional groups. As the surface of the aerogels becomes hydrophobic, the extent of moisture adsorption on the silica surfaces and thus the surface tension force arising from the leaving of the solvent from the wet gel would decrease significantly, and the possibility of obtaining monolithic aerogels is increased. [9].

Traditionally, adsorbents are porous materials with high specific surface areas, large pore volumes, well-developed pore distributions, and special pore surface chemistries. Silica aerogel, a unique material with wide applications has been increasingly researched as an adsorbent due to its high porosity (up to 99%) and ease of surface modification [11]. The applications of the silica aerogel have expanded into many fields. They are used as fillers for paints, varnishes, thermal and acoustic insulation materials adsorbents and catalyst supports and electronic materials such as Cerenkov detectors and sensor materials [12]. It shows high adsorption efficiencies for many different compounds in water [11].

2. EXPERIMENTAL

2.1. Apparatus

The samples were studied using infrared spectroscopy with FT-IR (4100 type A) manufactured by Jasco company, its measurement range from (400-4000 cm^{-1}) using the method of potassium bromide tablets, which is widely used for solid samples analysis. The samples were also studied by Scanning Electron Microscop model (Quanta 200) manufactured by (FEI) company. Nitrogen adsorption/desorption isotherms of the materials were determined the specific surface area was determined using Brunauer-Emmett-Teller (BET) method.

shaker model LSB-030S manufactured by LabTech company with maximum shaking speed (190 rpm) was used to shake the sample with the iron ions solutions.

2.2. Reagents and materials

All chemical materials used in this work were produced by Sigma Aldrich Company in analytical grade. The solutions were prepared with distilled water.

2.3. Samples Preparation

Silica wet gels were prepared with waterglass as starting materials. The waterglass was diluted with deionized water (waterglass/deionized water (v/v) = 1:4). The diluted solution went through an ion exchange column filled with strongly acidic type cation exchange resin to remove Na^+. The pH of the collected silica sol was in the range of (2–3). Then (1.0 mol/l) NaOH solution was added to the silica sol to raise its pH to 5 for gelation. The obtained silica sols were stirred for 1min, and then transferred into a plastic beaker where the sols aged into hydrogels within about 15 min.

2.3.1. Preparation of xerogel:

The next step was to immerse the hydrogels into deionized water and age them for 24 h at room temperature to strengthen the networks of the gels. The aged wet gel were dried at 180◦C for 2 h in an oven, and the dried material was xerogel (sample I).

2.3.2. Preparation of aerogel:

After gelation, the hydrogel were immersed into (50%) (H_2O/EtOH) solution and aged for 24 h at room temperature in order to further strengthen their networks. Then, (EtOH/TMCS/Hexane) mix solution was added to the strengthened wet gels to modify their surface chemistry property. After the preliminary experiments, the optimal molar ratio of pore (water/TMCS/EtOH/hexane) for modification was adopted as (2.5/0.8/1/1). With the completion of the reaction between the wet gel and the mixed solution and through extrusion of pore water, the modified gel sample was then dried at 80◦C for 2 h and then it was calcined at 500◦C for 30 min in an oven.

3. Results and discussion:

3.1. Mechanism of solvent exchange/surface modification:

In order to obtain high porous aerogel structure, elimination of capillary stress during drying is very important. In this study, the elimination of capillary stress was performed by pore water solvent exchange and surface modification of wet gel before ambient drying. (EtOH/TMCS/hexane) solution was used to replace the surface silanol groups (Si–OH) with alkyl, and to prevent the condensation and shrinkage of the gel structure during the APD process. When adding ethanol, hexane and TMCS to the wet gel, reactions occurred between the wet gel and (EtOH/TMCS/Hexane) solution. During the reaction of (EtOH/TMCS/hexane) solution with wet gel, a similar phenomena as illustrated in literature [13] can be observed: transparent yellow liquid (the aqueous HCl phase) coming out from the wet gel and staying in the hexane phase, while the resulting modified wet gels floated to the top of the derived solution of aqueous HCl phase mainly consisting of water extruded from the pores of wet gels and the formed HCl. The major reactions involved with surface modification were as follows [14]:

$$2(CH_3)_3\text{-Si-Cl} + H_2O\ (\text{porewater}) \rightarrow (CH_3)_3\text{-Si-O-Si-}(CH_3)_3 + 2HCl \qquad \text{equation (2)}$$

$$(CH_3)_3\text{-Si-Cl} + CH_3CH_2OH \rightarrow (CH_3)_3\text{-Si-O-}CH_2CH_3 + HCl \qquad \text{equation (3)}$$

$$2(CH_3)_3\text{-Si-O-}CH_2CH_3 + H_2O(\text{porewater}) \rightarrow (CH_3)_3\text{-Si-O-Si-}(CH_3)_3 + 2CH_3CH_2OH$$

equation (4)

$(CH_3)_3\text{-Si-O-Si-}(CH_3)_3 + 2HCl \rightarrow 2(CH_3)_3\text{-Si-Cl} + H_2O$ equation (5)

$(CH_3)_3\text{-Si-O-}CH_2CH_3 + HCl \rightarrow (CH_3)_3\text{-Si-Cl} + CH_3CH_2OH$ equation (6)

$(CH_3)_3\text{-Si-Cl} + \equiv\text{Si-OH} \rightarrow \equiv \text{Si-O-}(CH_3)_3 + HCl$ equation (7)

$(CH_3)_3\text{-Si-O-}CH_2CH_3 + \equiv\text{Si-OH} \rightarrow \equiv \text{Si-O-}(CH_3)_3 + CH_3CH_2OH$ equation (8)

It is clear that TMCS react with ethanol, pore water and Si–OH group in the wet gel. Because the reaction between the TMCS and pore water in the wet gel was so rapid, it would easily cause the gel to crack. Thus, during the process of solvent exchange/surface modification, controlling the reaction rate of the TMCS with the pore water is very important. Practically, the reaction between TMCS and ethanol decreases the reaction rate of TMCS with pore water, which is a favorable condition for obtaining crack-free aerogels. The molar ratio of (EtOH/TMCS/hexane) is a key factor in determining the properties of the silica aerogel. If the operation of adding ethanol, hexane solvent and TMCS modification reagent is appropriate, then monolithic silica aerogels with low density could be obtained. From the preliminary experiments, the optimum molar ratio of pore (water/TMCS/EtOH/hexane) was (2.5/0.8/1/1) for silica surface modification [11]. This modification mechanism has been applied by Schwerfeger's and et al. [13] and Shi and et al. [14]. After the modification process, the hydrophilic property of the internal surface was modified to hydrophobic by isopropoxytrimethylsilane and TMCS that react with the –OH of the internal surface.

3.2. Microstructure of silica aerogel and xerogel

Fig. 1 shows the SEM morphology of xerogel (sample I). After the serious volume shrinkage caused by drying, the unmodified xerogel did not show any porous microstructure under SEM observation.

Fig. 2 shows the SEM morphology of aerogel (sample II). The aerogel which was modified with surface methyl groups, exhibits a porous network structure.

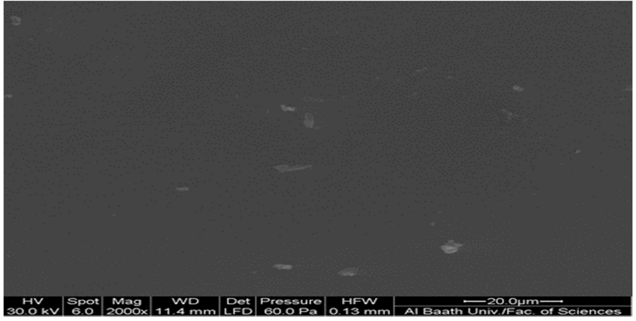

Figure (1): SEM picture of xerogel (sample I)

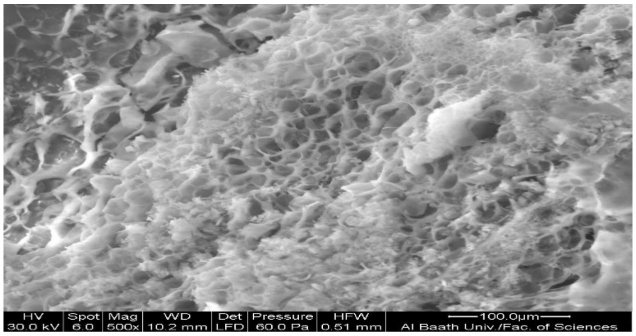

Figure (2): SEM picture of aerogel (sample II)

3.3. Textural properties of silica aerogels and xerogel:

Nitrogen adsorption/desorption method was used to analyze the textural properties of silica aerogels and xerogel. The specific surface area was determined using Brunauer-Emmett-Teller (BET) method. Pore size distribution and total pore volume of the materials were evaluated from the adsorption branch of nitrogen isotherms by using the Barrett–Joyner–Halenda (BJH) method. Xerogel, which did not undergo surface modification and therefore shrank greatly due to the capillary stress during the APD, showed a much smaller pore size and pore volume than of aerogel.

Table (1): experimental results of the specific surface areas, total pore volume and average pore diameter of the samples

Sample	BET surface area (m^2/g)	Pore volume (m^3/g)	Average pore diameter (A)
I	518.2	0.66	50.82
II	879	2.98	210

3.4. Infrared spectra of the aerogels and xerogel:

Fig. 3 shows the FT-IR spectra of the silica aerogel samples. The peaks at 3435 and 1630 cm^{-1} corresponding to O-H absorption band is possibly caused by physically adsorbed water. The absorption peaks near 1091 cm^{-1} are due to Si-O-Si vibrations, which will appear in any silica product. It is clearly seen that there is no adsorption peaks of $–CH_3$ because the methyl terminal groups were oxidized [11]. Shi and et al showed that in the range of ($350–450^0C$) there is a slow removal of the surface $-CH_3$ groups and residual organic components [15].

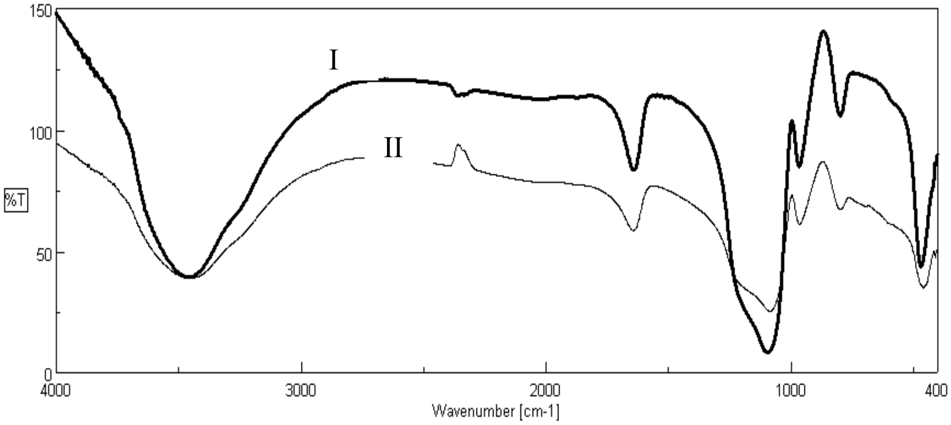

Figure (3): Infrared spectra of xerogel and aerogel.

3.5. Silica Aerogl adsorption of iron ions from its water solutions:

- A solution of iron ions was prepared at a concentration of (100 mg / l) starting from iron chloride.
- A weight of (0.1gr) of silicium oxide was taken to a (50 ml) erlenmyer.
- (30 ml) of the prepared iron ion solution were added to the silicium oxide sample and the erlenmyer then was put in a shaker at shaking speed (170 rpm).
- The amount of iron remaining in the solution was determined after one hour, two hours, four hours and then 24 hours using UV-VIS spectroscopy by forming the iron complex with theocyanate and preparing the standard series as follows:
    - A solution of Ammonium thiocyanate was prepared (15%).
    - A solution of iron ions was prepared at a concentration of (100 mg / l).
    - A standard series was prepared at (100 ml) volumetric flask as the following table:

Table (2): preparation of standard series

Standard	**blank**	**St_1**	**St_2**	**St_3**	**St_4**
C (mg/l)	0	0.2	1	2	3
$V_{(iron\ ions\ solution)}$ (ml)	0	0.2	1	2	3
$V_{(HCl)}$ (ml)	5	5	5	5	5
$V_{(Ammonium\ thiocyanate\ solution)}$ (ml)	25	25	25	25	25

The volume was added up to the mark with distilled water.

- (30 ml) of the shaked iron ions solution was took to a (100 ml) volumetric flask every time after one hour, two hours, four hours and 24 hours shaking.(5 ml) HCl and (25 ml) Ammonium thiocyanate solution were also added every time. The volume is added up to the mark with distilled water every time.

HCl was added to secure the best medium to form $Fe(SCN)_6^{3-}$ red complex.

$$Fe^{3+} + NH_4SCN \longrightarrow \begin{cases} Fe(SCN)^{2+} + Fe(SCN)_2^{+} + Fe(SCN)_3 + \\ Fe(SCN)_4^{-} + Fe(SCN)_5^{2+} + Fe(SCN)_6^{3-} \end{cases}$$

equation (9)

Table (3): Absorption of standard solutions

Standard	**St_1**	**St_2**	**St_3**	**St_4**
C (mg/l)	0.2	1	2	3
A	0.096	0.4	0.739	1.1

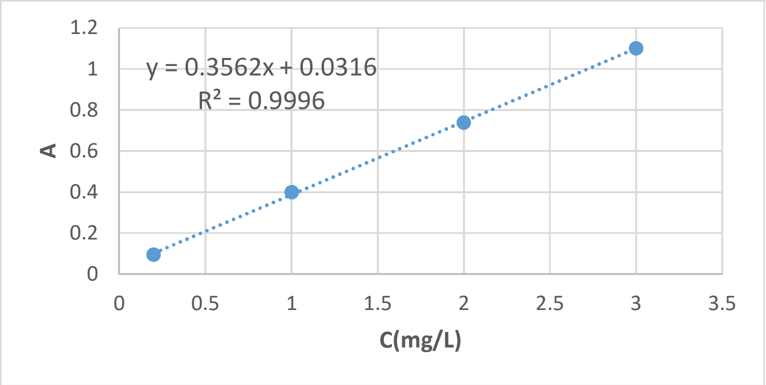

Figure (4): Adsorption changes with standard solution concentrations

Table (4):The quantities absorbed with time and the amount of iron absorbed in (1 gr) of the sample (I)

Sample weight (gr)	**Time (h)**	**A**	**Concentration of iron ions at diluted solution (mg/l**	**Concentration of iron ions at the prepared solution (mg/l)**	**Percentage of absorbed on the weighted sample (%)**	**Quantity of iron (mg) absorbed by (1gr) of the sample**
0.1275	0	1.1	2.999	86.318		
	1	0.954	2.589	84.131	13.665	107.453
	2	0.952	2.583	84.259	13.852	108.627
	4	0.932	2.527	84.259	15.724	123.302
	24	0.604	1.606	53.565	46.424	364.047

Table (5):The quantities absorbed with time and the amount of iron absorbed in (1 gr) of the sample (II)

Sample weight (gr)	**Time (h)**	**A**	**Concentration of iron ions at diluted solution (mg/l**	**Concentration of iron ions at the prepared solution (mg/l)**	**Percentage of absorbed on the weighted sample (%)**	**Quantity of iron (mg) absorbed by (1gr) of the sample**
0.1112	0	1.1	2.999			
	1	0.785	2.115	70.503	29.483	265.088
	2	0.753	2.025	67.509	32.478	292.017
	4	0.616	1.64	54.688	45.301	407.31
	24	0.556	1.472	49.073	50.917	457.803

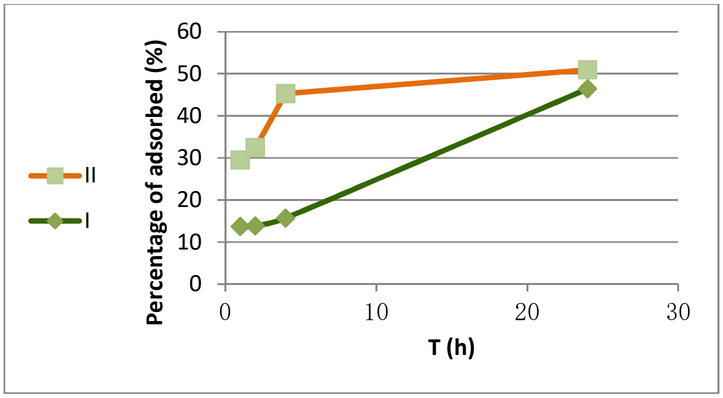

Figure (5): Absorbed percentage changes with time

We found that the bulk of the absorbed percentage is within the first hour. The value of the absorbed percentage in the sample (II) after 4 hours was very close to the value of the absorption percentage after 24 hours so we can say that we nearly got into saturation after four hours, while in the sample (I) The adsorption process continued after 4 hours to be very close to the value of the absorption percentage which was obtained after 4 hours in the sample (II).

3.6. Reusability of aerogel adsorbent:

To recycle The sample (II) (which was used for adsorption of iron ions from water) it was shaked for 2 hours by a shaker at shaking speed (170 rpm) in a solution containing (20 ml) distilled water with (5 ml of HCl at 60°C at shaking speed (170 rpm).

To determine the amount of the redux iron ions, the previous solution was carried after it became cool to a (100 ml) volumetric flask with (25 ml) of ammonium tiocyanate solution (15%) and HCl. The volume is added up to the mark with distilled water. the absorption of this solution was measured.

Table (6): The redux percentages

A	Redux percentages (%)
0.669	13.441

Then the sample was reused for adsorption of iron ions from a (100 mg/l) iron ion solution.

Table (7): The quantity absorbed with time and the amount of iron absorbed in (1 gr) of the sample (II) after recycling

The remaining weight of the sample (gr)	T (h)	A	Concentration of iron ions at diluted solution (mg/l	Concentration of iron ions at the prepared solution (mg/l)	Percentage of absorbed on the weighted sample (%)	Quantity of iron (mg) absorbed by (1gr) of the sample
0.0901	0	1.1	2.999			
	1	0.948	2.573	85.757	14.227	157.871
	2	0.861	2.328	77.616	22.37	248.232
	4	0.794	2.14	71.346	28.64	317.82
	24	0.775	2.087	69.568	30.419	337.554

Although the redux percentage of iron ions in the sample recycling method was relatively small we found that the percentage of absorbed on the weighted sample was relatively good (30.419 %).

4. Conclusions

In this study hydrophilic silica aerogel was prepared via a low cost ambient pressure drying procedure. It had high surface area, pore diameter and pore volume. It was effective as an absorbent for iron ions from its aqueous solution. The percentage of absorbed on the weighted recycling sample was relatively good (30.419 %).

Silica aerogel prepared via ambient pressure drying has great applications potential in the water treatment field.

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