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Optimisation of Glucose Templated Silica for Oil-Water Separation

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ABSTRACT

In this study, glucose is used as a template to manufacture microporosity in silica. Based on this objective, five different molar ratios of glucose (0%, 10%, 20%, 30% and 50%) were used for this experiment to maximise its affinity to adsorb oil droplets. The sample has been characterized using thermogravimetric analysis (TGA), Nitrogen Adsorption and Ultraviolet-Visible (UV-Vis) Spectroscopy. The adsorption of oil was tested in 1000 ppm oil-water emulsion in order to determine the performance of the templated silica. TGA analysis showed that 550 ℃ is a suitable temperature for material calcination for all the samples. N_2 adsorption showed the glucose templated silica (50%) had limited porosity, with a low surface area of 2 m^2/g. This is much lower than non-templated silica which was mesoporous, with an average pore diameter of 2.6 nm and a surface area of 272 m^2/g. Interestingly, despite the low porosity of the templated silica, high oil-water separations were achieved. This shows that glucose-templated silica is a promising material for oil-water separations.

Keywords: *oil-water separation; porous silica; glucose; sol-gel; adsorption*

1. INTRODUCTION

Despite substantial economic growth over the past century, people still lack access to clean drinking water in modern times. This is largely due to the dumping of industrial effluent into waterways. Crick *et al.* state that pharmaceutical, petrochemical and food processing industries along with domestic sewage produce oily wastewater which pollutes water resources without adequate treatment [1]. Silica is a porous material which plays a crucial role in many aspects of people's daily lives. It is chosen as it offers a high surface area to volume ratio which plays an important role for this research [2]. It also had been broadly analysed for technical applications. It has outstanding adsorption and heterogeneous catalysis properties [3, 4-6].

Sol-gel is one of the techniques used to synthesize an inorganic network at low temperature. This method produces homogenous materials on the nanoscale. Furthermore, reagents can be varied to tailor the pore size and morphology [7]. The sol-gel method is a series of hydrolysis and condensation reactions that are acid catalysed. Tetraethyl Orthosilicate (TEOS) is the most common precursor used in the sol-gel preparation of silica, and ethanol is used as the primary solvent. Ethanol is also a reactant in the sol-gel reactions. It is a suitable solvent for TEOS as it has appropriate kinetics for the reactions to be well controlled [8]. Further, it does not affect the structure as it is a like-for-like exchange with the ethoxy groups in TEOS. Water also plays a crucial role in the hydrolysis and condensation reactions.

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Glucose is being investigated in this study as a templating agent, with the aim of tailoring the porosity of silica. It is used as an additional precursor in this study. Once sol-gel processing is complete, the material is calcined at high temperatures in an air atmosphere. Glucose is combustible under these conditions and should leave porous voids in the silica structure [9].

The adsorption of oil from oil-water mixtures is used to study the effectiveness of glucose in enhancing the adsorption properties of silica [10]. An ideal support should have good physical strength and has a high degree of porosity with a large surface area. In this situation, silica is a suitable material for use as a support. As for glucose, since it combusts at low temperature and is inexpensive, it is used for the modification of silica in order to tailor the porosity.

2. METHODS AND MATERIAL

2.1 Preparation of Acid Catalysed Sol

21 mL of tetraethyl orthosilicate (TEOS) was placed into a 250 mL beaker. Then, 21 mL of ethanol was added into the beaker and the solution was stirred using a magnetic stirrer bar. Another solution was prepared with 28 mL distilled water, 1 mL of hydrochloric acid (HCl) and glucose. The amount of glucose was varied according to Table 1. After that, the solution was poured into the TEOS solution under continuous stirring. The two solutions were initially immiscible, but then mixed together after a few minutes. The solution was heated at 60˚C and then stirred for 1 hour and 15 minutes. The solution was subsequently dried in an oven at 100˚C for 24 hours.

Table 1: Molar Ratios of Glucose and Silica

Sample	Ratio of Glucose (%)	Glucose (mL)	TEOS (mL)
1	0	0	21.0
2	10	2.1	18.9
3	20	4.2	16.8
4	30	6.3	14.7
5	50	10.5	10.5

2.2 Preparation of Silica Powder

The gels were removed from the drying oven and were ground into a fine powder with a mortar and pestle. The powders were dried further under high vacuum overnight at 100℃. This material was utilised in all subsequent experiments.

2.3 Preparation of Oil-Water Separation

An oil-water mixture was prepared by pouring 1 gram of oil into 1 L of water. The mixture was then stirred continuously for 30 minutes at 100 rpm using an orbital shaker [10]. Silica powder was then added into the oil-water mixture. The solution was stirred again to get an emulsion for 1 hour. The adsorption of oil was investigated by analysing the adsorption of the oil-water mixture using ultraviolet-visible spectroscopy (UV-Vis).

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2.4 Sample Characterization

Thermogravimetric analysis (TGA) was performed using a model SDT-Q600. The sample was heated from room temperature to 1000 °C with a heating rate 5 °C min^{-1} in a platinum crucible. Heat treatment was conducted under instrument air flowing at 80 mL min^{-1}. Nitrogen sorption is usually used by several researchers for determining surface area and pore size distribution in a wide selection of porous solid materials [11]. Nitrogen adsorption was tested utilising a Micromeritics ASAP 2020 analyser. Adsorption was conducted at 77K for all the samples. Silica samples were degassed under vacuum at 200°C for a minimum of 8 hours. Absorbance measurements were performed using a Perkin Elmer Lambda 25 UV/Vis analyser.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

Figure 1 shows the TGA profile of all glucose templated silica materials. Multistage decomposition occurred in between 100℃ and 600℃. The total mass loss for each material increased with the amount of glucose used in preparation [12, 13]. This shows that glucose is in fact, combusting and was removed from the material during heating. Each material shows no further mass loss above 550℃, except for the 10% glucose sample, which achieves this state at 600℃. Given the purpose of adding glucose in silica is to remove it from the material to leave porosity, 550℃ has been selected as the calcination temperature for further experiments.

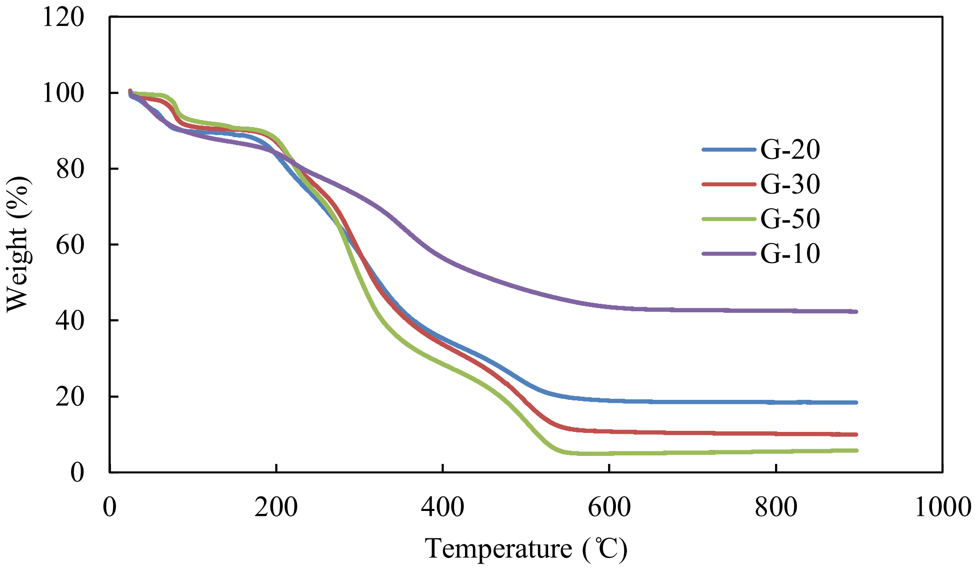

Figure 1: TGA Profile of Glucose Templated Silica Materials

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Kruk *et al.* reported similar findings when investigating the TGA profile of SBA-15. It is claimed that the major weight loss below 600℃ is due to the removal of the surfactant template [14]. However, this study investigates glucose-silica materials. Hence, it means that 50% of glucose has major weight loss at 94.2% compared to other ratios due to the desorption of glucose template. Thus, the glucose will be fully removed at 550℃ temperature [15]. Table 2 lists the weight loss of all materials tested at 600℃.

Table 2: Summary Results of TGA Analysis

Sample		Maximum Temperature (°C)	Weight Loss (%)
Glucose (%)	Silica (%)		
10	90	600	57.645
20	80	540	81.563
30	70	580	90.017
50	50	550	94.235

3.2 Nitrogen Sorption

Figure 2 displays the N_2 adsorption isotherm for the silica and 50% glucose templated silica. The pure silica exhibits a typical IUPAC Type-IV adsorption-desorption behaviour, which is the characteristic of mesoporous structure [16,17]. Type IV isotherms are indicative of materials with pores in the range of 1.5 – 100nm. The average pore diameter of the pure silica material was calculated to be 2.6 nm, while the BET surface area was calculated to be 272 m^2/g. These values correspond well with a study conducted by Paraknowitsch [18] who synthesized mesoporous silica with nitrogen-doped carbon and silica. The isotherm for the 50% glucose templated silica material, also shown in Figure 2, shows negligible adsorption of nitrogen. This isotherm is typical of dense materials that do not have porosity. This is likely due to the presence of glucose in the silica structure.

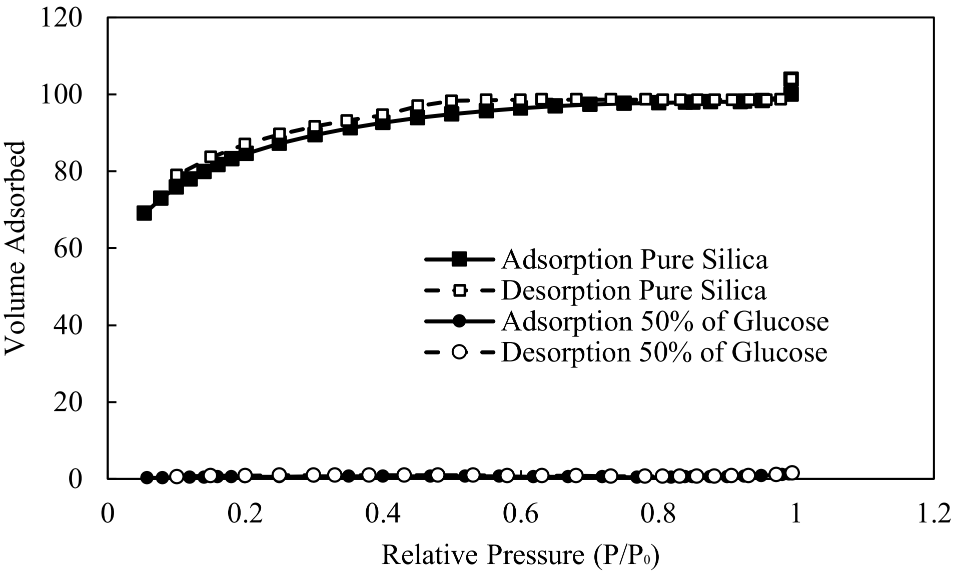

Figure 2: Isotherm of Silica and Glucose-Silica

Table 3 lists the details of the porous structure of both materials. It can be seen that the pure silica material has a higher surface area at 271.91 m^2/g compared with 2.2816 m^2/g for the 50% glucose templated silica. Pure silica has an average pore size at 2.5943 nm, whereas the 50% glucose templated silica has an average pore size of 3.9834 nm. It means that the number of pores present in the material affects the materials surface area. Since the sample of pure silica was analysed without adding some glucose, thus the pore size of this sample reduce and give high surface area. As for 50% of glucose, the pore size is higher due to the amount of glucose added during the experiment. This is also the primary reason for the materials lower surface area.

Table 3: Details of Porous Structure of Silica and Modified Silica with Glucose

Sample	Pure Silica (TEOS only without glucose)	50% glucose template with silica
Surface Area	271.9062 m^2/g	2.2816 m^2/g
Pore Volume	0.1607 cm^3/g	0.0023 cm^3/g
Pore Size	2.5943 nm	3.9834 nm

3.3 Ultraviolet-Visible Spectroscopy (UV-Vis) Analysis

This study tests oil-water separation to investigate the adsorption performance of the materials. The results of this analysis are displayed in Figure 3. The royal blue line shows the blank sample for oil and water only, with no silica present. This spectrum illustrated high absorbance across the wavelengths tested, with a maximum peak of 1.75 recorded at 250 nm. The high absorbance values suggest that no oil is adsorbed in the blank sample [19]. This makes intuitive sense since no adsorbent has been added to the oil-water mixture. For the glucose templated silica, the absorbance decreased as the amount of glucose in the material increased. This means that higher amounts of glucose used in the preparation of the material aid the adsorption of oil from oil-water mixtures.

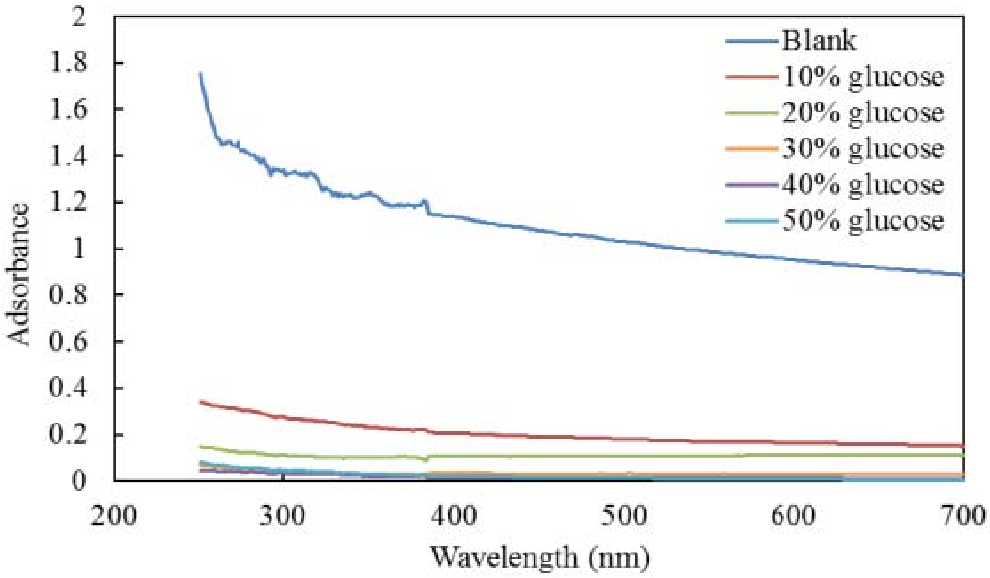

Figure 3: UV-Vis Results Before and After Oil-Water Separation Testing

In addition, the percentage of oil removal is calculated from the UV-Vis results via the peak at 250 nm [10]. The formula applied is demonstrated in Equation 1.

$$\text{Percentage oil removal (\%)} = \frac{\text{initial-final}}{\text{initial}} \text{ x } 100 \qquad (1)$$

As shown in Figure 4, the percentage removal of the sample at 50% glucose templated silica contributes the highest percentage approximately 96% as compared to the other material. Surprisingly, even the surface area of this material is much lower than pure silica, the other mechanism thought that residue of the decomposed glucose adsorbs oil droplets. The amount of glucose increased to reflect the oil removal percentage also rise until start to reach optimum value. This study shows the interesting results to be explored further.

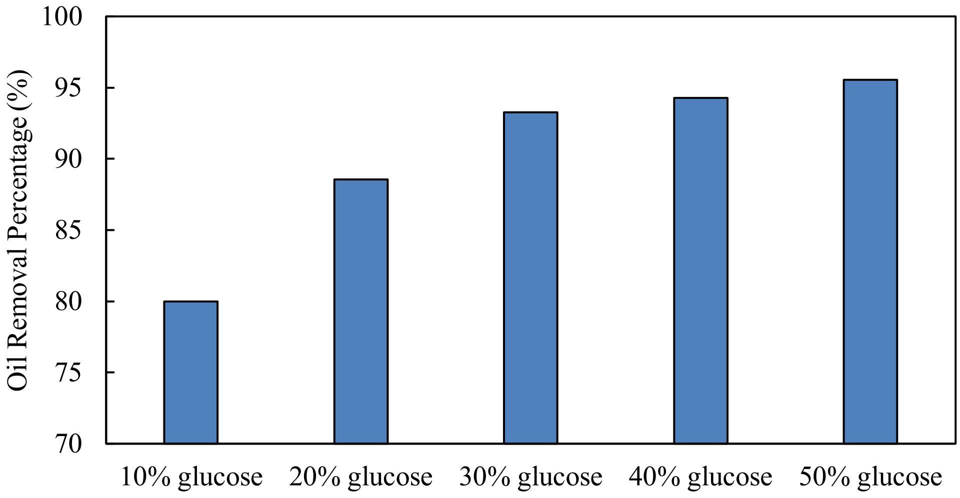

Figure 4: Oil Removal Percentage at Different Ratio of Glucose Templated

Table 4 outlines the observations made for each of the oil-water mixtures after one hour of adsorption testing. The qualitative observations from the adsorption test match well with the readings given by the UV/Vis experiment. Higher amounts of glucose added in the silica preparation process results in higher amounts of oil that get adsorbed to the material. This is because when certain oil passes through the sample with glucose, the oil will attach to the surface and cannot desorb. Hence, it will give clearer water if the amount of glucose increase and added it with silica.

Table 4: Observation of Simple Testing for Oil-Water Separation

Sample (%)	Observation
Blank (Oil and water)	Involve two layer (oil and water) and the oil in the surface water act as a polluted water
10	The solution becomes cloudy and the oil still present in the solution
20	The amount of oil in the water is constant and the solution becomes cloudy
30	A small amount of oil appeared in the water and the solution becomes cloudy
40	The solution becomes clear and the existence of oil in the water diminish
50	The solution becomes more clear and the existence of oil in the water diminish

4. CONCLUSION

The first objective of this study was to investigate the influence of glucose on the porosity of silica. The TGA and BET analysis were used for this purpose. As the optimum temperature was around 550 ˚C, the BET result can be analysed. Based on the result of the analysis, the average

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pore diameter of pure silica (without glucose) was 2.6 nm which falls in the mesoporous range. However, the size of the silica template with 50% of glucose shows that there is no size of porosity for this sample. It means that this sample has no porosity and densified. Since the glucose is integrated into the silica as a pore templating agent, with the purpose of enhancing porosity, it is concluded that the addition of glucose does not make the silica more porous.

The second objective was to investigate the influence of precursor glucose mass on the separation of oil from oil-water mixtures via adsorption. The performance was characterized using UV-Vis spectroscopy in order to check the existence of oil in the water. It was found that the templated silica materials which had higher amounts of glucose precursor achieved better oil separation performance. The 50% glucose templated silica achieved a high oil-water separation, with no suspended oil visible to the naked eye. This was confirmed by the low absorbance from the UV/Vis study. This highlights that glucose templated silica is a promising material for oil-water separations. Further optimization work including mechanism study should be undertaken, particularly in regards to increase material surface area, to further improve the performance of this material and a better understanding of the adsorption process.

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