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Removal of Oil Pollution in water using hydrophobic silica

Remoción de aceite en agua usando sílice hidrofóbica

SALAZAR-HERNÁNDEZ, Carmen[1]*†, SALAZAR-HERNÁNDEZ, Mercedes[2], HERNÁNDEZ-ARIAS, Lizeth Jocelyn[1] and MENDOZA-MIRANDA, Juan Manuel[1]

[1]Instituto Politécnico Nacional. Unidad Profesional Interdisciplinaria de Ingenierías Campus Guanajuato. Av. Mineral de Valenciana No. 200 Col. Fracc. Industrial Puerto Interior, C.P. 36275 Silao de la Victoria, Guanajuato, México.
[2]Departamento de Ingeniería en Minas, Metalurgia y Geología. Universidad de Guanajuato. Ex Hacienda de San Matías S/N Colonia San Javier, C.P.36020, Guanajuato, Gto. México.

ID 1st Author: *Carmen, Salazar-Hernández* / **ORC ID**: 0000-0002-6901-2937

ID 1st Coauthor: *Mercedes, Salazar-Hernández* / **ORC ID**: 0000-0001-8039-8124

ID 2nd Coauthor: *Lizeth Jocelyn Hernández-Arias* / **ORC ID**: 0000-0002-9509-9255

ID 3rd Coauthor: *Juan Manuel, Mendoza-Miranda* / **ORC ID**: 0000-0003-4777-767X

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Abstract

Nowadays the contamination in waters by oily substances turns out to be a problem of world-wide scope and although some methods of removal of oils in water exist; these present some limitations; therefore, this project proposes the use of hydrophobic silicas as absorbent materials for oily substances. Modified silicas (R-SiO_2) were synthesized using the Stöber method, modifying the surface by co-condensation. Tetraethyl-orthosilicate (TEOS) and two surface modifiers were used as silica former: Methyl-trimethoxysilane (MeTEOS) and n-octyl-triethoxysilane (nOctyl-TEOS). The R-SiO_2 were characterized by infrared spectroscopy identifying the modifying groups and their hydrophobicity was qualitatively evaluated according to the change in solubility in water. Finally, the removability of an automotive motor oil was evaluated by determining the amount of oil removed per gram of modified silica.

R-SiO_2, Hydrophobicity, Oil removal

Resumen

Hoy en día la contaminación en aguas por sustancias oleosas resultan ser un problema de ámbito mundial y aunque existen algunos métodos de remoción de aceites en agua; éstos presentan algunas limitantes por lo que, en este proyecto se propone el uso de sílices hidrofóbicas como materiales absorbentes para las sustancias oleosas. Las sílices modificadas (R-SiO_2) se sintetizaron empleando el método de Stöber realizando la modificación de la superficie por co-condensación. Se utilizó como formador de sílice el Tetraetil-ortosilicato (TEOS) y dos modificadores de superficie: Metil-trimetoxisilano (MeTMOS) y el n-octil-trietoxisilano (nOctil-TEtOS). Las R-SiO_2 se caracterizaron por espectroscopia de infrarrojo identificando los grupos modificadores y su hidrofobicidad se evalúo cualitativamente de acuerdo con el cambio de solubilidad en agua observada. Finalmente, se evalúo la capacidad de remoción de un aceite de motor automotriz determinando la cantidad de aceite removido por gramo de sílice modificada.

R-SiO_2, Hidrofobicidad, Remoción de aceite

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* Correspondence to Author (e-mail: msalazarh@ipn.mx)
† Researcher contributing as first author.

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Introduction

wastewater containing pollutant oil is commonly produced in a wide range of industries, such as oil extraction, petrochemical production, machinery manufacturing, and food production, causing groundwater to be directly affected by polluting oils (Escobar J, 2002), thus, the selective oil removal from water becomes an important issue for science and environmental engineering (García Pérez A, 2021). Current methods to removal waste oil from water can be divided into three methods as: 1) collecting oil from water surface, 2) mixing the wastewater with dispersing agents to promote the natural degradation of pollutant oil and 3) in situ polluting oils burning (Kumar Gupta R, 2017). However, these methods have different limitations, among them, the complete elimination of the pollutant oil. On the other hand, mesoporous silica has been explored as a removal system for different pollutants in water, for example, to remove heavy metals (Gutierrez-Valtierra M, 2019), pesticides (Moliner-Martínez, 2014), chlorinated compounds (Rodríguez D, 2013), colorants (Sienkiewicz A, 2019) among others. Thus, the aim of this paper is to evaluate modified silica with organic groups as a removal media for pollutant oils such as internal combustion engine oil.

Methodology

Synthesis of Silica Nanoparticles using Stöber's Method

100 mL of EtOH and 10 mL of water were placed in a vessel with stirring system and then 3 mL of NH3OH was added as a catalyst; taking care that the pH of the solution is lying between 9 and 10. Later, 10 g of TEOS (99.9% purity, Aldrich) were added and the solution was stirring for an hour and subsequently 12 h for aging. The solid obtained is filtered and washed using ethanol and dried for 6 h at 80ºC.

Silica Modification: Synthesis of R-SiO_2

The silica modification was carried out by Co-condensation; as shown in Figure 1; the polymerization of TEOS in an alkaline medium (pH 9-10) is carried out with the modifying agents; which were Methyl-trimethoxysilane (MeTMOS; 98% purity, Aldrich) and n-octyl-triethoxysilane (nOctyl-TEtOS; 97% purity, Aldrich).

The modifying agent was added to the TEOS solution in ethanol / water after 15 min of adding the TEOS. Table 1 shows the ratio of TEOS: modifying agent employed. The mixture is stirring for one hour and subsequently aged for 12 h, the solid obtained is filtered and washed with ethanol to dry at 80 ° C for 6 h.

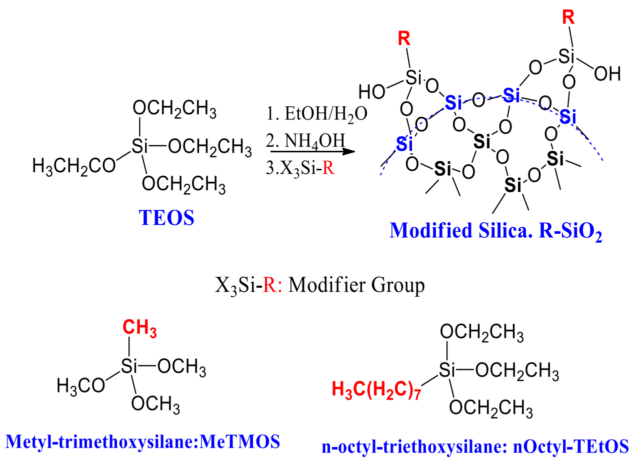

Figure 1 R-SiO_2 synthesis method

	TEOS	Modifier Group
MeTMOS	10 g	4.27 g
nOctyl-TEtOS	10 g	6.63 g

Table 1 TEOS / Modifying group used in the synthesis of R-SiO_2

R-SiO_2 Characterization

The chemical structure of silica and the addition of the modifier agent was studied by reflectance attenuation infrared spectroscopy (ATR-FT) using a Nicolet-iS10 Thermoscientific equipment, obtaining an average of 16 scans, with a 4 cm^{-1} resolution, and spectral window from 4000 to 600 cm^{-1}.

Oil Removal Capacity Measurement

One gram of combustion engine oil was poured into a beaker and modified silica nanoparticles were subsequently added. After the oil gelled, the mixture of silica and oil nanoparticles was placed on top of a mesh, and the measurement of the removal was carried out dividing the oil mass by the minimum mass of hydrophobic silica nanoparticles required for oil removal.

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Results

Infrared spectroscopic characterization of R-SiO_2

Figure 2 shows the silica and the modifying agents infrared spectra that were used; Table 2 shows the of the main peaks assignment; Furthermore, the modifying groups that will give the silica its hydrophobic properties are highlighted with a red circle. For methyl trimethoxysilane the hydrophobic characteristic is due by the methyl group (–CH_3); and in n-octyl-triethoxysilane the hydrophobic characteristic is due by group n-octyl (–CH_2 $(CH_2)_6CH_3$).

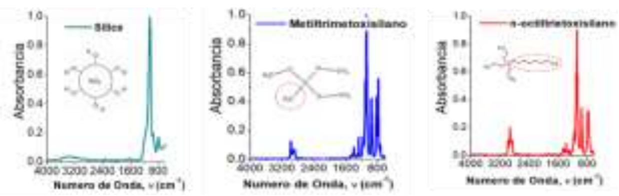


Figure 2 FT-IR reference spectrum for silica and modifying agents' materials

	Functional Group	Wavenumber (cm^{-1})
Silica	Si-O-Si	1150;570
	Free Si-OH	945
	hydrogen bridge Si-OH	3490-1600
MeTMOS	-CH3	2900-3100
		1400
	-Si-O	1100
	-Si-C	1200
nOctil-TEtOS	-CH_2 y CH_3	2900-3100
		1400
	-Si-O	1100
	-Si-C	1200

Table 2 IR-TF vibrational modes for silica and modifying groups

Figure 3 shows the modified silica spectra, the modifier group is highlighted in a circle. All silicas retain moisture on the surface in the form of free silanols as a thin shoulder present at 945 cm^{-1}; furthermore, the broad band at 3450 cm^{-1} indicates the presence of physisorbed water. Moreover, the siloxane base structure (Si-O-Si) is identified with the intense and wide peak observed around 1100 cm^{-1} and with the peak of moderate intensity at 600 cm^{-1}. Finally, the Si-C group (1200 cm^{-1}) of the modifier was observed with low intensity in SiO_2–Me and SiO_2–octyl.

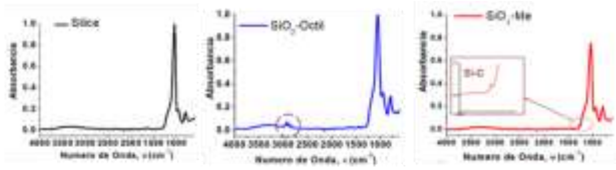


Figure 3 FT-IR spectrum of silica and modified silica (R–SiO_2)

Hydrophobic Behavior of R-SiO_2

Hydrophobicity was determined observing the change in solubility of silica in water; Thus, 0.3 g of silica and R-SiO_2 were added to 100 ml of distilled water, as shown in Figure 4. The silica precipitates towards to the bottom of the glass due to its poor solubility in water (Figure 4a). However, when the modifying groups are added, hydrophobic silicas were obtained that tend to float on the water surface (Figure 4b and c). According to these results, the degree of hydrophobicity has the following behavior: SiO_2 <SiO_2–Me <SiO_2–octyl.

Figure 4 Hydrophobicity test for silica and R–SiO_2

Evaluation of Oil Removal Capacity using R-SiO_2

Table 3 shows the qualitatively results of the adsorption of two grams of oil on the silicas. It is observed that the unmodified silica does not have the ability to remove oil, thus, the silica precipitates and the oil remains on the water. On the other hand, the modified silicas remove the oil efficiently, precipitating the silica and the trapped oil into the modified silica.

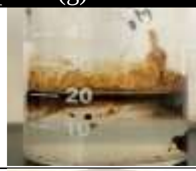
Sample	Amount of Silica required for absorption (g)	
SiO_2	Sin absorción	
SiO_2-MeTMOS	0.742	
SiO_2-nOcilTEtOS	0.752	

Table 3 Results of the amount of silica required to carry out the oil absorption at 25 ° C

The adsorption capacity of the silicas was determined according to Equation 1. Thus, table 4 summarizes the adsorption capacity of modified silicas, the highest removal was observed with the modified silica containing PDMS followed by the modified silica containg the methyl group and the lowest removal capacity was for the modified silica containing the octyl groups.

Figure 5 shows the ratio of the required mass of modified silica nanoparticles for the removal different amounts of oil. For example, according to the removal capacity of silicas, to remove 100g of oil, 35 g of SiO2-Me and 37g of SiO2-octyl are required;

Therefore, the removal capacity (C.R) was calculated as expressed in Equation 1 for the silicas studied and its values are indicated in Table 4. Thus, similar removal capacity was quantified for both methyl and octil modifier groups. On the other hand, it is observed that the unmodified silica does not have oil removal capacity, this due to its hydrophilic properties.

$$C.R = \frac{oil\ mass}{silica\ nanoparticle\ mass} \quad (1)$$

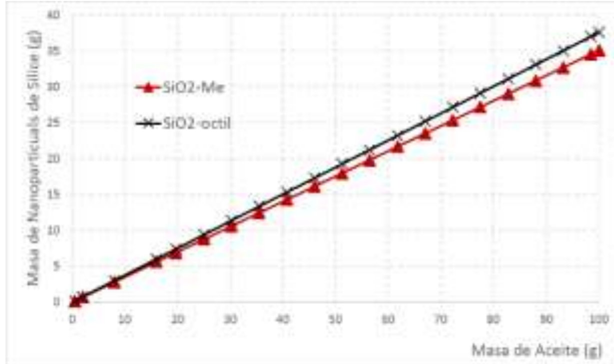


Figure 5 Amount of silica nanoparticles modified to remove oil

	Removal capacity ($g_{oil}/g_{silica\ nanoparticles}$)
SiO_2	---
SiO_2-Me	2.85
SiO_2-Octyl	2.66

Table 4 Oil removal capacity for R-SiO_2

Conclusions

Nanoparticles of mesoporous silica were modified coupling on the surface methyl (methyl-trimethoxysilane with the methyl group $-CH_3$) and octyl (n-octyl-triethoxysilane with the n-octyl group $-CH_2\ (CH_2)\ _6CH_3$) groups. The modified silicas show high hydrophobicity with the following behavior: SiO_2 <SiO_2–Me <SiO_2–octyl. The modified silica was characterized and contrasted with its precursors for its development, results shows that the modified silicas have a base structure of siloxanes (Si–O–Si) as well as the Si–C group for its modifiers with hydrophobic properties coupled in their structure. According to the results obtained, both modified silicas presented similar removal capacity, being slightly higher for SiO_2-Me.

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