

Synthesis and characterization of silica and magnetite nanoparticles for the adsorption of naphthenic acids

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Abstract

Produced water is the effluent generated in the largest volumes from oil and gas exploration. In Brazil, the treatment of produced water aims its discharge into the sea, and the removal of naphthenic acids is an important step in this process. Some treatment methods have been studied for this purpose, including adsorption. Adsorption is a compact treatment method that can be used on offshore platforms. In this study, silica nanoparticles and magnetic nanoparticles were synthesized for application as nanoadsorbents. Nanoparticles with hydrodynamic diameters between 40 and 600 nm and specific surfaces between 30 and 835 m²/g were obtained. Surface modifications allowed the production of nanomaterials with different surface potentials, as evidenced by zeta potential analysis. Among the synthesized samples, a calcinated mesoporous silica nanoparticle stands out due to its high specific surface, an important property for application in adsorption. In the adsorption of naphthenic acids, a positive surface potential is desirable for the interaction with the acids, which are found in produced water in a mostly deprotonated form. In this case, both the silica and the magnetite functionalized nanoparticles stand out. Magnetic nanoparticles, in particular, have potential for application in offshore environments due to their ease of collection after use by applying an electromagnetic field.

Keywords: Silica nanoparticles; magnetite nanoparticles; nanoadsorbents; naphthenic acid; produced water.

1. Introduction

Currently, the treatment of produced water represents one of the greatest challenges for the oil and gas industry. Conventional treatment has the main objective of removing dispersed oil; however, it demonstrates little efficiency in removing water-soluble organics (WSO) [1].

In 2018, Brazilian legislation was revised to establish a new methodology for characterizing produced water destined for disposal at sea, after its treatment. As a result of this change, WSO, mostly naphthenic acids, which had previously gone undetected by the former method, began to be detected during quantification. Adsorption is a promising treatment method for removing naphthenic acids from produced water, offering the potential to meet the requirements for disposal [1, 2].

This study aims to synthesize magnetic and silica nanoadsorbents for the adsorption of naphthenic acids. Notably, magnetic nanoadsorbents have the advantage of easy recovery after use by applying a magnetic field.

2. Methods

2.1 Synthesis of mesoporous silica nanoparticles

Mesoporous silica nanoparticles (mSiO₂) were synthesized by the modified Stöber method. The nanoparticles were precipitated with NH₄OH from the silica precursor TEOS in a water and ethanol solution containing CTAB. To remove the porosity-generating template, the nanoparticles were calcined at 600°C for 6 h (mSiO₂-c).

2.2. Surface modification of silica nanoparticles

The surface of the calcined silica nanoparticles was modified by the insertion of -OH groups (mSiO₂-cA), through their resuspension in a 0.01 mol/L NaOH solution and subsequent neutralization with acetic acid. Afterward, basic functional groups were inserted on its surface (mSiO₂-cA-NH₂) using APTMS.

2.3. Synthesis of magnetic nanoparticles

Magnetic magnetite nanoparticles (Fe₃O₄) were synthesized by the coprecipitation method in a basic medium, using a 1:1 ratio of Fe²⁺ and Fe³⁺. Then, the magnetic cores were encapsulated in silica (Fe₃O₄@SiO₂) by the modified Stöber method and functionalized with APTMS (Fe₃O₄@SiO₂-NH₂).

2.4. Characterization of nanoadsorbents

The nanoparticles were characterized by the following methods: thermogravimetric analysis (TGA) – Hitachi STA 7300 (ISI B&F – SENAI/CETIQT); Fourier transform infrared spectroscopy (FTIR) – PerkinElmer Frontier FT-IR/FIR (LAPINI – IMA/UFRJ); dynamic light scattering (DLS) and zeta potential - Anton Paar Litesizer 500 (LABEFIT – PEQ/COPPE/UFRJ); and textural analysis – MicrotracBel BELCAT II (ISI B&F – SENAI/CETIQT).

3. Results

3.1. Thermogravimetric analysis (TGA)

TGA analysis of silica nanoparticles (Fig. 1) was performed to verify CTAB removal and surface modification. CTAB removal by calcination is verified by the mass loss between 150 and 320 °C in the mSiO₂ sample, which is absent in the mSiO₂-c sample. This mass loss step can also be associated with the dehydroxylation of the silica's silanol groups [3]. Therefore, a surface activation step is necessary before functionalization with amino groups.

The activation of the mSiO₂-cA sample's surface introduces -OH groups, which hinder the adsorption of water from the environment. The activation can be verified by the decrease in the degradation peak related to water removal, compared to the mSiO₂-c

sample [4]. The functionalization of the mSiO₂-cA-NH₂ sample is confirmed by the mass loss between 350 and 600 °C related to the degradation of the aminopropyl. Additionally, the difference in residual mass between this functionalized sample and the unfunctionalized sample further supports this finding [5].

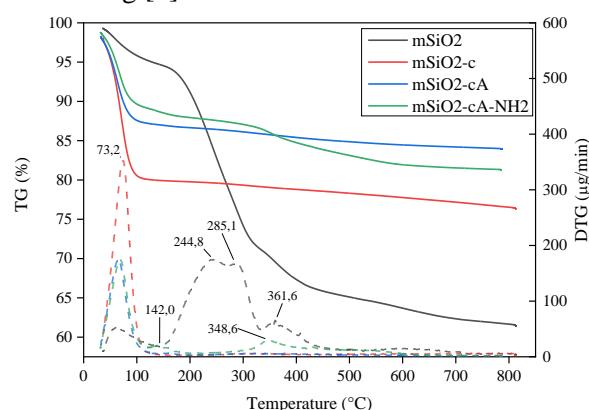


Fig. 1. Thermogravimetric analysis curves and their derivatives for silica samples.

3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis (Fig. 2) revealed the presence of silica-related bonds in all silica nanoparticles and the coated magnetite nanoparticles, with characteristic peaks at 1050, 965, and 800 cm⁻¹ [3]. This indicates the success of the encapsulation. In the magnetic samples, characteristic bonds of magnetite were observed at 620 and 600 cm⁻¹ [6]. Due to the low intensity of the signals and the overlapping of bands, it was not possible to confirm the functionalization through FTIR.

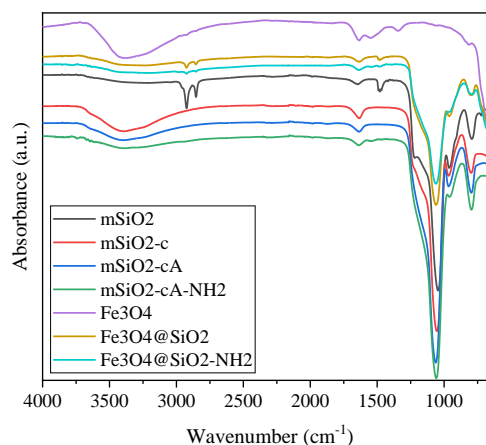


Fig. 2. FTIR spectra for silica and magnetite nanoparticles.

3.3. Zeta potential

The electrokinetic potential was used to evaluate the functionalization of the nanoparticles, through the correlation between their zeta potential and their surface properties (Fig. 3, Table 1). The mSiO₂ sample has a higher isoelectric point (6.3) than expected for silica (2.0) [7]. With the removal of CTAB, after calcination and activation, this value decreases to 3.4. The successful functionalization of the mSiO₂-cA-NH₂ sample can be verified by the increase in its isoelectric point to 7.7 [8]. The same behavior was observed for the magnetic nanoparticles, with an increase in the isoelectric point from 4.9 to 6.7 after functionalization [9].

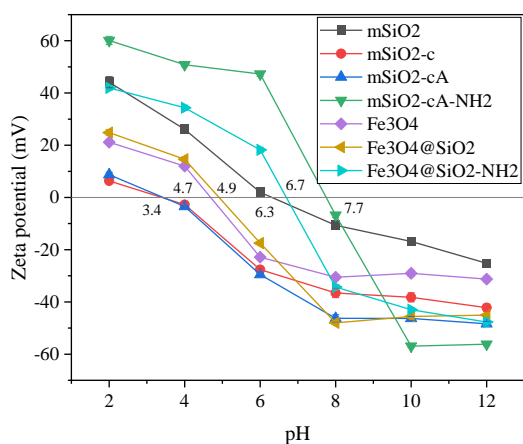


Fig. 3. Zeta potential for silica and magnetite nanoparticles.

Table 1. Isoelectric points and hydrodynamic diameters for silica and magnetite samples.

| Sample | Isoelectric point (mV) | Hydrodynamic diameter (nm) |
|---|------------------------|----------------------------|
| mSiO ₂ | 6.3 | 559.7 |
| mSiO ₂ -c | 3.4 | 542.6 |
| mSiO ₂ -cA | 3.4 | 519.4 |
| mSiO ₂ -cA-NH ₂ | 7.7 | 607.5 |
| Fe ₃ O ₄ | 4.7 | 40.5 |
| Fe ₃ O ₄ @SiO ₂ | 4.9 | 60.3 |
| Fe ₃ O ₄ @SiO ₂ -NH ₂ | 6.7 | 57.8 |

3.4. Dynamic light scattering (DLS)

The hydrodynamic diameters of the nanoparticles were obtained by DLS (Table 1). All silica nanoparticles presented hydrodynamic diameters of approximately 500 – 600 nm, as observed by other

authors [10]. On the other hand, the magnetic nanoparticles presented a change in hydrodynamic diameter from 40 to 60 nm after encapsulation in silica, indicating the success of the coating.

3.5. Textural analysis (BET)

The nitrogen adsorption isotherms at 77 K of the silica and encapsulated magnetite samples are classified as Type IV, characteristic of mesoporous materials (Fig.4). With the calcination of the silica sample, there was an increase in the specific surface from 30 to 835 m²/g. With activation and functionalization, this area decreased to 319 and 118 m²/g, respectively. Similarly, there was a decrease in the specific surface after functionalization of the Fe₃O₄@SiO₂ sample, from 115 to 49 m²/g, due to the insertion of functional groups on both the internal and external surface of the nanoparticles [11].

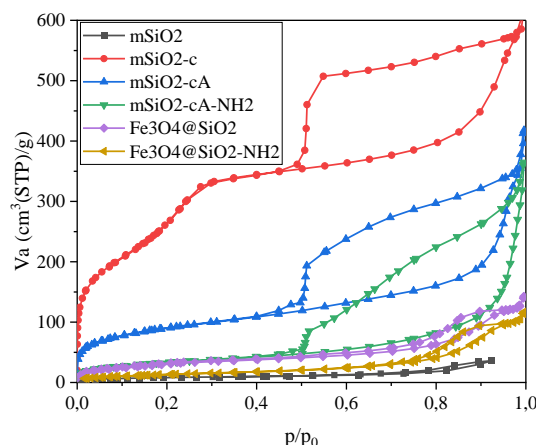


Fig. 4. N₂ adsorption and desorption isotherms at 77 K for the silica and magnetic samples.

4. Discussion and conclusions

Four silica nanoadsorbents and three magnetic nanoadsorbents were synthesized to be applied in the treatment of produced water, in the adsorption of naphthenic acids. The characterizations conducted indicate that the nanoparticles were successfully encapsulated in silica and that the surface modifications were effectively implemented.

For application as nanoadsorbents, samples with a higher specific surface are expected to have better performance [12]. In this case, the sample mSiO₂-c stands out, with a higher specific surface. In addition, samples with a positive surface charge are expected to interact more easily with naphthenic

acids, which are found in produced water mainly in their deprotonated form at $\text{pH} > \text{pK}_a \approx 5-6$ [13]. Thus, functionalized samples are expected to present better adsorption performance under these conditions.

Acknowledgements

The authors thank CAPES and FAPERJ for the scholarships and ISI B&F – SENAI/CETIQT for support with the analyses.

References

- [1] Candido, J.D.C., Weschenfelder, S.E., Ferraz, H.C., A review on the synthesis and application of magnetic nanoadsorbents to the treatment of oilfield produced water. *Brazilian J. Chem. Eng.* 2024, 41:1–21.
- [2] Smathers, C., Sabey, J., Reichert, A., Hallahan, G., Naphthenic Acid Removal in Offshore Oil Production. *Water Technology*. 2020.
- [3] Putz, A.-M., Cecilia, S., Ianăși, C., Dudás, Z., et al., Pore ordering in mesoporous matrices induced by different directing agents. *J. Porous Mater.* 2015, 22:321–331.
- [4] Lu, H.-T., Synthesis and characterization of amino-functionalized silica nanoparticles. *Colloid J.* 2013, 75:311–318.
- [5] Ruiz-Cañas, M.C., Corredor, L.M., Quintero, H.I., Manrique, E., et al., Morphological and Structural Properties of Amino-Functionalized Fumed Nanosilica and Its Comparison with Nanoparticles Obtained by Modified Stöber Method. *Molecules* 2020, 25:2868.
- [6] Asab, G., Zereffa, E.A., Abdo Seghne, T., Synthesis of Silica-Coated Fe₃O₄ Nanoparticles by Microemulsion Method: Characterization and Evaluation of Antimicrobial Activity. *Int. J. Biomater.* 2020, 2020:1–11.
- [7] Corredor, L., Maini, B., Husein, M., Improving Polymer Flooding by Addition of Surface Modified Nanoparticles, in: Day 1 Tue, October 23, 2018, SPE, 2018, pp. 1–21.
- [8] Schiestel, T., Brunner, H., Tovar, G.E.M., Controlled Surface Functionalization of Silica Nanospheres by Covalent Conjugation Reactions and Preparation of High Density Streptavidin Nanoparticles. *J. Nanosci. Nanotechnol.* 2004, 4:504–511.
- [9] Wang, B., Wei, Y., Wang, Q., Di, J., et al., Superhydrophobic magnetic core-shell mesoporous organosilica nanoparticles with dendritic architecture for oil-water separation. *Mater. Chem. Front.* 2020, 4:2184–2191.
- [10] Lanč, M., Sysel, P., Šoltys, M., Štěpánek, F., et al., Synthesis, preparation and characterization of novel hyperbranched 6FDA-TTM based polyimide membranes for effective CO₂ separation: Effect of embedded mesoporous silica particles and siloxane linkages. *Polymer (Guildf)*. 2018, 144:33–42.
- [11] Rafigh, S.M., Heydarinasab, A., Mesoporous Chitosan-SiO₂ Nanoparticles: Synthesis, Characterization, and CO₂ Adsorption Capacity. *ACS Sustain. Chem. Eng.* 2017, 5:10379–10386.
- [12] Huang, X., Young, N.P., Townley, H.E., Characterization and Comparison of Mesoporous Silica Particles for Optimized Drug Delivery. *Nanomater. Nanotechnol.* 2014, 4:2.
- [13] Facanali, R., Porto, N.D.A., Crucello, J., Carvalho, R.M., et al., Naphthenic Acids: Formation, Role in Emulsion Stability, and Recent Advances in Mass Spectrometry-Based Analytical Methods. *J. Anal. Methods Chem.* 2021, 2021:1–15.