**Manganese dioxide (MnO2) based Janus nanoparticles for emulsion stabilization with potential application for enhanced oil recovery**

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**Highlights**

* MnO2 nanoparticles were synthetized with different phases and geometries.
* Different MnO2 Janus nanoparticles were synthetized and characterized.
* The effect of amount surfactant in MnO2 Janus nanoparticles were studied.

**1. Introduction**

In the Oil - thermal recovery processes, various techniques are employed to heat the residual oil in the formation, resulting in reduction of the viscosity of crude oil which improves its mobility, facilitating its fluidity toward production wells [1, 2]. These kinds of techniques are mainly divided into two types: steam injection and in-situ combustion (ISC) [3]. One of the most advantageous yet complex thermal methods is in-situ combustion (ISC) process [1].

The transport of ultradispersed catalysts in the reservoir is essential to bring this material into contact with the crude [4]; the catalysts used can be based on transition metal nanoparticles (NP), which have a high catalytic activity [5]. However, the transport of particles in very narrow reservoirs can be a challenge, an important factor to consider is the permeability of the reservoir. Manganese dioxide (MnO2) is cheap and non-toxic [6], their diverse phases are successfully used in potential applications such as batteries, catalysis, water treatment, and chemical industry [7,8]. Additionally, when a material is present in a nanometric scale, it has larger surface areas compared to its macroscopic analogues [9].

Resasco [10] studied the application of hybrid nanoparticles in water/oil interfaces for improved recovery reactions and found that Janus particles are very effective to act as emulsion stabilizers and catalyst supports. It can be inferred that this type of nanomaterials could propagate in the flow of water through the porous media and reach the oleic phase [10]. The challenge of the oil industry is then to inject these catalysts into the reservoir through the porous medium without significantly affecting the permeability of the rock. For this purpose, it is essential that the catalytic systems form stable emulsions to transport them through the injector well [11]. Therefore, the main objective of this work is to formulate emulsions stabilized by Janus nanoparticles of manganese dioxide for their application in enhanced oil recovery.

**2. Methods**

α-MnO2, β-MnO2 and δ-MnO2 nanoparticles (NP) were prepared by a redox hydrothermal method with some modifications [12]. An aqueous solution composed of MnSO4·H2O and (NH4)2S2O8 with different ratios of reagents was charged into a Teflon-lined autoclave. The autoclave was kept in an oven at different temperatures for certain period and then cooled at room temperature. The obtained black slurry was filtered and dried with water and ethanol. The NP were mainly characterized by FT-IR and DLS.

 The as-obtained nanoparticles were selective surface functionalized through a Pickering emulsion [13] method in order to obtain Janus nanoparticles (JNP) and then a model emulsion was formed with an equal amount of oil and water.

With rheological tests as an index of fluency were chosen the best JNP for formulate emulsions and the percentage of functionalizing agent was varied to find a stable emulsion.

 **3. Results and discussion**

An easy method was performed to synthesize MnO2 nanoparticles from reagents with different charge ions, the characterization showed a narrow size distribution and the desired oxide on a nanometric scale. The synthesis also showed that the variation of reagent concentration and drying temperature affect the size and phase of nanoparticles, due to the change in the concentration of NH4+ and SO4- ions.

The synthesis of Janus manganese dioxide nanoparticles has not been widely studied, due to this finding the optimal fabrication conditions represented a challenge for the authors. The percentage of functionalizing agent was varied to analyze its effect on the JNP properties

**4. Conclusions**

In this work, the effect of the functionalizing agent in the stabilization of emulsions through Janus nanoparticles prepared by a Pickering emulsion method was studied. With this study, it is possible to understand the behavior of stable emulsions to be applied in different applications such as food, pharmaceutical, biochemistry, and the oil industry.

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