Magnetite nanoparticles and ferromagnetic bionanocomposites for crude oil removal from water

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Despite all the existing prevention systems in offshore platforms, oil spillage can occur Nyankson *et al* (2016). The main concern is to remove the oil as fast as possible and return the water to its original conditions. To remediate the water with crude oil, new technologies are being proposed, and the use of nanoparticles, that presents unique properties due to the high surface area, are showing its potential to be applied in this field. In addition, magnetic materials and magnetic nanoparticles can interact with the crude oil which then makes it easy to remove from the water by applying a magnetic field, using for example electromagnets Raj and Joy (2015). The main advantages of the hybrid magnetic materials are to utilize a high surface area (nanoparticles) with a material that has various functional groups (industrial waste), therefore, a higher capacity for contaminants are expected Saber *et al* (2015).

In this study, magnetite nanoparticles were produced by the co-precipitation method Panneerselvam *et al* (2011). The synthesis of MNP was carried out using a co-precipitation method (Molina *et al*., 2013) which consisted of the mixture of $FeCl_3 \cdot 6H_2O$ (4.0 mL) and $FeCl_2 \cdot 4H_2O$ (1.0 mL) both prepared in 1.0 mol/L HCl. This mixture was stirred for 30 min. at room temperature, while 200 mL of NH_4OH (0.7 mol/L) were gradually dropped in solution supported by a burette. The resulting suspension containing magnetite nanoparticles (MNP) separated using a neodymium magnet, washed with purified water and absolute ethanol, and dried in a desiccator. The bionanocomposite was obtained incorporating yeast biomass from ethanol industry on the synthetized nanoparticles suspension under heating the reactional medium at 80 °C (Panneerselvam *et al*. 2011; Raj and Joy, 2015). For this, around 2 g of the YB was added for each 250 mg of MNP. The synthetized materials were characterized by several techniques (XRD, SQUID, DLS, FTIR, SEM and elemental analyses), and compared to crude oil removal from aqueous.

The evaluation of oil uptake was performed using a fractional factorial design in which the effect of different parameters varied in two levels as following: magnetic material: MNP or YB-MNP; temperature: 5 or 45°C; contact time: 2 or 30 min; and mass of the magnetic material: 50 or 70 mg, performing eight different conditions.

The removal of oil was conducted by a two-layer procedure where around 0.2 g of oil sample were dispersed in 15 mL of ultrapure water disposed in Petri dishes, simulating an oil stains. Employing the conditions established by a fractional factorial design, the water containing the dispersed oil samples had their temperatures previously and masses of adsorbents were powdered over the dispersed oil and remained in contact the time stablished by the factorial design. After powdering YB-MNP or MNP on the dispersed oil over water, and let the uptake takes place, a neodymium magnet (50×50×25 mm; capable to endure 150 kg), covered with plastic film previously weighed, reached out for the oil on the surface. The oil and YB-MNP or MNP were immediately dragged by the magnet, leaving the solution. After that, the plastic films containing the oil and adsorbent material were lyophilized and weighted to determine the masses of oil removed from water in a gravimetric approach. All experiments were carried out in triplicate.

It seems to be predominantly a mechanical phenomenon, with a simple sprinkling of magnetic materials on oil stains, with a great potential for removal of oil from contaminated water. Therefore, this particular process does not fit peculiar cases of sorption of which studies such as isotherm models, thermodynamic, kinetic, or sorption capacity can be applied.

Figure 1 shows the XRD patterns of MNP and YB-MNP. The samples presented the six characteristic peaks assigned to Fe_3O_4 nanoparticles (JCPDS 20–596), confirming the absence of hematite or other iron hydroxides (Klug and Alexander, 1974). These diffractograms demonstrate that capping nanoparticles with YB did not lead to any phase change of the MNP. Crystallite sizes from 12.2 nm and 13.7 nm were obtained by Scherrer equation (Klug and Alexander, 1974) by taking into account the (311) Bragg reflection for the MNP and YB-MNP, respectively.

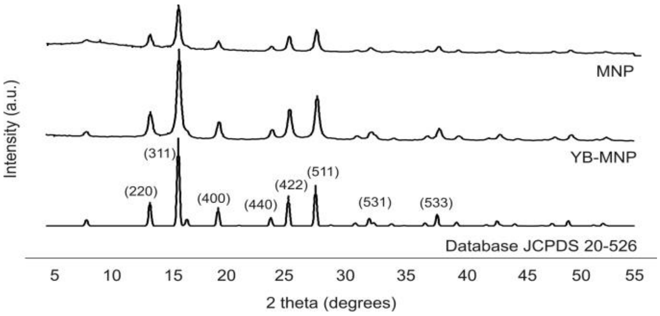

Figure 1. Powder X-ray diffractograms from representative MNP, YB-MNP and MNP from Database JCPDS 20-526 nanoparticles displaying the Bragg peak reflections of magnetite.

At lower temperatures, the removal capacity was better as shown in Figure 2, achieving the highest removal using 50 mg of magnetite nanoparticles at 5 °C with a contact time of 30 minutes (2157 ± 281 g/kg). However, the YB-MNP presented a most equalized response independent on temperature, contact time and masses used. This process of dragging is promoted by the thrust caused by the attraction of YB-MNP or MNP by the magnet in association with intermolecular forces among the oil molecules, which promotes spontaneous capillary action causing the remove of the oil from water due to adhesive and cohesive forces, such as London interactions (Israelachvili, 2011).

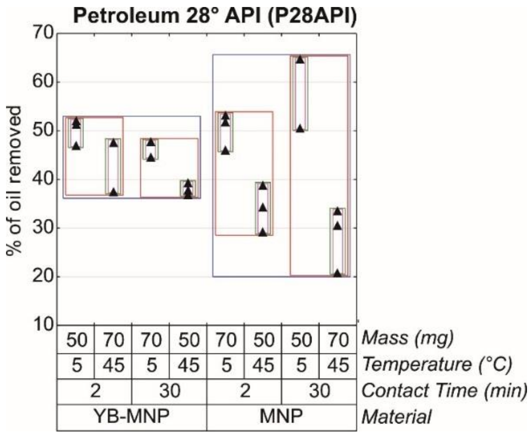

Figure 2. D-optimal design for crude oil by YB-MNP (yeast biomass coated by magnetite nanoparticles) and MNP (magnetite nanoparticles), n=3.

As seen in Figure 3, there are two relevant parameters, which affect the crude oil removal capacity: the temperature and the interaction between temperature and the material used.

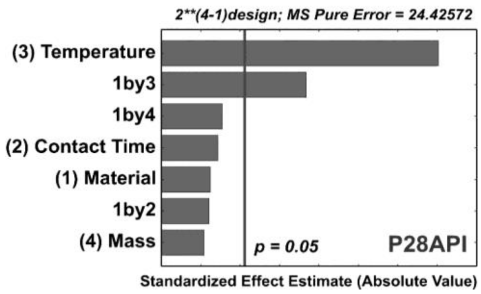

Figure 3. Pareto's graphic for crude oil (95% confidence).

This study proves that both materials, YB-MNP and MNP, are able to remove crude oil from aqueous solution, showing a removal capacity between 20% and 66%, which depend on the parameters involved in the process, specially temperature and the interaction between temperature and the material used.

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