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Development of Functionalized Magnetic Nanoparticles for Selective Extraction of Naphthenic Acid from Crude Oil

Functionalized magnetic nanoparticles (MNPs) are possible effective means for removing naphthenic acid (NA) from crude oil. In this work, magnetite nanoparticles functionalized with amine-containing ligands were used to selectively extract NA from model oil and from the heavy crude solution.

Nanoparticles were synthesized in the sonochemical process, by coprecipitation from the Fe2+ and Fe3+ solution in the basic pH. Further on, they were capped in the oleic acid (OA) to ensure proper dispersion of the material and functionalized with (3-Aminopropyl)triethoxysilane (primary amine) and N-[3-(Trimethoxysilyl)propyl]ethylenediamine (primary-secondary diamine). Two ligands varying in number of amine groups were used to assess the influence of the active sites concentration on the NA extraction. Non-functionalized nanoparticles were used as a reference.

Extraction procedure included dispersion of 1000 mg of nanoparticles in 100 ml of 4000 mg/l NA solution in heptane or 5% (vol.) solution of a South American heavy crude. Such suspension was then sampled over time to show decrease of the free NA concentration due to the acid-binding action of the MNPs. Subsequently, nanoparticles were removed from the NA solution using a permanent magnet and the acids were desorbed in DCM-MeOH-NH3(aq) (10:10:1 vol.). MNPs were then recycled for further removal of NA from the initial solution. Solutions were sampled after each extraction cycle to assess the effectiveness of the procedure.

Nanomaterials were characterized for their specific surface area, particle size, crystalline phases and thermal decomposition pattern. Moreover, synthesised particles were subject to FT-IR ATR to show effectiveness of the functionalization and titrated with HCl to ascertain concentration of the amine groups on the material surface. Liquid FT-IR using 0.1 mm NaCl cell was a principal technique for NA quantification. Readings for the model oil were calibrated using commercial NA mixture, whilst readings for the crude solutions give only relative values, taking initial concentration of acids as a reference.

Nanoparticles showed to be effective means for NA removal. MNPs functionalized with diamine turned out to be the most efficient type. Capacity of the acid extraction for this material reached up to 105 mg/g for the commercial NA mixture. Moreover, these results were repeatable when the nanomaterial was reused, proving that the MNPs are suitable for the reuse. Trials with the heavy crude solution showed that 4 extraction cycles are sufficient to lower the NA concentration to the quantification limit of the analytical method.
Measurements of the adsorption kinetics showed that, under proper agitation and initial NA concentration of 4000 mg/l, 3 minutes are sufficient for saturating 90% of the total NA binding capacity of the material. In such conditions, 30 minutes of agitation at 1500 RPM leads to complete stabilization of the NA levels in the liquid phase, so that they do not change significantly even after 24 hours.

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