Recyclable Amine-Functionalized Magnetic Nanoparticles for Rapid Demulsification of Crude Oil-in-Water Emulsions

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Fabrication of amine-functionalized magnetic nanoparticles

Fabrication of amine functionalized magnetic nanoparticles was accomplished by two steps. In the first step, bare magnetic nanoparticles (bare-MNPs) were prepared by co-precipitation under an alkaline condition. Subsequently, an aqueous APTES coating process was employed to coat amine group on the surface of bare-MNPs.

Synthesis of Iron Oxide Magnetic Nanoparticles

Iron oxide magnetic nanoparticles were prepared by a method reported previously.[30–33] Briefly, an amount of 2.15 g of $FeCl_2 \cdot 4H_2O$ and 5.87 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 100 mL DI-H_2O, resulting in a molar ratio of Fe^{2+} and Fe^{3+} at 1:2. Then, 0.125 g of citric acid monohydrate was added to it. After heating the solution up to 90^{o}C along with vigorous magnetic stirring, 37.5 mL of 20% ammonium hydroxide was loaded to establish alkaline conditions for the initiation of the nucleation of magnetic nanoparticles. Following the continuous reaction for 2 h at 90^{o}C, the resulting medium was then cooled down to room temperature. The synthesized bare magnetic nanoparticles were then washed with DI-H_2O three times and collected by a permanent magnet (0.44 T, K&J magnetics Inc., U.S.A.). During each washing step, ultra-sonication was applied to facilitate the dispersion of nanoparticles. Finally, the magnetic nanoparticles were redispersed in the DI-H_2O for amine functionalization.

Amine-functionalization of Iron Oxide Magnetic Nanoparticles

Amine-functionalization of iron oxide magnetic nanoparticles was accomplished by a coating method identified as APTES coating process.[32,33] During this procedure, an amount of 2.96 mL of APTES and 1.34 mL of glacial acetic acid were added into 28 mL of DI-H_2O at room temperature. After one hour of hydrolysis at acidic condition, the pH of the solution was adjusted to 8 by adding

2.5 N NaOH. Prior to amine-functionalization, 10 mL nanoparticle suspension (50 mg/mL) was sonicated (Branson digital sonifier, U.S.A.) for 10 min and added dropwise into the hydrolyzed APTES solution. Subsequently, DI-H_2O was added to reach a total volume of 100 mL. After 24 h of reaction at 65°C, the suspension was cooled down to room temperature. The amine-functionalized nanoparticles (NH_2-MNPs) were collected by a magnet, and washed three times with DI-H_2O. NH_2-MNPs were then re-suspended in DI-H_2O, and the pH of the suspension was adjusted to 4.5 by adding HCl (1 N), in order to maintain the stability of magnetic nanoparticles.

Adsorption isotherms

Langmuir and Langmuir-Freundlich (Sips) isotherms were adopted analyze the adsorption data, and were expressed by the following equations, respectively.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = \frac{q_m K_{LF} (C_e)^{1/n}}{1 + K_{LF} (C_e)^{1/n}} \quad (2)$$

In Langmuir model, q_e is the amount of crude oil adsorbed onto the NH_2-MNPs at equilibrium, C_e is the equilibrium oil concentration in the aqueous phase, q_{max} denotes as the maximum adsorption capacity of NH_2-MNPs corresponding to the complete monolayer coverage at the interface, and K_L is the Langmuir adsorption constant. This empirical model is for a monolayer adsorption (homogeneous adsorption), indicating that adsorption cannot take place once the reactive sites are occupied by the adsorbate. The Langmuir-Freundlich model is an integrated model combining both Langmuir and Freundlich isotherms for analyzing the adsorption results. K_{LF} is the L-F isotherm constant and q_m is the determined maximum adsorption capacity. The Langmuir-

Freundlich isotherm is generated on the basis of Freundlich isotherm, in which both monolayer and multilayer adsorptions can occur, and the surface of the adsorbent is considered as heterogeneous. But Langmuir-Freundlich isotherm includes an asymptotic property in which adsorption eventually reaches the maximum. If the heterogeneity factor (n) is unity, the Langmuir-Freundlich model becomes the conventional Langmuir isotherm.

The fitting lines using two different isotherms are presented in Figure 2S and the modelling parameters are shown in Table 1S. According to the results, the Langmuir-Freundlich isotherm is a suitable model to evaluate the adsorption of oil droplets onto the MNPs with R_{LF}^2 of 0.986. The predicted maximum adsorption capacity was estimated to be 1.49 $\times 10^5$ mg/g, indicating that 1 gram of NH_2-MNPs can demulsify approximately 149 gram of crude oil. This high value illustrates the superior capability of NH_2-MNPs for demulsifying oil droplets, which is due to the robust surface functionalization and finite size of the nanoparticles fabricated.

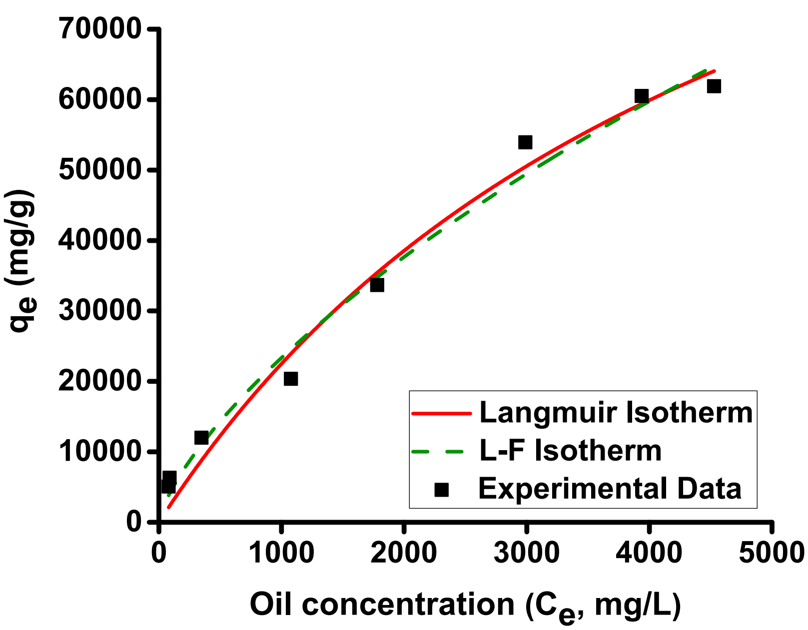

Figure 1S. Adsorption isotherm of crude oil to NH_2-MNPs and the fitting curves by Langmuir model, and Langmuir-Freundlich (L-F) model.

Table 1S. Fitting parameters of adsorption isotherm derived from Langmuir and Langmuir-Freudlich models at ambient temperature.

Langmuir			**Langmuir-Freundlich**			
q_{max}(mg/g)	K_L(L/mg)	R_L^2	q_m(mg/g)	K_{LF}(L/mg)$^{1/n}$	n	R_{LF}^2
1.34×10^5	2.0×10^{-4}	0.969	1.49×10^5	2.89	1.37	0.986

Demulsification Kinetics with and without a magnetic field

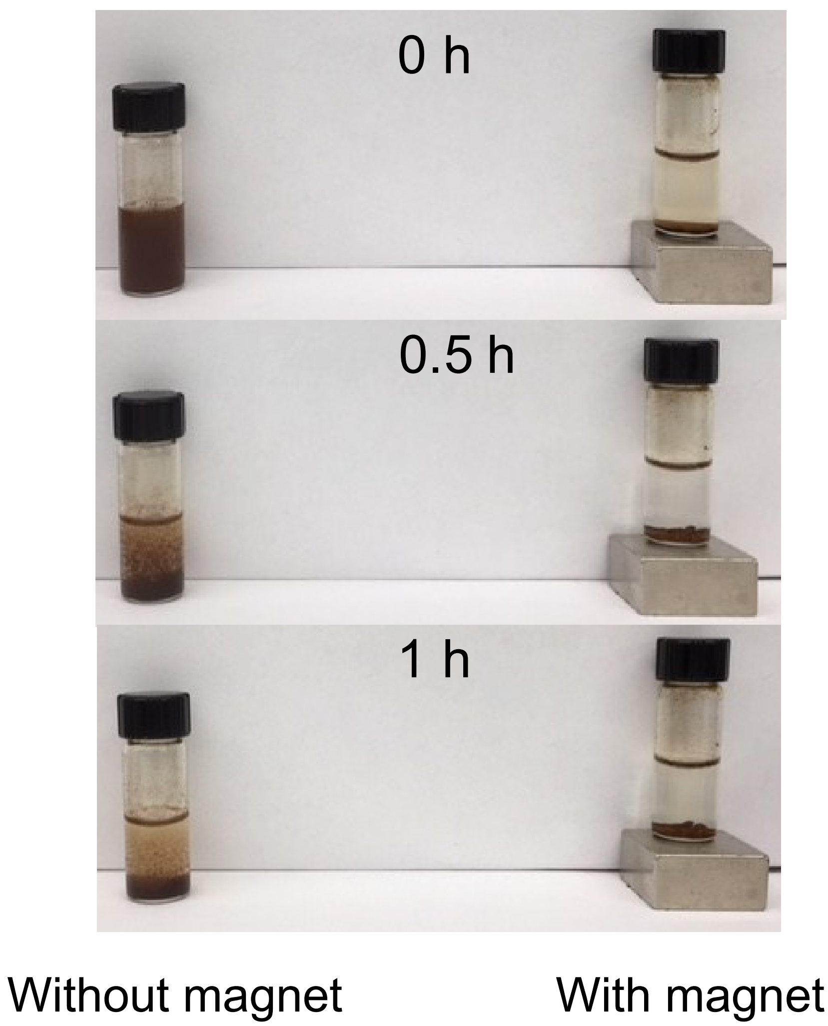

Figure 2S. Demulsification of crude oil emulsions with amine-MNPs with and without a magnetic field. The application of a magnetic field increases collision frequency which leads to faster demulsification.