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Removal of oil from crude oil-in-water emulsion by magnetically recyclable diatomite demulsifier

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Standard line of oil content and oil absorbance

1.0 mL of crude oil was dissolved in petroleum ether and the mixtures are diluted to different times. Then the oil absorbance at different oil concentration was tested at 225 nm, as shown in Fig. S1.

The polarizing optical microscope (POM) images of various samples

POM images of DM, high temperature treated DM and DM-APTES are shown in Fig. S2. It is obvious that all of them present typically perforated disk structures with the diameter of above 25 μm. Besides, the morphologies of DM particles remained intact after the thermal treatment (b) and surface modification (c), suggesting the strong
stability.

**Size distribution of DM samples**

Zeta potential analyzer was also carried out to measure the particle size of DM, as shown in Fig. S3. It is clearly seen that the DM particles presented wide size distribution. While most of particles concentrated in the range of 20-50 μm, demonstrating the reasonability of SEM and POM observations.

![Fig. S3 The size distribution of DM](image)

**The element mapping images of the M-DM**

The element mapping images of the M-DM sample are shown in Fig. S4. It can be seen that the C, O, Si, N, and Fe elements are distributed uniformly in the M-DM. The characteristic distribution of elements in a section of the M-DM surface further confirms the fact that the Fe₃O₄ NPs and amino groups have been successfully grafted onto the DM surface.
Stability analysis

TG analyses provided further supporting evidence of the assembly of APTES, Fe₃O₄ NPs and PEI have been successfully grafted onto the DM surface. The TG analysis result of DM, DM-APTES, DM-APTES@Fe₃O₄ and M-DM composite is shown in Fig. S5. It is found that DM has very high stability in nitrogen atmosphere and only little weight loss was observed in the range of 600-800°C. For the DM-APTES, the weight loss of 5.0wt % is mainly ascribed to the decomposition of aminopropyl and the dehydration of APTES layer. In addition, the weight loss of DM-APTES@Fe₃O₄ can be attributed to the stabilizer degradation of sodium acetate and the decomposition of aminopropyl and the dehydration of APTES layer. In the case of M-DM, multistep decomposition processes are observed. The first step taking place between 60°C to 200°C is mainly caused by the vaporization of crystal water. While the weight loss ranging from 200 to 550°C owes to the stabilizer degradation of sodium acetate, the weight loss that begins from 550°C most likely relates to the decomposition of
aminopropyl. All of these results demonstrated that the APTES, Fe$_3$O$_4$ NPs and PEI have been successfully grafted onto the DM surface.

![Fig. S5 TG analysis of various samples](image)

**Surface wettability test**

The surface wettability of samples can be reflected by the contact angle measurement. The DM, high temperature treated DM, DM-APTES, DM-APTES@Fe$_3$O$_4$ and M-DM solutions (dispersed in the ethanol) with the concentration of 2 mg/mL are respectively prepared and coated on the glass surface. Then the glasses were dried 12 h in vacuum drying oven to remove the ethanol. As shown in Fig. S6, the DM presented strong hydrophilicity with a contact angle of 22°. After the high temperature treatment, the contact angle of DM decreased to 2°, demonstrating high temperature could remove the attached organics on the DM surface and thus further improve the hydrophilicity of DM. While the DM-APTES layer displayed hydrophobility property with the contact angle value of 82°. Compared with DM-
APTES, the contact angles of DM-APTES@Fe₃O₄ and M-DM decreased to 60° and 56°, respectively. The reason was that the hydrophilic Fe₃O₄ and PEI have been grafted onto the DM-APTES surface. The difference of contact angle values revealed the variation of surface energy as a result of introducing hydroxyl, carboxyl and amino groups.

![Fig. S6 Contact angles of water drops on surfaces of various samples](image)

**Optimizing the mass ratios of DM to Fe₃O₄ in the M-DM**

The demulsification efficiency (DE) of M-DM with different mass ratios of DM-APTES to Fe₃O₄ at pH of 6.0 was tested and the results are shown in Fig. S7. It is seen that the DE increased with the increase of DM-APTES dosage. Thereinto, the DE reached the maximum when the dosage of DM-APTES was 0.1 g. Additional dosage increases of DM-APTES to 0.2, 0.3, 0.4 and 0.5g respectively would not further improve the DE. In addition, a portion of DM-APTES still resided in the mixed solution after the magnet separation. It is mainly due to the fact that -NH₂ of DM-APTES reacted with the -COOH groups of Fe₃O₄ NPs surface³⁴ to form the -CO-NH- covalent bond.
When excessive DM-APTES was added, no additional -COOH groups on the Fe$_3$O$_4$ NPs could react with the -NH$_2$ of DM-APTES, resulting in portions of DM-APTES were resided in the mixed solutions. Therefore, the optimal dosage of DM-APTES was determined as 0.1g. Under this condition, the prepared M-DM has excellent DE and magnetic recyclability.

![Graph showing the effect of mass ratios of DM-APTES to Fe$_3$O$_4$ on DE. The inserted photograph is the residual solution after magnet separation.]

Fig. S7 Effect of the mass ratios of DM-APTES to Fe$_3$O$_4$ on DE. The inserted photograph was the residual solution after magnet separation

References

