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Interfacially active and magnetically responsive composite nanoparticles with raspberry like structure; synthesis and its applications for heavy crude oil/water separation

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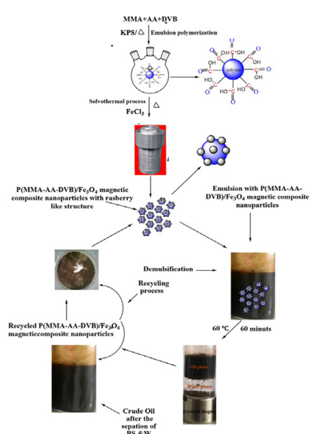
HIGHLIGHTS

- P(MMA-AA-DVB)/Fe_3O_4 Magnetic composite nanoparticles in micro scale were prepared by solvothermal process.
- P(MMA-AA-DVB)/Fe_3O_4 effectively attached to the stable emulsified water droplets in emulsion.
- The obtained composite nanoparticles expressed excellent recycling property for separation of water in crude oil emulsion.
- The recycled P(MMA-AA-DVB)/Fe_3O_4 retained its interfacial activity, surface morphology after demulsifiection.

GRAPHICAL ABSTRACT



Scheme. Procedures explaining the process of synthesis, demulsification and recycling of P(MMA-AA-DVB)/Fe_3O_4 magnetic composite nanoparticles.

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ABSTRACT

In the current study of interfacially active and magnetically responsive poly (methylmethacrylate-acrylicacid-divinylbenzene)/ironoxide magnetic composite nanoparticles with raspberry like surface morphology were designed and synthesized by direct soap free emulsion polymerization followed by solvothermal technique. Transmission Electron Microscopy (TEM), Fourier Transform Infrared spectroscopy (FT-IR), Vibrating Sample Magnetometer (VSM) and Thermo Gravimetric Analysis (TGA) were being used for the characterization of magnetic composite nanoparticle with proper surface morphology, nano scale particle size and high magnetic content. The prepared P(MMA-AA-DVB)/Fe_3O_4 nanoparticles showed excellent interfacial activity at the oil/water interface. The magnetic properties of P(MMA-AA-DVB)/Fe_3O_4 nanoparticles at the oil/water interface made the interfacial properties tunable and responsive to an external magnetic field which, showed quick separation of heavy oil and water emulsion within one hour. The magnetic property enabled the used magnetic composite nanoparticles to be recycled by magnetic separation and solvent washing. The recycled P(MMA-AA-DVB)/Fe_3O_4

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was found toretaining its interfacial activity and effectivity in the oil/water separation. The adsorption of P(MMA-AA-DVB)/Fe_3O_4 at the oil/water interface with their magnetic properties demonstrating enhanced coalescence of magnetically tagged water droplets and rapid separation of water droplets from the heavy crude oil and water emulsions by an external magnetic field.

1. Introduction

The formation of stable water in oil emulsion is a common problem in the petroleum industry which is most frequently resolved through the use of chemical demulsifier. The emulsions have stability ranging from a few minutes to years, depending upon the nature of crude oil and the extent of water. Surfactants such as asphaltenes, resins, carboxylic acids and solids such as clay and waxes stabilize these emulsions. It is important to demulsify these emulsions before transportation for refining [1,2]. Commercial demulsifiers are polymeric surfactants such as copolymers of polyoxyethylene and polypropylene or alkylphenol–formaldehyde resins or blends of different surface-active substances. These demulsifiers are surface-active agents and develop high surface pressures at crude oil/water interfaces, which results in the replacement of rigid films of natural crude oil surfactants by a film which is conducive to coalescence of water droplets [3,4]. The structure of these demulsifiers does affect their efficiency, i.e. the partitioning of the demulsifier between the phases, temperature, pH and salt content of the aqueous phase. Other parameters that influence the demulsifiers efficiency include the mode of injection of the demulsifier, the concentration of the demulsifier, the type of solvent carrier, the amount of water in the emulsion and the age of the emulsion [4–7].

The study of nanoparticles at fluid/fluid interfaces is technically important in many traditional industrial processes such as food formulation, crude oil extraction and mineral flotation [8]. The experimental and theoretical investigations elucidate the adsorption of nanoparticles at fluid/fluid interfaces and the stability of emulsions and foams derived from the nanoparticles interfacial adsorption [9,10]. A particularly promising set of materials in this context is stimuli-responsive polymers [11]. Combining these polymers with nanoscale inorganic materials is a strategy that has seen success in the development of composite materials with solvent- and temperature- tunable optical and electronic properties [12–14]. Magnetic nanoparticles like magnetite (Fe_3O_4) are powerful markers and carriers for diverse research and industrial applications due to their magnetic responses and convenient separation of a complex multiphase system by an external magnetic field. Further developing and assessing nanoscale inorganic materials which are hybridized with stimuli responsive materials, can be proved useful by employing them to the water/oil interface [15,16]. This interface is attractive with respect to the development of novel nanoscale inorganic materials because nanoparticles that are trapped at a water–oil interface can be modified using chemical operations in either of the two bulk phases. Self-assembly of nanoscale, inorganic materials at the water/oil interface has been used before to fabricate multilayered nanoparticles composite materials that combine the material properties of the individual nanoscale material [17]. Additionally, nanoscale inorganic materials capped with stimuli-responsive polymers and monolayers have been used to reversibly control the stability of emulsions in immiscible water/oil systems via temperature or pH modulation [18,19].

The main objective of the current study is to prepare an effective demulsifier which can break heavy oil and water emulsion in short time, at low temperature, reduced oil loss and which can be reuse several time. Herein, a completely new family of reusable nanoscale magnetic amphiphilic composites with a raspberry like structure is described. In our approach the magnetic composite nanoparticles possesses strong magnetic Fe_3O_4 with an interfacially active organic block co-polymer of P(MMA-AA-DVB). The Interfacial activity of P(MMA-AA-DVB) brings the magnetic composite nanoparticles at the oil/water interface to tag the emulsified water droplets and to effectively separate them by external magnet. The advantage of this new material is that it separates water in a short time of 1 h and at low temperature 60 °C with reduced oil loss and sludge formation. These composites can be magnetically recovered and reused several times. These composite demulsifier as they do not contaminate the treated emulsion and is a novel example of the application of nanotechnology in the field of oil and gas industry.

2. Experimental methods

2.1. Chemicals

Two different heavy crude oil samples with different physical parameters (Table 1) were provided by Chang Qin oil field in Gansu province. Ferric chloride ($FeCl_3{\cdot}6H_2O$), sodium acetate (NaAc), and acrylic acid (AA) were purchased from Tianjin Hongyan chemical reagent factory. Trisodium citrate (Na3Cit) was obtained from Guang Zhou Jin Hua Da chemical reagent Co. Ltd. Divinyl benzene (DVB) and methylmethacrylate (MMA) was purchased from Fu Yu chemical reagent Co. Ltd Tianjin. Ethylene glycol (EG) was purchased from Jin Shan Hua Shi Chengdu chemical. Potassium peroxy sulphate (KPS) was obtained from Sinopharm chemical reagent Co. Ltd Shanghai. All the reagents were of analytical grade and used without any further treatment.

2.2. Synthesis of the polymeric precursor and magnetic composite nanoparticle

Soap free emulsion polymerization was used for the preparation of P(MMA-AA-DVB) nanoparticles with (MMA) and (AA) as a monomer, (DVB) as a cross-linker and (KPS) as initiator [20]. The synthesis process is as follows: 6.00 g of MMA, 0.25 g AA and 0.90 g DVB were added to 80 mL water in a 150 mL round bottom flask which was properly assembled for heating under reflux. The mixture was heated from room temperature to 100 °C. 0.02 g of KPS dissolved in 20 mL deionized water was added to the solution. The polymerization reaction was kept under reflux for further 3 h. After the reaction completion the resultant P(MMA-AA-DVB) nanoparticles were dried by vacuum freezing.

Solvothermal process was used with some modification for the preparation of P(MMA-AA-DVB)/Fe_3O_4 magnetic composite nanoparticles in the presence of P(MMA-AA-DVB) [21]. For this purpose, 0.40 g of P(MMA-AA-DVB) nanoparticles, 2.00 g of $FeCl_3{\cdot}6H_2O$, 0.24 g of Na_3Cit and 1.60 g of NaAc were dispersed in 34 mL of ethylene glycol (EG) under ultrasonic irradiation and

Table 1
Physical parameters of crude oil samples.

Sample no.	Specific gravity	API gravity	Total water %	Asphalt content (wt %)
01	0.845	35.95	1.50	05.00
02	0.955	16.76	10.0	16.00