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Original Paper

Recent studies of Pickering emulsion system in petroleum treatment: The role of particles

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ABSTRACT

Pickering emulsions stabilized by solid particles have gained much attention, which afford high stability, low toxicity, controllable rheological properties and stimuli-responsive behavior compared to the traditional emulsions emulsified by surfactants. Those particles, as the core parts of the emulsion systems, play an important role in the fabrication and application of Pickering emulsion systems, making them attractive in petroleum fields. In this review, the influence of various particles on the stability and properties of Pickering emulsion systems as well as recent researches associated with the stimuli-responsibility of Pickering emulsion systems are introduced. Specifically, the design of functional particles and Pickering emulsion systems with super stabilities and controllable rheological properties are listed. Furthermore, some petroleum application of Pickering emulsion systems for enhanced oil recovery and spilled oil collection as well as the application as soft templates to fabricate oil-absorbing material and as three-phase microreactors that most likely for petroleum application are discussed, and the issues hindering the actual application of Pickering emulsion systems are also evaluated. This review charts a way for Pickering emulsion studies that could lead to a valid petroleum application through design of the particles served as the enhancers of Pickering emulsion stability for purpose of tailoring chemical flooding.

1. Introduction

With the rapid development of economy and industry, the disparity between demand and supply of crude oil put a serious challenge for the petroleum industry to produce the remaining oil with advanced technologies. In the actual oil extraction process, the highest natural driving oil recovery rate is only 20%–60%, therefore, it is of the importance to boost the oil extraction by developing enhanced oil recovery (EOR) technologies, such as water flooding, chemical flooding, and steam flooding (Gbadamosi et al., 2018). Among them, chemical flooding is commonly used strategy to enhance the oil extraction due to its facile, high efficiency, and low energy consumption by adding chemical agents in the EOR process. For now, the key aspects of chemical flooding researches are as follows: (1) improving the mobility ratio by reducing the viscosity of crude oil or increasing the viscosity of displacing fluid; (2) enhancing displacement efficiency through improving wettability and decreasing interfacial tension (Du et al., 2020). Compared with conventional water flooding, the emulsion flooding is reported that can efferently increase the recovery by more than 15% (Mandal et al., 2010), which is mainly ascribe to the combination of reduction in displacing liquid mobility and interfacial tension. Especially, emulsions stabilized by solid particles, also noted as Pickering emulsions, have gained much research interests in last few years. It is reported that those solid particles can effectively adjust the thermal stability and viscosity of emulsion systems, which are suitable for EOR applications (Katende et al., 2019; Li et al., 2018).

Solid particles in Pickering emulsion system have been indicated as substitutes or improvers for traditional polymer surfactants to stabilize the emulsion systems, which can be ascribed to their stronger tendency to be adsorbed irreversibly at immiscible biphasic interfaces (typical particle stabilizers are summarized in section 2) (Biswal et al., 2016). Compared with the traditional emulsions generated by surfactants, the Pickering emulsion systems exhibit superior performance in aspect of chemical stability, suitable rheologic property, low-cost and environmental safety

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(Nazari et al., 2015) owing to the unique incorporating particles properties, such as particular morphology, large specific surface area, and tunable topology and wettability (Liu et al., 2020). Thus, numerous works have been paid to investigate the effect of solid particles on generation, stability and properties of Pickering emulsion systems, including the wettability, morphology, and concentration of particles used, which provides an important mechanism foundation for the actual application of Pickering emulsion systems. Nowadays, the choose and design of practical solid emulsifier and multifunctional Pickering emulsion systems to promote the stability and rheological properties in chemical flooding at harsh reservoir conditions is still the research emphasis, which will offer the environmentally safely and promising strategy to boost the EOR process.

The design of novel and stable Pickering emulsion systems in the harsh conditions with varying pH, high salinity, and high temperature are of growing technical importance (Khalil et al., 2017). Especially, the high salinity/temperature conditions are often found in the oil reservoirs, which can achieve to 250,000 ppm TDS and 150 °C, respectively (Zhu et al., 2017). Mohamed et al. (2018) reported that using Cloisite as stabilizer to create the Pickering emulsion fluids. This emulsion fluids could still maintain stable under high temperature (over 100 °C) and high salinity (over 200,000 ppm) situations. For better application performance of Pickering emulsion systems, those stabilized particles are further decorated with certain abilities. Through modification of particles, the smart Pickering emulsion system is endowed with ability to response to various stimuli, such as pH (Dyab, 2012), magnetism (He et al., 2020), and temperature (Destribats et al., 2012). If the stabilizing behaviors of emulsion fluids can be smart control over a certain stimulation, it would maintain the fluid stability under complex oil reservoir conditions at EOR processes and oil tubing transportation efficiency. On the other hand, after being pumped back to the ground, the emulsion flooding could be smartly switched “off” to collapse for oil/water separation and simple processing in subsequent procedures to improve the quality of oil.

Furthermore, the smart Pickering emulsion systems also exhibit the significant potential on other aspects of oil recovery and transportation. The heavy oil emulsification, resulting from oil spill, bring serious consequences to the environment and make the oil more difficult to collection and removal. Based on the regular of emulsification, migration, and ripening of Pickering emulsion systems, a number of researches were conducted using special designed solid particles as medium to construct the smart Pickering emulsion systems, which could controllably stabilize, induce, ripen, and directional transport those micro-sized oil droplets in sea under magnetic fields to realize the spilled crude oil recovery (Song et al., 2018). Additionally, some researchers further used solid particles/Organism with catalytic ability or degradability as Pickering emulsifiers to stabilize those smart Pickering emulsion systems as micro-reactor platform in the oil treatment (Yang et al., 2015; Zhou et al., 2018). The smart Pickering emulsion systems offer the ideal three-phase contact area to maximum the treating efficiency. Generally, the internal phase is separated into a small and regular Pickering emulsion droplets, and each component is shelled with the confined space as well, which can effectively avoid the uneven mixing and offer an ideal condition for preparation in macroscopic quantity. Overall, the Pickering emulsion systems can serve as a strong and effective platform of industrialization prospects in petroleum and other fields.

In this work, the aim is to provide an up-to-date review on Pickering emulsion systems and their potential applications in petroleum field. The role of solid particles on the formation and characteristic of Pickering emulsion systems as well as the recent researches closely to the design of smart Pickering emulsion systems for petroleum application purpose will be introduced. Typically, we summarize the effect of solid particles on the performance of Pickering emulsion systems as mechanism foundation from the aspects of wettability, morphology, and concentration of particles used. Besides, the choose and design rules of practical solid emulsifier and smart Pickering emulsion systems to strengthen the fluid performances and rheological properties at EOR process is emphasized. Furthermore, we also discuss the applications of smart Pickering emulsion systems as magnetic transportation carriers and catalysis/degradation platforms for spilled oil treatment. This work summarizes the current researches and provides an outlook on expected future developments and major research directions.

2. The effect of particles on the preparation of Pickering emulsions

Different from conventional emulsions, Pickering emulsions are prepared via dispersing particles at biphasic interface instead of a surfactant. The sufficient reduction of the interfacial energy is considered as the driving force for the colloidal particles assembling. Those particles remain at the fluid-fluid interface can provide an electrostatic particle film as the effective mechanical barrier to stabilize the emulsified droplets (Zhang et al., 2017). To obtain the suitable Pickering emulsion systems, the effect of solid particles on the generation and characteristic of Pickering emulsions is need to be taken into consideration. Herein, we investigate the stability and morphology changes of Pickering emulsions in aspect of solid particles such as wettability, size, and shape.

2.1. Wettability of particles

According to previous works, the preferential wettability of solid particles played an essential part in the formation of Pickering emulsion systems (Huang et al., 2013; Tang et al., 2015; Griffith and Daigle, 2018). For the particles which are more easily wetted by water phase, they are prone to escape from the oil phase, thereby resulting in the interface curving towards the oil phase and generation of the separated oil droplets. In contrast, the situation with water droplets generated will occur for more hydrophobic particles used. In order to better understand the preferential wettability and predict the type of emulsion, the Young's equation (as follow Eq. (1)) was utilized to calculate the water contact angle (Tang et al., 2015).

$$\cos\theta_w = \frac{\gamma_{s/o} - \gamma_{s/w}}{\gamma_{o/w}} \tag{1}$$

where θ_w represents the contact angle at water phase, which is usually easy to be measured by three-phase contact angle photogoniometric method, and $\gamma_{s/o}$, $\gamma_{s/w}$, and $\gamma_{o/w}$ on behalf of the interfacial energies in solid-in-oil, solid-in-water, and oil-in-water interface, respectively. Generally, as displayed in Fig. 1, the boundary of preferential wettability for water and oil phase is 90°.When the $\theta_w < 90°$, the majority of particles will be wetted by water phase, inducing the formation of oil-in-water (O/W) emulsion system. And the water-in-oil (W/O) emulsion system can be obtained when particle with $\theta_w > 90°$ used. Besides, the particles with complete wetting in either phase are unable to stabilize the interface owing to the fact that those particles are completely immersive in single phase, failing to contact with both phases, and unable to maintain the stability of emulsion interface.

The stability of Pickering emulsions depends greatly on the particle behavior at biphasic interface. Some inorganic particles, such as graphene oxide (Li et al., 2009) and halloysite (Yu et al.,

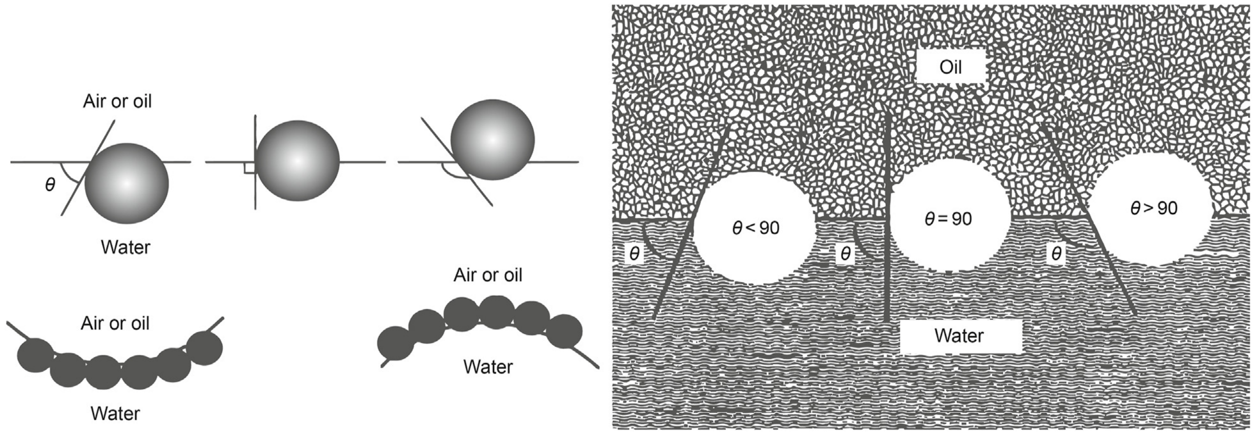

Fig. 1. (Left)Distribution of solid particles at water/oil interface. (Right) Particles positioning at oil/water interface (Umar et al., 2018).

2019a). are too hydrophilic to stay at the interface, which requires the appropriate hydrophobic modification to obtain the desire wettability to stabilize the emulsion systems. For example, the Binks's group has systematically examined the effect of SiO_2 particles wettability on the properties of Pickering emulsion formed. A series of modified silica particles with different wettability by silanization were fabricated to stabilize the toluene-in-water emulsion systems. The results indicated that the emulsion systems prepared by silica particles that were too hydrophilic or too lipophilic were unstable and quickly collapsed. Only used particles with contact angle between 60 and 80°, the stability of o/w emulsions was greatly improved (Binks and Lumsdon, 2000). Moreover, it has been proved by Kaptay that Pickering emulsifiers with a contact angles around 70-86° are the best candidate for generation of typic o/w emulsion systems. And for the stabilized w/o emulsion systems, the optimum θ_w require between 94 and 110° (Kaptay, 2006). Therefore, proper amphipathic properties of particles are required to stabilize the emulsion systems, which means particles could be well wetted by both oil/water phases at emulsion interface, resulting in the reduction in the interface tension and stabilization of emulsion systems. Design of particles with amphipathy is the key point of researches of Pickering emulsion systems.

Nowadays, anisotropic particles have attracted much attention in long-term Pickering emulsion stability. Typically, the Janus particles, two surfaces with different wettabilities, can be strongly adsorbed to the biphasic interface with surfaces toward to corresponding phase and provide better ability to stabilize the emulsion systems. Yang's group reported the inorganic Janus silica nanosheets with opposing wettabilities surfaces through three silanes self-assembled sol-gel process at emulsion interface (Liang et al., 2011). According to the thermodynamic study, it has been proven that when the emulsion droplets were covered by Janus silica nanosheets, the emulsion system exhibited the lowest energy state, suggesting the high stability of such emulsions. With the requirement of long-term stability of Pickering emulsion systems in multi-field applications, the customizable anisotropic wetting behavior and functions of Janus materials is the research hotpot. A number of novel Janus materials have been developed through emulsion template, self-assembly, and orientation coating (Wu and Ma, 2016). The Janus materials which modified using natural particles like clay and cellulose can obtain proper wettability and maintain partially original functions, which should be given priority.

2.2. Size of particles

In addition to the wettability, the size of solid particles also has been indicated that it is related to emulsion properties. Binks reported using hydrophobic latex particles with various arrange of sizes to investigated the interfacial behaviors of particles in the Pickering emulsion systems (Binks, 2002). As we can see from Eq. (2), they summarized that the amount of energy ΔE required to remove a spherical solid particle of radius R from the oil/water interface for small particles (less than 2 μm).

$$E = \pi R^2 \gamma_{O/W} (1 + \cos\theta_w)^2 \tag{2}$$

where the $\gamma_{o/w}$ stand for the interfacial tension between oil and water phases. Obviously, with the same wettabilities, the large particles require a larger desorption free energy. Besides, the nanoparticles are also reported can be adsorbed to the biphasic interface to stabilize the emulsion systems, however, the low ΔE requirement makes the nanoparticles easy to detached from the interface. In other words, it can be deduced that the ΔE free energy of spherical solid particle at the oil/water interface is always higher than the particles' thermal energy, even for nanosized particles.

Nan et al. (2014) prepared the uniform chitosan-coated alginate particles of three size (230, 550, and 1100 nm) to test the performance of Pickering emulsion systems. The results showed that all Pickering emulsions could maintain stable for more than half year and interestingly the as formed droplets diameters increased with increasing particle size, and then reach the balance. Indeed, although majority of particles can help to stabilize the emulsion, the particle diameter will affect the formed emulsion droplet size as well, thereby the emulsion stability. The experimental measurements carried by Binks indicated that the sedimentation stability of the Pickering emulsion systems (i.e., ratio of separated oil volume to total oil volume) decreased on the increasing the particle size ranging from 0.21 to 2.7 μm. Generally, the small size of solid particles can produce very fine emulsion systems, and in case of large particles, greater steric hindrance, so that larger emulsion droplets should result. In fact, the control of emulsion droplets size involves many other factors as well, such as phase viscosity, particle concentration, and shear force et. (Wu and Ma, 2016).

$$m_p = (16/3)\pi R_p \rho_p R_e^2 n_e \tag{3}$$

where the R_p and R_e represent the radius of the solid particles and emulsion droplets, respectively. n_e represent the number of droplets, m_p is the mass of the particles, and ρ_p stand for the density of particles.

According to Eq. (3), the desired concentration of solid particles is proportional to the average diameter of emulsified droplets, which means to achieve the same emulsion droplet diameter, lesser concentration of particles is required with smaller size of solid particles. Thus, the size of solid particles used is the highly effective factor to manipulate the emulsion droplet in meeting of application needs.

2.3. Shape of particles

In majority works, the solid particles utilized for preparing Pickering emulsion are spherical. While, for now, more and more non-spherical particles (including 2D sheets (Wei et al., 2018), cubes (Geng et al., 2019a) and rods (Firoozmand and Rousseau, 2016) have been used to obtained the super-stable Pickering emulsions with special surface properties.

Feng and Yin (2019) studied the effects of different shapes on interfacial behavior. They reported the silica ellipsoids as stabilizer for Pickering emulsion preparation. The results indicated that at high concentration, those ellipsoids could assemble into a triangular mesh structure, strengthening the framework of Pickering layer and prevent the emulsion from collapsing. Besides, the silica ellipsoids could form striped structure as well at a low condition. Compared with spherical particles, those silica ellipsoids were more effectively to stabilize the emulsion systems, and the stability of emulsion enhanced with the increasing aspect ratio of the particles. Russell et al. reported the using of 2D $Ti_3C_2T_x$ nanosheets to stabilize the Pickering emulsion system (Shi et al., 2019). The $Ti_3C_2T_x$ could quickly gather at the liquid-liquid interface, and assembled and jammed into a layer consisting of overlapping nanosheets, offering a robust barrier to inhibit the emulsion coalescence. Furthermore, the cellulose nanocrystals with aspect ratios between 15:1 to 100:1 were also observed to connect together and form netlike structures at the emulsion interface. Owing to the strong interaction between Pickering particles, the super-stable emulsion systems were obtained. In summary, the disorderly distribution and interaction between Pickering particles at emulsion interface can efficiently increase the ΔE energy and decrease the interfacial tension, thereby forming the long-term stable Pickering emulsion systems.

Various Pickering emulsion systems are introduced throughout the reported literature, spanning inorganic, and organic solid particles, the specific information of which are listed in Table 1. In general, wettability of solid particle is one of most important factors to prepare the stable Pickering emulsion system and the key to influence the type the formed emulsions. Some natural resources such as Clay, silica, and cellulose are widely used to develop the Pickering emulsion systems owing to their proper wettability, stability and cost. In some degree, to achieve the suitable wettability, the chemical modification on Pickering particles is usually required. Among them, the anisotropic modification with customized amphipathy and bi-functionals gain much research attention. Especially, the Janus particle emulsifier can be easily fabricated by emulsion template, which is suitable for industrial scale application. Furthermore, in order to manipulate the Pickering emulsion system like size and stability, the physical structure of Pickering particles need to be carefully chosen. For particle size is closely related to the size of droplet and dose of particles, and topography of particles can influence the stability and shape of emulsion droplets. To obtain the ideal Pickering emulsion system, although the polymer particles are well developed, the appropriate modification of natural particles like clay and cellulose with submicron and proper aspect ratios, which can obtain proper wettability and maintain partially original functions, should be given research priority.

3. Application of Pickering emulsion systems in oil recovery

Pickering emulsion systems have been developed in the enhanced oil recovery (EOR) process owing to the stability and the rheological characteristics even under the high temperature and pressure environment. The discussion emphasis of this part is placed on the design of the suitable solid particles and smart-response Pickering emulsion systems for meeting the thermal stability and proper rheological properties requirements in EOR process.

3.1. Manipulation of emulsion rheology

The rheological properties of oil fluids will affect the seepage characteristics in porous media, the swept volume, and displacement efficiency. For now, the formation of Pickering emulsion systems has been recognized as an alternate method to reduce the viscosity of heavy and extra heavy oils. In these Pickering emulsion systems, the crude oil is separated into independent droplets dispersing in the water phase. Compared with commonly used

Table 1
A brief summary of Pickering emulsifiers.

Particle type		Materials	Shape	Emulsion type	Ref.
Inorganic	Silica	SiO_2	Sphere	O/W and W/O	Mironova and Ilyin, 2018
	Clay	Montmorillonite	Bulk	O/W	Geng et al., 2019b
		Halloysite	Rod	O/W	Yu et al. (2019b)
		Sepiolite	Fiber	O/W	Geng et al., 2019b
		Hectorite	Bulk	O/W	Geng et al., 2019b
	Metal oxide	Fe_3O_4	Sphere	O/W	Yang et al. (2018)
		CuO	Rod	O/W	Kim et al. (2010)
		TiO_2	Sphere	O/W	Fessi et al. (2019)
	Carbon	Carbon nanotube	Rod	W/O	Menner et al. (2007)
		GO	Disk	O/W	Kim et al. (2010)
		Carbon black	Bulk	W/O	Saha et al. (2013)
		C_3N_4	Disk	O/W	Han et al. (2018)
Organic	Polymer	PS	Sphere	W/O	Vasantha et al. (2020)
		PNIPAM	Sphere	O/W or W/O	Dan et al. (2019)
	Polysaccharide nanocrystals	Cellulose nanocrystals	Fiber	O/W	Parajuli et al. (2020)
		Chitin	Fiber	O/W	Li et al. (2018)
		Starch nanocrystals	Fiber	O/W	Li et al. (2012)
	Organism	Bacteria	Rod	O/W	Firoozmand and Rousseau, 2016
		Enzyme	Sphere	O/W	Wang et al. (2020)
		Protein	Sphere	O/W	Huang et al. (2013)

heating oil strategy, it has been demonstrated that even in the cold areas, the Pickering emulsion systems can effectively transport the crude oil with a viscosity of more than 1 Pa s.

Mironova and Ilyin (2018) studied the influence of particles on the rheological and morphology behavior of crude oil emulsion systems. The hydrophilic SiO_2 and clay were used as emulsifier to stabilize the O/W emulsions. The results suggested the storage modulus exceeds the loss modulus in O/W emulsion system, and moduli of both are slightly lean upon deformation frequency. Those solid particles participated not only leaded to a significant increase in the effective viscosity of the emulsion, but also leads to the appearance of yield stress even in diluted emulsions. The yield stress increased with silica and clay content, which might reach 10–30 Pa. In the condition of shear stress exceed the yield stress, the viscosity of the formed Pickering emulsion would be reduced by 3–10 times when concentration of crude oil is 65 vol%. Generally, the effective viscosity of Pickering O/W emulsion can be adjusted by shear rate and solid particle concentration, which offers a promising method to optimize the component of crude oil emulsion systems for transportation. Considered the harsh condition in EOR process, Sharma et al. (2014) investigated whether the concentration of nanoparticles (SiO_2 and clay) would affect the viscosity of Pickering emulsions at high pressure and high temperature conditions. Compared with O/W emulsions produced by surfactant, Pickering emulsion systems displayed that the yield stress and viscosity are predominantly constant for varying pressure (from 0.1 to 30 MP) and temperature conditions (from 298 to 371 K). In such situation, the viscosity changes of this Pickering emulsion system can be predicted by Herschel-Bulkley model. Additionally, Kumar and Mandal (2018) formulated stable O/W Pickering emulsions consisting of clay and light mineral oil. The results showed that the Pickering emulsions had good thermal stability, and the viscosity remained stable under a wide range of temperatures (303–343 K). The storage modulus (G') and loss modulus (G'') of these Pickering emulsions increase with concentration of particles increased.

In the EOR process, the utilization of particles to eliminate the adverse effects on the rheological properties of the emulsion system caused by salinity has attracted great interest. Griffith and Daigle (2018) investigated the rheological properties of the Pickering bromohexadecane-in-brine emulsions emulsified by 6 nm silica nanoparticles modified with the low and high coverage of hydrophilic silane glymo, and determined the $G'0$ of such emulsions were greatly reduced by particles of which with a maximum coverage of glymo, which could effectively inhibit the Ca^{2+}/silanol site interactions. The research also showed that the particles involved help reduce the viscoelastic behavior of emulsion systems containing 50% oil volume fraction and 1 wt% $CaCl_2$ in brine phase, and with higher 70% oil volume fraction, the elastic storage modulus of emulsions could be reduced by utilizing particles modified with a higher concentration of glymo. This work concludes that the more hydrophilic of solid particles is favor to stabilize oil-in-brine system with higher oil volume fraction. Those results are also reported by similar emulsion system prepared by Katepalli et al. (2017).

On the other hand, Geng et al. try to investigate the effect of hydrophobic particles on the rheological properties of water-in-oil fluids as well at high temperatures (Geng et al., 2019a). Three different types of organoclays, including organo-hectorite (OSHCA), organo-sepiolite (OSEP), and organo-montmorillonite (OMMT) were fabricated via surface modification. The results of rheology indicated that the water-in-oil emulsion fluid stabilized by OSHCA has better rheological performance at high temperature than the other two organoclays, which underwent a state change from gel to liquid at 180 °C, and at 200 °C it back to a weak gel state again. The non-reactive Mg–OH surface groups and special reconstructed flocculation behavior of OSHCA were the key factors for adjustment of rheological properties of Pickering emulsion fluids at high temperature. Once again, the surface wettability of particles is demonstrated that it can efficiently manipulation of as-prepared emulsion rheological properties.

3.2. Enhanced oil recovery

The emulsion flooding is a strategy utilized to enhance the oil recovery through separating the oil into droplets with helping chemical reagents, which can change the interfacial properties of the displacing fluid, the, and the interaction mechanism between the displacement fluid and crude oil. (Mandal et al., 2010). Karambeigi et al. (2015) reported the using of core displacement experiments to investigated the EOR effect of Pickering emulsions. Those experimental data showed that compared with water flooding, the oil recovery rate was further improved to about 28%. The interface potential as well as non-Newtonian fluid characteristics of the Pickering emulsion systems contribute to the increase of the number of capillaries and oil recovery. In the EOR process, the formation of stable Pickering emulsion system is of great importance. Some emulsions stabilized by colloidal solid particle failed to use for EOR, because of the failure to be long-distance transported as required in reservoirs. Those emulsion fluids can block the pore throat thereby inhibiting the permeability of reservoir (Alomair et al., 2014). As mentioned above, salts from brine phase also have certain influence on emulsion fluid properties because salts can contact with interfacial particles and change the rheology of Pickering emulsion systems (Mironova and Ilyin, 2018), which will influence the original ability of Pickering particles as stabilizer so that they desorption from the interface and unable to emulsify the emulsion systems (Tzoumaki et al., 2011). Lately, Guang et al. (2018) developed a dispersed particle gel (DPG) soft heterogeneous compound (SHC) Pickering flooding system to promote the micro-profile control and displacement efficiency. The SHC flooding system composed of dispersed particle gel particles and partial surfactants could stand for the harsh reservoirs environment with the temperature of 80–110 °C and the salinity of 1×10^4–10×10^4 mg/L. This Pickering emulsion systems featured low viscosity and weak negative charge, and the particles, as stabilizer, can gather together into big aggregate and transform the wettability from partial hydrophobic to hydrophilic. Moreover, its IFT is less than 1×10^{-1} mN/m even after aging under high temperature. The SHC Pickering flooding system could stand high temperature and salinity and directly go through the porous media after deformation to get deep into the formation. As displayed in Fig. 2, Kumar et al. (2017) prepared surfactant-polymer-nanoparticle (SPN) Pickering emulsion systems using light mineral oil, consisting of silica nanoparticles (SiO_2), carboxy methyl cellulose (CMC), and certain amount of anionic surfactant. The results displayed viscosity and loss modulus value of emulsion system maintain stable over broad range of temperature from 30 °C to 100 °C, which indicate the better flow properties of the Pickering emulsion. The flooding experiment with a sand pack system indicated that the oil recovery of more than 24% is achieved using this Pickering emulsion system after conventional water flooding.

In numerical simulation experiments, DS Ma et al. (2013) set up a mathematical model of alkaline-surfactant-polymer (ASP) flooding with Pickering O/W emulsions and illustrated that emulsification by colloid particles can effectively promote the oil output and decrease the water cut, and this effect increases with increasing emulsification ability. Pillai et al. (2019) synthesized lysine grafted silica nanoparticle (LGS) to generate the O/W emulsion for fitting the EOR model. It was observed that the Winsor III microemulsion

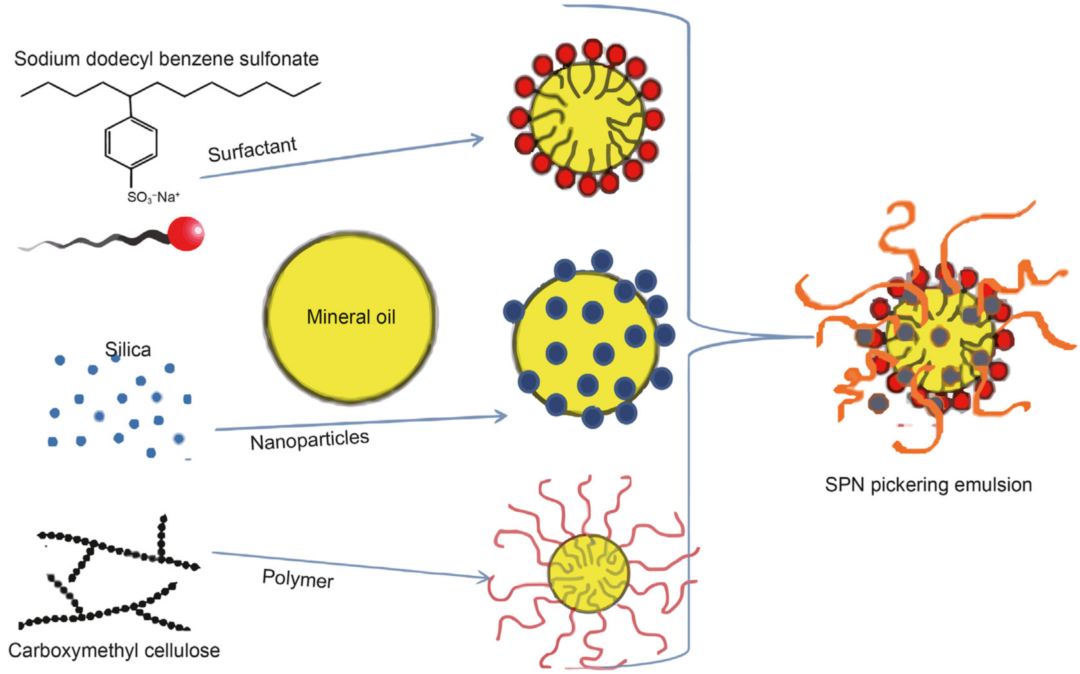

Fig. 2. SPN Pickering emulsion synthesis from mineral oil, SiO_2 nanoparticles, surfactant and cellulose (Kumar et al., 2017).

system, owing to its high oil solubility to bring ultra-low IFT, is considered to be the most ideal of all other microemulsion types. Using the expression of Chun Hush, it was found that the IFT of the microemulsion system with different LGS concentrations was in the ultra-low range of 10^{-5}. Sand-pack flooding experiments showed that in the presence of LGS, the additional oil recovery rate was 33.6%. Demikhova et al. (2016) exploited a filtration model to illustrate the process of Pickering emulsion fluids passing through porous media, and those calculation results summarized that the oil recovery promotion was owing to the wettability change caused by solid particles.

Furthermore, considering the complexity of flooding components in EOR process, Competitive or synergistic reactions may occur between surfactants and solid particles during Pickering emulsion stabilization. a series of works conducted by Ahmadi estimated of adsorption behavior of surfactants with various solid particles such as nano-silica and quartz. Generally, the chemical additive cost and emulsifier loss caused by reservoir rock are the main concerns in EOR processes. In those researches, the nonionic surfactants such as *Zyziphus spina christi* as synergistic stabilizer with particles were used to examine the adsorption behavior between surfactants and quartz (Ahmadi and Shadizadeh 2013, 2015) and the simulations were further applied into the real sandstone reservoir environment (Ahmadi and Shadizadeh, 2016). The results indicated with increasing concentration of introduced surfactant, the binding of surfactants and particles was enhanced, which could be ascribed to the strong electrostatic adsorption. During this process, the synergistic reaction is dominated and the viscosity of chemical flooding decrease thereby the ultimate recovery increased. Further increase of surfactant concentration increased the competitive stabilization of emulsion systems between particles and surfactant, which were no help to the recovery process. Those research results do much favor in making right surface modification of particles in order to suit the reservoir stimulation plans and the EOR process from carbonate reservoirs. Besides, it also provides a cost and environmentally friendly options to prepare emulsion flooding for use in EOR techniques.

Therefore, it can be summarized that the emulsion droplets emulsified by solid particles are small enough to pass through the rock pores from being trapped, and because those particles can be irreversibly adsorbed to the emulsion interface, the emulsion systems can remain stable under harsh reservoir environment. Additionally, by proper changing the surface wettability of particles, the rheological properties of emulsion fluids can be manipulated to meet the requirements of highly viscous oil phase transportation. However, there are still many factors need to be considered from the laboratory simulation to actual application, since the harsh reservoir conditions and the interaction between Pickering particles and natural surfactants from crude oil (e.g., asphaltene) may bring much challenging to the stability of Pickering emulsion systems and the particle emulsifying mechanism research. Thus, it is considered that comprehensive investigation of the constructions, properties and behaviors of the Pickering emulsion is essential part to understand the nature, control and application of petroleum emulsions.

3.3. Smart control for EOR

To obtain the good quality of oil, complicated separation processing needs to be performed for recovering the crude oil from the emulsion fluids, which are generally energy-consuming and high-cost. Herein, by introducing the stimuli-responsive particles whose wettabilities can be smartly changed through external triggers such as pH, temperature, and magnetic field (Yang et al., 2018) (Fig. 3), the smart Pickering emulsion systems can not only maximize the amount of oil separated from the mine, but also improve the separating and recovering efficiency. Also, the particle stabilizers can be easily retrieved and reused, which favor the establishment of a more sustainable and continue operation system. Therefore, this part will follow several smart Pickering emulsion systems designs (i.e., pH, temperature, and magnetic responsive) to investigate the enhanced recovery and separation process of oil although the researches are in laboratory stage.

Fig. 3. The controllable stabilization and destabilization of Pickering emulsion under electronic field (Yu et al., 2019b).

3.3.1. pH-responsive control

pH-responsive Pickering emulsion systems have attracted much research attentions in petroleum fields as one of the most common used smart systems, whose stabilizer particles can undergo behavior transforming in response to the changes of proton concentration through some chemical modification (Qin and Yong, 2019). Geng et al. (2019b) reported the using of pH-sensitive PAM nanogels to stabilize the Pickering emulsion and its controllable demulsification behavior by alkaline. Generally, a few of nanogels are sufficient to produce highly stable Pickering emulsion systems. The controllable collapsing of emulsion system can be ascribed to the fact that the pH-responsive PAM nanogels will hydrolyze the acrylamide involving in the polymer networks into carboxylate moieties with the stimulation of alkaline, which will change the zeta potential and promote the aggregation of PAM nanogels, realizing the fast separation of oil from water phase. Besides, the Pickering stabilizers including self-assembled or crosslinked microgels exhibit the ability to emulsify and demulsify emulsions with stimulation of pH as well (Morse et al., 2014; Tu and Lee, 2014). C Ma et al. (2013) described an amphiphilic copolymer polyurethane-*graft*-poly [2-(dimethylamino)ethylmethacrylate] (noted as PU-g-PDEM) which could self-assembly into core-shell nanoparticles in the water, where the hydrophilic PDEM blocks towards the outside and the lipophilic PU block binding within the core. The PDEM chains could shrink and collapse and cover the shell according to the increasing pH condition, which turned surface wettability of as-formed nanoparticles thereby inducing the demulsification of the Pickering emulsion systems. The quick pH-responsive performance renders the good oil/water separation efficiency, however, the much hydrophobic grafts make the particles tend to partially immerse into the oil phase, which will decrease the quality of oil.

Generally, the design of pH-responsive Pickering emulsion systems is most implementable owing to its simplicity and breadth of chemical modification available. Besides, the non-functionalized pH-responsive particles like GO (Kim et al., 2010), chitosan (Liu et al., 2012) and C_3N_4 (Han et al., 2018), can be utilized as emulsion stabilizer with facile and low-cost, which open the gate for the potential application in the petroleum industry.

3.3.2. Thermo-responsive control

Temperature is also a commonly studied stimuli model utilized to adjust the stability of Pickering emulsions systems. The temperature change can be easily achieved without changing the original chemical compositions, while the change of pH needs another addition of alkaline or acid to the emulsion system in some degree. The thermo-stimuli are usually related to the surface grafting with polymers which can exhibit special deformation or behavior, such poly (N-isopropylacrylamide) (PNIPAM) (Dan et al., 2019), and PS latex (Vasantha et al., 2020). PNIPAM is a thermo-sensitive polymer which is widely used as particle surface modifier for Pickering emulsion system, and its LCST (Lower Critical Solution Temperature) is usually 32 °C. Sun et al. (2016) reported that the controllable Pickering emulsion system stabilized by typical temperature-responsive PNIPAM microgels whose wettabilities and sizes are susceptible to the thermo. When temperature beyond the LCST, the microgels tend to shrink and to be hydrophobic and thereby resulting in the breakage of the stabilized Pickering emulsion system. Similarly, the Pickering emulsion system emulsified by PNIPAM brush graft-modified starch-based nanoparticles (NIPAM-g-SNP) was constructed by Pei et al. (2019). The PNIPAM-g-SNP exhibits the strong interfacial activity and can significantly reduce the IFTs of as-formed interfaces between toluene and water or n-hexane and water. The IFT value reach the bottom when temperature is close to the LCST, indicating the particle has the highest surface fraction occupying the interface at the LCST. As mentioned above, the size of emulsion droplets can be adjusted by concentration of Pickering particles, and increasing the PNIPAM-g-SNP concentration results in the tiny emulsion droplets. Notably, by adjusting the temperature, the properties of nanoparticles can be restored, therefore, the emulsification/demulsification process is controllable and reversible. Moreover, the halophilic functionalized latex utilized as temperature-responsive stabilizer for O/W emulsion system simulated the high salinity condition in EOR process are demonstrated by Vasantha et al. (2020). If the temperature above the upper critical solution temperature (UCST) (70 °C), the average diameter of latex particles shrinks from 383 nm to 334 nm and surface potential changing as well, which can break the emulsion system on demand through changing the surrounding environment.

However, the reservoir temperature is relevant complicated, which making the thermo-responsive particles unlikely to functionalize well to maintain the emulsion systems. Thus, the requirement for design of smart Pickering emulsion system which could stand for reservoir environment is highly request.

3.3.3. Alternative responsive control

Other stimuli, for example electric field, magnetic field, light intensity, and CO_2-responsive have been researched for the smart control of Pickering emulsion system behavior as well. Yang et al. (2018) investigated the utilization of interfacial active groups (3-aminopropyltriethoxy silane) coated magnetic nanoparticles ($Fe_3O_4@SiO_2{-}NH_2$) to stabilize the magnetic-responsive switchable Pickering emulsions system. Low particle concentrations (0.1–0.4 wt%) is sufficient to keep the O/W emulsion system stable for dozens of days. Stable O/W Pickering emulsion start to coalescence once introducing of a magnetic field, resulting the completely three phase separation in a few minutes. As reported by He et al. (2020a,b) that the cellulose-coated magnetic Janus NPs (MJ NPs) were used as stabilizers and carriers of W/O emulsion systems for transporting and separating the emulsified water droplets from crude oil phase under magnetic force. The MJ NPs with excellent interfacial activities could compete with asphaltene to stabilize the W/O Pickering emulsion systems, and could collect and separate about 95% emulsified water droplets (at dosage >0.75 wt%) from the crude oil products, indicating the potential application for petroleum emulsions dewatering.

Similar to the pH-responsive system, CO_2-responsive is a unique stimulus for smart emulsion control as its low cost, biocompatible and casual to implement. The response mechanism is the same, the CO_2 exists as carbonic acid form to increase the acidity of solutions when flowed into the reaction system. Guo and Zhang reported the using of N-dimethyl-N-dodecyl amine (noted as $C_{12}A$), a low-cost CO_2-sensitive agency, modified silica nanoparticles to investigate the stabilization of O/W Pickering high internal phase emulsion (HIPE) (Guo and Zhang, 2019). This Pickering emulsion system could maintain stable for more than 6 moths with CO_2, through alternately injecting carbon dioxide and nitrogen, the CO_2-sensitive $C_{12}A$ part could transform the structure between cationic and nonionic reversibly, and then attached on or detached from the silica particle surface leading to a reversible emulsion interface stability. Furthermore, the redox-responsive Pickering emulsion system produced by combination of silica nanoparticles and ferrocene ($FcCOC_{10}N$) was described by Yu et al. (2019a, 2019b). Simply, the stability of Pickering emulsion system could be manipulated through electrochemical reactions with ferrocene group in $FcCOC_{10}N$ structure avoiding the shortcomings of requiring additional reactants or changing the concentration of stabilizers.

Recently, multi-responsive Pickering stabilizers were also reported through a silica coated magnetic particles with tripe sensitive copolymers modification (Lv et al., 2020). The superparamagnetic core could prevent particles from aggregation during storage and able to rapidly separation at magnetic field. The modified thermo- and pH-sensitive copolymers shell is the key to control the emulsification/demulsification of as-formed O/W Pickering emulsion system. The combination of multiple response behaviors offers an effective strategy for both oil collection and recycling of Pickering stabilizers.

What needs to be pointed out is to the wettability and interfacial behavior of particles is always the key to the stability of Pickering emulsion systems. Starting from how to change the wettability or provide external energy to force the particles desorbing from the emulsion interface, it is easy to design smart particles and Pickering emulsion systems with stimuli-responsive properties. Although smart Pickering emulsion systems have been investigated for many years, there are still many factors inhibiting their applications. The main obstacles are multistep and complex modification of particles with suitable wettabilities and stimuli-responsive properties, and require fully understanding of its stabilization mechanism and interfacial interactions especially at the high temperature, high salt and complexed component environments. Thus, design of novel solid particles with simple and effective stimuli responsivity and compact knowledge of Pickering emulsion systems for oil recovery and separation is highly requested.

4. Application of Pickering emulsion systems in oil spill treatment

The low-concentration spilled oils appearing in the form of 0.04–50 μm emulsion droplets condition on the sea water are difficult to treat them through normal methods, for example centrifugation, skimming, and gravity separation, which cause serious damage to the ecological environment and risk human health. (Simonsen et al., 2018). Thus, this part will introduce a series of researches using solid particles as medium to stabilize, induce, and ripen the oil Pickering droplets to recovery the spilled crude oils under the external fields and the works using Pickering emulsion system to prepare structure-strengthened porous oil-absorbing materials and efficient biocatalysis/biodegradation microreactors for spilled oil treatment.

4.1. Oil spill recovery

To remove those traces of oil spills, Liang et al. (2011) reported the fabrication of Janus silica/Fe_3O_4 nanosheets and their application in oil droplets separation. Compared with traditional isotropic particles, those magnetic Janus nanoparticles with amphiphilic properties exhibit excellent interfacial activities and can be easily adsorbed at biphasic interfaces, which also enders this Pickering emulsion system controllable behavior under magnetic fields, achieving the goal of the efficient separation of micro-sized emulsified crude oils from the sea water. After that, a continues study was reported by Yu et al. (2015) about the using of magnetic porous silica-coated submicroparticles (MPSS) for dealing with the spilled oil issues. The MPSS with average diameter of 200 nm exhibited superoleophobicity and rapid magnetic response, enabling them to aggregate and remain at oil/water interfaces more than molecular surfactants. Those oil droplets covered by MPSS can be rapid separated within minutes at certain degree of magnetic field. Another study regarding to the spilled oil treatment by using effective particle strategy was carried out by Song et al. (2018a,b). The crescent-like magnetic Janus polymers with a concave hydrophobic surface and convex hydrophilic surface were designed through unique emulsion interfacial properties and selective surface assembly. Utilizing of the unique anisotropy in both morphology and chemical components in combination with magnetic response, the Janus particles could easily be adsorbed into the oil droplet surfaces and drag the oils realizing the spilled oil removal from the sea water (Fig. 4). Interestingly, the concave hydrophobic surface of Janus particles was functionalized as capture oil droplets, owing to the hydrophobic interaction. Then, the magnetic Janus particles accelerated the Ostwald ripening process and transform those small oil droplets into larger ones. Finally, the Janus particles adsorbed are sufficient to reduce the interfacial energy and the Pickering emulsion system reach the balance. Taking advantage of those topologies and wettabilities of the Janus particles, the effective and rapid oil droplets removal can be realized in less than 120 s with quite high separating efficiency of more than 99%.

Although lots of works have been paid to deal with oil spill problems using magnetic particles dominated Pickering emulsion strategy. The research process still limits to the laboratory stage, and the post treatment of separated oil and recovery of Pickering particles still have long way to go. Only few of study focus on developing the compact and facile systems for continuously quick emulsification and separation, which remains an engineering challenge in petroleum industry. Recently, Kumar et al. (2020) reported a novel and scalable method for continuous emulsification and demulsification of the O/W emulsion systems. This platform produced a porous packed bed made by low-cost sand to create the shear force for generating or demulsifying the Pickering emulsion systems, where the chitin nanocrystals were selected as emulsifier. The oleic and aqueous phase containing Pickering nanocrystals were co-injected continuously through the packed bed for fabrication of emulsion systems. On the contrary, the demulsification process was realized by injecting the Pickering emulsion system through another packed bed (Fig. 5). The wettabilities and sizes of san packed beds were altered according the demands, for example, hydrophilic packed bed was suitable for emulsification process since the non-wettability of sand could easily divide the oil phase into tiny droplets. Besides, the size of the emulsion droplets was a function of energy dissipation, which closely related to the flow rates and residence time at the emulsification process. On the other hand, demulsification process needed the lipophilic modified packed bed. In addition, this continues stabilization/demulsification process could generate Pickering heavy crude-in-water emulsion systems with proper viscosities, which could meet the reequipment of pipeline transportation. The recyclability of the chitin nanocrystal stabilizers during the whole process would make this method a promising scalable substitute to the current heavy oil dilution treatment as well. Some kinetic fitting models and process parameters are not established completely yet, the continues emulsification and separation platform provide ideas for industrial applications in heavy oil recovery, transportation and spilling oil treatment.

4.2. Pickering emulsions as templates to prepare materials used in oil spill treatment

In another strategy for oil spill treatment, the multi types of Pickering emulsion system are developed as template to prepare porous polymeric composite for oil removal (Yu et al., 2019c; Zhu et al., 2020). Zhang et al. (2018) used Pickering HIPE system stabilized Fe_3O_4 nanoparticles as template to prepare a hydrophobic polystyrene (PS) foam. The hydrophobic foam can collect the spilled oil through a physical adsorption way and the porous structure helps the accelerate the mass transportation and improve the adsorption capacity of oils. The incorporation of Fe_3O_4 nanoparticles not only bring magnetic responsive ability but also strengthen the mechanical behavior of as-formed foams. This magnetic foam exhibited a high oil selective adsorption capacity of 57 g g^{-1} towards the oil/water mixture. Besides, Using the ethyl cellulose nanoparticles (EC) stabilized Pickering emulsions templating method, a hierarchical porous cellulosic foam was produced (Bizmark et al., 2020). The microstructure of EC nanoparticles can effectively aggregate and cross at the interfacial which further enhance the completeness of pore structure of obtained materials. The results indicated this hierarchical porous material displayed a high oil-adsorbing selectivity toward the oil/water mixtures, and the ability to separate the oil from the stable emulsion system as well. Furthermore, some researchers utilized the assembly of particles at Pickering emulsion interfaces to construct the aerogel materials. For example, Russell et al. (2019) reported the using of 2D $Ti_3C_2T_x$ nanosheets to stabilize the Pickering emulsion system. The $Ti_3C_2T_x$ could quickly gather at the liquid-liquid interface, and assembled and jammed into a layer consisting of overlapping nanosheets. The $Ti_3C_2T_x$ aerogels were produced by simply freeze drying of the concentrated Pickering emulsion.

The as-formed aerogels were detected with approximately 15 mm pores and average density of 12.8 mg cm^{-3}, and the ability to carry a 20 g weight without obvious structure deformation, indicating the good mechanical strength. Besides, the excellent lipophilicity and hierarchical porous structure promise the $Ti_3C_2T_x$ aerogel a suitable application for absorbing oil, whose absorption of up to 9000% is found (toluene is selected as target oil).

In short, it is easy and convenient to fabricate bulk porous adsorbent materials using Pickering emulsion templating method,

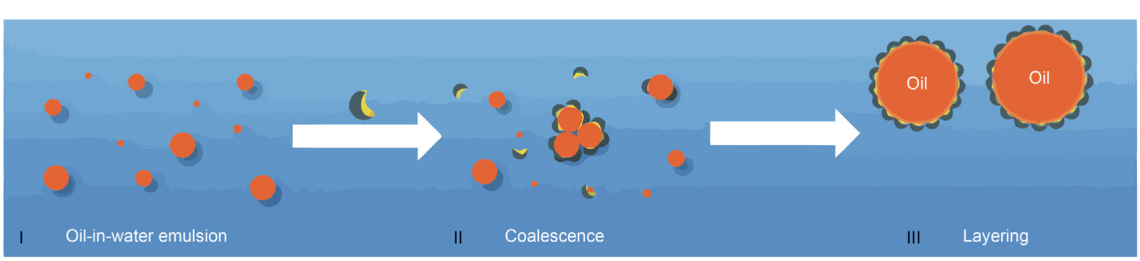

Fig. 4. Mechanism analysis of the Janus particle-mediated separation of tiny oil droplet (Song et al., 2018).

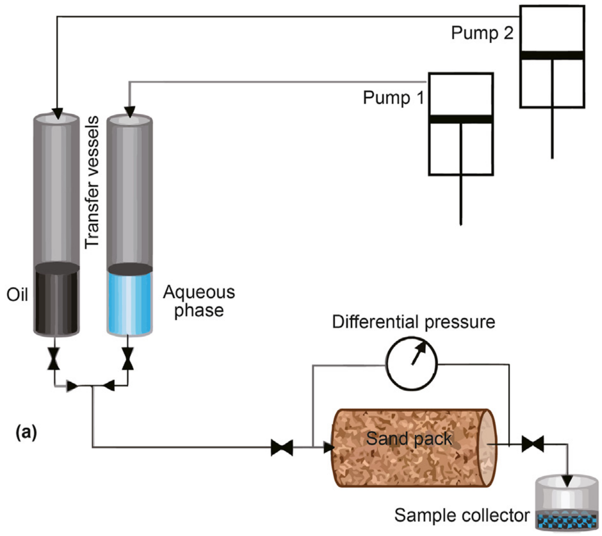

Fig. 5. Schematic representation of different setups for emulsion generation (a) and emulsion separation (b) (Kumar et al., 2020).

where each component is separated within a small and regular Pickering emulsion droplets, which can effectively avoid the uneven mixing and offer an ideal condition for preparation in macroscopic quantity. Thus, the Pickering emulsion systems can serve as a strong and effective method to develop various functionalized materials for industrial application purpose.

4.3. Pickering emulsions as microreactors for degradation of oil

Water pollution problems caused by oil substances such as oil spill have spurred industrial and environmental researchers to develop the efficient strategy for environment contamination. Sustainable chemistry known as green and highly efficient strategy has been widely used in environment treatment, which should follow those features: (1) a minimum number of byproducts and wastes, (2) safe and benign solvents and reactants, and (3) a high efficiency of mass transportation and catalytic processes (Wang and Wang et al., 2012; Zhou et al., 2018). The Pickering emulsion system can well meet these processes. In Pickering emulsion system, each separated droplet can be recognized as an individual microreactor, which can provide a large specific surface area for full interfacial contact between catalysts and reactants and reaction as well. Yang et al. (2015a,b) reported that the static Pickering emulsion system was adopted to investigate heterogeneous catalysis reaction, which was observed with excellent efficiency comparing to the normal two-phase reaction. For now, the Pickering emulsion systems provide an efficient platform to deal with those oil-containing environmental issues. Fessi et al. (2019) used unmodified TiO_2 nanoparticles as stabilize to form the 1-methylnaphthalene-in-water Pickering emulsion. Only 0.5% w/w of TiO_2 particles could successfully obtain the stable emulsion microreactors, which significantly reduce the dosage of catalyst. The results indicated that the small drop size could enlarge the interfacial contact aera for better reaction between the photocatalyst and organic contaminant, so that the photocatalytic degradation of 1-methylnaphthalene was 50 times higher than that of the non-emulsified system. Besides, Panchal et al. (2018) reported the construction of O/W Pickering emulsion system emulsified by halloysites nanotubes where the *Alcanivorax borkumensis*, hydrocarbon biodegraders, attached. The metabolic activity of this bacteria was demonstrated to be enhanced within the droplet microreactors. The proliferation of the bacteria on halloysite shows that it is a promising strategy to deal with spilled crude oil issues through biocataysis and bioremediation approach. Furthermore, a series of multi-functional Pickering emulsion microreactors have been developed on demand (Han et al., 2020; Yan et al., 2017; Herrera et al., 2020). For example, Wang et al. (2020) developed the smart dual-responsive Pickering emulsion microreactor using poly (N-isopropylacrylamide) (PNIPAM) grafted chitosan (noted as CS-g-PNIPAM) microgels as stabilizer. Such microreactor created an ideal carrier for enzyme loading and mild environment for biphasic biocatalysis. Zhou et al. (2018a,b) introduced another method to enhance the reaction rate of Pickering emulsion microreactor by placing the nanosized magnetic stirring bars made by magnetotactic bacteria within the emulsion droplet (Fig. 6). The introducing of magnetic particles not only accelerate the mass transportation process by mixing the materials thoroughly but only provide a routine to recover and separate the catalyst for recycle use.

Overall, the environmental issues caused by spilled oil bring much challenges to the treatment method. For those tiny emulsified oil droplets in the seawater, a series of magnetic particles with proper topology and wettability properties are developed to stabilize and induce the droplets coalescing into the bigger ones by accelerating the Ostwald ripening process under the magnetic field. The controllable stabilization/demulsification by changing the wettability of Pickering particles offer the opportunity for production and separation of the emulsified oil droplets continuously. Furthermore, taking advantages of unique individual three-phase structure, the Pickering emulsion systems can be expanded as polymerization templating for preparation of porous oil adsorbent materials, and ideal platforms for biocatalysis/biodegradation as well, which provide a promising industrial application in oil recovery and spilling oil treatment, especially with the trend of miniaturization of chemical reactors and the development of microfluidic technology.

5. Conclusions and prospects

Pickering emulsions as special system integrating of different immiscible phases by solid particles have drawn much attentions in the petroleum and gas industry. So far, numbers of researches have been carried among the academia and industry, and several factors of Pickering emulsion system have been examined in aspect of their roles in enhancing crude oils recovery and transportation, and

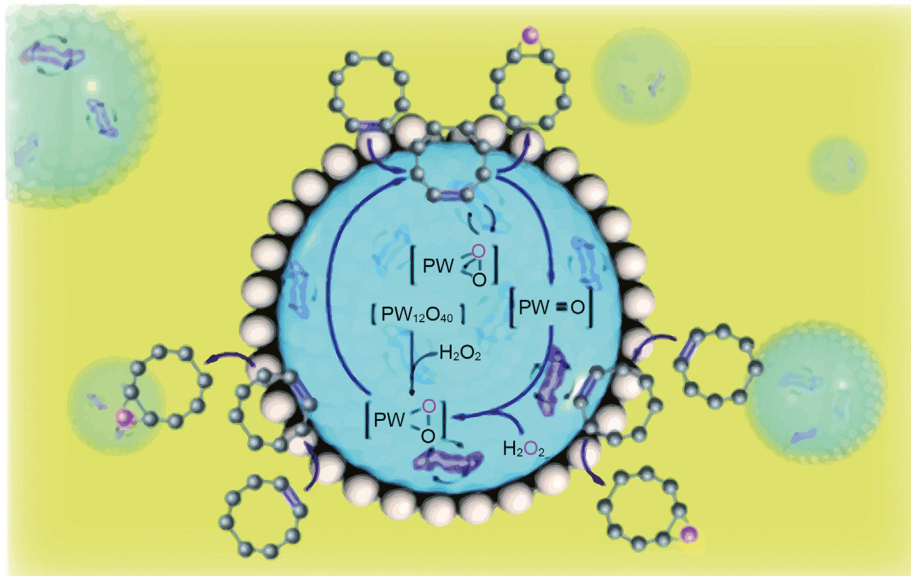

Fig. 6. Scheme illustration of the reaction in the Pickering emulsion system with nanoscale magnetic stirring bars (Zhou et al., 2018).

spilled oil removal as well. From this work, we overview the particle-stabilized emulsion system from its formation mechanism to the potential application in promoting the oil recovery and transportation, oil spills collection emulsion interfacial polymerization, enhanced biphasic catalysis performance, confined biocataysis and bioremediation, and preparation of porous bulk adsorbents as well. Based on those literature review, the following conclusions and prospects can be made:

1. Through manipulation of particle surface wettability, a highly stable emulsion system with suitable viscosity properties and small droplet dimeter can be obtained, where the increased dosage of particles can promote the viscosity of fluids and produce smaller droplets in some degree. From current study tendencies, we find that the research concept adopted by major researchers who investigated the particles-stabilized Pickering emulsion systems involve: (1) To achieve high separation performance, the solid particles are processed with complex fabrication steps, which inevitable increase the cost and bring many unpredictable factors to investigate the stabilizing mechanism. (2) Simulation of oil/water emulsion in the laboratory condition is not enough to reveal the particle emulsifying behavior since the synergistic effects between particles and composite from crude oil (e.g., asphaltene) may occur. (3) The triggering situation of stimuli-responsive stabilization and destabilization behavior should match the harsh reservoir conditions because the high temperature, high salt and complexed component environments may have significant influence on emulsion stability and disturb the responsive mechanism. Therefore, it is reasonable that full understanding the functionalized properties, compositions, and behaviors of these Pickering solid particles is essential part to investigate the nature, severity and type of petroleum emulsions, which also is fundamental in developing high-performance and cost-effective emulsification or demulsification strategy.
2. By design of specific topology and wettability properties of the magnetic particle, the difficult to handled micro-sized oil droplets can be separated from the water under magnetic field, where the hydrophobic magnetic particles can aggregate and stabilize the O/W interface thereby dragging the oil emulsion droplets under the magnetic field. Besides, the Pickering emulsion system can also serve as a soft template for preparing the bulk porous adsorbent. Those incorporated particles not only keep the integrity of porous structure and enhance the mechanical strength of as-formed materials, but also provide abundant active sites for capture oil from the water. So far, the research attentions are still need to be focused on the continues production and separation of oil from aqueous phase and the prediction model which able to evaluate the nature and separation kinetics behavior of petroleum emulsion adsorption.
3. The miniaturization of chemical reactors is a trend and change in the development of chemical engineering technology. With the rapid development of microfluidic technology, the emulsified droplet has been considered as the ideal microreactor for reaction because of the uniform and highly efficient mass transformation and reaction rate. For now, the Pickering emulsion systems have been demonstrated to be the ideal catalysis/degradation platform for enhancing the biphasic reaction. Each droplet in the Pickering emulsion systems is an individual microreactor, which greatly increase the specific surface area between targets and catalyst and prevent the reaction system from uneven mixing. Moreover, the droplet microreactor can effectively shield the reaction core from the external interference, creating a relatively mild environment for fragile biological materials like enzyme or bacteria, which extend the application occasion for those high-performance biocatalysis or biodegradation. Recently, the confined space in Pickering emulsion system is proven with special spatial and reactivity restrict for material formation or reaction, which cannot achieve by traditional synthetic strategy. Thus, it should be given priority.

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