

# Recent advances in the design and use of Pickering emulsions for wastewater treatment applications

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## Abstract

Pickering emulsions have recently emerged as versatile systems capable of targeting many applications of wastewater treatment. The unique properties, which include high emulsion stability, easy preparation, low toxicity, and stimuli-responsiveness, pave the way for advances in common pollutant control processes. This review aims to provide a comprehensive overview on different aspects in the Pickering emulsion design focusing on the key structural relations and their implications in specific applications. The first section is dedicated to the critical parameters governing the Pickering emulsion type, droplet size and stability. Furthermore, a section describing methods for demulsification and particle recovery is included, in which various stimuli have been explored. Finally, the most potent applications of Pickering emulsions such as photocatalytic degradation, adsorption, extraction, and separation of common wastewater pollutants are presented and discussed with a great deal of attention towards the efficacy, current limitations, and future potential. Recognizing the rise of innovative Pickering emulsion solutions is expected to induce profound effects facilitating the technology transfer to industrial processes.

**Keywords:** Pickering emulsion; photocatalysis; wastewater; surface functionalization

## 1. Introduction

Ever since the start of the industrialization era, the demand for freshwater resources has been increasingly growing, which poses many challenges for the developing nations facing rapid urbanization, population growth and chemical contamination problems<sup>1</sup>. It is estimated that around 4 billion people worldwide have no or little access to clean and sanitized water supply, and millions of people die of severe waterborne diseases annually<sup>2</sup>. As a result, both chemical pollution and global freshwater use were listed among the 9 critical problems referred to as planetary boundaries, defined by a group of leading environmental scientists<sup>3</sup>. Similarly, a report made by the United Nations Environment Programme (UNEP) stated that nearly all documented issues associated with the worldwide toxic contamination and their implications for human health can be related to industrial and mining activities<sup>4</sup>. One of the key underlying reasons behind these trends is the rapid expansion of industries that lack low-cost high efficiency water treatment technologies to treat the wastewater resulting in a discharge of micropollutants and contaminants into the natural water cycle<sup>5,6</sup>.

Depending on the industry, a diverse group of organic compounds can be found, including organic dyes, organic cyanides, heterocyclic compounds, and polycyclic aromatic hydrocarbons that are characterized by high toxicity and high-enough concentrations to be considered an environmental hazard<sup>7</sup>. A vast amount of water is also produced during oil and gas recovery, where the discharge water makes up the largest volume waste stream<sup>8-10</sup>. The composition of produced water tends to vary both in terms of salinity and the nature of organic compounds, but the most abundant organic compounds in produced waters are water-soluble low molecular weight organic acids and monocyclic aromatic hydrocarbons<sup>10</sup>. The presence of these compounds results in numerous adverse effects, including corrosion of production pipes and the overall toxicity of produced water<sup>11</sup>. Although the low molecular weight organic acids are known to be readily biodegraded by bacteria, fungi, and plants, various naphthenic acids (NAs), such as alkylated benzoic acids or alicyclic carboxylic acids, are difficult to remove by conventional methods<sup>10</sup>. At present, each of the industrially relevant organic wastewater treatment solutions (adsorption, chemical coagulation, biodegradation) suffers from multiple drawbacks making a "one size fits all" solution difficult to achieve<sup>12-14</sup>. The adsorption method is simple and versatile, but the pollutant is only transferred from one phase to another, without achieving the degradation effect<sup>15</sup>. What is more, regeneration of the adsorbent is limited. The chemical coagulation method can remove suspended solids effectively but lacks versatility for different compositions of wastewater<sup>16</sup>. Finally, the biological treatment, despite being the most efficient, is susceptible to high concentrations of pollutants that can affect the activity of microorganisms<sup>7</sup>. A common way to optimize the pollutant removal process involves the combination of all the approaches and is generally driven by the biological treatment within the integrated activated sludge treatment plant, where the sludge undergoes a series of mechanical and physiochemical steps, such as oil–water separation and coagulation<sup>17</sup>. Despite the complexity of the process flow, the use of reclaimed water is limited owing to the stringent and constantly variable pollutant level requirements<sup>18</sup>. A summary of requirements and applications for reclaimed water is given in Table 1

**Table 1** Requirements and applications for reclaimed water usage. As seen from the table, the pollutant levels are adjusted with respect to the risk for a direct human exposure to reclaimed water.

**Table 1** Requirements and applications for reclaimed water usage

<i>Water reuse</i>	<i>Treatment goals<sup>a,b</sup></i>	<i>Examples of applications</i>
<b>Urban use:</b> <i>Unrestricted</i>	≤10 mg/L BOD ≤ 2 NTU No detectable fecal coliform /100 mL 1 mg/l Cl <sub>2</sub> residual (min.)	Landscape irrigation (parks, playgrounds, school yards), fire protection, construction, ornamental fountains, recreational impoundments, in-building uses (toilets, air conditioning)
<b>Urban use:</b> <i>Restricted</i>	≤ 30 mg/l BOD ≤ 30 mg/l TSS ≤ 200 fecal coliform /100 ml 1 mg/l Cl <sub>2</sub> residual (min.)	Irrigation of areas where public access is infrequent and controlled (golf courses, cemeteries, residential, greenbelts)
<b>Agricultural irrigation:</b> <i>Food crops</i>	≤10 mg/L BOD ≤ 2 NTU No detectable fecal coliform /100 mL 1 mg/l Cl <sub>2</sub> residual (min.)	Crops grown for human consumption and consumed uncooked
<b>Agricultural irrigation:</b> <i>Non-food crops</i>	≤ 30 mg/l BOD ≤ 30 mg/l TSS ≤ 200 fecal coli/100 ml 1 mg/l Cl <sub>2</sub> residual (min.)	Fodder, fiber, seed crops, pastures, commercial nurseries, sod farms, commercial aquaculture
<b>Impoundments:</b> <i>Unrestricted</i>	BOD <sub>5</sub> : ≤10 mg/L ≤ 2 NTU No detectable fecal coliform /100 mL 1 mg/l Cl <sub>2</sub> residual (min.)	No limitations on body contact (lakes and ponds used for swimming, snowmaking)
<b>Impoundments:</b> <i>Restricted</i>	≤ 30 mg/l BOD ≤ 30 mg/l TSS ≤ 200 fecal coli/100 ml 1 mg/l Cl <sub>2</sub> residual (min.)	Fishing, boating, and other noncontact recreational activities
<b>Environmental enhancement</b>	Equivalent to restricted impoundments	Artificial wetlands, enhanced natural wetlands, and sustained stream flows
<b>Groundwater recharge</b>	Site-specific	Groundwater replenishment, saltwater intrusion control, and subsidence control
<b>Industrial reuse</b>	Equivalent to restricted impoundments	Cooling system makeup water, process waters, boiler feed water, construction activities, and washdown waters
<b>Potable reuse</b>	No detectable total coliform/100 ml 1 mg/l Cl <sub>2</sub> residual (min.) ≤ 2 NTU ≤ 2 mg/l TOC of wastewater origin	Blending with municipal water supply (surface water or groundwater)

<sup>a</sup>Adapted from <sup>19</sup>

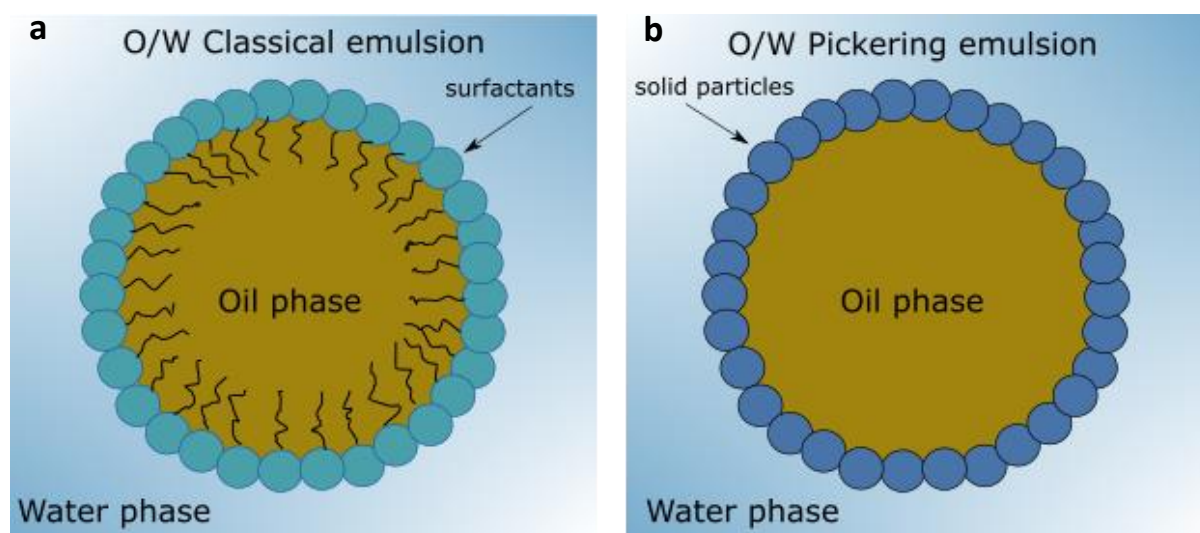
<sup>b</sup> BOD<sub>5</sub>: biochemical oxygen demand; NTU: nephelometric turbidity units; TSS: total suspended solids; TOC: total organic carbon.

Ultimately, the regulatory pressure imposed on the companies responsible for reclaiming this water and finding ways to release it back into the local environment creates a demand for research done on the development of low-cost and environmentally friendly methods that could serve a wide range of degradable pollutants<sup>20</sup>. Numerous advances have already been made on the laboratory scale treatment of organic acids by employing methods like nanofiltration<sup>21</sup>, membrane filtration<sup>22</sup>, ozonation<sup>23</sup>, or chemical coagulation<sup>24</sup>, but these processes are yet to be optimized for upscaling. Therefore, the implementation of novel degradation techniques of pollutants for wastewater treatment remains an important milestone for remediation of the large volumes of industrial effluents<sup>25</sup>.

The use of functional nanomaterials targeting wastewater treatment has recently emerged as one of the leading research fields that could facilitate the transition from the laboratory scale to various industrial plants worldwide<sup>26,27</sup>. The unique features like small particle size, high surface-to-volume ratio, high surface energy and the catalytic properties give rise to performance far superior to conventional wastewater treatment methods<sup>20</sup>. This potential has already been demonstrated by implementing nanomaterials in photocatalysis, adsorption, membrane filtration and chemical disinfection for an efficient pollutant degradation<sup>28</sup>. Among the nanoparticle systems applied for

these applications, emulsions stabilized by solid particles, so-called Pickering emulsions (PEs), have been identified to be perfectly suitable for environmental applications<sup>29,30</sup>. As a result, numerous PE systems have been developed claiming potential to replace the conventional wastewater treatment methods each of which posing individual requirements on the particle type, morphology, and functionality. For example, only the particles with a certain band gap can be used for photocatalysis, while a porous nature leading to high surface area is an essential criterion for PEs used as adsorbents. However, the main advantages originate from the emulsion stability, tunability and recyclability, opening a pool of innovative particle engineering strategies. The applicability of Pickering emulsions is not limited to the direct use of as-prepared emulsions – on the contrary, the emulsification can be exploited to produce high performance functional materials surpassing the limits of the PEs alone. Since the potential of PEs in wastewater treatment applications has just recently been realized, no reviews regarding the topic have been published. This review explores the roles, key parameters and the most potent applications associated with the use of Pickering emulsions in wastewater treatment.

## 2. Pickering emulsions: key parameters and stability



*Fig. 1 Comparison of a) classical and b) Pickering emulsions*

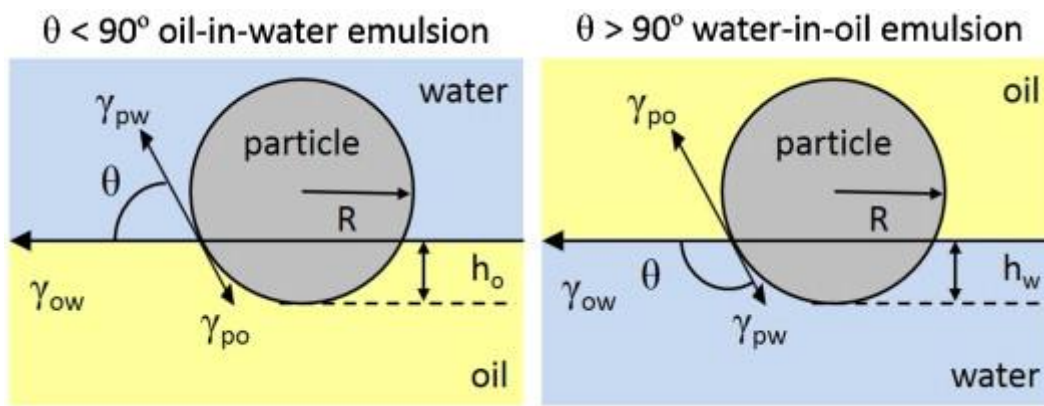
Pickering emulsions are emulsions in which particles accumulate at the interface between two immiscible liquids and act as stabilizers of the dispersed drops against coalescence (Fig. 1). While most emulsion-based applications are dominated by the use of conventional surfactants, Pickering emulsions have emerged as an alternative displaying very attractive properties including low cost, low toxicity, reduced environment pollution, increased stability, recycling ability and resistance towards pH or temperature changes<sup>31,32</sup>. Moreover, there has been a tremendous breakthrough in the use of PEs for a variety of catalytic applications offering advantages such as large active catalyst areas due to less particle agglomeration when adsorbed at liquid-liquid interfaces and the possibility to recover catalysts by demulsification<sup>29,33</sup>. Many studies have demonstrated flexibility of the system design by varying particle types, emulsion parameters and the morphology of Pickering emulsifiers making it possible to carefully adapt PEs for a wide range of applications<sup>34–38</sup>.

### 2.1. Emulsion stability

The feasibility of a certain Pickering emulsion system for pollutant treatment cannot be assessed without ensuring stability of the emulsion in a wastewater of interest. If successfully stabilized, the

emulsions exhibit a long-term stability against coalescence or Ostwald ripening<sup>39</sup>. Just like in the classical emulsions, both the design of formulation and the process of emulsification are of immense importance: the thermodynamically driven particle adsorption can be kinetically controlled by rheology and mass transfer of particles to interfaces<sup>40</sup>. Various stabilization theories have been proposed throughout the years, but the commonly accepted mechanism of stabilization is thought to be achieved by creation of a steric barrier composed of solid particles adsorbing at the oil–water interface<sup>32,41</sup>. This mechanism was supported by many studies via theoretical discussions and thermodynamic calculations<sup>42,43</sup>. Both theoretical and experimental relations have been derived pointing to the wettability and morphology of solid particles being the key parameters governing the stability of Pickering emulsions<sup>44</sup>. Additional parameters were found to be the oil type, particle concentration, size, phase volume fraction, pH and ionic strength<sup>31,32</sup>. The summary of these parameter relations will be briefly presented in the following sections.

## 2.2. Particle Wettability



**Fig. 2** Influence of a tri-phase contact angle on the Pickering emulsion type. Reprinted from<sup>45</sup> with permission from Elsevier.

It has been shown that although Pickering emulsions can be stabilized in a kinetic sense, they are not thermodynamically stable<sup>46</sup>. However, high degrees of packing and negative values of the Gibbs free energy of particle adsorption at the oil-water interface can be attained provided that particles exhibit partial wetting, which can be determined by evaluating a tri-phase contact angle  $\theta$  at the three-phase region between the particle, water phase and the oil phase (Fig. 2): if the particle is hydrophilic (contact angle  $< 90^\circ$ ), the water phase will be favored as the continuous phase, thus an oil-in-water (O/W) emulsion will be preferred<sup>47,48</sup>. Conversely, the hydrophobic particles (contact angle  $> 90^\circ$ ) will drive the formation of W/O emulsions. This phenomenon stems from the changes in the particle adsorption free energy (Eq. 1, spherical particle case), which defines the energy required for the solid particles to escape from the oil-water interface – the higher the energy, the stronger the adsorption to the interface. In general, Pickering emulsions show a much greater particle adsorption energy compared to classical surfactant-based emulsions<sup>40</sup>.

$$\Delta G_{ads} = \pi r^2 \gamma_{w-o} (1 - |\cos\theta|)^2 \quad (1)$$

Looking back at the equation, the highest energy is reached when the  $\cos(\theta) = 90^\circ$  and it steadily decreases as the contact angle moves away from that value. This results in the inability to form stable Pickering emulsions at very low and very high contact angles as the particles remain dispersed in their preferential phases<sup>49</sup>. Another aspect of the equation is the quadratic size dependency: since large particles have a larger area contacting oil and water, they possess a larger adsorption energy. Although this relationship alone undermines the potential use of nanoparticles for Pickering

emulsions, effects like higher packing density and enhanced surface area puts nanoparticles in the list of highly attractive Pickering emulsifiers<sup>50</sup>. The impact of particle wettability creates a demand for studies that are focused on surface modification of the solid particles with an aim to attain an amphiphilic character<sup>31,32</sup>. Several strategies exist in pursuit of the goal, but the most common approaches are physical adsorption and chemical grafting<sup>51-55</sup>.

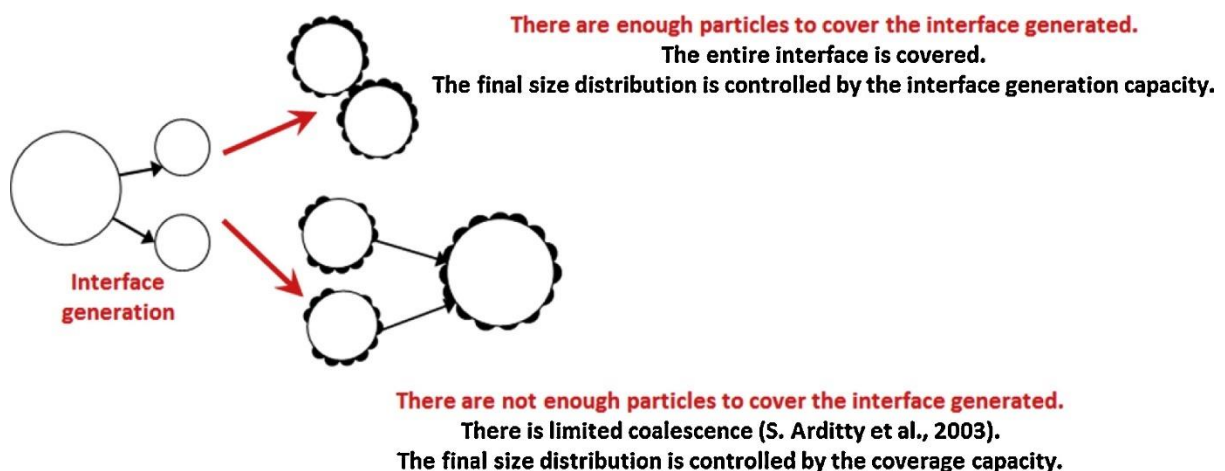
Having defined a tri-phase contact angle as an important descriptor affecting the kinetic emulsion stability, one should investigate the means of experimental characterization. A common way to express a tri-phase contact angle is by using Young's equation (2), which states that the contact angle is a function of the particle-liquid interfacial tensions  $\gamma_{p-o}$  and  $\gamma_{p-w}$ :

$$\cos(\theta_w) = (\gamma_{p-o} - \gamma_{p-w})/\gamma_{w-o} \quad (2)$$

Unfortunately, neither the classical contact angle measuring method by optical observation of drops deposited onto a solid surface nor the conventional interfacial tension measurements are feasible with submicron particles, therefore completely new analytical pathways had to be explored<sup>43,56</sup>. Two main categories of methods can be defined, namely the ensemble methods and single-particle methods, which are well explained in the literature<sup>57-59</sup>.

### 2.3. Oil type and volume fraction

The previously defined Young's equation illustrates the importance of the oil phase in terms of the interfacial tension exerted at the particle-oil and oil-water interfaces,  $\gamma_{p-o}$  and  $\gamma_{o-w}$ , respectively. These parameters would directly influence the particle adsorption energy thus the kinetic stability of the emulsions. In applications, where the emulsion formation in wastewaters can be performed in-situ (photocatalysis, adsorption), each hydrophobic component has a unique contribution to the overall interfacial tension of droplets. Consequently, the pollutants shall preferably be analyzed prior to the particle design activities so that an optimal emulsion stability window is found<sup>60,61</sup>. In general, numerous model oil phases have been explored including Pickering emulsions formed with silicone oil<sup>55</sup>, 1-methylnaphthalene<sup>62</sup>, hexadecane, heptane, or trichloroethylene<sup>63</sup>.

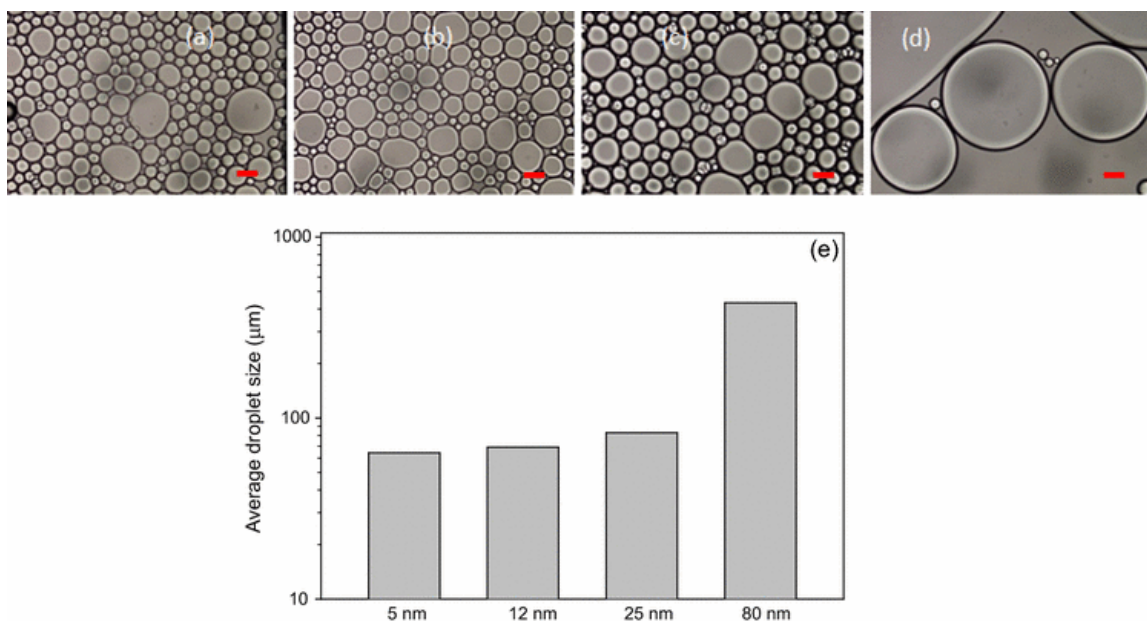


**Fig. 3** Typical representation of the mechanism controlling the size of a solid-stabilized emulsion. Reprinted from<sup>64</sup> with permission from Elsevier.

Another aspect that relates to the stability and the degradation performance is the volume fraction of oil, which affects the droplet size and the type of emulsions<sup>57,65,66</sup>. The variation of droplet size was observed by increasing the ratio of the oil phase in O/W PEs while keeping the graphene oxide particle concentration constant<sup>65</sup>. With the increasing dispersed phase ratios, the excess surface area of the droplets cannot be stabilized to the same extent without proportionally increasing the solid particle concentration, therefore larger droplets are being formed to compensate for the insufficient number of stabilizing particles (Fig. 3), an effect called “limited coalescence”<sup>67</sup>. This correlation has tremendous effects in most wastewater treatment applications as the processes are generally dependent on the effective surface area.

#### 2.4. Effects of particle concentration, shape, and size

Having highlighted the main criteria for solid particle adsorption leading to emulsion stability, one should consider other physiochemical parameters such as particle concentration, size, and shape, which are often used to optimize systems for a specific application. Although there have been many reviews on these trends<sup>32,40,57</sup>, certain parameters are more tunable than the others. For example, the concentration of solid particles has an inverse effect on the equilibrium emulsion droplet size as opposed to the volume fraction effect, thus in wastewaters containing high amounts of oil phase, it might be economically beneficial to vary the particle concentration instead of diluting the volume phase. In situations where emulsion stability is difficult to achieve, one can try to modify the particle shape such that the particle packing density would surpass the particle adsorption stabilization energies typically seen for the spherical particles<sup>68–70</sup>.



**Fig. 4** Effect of particle size on emulsion formation by sandpack flowing a) 5 nm, b) 12 nm, c) 25 nm, d) 80 nm (scale bar represents 100 μm), and e) average droplet size analysis. Reproduced from <sup>71</sup> with permission from Springer.

Finally, one of the key decisions in Pickering emulsion design is the size range of the stabilizing particles. Despite the interfacial adsorption energy scaling with the square of particle radius, it is known that both higher packing density and large catalytic surface areas can be achieved by decreasing the particle size<sup>72,73</sup>. However, it has been reported that having the particles too small may also have adverse effects on the emulsion stability due to variation of the wettability with respect to the particle size<sup>74</sup>. For their part, Binks & Lumdson showed that the stability of PEs against sedimentation increased upon particle size decrease<sup>73</sup>. In addition, for most practical applications it

is desired to be able to recover the stabilizing particles, therefore Levine et al. estimated that the solid particles should be, at least, one order of magnitude smaller in diameter than the smallest droplets<sup>49</sup>. Furthermore, the size-dependent particle mobility has implications on the final droplet size since, as discussed in the previous section, the equilibrium droplet size is influenced by the adsorption time at the interface as opposed to the rate of coalescence between the two droplets in the continuous phase<sup>64</sup>. The droplet size dependency on the particle size has been verified experimentally: emulsion droplet size was increasing as the particle size of silica nanoparticles became larger although the size difference between 5 and 12 nm was small (Fig. 4)<sup>71</sup>.

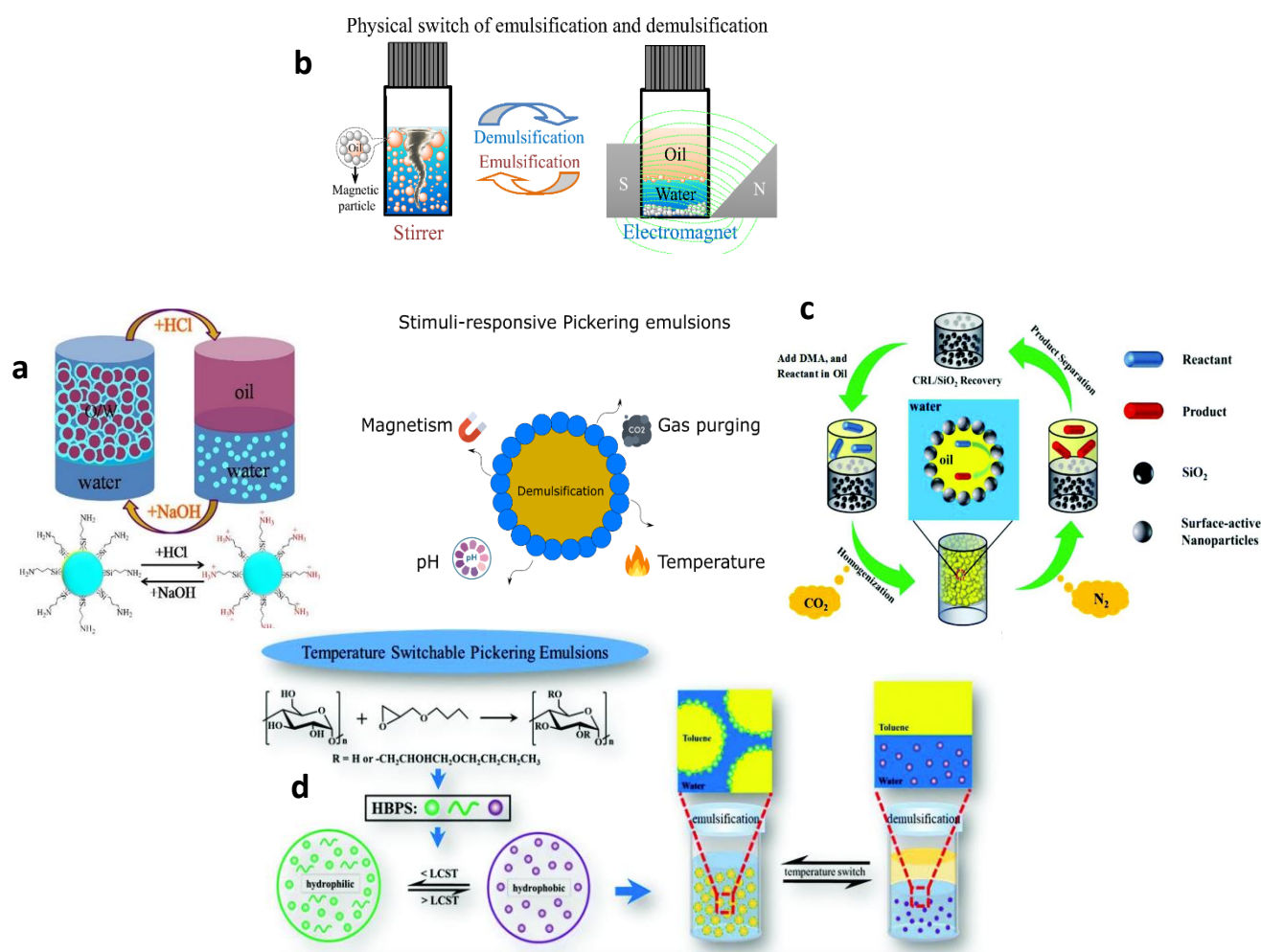
## 2.5. pH and ionic strength

Pickering emulsion sensitivity towards pH and ionic strength opens new possibilities for tailoring the emulsion stability windows owing to alterations in particle wettability and zeta potential<sup>75,76</sup>. For example, solid emulsifiers containing ionizable groups can change their hydrophilicity with respect to pH. This phenomenon was explored by Hao et al., where a pH-responsive emulsion system was developed by employing surface active titanium dioxide (TiO<sub>2</sub>) nanoparticles<sup>77</sup>. In the acidic range the particles were fully dispersed in an aqueous phase not being able to form emulsions, which was later made possible by increasing the pH value up to 7–8. Ionization of the moieties also affects the particle surface charge and the subsequent electrostatic interactions among them. The implications of that effect result in different spacing between the stabilizing particles at the oil-water interface, which subsequently leads to different stability profiles depending on the nature of the particle and the pH.

The charged nature of nanoparticles used for Pickering emulsions makes them extremely vulnerable to changes in the ionic strength as a consequence of the ion-induced electrostatic shielding effect that reduces their surface potentials triggering droplet coagulation or flocculation<sup>32,75</sup>. This results in reduction of the active surface areas needed for wastewater treatment applications limiting the practical use of Pickering emulsions in samples of high salinity and extreme pH values. In these situations, various means of particle modification can be applied to create a protective coating stabilizing the particles from aggregation<sup>33,78,79</sup>. The coated particles have been reported to demonstrate enhanced emulsion stability in high salinity conditions owing to the decreased repulsions and higher interfacial packing as opposed to the deionized water case<sup>80</sup>. Furthermore, numerous papers have demonstrated positive cases where salt was intentionally used in the design of Pickering emulsions. Li et al. showed that the decrease in zeta potential induced by added salts for pea protein microgel particles used as Pickering stabilizers would help a hydrophobic group to be embedded into the protein curl, resulting in a lower hydrophobicity<sup>81</sup>. There have also been instances of an intentional particle aggregation that would facilitate the migration of particles towards the oil-water interface in order to improve emulsion stability<sup>82,83</sup>. Finally, manipulations of NaCl concentration can induce an emulsion phase inversion and the amount of salt required for that would be dependent on the droplet size<sup>84</sup>.



### 3. Destabilization mechanisms



**Fig. 5.** Destabilization mechanisms by employing a) variations in pH (reprinted from<sup>77</sup> with permission from Elsevier), b) magnetic field<sup>85</sup>, c) CO<sub>2</sub>/N<sub>2</sub> stimulus (reprinted from<sup>86</sup> with permission from Royal Society of Chemistry), d) temperature differences (reprinted from<sup>87</sup> with permission from Royal Society of Chemistry).

The superior stability of Pickering emulsions can be seen as a disadvantage in most practical wastewater treatment applications owing to their recovery limitations<sup>88</sup>. The benefits of the increased reaction efficacy are often overshadowed by the difficulties in separating and removing the reaction products from the biphasic mixtures<sup>88–90</sup>. The commonly used catalyst recycling methods such as centrifugation and filtration face challenges when the particle size approaches sub-micrometer range leading to filter blocking, catalyst loss and oxidation problems<sup>88–90</sup>. Moreover, when it comes to Pickering emulsions, the demulsification energy barrier lies in the range of  $10^7 k_B T$  ( $k_B$  - Boltzmann constant) making it practically impossible to achieve<sup>91</sup>. Consequently, novel and cost-effective methods capable of regenerating solid emulsifiers are highly demanded. Various external-stimuli dependent approaches have been reported, including the use of pH<sup>61,77,92,93</sup>, CO<sub>2</sub><sup>86,94,95</sup>, temperature<sup>95,96</sup>, magnetic field<sup>97–99</sup>, ionic strength<sup>100</sup>, or their combinations<sup>93,95,101</sup> – some of them will be presented in this chapter.

In most cases, reversible emulsion breaking is achieved by introducing functional groups on the stabilizing particles that can interconvert between the structures exhibiting different wetting

properties<sup>102–104</sup>. The changes in wettability affect the adsorption Gibbs free energy making the presence of the particles at the tri-phase boundary layer thermodynamically unstable<sup>35</sup>. As a result, particles tend to redisperse in their preferred wetting phases<sup>32</sup>. For example, the presence of free amino groups along the backbone of chitosan turns it into a pH-tunable Pickering emulsifier which could adsorb at the interface of oil and water to stabilize O/W emulsions<sup>105</sup>. At pH < 6.0, chitosan was soluble in water and did not form emulsions with the oil phase, but when the pH surpassed 6, chitosan nanoparticles or micrometer-sized floccular precipitates were formed in situ acting as Pickering emulsifiers<sup>105</sup>. Another study by Low et al.<sup>101</sup> reported the dual behavior of Pickering emulsions made of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and poly[2-(dimethylamino) ethyl methacrylate], which could be emulsified/demulsified by tuning both the pH and magnetic field. A similar effect was demonstrated by employing a CO<sub>2</sub> sensitive surfactant, 4-butyl-4-(4- N,N-dimethylbutoxyamine) azobenzene bicarbonate, which can be interconverted between the charged and non-charged states with respect to the concentration of CO<sub>2</sub> dissolved in the water phase. What is more, the molecule is capable of interconverting between cis (more polar) and trans (less polar) isomers upon UV or blue light irradiation<sup>95</sup>. Both CO<sub>2</sub> and light irradiation are low cost, environmentally benign, and contamination free solutions that could overcome the current emulsifier recovery limitations. Yet another example of altering particle wetting properties is by introducing co-surfactants that could adhere to the surface of the stabilizing particles<sup>106</sup>. Alargova et al. argued that the adsorption of a drop-wise added sodium dodecyl sulfate (SDS) to foams, stabilized by hydrophobic polymer microrods induced the collapse of the foam followed by the efficient recovery of the microrods in the aqueous phase<sup>106</sup>. A summary of the aforementioned destabilization mechanisms is depicted in Fig. 5.

Although changing the particle wettability covers the majority of destabilization mechanisms, one can achieve similar results by disrupting the packing of the droplets. For example, Vashisth et al. showed that dodecane-in-water emulsions stabilized by silica nanoparticles can be demulsified by adding SDS into the mixture<sup>107</sup>. The added surfactant would compete for the oil-water interface by displacing the already existing particles. The hypothesis was backed by the previously reported results with proteins being displaced by surfactants due to reduction of the interfacial tension caused by surfactant adsorption<sup>108</sup>. A similar phenomenon was later demonstrated by Reynaert et al. where the decane-water interfacial layer stabilized by latex particles was characterized with and without SDS present. It was found that the presence of SDS disrupted the packing of the latex particles making the interfacial particle arrangement looser (more open)<sup>109</sup>.

The key parameters investigated in the previous sections will be critical when analyzing Pickering emulsions used for wastewater treatment applications. The tunability of PEs makes them very attractive for certain applications, but also difficult to control since many of these parameters are highly interlinked<sup>57</sup>. All other parameters being identical, different surface chemical composition could lead to different surface physicochemical properties, and consequently to different wetting properties and emulsion stability profiles<sup>32,35,36,57</sup>. Thus, systematic studies of independent variables and their implications for specific applications are of high interest. The most potent applications will be investigated in the following chapter.

## 4. Applications of Pickering emulsions for wastewater treatment

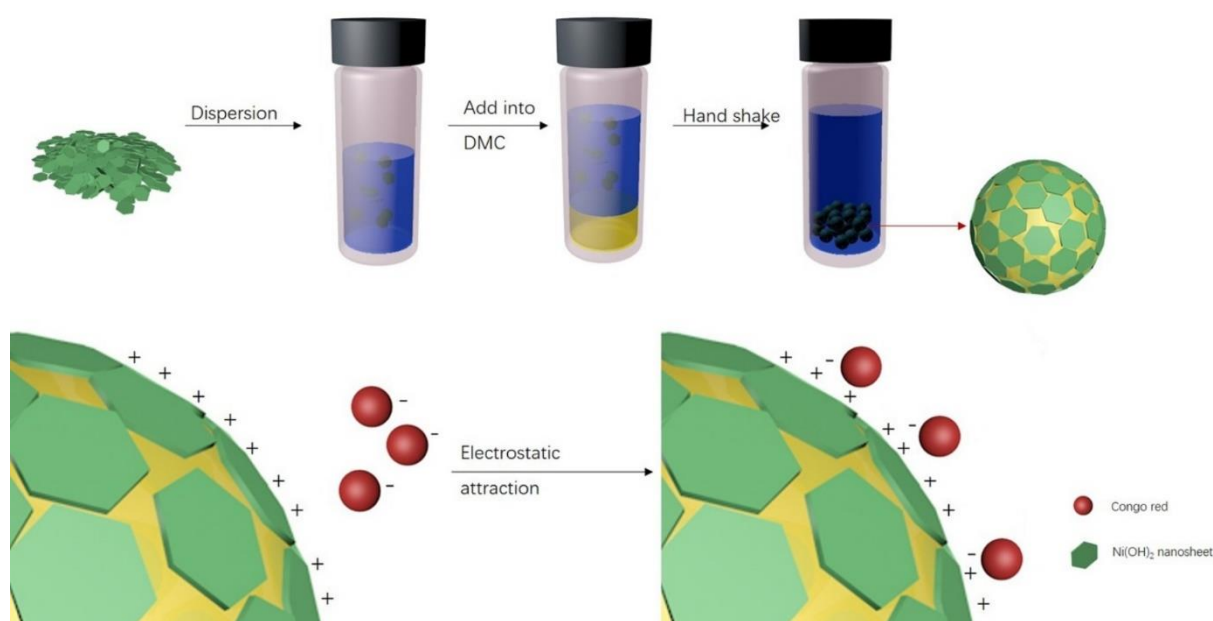
Pickering emulsions have become ideal candidates for wastewater treatment owing to their many attractive features, such as remarkable stability, tunability, low cost, low toxicity, easy recovery, and high performance due to high interfacial surface areas<sup>37,38,98,110,111</sup>. Various methods based on Pickering emulsions have been developed for removing contaminants from wastewater, including adsorption, photocatalytic oxidation, precipitation, coagulation/flocculation, chemical oxidation, biological processing, or membrane filtration. The adsorption processes were found to be a special case where the most potent techniques rely on the indirect use of Pickering emulsions yielding high performance functional adsorbents. **Table 2.** Pickering emulsion compositions and their applications in wastewater treatment Table 2 summarizes these applications with the corresponding target pollutants and emulsion architectures listed. Each of these techniques will be further analyzed focusing on both the working mechanisms and the examples demonstrating their performance in use.

**Table 2.** Pickering emulsion compositions and their applications in wastewater treatment

Application	Modifiers	Emulsion type	Composition	Target pollutant	Refs.	
Photocatalysis	NaF	O/W	TiO <sub>2</sub>	nitrobenzene	62	
		O/W	TiO <sub>2</sub>	Rhodamine B	112	
	hexylamine, continuous flow	O/W	TiO <sub>2</sub>	Nile red	113	
		O/W	TiO <sub>2</sub>	Rhodamine B	111	
		O/W	ZnO	nitrobenzene	114	
		W/O	Ag <sub>3</sub> PO <sub>4</sub> /BiPO <sub>4</sub>	Acid Blue 92	33	
Catalysis	H <sub>2</sub> O <sub>2</sub> mediated, N-doped	O/W	TiO <sub>2</sub> -rGO	MB	115	
		W/O	Janus-CNT	2-nitrophenol	116	
	NaBH <sub>4</sub> mediated, continuous flow	O/W	ACNF@Ag	4-NP, MB, MO	117	
		Adsorption	W/O	Ni(OH) <sub>2</sub> nanosheets	Rhodamine B	
			W/O	silica-oleic acid	lambda-cyhalothrin	118
Coagulation/flocculation	MIPFs	W/O	BA-MSN-PGM	luteolin	119	
		O/W	silica	Bisphenol A	120	
	polyHIPEs	W/O	Fe <sub>3</sub> O <sub>4</sub> @humic acid	Hg (II) ions	121	
	polyHIPEs	W/O	Poly(4-vinyl pyridine)	plutonium	122	
	O/W	Ag <sub>3</sub> PO <sub>4</sub> @palygorskite	tetradecane	123		
	O/W	CNC-g-AA-g-CA	MB	124		
	photo-induced polymerization	O/W	Pt@CdS	phenols	125	
	Extraction/separation	PELM	W/O/W	Fe <sub>3</sub> O <sub>4</sub>	4-methoxyphenol	97
		PELM	W/O/W	ASNWs	Cr (VI)	126
	Biological treatment	DVB as pre-polymer complex	O/W and W/O	HBPS-BGE	dimethyl blue/Nile red	87
O/W			Fe <sub>3</sub> O <sub>4</sub> + P.putida/P. denitrificans	phenols/DMF	127	
polyHIPEs		W/O	SRB-Poly(St-MTQ)	sulfates	128	
Bactericide	microcapsules	O/W	CTO/HAp/HACC/SA	E. coli and S. aureus	129	
	photocatalysis	O/W	epoxy acrylate copolymer@nano-TiO <sub>2</sub>	bacteria	130	
Steam generation	aerogels	O/W	CNF/PLA/PANI	salts, organic compounds	131	

CNT: carbon nanotubes; rGO: reduced graphene oxide; MB: methylene blue; ACNF: cellulose nanofibers with aldehyde groups; 4-NP: 4-nitrophenol; MO: methyl orange; MIPFs: molecularly imprinted polymer foams; BA-MSN: boronic acid suspended mesoporous silica nanoparticles; PGM: poly(glycidyl methacrylate); polyHIPEs: polymers from high internal phase emulsions; CNC-g-AA-g-CA: cellulose nanocrystals-ascorbic acid- citric acid; PELM: Pickering emulsion liquid membrane; ASNWs: amphiphilic silica nanowires; HBPS-BGE: 2-hydroxy-3-butoxypropyl starch with butyl glycidyl ether; P.putida: Pseudomonas putida; P.denitrificans: Paracoccus denitrificans; SRB: sulfate reducing bacteria; St-MTQ: styrene-MTQ silicone resin; CTO/HAp/HACC/SA: citronella oil loaded microcapsules with hydroxyapatite /quaternary ammonium salt of chitosan/sodium alginate; CNF/PLA/PANI: cellulose nanofibril/poly(lactic acid)/polyaniline;

## 4.1. Adsorption



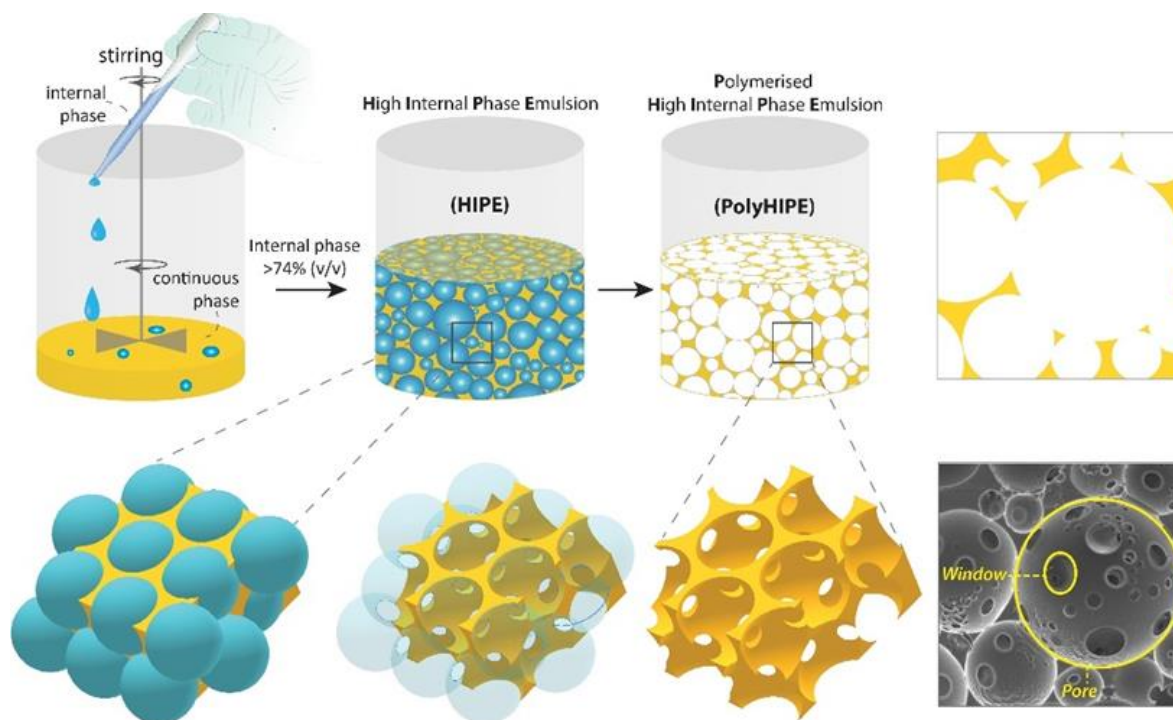
**Fig. 6** Preparation process of Ni(OH)<sub>2</sub> nanosheet stabilized Pickering emulsion with the electrostatic adsorption mechanism depicted. Reprinted from<sup>132</sup> with permission from Elsevier.

Adsorption is a common industrial method of pollutant removal from wastewaters being particularly effective when the pollutants are stable against other means of degradation, i.e., by using aerobic digestion, light, heat, or oxidizing agents<sup>133</sup>. Despite the process being rather inexpensive and simplistic, effective separation and regeneration of adsorbents is still considered a challenge<sup>134,135</sup>. Moreover, the eluent must be treated to avoid secondary pollution<sup>136</sup>.

To account for these problems, several Pickering emulsions have been designed to act as adsorbents that would overcome the separation and regeneration problem that would otherwise be present in the dispersed case<sup>132,137</sup>. A rather simplistic case is depicted in **Fig. 6**, where the electrostatically-driven adsorption of Congo red dye was evaluated by utilizing Ni(OH)<sub>2</sub> nanosheets as Pickering emulsifiers together with dichloromethane as the oil phase<sup>132</sup>. The intention was to promote the settling rate of the saturated adsorbent owing to the high density of the oil phase, but the adsorption rate had to be accounted for by tuning the droplet sizes such that the adsorbent would not settle before having captured the dye molecules. The produced emulsion exhibited a much higher adsorption capacity and a faster settling rate compared to Ni(OH)<sub>2</sub> dispersed in the water phase. The difference was explained by the embedding effect between the bare nanosheets during deposition, which would effectively reduce the number of active sites for adsorption as opposed to the ordered emulsion structure. More examples include iron oxide-modified magnetically separable emulsions targeting rhodamine B (RhB)<sup>138</sup> or layered hexaniobate emulsions, capable of adsorbing both water-soluble and lipophilic dyes<sup>139</sup>.

Although direct adsorption systems have been known, their complexity and performance limitations did not lead to further attempts to commercialize the process. However, the most prominent adsorbents are generally made by applying Pickering emulsions indirectly<sup>137,140</sup>. The functional porous materials made by templating Pickering emulsions have gained considerable attention owing to their tunable porous structure, surface properties and high specific surface area<sup>140</sup>. The main group of highly porous adsorbents based on Pickering emulsions are so-called polyHIPEs: polymeric high internal phase emulsions (Fig. 7**Error! Reference source not found.**)<sup>141</sup>. This type of materials

has already demonstrated potential for removal of heavy metal ions<sup>142</sup>, organic contaminants (i.e., dyes, surfactants, pesticides) and for oil spillings<sup>140</sup>.



**Fig. 7** Fabrication steps of the Polymerized High Internal Phase Emulsion (PolyHIPE). (a,b) The gradual addition of the internal phase into the continuous phase while the system is mixed, c) polymerization of the high internal phase emulsion (HIPE), d) 2D projection of PolyHIPE, e-g) the formation of the pores and windows, and h) scanning electron microscopy image<sup>141</sup>

A vast number of different adsorbents has been fabricated by utilizing Pickering emulsions as precursors relying on the polyHIPEs technology<sup>140</sup>. Pan et al. used a common pesticide  $\lambda$ -cyhalothrin in the continuous phase coupled with the polymerizable PEs to synthesize polyHIPEs with an enhanced recognition towards the pollutant<sup>118</sup>. The adsorption results indicated favorable adsorption kinetics and high adsorption selectivity. Similarly, a cis-diol specific adsorbent system can be designed by functionalizing silica NPs with boronic acids, which are known for their affinity towards the formation of complex compounds with carbohydrates<sup>119</sup>. Another study showed that bisphenol A could be selectively adsorbed by synthesizing molecularly imprinted multicore rattle-type microspheres through a facile Pickering emulsion polymerization using silica nanoparticles<sup>120</sup>.

When it comes to removal of heavy metal ions, adsorbents must possess a hydrophilic character<sup>140</sup>. Several ways of introducing hydrophilic moieties have been proposed, but the most prevalent one is the post-synthesis modification of hydrophobic polyHIPEs. Mert et al. formulated styrene/divinylbenzene (ST/DVB) based polyHIPEs stabilized by humic acid-modified oxide magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@HA$ ) that showed a high adsorptive capacity for Hg (II) ions<sup>121</sup>. Another approach was realized by Pribyl et al., where polyHIPE foams were surface-grafted with a brush of a polymer containing ion-exchange sites designed to remove plutonium<sup>122</sup>. The post-modified polyHIPEs strategy although being quite effective, remains tedious and costly to be produced on a large scale<sup>140</sup>. Due to this reason, there has been an increasing interest in O/W polyHIPEs as opposed to conventional W/O systems, which require post-modification<sup>141</sup>. For instance, a series of magnetic O/W polyHIPEs were prepared through a free-radical grafting polymerization method by immobilizing surface-modified iron oxide nanoparticles<sup>143</sup>. The subsequent grafting of acrylic acid

onto hydroxypropyl cellulose tailored the specific adsorption sites towards  $\text{Rb}^+$  and  $\text{Cs}^+$  ions. Furthermore, the use of stabilizing magnetic nanoparticles is extremely advantageous for adsorbent recovery. Finally, tunability of the pore geometry, simplicity of the synthesis and versatility towards a wide range of ions metal ions makes the polyHIPEs technology very attractive for advanced adsorbent development. There is, however, a theoretical Pickering emulsion porosity limitation of 74.048% dictated by the highest possible dispersive phase volume<sup>141</sup>. In order to surpass this limit and further enhance the adsorption capacity, multi-hollow structures in the polymer microspheres or double emulsion systems can be fabricated. In these systems droplets of the dispersed phase themselves contain even smaller droplets<sup>144</sup>.

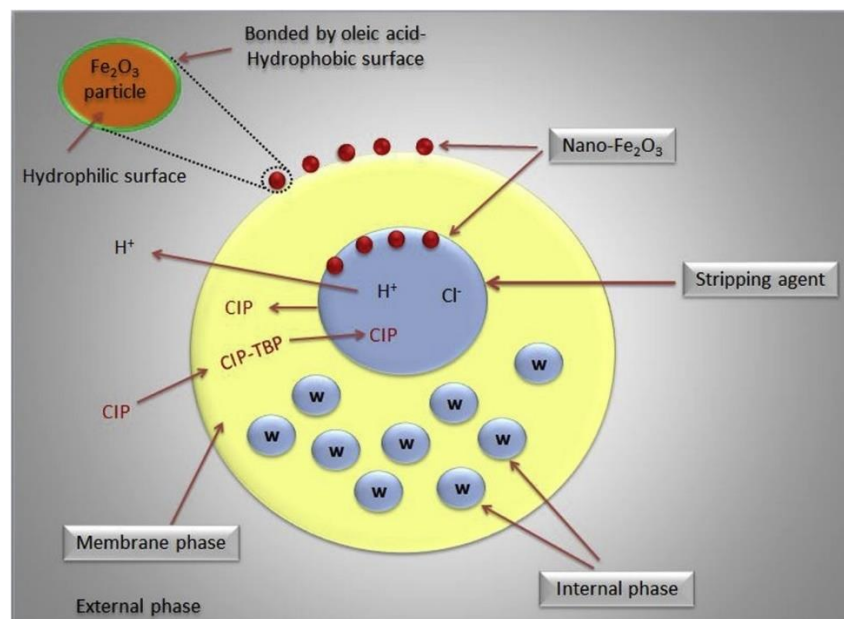
#### 4.2. Coagulation/flocculation

Typical inorganic or synthetic wastewater treatment flocculants despite being highly effective and relatively cheap, lack biodegradability hence cause secondary pollution to the environment<sup>145</sup>. Other drawbacks include a large amount required for efficient flocculation, high sensitivity to pH, inefficiency towards very fine particles, and applicability only to selected disperse systems<sup>145,146</sup>.

The carboxylated cellulose nanocrystals (CNCs) can address these challenges by utilizing their strong electrostatic adsorption between anionic carboxyl groups and cationic dyes or suspended particles that would in turn exert strong enough attractive forces to overcome the electrostatic repulsion<sup>124</sup>. Kaolin suspension (wastewater model system) was coagulated by forming O/W Pickering emulsions, stabilized by CNCs with a variable carboxylic group density. It was found that indeed, more anionic groups on the CNC surfaces enhanced the electrostatic adsorption due to charge neutralization leading to a more effective turbidity reduction.

Alternatively, a new reaction system for the simultaneous removal of aromatic contaminants from wastewater was demonstrated by carrying out a photo-induced oxidative polymerization of phenolic substrates via a chain growth mechanism, thereby providing a path for pretreating water by flocculating out contaminants with a concurrent generation of hydrogen<sup>125</sup>. The propagating polymer chain would exhibit a decreasing water-solubility pattern with each added monomer up to a point, where a poly-phenolic Pickering emulsion from the contaminants originally found in wastewater could be formed. Additionally, the reaction results in generation of hydrogen gas, which can be utilized as a useful byproduct. Further development is still needed to replace the currently used Pt@CdS substrate with particles composed of less toxic and more earth abundant materials to make the system viable for water cleaning.

### 4.3. Extraction/separation

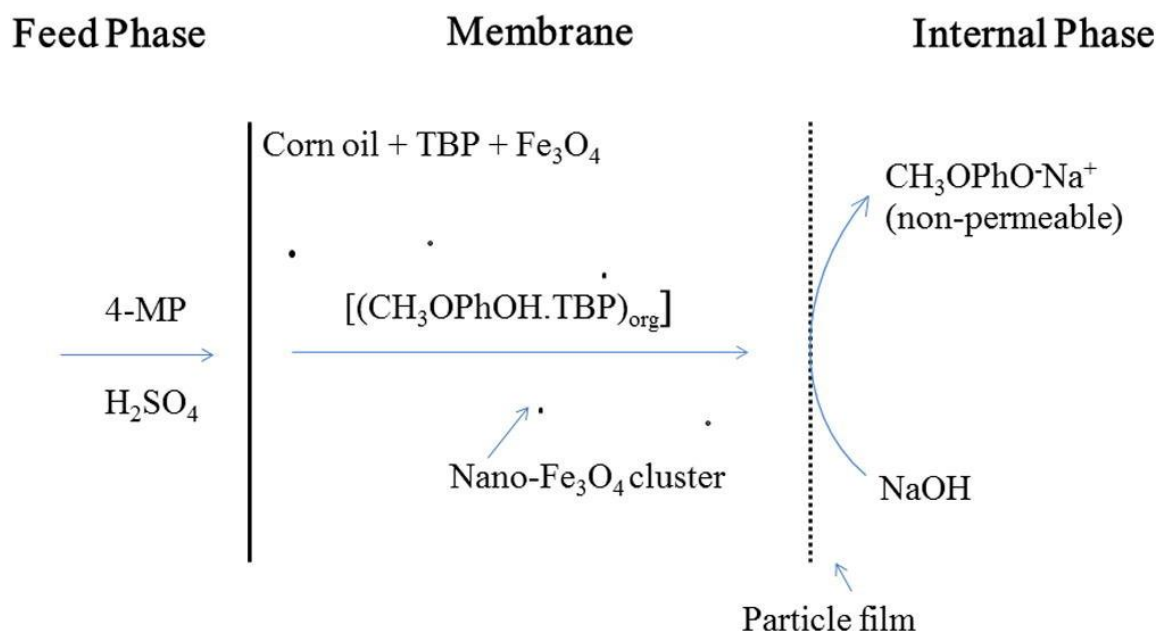


**Fig. 8** Extraction mechanism of a PELM system. Reprinted from <sup>147</sup> with permission from Elsevier.

Methods like microfiltration, ultrafiltration, and reverse osmosis are very well established in the wastewater treatment process, but the limitations such as low efficiency, difficult operating conditions and high maintenance costs create an interest for alternative solutions<sup>37</sup>. Emulsion liquid membranes (ELMs) have recently emerged as potential substitutes used in separation and extraction processes owing to their simplicity, high selectivity, rapid extraction, and low energy consumption<sup>148–150</sup>. ELM technology typically relies on a conventional W/O surfactant-stabilized emulsion dispersed in an external feed phase, which is usually aqueous<sup>37</sup>. The oil phase is then considered to be the liquid membrane separating the two miscible phases. Therefore, ELM based extraction systems can be thought as equivalent to double emulsions that exist as W/O/W (water-in-oil-in-water) and O/W/O (oil-in-water-in-oil)<sup>151</sup>. The separation is achieved by transporting species across the oil phase so that they would be trapped inside the internal aqueous phase. The W/O emulsion can afterwards be broken up through various stimuli to release the contents of the internal phase. Despite the appealing concept, commercialization of ELM has been limited due to instability of emulsions and the difficulty of demulsification after extraction<sup>148,149</sup>.

Adaptation of an ELM template to Pickering emulsions has been found to be an option that would circumvent the main drawbacks of a typical ELM system. Pickering emulsion liquid membrane (PELM) concept replaces surfactants used in ELM with solid nanoparticles that provide higher emulsion stability and easier demulsification owing to their wide range of particle functionalization pathways<sup>152</sup> (**Error! Reference source not found.**). Only a handful of studies so far considered using PELMs for wastewater treatment most notably by using magnetic particles as emulsifiers<sup>97,147</sup>. One instance of a PELM-like system was demonstrated by using Fe<sub>2</sub>O<sub>3</sub> particles as co-emulsifiers in ELMs to characterize the stability and efficiency in extracting lead ions (Pb<sup>2+</sup>) from aqueous solutions. The method was proven to be useful for improving the membrane stability (emulsion breakage as low as 0.3 %) with Pb<sup>2+</sup> extraction efficacy up to 97.2 % <sup>152</sup>. Alternatively, Lin et al. made use of a nano-Fe<sub>3</sub>O<sub>4</sub> PELM system that could extract over 86% of 4-methoxyphenol (4-MP) from wastewater<sup>97</sup>. The working mechanism of extraction is depicted in Fig. 9: 4-MP in the feed phase diffuses to the O/W interface of the membrane and reacts with the tri-n-butyl phosphate (TBP) carrier capable of

forming an oil-soluble complex with 4-MP. The complex then diffuses across the oil phase of the membrane to reach the internal W/O interface, where it forms a salt which cannot diffuse back into the oil phase. As a result, 4-MP is selectively extracted by the carrier from the external feed phase to the internal phase. The system can then be demulsified by applying magnetic field or centrifugation. In fact, the proven efficacy of centrifugation as a feasible destabilization route facilitates the expansion of emulsifiers beyond magnetic particles.



**Fig. 9.** Schematic diagram of 4-MP extraction by PELM technology. Reprinted from<sup>97</sup> with permission from Elsevier.

One example of non-magnetic PELMs by Perumal et al.<sup>126</sup> indicated that amphiphilic silica nanowires (ASNWs) can be used as PELM surfactants for extraction of  $\text{Cr}^{6+}$  ions. The prepared PELM was very effective in the extraction of chromium at lower concentrations although lacked the means of recovery. ASNWs were also reported to be suitable for the removal of both  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  indicating a superior performance compared to alumina or sorbitane monooleate (SPAN 80). Regardless of being in the early phase of development, PELM technology shows a high potential for becoming a viable extraction technique used in wastewater treatment.

Aside from liquid membranes used for pollutant separation, a new group of super wettable materials has emerged addressing the drawbacks of conventional techniques, such as gravity separation, skimming, and flotation<sup>87</sup>. A major industrial challenge is the effectiveness of emulsion separation, which can be targeted by utilizing extreme values of wettability thus providing excellent material properties for the separation of different water-oil mixtures<sup>87,140</sup>. Thermoresponsive 2-hydroxy-3-butoxypropyl starch (HBPS) was produced and later surface-modified by Pickering emulsion polymerization to produce super wettable porous spheres used for oil/water separation<sup>87</sup>. By changing the temperature, one could emulsify (below the lower critical solution temperature (LCST) and demulsify (above LCST) oil/water mixtures by exploiting changes in polymer wettability with respect to temperature. The polymer spheres would then serve as a porous layer for separation: during the separation of stable water-in-oil emulsions, the oil phase would freely pass through the layered spheres, whereas the water droplets would be repelled. Conversely, the dispersed oil phase in oil-in-water emulsions would be adsorbed by the polymer spheres forming a thick layer that could only be penetrated by water when a vacuum pump is used. According to the initial results indicating the separation efficiency of 99.9%, it is believed that super wettable

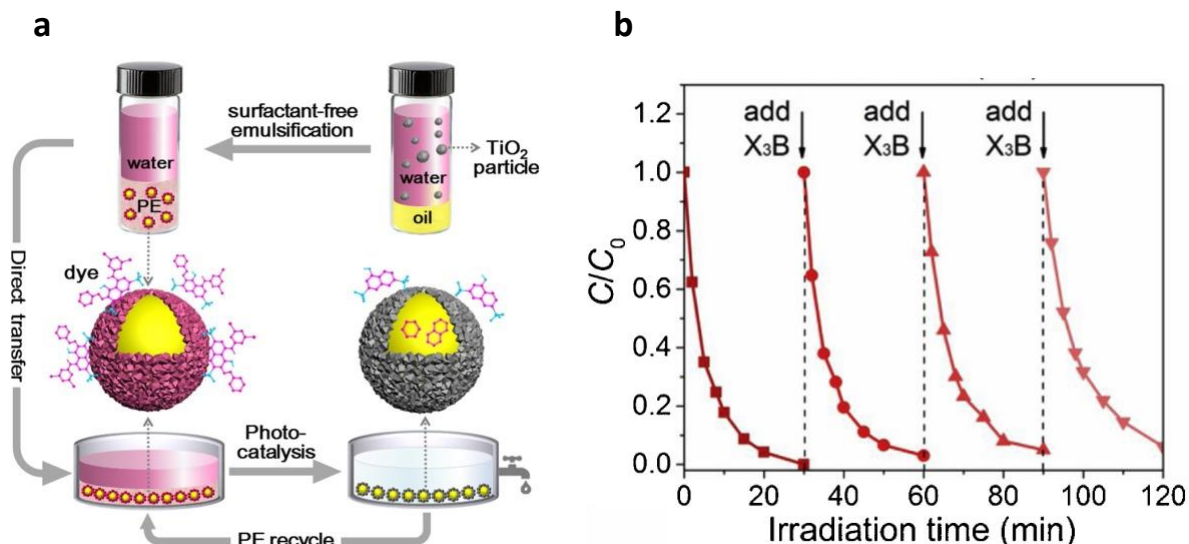


materials could become the future state-of-the-art technology used in separation of complex fluids<sup>87</sup>.

#### 4.4. Photocatalysis

Over the last few decades, there has been a great interest in developing photocatalysts with high catalytic efficiency and good stability towards common pollutants in industrial waste waters around the globe<sup>153</sup>. The evolution of advanced oxidation processes (AOPs) has drawn attention towards the photocatalytic means of generating radical species, which would then unselectively decompose organic pollutants making the contaminants be quickly and efficiently fragmented and converted into small inorganic and organic molecules<sup>154</sup>. Even though the formation of highly oxidizing active oxygen species through light induced redox reactions allows degradation of almost every organic substrate, its full potential has not been reached yet<sup>62</sup>. For example, the efficiency of photocatalysis drops as the contaminant concentration drops<sup>155</sup> or if hydrophobic organic pollutants poorly adsorb onto the hydrophilic surface of the photocatalyst making the reaction kinetically hindered<sup>156</sup>. In general, the photocatalytic efficacy is highly dictated by the interfacial phenomena, therefore enhancing the contact area between contaminants and photocatalysts would be an effective route to improve the photocatalytic activity<sup>114</sup>.

Considering these challenges, the benefits associated with the photocatalytic nanoparticles become obvious owing to their large catalytically active surface areas, broadening of the band gap and faster spatial charge-transfer<sup>157</sup>. These assumptions were confirmed by Koci et al., where a clear nanoparticle size dependency was observed - as the particles got smaller, both the charge-carrier dynamics and light absorption efficiency of TiO<sub>2</sub> nanoparticles improved, leading to an exponential increase in the catalytic activity<sup>158</sup>. An elegant way to reduce droplet sizes and enhance the contact between photocatalysts and pollutants is by employing Pickering emulsions, which rely on the solid photocatalyst particles as emulsion stabilizers. The system is then composed of small and stable nanoparticles surrounding hydrophobic droplets - a matrix made of photocatalytic micro-reactors, that can be recoverable by demulsification<sup>36,62,159</sup>. The advantages deriving from the use of stable, cheap, and abundant nanoparticles combined with the increased photocatalytic activity show a high potential in developing universal methods for effective degradation of organic pollutants in wastewater through photocatalysis<sup>36</sup>.



**Fig. 10** a) Schematic of an o/w Pickering emulsion formation from super hydrophilic  $\text{TiO}_2$  coated with sulfonate-carrying pollutants for photocatalytic dye degradation testing, b) Four photocatalytic cycles of reactive brilliant red ( $\text{X}_3\text{B}$ ) degradation in the PE system with the same catalysts recovered. Reprinted from <sup>38</sup> with permission from Elsevier.

Pickering emulsions have shown promising results as photocatalytic systems for the degradation of organic contaminants in wastewater treatment. A classical example of the superior PE performance over the dispersed particle system was presented by Fessi et al., where 1-methylnaphthalene-(1-MN) was exploited both as an oil phase and as a target pollutant<sup>62</sup>. In this case, the water dispersed bare  $\text{TiO}_2$  nanoparticles would adsorb on the surface of the pollutant droplets acting as small microreactors with an enhanced contact area and photodegradation efficacy<sup>62</sup>. The degradation rate was compared between the blank ( $\text{TiO}_2$  free), non-emulsified and emulsified conditions in the presence of  $\text{TiO}_2$ . It was found that around 95% of (1-MN) could be degraded after 24 h of UV irradiation, compared with only 25% in the non-emulsified system. Substantial research is also done on the water-soluble dye removal from the wastewaters containing Nile red, Methylene blue and Rhodamine B<sup>111–113</sup>. A very interesting case was presented by Q. Li et al., where the wetting of bare  $\text{TiO}_2$  particles was in situ tuned by the adsorbing sulfonate groups from the reactive brilliant red ( $\text{X}_3\text{B}$ ) molecules (

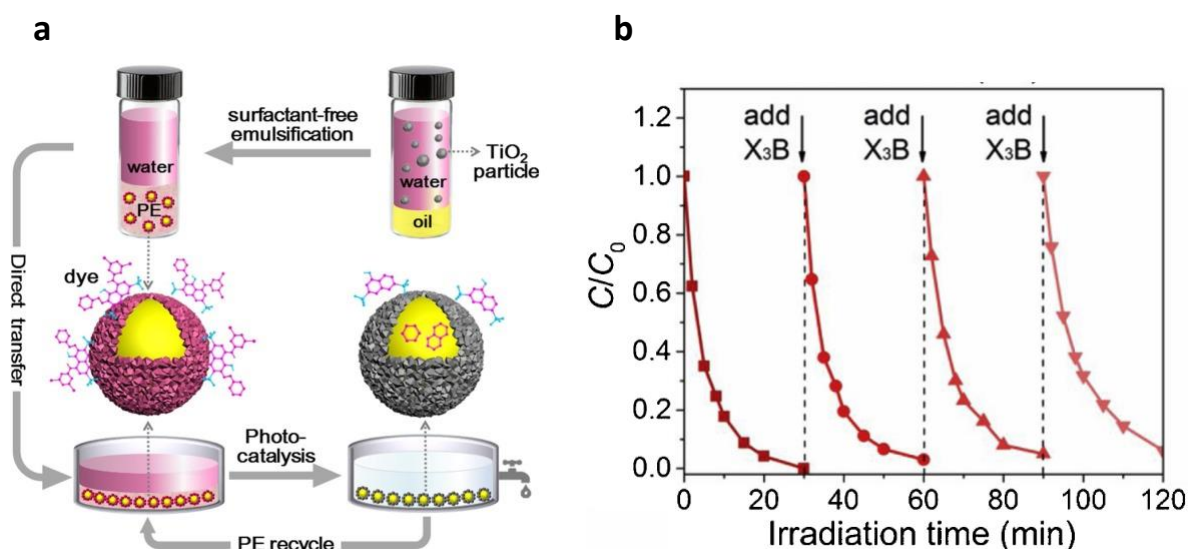


Fig. 10 a) Schematic of an o/w Pickering emulsion formation from super hydrophilic TiO<sub>2</sub> coated with sulfonate-carrying pollutants for photocatalytic dye degradation testing, b) Four photocatalytic cycles of reactive brilliant red (X<sub>3</sub>B) degradation in the PE system with the same catalysts recovered. Reprinted from <sup>38</sup> with permission from Elsevier.

a)<sup>38</sup>. The adsorbed pollutants reduced the hydrophilicity of bare titania, thus empowering titania to be an emulsifier capable of forming stable emulsions between water and dichloromethane. The prepared Pickering emulsions would then undergo a photocatalytic decomposition of titania-coated sulfonate-carrying pollutants, which would gradually demulsify the system providing excellent recyclability for reuse after irradiation (

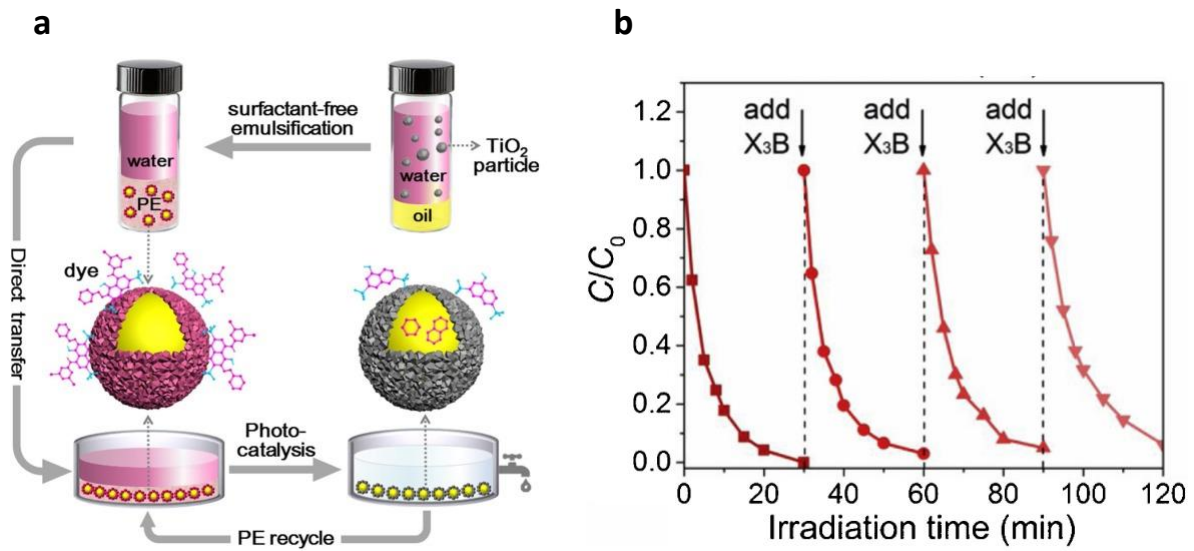


Fig. 10 a) Schematic of an o/w Pickering emulsion formation from super hydrophilic TiO<sub>2</sub> coated with sulfonate-carrying pollutants for photocatalytic dye degradation testing, b) Four photocatalytic cycles of reactive brilliant red (X<sub>3</sub>B) degradation in the PE system with the same catalysts recovered. Reprinted from <sup>38</sup> with permission from Elsevier.

b). As an alternative to TiO<sub>2</sub>, Wu et al. proved that the modified zinc oxide (ZnO) nanoparticles are perfectly feasible for photocatalytic applications of organic contaminants in wastewaters<sup>114</sup>.

Photocatalytic applications involving PEs are not just limited to the use of metal-oxide emulsifiers – complex compounds have been made with superior properties compared to conventional materials used for Pickering emulsions. One famous example has been demonstrated by Mohaghegh et al.<sup>33</sup>, where a novel p-n junction Ag<sub>3</sub>PO<sub>4</sub>/BiPO<sub>4</sub>-based Pickering emulsion coupled with either graphene or hydrophobic multi-walled carbon nanotubes was formed. The measured Acid Blue 92 dye degradation with respect to irradiation time indicated a highly effective photocatalytic activity far superior to the dispersed control case. The improvement was attributed to an enhanced migration of the produced O<sub>2</sub>, which is more soluble in the oil phase than in water. The self-induced removal of the product shifted the equilibrium to the product formation side thus improving the rate of pollutant degradation. More studies have been done by using graphene oxide (GO) and its composites by exploiting the benefits of highly efficient electron transfer and smooth connection between materials hence improving the photocatalytic degradation performance<sup>115</sup>.



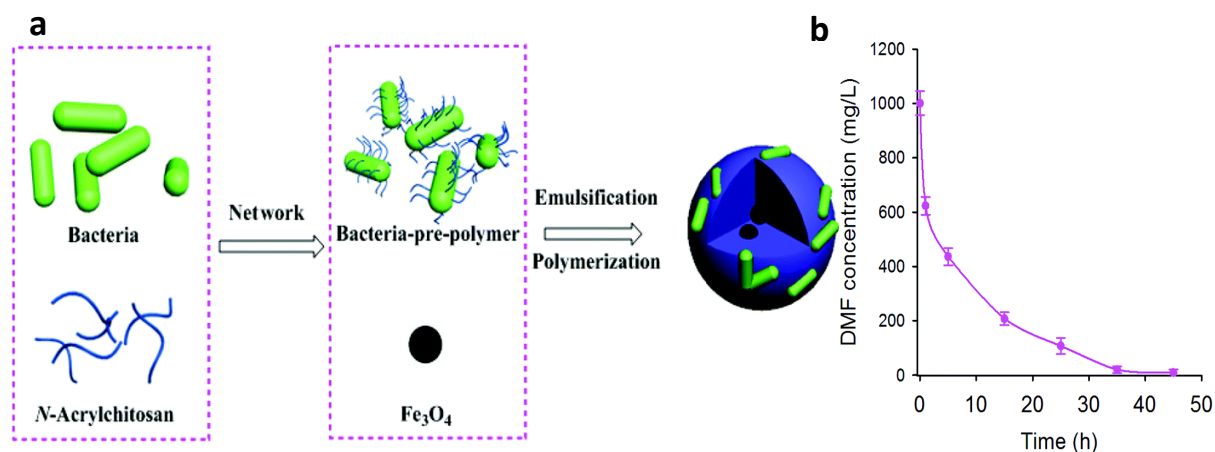
**Fig. 11.** Schematic of coupling process of adsorption, extraction, and photocatalysis. Reprinted from <sup>111</sup> with permission from Elsevier.

Regarding the combined adsorption-photocatalysis approach, X. Zhang et al. fabricated amphiphilic graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) to degrade rhodamine B (RhB) dye from wastewaters (Fig. 11 **Error! Reference source not found.**)<sup>111</sup>. The dye molecules could be captured by g-C<sub>3</sub>N<sub>4</sub> acting as a Pickering emulsifier-adsorbent, which would simultaneously photodegrade RhB upon irradiation. The process does not require any stirring or secondary treatment, which are needed in conventional wastewater treatment processes. Under visible light irradiation, the conversion of RhB removal reached 100% within 25 min and the used PEs could be reused without any reduction in performance. Another example was shown by preparing a composite made of highly absorbent palygorskite (PAL) clay particles and silver phosphate (Ag<sub>3</sub>PO<sub>4</sub>), which is a common photocatalyst<sup>123</sup>. The targeted removal of tetradecane indicated a 4.9 times higher efficiency compared to Ag<sub>3</sub>PO<sub>4</sub> particles alone. Adsorption also played a big role in enhancing the photocatalytic degradation of TiO<sub>2</sub>-graphene oxide composite towards methylene blue<sup>115</sup>. Many mesoporous voids acting as adsorption chambers were created by growing TiO<sub>2</sub> nanoparticles on the interface of O/W type GO Pickering emulsions. Overall, the combined strategy has been proven to be highly effective due to the individual contributions of the components constituting the composites.

The overall strategy of bridging advances in the research of photocatalytic Pickering emulsions is defined by two main paths of development: improving photocatalyst performance to meet industrial requirements or enhancing the mass transfer of low-concentration pollutants to intensify the process<sup>160-162</sup>. Although the former has been studied quite extensively in recent years, a substantial pollutant degradation process takes place in the order of hours, which is too long to be implemented in industry<sup>111</sup>. Nevertheless, recent success in pursuing the mass transfer route opened new possibilities for the enhanced photocatalytic timescales<sup>160,163,164</sup>.

## 4.5. Biological treatment

Among the pool of industrial methods used to remove soluble organic pollutants from wastewater, the biological treatment techniques are known to be the most cost-effective<sup>7,165,166</sup>. These methods can withstand a wide range of concentrations, produce harmless species, and show a high removal efficiency<sup>167–169</sup>.



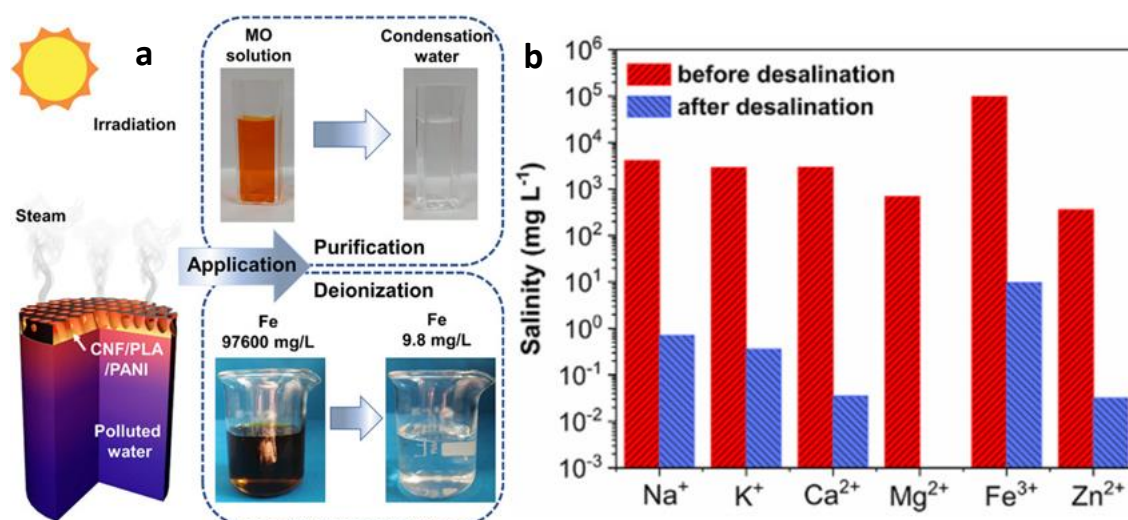
**Fig. 12.** a) Schematic illustration of the preparation and structure of the magnetic bacteria–polymer (MPB) composite, b) The adsorption–biodegradation process of DMF by MPB. Reprinted from<sup>127</sup> with permission from Royal Society of Chemistry.

Immobilized microorganism technology has recently emerged as a feasible water treatment alternative offering advantages, such as high cell density, easy recovery, high microbial stability, and the possibility to run the process continuously<sup>170</sup>. As a result, numerous groups have evaluated the use of natural and artificial microbial supports in bioreactors<sup>171–173</sup>. One potent research branch focusing on biomass immobilization makes use of Pickering emulsions acting as multifunctional substrates enabling effective adsorption, separation, and biological degradation of wastewater pollutants. For example, Cai et al. covalently immobilized two types of bacterial cells (*Pseudomonas putida* and *Paracoccus denitrificans*) on the surface of functional polymer particles to effectively degrade phenols and N,N-dimethylformamide (DMF) as model systems (Fig. 12a)<sup>127</sup>. Additionally, iron oxide nanoparticles were added to the oil phase before the polymerization providing a pathway for the bacteria–polymer composites to be separated by magnetic field. The pollutant removal profile is illustrated in Fig. 12b: sharp reduction in DMF concentration is initially attributed to adsorption followed by biodegradation by the MPB ultimately reaching negligible values in concentration. The removal of phenols followed a very similar trend to the removal of DMF as discussed above. Not only could the final composite effectively adsorb and remove organics from the aqueous solutions, but the magnetic separability also made the system fully reusable with no secondary pollution created. The same principle was later applied in fabricating bacteria-immobilized Pickering emulsions for desulfurization and oil-removal<sup>128,174</sup>.

#### 4.6. Other applications: steam generation, catalysis, bactericide

Having defined the main development areas of Pickering emulsions in wastewater treatment applications, one could analyze alternative ideas deepening our knowledge and exposing new principles that can later be incorporated into the most potent pollutant degradation techniques.

Pickering emulsions have become universal templates in particle engineering that can be utilized in the production of bactericidal materials, such as composites, microcapsules, or porous scaffolds. For instance, citronella oil (CTO), a well-known antibacterial agent<sup>175</sup>, was loaded to produce composite microcapsules with hydroxyapatite (HAp)/quaternary ammonium salt of chitosan (HACC) and sodium alginate (SA) shells in pursuit to inhibit *E. coli* and *S. aureus* growth used as model bacteria found in wastewaters. The fabrication was performed under ambient conditions without the use of surfactants and with the composites exhibiting excellent thermal stability. The prepared microcapsules showed a sustained release activity and displayed a significant bacterial inhibition effect<sup>129</sup>. An alternative particle design targeting antibacterial activity towards *E. coli* and *S. aureus* was realized by making grafted xanthan gum with poly(vinylimidazole) (XG-g-PVI) nanocomposites in the presence of different Montmorillonite (MMT) nanoclays<sup>176</sup>. MMT is known for its charged layer structure making it a great adsorbent for contamination removal in wastewaters. What is more, the cross-linked nanocomposites made of antibacterial thermally stable synthetic polymers such as poly(vinylimidazole) (PVI) with XG would furthermore enhance the mechanical strength and adsorption efficacy of the resulting structure. Lastly, the photocatalytic properties of TiO<sub>2</sub> were exploited to synthesize antibacterial epoxy acrylate copolymer@nano-TiO<sub>2</sub> composite particles (PKE@NT) by carrying out Pickering emulsion polymerization<sup>130</sup>. Apart from the antibacterial properties, the resulting emulsion demonstrated high adhesion and water absorption properties making them suitable for waterborne antibacterial and humidity controlling interior coatings. The generic approach of introducing bactericidal species into Pickering emulsions provides unique opportunities for environmentally friendly and energy-efficient wastewater treatment applications.



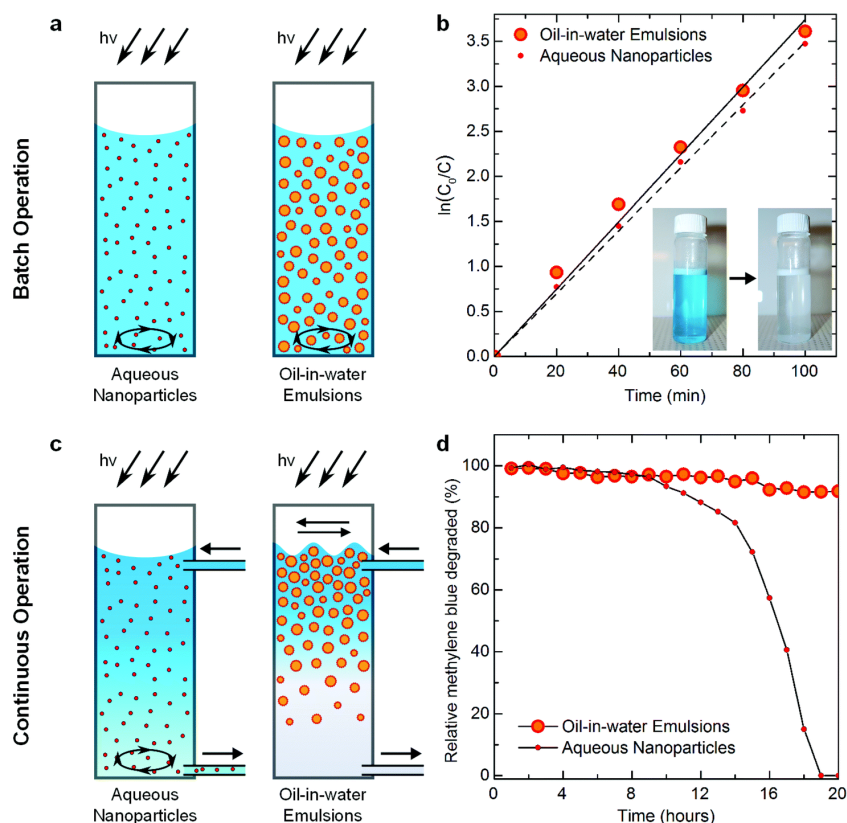
**Fig. 13.** a) Working mechanism of CNF/PLA/PANI aerogel assisted water treatment, b) Ion concentration change before and after desalination Reprinted with permission from<sup>131</sup>. Copyright 2020 American Chemical Society.

A novel water evaporation-based technology was displayed by S. Li et al.<sup>131</sup>, where Pickering emulsions were used to synthesize a light absorbing cellulose nanofibril/poly(lactic acid)/polyaniline (CNF/PLA/PANI) hybrid aerogel as a self-floating photothermal device for solar steam generation

(Fig. 13a). The evaporation was carried out under the irradiation of 1 sun with the aerogel maintaining temperatures up to 105 °C, which resulted in an evaporation rate up to 1.58 kg m<sup>-2</sup> h<sup>-1</sup>. Overall, the aerogel exhibited an excellent performance durability and structural integrity over the multiple cycles it was used. The experiments carried out on 3 wt. % mixed salt solutions indicated a noticeable reduction in the concentrations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> making the purified water compliant with the WHO safe drinking water standard and the US Environmental Protection Agency (EPA) standard (Fig. 13b)<sup>177</sup>. The same principle can be further expanded into organic pollutant removal: the absorption peaks at 464 and 550 nm corresponding to water contaminated with methyl orange and rhodamine B, respectively, disappeared after collecting the purified water. These observations confirmed high purification ability of CNF/PLA/ PANI aerogels towards a wide range of pollutants in wastewater.

Finally, despite the photocatalytic route for organic pollutant degradation being regarded as the leading catalytic approach, other types of catalytic reactions can be just as useful to exploit. Janus-like amphiphilic carbon nanotubes (CNTs) were tested as catalysts in the oxidation of 2-nitrophenol (2-NP) with hydrogen peroxide<sup>116</sup>. The reaction would take place at the biphasic oil-water interface, where 2-NP would be continuously fed from the oil phase due to the disappearance of it in the aqueous phase. Similarly, Ag-decorated cellulose nanofibers (ACNF@Ag) were used as Pickering emulsifiers to demonstrate the feasibility of continuous flow catalysis by reducing organic pollutants (4-nitrophenol (4-NP), methylene blue (MB), and methyl orange (MO)) with sodium borohydride (NaBH<sub>4</sub>)<sup>117</sup>. Very high conversion rates were obtained for 4-NP (>98%, 50 h), MB (>99%, 30 h), and MO (>96%, 40 h). This example illustrates the potential of Pickering emulsion-based continuous flow approach as a viable framework for other means of industrial wastewater treatment solutions.

## 5. Pickering emulsions in flow



**Fig. 14** Comparison of an oil-in-water SNPR with a dispersed aqueous nanoparticle suspension under batch and continuous operation. (a) Schematics of methylene blue degradation in a well stirred (fully dispersed) batch reactor using aqueous and emulsion-based photocatalysts. (b) Dye degradation over time for both fully dispersed batch reactors. (c) Schematics of methylene blue degradation in continuous reactors with aqueous and emulsion-based photocatalysts. (d) Comparison of the percentage of methylene blue degraded over time for each reactor with a continuous inlet flow of 60 mL h<sup>-1</sup> of 4 μM methylene blue. Reprinted from<sup>113</sup> with permission from Royal Society of Chemistry.

The majority of applications presented in this review have been based upon wastewater treatment under batch operation, which is not the preferred mode of operation for industrial applications<sup>178</sup>. The product separation and emulsion regeneration challenges are often tackled with advanced particle engineering techniques, which are cost inefficient. Having a continuous flow system would remove the need for sophisticated materials, increase the conversion, selectivities and simplify the product separation by enabling the collection of the treated water at the outlet of the reactor<sup>113</sup>. Furthermore, focusing on mass-transfer limitations is becoming a more effective route in Pickering emulsion development for targeted applications<sup>113,179,180</sup>.

A pioneering work was done by Burdyny et al. demonstrating the enhanced photocatalytic performance in flow by titania stabilized Pickering emulsions<sup>113</sup>. Initially, the degradation of methylene blue under batch conditions was tested to compare the dispersed and emulsified systems both yielding similar reaction rates (Fig. 14a and b). Then, the same conditions were tested in continuous operation indicating a large difference between the dispersed and emulsified systems (Fig. 12c and d). It was later discovered that the dispersed particles were disappearing with the renewal of the continuous case, whereas the emulsion droplets were sufficiently buoyant to maintain the lower portion of the reactor effectively nanoparticle free. As predicted, the collected outlet stream contained only reaction products, and enabled steady-state operation with no detectable loss of photocatalyst. The study illustrates the stability and scalability of the process



aiming to reduce the costs and complexity of the most state-of-the-art solutions being published. Several other reports on the PE stability, droplet sizes and catalytic performance under continuous flow have been published in the recent years, but its full potential has not been fully explored yet<sup>29,164,181,182</sup>.

## 6. Outlook

There has been a breakthrough in the last couple of decades in terms of the research effort put into developing functional materials based on Pickering emulsions. The emulsions can nowadays be synthesized in various forms and shapes ranging from simplistic O/W emulsions with spherical particles to microbowl-stabilized double emulsions. The original purpose of these emulsions has also been changing from the direct usage to well-defined framework structures used for subsequent polymerization and fabrication of novel materials.

With the rise of potential uses of Pickering emulsions, many studies are now focused on optimizing the current PE systems by improving the emulsion stability and tailoring the functional properties for a cost-effective and easily scalable solution in an industrial setting. Understanding the influence of key descriptors such as particle wettability, concentration or oil/water volume fraction is crucial for the development of novel wastewater treatment systems that could compete with the conventionally used methods. Besides, there is still enough room for fabricating novel materials with interesting properties and morphologies. For example, only a few examples exist with Janus particles, which could combine several pollutant degradation techniques together. Another interesting field is the use of organic and bioparticles to stabilize emulsions: some bioparticles (e.g., starch) have already been reported to act as Pickering emulsifiers. While the conventional surfactants for emulsions stability are efficient, it is necessary to phase them out to reduce volatile organic compounds and carbon footprints. Incorporating these particles into wastewater treatment processes would eliminate the need for sophisticated particle recovery steps as well as provide a cheap, bio-friendly, and simplistic alternative.

More fundamental studies on emulsion stability could help to assess the impacts of varying particle shape and morphology since most studies rely on the behavior described for spherical particles. This research could be extended to mass transfer effects, which are becoming more important with the approaching limits of particle efficacy. A comprehensive analysis of packing effects and their implications on pollutant mass transfer across the particle-stabilized interfaces could help to design effective Pickering emulsion systems.

Regarding the individual applications, much effort has been made to develop porous adsorbents based on the polyHIPEs technology as well as the photocatalytic PEs focused on pollutant degradation in wastewaters. Despite the progress, there are still many technological and economic obstacles that impede the transition from the laboratory scale to industry as the proposed techniques are generally too costly and complex for upscaling. The photocatalytic route, for instance, could be improved in terms of the light absorption ranges, reusability, and the costs of material production. Similar trends exist for other applications, where cost-effectiveness remains a challenge even though the mechanism of action is much more efficient compared to the currently used analogs. Recently, Pickering emulsions have been used to carry out catalytic reactions in a continuous flow setup, which would enable the polluted water to be injected from the inlet and the purified water collected from the outlet<sup>113</sup>. The proven feasibility of the application would eliminate the need for separation of the purified water as opposed to the static approach, which is both time-

and energy-consuming. Furthermore, the systems used for the applications could be greatly simplified for a potential technology transfer to industry.

## 7. Conclusions

Pickering emulsions have emerged as a versatile framework used for the preparation of functional materials suitable for various means of wastewater treatment. The unique features such as high surface area, stability, easy production and tunability make them very attractive as precursors in applications alternative to traditional methods that often suffer from performance and recovery limitations. Despite the individual challenges, the extrapolated benefits each method could bring on an industrial scale puts this field at the forefront of research interest.

The primary objective in fabricating these materials has been identified to be the ability to form stable emulsions, which is a challenge on its own due to a highly interlinked nature of the critical emulsion stability parameters. Analysis of these parameters enlightened the importance of particle wettability, morphology, oil/water volume fraction, concentration, size, shape, the ionic strength, and the pH opening wide opportunities for tuning the emulsions type, droplet sizes and their stability. A wide range of demulsification methods has been presented resulting from surface functionalization of solid particles. These methods serve as a basis for reusability and efficient particle recovery.

Given the progress made in the development of Pickering emulsions, more studies are needed on the optimization of the developed methods aiming to create cost-effective and easily scalable systems offering advantages over the conventionally used wastewater treatment techniques. The increased knowledge of Pickering emulsions and their applications is expected to promote their use in industry.

## 8. Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## 10. Bibliography

1. Kim, K. H. & Ihm, S. K. Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review. *J Hazard Mater* **186**, 16–34 (2011).
2. Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J. & Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catal Today* **147**, 1–59 (2009).
3. Rockström, J. *et al.* Planetary Boundaries: Exploring the Safe Operating Space for Humanity. **14**, (2009).
4. Harris, J. *et al.* The Top Ten of the Toxic Twenty Blacksmith Institute's The World's Worst Toxic Pollution Problems Produced in collaboration with Green Cross Switzerland.
5. Wintgens, T., Salehi, F., Hochstrat, R. & Melin, T. Emerging contaminants and treatment options in water recycling for indirect potable use. *Water Science and Technology* **57**, 99–107 (2008).
6. Suárez, S., Carballa, M., Omil, F. & Lema, J. M. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Rev Environ Sci Biotechnol* **7**, 125–138 (2008).
7. Fan, J., Wu, H., Liu, R., Meng, L. & Sun, Y. Review on the treatment of organic wastewater by discharge plasma combined with oxidants and catalysts. *Environmental Science and Pollution Research 2020 28:3* **28**, 2522–2548 (2020).
8. Nzila, A., Razzak, S. A., Zhu, J., Bhamidimarri, R. & Tota-Maharaj, K. Bioaugmentation: An Emerging Strategy of Industrial Wastewater Treatment for Reuse and Discharge. *International Journal of Environmental Research and Public Health 2016, Vol. 13, Page 846* **13**, 846 (2016).
9. Mishra, L., Paul, K. K. & Jena, S. Coke wastewater treatment methods: Mini review. *Journal of the Indian Chemical Society* **98**, (2021).
10. Neff, J., Lee, K. & DeBlois, E. M. Produced Water: Overview of Composition, Fates, and Effects. in *Produced Water* (2011). doi:10.1007/978-1-4614-0046-2\_1.
11. Thomas, K. v., Langford, K., Petersen, K., Smith, A. J. & Tollefsen, K. E. Effect-directed identification of naphthenic acids as important in vitro xeno-estrogens and anti-androgens in North Sea offshore produced water discharges. *Environ Sci Technol* **43**, 8066–8071 (2009).
12. Casani, S., Rouhany, M. & Knøchel, S. A discussion paper on challenges and limitations to water reuse and hygiene in the food industry. *Water Res* **39**, 1134–1146 (2005).
13. Bixio, D. *et al.* Wastewater reuse in Europe. *Desalination* **187**, 89–101 (2006).
14. Dias, E. M. & Petit, C. Towards the use of metal-organic frameworks for water reuse: a review of the recent advances in the field of organic pollutants removal and degradation and the next steps in the field. (2015) doi:10.1039/c5ta05440k.
15. Awad, A. M. *et al.* Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *Sep Purif Technol* **228**, 115719 (2019).

16. Ashraf, M. I. *et al.* Integrated treatment of pharmaceutical effluents by chemical coagulation and ozonation. *Sep Purif Technol* **158**, 383–386 (2016).
17. Yang, M. & Zheng, S. Pollutant removal-oriented yeast biomass production from high-organic-strength industrial wastewater: A review. *Biomass and Bioenergy* vol. 64 356–362 Preprint at <https://doi.org/10.1016/j.biombioe.2014.03.020> (2014).
18. Sun, G. *et al.* Enhanced removal of nitrate and refractory organic pollutants from bio-treated coking wastewater using corncobs as carbon sources and biofilm carriers. *Chemosphere* **237**, (2019).
19. Epa, U., Supply, W., Resources Division, W. & Smith, C. 2012 Guidelines for Water Reuse. (2012).
20. Jain, K., Patel, A. S., Pardhi, V. P. & Flora, S. J. S. Nanotechnology in Wastewater Management: A New Paradigm Towards Wastewater Treatment. *Molecules* **2021**, Vol. 26, Page 1797 **26**, 1797 (2021).
21. Peng, H., Volchek, K., MacKinnon, M., Wong, W. P. & Brown, C. E. Application on to nanofiltration to water management options for oil sands operation. *Desalination* **170**, 137–150 (2004).
22. Kim, E. S., Liu, Y. & Gamal El-Din, M. Evaluation of membrane fouling for in-line filtration of oil sands process-affected water: The effects of pretreatment conditions. *Environ Sci Technol* **46**, 2877–2884 (2012).
23. Martin, J. W. *et al.* Ozonation of oil sands process-affected water accelerates microbial bioremediation. *Environ Sci Technol* **44**, 8350–8356 (2010).
24. Pourrezaei, P. *et al.* The Impact of Metallic Coagulants on the Removal of Organic Compounds from Oil Sands Process-Affected Water. *Environ. Sci. Technol* **45**, 8452–8459 (2011).
25. Wang, B. *et al.* Occurrences and Behaviors of Naphthenic Acids in a Petroleum Refinery Wastewater Treatment Plant. (2015) doi:10.1021/es505809g.
26. Fauzi Ismail, A. & Sean Goh, P. Chemistry in the Environment Series No. 3 Functional Hybrid Nanomaterials for Environmental Remediation Edited by. (2021) doi:10.1039/9781839165283-00001.
27. Zhang, Y. *et al.* Nanomaterials-enabled water and wastewater treatment. *NanoImpact* **3–4**, 22–39 (2016).
28. Chenab, K. K., Sohrabi, B., Jafari, A. & Ramakrishna, S. Water treatment: functional nanomaterials and applications from adsorption to photodegradation. *Mater Today Chem* **16**, (2020).
29. Rodriguez, A. M. B. & Binks, B. P. Catalysis in Pickering emulsions. *Soft Matter* vol. 16 10221–10243 Preprint at <https://doi.org/10.1039/d0sm01636e> (2020).
30. Bago Rodriguez, A. M. & Binks, B. P. Capsules from Pickering emulsion templates. *Curr Opin Colloid Interface Sci* **44**, 107–129 (2019).
31. Binks, B. P. & Lumsdon, S. O. Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir* **16**, 8622–8631 (2000).

32. Aveyard, R., Binks, B. P. & Clint, J. H. *Emulsions stabilised solely by colloidal particles*. *Advances in Colloid and Interface Science* vol. 100 (2003).
33. Mohaghegh, N., Tasviri, M., Rahimi, E. & Gholami, M. R. A novel p-n junction Ag<sub>3</sub>PO<sub>4</sub>/BiPO<sub>4</sub>-based stabilized Pickering emulsion for highly efficient photocatalysis. *RSC Adv* **5**, 12944–12955 (2015).
34. Thompson, K. L. *et al.* Vermicious thermo-responsive Pickering emulsifiers. *Chem Sci* **6**, (2015).
35. Gonzalez Ortiz, D., Pochat-Bohatier, C., Cambedouzou, J., Bechelany, M. & Miele, P. Current Trends in Pickering Emulsions: Particle Morphology and Applications. *Engineering* vol. 6 468–482 Preprint at <https://doi.org/10.1016/j.eng.2019.08.017> (2020).
36. Qu, Y., Sun, D. & Yu, Y. Interfacial engineering in Pickering emulsion photocatalytic microreactors: From mechanisms to prospects. *Chemical Engineering Journal* vol. 438 Preprint at <https://doi.org/10.1016/j.cej.2022.135655> (2022).
37. Hussein, M. A., Mohammed, A. A. & Atiya, M. A. Application of emulsion and Pickering emulsion liquid membrane technique for wastewater treatment: an overview. *Environmental Science and Pollution Research* vol. 26 36184–36204 Preprint at <https://doi.org/10.1007/s11356-019-06652-3> (2019).
38. Li, Q. *et al.* One-step construction of Pickering emulsion via commercial TiO<sub>2</sub> nanoparticles for photocatalytic dye degradation. *Appl Catal B* **249**, 1–8 (2019).
39. López-Pedrouso, M., Lorenzo, J. M., Moreira, R. & Franco, D. Potential applications of Pickering emulsions and high internal-phase emulsions (HIPEs) stabilized by starch particles. *Curr Opin Food Sci* **46**, (2022).
40. Li, W. *et al.* Recent Advances on Pickering Emulsions Stabilized by Diverse Edible Particles: Stability Mechanism and Applications. *Front Nutr* **9**, 738 (2022).
41. Monégier du Sorbier, Q., Aimable, A. & Pagnoux, C. Influence of the electrostatic interactions in a Pickering emulsion polymerization for the synthesis of silica-polystyrene hybrid nanoparticles. *J Colloid Interface Sci* **448**, 306–314 (2015).
42. Menon, V. B. & Wasan, D. T. Characterization of oil–water interfaces containing finely divided solids with applications to the coalescence of water-in-oil Emulsions: A review. *Colloids and Surfaces* **29**, 7–27 (1988).
43. Binks, B. P. & Clint, J. H. Solid Wettability from Surface Energy Components: Relevance to Pickering Emulsions. (2002) doi:10.1021/la011420k.
44. Binks, B. P. & Horozov, T. S. *Colloidal particles at liquid interfaces*. *Colloidal Particles at Liquid Interfaces* vol. 9780521848466 (2006).
45. Rayner, M. *et al.* Biomass-based particles for the formulation of Pickering type emulsions in food and topical applications. *Colloids Surf A Physicochem Eng Asp* **458**, 48–62 (2014).
46. Aveyard, R. Can Janus particles give thermodynamically stable Pickering emulsions? *Soft Matter* **8**, 5233–5240 (2012).

47. Binks, B. P. Particles as surfactants—similarities and differences. *Curr Opin Colloid Interface Sci* **7**, 21–41 (2002).
48. Binks, B. P. Colloidal Particles at a Range of Fluid-Fluid Interfaces. *Langmuir* **33**, 6947–6963 (2017).
49. Levine, S., Bowen, B. D. & Partridge, S. J. Stabilization of emulsions by fine particles I. Partitioning of particles between continuous phase and oil/water interface. *Colloids and Surfaces* **38**, 325–343 (1989).
50. Larson-Smith, K. & Pozzo, D. C. Pickering Emulsions Stabilized by Nanoparticle Surfactants. (2012) doi:10.1021/la301896c.
51. Chevalier, Y. & Bolzinger, M. A. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids Surf A Physicochem Eng Asp* **439**, 23–34 (2013).
52. Binks, B. P., Rodrigues, J. A. & Frith, W. J. Synergistic interaction in emulsions stabilized by a mixture of silica nanoparticles and cationic surfactant. *Langmuir* **23**, 3626–3636 (2007).
53. Binks, B. P. & Rodrigues, J. A. Enhanced stabilization of emulsions due to surfactant-induced nanoparticle flocculation. *Langmuir* **23**, 7436–7439 (2007).
54. Midmore, B. R. Preparation of a novel silica-stabilized oil/water emulsion. *Colloids Surf A Physicochem Eng Asp* **132**, 257–265 (1998).
55. Kawazoe, A. & Kawaguchi, M. Characterization of silicone oil emulsions stabilized by TiO<sub>2</sub> suspensions pre-adsorbed SDS. *Colloids Surf A Physicochem Eng Asp* **392**, 283–287 (2011).
56. Frelichowska, J., Bolzinger, M. A. & Chevalier, Y. Pickering emulsions with bare silica. *Colloids Surf A Physicochem Eng Asp* **343**, 70–74 (2009).
57. Albert, C. *et al.* Pickering emulsions: Preparation processes, key parameters governing their properties and potential for pharmaceutical applications. doi:10.1016/j.jconrel.2019.07.003i.
58. Arnaudov, L. N., Cayre, O. J., Cohen Stuart, M. A., Stoyanov, S. D. & Paunov, V. N. Measuring the three-phase contact angle of nanoparticles at fluid interfaces. *Physical Chemistry Chemical Physics* **12**, 328–331 (2009).
59. Isa, L., Lucas, F., Wepf, R. & Reimhult, E. Measuring single-nanoparticle wetting properties by freeze-fracture shadow-casting cryo-scanning electron microscopy. *Nature Communications* **2011 2:1** **2**, 1–9 (2011).
60. Binks, B. P. & Lumsdon, S. O. Effects of oil type and aqueous phase composition on oil–water mixtures containing particles of intermediate hydrophobicity. *Physical Chemistry Chemical Physics* **2**, 2959–2967 (2000).
61. Read, E. S., Fujii, S., Amalvy, J. I., Randall, D. P. & Armes, S. P. Effect of varying the oil phase on the behavior of pH-responsive latex-based emulsifiers: Demulsification versus transitional phase inversion. *Langmuir* **20**, 7422–7429 (2004).
62. Fessi, N. *et al.* Photocatalytic degradation enhancement in pickering emulsions stabilized by solid particles of bare TiO<sub>2</sub>. *Langmuir* **35**, 2129–2136 (2019).
63. Tsuji, S. & Kawaguchi, H. Thermosensitive pickering emulsion stabilized by poly(N-isopropylacrylamide)-carrying particles. *Langmuir* **24**, 3300–3305 (2008).

64. Tsabet, È. & Fradette, L. Effect of the properties of oil, particles, and water on the production of Pickering emulsions. *Chemical Engineering Research and Design* **97**, 9–17 (2015).
65. He, Y. *et al.* Factors that affect pickering emulsions stabilized by graphene oxide. *ACS Appl Mater Interfaces* **5**, 4843–4855 (2013).
66. Liu, F. & Tang, C.-H. Phytosterol Colloidal Particles as Pickering Stabilizers for Emulsions. (2014) doi:10.1021/jf404930c.
67. Arditty, S., Whitby, C. P., Binks, B. P., Schmitt, V. & Leal-Calderon, F. Some general features of limited coalescence in solid-stabilized emulsions. *The European Physical Journal E* **2003 11:3 11**, 273–281 (2018).
68. Basavaraj, M. G., Fuller, G. G., Fransaeer, J. & Vermant, J. Packing, Flipping, and Buckling Transitions in Compressed Monolayers of Ellipsoidal Latex Particles. (2006) doi:10.1021/la060465o.
69. Donev, A. *et al.* Improving the Density of Jammed Disordered Packings Using Ellipsoids. *Science (1979)* **303**, 990–993 (2004).
70. Rao Dugyala, V., Daware, S. v & Basavaraj, M. G. Shape anisotropic colloids: synthesis, packing behavior, evaporation driven assembly, and their application in emulsion stabilization. doi:10.1039/c3sm50404b.
71. Kim, I., Worthen, A. J., Johnston, K. P., DiCarlo, D. A. & Huh, C. Size-dependent properties of silica nanoparticles for Pickering stabilization of emulsions and foams. *Journal of Nanoparticle Research* **18**, 1–12 (2016).
72. Nan, F. *et al.* Preparation of uniform-sized colloidosomes based on chitosan-coated alginate particles and its application for oral insulin delivery. *J Mater Chem B* **2**, 7403–7409 (2014).
73. Binks, B. P. & Lumsdon, S. O. Pickering emulsions stabilized by monodisperse latex particles: Effects of particle size. *Langmuir* **17**, 4540–4547 (2001).
74. Ge, S. *et al.* Characterizations of Pickering emulsions stabilized by starch nanoparticles: Influence of starch variety and particle size. *Food Chem* **234**, 339–347 (2017).
75. Tang, M., Wu, T., Xu, X., Zhang, L. & Wu, F. Factors that affect the stability, type and morphology of Pickering emulsion stabilized by silver nanoparticles/graphene oxide nanocomposites. *Mater Res Bull* **60**, 118–129 (2014).
76. Feitosa, E. *et al.* Structural organization of cetyltrimethylammonium sulfate in aqueous solution: The effect of Na<sub>2</sub>SO<sub>4</sub>. *J Colloid Interface Sci* **299**, 883–889 (2006).
77. Hao, Y. *et al.* A pH-responsive TiO<sub>2</sub>-based Pickering emulsion system for in situ catalyst recycling. *Chinese Chemical Letters* **29**, 778–782 (2018).
78. Rodrigues, E. C., Morales, M. A., de Medeiros, S. N., Suguihiro, N. M. & Baggio-Saitovitch, E. M. Pluronic® coated sterically stabilized magnetite nanoparticles for hyperthermia applications. *J Magn Magn Mater* **416**, 434–440 (2016).
79. Suk, J. S., Xu, Q., Kim, N., Hanes, J. & Ensign, L. M. PEGylation as a strategy for improving nanoparticle-based drug and gene delivery. *Adv Drug Deliv Rev* **99**, 28 (2016).

80. Hatchell, D., Song, W. & Daigle, H. Examining the role of salinity on the dynamic stability of Pickering emulsions. *J Colloid Interface Sci* **608**, 2321–2329 (2022).
81. Li, S. *et al.* Edible mayonnaise-like Pickering emulsion stabilized by pea protein isolate microgels: Effect of food ingredients in commercial mayonnaise recipe. *Food Chem* **376**, (2022).
82. Liu, F. & Tang, C. H. Soy protein nanoparticle aggregates as pickering stabilizers for oil-in-water emulsions. *J Agric Food Chem* **61**, 8888–8898 (2013).
83. de Folter, J. W. J., van Ruijven, M. W. M. & Velikov, K. P. Oil-in-water Pickering emulsions stabilized by colloidal particles from the water-insoluble protein zein. *Soft Matter* **8**, 6807–6815 (2012).
84. Binks, B. P. & Lumsdon, S. O. Catastrophic phase inversion of water-in-oil emulsions stabilized by hydrophobic silica. *Langmuir* **16**, 2539–2547 (2000).
85. Yang, H. *et al.* Rapid demulsification of pickering emulsions triggered by controllable magnetic field. *Scientific Reports* 2020 10:1 **10**, 1–7 (2020).
86. Yu, S. *et al.* Biphasic biocatalysis using a CO<sub>2</sub>-switchable Pickering emulsion. *Green Chemistry* **21**, 4062–4068 (2019).
87. Wang, C. *et al.* Superwetable porous spheres prepared by recyclable Pickering emulsion polymerization for multifarious oil/water separations †. (2021) doi:10.1039/d0gc04147e.
88. Li, Z. *et al.* Light-Responsive, Reversible Emulsification and Demulsification of Oil-in-Water Pickering Emulsions for Catalysis. *Angewandte Chemie - International Edition* **60**, 3928–3933 (2021).
89. Yang, Y., Priyadarshani, N., Khamaturova, T., Suriboot, J. & Bergbreiter, D. E. Polyethylene as a nonvolatile solid cosolvent phase for catalyst separation and recovery. *J Am Chem Soc* **134**, 14714–14717 (2012).
90. Yang, H., Zhou, T. & Zhang, W. A Strategy for Separating and Recycling Solid Catalysts Based on the pH-Triggered Pickering-Emulsion Inversion. *Angewandte Chemie* **125**, 7603–7607 (2013).
91. Du, K., Glogowski, E., Emrick, T., Russell, T. P. & Dinsmore, A. D. Adsorption energy of nano- and microparticles at liquid-liquid interfaces. *Langmuir* **26**, 12518–12522 (2010).
92. Huang, J., Cheng, F., Binks, B. P. & Yang, H. PH-Responsive Gas-Water-Solid Interface for Multiphase Catalysis. *J Am Chem Soc* **137**, 15015–15025 (2015).
93. Wang, F. *et al.* Dual pH-and Light-Responsive Amphiphilic Random Copolymer Nanomicelles as Particulate Emulsifiers to Stabilize the Oil/Water Interface. *Journal of Physical Chemistry C* **122**, 18995–19003 (2018).
94. Shi, Y. *et al.* Highly Efficient and Reversible Inversion of a Pickering Emulsion Triggered by CO<sub>2</sub>/N<sub>2</sub> at Ambient Conditions. *ACS Sustain Chem Eng* **6**, 15383–15390 (2018).
95. Jiang, J., Ma, Y., Cui, Z. & Binks, B. P. Pickering Emulsions Responsive to CO<sub>2</sub>/N<sub>2</sub> and Light Dual Stimuli at Ambient Temperature. *Langmuir* **32**, (2016).



96. Binks, B. P., Murakami, R., Armes, S. P. & Fujii, S. Temperature-Induced Inversion of Nanoparticle-Stabilized Emulsions. *Angewandte Chemie International Edition* **44**, 4795–4798 (2005).
97. Lin, Z., Zhang, Z., Li, Y. & Deng, Y. Magnetic nano-Fe<sub>3</sub>O<sub>4</sub> stabilized Pickering emulsion liquid membrane for selective extraction and separation. *Chemical Engineering Journal* **288**, 305–311 (2016).
98. Mohammed, S. A. M., Zouli, N. & Al-Dahhan, M. Removal of benzoic acid from wastewater by pickering emulsion liquid membrane stabilized by magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles. *Desalination Water Treat* **68**, (2017).
99. Zhang, J., Li, Y., Bao, M., Yang, X. & Wang, Z. Facile Fabrication of Cyclodextrin-Modified Magnetic Particles for Effective Demulsification from Various Types of Emulsions. *Environ Sci Technol* **50**, 8809–8816 (2016).
100. Zhao, C. *et al.* Ca<sup>2+</sup> ion responsive pickering emulsions stabilized by PSSMA nanoaggregates. *Langmuir* **29**, 14421–14428 (2013).
101. Low, L. E., Ooi, C. W., Chan, E. S., Ong, B. H. & Tey, B. T. Dual (magnetic and pH) stimuli-reversible Pickering emulsions based on poly(2-(dimethylamino)ethyl methacrylate)-bonded Fe<sub>3</sub>O<sub>4</sub> nanocomposites for oil recovery application. *J Environ Chem Eng* **8**, (2020).
102. Bai, R. X. *et al.* Light-Triggered Release from Pickering Emulsions Stabilized by TiO<sub>2</sub> Nanoparticles with Tailored Wettability. *Langmuir* **32**, 9254–9264 (2016).
103. Dyab, A. K. F. Destabilisation of Pickering emulsions using pH. *Colloids Surf A Physicochem Eng Asp* **402**, 2–12 (2012).
104. Bai, Y. *et al.* Pickering emulsion strategy to control surface wettability of polymer microspheres for oil–water separation. *Appl Surf Sci* **566**, 150742 (2021).
105. Liu, H., Wang, C., Zou, S., Wei, Z. & Tong, Z. Simple, reversible emulsion system switched by pH on the basis of chitosan without any hydrophobic modification. *Langmuir* **28**, 11017–11024 (2012).
106. Alargova, R. G., Warhadpande, D. S., Paunov, V. N. & Velev, O. D. Foam superstabilization by polymer microrods. *Langmuir* **20**, (2004).
107. Vashisth, C., Whitby, C. P., Fornasiero, D. & Ralston, J. Interfacial displacement of nanoparticles by surfactant molecules in emulsions. *J Colloid Interface Sci* **349**, 537–543 (2010).
108. Mackie, A. R., Ridout, M. J., Moates, G., Husband, F. A. & Wilde, P. J. Effect of the interfacial layer composition on the properties of emulsion creams. *J Agric Food Chem* **55**, 5611–5619 (2007).
109. Reynaert, S., Moldenaers, P. & Vermant, J. Control over colloidal aggregation in monolayers of latex particles at the oil-water interface. *Langmuir* **22**, (2006).
110. Voisin, H., Falourd, X., Rivard, C. & Capron, I. Versatile nanocellulose-anatase TiO<sub>2</sub> hybrid nanoparticles in Pickering emulsions for the photocatalytic degradation of organic and aqueous dyes. *JCIS Open* **3**, (2021).

111. Zhang, X. *et al.* One-step dye wastewater treatment by combined adsorption, extraction, and photocatalysis using g-C<sub>3</sub>N<sub>4</sub> pickering emulsion. *Colloids Surf A Physicochem Eng Asp* **644**, (2022).
112. Anusuyadevi, P. R., Riazanova, A. v., Hedenqvist, M. S. & Svagan, A. J. Floating photocatalysts for effluent refinement based on stable pickering cellulose foams and graphitic carbon nitride (g-c<sub>3</sub>n<sub>4</sub>). *ACS Omega* **5**, 22411–22419 (2020).
113. Burdyny, T., Riordon, J., Dinh, C. T., Sargent, E. H. & Sinton, D. Self-assembled nanoparticle-stabilized photocatalytic reactors. *Nanoscale* **8**, 2107–2115 (2016).
114. Wu, W., Gao, S., Tu, W., Chen, J. & Zhang, P. Intensified photocatalytic degradation of nitrobenzene by Pickering emulsion of ZnO nanoparticles. *Particuology* **8**, 453–457 (2010).
115. Zhang, S., Xu, J., Hu, J., Cui, C. & Liu, H. Interfacial Growth of TiO<sub>2</sub>-rGO Composite by Pickering Emulsion for Photocatalytic Degradation. *Langmuir* **33**, 5015–5024 (2017).
116. Diaz de Tuesta, J. L. *et al.* Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide. *Catal Today* **356**, 205–215 (2020).
117. Peng, F., Xu, J., Xu, H. & Bao, H. Electrostatic Interaction-Controlled Formation of Pickering Emulsion for Continuous Flow Catalysis. *Cite This: ACS Appl. Mater. Interfaces* **13**, 1872–1882 (2021).
118. Pan, J. *et al.* Molecularly imprinted polymer foams with well-defined open-cell structure derived from Pickering HIPEs and their enhanced recognition of  $\lambda$ -cyhalothrin. *Chemical Engineering Journal* **253**, 138–147 (2014).
119. Pan, J. *et al.* Wulff-type boronic acids suspended hierarchical porous polymeric monolith for the specific capture of cis-diol-containing flavone under neutral condition. *Chemical Engineering Journal* **317**, 317–330 (2017).
120. Wang, Z. *et al.* Polymerization induced shaping of Pickering emulsion droplets: From simple hollow microspheres to molecularly imprinted multicore microrattles. *Chemical Engineering Journal* **332**, 409–418 (2018).
121. Mert, E. H., Yildirim, H., Üzümcü, A. T. & Kavas, H. Synthesis and characterization of magnetic polyHIPEs with humic acid surface modified magnetic iron oxide nanoparticles. *React Funct Polym* **73**, 175–181 (2013).
122. Pribyl, J. *et al.* Photoinitiated Polymerization of 4-Vinylpyridine on polyHIPE Foam Surface toward Improved Pu Separations. *Anal. Chem* **89**, 14 (2017).
123. Han, C., Li, Y., Wang, W., Hou, Y. & Chen, D. Dual-functional Ag<sub>3</sub>PO<sub>4</sub>@palygorskite composite for efficient photodegradation of alkane by in situ forming Pickering emulsion photocatalytic system. *Science of the Total Environment* **704**, (2020).
124. Song, M.-L. *et al.* Multibranch Strategy To Decorate Carboxyl Groups on Cellulose Nanocrystals To Prepare Adsorbent/Flocculants and Pickering Emulsions. (2019) doi:10.1021/acssuschemeng.8b06671.
125. Hafenstine, G. R. *et al.* Solar Photocatalytic Phenol Polymerization and Hydrogen Generation for Flocculation of Wastewater Impurities. (2019) doi:10.1021/acsapm.9b00210.

126. Perumal, M., Soundarajan, B. & Thazhathuveetil Vengara, N. Extraction of Cr (VI) by pickering emulsion liquid membrane using amphiphilic silica nanowires (ASNWs) as a surfactant. *J Dispers Sci Technol* **40**, 1046–1055 (2019).
127. Cai, Y. *et al.* A novel strategy to immobilize bacteria on polymer particles for efficient adsorption and biodegradation of soluble organics. *Nanoscale* **9**, 11530–11536 (2017).
128. Li, Y., Feng, X., Zhang, T., Zhou, X. & Li, C. Preparation of magnetic macroporous polymer sphere for biofilm immobilization and biodesulfurization. *React Funct Polym* **141**, 1–8 (2019).
129. Wang, J. *et al.* Fabrication of sustained-release and antibacterial citronella oil-loaded composite microcapsules based on Pickering emulsion templates. *J Appl Polym Sci* **135**, 46386 (2018).
130. Zhai, W. *et al.* Preparation of epoxy-acrylate copolymer@nano-TiO<sub>2</sub> Pickering emulsion and its antibacterial activity. *Prog Org Coat* **87**, 122–128 (2015).
131. Li, S. *et al.* Cellulose Nanofibril-Stabilized Pickering Emulsion and in Situ Polymerization Lead to Hybrid Aerogel for High-Efficiency Solar Steam Generation. *ACS Appl Polym Mater* **2**, 4581–4591 (2020).
132. Yan, B. *et al.* Hexagonal Ni(OH)<sub>2</sub> nanosheets for stabilizing Pickering emulsion and Congo red adsorption. *Colloids Surf A Physicochem Eng Asp* **598**, 124828 (2020).
133. Crini, G. Non-conventional low-cost adsorbents for dye removal: A review. (2005) doi:10.1016/j.biortech.2005.05.001.
134. Zhou, Y., Lu, J., Zhou, Y. & Liu, Y. Recent advances for dyes removal using novel adsorbents: A review. *Environmental Pollution* **252**, 352–365 (2019).
135. Qadeer, R. Adsorption behavior of ruthenium ions on activated charcoal from nirtic acid medium. *Colloids Surf A Physicochem Eng Asp* **293**, 217–223 (2007).
136. Piaskowski, K., Świdarska-Dąbrowska, R. & Zarzycki, P. K. Dye Removal from Water and Wastewater Using Various Physical, Chemical, and Biological Processes. *J AOAC Int* **101**, 1371–1384 (2018).
137. Yan, B. *et al.* One-step preparation of hydroxyapatite-loaded magnetic Polycaprolactone hollow microspheres for malachite green adsorption by Pickering emulsion template method. *Colloids Surf A Physicochem Eng Asp* **639**, 128347 (2022).
138. Sun, N. *et al.* Dual-Responsive Pickering Emulsion Stabilized by Fe<sub>3</sub>O<sub>4</sub> Nanoparticles Hydrophobized in Situ with an Electrochemical Active Molecule. *Colloids Surf A Physicochem Eng Asp* **608**, 125588 (2021).
139. Nakato, T. *et al.* Pickering emulsions prepared by layered niobate K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> intercalated with organic cations and photocatalytic dye decomposition in the emulsions. *ACS Appl Mater Interfaces* **4**, 4338–4347 (2012).
140. Zhu, Y., Wang, W., Yu, H. & Wang, A. Preparation of porous adsorbent via Pickering emulsion template for water treatment: A review. *J Environ Sci (China)* **88**, 217–236 (2020).

141. Aldemir Dikici, B. & Claeysens, F. Basic Principles of Emulsion Templating and Its Use as an Emerging Manufacturing Method of Tissue Engineering Scaffolds. *Front Bioeng Biotechnol* **8**, 875 (2020).
142. Mert, E. H., Kaya, A. & Yıldırım, H. Preparation and Characterization of Polyester-Glycidyl Methacrylate PolyHIPE Monoliths to Use in Heavy Metal Removal. *Des Monomers Polym* **15**, 113–126 (2012).
143. Zhu, Y. *et al.* Fast and high-capacity adsorption of Rb<sup>+</sup> and Cs<sup>+</sup> onto recyclable magnetic porous spheres. *Chemical Engineering Journal* **327**, 982–991 (2017).
144. Yang, S., Liu, H. & Zhang, Z. Fabrication of novel multihollow superparamagnetic magnetite/polystyrene nanocomposite microspheres via water-in-oil-in-water double emulsions. *Langmuir* **24**, 10395–10401 (2008).
145. Lee, C. S., Robinson, J. & Chong, M. F. A review on application of flocculants in wastewater treatment. *Process Safety and Environmental Protection* **92**, 489–508 (2014).
146. Okaiyeto, K., Nwodo, U. U., Okoli, S. A., Mabinya, L. v. & Okoh, A. I. Implications for public health demands alternatives to inorganic and synthetic flocculants: bioflocculants as important candidates. *Microbiologyopen* **5**, 177–211 (2016).
147. Mohammed, A. A., Atiya, M. A. & Hussein, M. A. Studies on membrane stability and extraction of ciprofloxacin from aqueous solution using pickering emulsion liquid membrane stabilized by magnetic nano-Fe<sub>2</sub>O<sub>3</sub>. *Colloids Surf A Physicochem Eng Asp* **585**, 124044 (2020).
148. Ng, Y. S., Jayakumar, N. S. & Hashim, M. A. Performance evaluation of organic emulsion liquid membrane on phenol removal. *J Hazard Mater* **184**, 255–260 (2010).
149. Chaouchi, S. & Hamdaoui, O. Extraction of Priority Pollutant 4-Nitrophenol from Water by Emulsion Liquid Membrane: Emulsion Stability, Effect of Operational Conditions and Membrane Reuse. <http://dx.doi.org/10.1080/01932691.2013.844704> **35**, 1278–1288 (2014).
150. Mahmoodi, R., Mohammadi, T. & Moghadam, M. K. Separation of Cd(II) and Ni(II) ions by supported liquid membrane using D2EHPA/M2EHPA as mobile carrier. *Chemical Papers* **68**, 751–756 (2014).
151. Laki, S. & Kargari, A. Extraction of Silver Ions from Aqueous Solutions by Emulsion Liquid Membrane. *Journal of Membrane Science and Research* **2**, 33–40 (2016).
152. Salman, H. M. & Mohammed, A. A. Extraction of lead ions from aqueous solution by co-stabilization mechanisms of magnetic Fe<sub>2</sub>O<sub>3</sub> particles and nonionic surfactants in emulsion liquid membrane. *Colloids Surf A Physicochem Eng Asp* **568**, 301–310 (2019).
153. Ren, G. *et al.* Recent Advances of Photocatalytic Application in Water Treatment: A Review. *Nanomaterials 2021, Vol. 11, Page 1804* **11**, 1804 (2021).
154. Murgolo, S. *et al.* Degradation of emerging organic pollutants in wastewater effluents by electrochemical photocatalysis on nanostructured TiO<sub>2</sub> meshes. *Water Res* **164**, (2019).
155. Bergamini, R. B. M., Azevedo, E. B. & Araújo, L. R. R. de. Heterogeneous photocatalytic degradation of reactive dyes in aqueous TiO<sub>2</sub> suspensions: Decolorization kinetics. *Chemical Engineering Journal* **149**, 215–220 (2009).

156. Bellardita, M. *et al.* Photocatalysis in dimethyl carbonate green solvent: degradation and partial oxidation of phenanthrene on supported TiO<sub>2</sub>. *RSC Adv* **4**, 40859–40864 (2014).
157. Guo, Q. *et al.* Elementary photocatalytic chemistry on TiO<sub>2</sub> surfaces. *Chem Soc Rev* **45**, 3701–3730 (2016).
158. Kočí, K. *et al.* Effect of TiO<sub>2</sub> particle size on the photocatalytic reduction of CO<sub>2</sub>. *Appl Catal B* **89**, 494–502 (2009).
159. Zhai, W., Li, G., Yu, P., Yang, L. & Mao, L. Silver Phosphate/Carbon Nanotube-Stabilized Pickering Emulsion for Highly Efficient Photocatalysis. *Journal of Physical Chemistry C* **117**, 15183–15191 (2013).
160. Szczepanik, B. Photocatalytic degradation of organic contaminants over clay-TiO<sub>2</sub> nanocomposites: A review. *Appl Clay Sci* **141**, 227–239 (2017).
161. Li, H., Tu, W., Zhou, Y. & Zou, Z. Z-Scheme Photocatalytic Systems for Promoting Photocatalytic Performance: Recent Progress and Future Challenges. *Advanced Science* **3**, 1500389 (2016).
162. Nasr, M., Eid, C., Habchi, R., Miele, P. & Bechelany, M. Recent Progress on Titanium Dioxide Nanomaterials for Photocatalytic Applications. *ChemSusChem* **11**, 3023–3047 (2018).
163. Li, D., Kassymova, M., Cai, X., Zang, S. Q. & Jiang, H. L. Photocatalytic CO<sub>2</sub> reduction over metal-organic framework-based materials. *Coord Chem Rev* **412**, 213262 (2020).
164. Sambiagio, C. & Noël, T. Flow Photochemistry: Shine Some Light on Those Tubes! *Trends Chem* **2**, 92–106 (2020).
165. Han, X., MacKinnon, M. D. & Martin, J. W. Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* **76**, 63–70 (2009).
166. Misiti, T. M., Tezel, U., Tandukar, M. & Pavlostathis, S. G. Aerobic biotransformation potential of a commercial mixture of naphthenic acids. *Water Res* **47**, 5520–5534 (2013).
167. Nuhoglu, A. & Yalcin, B. Modelling of phenol removal in a batch reactor. *Process Biochemistry* **40**, 1233–1239 (2005).
168. Shetty, K. V., Kalifathulla, I. & Srinikethan, G. Performance of pulsed plate bioreactor for biodegradation of phenol. *J Hazard Mater* **140**, 346–352 (2007).
169. Vázquez-Rodríguez, G., Youssef, C. ben & Weissman-Vilanova, J. Two-step modeling of the biodegradation of phenol by an acclimated activated sludge. *Chemical Engineering Journal* **117**, 245–252 (2006).
170. Chen, H. Y., Guan, Y. X. & Yao, S. J. A novel two-species whole-cell immobilization system composed of marine-derived fungi and its application in wastewater treatment. *Journal of Chemical Technology & Biotechnology* **89**, 1733–1740 (2014).
171. Feng, Y., Racke, K. D. & Bollag, J. M. Use of immobilized bacteria to treat industrial wastewater containing a chlorinated pyridinol. *Applied Microbiology and Biotechnology* **47**:1, 73–77 (1997).
172. Kariminiaae-Hamedani, H.-R., Kanda, K. & Kato, F. Wastewater treatment with bacteria immobilized onto a ceramic carrier in an aerated system. *J Biosci Bioeng* **95**, 128–132 (2003).

173. Ławniczak, Ł., Kaczorek, E. & Olszanowski, A. The influence of cell immobilization by biofilm forming on the biodegradation capabilities of bacterial consortia. *World J Microbiol Biotechnol* **27**, 1183–1188 (2011).
174. Cheng, H. *et al.* Multi-functional magnetic bacteria as efficient and economical Pickering emulsifiers for encapsulation and removal of oil from water. *J Colloid Interface Sci* **560**, (2020).
175. Wei, L. S. & Wee, W. Chemical composition and antimicrobial activity of *Cymbopogon nardus* citronella essential oil against systemic bacteria of aquatic animals. *Iran J Microbiol* **5**, 147 (2013).
176. Abu Elella, M. H. *et al.* Innovative bactericidal adsorbents containing modified xanthan gum/montmorillonite nanocomposites for wastewater treatment. *Int J Biol Macromol* **167**, 1113–1125 (2021).
177. *Guidelines for THIRD EDITION Drinking-water Quality*. (2004).
178. Wiles, C. & Watts, P. Continuous process technology: a tool for sustainable production. *Green Chemistry* **16**, 55–62 (2013).
179. Wang, F. *et al.* Pickering medium internal phase emulsions based on natural clay particles: Route to a macroporous adsorbent. *J Mol Liq* **322**, 114995 (2021).
180. Fessi, N. *et al.* Pickering Emulsions of Fluorinated TiO<sub>2</sub>: A New Route for Intensification of Photocatalytic Degradation of Nitrobenzene. *Langmuir* **36**, 13545–13554 (2020).
181. Zhang, M. *et al.* Ionic Liquid Droplet Microreactor for Catalysis Reactions Not at Equilibrium. *J Am Chem Soc* **139**, 17387–17396 (2017).
182. Griffith, C. & Daigle, H. A comparison of the static and dynamic stability of Pickering emulsions. *Colloids Surf A Physicochem Eng Asp* **586**, 124256 (2020).