Water Reuse

Removing free-floating oil from water using cationic polymers/surfactant-modified silica

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ABSTRACT

The purpose of this work was to evaluate the efficiency of oil sorption of silica particles modified by three different types of cationic polymers and a cationic surfactant. Low-molecular-weight polyethyleneimine (LPEI), high-molecular-weight polyethyleneimine (HPEI), polydiallyldimethylammonium chloride (PDM), and cetyltrimethylammonium bromide (CTAB) were used to modify the silica particles and then compared their performances for oil removal. The scanning electron microscope and zeta potential measurements were used to analyze the surface characteristics of unmodified and modified silica particles. Adsorptions of motor oil and palm oil on the modified silica particles have been investigated under various parameters such as the silica particle size, the oil concentration, the polymer/surfactant concentrations, and the pH. The results have shown that the modified silica particles enhanced the oil sorption ability by approximately 10–20 times depending on the size of silica particles, pH, and the type of polymer/surfactant used when compared with the unmodified silica particles. The highest palm oil adsorption values of LPEI-silica, HPEI-silica, PDM-silica, CTAB-silica, and unmodified silica were 2.40, 2.10, 1.95, 1.50, and 0.15 g/g_{silica}, respectively. Moreover, the oil sorption of the modified silica particles was increased by approximately 30–50% for the smallest-sized silica particles.

Key words: adsorption efficiency, cetyltrimethylammonium bromide, oil removal, polydiallyldimethylammonium chloride, polyethyleneimine, silica particles

HIGHLIGHTS

- Cationic polymers/surfactant-modified silica particles can enhance the oil sorption by approximately 10–20 times.
- Polymer/surfactant-modified silica can be used to remove both fresh and used oil.
- Low molecular weight of the cationic polymer performed the outstanding oil sorption performance.
- Oil sorption on small particles was 30–50% higher than that of the large particles.
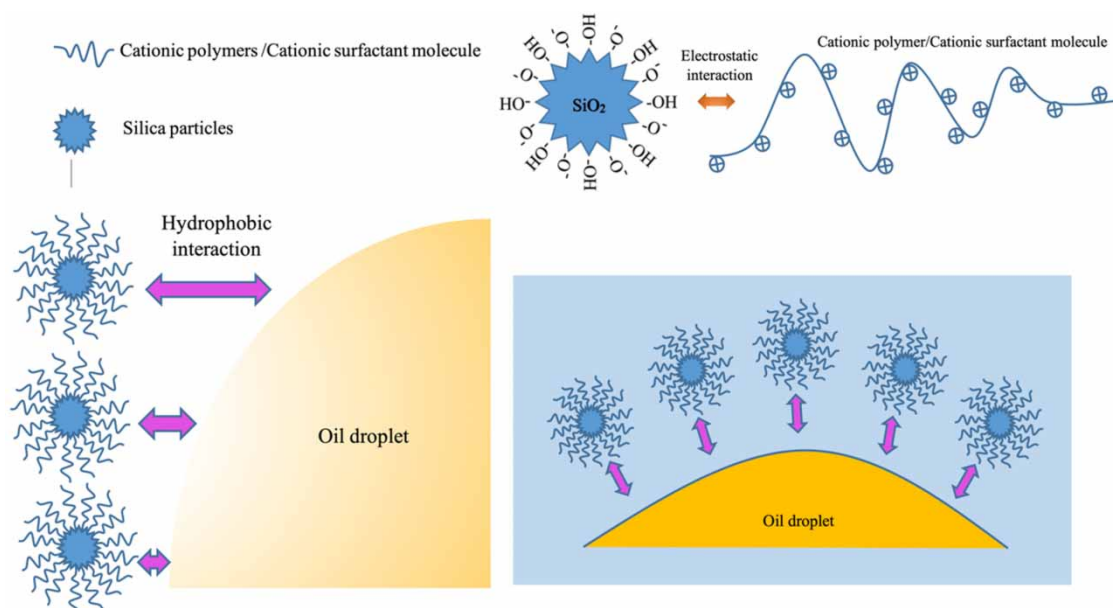
1. INTRODUCTION

Wastewater treatment is currently an important aspect of investigations to meet the targets for sustainable development and clean technology. There are several pollutants that can harm the environment, and oil spill is one of them that can cause severe environmental problems (Putatunda *et al.* 2019). The oil contamination to water emanates from a variety of sources, such as the crude oil production, the oil refining, the waste from the petrochemical industry, the oil running off from roads, the metal processing, the palm oil industry, and the waste from restaurants (German & Svensson 2005; Abd El-Gawad 2014). Some oil components can persist in the environment for a long time when accumulated in sediments, sea life, and wildlife (Akpor *et al.* 2014). Cleaning-up and removing oil spills are difficult, and depends on many factors, especially the type of oil spilled and the temperature of the water (affecting evaporation and biodegradation). Moreover, physical cleaning-up of oil spills is also very expensive (Doshi *et al.* 2018). There are several methods available for the treatment of oil–water emulsions, for example, the coagulation/flocculation followed by air flotation and chemical de-emulsification (Welz *et al.* 2007). These methods are considered as primary methods for water treatment. Meanwhile, there are various methods of oil and grease removal, for example solvent addition (Ahmad *et al.* 2003), coagulation and flocculation with chemicals (Santo *et al.* 2012), electrocoagulation/electroflotation (Yang 2007), and sorption (Ribeiro *et al.* 2003). Adsorption is one of the effective methods for oil spill/oil–water emulsion removal. Various adsorption materials such as plant materials (Deschamps *et al.* 2003), fabric (Anupriyanka *et al.* 2020), foam (Ng *et al.* 2020), polymeric membranes (Krasian *et al.* 2019), bentonite organoclays, and vermiculite (Mueller *et al.* 2003) have been examined for their oil adsorption capacities. Silica in particulate form is an essential biocompatible material that makes it a suitable candidate for several applications when assisted by the surface modification treatment, such as drug delivery (Slowing *et al.* 2008), encapsulating agent for magnetic resonance imaging (Kim *et al.* 2008), dye removal (Ebadi & Rafati 2015), and oil adsorption (Santos *et al.* 2018).

The objective of this study was to remove oil floating on top of the water using the technique based on oil sorption on the modified silica particles. In previous work, polyethyleneimine (PEI)-modified silica particles have shown the potential for use in soybean oil removal (Janhom 2010), while more recent work has emphasized simple surface modification of silica particles using cationic polymers and/or cationic surfactant and subsequently examined their use for oil removal to achieve completeness of oil sorption on the modified silica particles. The investigated factors influencing the oil sorption ability included the types of oil adsorbed, the type of polyelectrolytes, and surfactant used for modification, as well as the size of the silica particles. In this study, the modification of silica particles of two sizes by three different types of cationic polymers and a cationic surfactant was carried out. Consequently, the adsorption of various types of oils was investigated and compared under

different process parameters including the initial oil concentration, the polymer/surfactant concentration, and the pH. Furthermore, the surface characteristics and the surface charge of virgin silica, low-molecular-weight polyethyleneimine (LPEI)-silica, high-molecular-weight polyethyleneimine (HPEI)-silica, polydiallyldimethylammonium chloride (PDM)-silica, and CTAB-silica were investigated using SEM and the zeta potential. The adsorption characteristics of oil and the modified silica particles were monitored using a stereo microscope.

2. MATERIALS AND METHODS

2.1. Silica particle preparation and chemicals

Particles of silica gel with sizes ranging from 0.063 to 0.200 mm purchased from Merck and 2 to 4 mm from Riedel-de Haën were used in this study. Polyethyleneimine solutions, 50% (w/v) in H_2O of M_w 2,000 (LPEI) and M_w 750,000 (HPEI), PDM 35% (w/v) in H_2O $M_w < 100,000$ (PDM), and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. The chemicals used for pH control were sodium hydroxide and hydrochloric acid purchased from Fisher Scientific. Semi-synthetic 10 W-30 motor oil (Mobil Super 2000) for diesel engines was used as the fresh motor oil. The used motor oil in this study was the same type of fresh motor oil which was used for 3 months (9,680 km) in a Hyundai H1. Additionally, palm oil (Yok Brand, Thailand) was used as the representative of the cooking oil. The used palm oil was the same type of fresh oil which was used three times for frying chicken (filtered with no.1 paper before each use).

2.2. Preparation of modified silica with three cationic polymers and a cationic surfactant

2.2.1. Adsorption of PEI on silica

Silica particles with size ranging from 0.063 to 0.200 mm and 2 to 4 mm, representative of small- and large-silica groups, were washed three times in distilled water and subsequently dried at 80 °C for 24 h. LPEI and HPEI were diluted with distilled water using concentrations ranging from 0.10 to 10 mg/ml. The calibration curves for all kinds of PEI solutions were made by mixing PEI standard solutions with 5.00 ml of 0.50% (w/v) copper sulfate. The absorbance of PEI/Cu complex with various PEI concentrations was quantified using a UV–vis spectrophotometer at wavelength 615 nm. The adsorption of PEI on silica particles was studied by immersing 1 g of silica particles in the PEI solution ranging from 0.10 to 10 mg/ml at ambient temperature for 1 h. The absorbance of PEI/Cu complex was quantified, and hence, the amount of residual PEI was determined.

2.2.2. Adsorption of PDM on silica particles

The adsorption of PDM on silica particles was studied by spectrophotometry based on a diazotization-coupled ion pair (Mwangi *et al.* 2012). The absorbance of standard solutions of PDM ion pair in the range of 0.1–25.0 mg/l was measured at a wavelength of 230 nm for setting up the calibration curve. The adsorption of PDM on silica particles was done by immersing 1 g of silica particles in the PDM solution ranging from 0.1 to 25.0 mg/l at ambient temperature for 1 h. PDM solutions were added with 5 ml of coupled azo dye to those variety concentrations of PDM solutions to form a colloidal material. The colloid was then filtered with a sintered glass crucible and dissolved in 10 ml of dimethylformamide. The resulting mixture was quantified using a UV–Vis spectrophotometer.

2.2.3. Adsorption of CTAB on silica

The standard solutions of CTAB in the range of 0.10–150.0 mg/l were prepared in distilled water for setting up the calibration curve. An aliquot of the solution containing the standard solution of CTAB, 2.0 mL of 0.0010 mol/l CAS solution, 1.0 ml of 5.0 mg/l Al^{3+} solution, 0.4 ml of 1% (v/v) Triton X-100 solution, and 2.0 ml of pH 5.4 acetate buffer solution was transferred into a 10.0 ml volumetric flask. The solution was then diluted to the desired proportion by distilled water. A portion of the solution was transferred into a 1.0 cm quartz cell to measure the absorbance at the wavelength of 612 nm against a blank solution that was also prepared using the same method. In the adsorption study, 1 g of silica particles was immersed in the CTAB solution, ranging from 0.10 to 10 mg/ml at ambient temperature for 1 h. Initial and residual concentrations of CTAB in the adsorption study were determined using the same method that was used for calibration curve preparation (Afkhami *et al.* 2010).

2.2.4. Modification of silica with three cationic polymers and a cationic surfactant

Silica particles with sizes ranging from 0.063 to 0.200 mm and 2 to 4 mm, representative of small- and large-silica groups, respectively, were washed three times using distilled water and subsequently dried at 80 °C for 24 h. LPEI, HPEI, PDM,

and CTAB were diluted using distilled water to the concentration ranging from 0.1 to 3.0 mg/ml. LPEI-silica, HPEI-silica, PDM-silica, and CTAB-silica were prepared by separately immersing 1 g of silica particles in 100 ml of polymers or surfactant solutions for 1 h. Finally, they were washed with distilled water for three times and subsequently dried in normal atmosphere.

2.3. Characterization of modified silica

2.3.1. FT-IR spectra determination

The FT-IR spectra of the unmodified and polymer/surfactant-modified silica were obtained by the powder-pressed KBr pellet method using a Bruker tensor 27 spectrophotometer operating in the transmission mode with a resolution of 4 cm^{-1} over the range of 4,000–500 cm^{-1}.

2.3.2. Zeta potential measurement

The washed silica particles, spreading to a size of 0.063–0.200 mm, were screened using a 63-μm mesh sieve, obtaining particles having a size smaller than 0.063 mm. This screening was carried out to obtain very fine silica particles for the preparation of a colloidal solution of silica particles. The screened silica particles were modified by three cationic polymers and a cationic surfactant and left to dry in the air. Solutions containing 0.10% (w/v) solids were prepared in 0.0010 M KCl (the supporting electrolyte) at various pH values and stirred with magnetic stirrer for 10 min. The reagents used for controlling the pH were HCl, 0.1 mol/l, and KOH, 0.1 mol/l. Then the zeta potential of each sample was measured as a function of the pH change using a nanoparticle analyzer (HORIBA; SZ-100-S).

2.3.3. Surface area analysis

To evaluate the changes of silica particle surface after pretreatment by polymers and surfactant, the specific area of the unmodified and modified silica particles of the small and large particle groups was examined using the Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption using an Autosorb 1 MP instrument. Samples of 0.03 g were weighed and placed into a sample tube and degassed under vacuum at 100 °C for 7 h.

2.4. Oil sorption study

2.4.1. Physical properties of oils

The density values of the palm oil and the motor oil samples were measured using 10 ml specific gravity bottles. The viscosity values of the fresh oil and the used oil were measured at 25 °C with a Brookfield rheometer (Model DV-III).

2.4.2. Sorption study of oil on modified silica

The palm oil, the used palm oil, the motor oil, and the used motor oil were used to evaluate the adsorption capability of the modified silica particles. Oil–water mixtures were prepared by mixing oil and deionized water to concentrations ranging from 0.50 to 10.0 g$_{oil}$/100 ml and stirred using a 1,500 rpm magnetic stirrer for 20 min at 25 °C. HCl (0.10 M) and NaOH (0.10 M) were used to adjust the pH of the silica mixtures to 3–11.

One gram of the modified silica particles was added into the oil–water mixtures and stirred for 15 min. After the oil–water mixture completely separated from the oil-adsorbed silica particles for 5 min, the amount of oil adsorbed by the modified silica particles was measured by the extraction technique using hexane and solvent evaporation. The weights of the oil-containing samples were then measured to examine the oil adsorption capacity of each case. The sorption capacity and % removal were calculated according to the following Equations (1) and (2), respectively.

$$q = \frac{(m_{\text{Before-extracted}} - m_{\text{After-extracted}})}{m_{\text{MSP}}} \tag{1}$$

$$\% \text{ Removal} = \frac{m_{\text{Before-extract}} - m_{\text{After-extracted}}}{m_{\text{Before-extracted}}} \times 100 \tag{2}$$

where m_{MSP} is the mass of the modified silica particles (g), $m_{\text{Before-extracted}}$ is the mass of the oil-modified silica particles before oil extraction (g), $m_{\text{After-extracted}}$ is the mass of oil after oil extraction (g), and q is the sorption capacity (g$_{oil}$/g$_{MSP}$). Each experimental batch was repeated three times, and the average final concentration was given as the reported value.

2.5. Investigation of the sorption of oil on the modified silica particles

Palm oil or motor oil (0.50–1.5 g) was mixed with 100 ml of distilled water in each batch contactor, stirred for 15 min, and then left for 5 min. Then, 1 g of the modified small/large-silica particles was added into the oil/water mixture and stirred for 1 min. To examine the oil sorption behavior of silica particles, a polarizing microscope (Nikon Optiphot-2 Pol) and a stereo microscope (Nikon SMZ-U) were used to take photographs of the oil-modified silica particles. The size of oil droplets covered by silica in the photos was measured using ImageJ analysis software.

3. RESULTS AND DISCUSSION

3.1. Modification of silica particles using three cationic polymers and a cationic surfactant

The investigations on the modification of silica particles by cationic polymers/cationic surfactant are carried out to evaluate their use for an application on oil removal. Silica particles are simply modified by immersion in each of the cationic polymer solutions or the cationic surfactant solution and subsequently dried in an oven at 80 °C. SEM images of the virgin silica, LPEI-silica, CTAB-silica, PDM-silica, and HPEI-silica samples at different resolutions are shown in Figure 1. The surfaces of both unmodified and modified silica particles are irregular, but no visible pores can be seen, although the modified silica particle surface is almost the same as that of the unmodified one. However, the images presented in Figure 1 show the conglutination and dissolution of the small particles on the modified silica surface that can be described as a polymer/surfactant addition due to the treatment processes. The appearance of the small particles can be observed on the modified silica surface in the high-magnification images, as shown in Figure 1 (b_2,c_2). The figures clearly demonstrate that the modified surface is different from the surface of the unmodified sample.

Figure 2 shows the FT-IR spectra of the unmodified and modified silica. For the unmodified silica (Figure 2(a)), the strong absorption band at 1,093 cm^{-1} is attributed to the stretching asymmetric vibrations of the Si–O–Si band (Pérez-Quintanilla et al. 2007). The absorption peak at 808 cm^{-1} is assigned to the bending vibrations of the Si–O–Si group, meanwhile the absorption peak at approximately 958 cm^{-1} is related to the Si–O– groups. In the case of LPEI-silica, the FT-IR spectrum is shown in Figure 2(b), where the existence of PEI on the silica particles is confirmed by the presence of the absorption features due to PEI at 1,579–1,647 cm^{-1}. This peak is assigned to the bending of N-H_2. The two bands at 2,833 and 2,928 cm^{-1} agree well with the C–H_2 absorption bands. The peak at 1,485 cm^{-1} is assigned to the symmetrical bending mode of NH_3^+ in the Si–O ··· NH_3^+ groups. Note that the characteristic peak of Si–O–Si at 958 cm^{-1} became weaker after samples surface modification. The FT-IR spectrum of CTAB-silica is shown in Figure 2(c). The typical stretching vibrations of C–H are found at 2,880 and 2,945 cm^{-1} corresponding to the –CH_2 and –CH_3 in the CTAB, respectively. The different absorption features in the spectra suggest that PEI and CTAB existed and interacted with the hydroxyl groups on the surface of the silica particles. Note that the shifting of IR spectra is not found in the case of PDM-silica, as seen in Figure 2(d). This indicates that PDM dose neither interacts nor forms new bonds on the silica particle surface, which is similar to the results found on the treatment of PDM on clay particles (Nguyen et al. 2019).
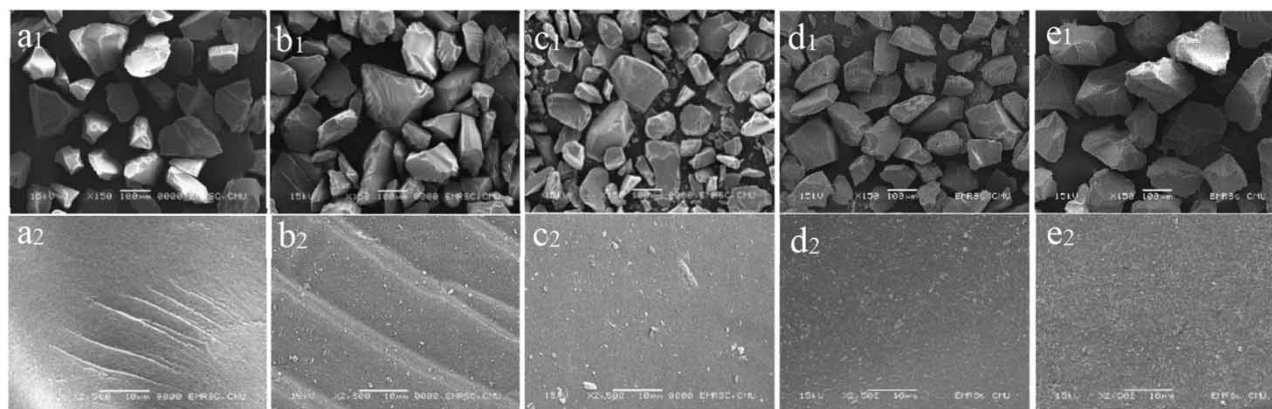
Figure 1 | SEM images of the unmodified silica (a_1, a_2), LPEI-silica (b_1, b_2), CTAB-silica (c_1, c_2), PDM-silica (d_1, d_2) and HPEI-silica (e_1, e_2) samples with different resolutions.
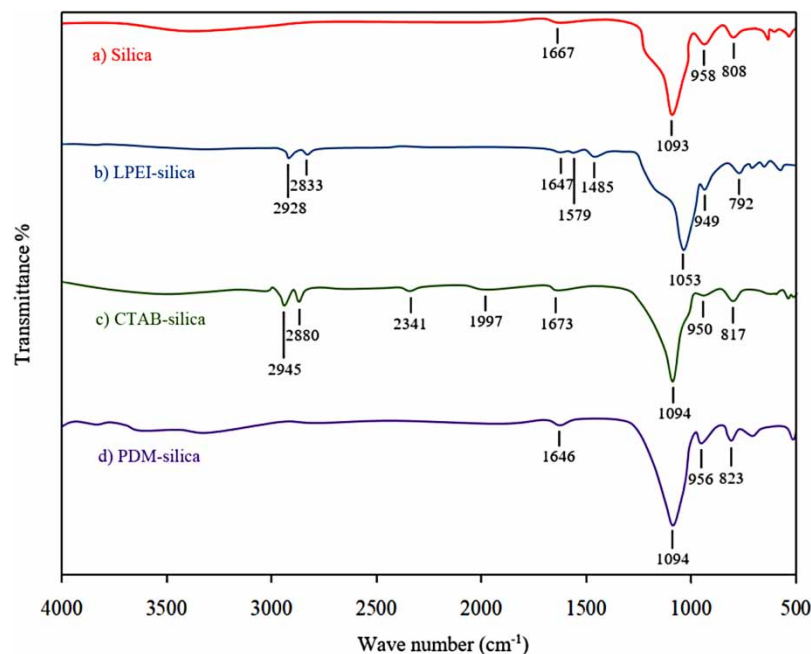
Figure 2 | FT-IR spectra of the unmodified silica (a), LPEI-silica (b), CTAB-silica (c), and PDM-silica (d).

3.2. Surface charge analysis

The zeta potential (ζ) is an important factor used to describe the electrokinetic property of silica particles. The ζ values of the unmodified silica, LPEI-silica, HPEI-silica, PDM-silica, and CTAB-silica as a function of pH are shown in Figure 3. The results demonstrate that the unmodified silica particles exhibit a negative charge on the surface over the pH range of 2–12. The results also report additional information that the negative charge on the silica surface tends to increase with an increasing silanol group formed on the silica surface (Lowe *et al.* 2015). However, the negative charge of the CTAB-silica surface slightly decreases and approaches zero after being treated with the cationic surfactant. This finding indicates that the treatment of silica with the cationic surfactant leads to a reduction of the negative charge on the silica surface by means of a neutralization of the surface by the cations of the surfactant (Tyrode *et al.* 2008). In addition, the zeta potential of silica particles modified by cationic polymers, LPEI, HPEI, and PDM, is investigated. The results show that the cationic polymer-modified silica surfaces have positive charges over the pH range of 2–12, indicating that cationic polymers interact
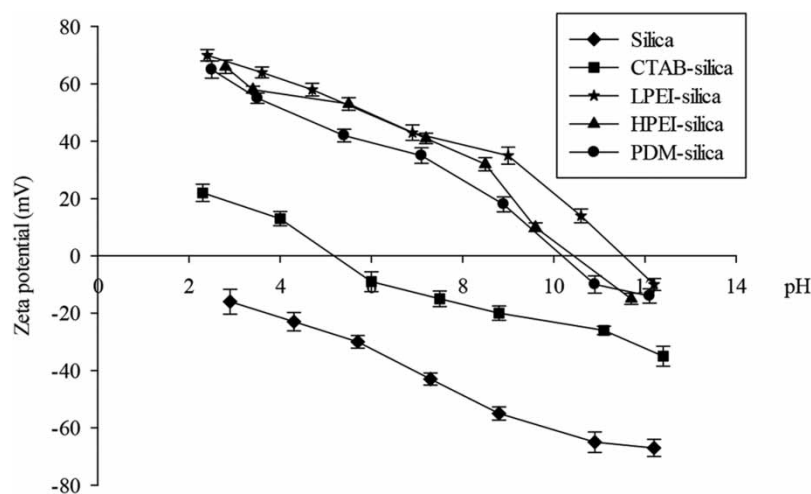
Figure 3 | The zeta potential of virgin silica compared with the modified silica particles.

with the silica surface by electrostatic and non-Coulombic interactions between PEI and silica (Meszaros *et al.* 2002). Our result is similar to that found during the modification of silica particles with LPEI for soybean oil removal (Janhom 2010). Note that the modification of silica particles using PEI generates more positive charge on silica particle surfaces than that using the other compounds.

The specific surface area values of small- and large-silica samples, initially around 0.2 and 150 m^2/g, respectively, change slightly after the treatment, as shown in Figure 4. These results are inconsistent with the SEM images shown in Figure 1 displaying the disappearance of porosity on the silica particles.

The adsorption of cationic polymers and the cationic surfactant on the small-silica particles are demonstrated by the isotherm, as shown in Figure 5(a). It reveals that the adsorption isotherms of HPEI and LPEI on silica particles at ambient temperature are the Langmuir type as shown in Figure 5(b). It is indicated that HPEI/LPEI forms a single layer on the surface of silica particles, while PDM and CTAB deviate away from this model. The adsorption of cationic polymers and cationic surfactant can be explained in detail based on the interaction between the surface charge of silica and functional groups of polymer/surfactant which contributes to the change of charge accumulation on the silica surface after treatment. The figure also shows that HPEI has the highest adsorbed amount on silica particles at around 140 mg/g, followed by LPEI, PDM, and CTAB, respectively.
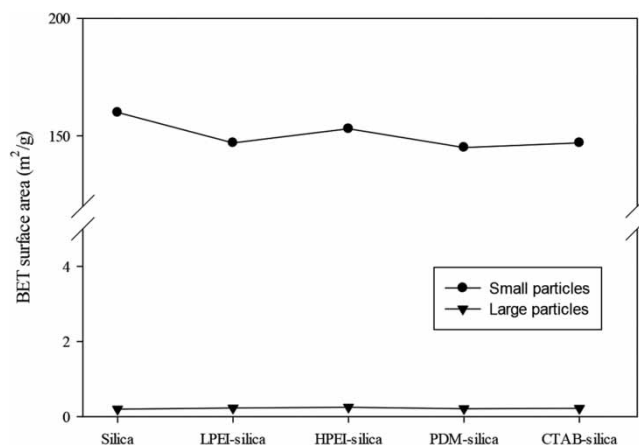
Figure 4 | Specific surface area of virgin and the modified silica particles (according to BET; 5-Pt. measurement).
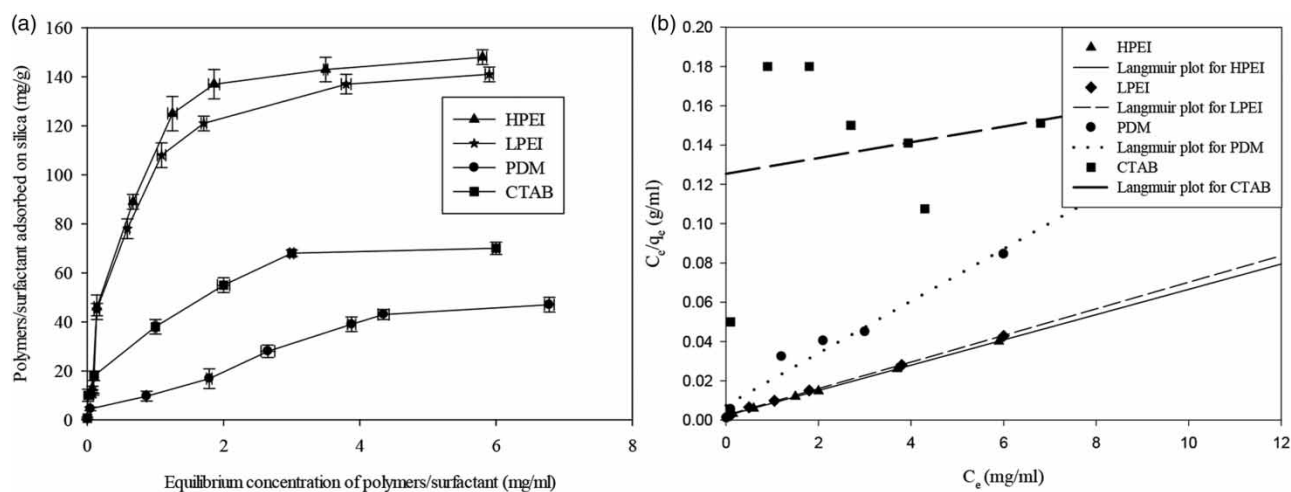
Figure 5 | Adsorption isotherm (a) and Langmuir plot (b) of polymers/surfactant on the small-silica particles at ambient temperature.

3.3. Physical properties of oils

The oils used for oil removal studies are palm oil, used palm oil, motor oil, and used motor oil. The physical properties of cooking oil and motor oil are shown in Table 1. It is demonstrated that the fresh cooking oil and the fresh motor oil have lower density and viscosity than the used oils, which affect the sorption ability of adsorbent (Shan *et al.* 2020).

3.4. Sorption study of oil on modified silica

The sorption ability of the used oil and the fresh oil on the unmodified and modified silica particles was separately examined under ambient temperature. Photographs of the palm oil sorption on the unmodified small- and large-silica particles are shown in Figure 6(a) and 6(b). The results demonstrate that the oil in an oil–water mixture cannot be adsorbed on the unmodified silica particles but can be successfully adsorbed on the modified particles for all different oil types. Examples of the adsorption study of palm oil and motor oil on the modified silica particles are shown in Figure 6(c) and 6(d). The figure shows that palm oil and motor oil in the oil–water mixture, floating on the water, can be adsorbed on the modified silica particles, leading to those particles settling down to the bottom of the beaker. This demonstrates the potential of using cationic polymer/surfactant-modified silica particles for oil removal. After the oil adsorption process takes place the oil floating on the water surface is drawn in contact with the silica particles by the centrifugal force of the magnetic stirrer. The oil droplets are covered with the modified silica particles and sink to the bottom. When the clean water is separated, the oil-covered silica particles located at the bottom of the container are extracted by using the solvent, and silica may possibly be recycled.

The adsorption characteristics of various types of oil of both small- and large-silica particles after modification are thoroughly studied. The interaction of oil droplets and the modified silica particles is examined using a polarizing stereo microscope. The sorption behaviors of oil on the modified small-silica particles can be noticed, in which the modified silica particles interact with the oil droplets in oil–water mixture and surround the droplets to form silica-oil balls which subsequently sink to the bottom, as shown in Table 2. Note that the oil sorption ability of the modified silica particles tends to increase with the increasing of the silica-oil ball size. While this phenomenon cannot occur in the case of the modified large-silica particles because their sizes are larger than the oil droplets, only a combination of oil with the modified silica particles

Table 1 | Physical properties of palm oil and motor oil at 25 °C
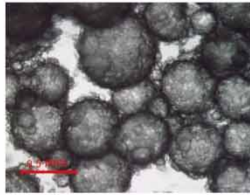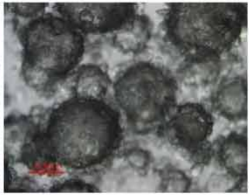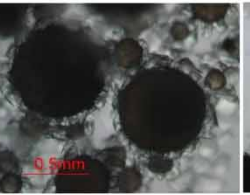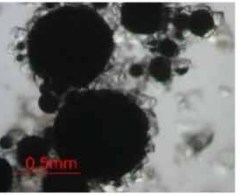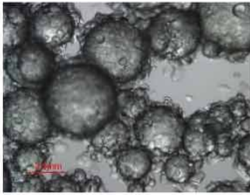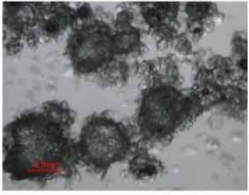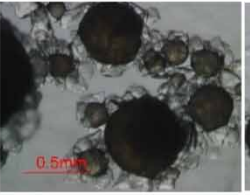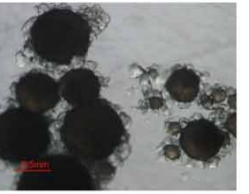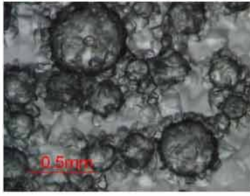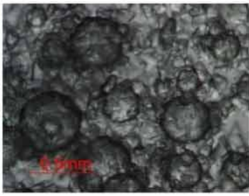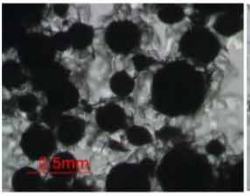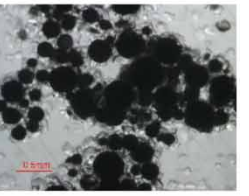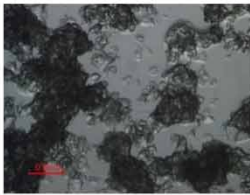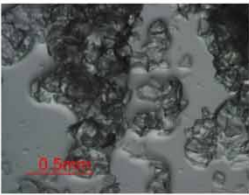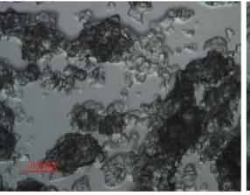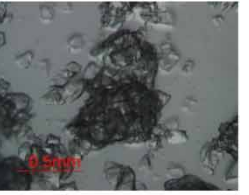
Parameter	Fresh palm oil	Used palm oil	Fresh motor oil	Used motor oil
Density (g/cm^3)	0.9120	0.9724	0.8992	0.9231
Viscosity (cp)	30.32	36.45	72.14	97.89
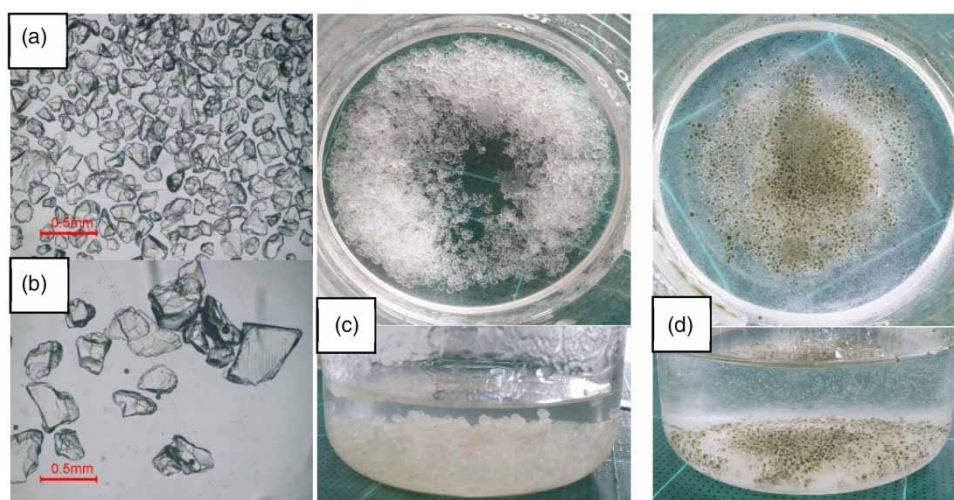
Figure 6 | Unmodified, small (a) and large (b) silica particles, and the adsorption of palm oil (c) and motor oil (d) on the modified small-silica particles.

**Table 2** | Adsorption characteristics of the various types of oil of the modified small-silica particles

Modification of silica particles	Palm oil	Used palm oil	Motor oil	Used motor oil
LPEI-silica				
HPEI-silica				
PDM-silica				
CTAB-silica				

can be seen as shown in Table 3. Since the sorption characteristics of all types of oil are similar, the palm oil sorption on the modified small-silica particles is used as a representative example, and this is what is shown in Table 2.

The oil droplets in the oil–water mixture are continuously adsorbed and pulled down to the bottom by gravity due to the weight of the silica particles. From Table 2, it can be noticed that the amount of remaining oil floating on top of the water after being treatment by the modified large-silica particles is higher than after treatment by the modified small-silica particles.

Considering the adsorption of oil on the modified small-silica particles, it is found that the modification of silica particles by LPEI results in the occurrence of silica-oil balls for all types of oil, and the size of the silica-oil balls tends to decrease in the cases of the silica particles modified by HPEI and PDM. In the case of removal of the oil by the CTAB-silica particles, one can see only the merging of oil and modified silica, but rarely see the silica-oil balls. This phenomenon can be ascribed by the low charge density of the CTAB coating on the silica particles which results in the low interaction between the oil droplets and the CTAB-silica, leading to the disappearance of silica-oil balls. Illustration models of interactions between oil droplets with the modified large-/small-silica particles are presented in Figure 7.

For the modified large-silica particles, the oil seems to mix only with the treated silica and sinks to the bottom. Meanwhile for the modified small-silica particles, the oil encloses the treated silica similarly to the silica-oil ball and floats at the surface. Therefore, the oil adsorption of the latter is higher than the former, implying the modified small-silica particles might be a better adsorbed substance for oil droplets than the bigger ones.

Table 3 | Examples of adsorption characteristics of palm oil of the modified large-silica particles
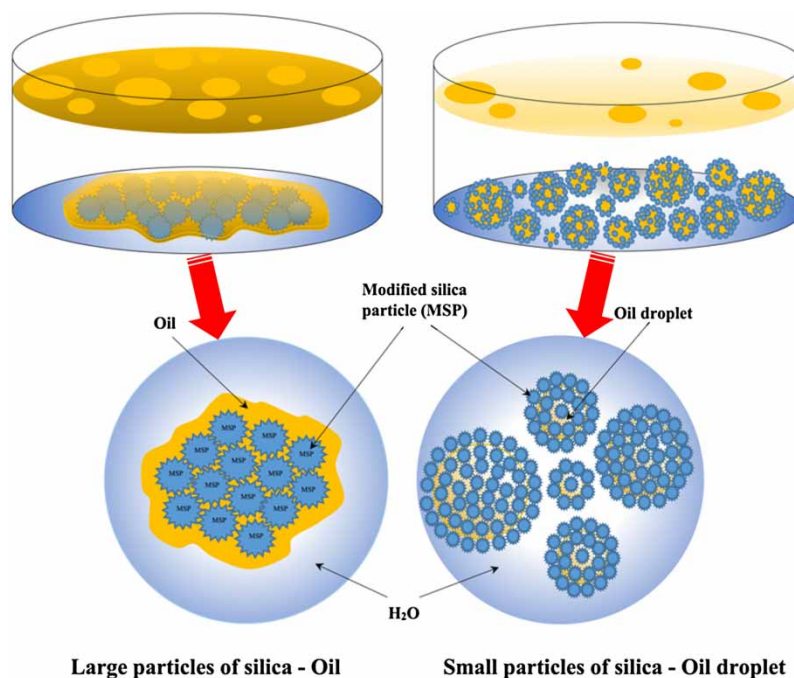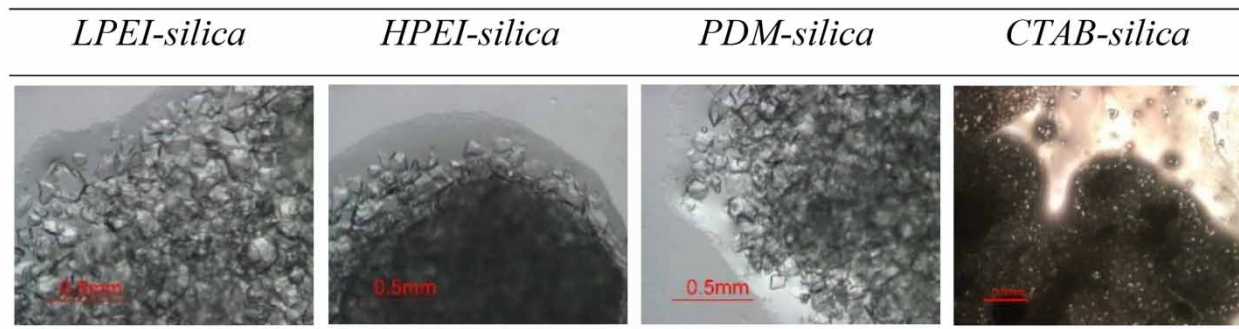
Figure 7 | Illustration model of the interactions between oil droplets with the modified large-/small-silica particles.

Fresh palm oil and small-silica particles were further used to determine factors affecting the oil sorption, for example, the oil concentration, the molecular weight of the polymer, the polymer/surfactant concentrations, and the pH. The influences of the residue oil concentration in the oil–water mixture to the oil adsorption on the silica particles are shown in Figure 8.

It can be clearly seen that oil from the oil–water mixture is rarely absorbed on the unmodified silica particles. However, the modifications of silica particles using those three cationic polymers and a surfactant obviously lead to the increase of oil sorption on the silica particles. An increase in oil concentration in oil–water mixture results in an increase in palm oil adsorbed on the modified silica particles. It can be observed that the modified silica can adsorb the palm oil better than the unmodified silica. The maximum amount of oil adsorbed by each modified silica is at the same range of the residue oil concentration, at approximately 0.03 g/ml. The maximum amounts of palm oil adsorbed on LPEI-silica, HPEI-silica, PDM-silica, CTAB-silica, and unmodified silica are 2.40, 2.10, 1.95, 1.5, and 0.15 g/g_{silica}, respectively. It can be observed that the removal of palm oil by the LPEI-silica exhibits the highest oil sorption efficiency. Considering the effect of molecular weight of PEI on palm oil removal, one can see that the maximum of adsorbed amount of palm oil on LPEI-silica is higher than that obtained by
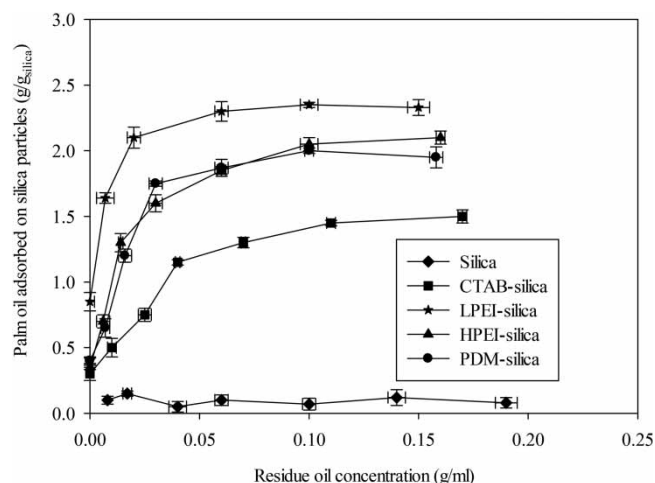
Figure 8 | Adsorption isotherms of palm oil on various types of the modified silica particles.

HPEI-silica. The adsorption of palm oil on LPEI-silica can be attributed to the hydrophobic interaction between the oil and the PEI molecule and to the charge interaction between the dissociated carboxyl group on the fatty acid molecule and the cationic charge on PEI chain (Janhom 2019). According to the results showing that the adsorbed amount of HPEI on silica particles is maximum (Figure 5), the hydrophobic interaction and the charge interaction between oil and HPEI-silica particles should be greater than the others, and consequently, the oil interacting with the HPEI-silica particles should be greater than the others as well. However, it does not seem to be as predicted, as the amount of oil sorption on HPEI-silica particles is lower than the adsorption on LPEI-silica particles. This result suggests that the adsorption ability of PEI-silica particles on oil droplets not only depends on the amount of polymer adsorbed on the silica surface, there may also be other parameters affecting this phenomenon.

The characteristic of the oil droplet adsorption by the modified silica is shown in Figure 9. In this figure, the covering by all types of modified silica particles on the oil droplet is visible. It is found that the adsorption of LPEI-modified silica particles on the oil droplet is more significantly consistent than the others. One can clearly notice the vacant position on the oil droplets covered by HPEI-silica particles and PDM-silica particles, as indicated by the red arrows in Figure 10(b) and 10(c). These results indicate that the densities of HPEI and PDM-silica particles on the oil droplets is lower than those of LPEI-modified silica particles. Apart from the hydrophobic and charge accumulation which affect the interaction between the oil and the PEI-molecule-adsorbed silica enhancing the stickling of the modified silica to the oil droplets, perhaps the steric effect associated to the size of polymer adsorbed on the silica surface might also influence the oil absorption ability on the modified silica particles as shown by the schematics diagram in Figure 10. This phenomenon can be ascribed to the steric effect from HPEI adsorbed on the silica particles, preventing the HPEI-silica particles cover on the oil droplet, thus suppressing the interaction between the modified silica particles and the oil droplet. On the other hand, LPEI-silica particle seems to move easier and interacts with the oil droplet, as shown in the schematics diagram below. Therefore, LPEI-silica particles easily interact with oil droplets, resulting in more sorption efficiency of the modified silica particles for the oil removal process.

Similar to the case of HPEI-silica, PDM-silica also achieves the same success for the oil adsorption, ascribable to the same reasons as those of HPEI-silica. The explanation of the palm oil adsorption on CTAB-silica can be ascribed to the interaction between CTAB-silica particles, where a hydrophobic part of the CTAB molecule interacts with a hydrophobic part of palm oil. The polymer and surfactant concentrations in the oil–water mixture affecting the oil sorption ability are also studied as the results shown in Figure 11. The maximum palm oil amounts adsorbed for LPEI-silica, HPEI-silica, and PDM-silica are saturated at 2.3, 2.0, and 1.8 g/g_{silica}, respectively, when silica particles are modified by various types of polymers at a concentration of ~2 mg/ml. These results show the higher potential of LPEI-silica for oil removal than the others. In addition, the modification of silica using CTAB at various concentrations for oil removal is also investigated as also shown in Figure 11. The results reveal that the plateau of the saturation of palm oil adsorbed on CTAB-silica occurred at 1.4 g/g_{silica} when the CTAB concentration is 1 mg/ml.
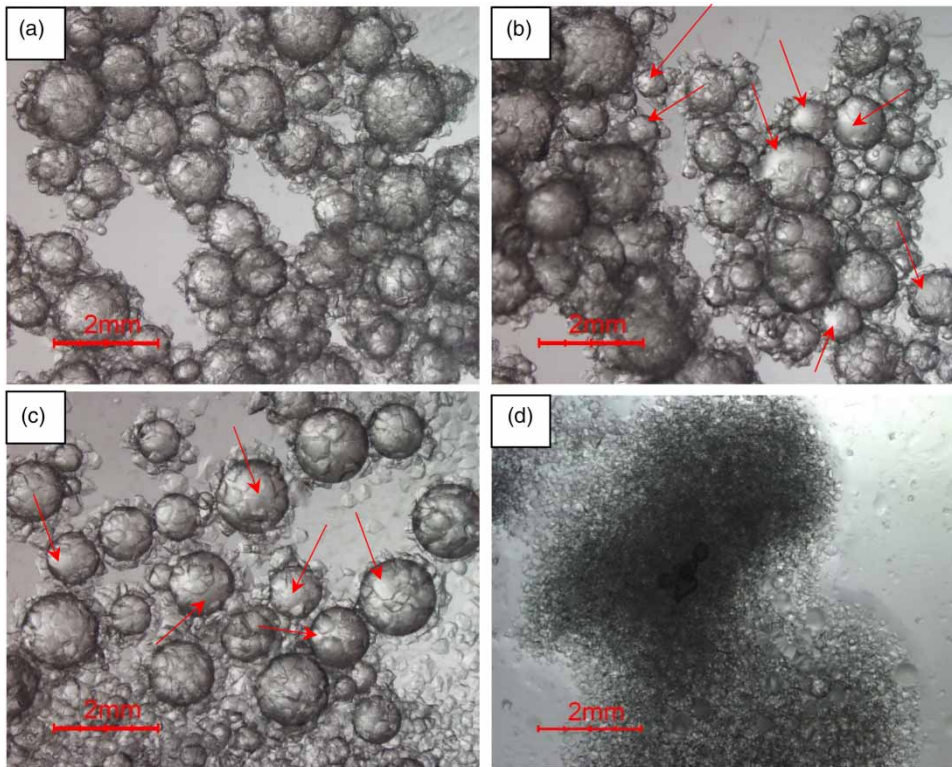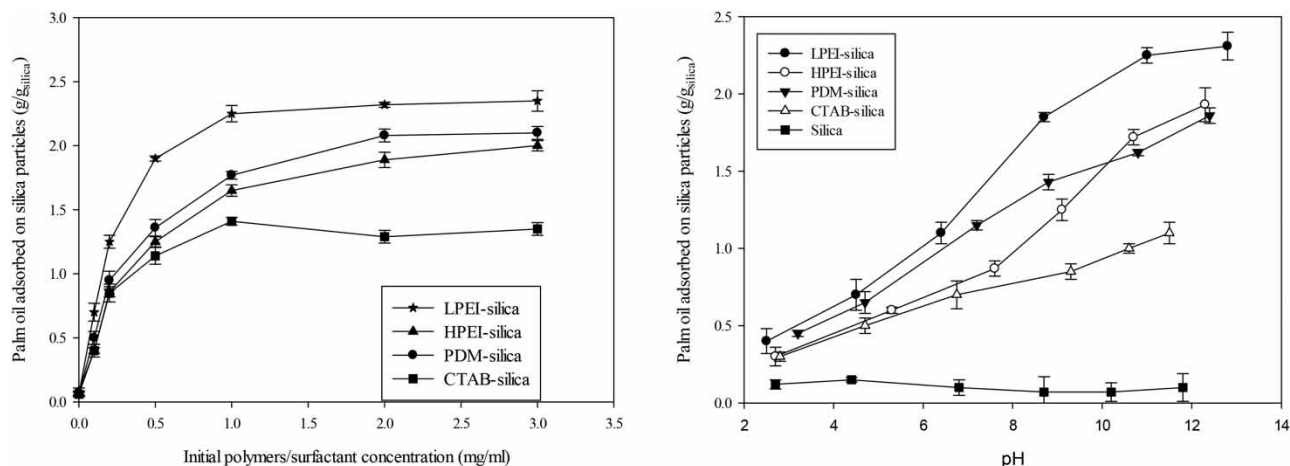
Figure 9 | The covering of modified silica particles on the oil droplet: (a) LPEI-silica, (b) HPEI-silica, (c) PDM-silica, and (d) CTAB-silica.
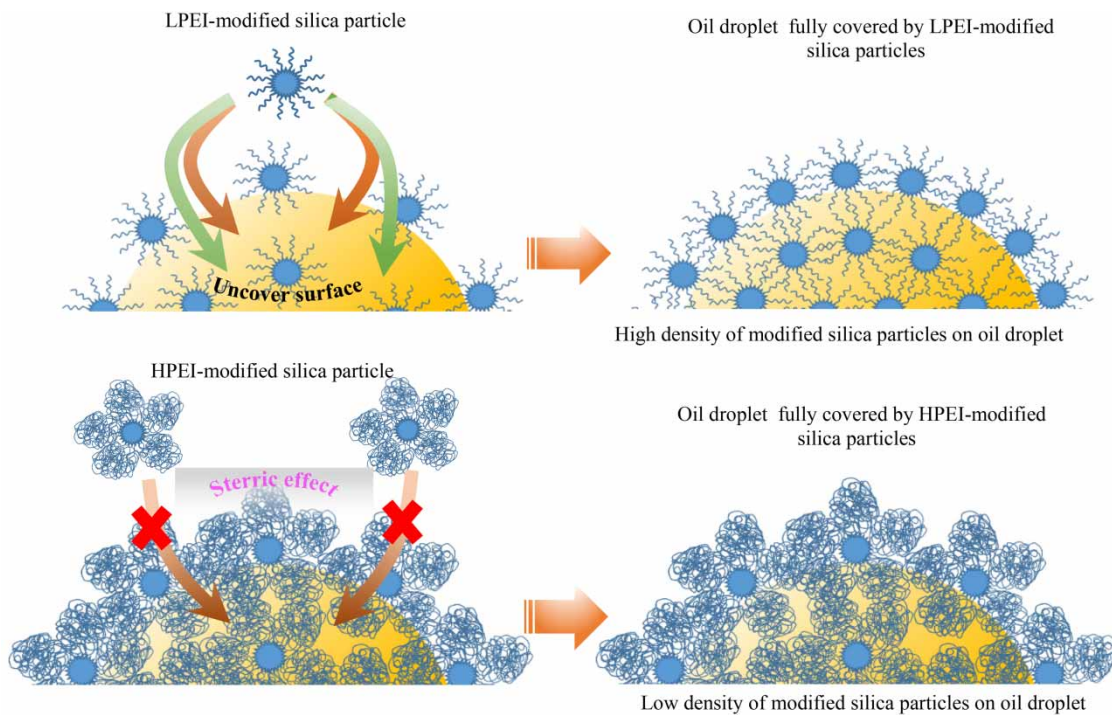

Figure 10 | Comparison of the covering of LPEI-modified silica particle/HPEI-modified silica particles on the oil droplet.

Figure 11 | Adsorption of palm oil on cationic polymers and surfactant-modified silica particles at different polymer concentrations and pH.

Tests of palm oil adsorption on unmodified and modified small-silica particles at various pH values ranging from 2 to 13 are carried out and the results are given in Figure 11(right). The figure reveals that the adsorption of palm oil on silica particles at all pH values is very low. However, it can be observed that the amount of palm oil adsorbed on the modified silica particles tends to increase with increasing pH. This result can be ascribed to the fact that the adsorption of palm oil on polymer-modified silica depends on both the hydrophobic interaction between oil-polymer and the increasing dissociation of the carboxyl group of the fatty acid molecule at higher pH values. In addition, the zeta potential of palm oil is negative at high pH (Taha *et al.* 2018), which is another reason for palm oil interacting with silica particles modified with the positive polymer. Therefore, it leads to the enhancement of palm oil adsorption on polymer-modified silica particles. However, the adsorption of the oil on polymer-modified silica surface tended to be constant above pH 10. A reduction of polymer charge density occurs at higher pH values due to the protonated PEI on the polymer-modified silica (Meszaros *et al.* 2002). In the case of CTAB-silica, increasing the pH results in the enhancement of CTAB adsorption on silica particles due to the protonated sites on the silica surface decreasing with increasing pH. Thus, the amount of palm oil adsorbed at higher pH is raised as the amount of CTAB adsorbed on the silica surface increases. The interaction mechanism of silica particle modification using polymers/surfactant and oil sorption on the modified silica particles can be described by the schematic diagrams as shown in Figure 12.
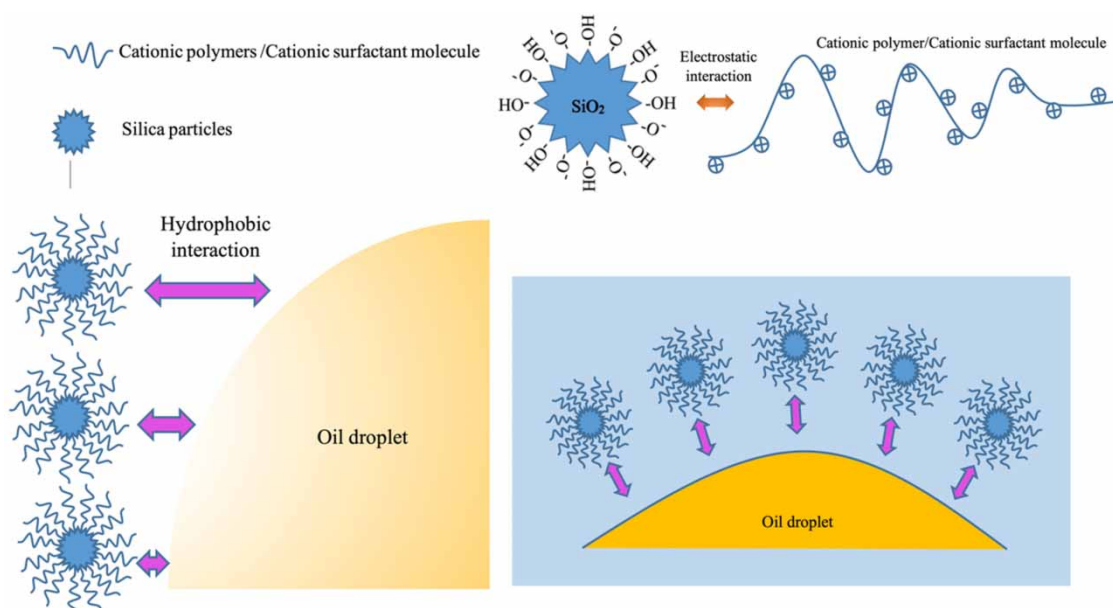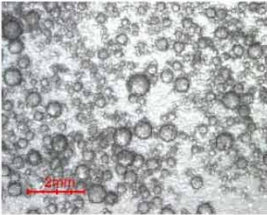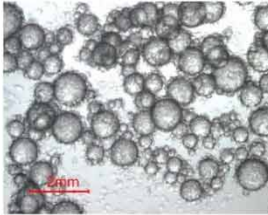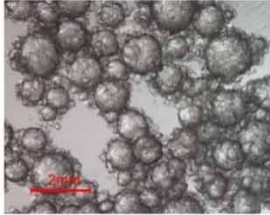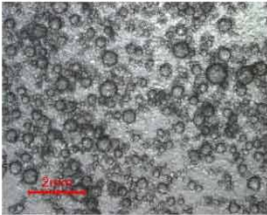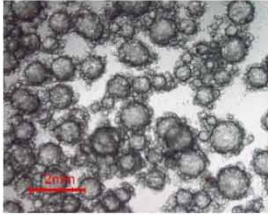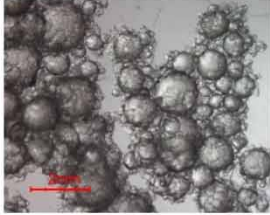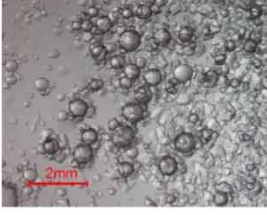

Figure 12 | Schematic diagrams of the interactions between cationic polymers/surfactant-modified silica particles and oil droplets.

3.5. Investigation of the sorption of oil on the modified silica particles

The size of oil droplets covered by modified silica are investigated using a polarizing microscope and a stereo microscope and measured using Image J analysis software as shown in Table 4. The results reveal that the size of oil droplets covered by

Table 4 | Adsorption characterization of the palm oil on various modified silica particles at various concentrations of polymers/surfactants

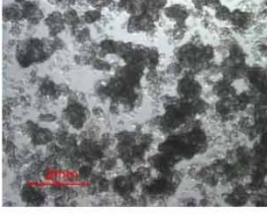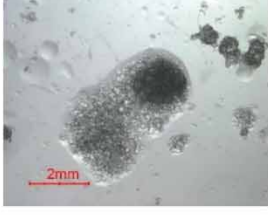| Modification of silica particles	Various concentration of polymers/surfactant		
LPEI-silica	100 ppm Avg. oil drop size 0.419 mm SD 0.119 Count no. 61	500 ppm Avg. oil drop size 0.742 mm SD 0.226 Count no. 57	1000 ppm Avg. oil drop size 1.106 mm SD 0.259 Count no. 40
HPEI-silica	100 ppm Avg. oil drop size 0.325 mm SD 0.0987 Count no. 81	500 ppm Avg. oil drop size 0.812 mm SD 0.208 Count no. 51	1000 ppm Avg. oil drop size 1.076 mm SD 0.351 Count no. 27
PDM-silica	100 ppm Avg. oil drop size 0.542 mm SD 0.149 Count no. 27	500 ppm Avg. oil drop size 1.088 mm SD 0.361 Count no. 23	1000 ppm Avg. oil drop size 1.053 mm SD 0.293 Count no. 25
CTAB-silica	0.10 mM Oil drop size (ND)	0.50 mM Oil drop size (ND)	1.0 mM Oil drop size (ND)
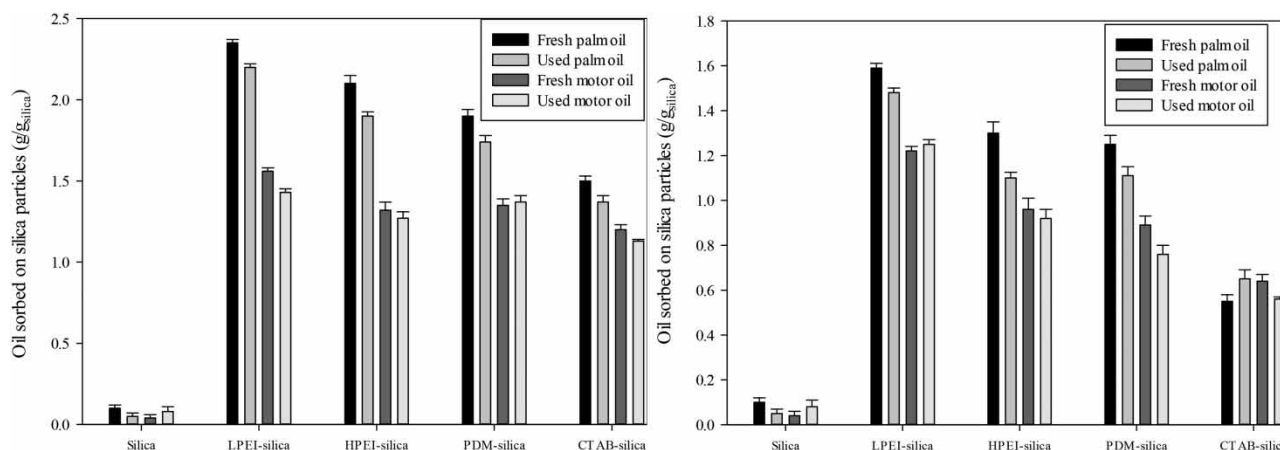
Figure 13 | The sorption of various types of oil on unmodified and modified small-silica particles (left) and unmodified and modified large-silica particles (right).

modified silica tends to increase with the polymer concentration using the pretreatment process. It can be clearly seen that CTAB coating on the silica particles leads to the disappearance of silica-oil balls. In addition, it is also found that the amount of silica-oil ball that is produced correlates to the oil sorption efficiency when considered together with Figure 8.

The adsorption of various types of oil on unmodified and modified silica particles is investigated, as shown in Figure 13. It is found that the sequence in descending order of oil sorption on both small- and large-silica particles after modification is as follows: fresh palm oil, used palm oil, fresh motor oil, and used motor oil. The figure reveals that the palm oil can be adsorbed by the modified silica particles better than the motor oil. This may be due to the hydrophobic interaction and the dissociation of the carboxyl group of palm oil supporting the interaction with the modified silica particles for the former, but only hydrophobic interaction occurs alone in the case of motor oil.

Moreover, one can see that both fresh palm oil and fresh motor oil exhibit higher oil-adsorbed amounts than the used ones. This finding can be attributed to the higher viscosity of the used oils resulting in less sorption capacity and less separation that occurs during the silica modification process settling at the bottom for the cases of oil removal from an oil–water mixture. Our result is in contrast to the case of the study on the oil adsorption on untreated and treated cotton cloths, which demonstrates that higher oil viscosity results in greater sorption capacity for the direct adsorption of oil onto the adsorbent without water (Janhom 2019). However, we can assume that the smaller-sized silica particles are approximately 30–50% more effective in their performance as oil adsorbents than the corresponding larger-sized silica particles. In conclusion, LPEI-silica contained amounts of oil sorption approximately 10–20 times higher than unmodified silica depending on the size of the silica particle and the type of oil. This is in conformity with the other reports that state that the oil sorption efficiency is affected by the size of the particles (Ikenyiri & Ukpaka 2016). The increase of oil sorption can be attributed to the higher surface area values of the modified small-silica particles resulting in better covering on the oil droplet, which leads to the higher efficiency for oil removal.

4. CONCLUSIONS

In this work, polymer/surfactant-modified silica particles were investigated and confirmed to be a new type of potential sorbent for various types of oil from oil–water mixtures. This work revealed that the modified silica particles can be applied to the oil removal process for all types of oil. In addition, the advantage of LPEI modification with respect to that of cationic polymers/surfactants for enhancing the oil sorption ability of silica particles was clearly demonstrated. LPEI-silica yielded 10–20 times higher amounts of oil sorption than unmodified silica depending on the size of the silica particles and the type of oil. The modification of silica particles by LPEI has the highest oil sorption efficiency, followed by HPEI-silica, PDM-silica, and CTAB-silica, respectively. It was discovered that the interaction between modified silica particles and oil produced the silica-oil balls for all types of oil. However, the size of silica-oil balls tended to decrease when changing the polymer-modifying agent from LPEI to be HPEI, PDM, and CTAB, respectively. This work also revealed that the amount of oil sorption on the modified small-silica particles was approximately 30–50% higher than that of the modified large-silica particles.

The oil sorption ability results confirmed the possibility of using cationic polymer to adapt the silica particles for oil removal applications.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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