Increasing the hydrophobicity of filter medium particles for oily water treatment using coupling agents

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Abstract

Generally, increasing the hydrophobicity of filter media leads to enhanced oil removal by filtration. In this study, the hydrophobicity of quartz sand filter media was increased by modifying the particles with titanate and silane coupling agents (DN101 and KH550) by dry processing. The results show that the quartz sand particle surfaces were uniformly covered with the coupling agents after surface modification, and many fine particles were observed. The optimised parameters for the surface modification procedure were a DN101:KH550 ratio of 1:2, total coupling agent amount of 1.0 wt%, reaction temperature of 60 °C and reaction time of 50 min. Under these conditions, the water contact angle on the filter media surface increased from 40.1° to 82.9°, and the effluent oil concentration decreased from 4.74 mg/L for the unmodified filter media to 2.99 mg/L for the modified filter media when the influent oil concentration was 17.3 mg/L. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy results show that DN101 and KH550 formed chemical bonds with the quartz sand surface groups, resulting in the formation of a uniform, stable coating on the surface.

Keywords: Chemical engineering, Chemistry
1. Introduction

Oily wastewater is commonly produced in a wide range of industries, such as oil extraction, petrochemical production, machinery manufacturing, and food production [1, 2, 3, 4]. Deep bed filtration is an economic, efficient oily wastewater treatment technology that is particularly suited to removing oil pollutants with diameters of less than 10 μm [5]. The wettability of the filter media is a key factor affecting the oil removal efficiency of this technology. Generally, the oil removal efficiency increases as the lipophilicity and hydrophobicity of the filter media increase [6, 7, 8, 9]. Filter media surfaces can be modified with coupling agents to increase their hydrophobicity [10]. These coupling agents have at least two types of functional groups with distinct properties; one of these groups undergoes alcoholysis to generate a hydroxyl group, which can then react with a hydroxyl group on the filter media surface via a condensation reaction, and the other group interacts with the surrounding fluid [11, 12, 13], improving the hydrophobicity of the filter media.

In one type of surface modification method, particles or powders are dispersed in a coupling agent solution under stirring, which allows the modification reaction to occur in the liquid phase. This method, which is called wet modification [13, 14, 15], requires a large volume of coupling agents, leading to severe environmental pollution, and is therefore mainly used in laboratory research. Therefore, in this study, a modification technique called dry processing was used. This method involves spraying a coupling agent solution onto the surfaces of sufficiently dispersed dry filter media using suitable equipment and can therefore overcome the disadvantages of wet modification. Accordingly, it is used in both basic research and industrial applications. In this study, quartz sand filter media was modified with the titanate coupling agent DN101 and silane coupling agent KH550, and the effects of the modification on its hydrophobicity were evaluated by measuring the water contact angle on the filter media surface. In addition, the dynamic oil removal performance and stability of the modified filter media were also investigated.

2. Experimental

2.1. Materials and reagents

The titanate coupling agent DN101 (isopropyl dioleic (dioctyl phosphate) titanate) and the silane coupling agent KH550 (3-triethoxysilylpropylamine) were purchased from Nanjing Pinning Coupling Agent Co., Ltd. (China). Quartz sand was purchased from Hongda Filter Plant (Henan Province, China). Analytically pure 65–68% nitric acid, isopropanol and cyclohexane were used in the experiments, and distilled water was prepared in the lab. Kunlun Tiange SD40-type gasoline engine oil was obtained from Petro China Lubricant Company.
2.2. Experimental procedures

The quartz sand was sieved to a particle size of 0.45–0.9 mm and then boiled in distilled water for 30 min, rinsed with deionised (DI) water repeatedly, and dried at 110 °C in an oven. After cooling, the quartz sand was immersed in 1 M nitric acid for 24 h and then anhydrous ethanol for 30 min. Then, it was rinsed with water and dried in an oven to obtain the pretreated sample. The alcoholysed DN101 solution was prepared by stirring a 15:85 DN101:isopropanol mixture at 20 °C for 40 min. KH550 solutions with different concentrations were prepared using deionised water and ethanol as the solvents (ethanol was employed only to dissolve KH550) and then hydrolysed under stirring at 20 °C. During hydrolysis, the conductivity of the KH550 hydrolysate was measured to ensure that it remained constant. The pretreated quartz sand (1,300 g) was placed in a mixer (SHR-5, Laizhou Xingge’er Chemical plastics machinery Co. Ltd, China) and preheated under stirring at a given rotation speed and temperature. Then, a certain amount of the alcoholysed DN101 solution and KH550 hydrolysate were added to the sand, and the mixture was stirred at a constant temperature for a given amount of time. After cooling, the mixture was removed from the mixer and again sieved through a 0.45–0.9 mm-mesh stainless steel screen. The sieved mixture was rinsed repeatedly with tap water and finally dried at 110 °C.

2.3. Wettability measurements

The water contact angle on the filter media was measured to assess the effects of the surface modification on the filter media hydrophobicity. According to the Laplace-Young equation [16] for the particle packed bed, the wetting contact angle of a liquid on a solid particle surface is:

$$\cos \theta = \frac{g w_r r_s}{2 \gamma_{GL} \pi R^2 e}$$

(1)

where $\theta$ (°) is the static contact angle of the wetting liquid on the filter media surface; $g$ (m/s$^2$) is the acceleration of gravity; $r_s$ (m), $R$ (m) and $e$(%) are the effective radius, inner diameter and porosity, respectively, of the packed bed; $w$ (g) is the liquid mass in the capillary at equilibrium; and $\gamma_{GL}$ (mN/m) is the surface tension of the wetting liquid.

Because $r_s$ is difficult to measure, Eq. (1) cannot be used to directly calculate the contact angle. However, for a given packed bed, $r_s$ is a constant [17]. When water and cyclohexane are the wetting liquids, the following equation can be derived:

$$\frac{\cos \theta_W}{\cos \theta_O} = \left( \frac{g w_{wW} r_{wW}}{2 \gamma_w \pi R_{w}^2 e_w} \right) / \left( \frac{g w_{eO} r_{eO}}{2 \gamma_{O} \pi R_{O}^2 e_O} \right)$$

(2)
where $\theta_W$ and $\theta_O$ (°) are the water and cyclohexane contact angles, respectively, on the filter media; $w_{eqW}$ and $w_{eqO}$ (g) are the water and cyclohexane masses, respectively, at equilibrium in the same packed bed; $\gamma_W$ (72.8 m N/m at 20 °C) and $\gamma_O$ (25.5 m N/m at 20 °C) are the water and cyclohexane surface tensions, respectively. The W and O subscripts denote the corresponding variables for water and cyclohexane, respectively. For a packed bed with the same filter media, $r_{SW} = r_{SO}$, $R_W = R_O$, and $\varepsilon_W = \varepsilon_O$.

Assuming that cyclohexane is a perfect wetting liquid, its contact angle on the solid particles is 0° [18], i.e., $\theta_O = 0°$, and $\cos \theta_O = 1$. Therefore, the following equation can be derived:

$$\theta_W = \arccos \left( 0.350 \frac{w_{eqW}}{w_{eqO}} \right)$$

Thus, the wetting contact angles on the filter media surface before and after modification can be calculated using Eq. (3). The details of the water and cyclohexane weight measurements in the filter media packed bed can be found in the literature [19].

### 2.4. Characterisation

The surface morphology of the filter media was characterised by scanning electron microscopy (SEM, JSM-5600LV, JEOL, Japan). The filter media chemical structure was analysed by Fourier transform infrared spectroscopy (FTIR, Bruker, Germany). A multi-functional X-ray photoelectron spectrometer (XPS, PHI-5702, Physical Electronics, USA) was used to quantitatively determine the elemental and functional group contents at the filter media surface.

### 2.5. Oil removal experiments

The dynamic filtration experiments were performed as follows: two Plexiglas filtration columns (33 mm diameter) were filled with 30 cm of a (pebble) graded gravel layer and then 90 cm of the unmodified (modified) quartz sand filter media. Downflow filtration of the prepared emulsified oily wastewater was performed at a given filtration rate, and the effluent oil concentration was measured to calculate the oil removal efficiency.

### 2.6. Filter media stability

The stability of filter media affects its oil removal efficiency in the later stages of use. To test the filter media stability, it was continuously backwashed in the filtration column at a rate of 26.9 L/(s·m²) (same as the actual backwashing rate after filtration) with an expansion height of 36% for 24 h and 48 h, and then its wettability was
measured. This measurement was used as a metric to determine if the filter media maintained a high wastewater treatment efficiency after filtration for long periods of time. One backwashing required 7 min; therefore, 24 h of backwashing was equivalent to 200 filtration cycles. Similarly, 48 h of backwashing was equivalent to 400 filtration cycles.

3. Results and discussion

3.1. Modification mechanism

DN101 is alcoholysed in the presence of an alcohol to produce a hydroxyl group. KH550 hydrolys in the presence of water to generate silanol (Si(OH)₃) groups. The hydroxyl groups produced from the alcoholysis and hydrolysis of the coupling agents react with the hydroxyl groups on the quartz sand surface via condensation reactions [20, 21], as shown in Fig. 1, resulting in the grafting of the DN101 long-chain alkyl and KH550 aminopropyl groups to the quartz sand surface.

3.2. Effects of the DN101:KH550 ratio

The effects of the DN101:KH550 ratio on the water contact angle on the filter media surface were investigated at a reaction temperature of 60 °C, reaction time of 50 min and total DN101 and KH550 amount of 1.0 wt%, and the results are shown in Fig. 2. Clearly, the ratio of the two coupling agents significantly impacted the modification results. The optimal DN101:KH550 ratio was determined to be 1:2. The water contact angle varied with the DN101:KH550 ratio due to differences in the DN101 and KH550 functional group chain lengths. Using a combination of coupling agents led to a reduction in the steric hindrance between the grafted molecules and thus an effective increase in their amount.

![Fig. 1. Schematic illustration of the condensation reactions between the coupling agents and the quartz sand surface.](https://doi.org/10.1016/j.heliyon.2018.e00809)
3.3. Effects of the total amount of DN101 and KH550

The effects of the total amount of DN101 and KH550 on the water contact angle on the filter media surface were investigated at a reaction temperature of 60 °C, reaction time of 50 min and DN101:KH550 ratio of 1:2, and the results are shown in Fig. 3. The water contact angle on the filter media surface first increased and then decreased.

Fig. 2. Effect of the DN101:KH550 ratio on the water contact angle.

Fig. 3. Effect of the total amount of DN101 and KH550 on the water contact angle.
with increasing total amount of the two coupling agents. When the total amount of the coupling agents was small, the surface reaction was incomplete, and some Si–OH groups were exposed on the filter media surface, which affected the filter media hydrophobicity [22]. In contrast, when the total amount of the coupling agents was too high, the surface was saturated, and the hydroxyl groups of some of the coupling agents pointed towards the surrounding fluid [23, 24]. The optimal total amount of the coupling agents was determined to be 1.0 wt%; the water contact angle on the filter media surface increased from 40.1° for the unmodified quartz sand to 82.9° for the quartz sand modified with this amount of the coupling agents.

3.4. Effects of the reaction temperature

The effects of the reaction temperature on the water contact angle on the filter media surface were investigated using a reaction time of 50 min, DN101:KH550 ratio of 1:2 and total amount of DN101 and KH550 of 1.0 wt%, and the results are shown in Fig. 4. The water contact angle on the filter media surface first increased and then decreased with increasing reaction temperature. The maximum water contact angle and, thus, the highest filter media surface hydrophobicity was observed at a reaction temperature of 60 °C. At low temperatures, the energy provided to the system was insufficient to overcome the activation energy of the coupling reaction. Accordingly, the activity of the coupling agents was low, and the improvement in the surface hydrophobicity was poor. In contrast, the coupling agents can self-polymerise, decompose or be carbonised at high temperatures. Consequently, the coupling reaction did not occur at high temperatures. Therefore, the optimal reaction temperature for modifying the filter media was 60 °C.

![Fig. 4. Effect of the reaction temperature on the water contact angle.](https://doi.org/10.1016/j.heliyon.2018.e00809)
3.5. Effects of the reaction time

The effects of the reaction time on the water contact angle on the filter media surface were investigated at a reaction temperature of 60 °C, DN101:KH550 ratio of 1:2 and total amount of DN101 and KH550 of 1.0 wt%, and the results are shown in Fig. 5. The conversions of the reactions between the coupling agents and quartz sand increased, and the water contact angle on the filter media surface gradually increased with increasing reaction time. The maximum water contact angle on the modified quartz sand surface and, thus, the highest surface hydrophobicity was observed at a reaction time of 50 min. When the reaction time was further increased, the water contact angle decreased. This result is likely due to the desorption of the grafted organic molecules from the filter media surface under stirring, leading to a decrease in its lipophilicity and hydrophobicity. Therefore, the optimal reaction time was determined to be 50 min.

3.6. Structural characterisation

As shown in the SEM images of the filter media before and after modification in Fig. 6, the unmodified quartz sand had a coarse surface with many irregular angular features, grooves and pits. An anisotropic crystalline structure was clearly observed, and the surface porosity was underdeveloped. After modifying the filter media surface with a uniform layer of the coupling agents, the surface was smoother with no angular features, yet still coarse. Furthermore, the pores were still underdeveloped. The FTIR spectra of the filter media before and after modification are shown in Fig. 7. The unmodified quartz sand exhibited a hydroxyl peak at 3734 cm⁻¹ [25].

![Fig. 5. Effect of the reaction time on the water contact angle.](image-url)
Fig. 6. SEM micrographs of the quartz sand (a, b) before and (c, d) after modification.

Fig. 7. FTIR spectra of the quartz sand (a) before and (b) after modification.
The strong band at 1200–1100 cm\(^{-1}\) and the peak at 472 cm\(^{-1}\) corresponded to the Si-O-Si asymmetric stretching and bending vibrations, respectively. The peaks at approximately 3415 cm\(^{-1}\) and 1627 cm\(^{-1}\) corresponded to the O-H stretching and bending modes, respectively, of adsorbed water molecules. The Si-OH stretching mode at the quartz sand surface overlapped with the water stretching vibration at approximately 3415 cm\(^{-1}\), resulting in peak broadening at this frequency. The DN101 and KH550 C-H peaks were observed at 2918 cm\(^{-1}\) and 2850 cm\(^{-1}\), respectively, in the modified quartz sand spectrum. The C-H bending vibration was observed at 1450 cm\(^{-1}\), and the peak at 1726 cm\(^{-1}\) corresponded to the DN101 ester C=O stretching mode. The peak at 3734 cm\(^{-1}\) that was attributed to the hydroxyl groups on the unmodified quartz sand surface disappeared after surface modification, indicating that these groups reacted with DN101 and KH550\[25\]. These results show that DN101 and KH550 were chemically bonded to the quartz sand surface\[25\].

Fig. 8 shows the XPS spectra of the quartz sand before and after modification. The results show that the unmodified quartz sand consisted of 69.55% O (532.8 eV) and 30.45% Si (103.5 eV). After the dry modification of the surface by DN101 and KH550, the O (536.4 eV), Si (103.0 eV), C (284.9 eV) and Ti (466.4 eV) concentrations at the quartz sand surface were 44.33%, 18.46%, 36.61% and 0.60%, respectively. The Si concentration at the modified quartz sand surface was significantly lower than that at the unmodified surface, due to the layer of coupling agents on the surface after the grafting process. Additionally, the presence of Ti at the filter media surface confirms that the coupling agents were successfully grafted to the filter media surface.

3.7. Oil filtration experiments

When an influent oil with a concentration of 17.3 mg/L was filtered through the column for 4 h at a rate of 4 m/h, the effluent oil concentration was 4.74 mg/L for the unmodified filter media and 2.99 mg/L for the modified filter media. Thus, the oil...
concentration decreased by 36.9% when the modified filter media was used instead of the unmodified filter media, indicating that modifying the filter media greatly enhanced its oil removal efficiency.

3.8. Working life of the filter media

The stability measurements show that the water contact angle on the filter media surface decreased from 82.9° to 81.0° after 24 h of backwashing and to 80.6° after 48 h of backwashing, i.e., the total decrease in the water contact angle was only 2.3° after 48 h, thus demonstrating the excellent stability of the filter media. With prolonged backwashing, the water contact angle gradually decreased until it finally plateaued at a value much higher than 40.1°, which was the value measured on the unmodified quartz sand surface. This result indicates that the modified filter media was highly stable.

4. Conclusions

A combination of titanate and silane coupling agents were used to modify quartz sand filter media by dry processing. The optimal modification conditions were determined to be a DN101:KH550 ratio of 1:2, total modifier amount of 1.0 wt%, reaction temperature of 60 °C and reaction time of 50 min. Under these conditions, the water contact angle on the filter media surface increased from 40.1° for the unmodified surface to 82.9° for the modified surface, thus greatly improving the filter media wettability. After modification, the coupling agents were chemically bonded to the filter media surface, and the modified filter media therefore exhibited excellent stability. The surface modification greatly improved the oil removal efficiency of the filter media in oily wastewater treatment.

Declarations

Author contribution statement

Wei Bigui: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Cheng Yue: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Liu Jianlin, Zhang Hongwei, Dai Liang: Performed the experiments; Analyzed and interpreted the data.

Chang Qing: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.
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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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