Synthesis and application of the drilling mud additive in the presence of surfactants

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Abstract
Drilling fluid is the most important lifeline of the drilling operation, that main task is facilitate the cuttings removal of the drilling. There are varieties of drilling fluids such as sodium bentonite based-drilling fluid is called “mud” and drilling foam or surfactant based-drilling fluid is called “soap”. The present work aims are study on the modified drilling mud properties by using the TiO2 / Polyacrylamide (PAM) as a nanocomposite additive. This additive was obtained through the aqueous solution polymerization of acrylamide monomer in the presence of TiO2 nanoparticles and high hydrophilic-lipophilic balance (HLB) surfactants such as sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan mono-oleate (Tween 80). At first, the TiO2 / PAM nanocomposite was characterized by XRD, UV-Vis, FTIR, DLS and SEM. Then the viscosity, density -specific gravity- and filtration properties of the modified drilling mud were investigated in different amount of nanocomposite compounds. The results indicated that the density, fluid loss and filter cake thickness of the modified drilling mud were decreased with the increase of the surfactant concentration, whereas the viscosity was increased. With the increasing amount of SDS from 0.1 to 1.2 g in the synthesis process, the viscosity was increased approximately 4 cP and the density was decreased about 0.1 specific gravity. The nanoparticle and HLB value were affected in the filtration properties, but in general, that improved the fluid loss and filter cake thickness about 28 and 38% compared the based drilling mud, respectively.

Key words: Drilling mud; Nanocomposite; Polyacrylamide; Surfactant; TiO2.

INTRODUCTION
The drilling fluids are using for drilling deep wells to clean and maintain hole integrity, transport the rock cuttings, lubricate and cool the drill bit, and control the formation pressures. The different drilling fluids such as water-based fluids, oil- or synthetic-based fluids, and pneumatic fluids are using in the drilling operations. Among these drilling fluids, the water-based fluids have the most widely usage in drilling, which are obtained by adding bentonite to the water [1, 2].

The water-soluble polymer additives are using to improve the water-based drilling fluid properties include natural polymers like xanthan gum [3], guar gum [4], or modified natural polymers like polyanionic cellulose [5] or sodium carboxymethyl cellulose (NaCMC) [6, 7] enhance the drilling process. In fact, these compounds are not stable in the high temperatures and salty environments. Therefore, the water-soluble synthetic polymers additives are being produced to solve these problems. Dairanieh and Lahalih [8] had used the methyl cellulose and poly(vinyl alcohol) in the drilling mud to improve the yield point and stability against the shear. Nanoparticles have also been used as drilling fluids additives, mention carbon black [9] and palygorskite [10] nanoparticles. In addition, natural polymer nanoparticles like polyanionic cellulose polymer [11] and carboxymethyl cellulose nanoparticles...
[12] are being used to reduce the water loss and mud cake thickness. The Foam has been used as the drilling mud in the major drilling processes. In most cases, the foam drilling offers many advantages such as increased productivity by reducing formation damage, increasing drilling rate, and reducing operational difficulties associated with drilling in the reservoirs at low pressure (e.g., differentially stuck pipe). Luo et al. [13] studied applications of the foam drilling fluids in fracture and complex formations. The Foam is a continuous liquid phase that surrounds the gaseous phase. The surfactants can be used for this purpose, and the foams can have extremely high viscosity. In general, their viscosity is greater than either liquid or gas that was constituting them [14, 15]. Ozbayoghlu [16] introduced more accurate model for estimating the pressure drop of foam flowing through the bit and showed the same flow conditions and pressure drop were decreased whit increasing of the foam quality. Drilling fluids manufacturers may also have added the Partially Hydrolyzed Polyacrylamide (PHPA) [17] and Polyanionic Cellulose [6] polymers in the drilling foam. Moreover, in our previous work, the Al₂O₃/ Polyacrylamide (PAM) and TiO₂/PAM nanocomposite were synthesized without surfactants and were investigated the drilling fluids properties in the different additive concentrations [18-20].

In this study, TiO₂/PAM nanocomposite was produced by the solution polymerization method in the presence of high HLB surfactants such as sodium dodecyl sulfate (SDS) and Polyoxyethylene sorbitan mono-oleate (Tween 80) to improve the rheological properties of water-based drilling muds. The drilling mud properties such as viscosity, density and foaming behavior are investigated. Surfactants are effective in the increasing the stability and foaming behavior of modified water-based drilling mud.

**EXPERIMENTAL**

**Materials**

Acrylamide (AM) monomer, potassium peroxysulfate (KPS) and sodium dodecyl sulfate (SDS) were purchased from Merck Chemical Co. Polyoxyethylene sorbitan mono-oleate (Tween 80) was purchased from AppliChem. Nano-TiO₂ with an average particle size of 10-15 nm and a specific surface area of 100-150 m² g⁻¹ was purchased from TECNAN Ltd. Natural bentonite was supplied by National Iranian Drilling Co.

**Synthesis method**

The TiO₂/PAM nanocomposite was synthesized by polymerization method solution. There are two main solutions for making synthesis process. The first, SDS and water were stirred for 5 min at room temperature. For second one, Nano-TiO₂ was stirred in the mixture of distilled water and Tween 80 for 5 min at room temperature and ultra-sonicated in an ice bath for 10 min (output power 120 w, work time 2s, pause time 1s) to obtain the homogenous dispersion. Acrylamide and distilled water was stirred for 5 min and then, these solutions were mixed together to obtain the second solution. Then, all of these solutions were mixed for 10 min by magnetic stirring to achieve a stable solution with monomer and nanoparticle. Then, the KPS was dissolved in the mixture solution and was poured into the glass batch reactor that was equipped by the condenser and mechanical stirrer in a water bath, under nitrogen atmosphere. The reaction was performed at 70 °C for 20 min under stirring rate 300 rpm in the whole process. Fig. 1 shows a schematic of this process. When the polymerization process was finished, the polymer nanocomposite was dried in ambient temperature. The recipes that used for preparation of different samples were shown in Table 1.

**Sample preparation**

The nanocomposites were added in the mixture of 350 mL distilled water and 10 g natural bentonite while being stirred at 11000 RPM by a commercial Hamilton Beach stirrer to obtain the modified drilling mud.

**Characterization**

Horiba LB-550 particle size analyzer uses, Dynamic Light Scattering (DLS) measurements were used for measuring particle size over the range of 0.001-6 µm. X-ray diffraction (XRD) pattern was obtained by Bruker D8- Advance instrument with Cu Kα radiation (40 kV, 40 mA). The UV-Vis spectra of the samples were obtained by using a SHIMADZU UV-1800 UV-Vis spectrophotometer achieves a resolution of 1 nm. Infrared spectra (IR) was carried out on PerkinElmer RX I Fourier transform infrared (FTIR) spectrometer. Scanning electron microscopy (SEM) was performed using a Cambridge S-360 SEM.

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Viscosity measurements

Drilling fluids viscosities were measured by the Brookfield DV-II+Pro viscometer with an ultra-low adapter (ULA 316 s/s) at given shear rates.

The adapter consists of a cylindrical sample holder, a water jacket and spindle. The viscometer drives the spindle immersed in the sample holder containing the test fluid sample and can provide a rotational speed that can be controlled to vary from 0.1 to 200 rpm to yield the shear rate from 0.1223 to 244.6 1/s. It measures viscosity by measuring the viscous drag of the fluid against the spindle when it rotates.

Drilling mud filtration measurements

The fluid loss and filter cake thickness of the drilling muds were studied at different surfactant concentrations. The modified drilling muds were filtered through Schleicher & Schuell No. 1505 filter paper using low pressure and temperature (LPLT) filter press apparatus at 100 psi pressure and 25 °C temperature, and the fluid loss was measured after 30 min. The filter cake thickness was measured by the digital caliper.

RESULTS AND DISCUSSION

Characterization of TiO$_2$/PAM nanocomposite

For determining the crystallite structure, we used the XRD technique. Fig. 2 shows the XRD patterns the TiO$_2$/PAM nanocomposite. Three diffraction intensity at 2θ=25.30°, 38.60° and 48.05° for TiO$_2$/PAM indicates the larger amount
of anatase crystal phase existed in the PAM.

The FTIR spectra of TiO$_2$/PAM nanocomposite has been shown in Fig. 3. The absorption peaks at 1329 cm$^{-1}$ and 1094 cm$^{-1}$ are induced by C–O–H deformation vibration and Ti–O–C vibration, which indicates TiO$_2$ has reacted with PAM by –OH.

Fig. 4 shows the particle size distribution of TiO$_2$ nanoparticles. The median and mode size of particles are 18.3 nm and 16.1 nm, respectively.

The UV-Vis spectra of the PAM and TiO$_2$/PAM nanocomposite have been shown in Fig. 5. As it was indicated in Fig. 5, UV-Vis spectrum of TiO$_2$/PAM in aqueous solution showed high absorbency in the range of 300-400 nm, and contained characteristic of TiO$_2$ group band ($\lambda = 325$ nm), which belongs to the TiO$_2$ segment in the polymer chain [21]. This indicated that TiO$_2$ has been incorporated with the PAM molecules.

Fig. 6(a) and (b) show the SEM micrographs of the pure PAM (SS-0) and TiO$_2$/PAM nanocomposite (SS-5), respectively. Fig. 6(a) shows the smooth surface of pure PAM. The comparison of these two images shows that the TiO$_2$ grains appear on the surface and the inside of the PAM.
Fig. 4: Particle size distribution of TiO$_2$ nanoparticles.

Fig. 5: UV-Vis spectra of the PAM and TiO$_2$/PAM nanocomposite.

Fig. 6: SEM images of (a) pure PAM, (b) TiO$_2$/PAM nanocomposite.
The viscosity, foaming behavior and filtration properties of the drilling mud

The amphiphilic surfactants are characterized by the hydrophilic-lipophilic balance (HLB): a relative ratio of the polar and non-polar groups in the surfactant. This means, the balance between the oil soluble and water-soluble moieties in a surface-active molecule, and is expressed as the “hydrophilic-lipophilic balance”.

The HLB number of a mixture composed of \(x\)% of surfactants of HLB A and \(y\)% of surfactants of HLB B is obtained by the following formula [22].

\[
HLB (A + B) = \frac{(A x + B y)}{(x + y)}
\]  

(1)

The HLB value of SDS is 40. It dissolves in the water very well, that is a common additive to the most heterogeneous systems, and to almost all common detergents, shampoo etc. Also, the HLB value of Tween 80 is 15. It is used in detergents systems and oil-in-water emulsifying agents. In this experiment, the TiO\(_2\)/PAM was synthesized with different amounts of high HLB surfactants as shown in Table 1. The viscosity and density of the drilling muds show in Fig. 7. Density is expressed as a specific gravity (SG) according to:

\[
(SG=\rho)/\rho_0
\]  

(2)

Where \(\rho\) is the density of substance and \(\rho_0\) is the density of reference substance. The reference substance is distilled water with 0.99 g/ml density. The results indicate that the viscosity and density of the sample SS-0 is higher than other samples. By adding the nanoparticles to the system (Sample SS-1), the viscosity is decreased about 14 cP, while there is no significant change in the density. However, by adding the surfactants, increase in the viscosity and decrease in the density. In addition to, Fig. 8 shows the reduction of SG by increasing the HLB value. Therefore, the foaming behavior can be change with the amount of surfactants.

![Fig. 7: Viscosity and specific gravity of the samples.](image)

![Fig. 8: HLB value and specific gravity of the samples.](image)
small amount of TiO2 nanoparticles in the synthesis indicate that the fluid loss decreases by adding a cake thickness, respectively. The results in Table 2 about 28 and 38% for the fluid loss and the filter cake thickness, respectively. It has been shown that enhances the filtration properties of the modified drilling mud. Table 2 demonstrates that the enhancement is ±0.03 mm for the fluid loss and filter cake thickness, experimentally. The preparation and three separated measurements in the same experimental condition were described in the section 2. The standard error is about ±0.85 ml and experimental condition. The characterization study such as XRD, FTIR, UV–Vis, SEM and DLS were confirmed that the production of nanocomposite. The comparison between the PAM and nanocomposite has been shown the fluid loss and filter cake thickness were decreased about 28 and 38%, respectively. In the nanocomposite samples with increasing concentration of the surfactants and thereby increase the HLB value of the drilling mud, the level of foam formation is increased. The specific gravity is decreased and the viscosity is increased in the presence of foam in this system about 42 and 45%, respectively.

CONCLUSION

The polymer nanocomposites are usually used to control the viscosity, fluid loss and filter cake thickness of water based-drilling muds. Foam was considered as a weight reduction agent in the drilling operations. In this present work, various samples such as PAM and TiO2/PAM nanocomposites have been synthesized by the solution polymerization method as additives for the drilling muds samples. The characterization study such as XRD, FTIR, UV–Vis, SEM and DLS were confirmed that the production of nanocomposite. The comparison between the PAM and nanocomposite has been shown the fluid loss and filter cake thickness were decreased about 28 and 38%, respectively. In the nanocomposite samples with increasing concentration of the surfactants and thereby increase the HLB value of the drilling mud, the level of foam formation is increased. The specific gravity is decreased and the viscosity is increased in the presence of foam in this system about 42 and 45%, respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

Table 2: Drilling mud filtration properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SS-0</th>
<th>SS-1</th>
<th>SS-2</th>
<th>SS-3</th>
<th>SS-4</th>
<th>SS-5</th>
<th>SS-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid loss (ml)</td>
<td>50.00</td>
<td>46.00</td>
<td>44.00</td>
<td>41.00</td>
<td>38.00</td>
<td>36.00</td>
<td>36.00</td>
</tr>
<tr>
<td>Filter cake (mm)</td>
<td>1.56</td>
<td>1.06</td>
<td>1.04</td>
<td>1.00</td>
<td>1.00</td>
<td>0.98</td>
<td>0.96</td>
</tr>
</tbody>
</table>

REFERENCES


