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# Synthesis of Titania-Bentonite Nanocomposite and its Applications in Water-Based Drilling Fluids

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Titania or TiO<sub>2</sub>-bentonite nanocomposite was synthesised by environmental friendly and cost effective hydrothermal method. Synthesised nanocomposite was successfully characterised by Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD). The target of the study was to enhance the rheological behaviour of the water-based drilling fluid (WBDF) by using synthesised nanocomposite. The experimental results revealed that Titania-bentonite nanocomposite exhibited better rheological characteristics than conventional WBDF. Rheological properties in particular yield point (YP) and 10-min gel strength (10-min GS) were improved by 57 % and 40 % compared to basic drilling fluid after addition of 1.0 g of the synthesised nanocomposite at 65.56 °C. API filtrate loss volume and High Pressure High Temperature (HPHT) filtrate loss volume were slightly reduced by 10 %, and 9.2 %. These scientific results can be used to formulate enhanced WBDF at elevated temperatures.

# 1. Introduction

Gulf of Mexico to Southeast Asia, petroleum and natural gas engineers are exploring deeper, extreme temperatures and pressures, pushing the drilling technologies to the wall than ever before. Conventional drilling fluids additives destabilised the rheological properties at elevated temperature conditions.

Polymers were routinely used in drilling fluids and considered to be good heat insulator. It could not heat transfer through drilling fluid system and deteriorated at high temperature (Mao et al., 2015). Oil-based drilling fluid (OBDF) was commonly used to drill HPHT wells. OBDF raised environmental problems and it was restricted in environmental alerted areas (Young and Rabke, 2006). OBDF formulated for shale drilling mainly contained quaternary ammonium salts which destabilise at high temperature (Silva et al., 2014). Various researchers focused on the use of nanoscale additive, in particular the multi-walled carbon nanotube (Aftab et al., 2016a), nanosilica (Pham and Nguyen, 2014), ZnO (William et al., 2014), and GO (Kosynkin et al., 2011), to improve the rheological behaviour of drilling fluids. Nanosilica has been successfully used for shale inhibition due to their better physical plugging and hydrophobic nature (Cai et al., 2012). Single sphere nanoparticles based drilling fluids have some limitations. Due to the very tiny size of nanoparticles, it raised van der Waals' forces and developed the problems of sedimentation. It cannot homogeneously disperse in the drilling fluids and minimised drilling fluids efficiency. Mao et al. (2015) made efforts to synthesise polymer based nanosilica composite, it was found that rheological and shale inhibition characteristics of WBDF were enhanced.

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Aftab et al.(2016b) synthesised ZnO nanoparticles-acrylamide composite and examined that AV, 10-s GS, API filtrate loss volume and lubricity were improved with the addition of synthesised composite. Abdo et al.(2014) synthesised ZnO-clay nanocomposite and added in WBDF, it was measured that the rheological properties of drilling fluids were stable at high temperature conditions. The development of drilling fluids with enhanced rheological and shale inhibition behaviour at high temperature is still a big challenge. Green behaviour of TiO<sub>2</sub> nanoparticles has attracted a lot of research interest. It has better electronics properties, chemical stability, and low costs. However, it raised agglomeration which may form large particles (Cao et al., 2016). It may lower down the dispersion, reduce viscosity and thermal transition characteristics of the fluids. Researcher modified TiO<sub>2</sub> nanoparticles to enhance its chemical stability and heat transfer qualities. TiO<sub>2</sub> nanoparticles are deposited over bentonite clay to prevent the nanoparticles agglomeration. In result, it may improve the chemical and thermal behaviour of the nanoparticles (Yang et al., 2008). Bentonite is composed of the smectite mineral. It is economical and widely available. It is chemically and physically modified. Bentonite is commonly used in drilling fluids. The function of bentonite is to provide better rheological behaviour in particular increase viscosity and cool the drilling bit (Grolms, 2015). It was the reason TiO<sub>2</sub> nanoparticles were deposited over bentonite.

In the present study, TiO<sub>2</sub>-bentonite nanocomposite was developed. Structural and morphological characterisation of the synthesised nanocomposite were carried out by using conventional characterisation techniques such as XRD and SEM. Rheological properties were determined at elevated temperature to evaluate the potential of the synthesised nanocomposite as a WBDF additive. As per our knowledge no study has been reported so far over the use of TiO<sub>2</sub>-bentonite nanocomposite as a drilling fluid additive.

# 2. Materials and methods

## 2.1 Material

Fluorine doped tin oxide (FTO) substrate, titanium tetraisopropoxide (TTIP), 37 % HCI were purchased from Sigma Aldrich for synthesis of TiO<sub>2</sub> nanoparticles. Bentonite drilling fluid additive provided by Scomi Oiltools for the synthesis of TiO<sub>2</sub>-bentonite nanocomposite. KCI, NaOH, flowzan, filtrate reducer, and barite were provided by Somi Oiltools and used for the preparation of basic and the synthesised nanocomposite based drilling fluids.

#### 2.2 Synthesis of TiO<sub>2</sub>-bentonite nanocomposite

In this typical process, 1.5 mL of TTIP, 23 mL of 37 % HCl and 40 mL of deionised water were mixed and stirred for 35 min. Then solution was transferred in to Teflon vessel of 125 mL and sealed in autoclave and placed in preheated oven at 120 °C for 11 to 12 h. Then, synthesised TiO<sub>2</sub> nanoparticles were filtered and dried in preheated oven 50 °C for 20 min. Synthesised TiO<sub>2</sub> nanoparticles and bentonite were used for the synthesis of the TiO<sub>2</sub>-bentonite nanocomposite. 1 g of synthesised TiO<sub>2</sub>, 1 g of bentonite, and 40 mL of deionised water were mixed at constant stirring for 30 min. The solution was transferred in 100 mL reagent bottle and capped. The reagent bottle placed in the hot tub and sonicated for 1.5 to 2 h at 70 °C. Later, synthesised TiO<sub>2</sub>-bentonite nanocomposite was filtered and dried at 70 °C for 20 min.

#### 2.3 Development of basic drilling fluid and synthesised nanocomposite drilling fluids

25 g of KCl was added in 260 mL of fresh water and mixed by using IKA Rw 20 N mixer for 5 min. 0.13 g of NaOH was added in to the solution and mixed for 3 min. Then, 1 g of flowzan was added into the solution and mixed for 4.0 min. 1.5 g of the filtrate reducer was added into the solution and mixed for the period of 5 min. Later, 190 g of barite was added in to the solution and mixed for the 30 min as provided in Table 1. In the last, 1 : 1 of synthesised nanocomposite was put into 50 mL regent bottle containing 30 mL of fresh water at the different concentrations and sonicated for another 25 min.

Materials	Basic drilling fluid	0.2 g	0.4 g	0.6 g	0.8 g	1.0 g	Mixing time
Fresh water, mL	290	290	290	290	290	290	-
KCI, g	25	25	25	25	25	25	5
NaOH, g	0.13	0.13	0.13	0.13	0.13	0.13	3
Flowzan, g	1.0	1.0	1.0	1.0	1.0	1.0	6
PC, g	1.5	1.5	1.5	1.5	1.5	1.5	5
Barite, g	190	190	190	190	190	190	30
Synthesised nanocomposite, g	0	0.2	0.4	0.6	0.8	1.0	20

Table 1: Formulation of basic and synthesised composite drilling fluids

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## 2.4 Rheological properties

Rheological properties examined the behaviour of drilling fluids at static and dynamic conditions. PV (plastic viscosity), and YP (yield point) were determined by using Fann viscometer. The viscometer determined the shear rates of drilling fluids at different dial reading of 600, 300, 200, 100, 6, 3 revolutions per min (RPM). PV identified the initial resistant to the fluid flow. YP indicated the ability of drilling fluids to remove drill cuttings from sub surface to surface. 10-sec and 10-min GS (gel strength) determined the ability of drilling fluid to suspend drilled cuttings.

## 3. Results and discussion

## 3.1 Structural characterisation of TiO2bentonite nanocomposite

XRD determined the major, minor and traces of the compound in the material. TiO<sub>2</sub>-bentonite nanocomposite was dried at atmospheric temperature before sent for the XRD. It was conducted by using Rigaku smart lab x-ray diffractometer R&D 100. Figure 1(a) shows the diffraction pattern of TiO<sub>2</sub> nanoparticles and bentonite synthesised composite material. SEM was conducted to determine morphology of the synthesised nanocomposite in particular deposition of TiO<sub>2</sub>nanoparticles over bentonite clay. Synthesised nanocomposite was dried at atmospheric temperature and coated with platinum coater for 10 - 15 min before SEM.TiO<sub>2</sub> nanoparticles were incorporated within the bentonite (Figure 1(a)) matrix resulting TiO<sub>2</sub>-Bentonite composite (Figure 1(b)). Bentonite is naturally dynamic colloids, due to their result of shape and halfway owing to their subatomic structure which brings about high negative charges on basal surfaces and positive charges on edges of clay (Darley and Gray, 1988). Thus, deposition of TiO<sub>2</sub> nanoparticles may result from attraction between negative sites of the TiO<sub>2</sub> nanoparticles and positive site on the edge of clay platelets.



Figure 1: Characterisation: (a) XRD of  $TiO_2$ -bentonite nanocomposite (b) SEM of bentonite (c) SEM of  $TiO_2$ -bentonite nanocomposite

## 3.2 Effect of synthesised nanocomposite on rheological properties of WBDF at 26.67 °C and 65.56 °C

Rheological behaviour of WBDF system was improved with the increase in the concentration of the synthesised composite. PV, YP, 10-sec GS and 10-min GS were increased with the increase in the concentration of the synthesised composite. PV was enhanced with the addition of synthesised nanocomposite. PV of basic drilling fluids was found within acceptable range (20 to 29 mPa.s) at both ambient and 65.56 °C. PV had a little increased from 26 to 28 mPa.s at 65.56 °C conditions after addition of synthesised composite as provided in Figure 2(a). Bentonite contains montmorillonite clay which expands 10 time to its volume, resulting better

viscosity and thixotropic properties to the drilling fluids (Peng et al., 2013). TiO<sub>2</sub> nanoparticles increased the viscosity of the system at elevated temperature due to their nano size and better heat transfer characteristics (Turgut et al., 2009). YP was increased with the addition of synthesised nanocomposite at 65.56 °C conditions. YP of basic drilling fluid was found within acceptable range (13 to 21 Pa) at 26.67 °C conditions. Basic drilling fluid displayed decrease in YP with increase in the temperature.



Figure 2: Effect of synthesised composite over (a) PV, (b) YP, (c) 10-s GS, and (d) 10-min GS

YP of basic WBDF was reduced from 14 to 6 Pa at 65.56 °C. It was improved from 6 to 12 Pa with the addition of 1 g of synthesised nanocomposite at 65.56 °C Figure 2 (b). This progress can be attributed to bentonite and TiO<sub>2</sub> nanoparticles. Higher concentrations of synthesised material yielded mild degree of attraction between clay-clay platelets and clay platelets-TiO<sub>2</sub> nanoparticles, resulting better YP and GS. Synthesised material contained bentonite material. YP displayed significant results compared to PV. Hiller (1963) demonstrated that drilling fluids showed decrease in both PV and YP when fully deflocculated, increase in YP and decrease in PV when flocculated at 176.67 °C. 10-s and 10-min GS were improved with the addition of synthesised nanocomposite. 10-s GS of basic drilling fluid was found at 2.8 Pa at 65.56 °C. Basic drilling fluid showed 10-s GS was below the acceptable range (3 to 5 Pa) at 65.56 °C BHFT. It was improved from 2.8 to 5.2 Pa at 65.56 °C with the addition of 1.0 g of the synthesised nanocomposite as shown in Figure 2(c). 10-min GS of basic drilling fluid was found at 4.0 Pa.s at 65.56 °C. It was below the acceptable range at 1 g of the synthesised nanocomposite as provided in Figure 2(d).

# 3.3 Effect of the synthesised nanocomposite over API and HPHT filtrate loss volume

API and HPHT filtrate loss volume were reduced with the addition of synthesised nanocomposite. API filtrate volume loss of basic drilling fluid was found to be 5.6 mL. It was above acceptable range. Acceptable range of API filtrate loss volume is < 5 mL. Figure 3(a) shows that API filtrate loss volume was reduced from 5.6 to 5 mL after adding 1 g of the synthesised nanocomposite.



Figure 3: Effect of synthesised nanocomposite over (a) API filtrate loss volume (b) HPHT filtrate loss volume

The reduction in the API filtrate loss volume was due to the increase in the viscosity of drilling fluid system resulting viscous filtrate and formation of impermeable thin filter cake containing synthesised nanoparticles. HPHT filtrate loss volume was decreased with the addition of synthesised nanocomposite. Despite the fact that filtrate reducer was used, HPHT filtrate loss volume of basic drilling fluid was found to be 13.5 mL. According to Simpson (1974) observation, increase in temperature can increase the filtrate volume in many ways, for instance, it decreases filtrate viscosity, and thus filtrate loss volume was reduced from 13.5 to 11.8 mL with 1 g of synthesised nanocomposite as illustrated in Figure 3(b). It may be possible that the synthesised composite improved the viscosity of filtrate and heat transfer behaviour of the drilling fluid system.

# 4. Conclusion

TiO<sub>2</sub>-bentonite nanocomposite was synthesised and analysed with conventional characterisation techniques. It is observed that synthesised composite improved the performance of WBDF with its increasing concentration. Rheological properties of drilling fluid such as YP, 10-s GS, 10-min GS improved with the addition of synthesised nanocomposite. API and HPHT filtrate loss volume reduced with the addition of the synthesised nanocomposite. The next phase of the study will be to examine the behaviour of the synthesised TiO<sub>2</sub>-bentonite nanocomposite WBDF at high temperature.

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