Abstract
There have been some doubts about the reality of events that unfolds as nanoparticle (NP) travels in a porous media. A good understanding of this will alleviate this challenge, give a clue on how to enhance the delivery and recovery of nanoparticles, wettability alteration mechanism, and optimisation of nanofluid concentration during nanofluid flooding. Adsorption, desorption, blocking and migration are the main phenomena of nanofluid transport mechanism in porous media. Here, we are concerned with a review and simulation (of NP adsorption) of the afore mentioned phenomena which occurs whenever nanofluid travels through a porous media. Theoretical analysis of these phenomena is presented along with governing mathematical models. Also, results of some NPs’ adsorption simulation are shown to consolidate existence of adsorption, quantification of adsorption energy per NP type and suggest the inclusion of NP type as a variable into NP transport models since there is variance in adsorption energy per NP. Gravity force, permeabilities (absolute, relative and effective), capillary pressure, porosity, density, viscosity, saturation, concentration and interfacial tension (IFT) are parameters considered for phenomena description while Brownian diffusion mechanism is the co-opted mechanism.

Keywords: Nanoparticles; Phenomena; Porous media; Transport mechanism; Mathematical model.

1. Introduction

The current findings on research has shown a great deal of improvement in enhanced oil recovery, using nanotechnology [1-2]. Precisely, the use of nanoparticles in EOR although on the laboratory scale, has proven to be better than existing EOR techniques as it improves properties (viscosity, density, etc.) of injected fluid and fluid-rock interaction [3]. This improvement is largely due to its small size (‘nanometre’ means one-billionth of a metre) [2].

Therefore, a definite mathematical representation of nanofluid transport in porous media is needed to effectively optimise the delivery and recovery of NPs. Pore radii of a porous medium range from 6 - 6.3(10^4 nm) compare to nanoparticle size (1-100 nm), which ordinarily suggest an easy flow of NP through the pores, but it is not generally so due to some influential factors. Pore throat may be blocked during transportation of NP if particle size is larger than the pore (mechanical entrapment) [2,4]. The stability of NP in suspension and its movement is due to van der Waals forces and Brownian motion respectively [2,5]. There will not be aggregation of NP provided the repulsive forces between the particles are higher than the attractive forces [6].
Some NP gets stacked to pore surfaces while some to the pore throat leading to NP retention, thereby effecting some changes (wettability alteration, change in relative permeability) to the porous medium. Log-jamming (accumulation) characterises pore throat blockage leaving a narrow area for flow. This process depends on concentration of NP, flowrate, and diameter of pore throats \[7\]. At times some of the stacked NP are released back into the flowing fluid; a process referred to as desorption. The phenomena of nanofluid transport in a porous media are summarised into four as; adsorption, desorption, blocking and migration \[3, 8\].

This paper intends to present mathematical models for the different phenomena involved in NP transport by incorporating Brownian motion theory into the governing principle of fluid flow and present some simulation results of adsorption of some NPs. Fig. 1 illustrates the features of porous media with NP interaction.

2. Transport model for NP flow in porous media

Dispersion effect was neglected by \[9\] when formulating his model on the transport of particles (greater than one micron) through porous media since \[10\] has established that particle dispersion is negligible once NP is greater than one micron. Since NP considered here is in the range of 1-100nm, Brownian diffusion is considered, and the continuity equation for hydrophilic (NP that exists in water phase) NP size interval \(i\) in phase \(l\) in a porous media is given by \[11\] as;

\[
U_l \frac{\partial C_{i,l}}{\partial x} + \phi S_l \frac{\partial C_{i,l}}{\partial t} - \frac{\partial}{\partial x} \left( \phi S_l D_{i,l} \frac{\partial C_{i,l}}{\partial x} \right) + R_{i,l} = 0
\]

(1)

With initial condition; \(C_i(x,0) = C_{i0} = 0; \ t = 0\)

and boundary condition; \(C_i(0,t) = C_{i,in} = 0; \ x = 0; \ C_i(L,t) = C_{i,L} = 0; \ x = L\)

where \(i = 1, 2 ... n\), \(x\) is the distance from the inlet of the sand core; \(t\) is time; \(C\) (wt. %) is particle concentration; \(\phi\) is the porosity of the porous media; \(S_l\) is saturation of phase; \(l, u_l\) is the pore velocity of phase; \(l, D_{i,l}\) is the dispersion coefficient of NP in size interval \(i\) in phase \(l\). Phase \(l\) is fluid.

3. Phenomena involved in NP transport

3.1. Adsorption and desorption

Adsorption is the stacking of NP to the pore surface (wall) or pore throat of a porous media while desorption is the reverse. Force of attraction between NP and pore walls leads to adsorption of NP to the pore wall while desorption is due to repulsion force \[8\]. Fig. 2 gives information on areas where stackings can occur in porous media. NP could be caught up in the air-water interface, solid-water-air interface, within the pores, at pore-mouth and even at portion of the rock where there is no continuous flow (dead zone).

Figure 2. NP Possible attachment zone

The aftermath of adsorption/desorption are; changes in relative permeabilities, wettability alteration and reduction of surface tension thereby enhancing oil mobility and displacement efficiency of NP leading to improved oil production as experimentally proven by \[12\]. Also, increase in concentration of NP enhances adsorption leading to wettability alteration due to a reduction of contact angle \[13\]. Although adsorption/desorption has been largely reported to be of positive effect by \[14\] because; as a key parameter, wettability dictates location, movement and spreading of fluids in porous media \[8\], but it could be adverse too since it could
lead to a decrease in porosity \cite{12}. These mechanisms practically determine the quantity of nanoparticle that will be recovered after nanofluid flooding. Even under the assumption that there is no NP decay, it is practically impossible to recover the quantity of injected NP. There are three types of filtration mechanisms (surface, straining, physical-chemical) that describes these processes. \cite{15} considered desorption and adsorption rates to develop the filtration model (reaction term):

\[
\frac{\partial S}{\partial t} = K_{\text{dep}} \left(1 - \frac{S}{S_{\text{max}}} \right) C - \frac{\rho_b}{\phi} K_{\text{det}} S
\]

\[
(2)
\]

\(\rho_b\) = bulk density of porous media; \(\phi\) = porosity of porous media; \(S\) = adsorption; \(D\) = dispersion coefficient; \(K_{\text{dep}}\) = adsorption rate; \(K_{\text{det}}\) = desorption rate; \(t\) = temporal variable; \(S_{\text{max}}\) = maximum retention capacity, which can be determined by the specific surface area based on the monolayer principle.

The reaction term is proposed by Langmuir \cite{16} and is the basis for adsorption simulation in material studio software which is used to simulate the adsorption of some nanoparticle to the sandstone surface. Table 1 shows the adsorption strength of NPs with the negative signs reflecting that all the NPs have adsorption tendencies.

Table 1. Mono nanoparticle (NP)

<table>
<thead>
<tr>
<th>NP</th>
<th>PaO</th>
<th>PaO2</th>
<th>NiO</th>
<th>GeO2_alpha</th>
<th>BaO2</th>
<th>TiO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy</td>
<td>-0.37</td>
<td>-10.19</td>
<td>-0.09</td>
<td>-8.70</td>
<td>-9.09</td>
<td>-5.63</td>
</tr>
</tbody>
</table>

Table 1 show case the adsorption capacity of NP to vary from NP to NP as different NPs have different absorption capacity. Different NPs have different adsorption energies suggesting their tendencies to change porous medium properties; from oil-wet to water-wet, which is good news to oil and gas industry. Table 2. reflects a higher adsorption for hybrid NPs compare to mono NPs.

Table 2. Hybrid nanoparticle (NP)

<table>
<thead>
<tr>
<th>Dielectric NP</th>
<th>PaO</th>
<th>Magnetic NP</th>
<th>PaO2</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO2_alpha</td>
<td>-25.05579554</td>
<td>-35.79411051</td>
<td>-24.61846131</td>
<td></td>
</tr>
<tr>
<td>BaO2</td>
<td>-35.26376585</td>
<td>-27.13185291</td>
<td>-23.67020279</td>
<td></td>
</tr>
<tr>
<td>TiO3</td>
<td>-28.58768845</td>
<td>-27.42858077</td>
<td>-23.66050692</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 reveals a higher adsorption capacity for hybrid NPs which may also be good depending on goals to be achieved. \cite{13} presented an empirical model relation to contact angle (a major factor for wettability alteration);

\[
\theta = \frac{\theta_0}{(aC+1)}
\]

\[
(3)
\]

where: \(C\) is nanoparticle concentration (wt%); \(a\) = rock surface factor; \(\theta_0\) = initial contact angle; and \(\theta\) = contact angle (°).

3.2. Migration and blocking

Understanding the movement of NP and factors influencing such movement is crucial for NP recovery. The tiny linked channels that are found in permeable rocks are called pores, and space, where they are contained, is the pore space. The narrower passages linking pore bodies are the pore throats \cite{17}. Migration is a phenomenon used to describe the movement of NP through the pores, pore throats, and rock surfaces while interacting with other fluids. The movement is dictated by Brownian motion, as NP moves freely \cite{2,5}. At a point in time, there tend to be a reduction in concentration of NP as retention sets in due to two major activities: NP with a larger radius than the pore throats cover the mouth of the pore throat leading to surface deposition of NP on pore bodies and NP smaller in size compare to pore throat aggregate in the pore throat as NP propagates. These two activities are reportedly known as mechanical entrapment (straining) and log-jamming (accumulation) respectively \cite{2,7}, while the
The entire process is referred to as blocking \([3,8]\). We consider Langevin equation to represent the migration phenomenon due to Brownian motion with a mathematical model starting with Newton equation for particulate movement:

\[
m \frac{dv(t)}{dt} = F(t)
\]

where: \(M=\) mass; \(v(t)=\) velocity; \(t=\) time and \(F(t)=\) total force.

For Brownian particle interacting with the surrounding medium, \(F(t)\) is a combination of friction force \(-\gamma v(t)\) (dominant) and random force \(\xi(t)\). Where \(\gamma = 6\pi \eta a\) (\(\eta = \) viscosity, \(a = \) particle radius) is friction coefficient given by Stokes [18]. Therefore, model for Brownian particle is;

\[
\frac{dx(t)}{dt} = v(t); \quad \frac{dv(t)}{dt} = -\frac{\gamma}{m}v(t) + \frac{1}{m} \xi(t)
\]

But \(\xi(t)\) is due to density variation, if we assume that there’s no variation then, (5) becomes;

\[
\frac{dv(t)}{dt} = -\frac{6\pi \eta a}{m}v(t)
\]

Which has the solution;

\[
v(t) = e^{-\frac{6\pi \eta a}{m} t}v(0), \quad \tau_B = \frac{m}{\gamma} = \frac{m}{6\pi \eta a}
\]

Considering effects of pressure \(P\), gravity \(g\), absolute permeability \(k\), relative permeability \(k_r\), viscosity \(\mu\) and depth \(Z\); differential Darcy law is engaged in describing the velocity of NP in porous media [19];

\[
u = -\frac{k}{\mu} (\nabla P - \rho g \nabla Z)
\]

Blocking phenomena results in NP retention \((R)\) and are classified as; deposition on the pore body and accumulation in the pore throats. Model of [3,9] was modified with the assumption that NP is hydrophilic (phase restricted) to obtain;

\[
R_i = \frac{\partial \sigma_i}{\partial t} + \frac{\partial \sigma_i^*}{\partial t}
\]

\(\sigma_i\) is a mass of NP i in contact with water phase on the surface of the pore per unit bulk volume of rock, \(\sigma_i^*\) is mass of NP i captured in pore throats caused by plugging and bridging.

There is a value for velocity (critical) that determines when NP is both retained and entrained. Specifically, only retention occur below this value while NP is retained and entrained simultaneously when velocity is above this critical value \([3,20]\). [9] modified the work of [20] to develop a model for surface deposition as;

\[
\frac{\partial \sigma_i}{\partial t} = k_{re,i} u_w \sigma_i; \quad u_w \leq u_{wc}
\]

\[
\frac{\partial \sigma_i}{\partial t} = k_{re,i} u_w \sigma_i - k_{en,i} \sigma_i (u_w - u_{wc})
\]

\[
u_w > u_{wc}
\]

where: \(k_{re}\) and \(k_{en}\) are retention and entrainment rate constants respectively; and \(u_{wc}\) is the critical velocity; With the initial condition; \(\sigma_i = 0; \ t = 0\).

For pore throat entrapment, the rate equation is;

\[
\frac{\partial \sigma_i^*}{\partial t} = k_{pt,i} u_w \sigma_i
\]

where: \(k_{pt}\) is rate constant for pore throat blocking with the initial condition; \(\sigma_i = 0; \ t = 0\).

4. Conclusion

Theoretical analysis with simulation and mathematical models for the different phenomena involved in NP transport has been presented by incorporating Brownian motion theory into the governing principles of the migration phenomenon. These phenomena may also be applied in describing the process of nutrient release into the soil. Assuming a constant density (no variation of mass) in equation (8); implies that velocity of Brownian particle vanishes at long durations \((t \to \infty)\), it may not be required for cases of long time NP migrations. Reduction of mass of NP may not be solely dependent on retention and entrainment as condition like NP
decay may also play a role. Therefore, NP decay could be taken into consideration in future modelling of NP transport.

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References


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