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Experimental assessment of graphene oxide adsorption onto sandstone reservoir rocks through response surface methodology

Hamideh Radnia[a], Ali Reza Solaimany Nazar[a,*], Alimorad Rashidi[b]

[a] Chemical Engineering Department, University of Isfahan, Isfahan, Iran
[b] Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

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ABSTRACT

This study mainly deals with the adsorption behavior of the graphene oxide (GO) onto sandstone which is an important factor for applying a material in chemical enhanced oil recovery methods. The combined effects of initial GO concentration, salinity and pH of the solution are assessed by adopting response surface methodology. The results show that the GO concentration has a stronger influence on the GO adsorption than those of the initial pH and salinity. The effect of pH on the GO adsorption becomes significant at high GO concentrations and low salinities. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is applied to explain the observed trend of GO adsorption under various salinity and pH conditions. Reduction in the height of energy barrier and formation of a secondary minimum are responsible for increasing the GO adsorption at lower pH values and moderate salinities (1 wt.%). The contact angle measurement of the rock surface treated in GO solution at optimum conditions (GO concentration of 0.89 mg/mL, salinity of 5 wt.% and pH of 6.74) shows that the adsorbed GO can alter the wettability of sandstone from strongly oil wet (150°) to intermediate conditions (90°).

1. Introduction

Enhanced oil recovery (EOR) is a potential tool usually applied to recover extra oil from the subsurface reservoir by altering the rock and *in situ* fluid properties. Almost one-fourth of the world's sedimentary rocks are sandstone. Injecting an agent into reservoirs called chemical enhance oil recovery is the most common technology for enhancing oil recovery in sandstone reservoirs [1].

Chemical EOR improves oil recovery due to several mechanisms: decreasing the oil/water interfacial tension (IFT) via increasing the capillary number which results in larger amounts of oil displacement from pores; increasing the viscosity of the sweeping fluid relative to that of the oil, leading to decrease in mobility ratio which is suitable for enhancing oil recovery; and altering the wettability of the reservoir rock to become more water-wet which can improve the microscopic displacement of trapped oil in the rock pores [2–4].

Recently, the use of nanoparticles has attracted major of interest for EOR applications [5–10]. A new view of oil displacement from a solid substrate using nanoparticle dispersions is based on a novel concept of nanoparticle structuring in the wedge film which is proposed by Wasan and Nikolov [11–13]. The nanoparticle structuring phenomenon increases the structural disjoining pressure in the wedge film. The disjoining pressure can act as driving force for wettability alteration during nanofluid flooding and expel oil from rock surface [14–16].

The interaction between nanoparticles and reservoir rock plays an important role in the performance of nanofluids for EOR applications. A deep understanding of this aspect helps to design a more successful nanoparticle assisted EOR process. Well-designed nanoparticles are able to adsorb at the oil–water interfaces in the rock pores while travelling through reservoir rocks. This can decrease the IFT and produce fine oil in water emulsion droplets, which is suitable for EOR. However, in conjunction with IFT reduction mechanism, wettability alteration of reservoir rock by nanoparticles can also enhance the oil recovery.

The transport and retention of different nanostructures have been investigated in literature. The adsorption behavior of SiO_2 nanoparticles in a low permeability core was studied through displacement tests by Lu et al. [17]. They concluded that nanoparticles tend to attach to the pore surface of the rock and change the wettability of the cores to a strongly water-wet condition. Iqbal et al. [18] designed and prepared magnetite nanoparticles grafted with sulfonated copolymers. Using the polymer provides electrosteric stabilization between the nanoparticles and weakens the interactions of the nanoparticles with sandstone surfaces. Choi et al. [19] prepared hydrophobically associative zwitterionic

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* Corresponding author.
E-mail addresses: asolaimany@eng.ui.ac.ir, asolaimany@yahoo.com (A.R. Solaimany Nazar).

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Nomenclature

A	Hamaker constant (J)
Adeq Precision	Adequate precision
Adj. R^2	Adjusted R^2
ANOVA	Analysis of variance
b_i	Linear effect
b_0	Intercept
b_{ii}	Squared effect
b_{ij}	Interaction effect
C_e	Equilibrium concentration of the solution (mg/mL)
C_0	Initial concentration of the solution (mg/mL)
CCD	Central composite design
DLVO theory	Derjaguin–Landau–Verwey–Overbeek theory
e	Electron charge (-1.60×10^{-19} C)
EDS	Energy dispersive spectroscopy
EOR	Enhanced oil recovery
FESEM	Field emission scanning electron microscopic system
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
H	Separation distance between GO particle and sand surface (m)
I	Ionic strength of the background electrolyte (mol/L)
IFT	Interfacial tensions
K	Number of factors
k_B	Boltzmann's constant (1.38×10^{-23} J/K)
LSD	Least significant difference bars
M	Mass of used sand (g)
N_A	Avogadro number (6.02×10^{23} atoms/mol)
Pred. R^2	Predicted R^2
Prob. $> F$	Proportion of time or probability expected to obtain the stated F value
r_p	Radius of GO particle (m)
R^2	Coefficient of determination
RSM	Response surface methodology
Std. dev.	Standard deviation
T	Temperature (333 K)
TEM	Transmission electron microscopy
V	Initial volume of the solution (mL)
V_{DLVO}	Total interaction energy between two surfaces (J)
V_{EDL}	electrostatic double layer potential energies (J)
V_{VDW}	van der Waals potential energies (J)
x_i	Dimensionless coded value of the ith independent variable
X_i	ith independent variable
X_j	jth independent variable
X_0	Value of X_i at the center point
X_1	First factor, GO concentration (mg/mL)
X_2	Second factor, salinity (wt.%)
X_3	Third factor, pH
XRD	X-ray diffraction
Y	Experimental response

Greek symbols

$\pm\alpha$	Axial points
Δx	Step change value
ε_0	Vacuum permittivity (8.85×10^{-12} $C^2/(J\,m)$)
ε_r	Dimensionless relative dielectric permittivity constant of water (78.4)
ζ	Zeta potential
K	Inverse of the diffuse layer thickness ($1\,m^{-1}$)
λ	Characteristic wavelength of GO particle (10^{-7} m)
$\lambda_{\max}$	Wavelength that the absorption peak is observed in UV spectra
ψ_1	Surface potentials of GO (V)
ψ_2	Surface potentials of sand (V)

polymer-coated silica nanoparticles. The core flooding experiment demonstrated that this nanofluid could enhance oil recovery along with lowering the injection pressure due to the formation of the wedge film between the oil and the rock surface. There are other studies investigating the interaction of nanoparticles with rock surface. The studied nanoparticles are silica in an oilfield polymer polyacrylamide [20], silica with mixture of surfactant and polymers [21] and titanium oxide nanoparticles [22,23].

The previous researches showed that graphene oxide (GO) [24, 25] and also its hybrids with metal nanoparticles [26,27] have an ability to form emulsions by altering interfacial tension between oil and water phases. GO is offered as an attractive opportunity for enhanced oil recovery in deep subsurface due to its suitable dispersion stability at high salinity brines [28]. There are a number of researches dealing with modifying the GO surface in order to improve its stability at high temperature and salinity. In this case, Zuniga et al. [29] proposed a method for covalently functionalization of GO with a kind of zwitterionic polymer to improve its stability. Luo et al. [30] also produced a nanofluid of graphene based amphiphilic Janus nanosheets for chemical flooding. They investigated the colloidal stability of this nanofluid in another research work [31].

The interaction between GO and solid surfaces is a main challenge for successful propagation of GO through porous media. Adsorption of GO onto the rock or sand affects qualitatively and economically the performance of flooding processes. This makes it less effective in IFT reduction during EOR applications. This negative effect can be partly compensated, if the adsorbed GO can alter the wettability of the rock from oil wet to water wet conditions.

To the best of our knowledge, there is no study on the GO and sandstone interaction for oil reservoir applications. In this study the central composite design (CCD) under response surface methodology (RSM) is adopted to determine the optimum conditions for minimizing the GO adsorption onto sandstone in terms of the independent factors of initial GO concentration, salinity and pH of the solution. In comparison to our experimental studies, the attachment behavior of GO onto sandstone are related to theoretically determined Derjaguin–Landau–Verwey–Overbeek (DLVO) energy interaction profiles. The effectiveness of GO dispersion in altering the wettability of sandstone to preferential water-wetting is also assessed through the contact angle measurements.

2. Experimental

2.1. Materials

Graphite powder, sodium nitrate, potassium permanganate, sulfuric acid, hydrochloric acid, 30% hydrogen peroxide, sodium chloride, sodium hydroxide and toluene are purchased from Merck (Germany). All reagents are analytic grade.

2.2. Sandstone samples

Sandstone cores are obtained from one of Iranian southwest oil fields. All core plugs are cleaned by toluene and methanol in a Soxhlet extractor. The cores are crushed and characterized using

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