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Full Length Article

Demulsification of water in oil emulsion using ionic liquids: Statistical modeling and optimization

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ABSTRACT

In this research, the performance of three ionic liquids namely Trioctylmethylammonium chloride, Trioctylmethylammonium bromide and 1-Hexadecyltrimethylammonium bromide are evaluated as the demulsifier agents to break crude oil emulsion through the bottle test method. Then, the response surface method (RSM) is applied to investigate the effect of demulsifier concentration, temperature, pH and fresh water ratio on the dehydration efficiency of the prepared agents. The experiments are designed based on the central composite design method (CCD). To find the optimum conditions of input variables, an accurate model is developed to predict the dehydration efficiency of agents based on the statistical testing of various models by the analysis of variance (ANOVA). The results shows that temperature and pH of aqueous phase are two main parameters in the demulsification process and the maximum dehydration is attained at neutral value of pH and nearly the maximum temperature in the all samples. Then, the optimum operating conditions of agents are determined by RSM.

1. Introduction

Generally, the extracted crude oil from reservoir contains some impurities such as water and sediment [1]. In addition, it consists of a series of hydrocarbons such as alkenes, naphthenes, and aromatic compounds as well as phenols, carboxylic acids, and metals. Some of these components such as asphaltene, resin, wax, and naphthenic acids may accumulate at the water-oil interface [2] and form a stable film around the droplets that hinder the water droplets to coalescence and cause to form stable water in oil emulsion [3]. The stability of the emulsion depends on the several factors, including the heavy material in crude oil, solids (e.g., clays, scales and corrosion products), temperature, pH, water droplet size and oil to brine ratio. Viscosity, interfacial tension and difference in density between two phases are considered as other important factors [3,4]. The presence of water in oil causes several problems in the handling and processing stages such as corrosion, fouling in pipelines, equipment, and poisoning of catalysts in the refinery processes [5]. Thus, it is necessary to break the emulsion and separate water from crude oil [6,7]. Chemical demulsification is the common method for destabilizing the emulsion by the surface-active compounds that known as demulsifier agent. The emulsifier molecules at the interface are replaced with the demulsifier and it destroys the stable film around the water droplets [4,8,9]. Finding the principle and essential parameters that destabilize water in oil emulsion are the major challenges in the oil processing. In this regard, many studies have been reported recently. Mohammed et al. investigated the effect of chemical demulsification on the water in oil emulsion via bottle test and microscopic examinations [10]. The results showed that agent overdosing has a reverse effect on the demulsification efficiency. Zaki et al. studied the effect of temperature, NaCl concentration, pH, and solvent type on the demulsification efficiency of the propylene oxide (PO)-ethylene oxide (EO) block copolymers [11]. The results showed that the high temperature and low salinity of the aqueous phase increase demulsification efficiency. The maximum demulsification efficiency was obtained when the pH value of the emulsion's aqueous phase approaches to seven. Abdul-Wahab et al. evaluated the effect of temperature, settling time, mixing time, chemical dosage, and dilution rate on the desalting and dehydration process [12]. The results indicated that the settling time and dilution water are the common variables in estimating both the salt removal and water cut efficiencies. Fortuny et al. investigated the effect of pH, salt and water contents on the microwave demulsification process [13]. The experimental results showed that the maximum demulsification was achieved under the highest temperature at natural environment. Mahdi et al. experienced the effect of demulsifier concentration, temperature, wash water dilution ratio, settling time and mixing time on performance of the desalting and

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dehydration process by using fractional factorial design [14]. The results showed that salt removal efficiency approaches to 93.28% at the optimal condition. Zhang et al. investigated the enzymatic demulsification of the oil emulsion [15]. The response surface methodology (RSM) was used to maximize the dehydration efficiency and minimize enzyme concentration. Vafajoo et al. studied the effect of temperature, injected chemical demulsifier and pH on an electrostatic desalter [16]. Nour et al. investigated the effect of microwave power, concentration of demulsifier and time processing on the demulsification efficiency of crude oil [17]. Then, the optimal condition of variables was determined by response surface methodology (RSM). Amirabadi et al. investigated the demulsifying performance of a bio-demulsifier to break water in heavy crude oil emulsion [18]. RSM was used to find the optimal values of pH, temperature, carbon source, and carbon concentration. Kundu et al. evaluated the effect of oil concentration, surfactant concentration, stirring intensity and mixing time on the stability of oil/water emulsion considering an integrated hybrid algorithm (GA) and response surface methodology [19].

It is concluded from the literature that concentration of demulsifier, temperature, dilution water and pH have a significant effect on the demulsification efficiency. Due to the unique properties of ionic liquids likes non-volatility, non-flammability, thermal stability and being liquid at room temperature, they are a suitable candidate to apply as demulsifier agent [20,21]. Ionic liquids are cationic demulsifier with amphiphilic characteristics containing a charge head and long alkyl chain(s) as the tail [22]. The present work investigates the effect of demulsifier concentration, temperature, pH and fresh water on demulsification efficiency of water in oil emulsion to find the optimum operating condition of crude oil demulsification by some ionic liquids. Three ionic liquids namely Trioctylmethylammonium chloride, Trioctylmethylammonium bromide and 1-Hexadecyltrimethylammonium bromide have been selected and the dehydration efficiency of the selected agents are compared through the bottle test method. The central composite design (CCD) of response surface methodology (RSM) has been used to design the required tests and optimize the water removal efficiency.

2. Material and methods

2.1. Material

The crude oil emulsion was supplied from Sarvestan oil field in Iran. Table 1 shows the characteristics of the supplied crude oil. The chemical composition of the crude oil is shown in Table 2.

Trioctylmethylammonium chloride (TOMAC) and Trioctylmethylammonium bromide (TOMAB) were supplied from Sigma-Aldrich Company and 1-Hexadecyltrimethylammonium bromide (CTAB) with 99% purity was supplied from Merck Company. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) and the required solvents such as methanol, toluene, and xylene were supplied from Kimia Mavad Company. Table 3 shows the molecular structure of the selected ionic liquids.

Table 1
The characteristics of the crude oil.

Physical characterization/mass percentage	Value
API gravity at 15 °C	27.34
Viscosity at 15 °C (mPa s)	14
Pour point (°C)	−16
Salt content of the crude oil (mg/L)	1200
Saturates (wt%)	45
Aromatics (wt%)	32
Resins (wt%)	8
Asphaltenes (wt%)	5
Water and residue (wt%)	10

Table 2
Chemical composition of the supplied crude oil.

Component	Mole fraction
C_1	0.0021
C_2	0.0042
C_3	0.0270
IC_4	0.0109
NC_4	0.0380
IC_5	0.0224
NC_5	0.0303
C_6	0.0548
C_7^+	0.8095
H_2S	0.0005
CO_2	0.0003
N_2	0.0000

2.2. Water cut measuring

The water content of the supplied crude oil from Sarvestan oil field was measured by the centrifuge procedure through ASTM D4007-02 test method. The supplied crude oil, xylene and industrial chemical demulsifier (CHIMEC 2642D) were mixed and injected into the cone-shaped centrifuge tubes. The mixture was centrifuged by Eppendorf 5810R Centrifuge at 2000 rpm for 15 min. Then the volume of the separated water and sediment layer at the bottom of the tubes were measured.

2.3. Bottle test method

The common method to determine the emulsion stability in the lab scale is the bottle test. The crude oil and fresh water were mixed in an electric mixer to facilitate the dissolution of salt in the dilution water [23]. To prepare demulsifier agents, hydrophobic ionic liquid as TOMAC was dissolved in xylene and the hydrophilic ionic liquids like TOMAB and CTAB were dissolved in methanol, to prompting the rapid solubility of the demulsifiers in the oil and better separation of the phases. Then, the prepared solution was mixed with the crude oil emulsion. After mixing for 5 min, the prepared samples were placed in an electric oven at a fixed temperature for 12 h. Then, the phase separation was monitored to obtain the water separation capacity. The tests were designed at various demulsifier concentrations, temperatures, pH and fresh water ratio. The demulsification efficiency was calculated by [24]:

$$DE = \frac{V}{V_0} \times 100 \qquad (1)$$

where V and V_0 are volume of the separated water through bottle test and water cut in the prepared mixtures, respectively.

3. Experimental design

Response surface methodology (RSM) is a collection of mathematical and statistical methods that are based on the fit of empirical models to the experimental data [25,26]. The most popular RSM design is the central composite design (CCD) that has three groups of design points namely two-level factorial or fractional factorial design points, axial points and center points [27]. The experimental data from the CCD model were analyzed by following equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{\substack{i \\ i<j}} \sum_{j} \beta_{ij} x_i x_j + \varepsilon \qquad (2)$$