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Separation of Emulsified Oil from Industrial Wastewater Using Poly Silicate Ferro-Aluminum Sulphate (PSFAS): A Novel Methodology for the Attainment of Very High Separation Efficiency

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Research Article

Keywords: Coagulants, Flocculants, Turbidity, Alkalinity

Posted Date: December 8th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-693209/v1

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Abstract

The large amount of wastewater generated from textile industries, petroleum industries, chemical industries contains heavy metals, suspended solids, hazardous waste, oils, fatty acids, dyes, pigment etc. It is very important to improve the quality of contaminated water before it discharges into the water sources or use. In the current work, an efficient methodology has been developed to separate emulsified oil from wastewater. The emulsified oil is tried to separate by using poly silicate Ferro aluminium sulphates, a flocculent. In addition to the above, the maximum separation efficiency for the devolved process is also revealed. Using PSFA, up to 93.5 % separation efficiency is achieved, and the discussed methodology can separate emulsified forms of the oil without altering the efficiency. The dissolved solid and metal content are also considered as the controlling parameters for the separation efficiency. The optimum TDS and the metal content must be maintained at 560 mg/L and 2 mg/L, respectively, to attain maximum separation efficiency.

1. Introduction

Waste water from chemical industries contains heavy metals, organic and inorganic materials, fertiliser, petrochemicals, and many other additives that highly impact natural water bodies and must be prevented from entering into the water cycle; otherwise, deadly impact on the aquatic Ecosystem. Various processes are available to treat water like adsorption, aeration, sedimentation, screening, disinfection, chemical oxidation etc.(Li et al. 2011; Osman 2014; Chaitali Gohatre 2016; Colla et al. 2016; EH et al. 2018).

Industrial wastewater contains oil and grease, and these are considered threatening to aquatic animals, marine animals, and human beings. Therefore, before discharge to the main water stream, the oil and grease present in the industrial wastewater need to separate. Among various forms of oil, the oil which is present as a separate layer or presents as a bulk quantity can be separated easily by following the methodology described in the literature (Hassler 2011; Li et al. 2014; Xue et al. 2014; Razali et al. 2015). However, the emulsified form of the oil is very difficult to separate efficiently. Therefore, an attempt has been made to separate the emulsified oil from the industrial wastewater up to 99% (S. Liubartsevaa et al. 2015; Xiong et al. 2015).

In the effluent, the emulsified oil forms a physical hydro-bonding with the nearest water molecules. The discussed attachment is physical attachment, defined by the attractive force between the emulsified oil and the water. For the removal of emulsified oil in the effluent stream, the physical hydro-bonding needs to break. The detachment mentioned above is performed by using additives which creates a strong electrostatic force between the additive and the oil. The described mechanism is depicted with the help of the following schematic. (Fig. 1)

Stage 1: Oil and water interaction in the effluent.

Stage 2: Oil and water separation in the effluent

After separating emulsified oil, the density of oil increases compared to water due to the attachment of strong metallic ions with the oil molecules. Furthermore, for the agglomeration of separated oil droplets, strong interactions among the oil droplets are required, and this is done by adjusting the pH. After that, due to gravity, the flocs settle, and an effluent stream free from oil and grease is obtained (Lin et al. 2007; Choi et al. 2009; King et al. 2015; S. Liubartsevaa et al. 2015).

In the current work, using the above-discussed mechanism, the emulsified form of the oil is tried to remove very efficiently, and the proposed process has not been disclosed in the literature, and the obtained separation efficiency is also much higher than the reported value. Furthermore, the additive consumption rate is comparatively lower than the data reported in the literature (GUPTA, Vinod Kumar, ALI, Imran, SALEH, Tawfik A.; Gu and Li 1998; Teduka and Nishioka 2014; Zhu et al. 2016; Wu et al. 2018).

It is a highly effective process for removing colloidal, soluble, and suspended particles as well as other types of pollutants such as organic compounds, colour, micro pollutants, fat, and oils, by aggregating macro and micro particulates into larger ones and then sedimenting them(EH et al. 2018). This process helps to reduce the organic matter, pH, turbidity, alkalinity, oil concentration and increase the dissolved oxygen level.

2. Experimentation

2.1 Material and Methods

Industrial wastewater containing emulsified oil and grease, calcium oxide, and poly-silicate and Ferro-aluminium sulphate were used in the current work. The wastewater collected from the industry was initially analysed, and the obtained results have been presented in Table 1. The composition stated below is diluted by using distilled water to prepare the various industrial wastewater composition. In addition to the above, poly-silicate and Ferro-aluminium sulphate and calcium hydroxide were prepared. The PSFAS was prepared using Sodium Silicate $Na_2SiO_3.9H_2O$ (MW 284.22), Ferrous Sulphate $FeSO_4$ (MW 278.02), Aluminium Sulphate $Al_2(SO4)_3.18H_2O$ (MW 666.41), Sulphuric acid H_2SO_4 (MW 98.07). The flocculent was prepared by following the methodology reported in the literature, and after preparing the composition, it was ensured using FT-IR analysis.

2.2 Experimental procedure

The experimental setup used in the experimentation is presented in Fig. 3. It contains a reactor (20L) which is fitted with an air distributor at the bottom. In addition to the above, the reactor is also fitted with pH and temperature indicators. The reactor is connected with the tank, where separation (20 L) is achieved based on density difference. Finally, the sludge from the separator goes to the filter press. In addition to the above, two dosing pumps are used to feed calcium hydroxide and PSFAS intermittently as per the experimentation design.

Table 1
Composition of wastewater

Name of the parameter	Concentration (mg/L)
Oil and Grease	609
Suspended solids	700
Ammonia as (N_2)	060
Phenol	007
Chromium (VI)	003
COD	500
BOD	110
Cyanide	004
Fluoride	014
Lead	2

2.3 Flocculent Preparation Procedure

The flocculant used in the experiment was PSFA. In preparation for PSFA, 1.7g sodium silicates, 27.80g ferrous sulphate, and 99.96g were initially combined in a glass reactor. The reactor was then filled with 230 mL 98% weight sulphuric acid and then gently filled with 230 mL tap water while stirring. Finally, the solution was agitated for 1.5 hours to obtain the final PSFA flocculant. The flocculant was solid and white or yellow in colour, and it retained its properties for at least three months. In practical coagulation experiments, a stock solution of 20% PSFA was prepared using tap water (density: 1.0866 g/mL, pH: 0.41). $Al_2(SO_4)_3$ was dissolved in tap water to make a 20% coagulant solution (density: 1.1238 g/mL, pH: 2.51).(Li et al. 2011).

2.4 Experimental Procedure

After mixing the flocculent mentioned above, the pH, turbidity, total dissolved solids, alkalinity, metal content and dissolved oxygen content of the waste eater alter. Therefore, before using the PSFAS in the oil-water separation process, the variation of the parameters mentioned above regarding additive dosing amount needs to be investigated. The quantity of additives required to create the favourable condition for the higher removal efficiency needs to be monitored, and other additives are used to attain higher efficiency if the ambience is not in the favourable direction.

2.5 Variation of pH

The variation of pH with the PSFAS concentration is presented in Table 2. It indicated the transition from basic region to acidic with the increasing concentration of PSFAS. The study on the effect of pH is necessary for oily wastewater because solubility depends on it. Suppose the pH value higher than 7, then lesser the solubility and vice versa. When the pH value is high, the charge of the flocculant types becomes less positive, making them less attractive to anionic organic compounds and decreasing the likelihood of floc formation.

Table 2
The variation of pH with PSFA

Sl.No.	Flocculant dosage(mg/L)	pH values
1	0	7.2
2	5	6.95
3	20	6.30
4	35	5.56
5	55	5.2
6	70	6.5
7	90	4.95
8	120	3.5
9	140	3.4

2.6 Variation of TDS

TDS is a mixture of dissolved solids that contains solid or metal such as potassium, calcium, carbonates, fluorides, magnesium, and many more. In addition to the above, it also comprises heavy toxic metals like mercury, lead, and arsenic. These toxic chemicals are extremely hazardous to health. The reduction rate in TDS due to the use of PSFAS is presented in Table 3. As the flocculent dose is increased, the TDS content declines in the wastewater. If we increase flocculant, further TDS increases due to an increase in a solute particle of flocculant; this helps to reduce the efficiency of TDS removal.

Table 3
The variation of TDS with PSFA

Sl.No.	Flocculant dosage(mg/L)	Total Dissolved Solvent(mg/L)
1	0	570
2	5	558
3	20	481
4	35	445
5	55	363
6	70	398
7	90	402
8	120	428
9	140	498

2.7 Variation of DO

The DO presents in the wastewater decides the final BOD and COD before the treatment on sets (Table 4). Generally, Bacteria and microorganisms use this dissolved oxygen to degrade the organic matter and decrease the oxygen level in the sample. The DO values at different doses of PSFAS are illustrated in Table 4. The optimum concentration depicting the maximum DO in water is 6–7 mg/L. After the maintained value and concentration, the DO reaches the plateau region.

Table 4
The variation of DO with PSFAS

Sl. No.	Flocculant dosage(mg/L)	Dissolved Oxygen
1	0	3.9
2	5	4
3	20	4.2
4	35	4.8
5	55	5.6
6	70	5.9
7	90	6.3
8	120	6.6
9	140	6.8

2.8 Variation of Alkalinity, Turbidity and Metal content

Alkalinity is a measurement of dissolved alkaline substances in water (higher than 7.0 pH). It tells us the water's ability to neutralise the acid. The variation of alkalinity with PSFAS is presented in Table 5. As the flocculent dose increases, alkalinity in water decreases up to 200, and further variation is insignificant. In addition to the above, the variation of turbidity with flocculent dose is presented in Table 6. As a dose of flocculent increases, turbidity decreases, and after a certain value, it almost remains constant due to the destabilisation of solid particles. Furthermore, the reduction in metal contents such as Pb and chromium hexavalent is also noticed (Table 7)

Table 5
The variation of alkalinity with PSFAS

Sl No	Flocculant dosage(mg/L)	Alkalinity(mg/L)
1	0	350
2	5	330
3	20	290
4	35	250
5	55	225
6	70	200
7	90	190
8	120	180
9	140	174

Table 6
The variation of turbidity with PSFAS

Sl. No.	Flocculant dosage(mg/L)	Turbidity (NTU)
1	0	150
2	5	142
3	20	120
4	35	98
5	55	75
6	70	59
7	90	44
8	120	42
9	140	39

Table 7
The variation of metal content with PSFAS

Sl No.	Flocculant dosage(mg/L)	Metal element Lead(mg/L)
1	0	2.0
2	5	1.2
3	20	0.93
4	35	0.8
5	55	0.71
6	70	0.66
7	90	0.6
8	120	0.59
9	140	0.51

3. Results And Discussion

In the current work, the oil's separation efficiency is considered a parameter defining the effectiveness of the designed process. Therefore, the variation of the parameter mentioned earlier at various ambiences tries to identify the best or optimum operating condition for the highest efficiency attainment (Eq. 1). In the current investigation, by using the following equation, the separation efficiency is calculated.

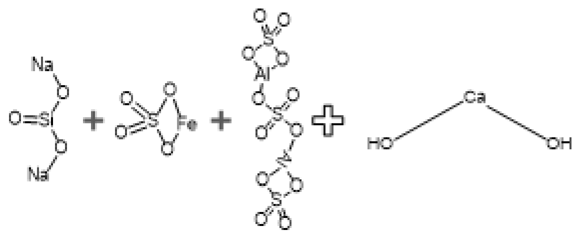
$$\text{Separation efficiency} = \frac{C_o - C_f}{C_f} \qquad (1)$$

3.1 The Effect of PSFAS Dose

The variation of separation efficiency is calculated by following Eq. 1, with PSFAS doses, presented below Fig. 4. It indicates the separation efficiency increase up to 92% with the increasing PSFAS concentration (40 mg/L). Further increment in PSFAS concentration, the separation efficiency becomes almost constant. The interaction between the flocculent and other additives used to maintain favourable conditions needs to be analysed.

The separation depends on the intensity of electrostatic force of attraction between the oil droplet and water in terms of hydro bonding and surface charges due to the addition of flocculants and calcium hydroxide. Beyond 40 mg/L, it is expected that the unbalanced charges still exist in the water, and as a consequence, the flocculation process is hampered, and the efficiency remains almost unaltered. For the further better understanding, the involved reactions are analysed, and the associated physical process is tried to interpret using a schematic diagram

The coagulant helps to neutralise the charge which is present on the colloidal particles. Most colloidal particles have a negative charge; therefore, coagulants must have a positive charge for neutralisation. Initially, surface electrical charges repel each other because the suspension of colloidal particles is very slow. After complete neutralisation, 'Van der Waals' force acts between them, which help in the formation of micro flocs



(2)

OH^{2-} ion replaces Na and SO_4, and as a result, surface charge creates on the surface of the flocculent (Eq. 2). After this modification, on the surface of the PSFAS, a negative charge accumulates. Around the sol, Ca^{+2} ions are oriented. Finally, the electrical force of attraction binds the sol with Ca^{+2} ions and flocs form. The described mechanism is presented in below schematic diagram (Fig. 5).

3.2 The effect of pH

The variation of separation efficiency with pH is presented in Fig. 6. It illustrates that the separation efficiency enhances with the increasing pH up to 8; further increment declines the separation efficiency. Up to pH = 8, the unbalanced surface charges in the mixture decreases and above the stated value, it augments. Due to this, after pH = 8, the flocculation process is hampered and, consequently, the separation efficiency. From the nature of the variation, it can be commented that the critical pH is around 8 for the PSFAS as the flocculent.

3.3 The effect of dilution

To identify the role of dissolved solids and metal concentration in the separation process, five different samples were prepared by mixing distilled and deionised water with wastewater collected from the industry. By mixing the deionised water, the concentration of dissolved solids and the metals in the wastewater were varied.

The variation of separation efficiency with the PSFAS doses at different dilutions is presented in Fig. 7. From Fig. 7, it is identified that the separation efficiency increase with the increasing dilution rate up to 20% due to enhancement in mass transfer from the bulk of the wastewater to the sol. Further increment reverses the trend, and this could be due to the hamper in the flocculation process due to the decrement in the balanced surface charges forming the flocs.

3.4 The effect of temperature

The separation efficiencies were determined at various wastewater temperatures. The obtained information is presented in following Fig. 8. It indicates that at a higher temperature, the separation efficiency enhances due to an increment in the reaction rate or decrement in the threshold energy. Temperature above 45°C, the variation in the separation efficiency is almost insignificant. This could be the contribution of the instability created in the formed flocs at a higher temperature

3.5 Comparative Study

To check the effectiveness of PSFAS, the separation efficiency achieved in the current case has been compared with the data achieved in case aluminium sulphate and ferrous sulphate are used as the flocculants (Fig. 9). The reactions associated (equations 3–5) with the flocculants mentioned above are presented below to understand the separation mechanism better.

$$Al(SO_4)_3.14H2O + 3Ca(OH)_2 = 2\ Al(OH)_3 + 3CaSO_4 + 14\ H_2O \quad (3)$$

$$FeSO_4\ .7H_2O + Ca(OH)_2 = Fe(OH)_2 + CaSO_4 + 7H_2O \quad (4)$$

$$Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3 \quad (5)$$

Ferrous hydroxide is relatively soluble, and therefore it is further oxidised to form ferrous hydroxide to make it insoluble. During the first reaction, the positive surface charge creates, and this separates oil from the water, and then it neutralises with the negative charge of colloids. In aluminium sulphate, similar types of behaviour are expected, and the flocs from in a single step. However, in the current case, the creation of surface charge is comparatively lower than in the other case.

Poly Silicate Ferro Aluminium Sulphate creates a huge amount of surface charges compared to the other two cases and helps to neutralise the charge present on the colloidal particles. Most colloidal particles have a negative charge; therefore, coagulants must have a positive charge for neutralisation. Initially, surface electrical charges repel each other because the suspension of colloidal particles is very slow. After complete neutralisation, ‘Van der Waals’ force acts between them, which help in the formation of micro flocs.

3.6 Rate Expression

The variation of oil concentration with the time is illustrated in Fig. 10. The correlation between time and oil concentration is determined from the displayed experimental data using the curve fitting technique.

The very high determination coefficient value (0.99) ensures the appropriate data fitting. The obtained equation is presented below

$$Co = 625.06 - 40.56\,t + 0.72\,t^2 \quad (6)$$

$$\frac{\partial Co}{\partial t} = -40.56 + 1.42t \quad (7)$$

$$\frac{\partial Co}{\partial t} = k_1 + k_2 = k_2\left[\left(\frac{k_1}{k_2}\right) + t\right] \quad (8)$$

$$\frac{\partial Co}{\partial t} = k_2\left[k_3 + t\right] \quad (9)$$

4. Conclusions

Based on the various investigations performed and their corresponding discussion, the followings are the conclusion:

- Using PSFA, up to 93.5 % separation efficiency is achieved, and the discussed methodology can separate emulsified forms of the oil without altering the efficiency.
- For the attainment of maximum separation efficiency, the pH of the solution must be maintained at around 8 to achieve proper flocculation.
- The dissolved solid and metal content are also considered as the controlling parameters for the separation efficiency. The optimum TDS and the metal content must be maintained at 560 mg/L and 2 mg/L, respectively, to attain maximum separation efficiency.
- PSFAS helps to improve all parameter which was responsible to the settling time of sludge particle.
- With the addition of flocculent, the pH, turbidity, TDS, alkalinity, DO, and metal content also alter
- PSFA also helps to reduce metal such as the lead up to 74.5%.
- The kinetics for the interaction of oil and wastewater has been developed, and the determination coefficient value indicates the suitability of the correlation.

Abbreviations

Subscripts

c_o = initial concentration

c_f = final concentration

k_1 = rate constant,

k_2 = rate constant,

k_3 = , *min*

Acronyms

PSFA = Ploy silicate Ferro Aluminate

PSFAS = Poly silicate Ferro Aluminium sulphate

TDS = Total dissolved solids

DO = Dissolved oxygen

Declarations

Conflict of interest

The author declares no conflict of interest.

Funding statement

The author received no specific funding for this work.

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

All authors agreed to publish

Authors Contributions

SSM conceptualized, designed the experiment and prepared the first draft. SA did the experimental work. KPRK and AS reviewed the draft, part of conceptualization. All the authors read the final draft and finalised.

Availability of data and materials

Everything available in the manuscript

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Figures

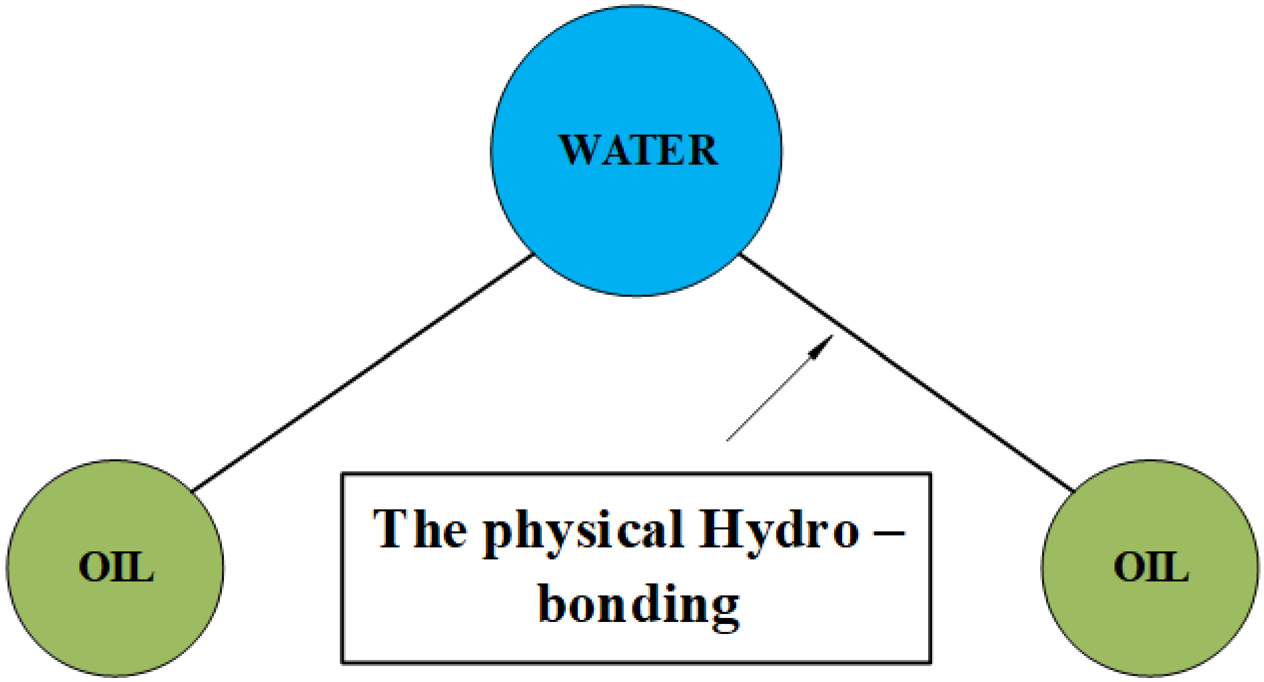

Figure 1

Schematic of oil and water interaction

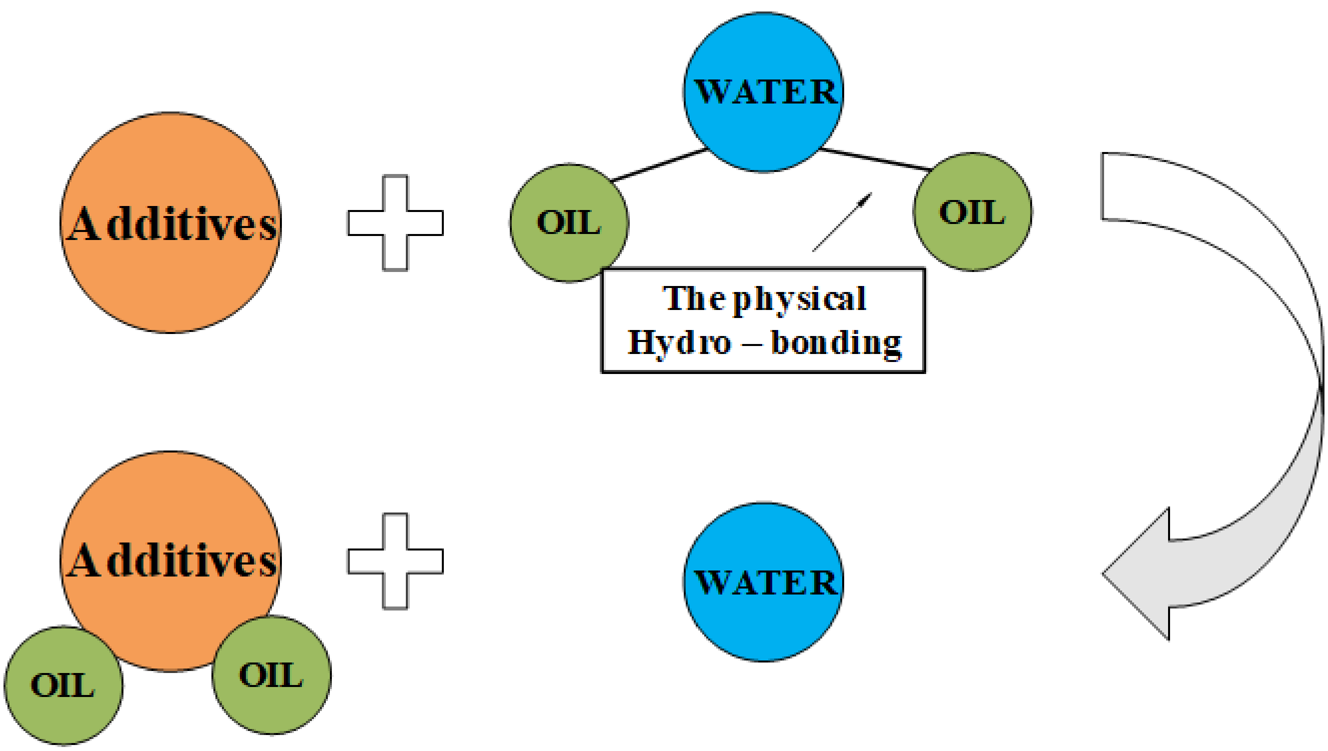

Figure 2

Schematic representation of oil-water separation

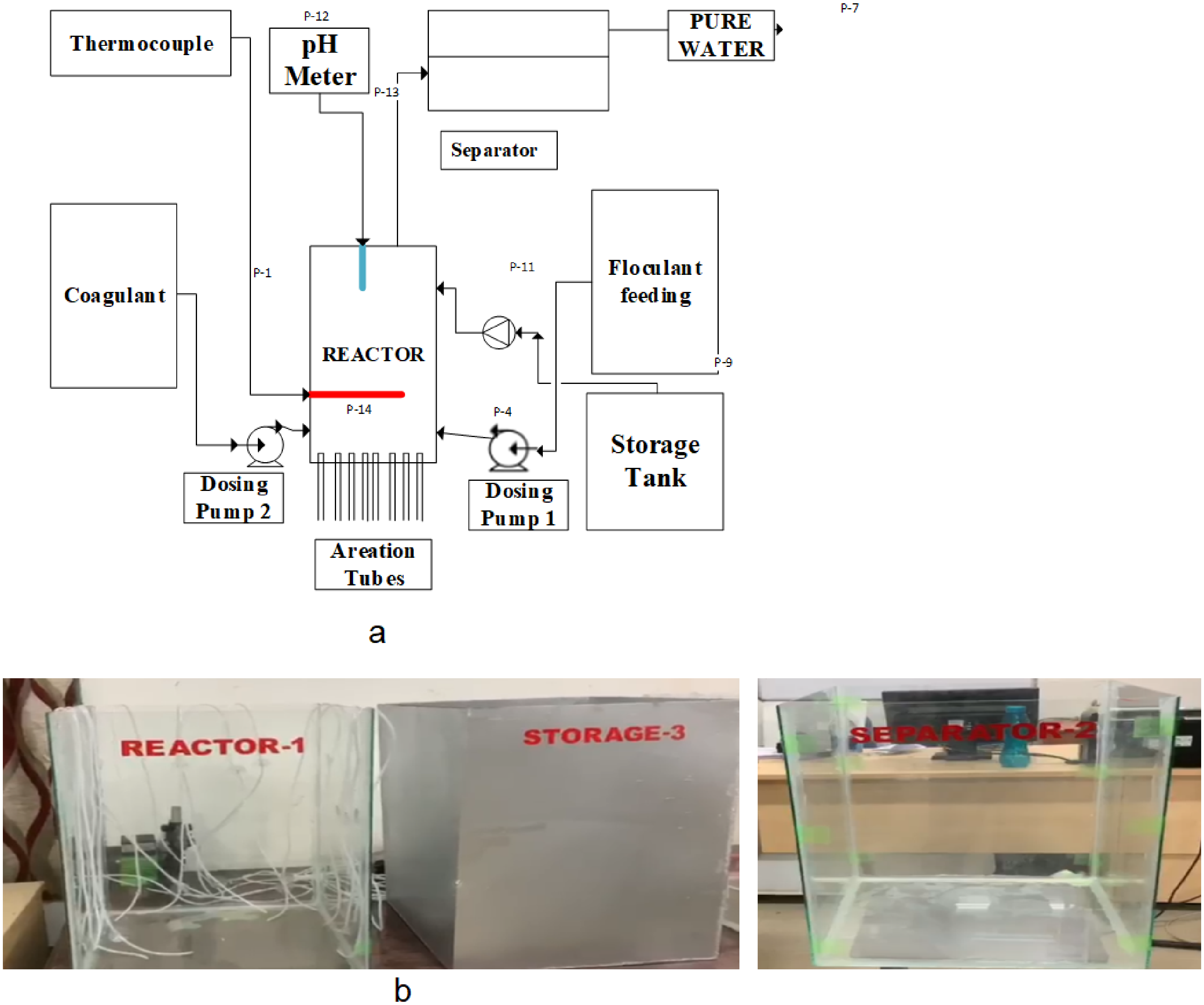

Figure 3

(A): The schematic diagram of the experimental setup (B): Images of the various components of the experimental setup

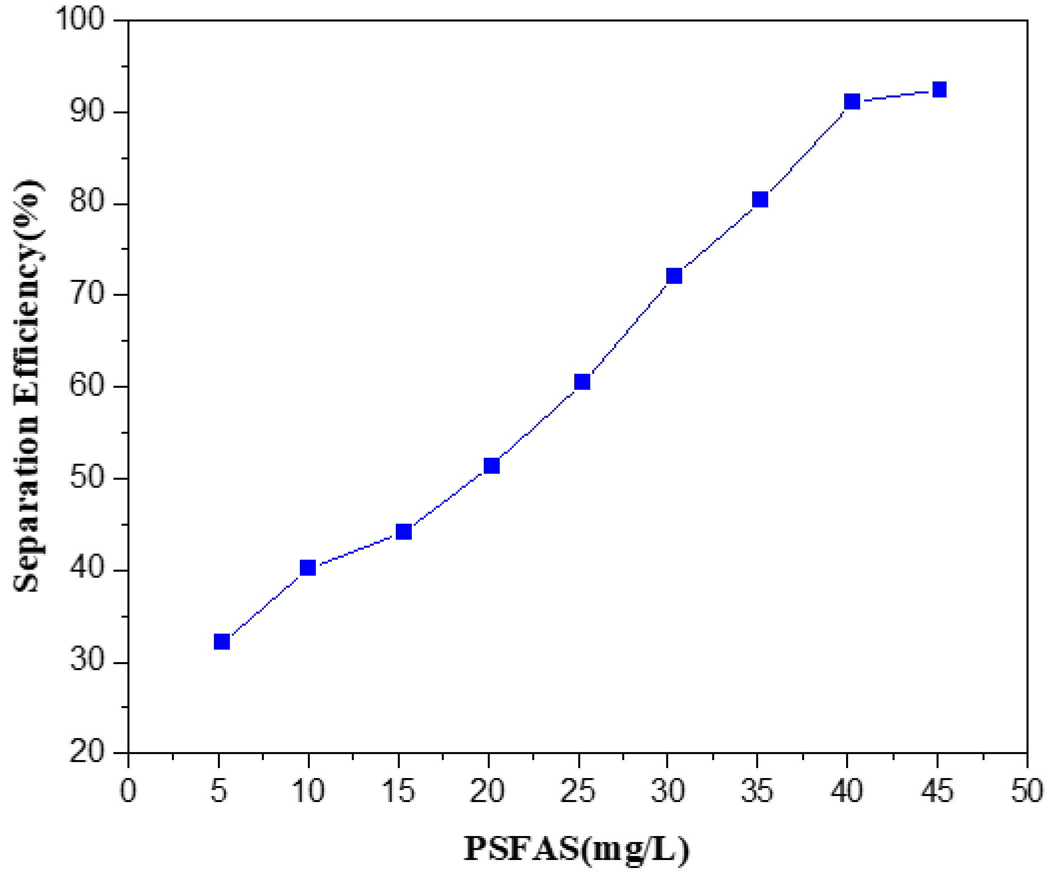

Figure 4

The variation of separation efficiency with PSFAS doses

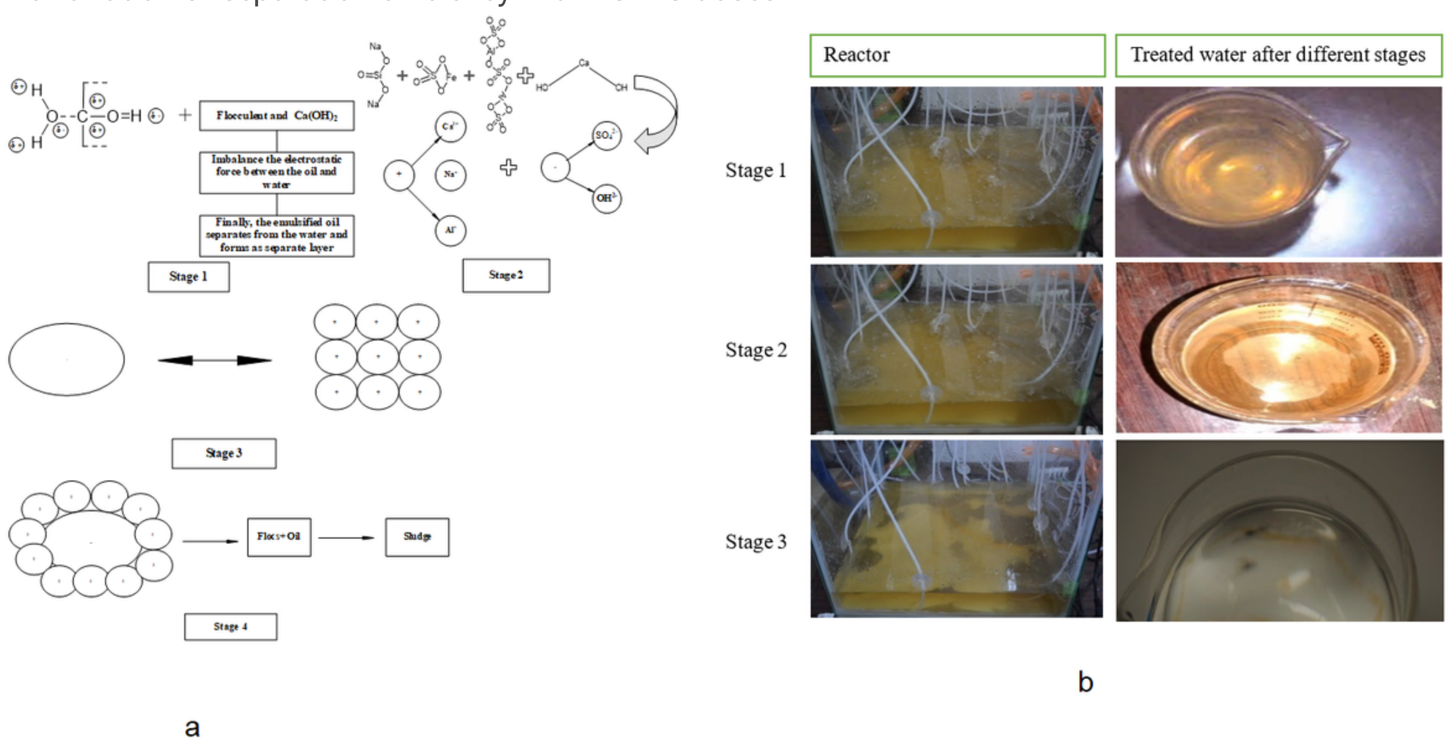

Figure 5

A: Schematic depicting the separation mechanism B: Images corroborating the various stages depicted in 5(A)

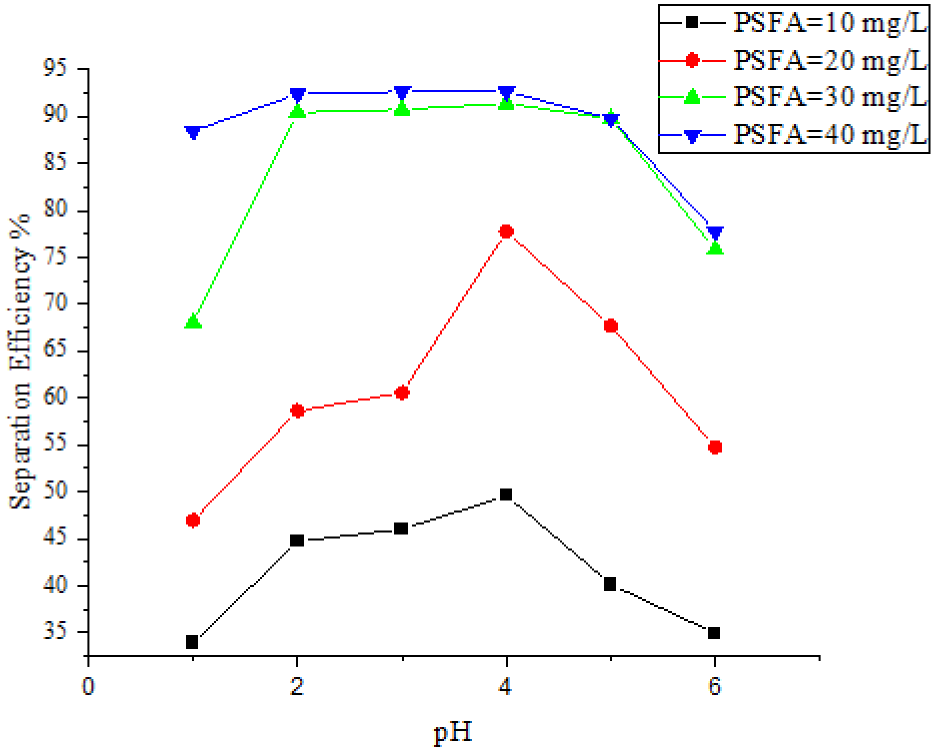

Figure 6

The variation of separation efficiency with pH

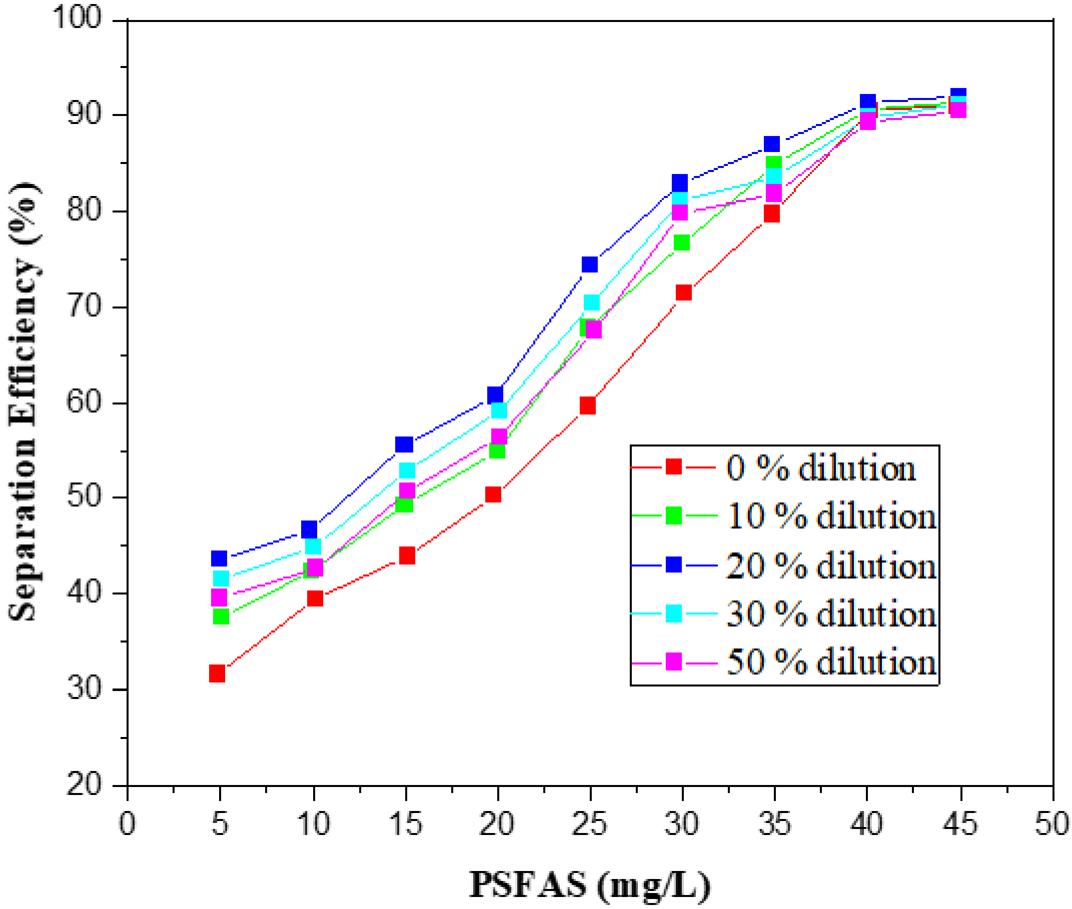

Figure 7

The variation of separation efficiency with a dilution rate

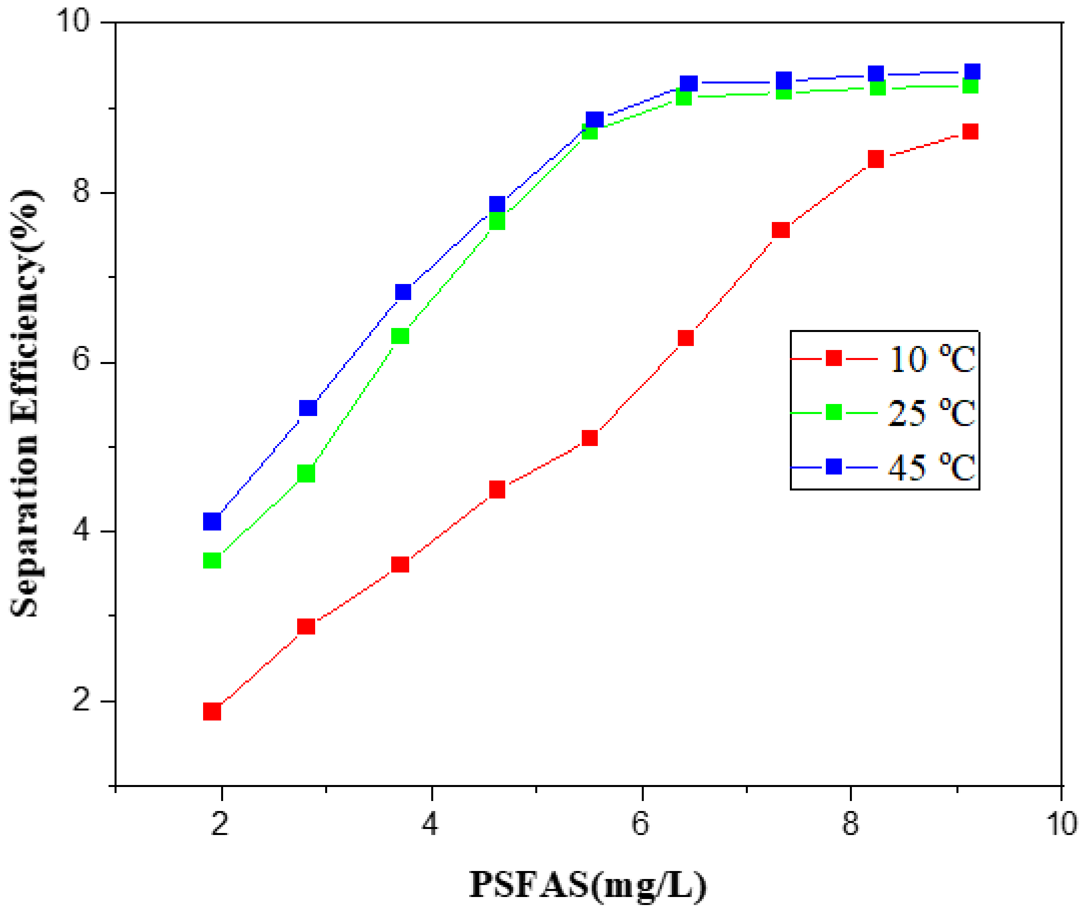

Figure 8

The variation of separation efficiency with water temperature

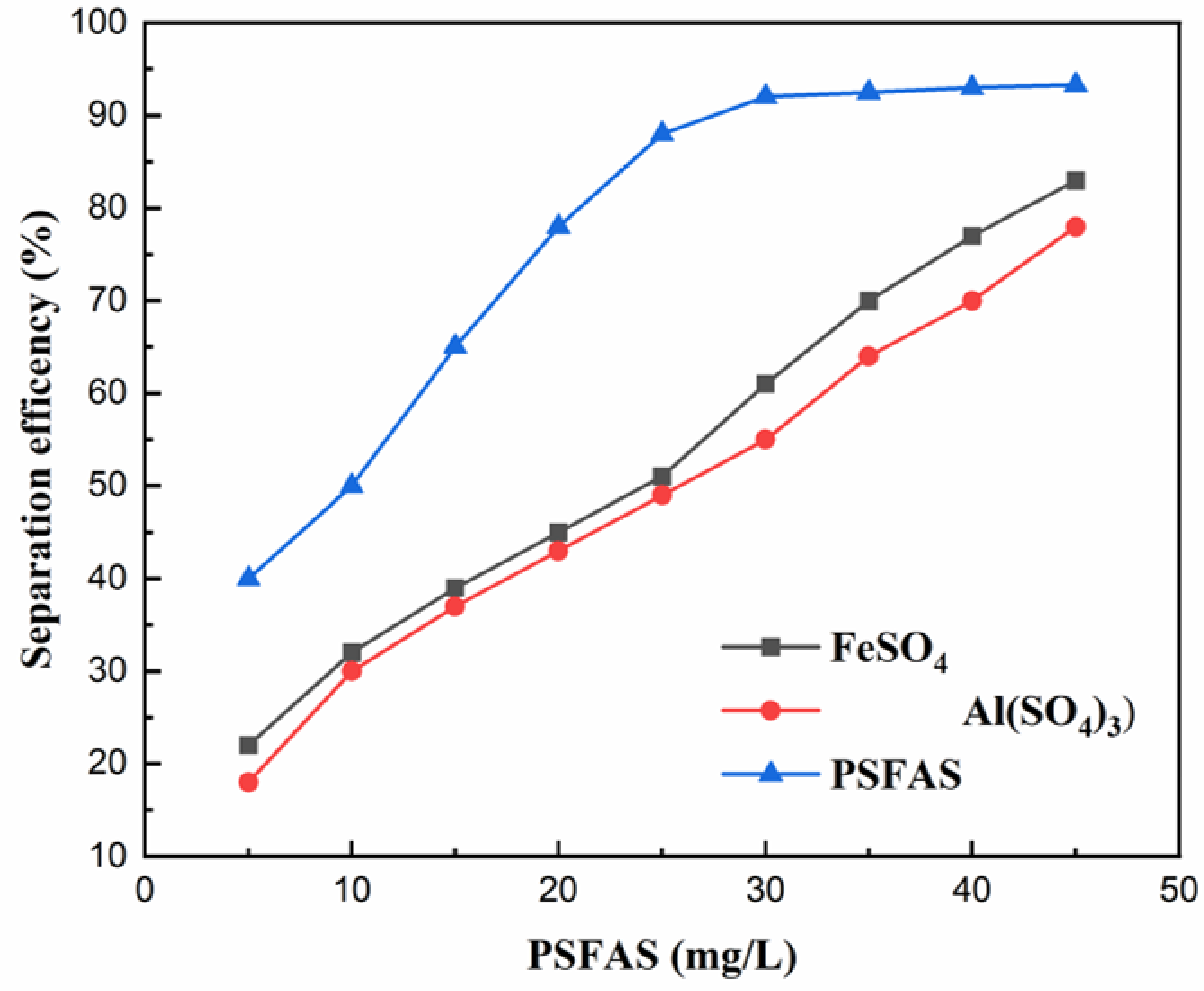

Figure 9

Comparative study

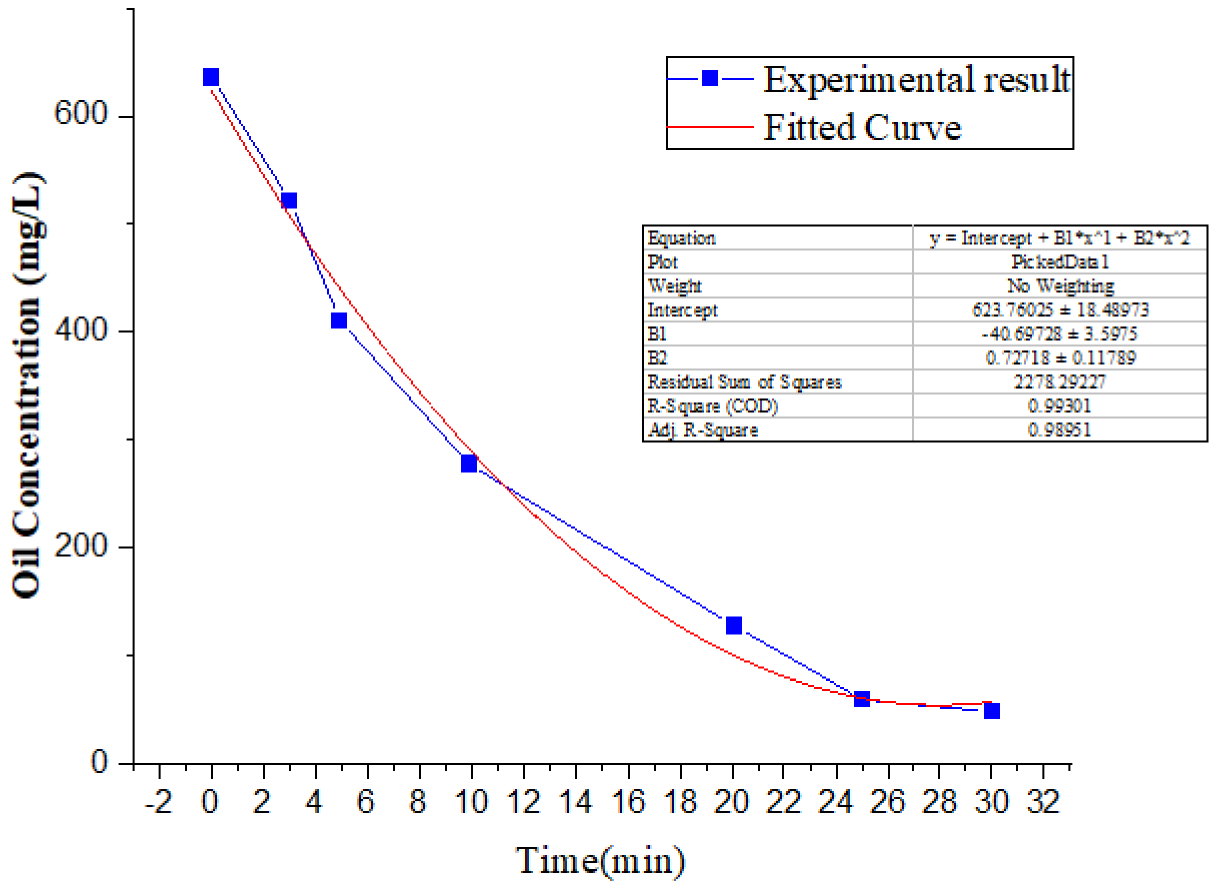

Figure 10

The variation of oil concentration with time