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# Modeling and optimization of oil refinery wastewater chemical oxygen demand removal in dissolved air flotation system by response surface methodology

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**ABSTRACT**

In this present study the dissolved air flotation (DAF) system was investigated for the treatment of Kermanshah Oil Refinery wastewater. The effect of three parameters on flotation efficiency including flow rate (outflow from the flotation tank), saturation pressure and coagulant dosage on chemical oxygen demand (COD) removal was examined experimentally. All the experiments were done under a certain time (in this case 3 min). After final testing maximum COD removal efficiency was obtained 67.86%. In the next step of study, response surface method (RSM) was applied to model oil refinery wastewater COD removal as a function of flow rate, saturation pressure and coagulant dosage. Coefficient of determination, $R^2$, showed that the RSM model can explain the variation with the accuracy of 0.996, indicating there was strong correlation. Moreover, process optimization was performed to predict the best operating conditions using RSM method, which resulted in the maximum COD removal of the oil refinery wastewater. The maximum COD removal of oil refinery wastewater was estimated by RSM to be 67.87% under the operational conditions of flow rate (3.76 – 3.86 L/min), saturation pressure (4.99 - 5bar) and coagulant dosage (24.16 – 24.79 mg/L).

## 1. Introduction

Dissolved air flotation (DAF) is a wastewater treatment process that clarifies wastewaters (or other waters) by the removal of suspended matters [1, 2]. Air bubbles are introduced near the bottom of the basin containing the water to be treated. As the bubbles move upward through the water, they become attached to particulate matter and floc particles, and the buoyant force of the combined particle and air bubbles will cause the particles to rise to the surface [3, 4]. The released air forms tiny bubbles which adhere to the suspended matter causing the suspended matter to float to the surface of the water where it may then be removed by a skimming device [5]. Thus, particles that have a higher density than the liquid can be made to float. Particles that rise to the surface are removed for further processing as residuals, and the clarified liquid is filtered to remove any residual particulate matter [6]. DAF has been used for several decades in wastewater treatment as an alternative clarification method to sedimentation. It is more efficient than sedimentation in removing turbidity, COD, color and suspended particles from wastewaters [7]. In the DAF system, the removal is achieved by dissolving air in the water or wastewater under pressure and then releasing the air at atmospheric pressure in a flotation tank or basin. The increased dissolved air concentration in water at elevated pressure is the fundamental principle that allows the formation of microbubbles [8, 9]. The amount of air released into the system can be calculated using Henry's law, by having the saturation pressure and the amount of recycled fluid flow. Zouboulis and Avranas (2000)

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investigated the treatment of oil/water emulsions containing n-octane by DAF. The results showed that utilization of polyelectrolytes was not able to effectively treat the emulsions, while the addition of ferric chloride and the subsequent use of DAF were found very efficient [10]. Al-Shamrani et al. (2002) studied the roles of aluminum and ferric sulphates as destabilizing agents for oil-water emulsions that were stabilized by a non-ionic surfactant in terms of oil removal. They found out that relatively low average mixing speeds for coagulation and flocculation are essential for efficient operation [11]. The physicochemical treatment of cutting oil emulsion using coupling coagulation and DAF was investigated by Bensadok et al. (2007). In their study, under the optimal conditions (average diameter of air micro bubbles (50 µm), saturation pressure equal to 6.5 bars) they could achieve optimal flotation effectiveness [12]. Tansel and Pascual (2011) used DAF to remove emulsified fuel oils from brackish and pond water. They indicated that DAF process can be effective both with and without the use of coagulants for removing petroleum hydrocarbons from brackish and pond waters [13]. Karhu et al. (2014) applied DAF for treatment of highly concentrated O/W emulsions. Their results showed that the COD decrease was 70% with an optimal coagulant polydiallyldimethylammonium chloride dosage (200 ppm) with the TSC value quite neutralized [14]. The removal of chromium from aqueous solution and plating wastewater using DAF was studied by Esmaeili et al. (2014). They successfully removed 98% chromium from aqueous solution and plating wastewater for poly aluminum chloride [15]. Jessica et al. (2014) studied chemical coagulation with ferric chloride (FeCl3) and adsorption organically in a completely stirred tank reactor (CSTR) configuration as pre-treatment for DAF for the removal of dissolved and dispersed oils from produced water. Finally, they successfully reduced concentrations of dispersed oil in clarified water and naphthalene concentration [16]. Kermanshah Oil Refinery (in Iran) produces large amounts of oily wastewater annually. On the other hand, the refinery due to being located in the city of Kermanshah and on the other because of the lack of appropriate technology produces considerable environmental pollution. Hence, refinery wastewater treatment with novel and advanced methods is a very important issue. In this work, the effects of input variables such as flow rate, saturation pressure and coagulant dosage on DAF process were investigated. Also, response surface methodology (RSM) was used for modeling the COD removal data.

## 2. Materials and methods

### *2.1. Materials and analytical tests*

The samples used in this study were obtained from Kermanshah Oil Refinery. Some characteristics of the wastewater used in this study are shown in Table 1. Poly aluminum Chloride (PAC) with purity of 30% as coagulant was supplied by Foodchem Company, China. Sulfuric acid with purity of 98%, Potassium dichromate, Silver sulfate, Mercury sulphate and Potassium hydrogen phthalate were supplied from Merck Company, Germany and were used to measure COD. Spectrophotometer (UV-2100, Unico, USA) was used to analyze the samples.

**Table 1.** Some characteristics of the wastewater used in this study

| Characteristic | Amount |
|---|---|
| pH | 8 |
| Chemical oxygen demand (mg/L) | 452 |
| Color (PtCo Unit) | 2250 |
| Turbidity (NTU) | 106 |
| Dissolved oxygen (mg/L) | 1.3 |
| Suspended solids (mg/L) | 120 |
| Alkalinity (mg/L as $CaCO_3$) | 7100 |
| Ammoniacal nitrogen (mg/L) | 1010 |

### *2.2. Experimental apparatus*

The experimental apparatus is presented schematically in Figure 1. It consists of an 8L stainless steel saturation vessel and a flotation tank (a Plexiglas column with 9cm diameter and 80cm height). Saturation vessel was attached through plastic tubes and two pressure relief valves to flotation tank. Air was supplied to the bed from the bottom by an air compressor (Air-Tech euro 210/24, Italy). A high pressure pump (PM series, Pentax, Italy) supplied required pressure into saturation vessel. Also, a pressure gauge (DP GUGG, WIKA, Germany) for measurement of the pressure into saturation vessel and flow meter (F-2000, Blue-White, USA) for measurement of wastewater flow rate were used.

### *2.3. Experimental procedures*

For each experiment, 3 Liters of wastewater was poured into the flotation tank. Then, the high pressure pump was operated until wastewater was pumped in saturation vessel. To adjust the pressure in saturation vessel compressor was turned on, and then the flow rate was regulated by two pressure relief valves (in a determined value). Wastewater with a certain flow rate was under aeration for 3 min until the resulting system was steady-state. Finally, COD of samples were measured and analyzed by the ASTM-D5220 method (closed reflux, colorimetric method) mentioned in "Standard Methods" [17].

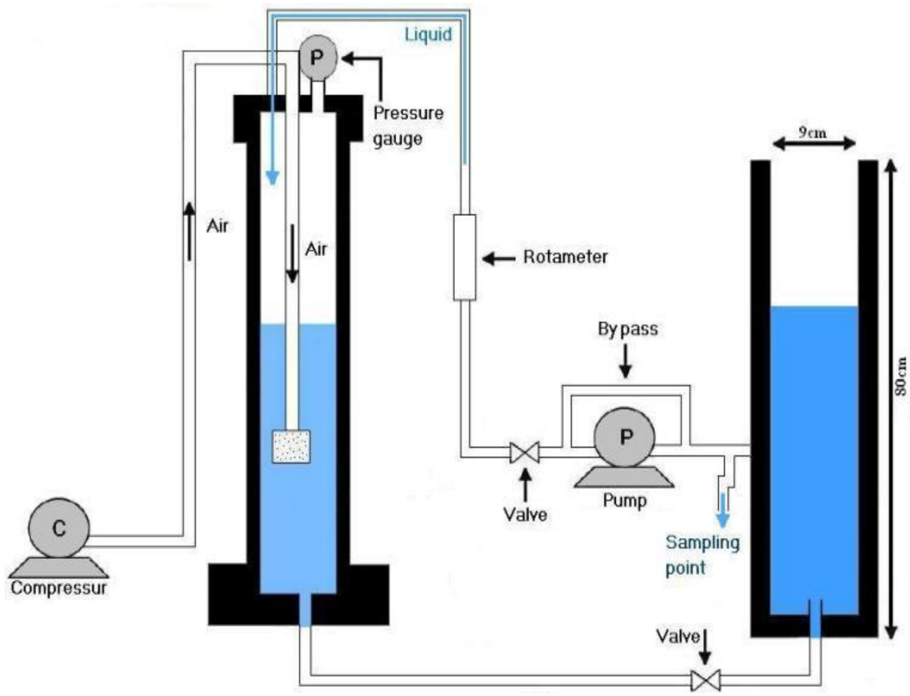


**Fig. 1.** Schematic of experimental scale DAF apparatus.

*2.4. Design of experiments*

The software Design Expert (Design Expert 7.0.0.1, Statease, USA) was applied for the experimental design, statistical analysis of data, development of regression models and optimization of process conditions. The response surface methodology (RSM) was used for fitting a quadratic surface and to analyze the interactions among the parameters. The COD removal was selected as the studied response and flow rate, saturation pressure and coagulant dosage were chosen as the studied factors. All three factors were at each of the three levels. The most appropriate design to conduct such a 3-factor-3- level set of experiments was the 17-trial set of box-behnken design (BBD) combined with RSM (Table 2). The detailed processing conditions are summarized in Table 3.

**Table 2.** Levels of independent parameters chosen for BBD

| Variables | Unit | Symbols | Coded Levels | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | +1 |
| Flow rate | L/min | $X_1$ | 2 | 3 | 4 |
| Saturation pressure | bar | $X_2$ | 3 | 4 | 5 |
| Coagulant dosage | mg/L | $X_3$ | 20 | 25 | 30 |

**Table 3.** The design of experiments using BBD method

| Experiments | Parameters | | | COD removal (%) | |
|---|---|---|---|---|---|
| | **$X_1$** | **$X_2$** | **$X_3$** | **Experimental** | **RSM** |
| 1 | 2 | 3 | 25 | 60.10 | 60.15 |
| 2 | 2 | 4 | 20 | 61.68 | 61.57 |
| 3 | 2 | 4 | 30 | 60.12 | 59.95 |
| 4 | 2 | 5 | 25 | 62.40 | 62.63 |
| 5 | 3 | 3 | 20 | 62.86 | 62.92 |
| 6 | 3 | 3 | 30 | 61.24 | 61.36 |
| 7 | 3 | 4 | 25 | 65.44 | 65.52 |
| 8 | 3 | 4 | 25 | 65.73 | 65.52 |
| 9 | 3 | 4 | 25 | 65.39 | 65.52 |
| 10 | 3 | 4 | 25 | 65.42 | 65.52 |
| 11 | 3 | 4 | 25 | 65.60 | 65.52 |
| 12 | 3 | 5 | 20 | 66.19 | 66.07 |
| 13 | 3 | 5 | 30 | 65.31 | 65.25 |
| 14 | 4 | 3 | 25 | 63.49 | 63.26 |
| 15 | 4 | 4 | 20 | 65.12 | 65.29 |
| 16 | 4 | 4 | 30 | 64.40 | 64.51 |
| 17 | 4 | 5 | 25 | 67.86 | 67.81 |

The following second order polynomial equation (Eq. (1)) was utilized to predict the chosen responses as a function of independent variables and the interaction among them [18]:

$$Y = \eta_0 + \sum_{i=1}^{k} \eta_i \varphi_i + \sum_{i=1}^{k} \eta_{ii} {\varphi_i}^2 + \sum_{i<j}^{K} \sum_{j=1}^{k} \eta_{ij} \varphi_i \varphi_j + e \quad (1)$$

Where y is the predicted dependent variable, $\eta_0$ is a constant, $\eta_i$ is the linear effect of $\varphi_i$, $\eta_{ii}$ is the linear interaction between $\varphi_i$ and $\varphi_j$, $\eta_{ij}$ is the quadratic effect of interactions between $\varphi_i$ and $\varphi_j$ and e is the statistical error.

## 3. Results and discussion

### *3.1. RSM Results*

A $3^3$ BBD was employed to determine the simple and combined effects of three operational variables on COD removal. The variations in COD removal under different combinations are presented in Table 3. $F_{statistics}$ and p-value were employed for statistical testing of various models to predict the desired model. Selection of adequate models is shown in Table 4. If p> F-value is less than 0.05, the model is considered to be statistically significant and the higher the value of correlation coefficient ($R^2$, adj $R^2$ and pred $R^2$), the higher the desirability of the model to describe the relationship between variables. The significant model for COD removal is quadratic. The value of $R^2$ equal to 0.996 shows that 0.4% variations in COD removal can be explained by the model. Moreover, adj-$R^2$ and coefficient of variation (C.V) were estimated to check the model adequacy. A high adj-$R^2$ for COD removal demonstrates that non-significant terms have not been included in the model. Analysis of Variance (ANOVA) was performed for statistical testing of the selected model to identify the significant terms in the model. The ANOVA table for the reduced quadratic model is shown in Table 4 for COD removal. F-values of 200.51 show that the models are significant. Low CV values for the proposed model indicate the precision and reliability of the experimental runs. Adequate precision (Adeq) measures the signal-to-noise ratio (S/N), with a ratio greater than 4 being desirable. For the proposed models, Adeq is 48.227, which suggests a very good S/N ratio. The comparison between predicted and actual values for the response variables also indicated that the proposed quadratic regression models were suitable to determine optimum formulation for COD removal.

**Table 4.** ANOVA analysis for the COD removal

| Source | Std. Dev. | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | p-Value | PRESS | Remarks |
|---|---|---|---|---|---|---|---|
| *Adequacy of the model tested* | | | | | | | |
| Linear | 1.24 | 0.757 | 0.701 | 0.624 | 0.0002 | 30.66 | |
| 2FI | 1.36 | 0.774 | 0.638 | 0.392 | 0.0001 | 49.74 | |
| Quadratic | 0.21 | 0.996 | 0.991 | 0.953 | 0.1193 | 3.85 | Suggested |
| Cubic | 0.14 | 0.999 | 0.996 | | | + | Aliased |
| **Source** | **Coefficient estimate** | **Sum of squares** | **Degree of freedom** | **Standard error** | **Mean square** | **F Value** | **p-Value** |
| Model | 65.52 | 81.46 | 9 | 0.095 | 9.05 | 200.51 | <0.0001 |
| $X_1$ | 2.07 | 34.32 | 1 | 0.075 | 34.32 | 760.28 | <0.0001 |
| $X_2$ | 1.76 | 24.75 | 1 | 0.075 | 24.75 | 548.17 | <0.0001 |
| $X_3$ | -0.60 | 2.86 | 1 | 0.075 | 2.86 | 63.27 | <0.0001 |
| $X_1X_2$ | 0.52 | 1.07 | 1 | 0.11 | 1.07 | 23.73 | 0.0018 |
| $X_1X_3$ | 0.21 | 0.18 | 1 | 0.11 | 0.18 | 3.91 | 0.0886 |
| $X_2X_3$ | 0.19 | 0.14 | 1 | 0.11 | 0.14 | 3.03 | 0.1251 |
| $X_1^2$ | -1.56 | 10.27 | 1 | 0.10 | 10.27 | 227.50 | <0.0001 |
| $X_2^2$ | -0.49 | 1.02 | 1 | 0.10 | 1.02 | 22.56 | 0.0021 |
| $X_3^2$ | -1.12 | 5.32 | 1 | 0.10 | 5.32 | 117.89 | <0.0001 |
| Residual | | 0.32 | 7 | | 0.045 | | |
| Std. Dev. | 0.21 | | | | | | |
| Mean | 64.02 | | | | | | |
| C.V.%* | 0.33 | | | | | | |
| Adeq Precision | 48.227 | | | | | | |

+Case(s) with leverage of 1.0000: PRESS statistic not defined

*C.V.% is Coefficient of Variation.

The final mathematical models for COD removal, which can be used for prediction within same design space in terms of coded factors, are given as follows:

$$\text{COD removal (\%)} = +65.52 +2.07X_1 +1.76X_2 -0.60X_3 +0.52X_1X_2 +0.21X_1X_3 +0.19X_2X_3 -1.56X_1^2 -0.49X_2^2 - 1.12X_3^2 \quad (2)$$

From the above equation, it is obvious that linear terms ($X_1$, $X_2$, $X_3$), interactive term ($X_1X_2$) and quadratic terms ($X_1^2$, $X_2^2$, $X_3^2$) have the largest effects on COD removal due to its higher F values as well as low p-values.

### *3.2. Experimental Results*

Figure 2 is the response surface, indicating the influence of flow rate and saturation pressure on the COD removal at the fixed coagulant dosage. At a certain pressure, the COD removal improved with the growth of flow rate, most probably due to the boosted mass transfer rate [19]. Pressure expressed a positive linear effect on the COD removal. The effect of pressure depends on the solubility of used gases in liquids. More gases are soluble in liquid at higher pressures than at lower pressures, i.e., extra gases dissolve at a high pressure and discharge when the pressure is reduced [15, 20]. There was appreciable interaction between flow rate and saturation pressure. At low flow rate values, saturation pressure was low when the COD removal reached low amount. Though, at higher flow rate levels, saturation pressure was high when the COD removal achieved greatest quantity (Eq. 2).

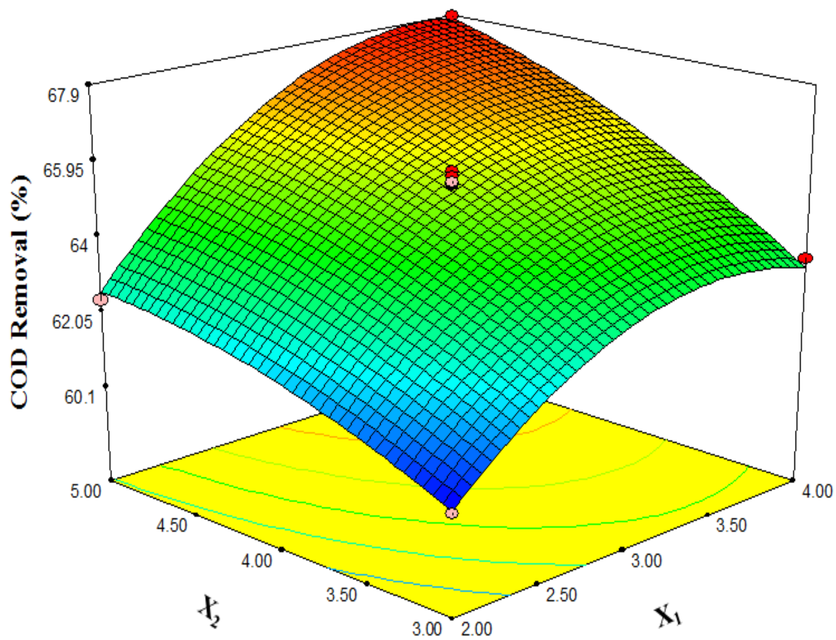


**Fig. 2.** Surface plot (COD removal, flow rate, and saturation pressure).

Figure 3 is the response surface, depicting the influence of flow rate and coagulant dosage on the COD removal at the fixed saturation pressure. At low coagulant dosage values, the COD removal improved with the growth of coagulant dosage, most probably due to production of small and light flocs. Whereas, at higher than the optimum value of coagulant dosage the COD removal declined with the rise of coagulant dosage, most likely due to the produced colloids which may have restabilized [21] and produced bigger and heavier flocs.

Figure 4 is the response surface, implying the effect of saturation pressure and coagulant dosage on the COD removal at the constant flow rate. At low saturation pressure, coagulant dosage was high when the COD removal approached maximum value [20]. However, at higher saturation pressure levels, coagulant dosage was small when the COD removal attained highest measure [19].

### *3.3. Process optimization*

The conditions were optimized based on the best combination of factor levels that obtain maximum amounts for the studied response. The chosen criteria for optimization goal were ‘maximize’ for response (COD removal) and ‘in range’ for input factors. Among 25 proposed solutions, the top 23 solutions were expressed with higher desirability. The distinguished optimal conditions were the flow rate (3.76 – 3.86 L/min), saturation pressure (4.99 - 5 bar) and coagulant dosage (24.16 – 24.79 mg/L) with the peak desirability value 100%. The maximum COD removal was 67.87%.

The predictability of the optimized model was evaluated using five independent experimental runs. Table 5 summarized the results and indicated excellent confidence between the predicted and measured value.

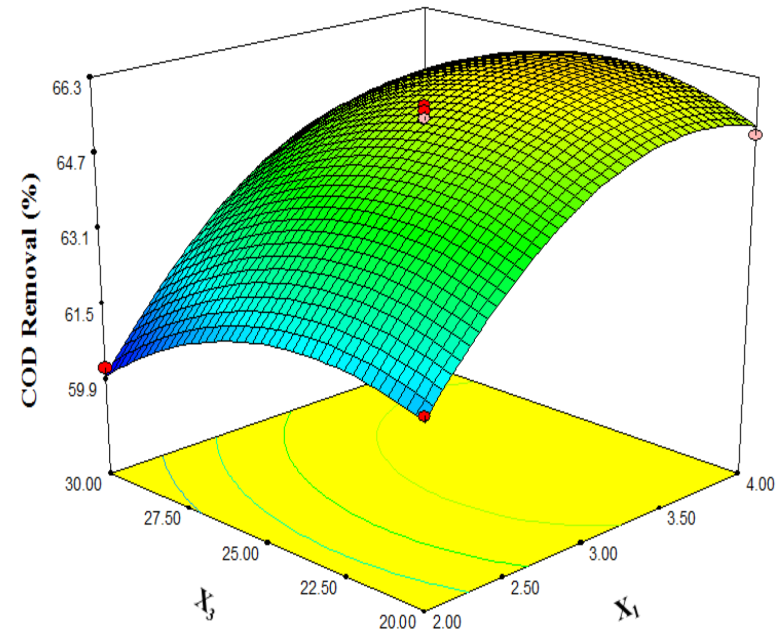


**Fig. 3.** Surface plot (COD removal, flow rate, and coagulant dosage).

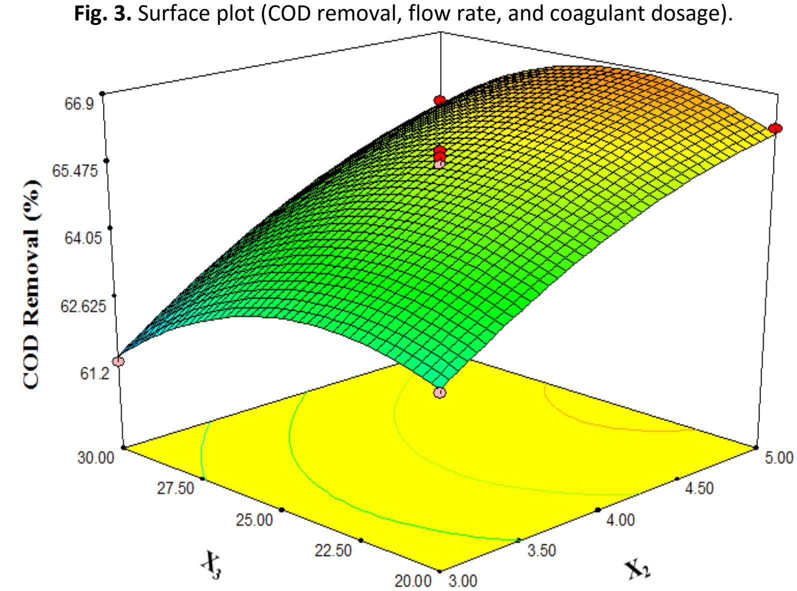


**Fig. 4.** Surface plot (COD removal, saturation pressure, and coagulant dosage).

**Table 5.** The predictability of the optimized model using five independent experimental runs

| Run | Parameters | | | COD removal (%) | |
|---|---|---|---|---|---|
| | $X_1$ | $X_2$ | $X_3$ | Experimental | Predicted |
| 1 | 2 | 3 | 20 | 59.60 | 60.02 |
| 2 | 2 | 4 | 25 | 62.56 | 61.88 |
| 3 | 3 | 3 | 25 | 63.45 | 63.26 |
| 4 | 4 | 3 | 20 | 63.66 | 62.71 |
| 5 | 4 | 4 | 25 | 66.09 | 66.02 |

## 4. Conclusions

COD removal from Kermanshah Oil Refinery wastewater using DAF system was investigated. All the experiments were done using poly aluminum chloride (PAC) as coagulant. In the present research the following factors were studied: flow rate, saturation pressure and coagulant dosage.

The following conclusions can be understood from this experimental study:

- Flow rate has significant impact on reduction of the COD.

- Any increase in the saturation pressure will improve the reduction of COD.
- In the case of coagulant dosage, the COD removal increases with the coagulant dosage until it reaches the highest value, the COD removal then starts to drop as coagulant dosage is increased. Therefore, the optimum coagulant dosage for Kermanshah Oil Refinery wastewater treatment was 25mg/L.

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