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# Treatment of Spent Caustic Effluent of Oil Refinery with Catalytic Oxidation and Optimization of Relevant Parameters using Response Surface Methodology

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**Abstract:** Caustic soda is a substance used for sweetening hydrocarbon products in oil refinery, gas and petrochemical units. The caustic soda-generated salts are increasingly formed during the process of removing impurities like mercaptans, sulfides and nitrates, which eventually leave process system through spent caustic discharge. Spent caustic discharge into environment is prohibited due to the presence of compounds like organic and toxic substances, sulfide salts, mercaptans as well as high chemical oxygen demand (COD), emphasizing the need to treat such effluents. The present study aimed to employ catalytic wet air oxidation method for treatment of spent caustic effluent collected from Bandar Abbas oil refinery and optimize related parameters. Experimental processes were performed in a 500-ml batch reactor. Catalyst concentration, residence time and stoichiometric air flow parameters were optimized by Box-Behnken design. Based on our findings, optimal conditions for this process were the catalyst concentration of 117.1 mg/kg, the residence time of 2.8 h and the stoichiometric air flow of 4.3 l/h, with a maximum reduction of spent caustic COD of 42.%. The results of optimization experiments were analyzed by Design Expert 11 software, the results of which documented that the three mentioned parameters had the greatest effect on reducing spent caustic COD. Prolonging residence time had no significant impact on COD removal. Polynomial equation based on the three mentioned variables was presented to predict the spent caustic COD changes. In this treatment method, in addition to a significant reduction in COD, the available toxic substances also reached less than 1 mg/l.
**Keywords:** Box-Behnken Design, Catalytic Oxidation, Spent Caustic, Treatment.



## 1. Introduction

Oil refineries and chemical industries are among the plants that generate a variety of hazardous and treatment required wastes (Alishiri et al., 2020). These units typically employ sodium hydroxide (NaOH), also known as lye and caustic soda, as chemical cleaning solutions to remove sulfur compounds such as hydrogen sulfide, cresylic acids, mercaptan, and naphthenic acid (Esmaeilzadeh et al., 2020).. The wastewater solution obtained from this process is called spent caustic (De Angelo et al. 1983; Kumfer et al. 2010). The spent caustic effluent is a brown liquid with a pungent odor, usually made of sodium hydroxide, water, sulfur compounds, naphthenates, cresylic acids and other contaminants, which has high salinity, high alkalinity and high sulfur content. The spent caustic effluent needs to be discharged to the environment by choosing a suitable treatment process. The mean spent caustic pH is usually higher than 12; depending on its origin, this wastewater contains large amounts of hydrogen sulfide, mercaptan and phenol (Maugans et al. 2010y; Karimi et al. 2017). The characteristics of spent caustic types are listed in Table 1 (Ahmadpour et al. 2016).

Table 1: Profile of spent caustic produced in refinery industries

| | Sulfidic Spent caustic | Naphthenic Spent caustic | Cresylic Spent caustic |
|---|---|---|---|
| Chemical oxygen demand (COD)(ppm) | 5,000-90,000 | 50,000-100,000 | 150,000-240,000 |
| Total organic carbon(TOC)(ppm) | 3,000-20 | 10,000-24,000 | 24,000-60,000 |
| Sulfides(ppm) | 2,000-52,000 | <1 | 63,000-0 |
| Sulfite(ppm) | 1,5-500 | 4-8 | 1,500-800 |
| Mercaptans(ppm) | 0-30,000 | <30 | 0-5,400 |
| Thiosulfate(ppm) | 0-4,000 | 1,200-70 | 10,000-13,000 |
| Total phenol(ppm) | 2-30 | 1,000-1,900 | 14,000-19,000 |

According to the United States Environmental Protection Agency (US EPA) in the Resource Conservation and Recovery Act (RCRA), the spent caustic is classified as hazardous waste due to its high concentration of toxic materials and malodor (Shih-Hsiung et al. 2001).

Multiple methods are available for the treatment of spent caustic effluent, including incineration, biological approaches, classical oxidation, advanced chemical oxidation process (AOP), and wet air oxidation (WAO), each of which can be employed individually or concurrently. Waste incineration stands for the treatment of effluents containing chemical oxygen demand (COD) higher than 100 g/l. However, the use of this method is limited because of its high energy consumption and the release of hazardous compounds such as furans and dioxins (Luan et al. 2012).

Biological approaches are widely used method for the treatment of various waste effluents, but not suitable for effluents with the COD concentration of more than 10,000 mg/l (Hawari et al. 2015).

In the classical oxidation processes, an oxidizer is directly appended into the effluent under ambient pressure and temperature to eliminate the contaminants. The most common oxidizers in this method are chlorine, chlorine dioxide, oxygen, persulfate, permanganate, ozone and hydrogen peroxide ($H_2O_2$).

Despite the advantages, these processes have some disadvantages such as high cost and toxic byproduct generation. Therefore, the effluent compounds generating such byproducts must be separated from those ones using effective techniques like adsorption prior to adding oxidant (Mortazavian, 2017).

The AOP method is a combination of ozone ($O_3$) + Ultraviolet light (UV), $O_3$ + $H_2O_2$ and UV + $H_2O_2$, all of which aim to form hydroxyl radicals, and have robust oxidizing potential and also convertibility of non-biodegradable pollutants into biodegradable non-toxic substances. Unlike other methods, this one has potential to eliminate the organic and inorganic contaminants such as aromatic carboxylic acids. The AOP requires co-processes to achieve high efficiency. Thus, these systems are complex and expensive (Bahrami 2016; Bakhshandeh 2017).

The WAO process is performed under high temperatures and pressures. Most WAO-related developmental efforts in the United States began about 50 years ago and have expanded in recent years. This method is employed in the treatment of industrial effluents such as caustic solutions from washing towers and also in the production of useful products such as acetic acid (Luck 1999; Hii 2014). This technique is also applied to treat wastewaters with the COD content of 200,000 mg/l, but it requires huge energy and is commonly considered as a pretreatment process (Claude 1998; Naizy 2008). One of the main bottlenecks of the WAO process is the defect in the complete oxidation of organic compounds because various low-molecular weight oxygen compounds (such as acetic acid, propanoic acid, as well as methanol, ethanol, and acetaldehyde) are either present in the feed or formed during the process, which are difficult to convert to carbon dioxide (Mortazavian, 2017; Bhargava et al. 2006).

To control the volatile organic compounds, the catalytic oxidation has attracted further attention due to its high efficiency at relatively low temperatures and its ease of use in various processes. Different oxidizers such as $H_2O_2$ and Fenton's reagent (a solution of $H_2O_2$ mixed with ferrous iron catalyst) are applied for conversion and degradation of organic matter (Mohammadizadeh, 2018). Due to the fact that the efficiency of the WAO process is suitable at the temperatures of 200-325°C and the pressures of 50-150 Bar, this process does the same work when using iron catalysts and robust oxidizers such as $H_2O_2$ at 230°C and 35-Bar pressure. The catalytic oxidation process is based on the capacity of these oxidizers to chemically degrade hydrocarbons and based on the formation of free radicals such as hydroxyl radicals, thus oxidizing the organic matter of interest (Debellefontaine et al. 1996).

In fact, the presence of a catalyst causes the oxidation of resistant compounds such as acetic acid at lower temperatures and pressures than when the process is performed in the absence of a catalyst, indeed as one of the most appropriate methods to eliminate these contaminants (Heponiemi, 2015).

Therefore, the catalytic wet air oxidation (CWAO) process has lower energy consumption and higher oxidation efficiency compared to the conventional WAO process, increasing the reaction rate and reducing the reaction time (Luck 1999; Levec 2007).

The expansion of studies on catalytic oxidation processes began in the United States in the mid-1950s, which are based on homogeneous catalysts (such as iron or copper) or on heterogeneous catalysts. In some cases, the overall performance of the CWAO process can be closely similar to the oxidation process using a supercritical point of water, for example at a pressure of about 25 MPa and a temperature of about 550°C. Exploiting homogeneous and heterogeneous catalysts can significantly improve the oxidation efficiency of the aqueous phase. A number of Japanese companies have developed catalytic oxidation technology using noble metals based on titanium oxide or titanium zirconium. European researchers also focused on the application of homogeneous catalysts. It is really important to select appropriate catalysts for environmental protection because proper catalysts prevent the production and the release of unwanted intermediate pollutants through a change in the process pathway (Luck 1999).

A study recruiting analytic hierarchy process (AHP) and adopting a prospective to the advantages and disadvantages analyzed the best method of caustic wastewater treatment. Four parameters of technical feasibility, efficiency, treatment time and cost as the criteria of this process and four industrial options of advanced oxidation, catalytic oxidation, biological method and wet air oxidation as the best methods were selected for the caustic wastewater treatment within the AHP. After evaluation and pairwise comparison of different criteria and options in Expert Choice software, cost and return criteria had 43 and 23.3% priority, respectively, and the catalytic oxidation (catalyst based on metal phthalocyanines such as cobalt, vanadium and molybdenum) with 35.8% efficacy had the highest preference over other methods (Karimi 2017).

In a study, the spent caustic effluent collected from a Chinese refinery containing COD content of 250,781 mg/l in a one-liter steel reactor underwent WAO and a catalyst at a temperature of 150-200°C and a pressure of 0.2-2.5 MPa. The results showed that a decrement rate of feed COD was 75% in the WAO process at a temperature of 200°C, pressure of 2 MPa and the stirring speed of 300 rpm and 95% in the CWAO process using the composite catalyst of MnOx-CeOx/$\gamma$-$Al_2O_3$ (Chen and Cheng 2013). In a study to optimize the treatment and recovery of spent caustic in the Olefine Unit of Tabriz Petrochemical Complex, the feed was first tested and treated by COD of 30,000 mg/l and 360 mg/L amount of $S^{2-}$ in a 500-ml batch bubble column reactor under CWAO using IVKAZ catalyst (cobalt phthalocyanine) at 90-110°C, airflow of 7-10 L/min and reaction time of 20-30 minutes under ambient pressure. The output flow from this reactor was then fed into a precipitation stirred tank reactor by adding lime to perform precipitation process under ambient pressure and temperature. The full factorial method was used for experimental design and the response surface methodology (RSM) was applied to optimize the test results. Experimental results showed that the COD concentration was decreased to 5000 mg/L and the $S^{-2}$ content also to 362 mg/L at the temperature of 90ºC, the air flow of 7 L/min and the reaction time of 30 min. The amount of caustic was also increased from 1% wt to 6% wt (Karimi et al. 2017).

A study analyzed the recovery and treatment of sulfidic spent caustic in the Olefine Unit of Tabriz Petrochemical Complex using the AHP. Selective parameters for AHP included cost, environmental considerations, availability and scaling, and alternative methods involved WAO, biological and catalytic methods. Among the alternative techniques, the catalytic method with 54.4% was selected as the best approach for recovery and treatment of spent caustic through AHP. Then, the experiments were performed by CWAO using IVKAZ catalyst in two batch bubble column reactor and precipitation stirred tank reactor.

The best value for NaOH recovery with an initial weight of 4% wt was 13.4% wt, output $S^{2-}$ under optimal conditions decreased from 81 g/l to 36 g/l and the COD amount from 160 g/l to 52 g/l (Karimi et al. 2016).

In a study for the treatment of naphthenic spent caustics gathered from phase 4 and 5 refineries of South Pars (Assaluyeh, Iran) with initial COD of 24000 mg/l and $S^{2-}$ content of 4493 mg/l, the amount of 50 ml of feed underwent CWAO using liquid cobalt sulfonated phthalocyanine catalyst 30%wt (Rangineh Pars Catalyst Company) at the concentrations of 500, 1250 and 2000 mg/l, stoichiometric air flow of 3, 6 and 9 l/h, and the residence time of 1, 2 and 3 hours. The reactor used was a batch reactor and the process parameters were selected to be catalyst concentration, stoichiometric air flow and residence time. Optimization experiments were designed using the Box-Behnken design (BBD) method by Design-Expert 7.0 Software. Experimental results showed that the COD concentration decreased to 15000 mg/l and $S^{-2}$ to 59.874 mg/L at the optimum point of the catalyst with a concentration of 2000 mg/l, residence time of 2.37 hours and stoichiometric air flow of 9 l/h (Mohammadizadeh 2018). The problem with this method was the consumption of high catalyst concentration in experiments.

Mercaptans and sulfides can be oxidized in the presence of air/oxygen using metal phthalocyanine catalysts (molybdenum, vanadium, cobalt and manganese) in an alkaline medium. Metal phthalocyanine derivatives are used as homogeneous catalysts for liquid-liquid sweetening and treatment and alkaline reduction in the extraction of mercaptans from light distillation products other petroleum products such as heavy naphtha, FCC gasoline, ATF and heavy oil (Mohammadizadeh 2018; Rathore et al. 2011).

Catalytic Wet Air Oxidation (CWAO) is a low-pressure and low-temperature process in the presence of a catalyst, as a licensed and technological approach. The main practices of this method are called Merox process (mercaptan oxidation). Due to the operating conditions of low temperature and pressure, the CWAO is considered as a process with low investment expenditure and is important in the treatment of spent caustic and other effluents. In oil refineries, cobalt phthalocyanine acts as an effective catalyst in mercaptan oxidation and spent caustic reduction. The role of this process in Bandar Abbas oil refinery and most refineries is to treat the spent caustic effluent and also to convert salts to disulfide.

According to the previous studies, the spent caustic effluent has been treated by the CWAO method under the operating conditions of high temperature and high pressure, as well as high catalyst concentration, while the present study has taken advantage of the operating conditions of low temperature and pressure and low catalyst concentration, thereby reducing the investment expenditure.

## 2. Materials and Methods

### *Examination and sampling methods*

The spent caustic samples in this study were collected from Unit 51 of the Bandar Abbas Oil Refinery, Iran. At the baseline, the samples were taken from the inlet of Unit 51 in a 20-liter container at once by the Research Institute of Petroleum Industry. The samples were then transferred to the laboratory of the Research Institute of Petroleum Industry, and kept in a dry, cool, and heat-free environment.

The spent caustic specimens were treated by the CWAO method using a 500-ml cylindrical reactor made of Grade 316 stainless steel capable of withstanding up to 20-bar pressure and equipped with a pressure relief valve (Figure 1). First, 100 ml of the spent caustic sample was weighed using a Mettler Toledo's JB1603 carat scale (Switzerland), and poured into the reactor according to the determined concentration of IVKAZ solid catalyst (VENIUSS Co., Russia). A magnetic stirrer was used to mix feed and oxygen. The reactor was then placed on a heater. After the system reached a temperature of 50°C and a pressure of 8 Bar, 35 tests were performed based on the test design to achieve the desired result. The COD and $S^{2-}$ concentrations were analyzed for 35 samples. The results of the COD analysis of 16 tests are given in the test design table. Moreover, three tests were performed

COD 64100

such as LPG, pentane and light naphtha. These catalysts are also applied as heterogeneous catalysts for refining for the treated effluent sample at the optimal conditions and a general analysis was carried out. According to the test design, the feed containing different concentrations of catalyst (50, 100 and 150 ppm) was exposed to a certain amount of stoichiometric air flow (2, 4 and 6 l/h) monitored by the air mass flow controller at different residence time periods (1, 2 and 3 h). In order to measure the COD content, 0.2 ml of the treated effluent sample was diluted with 0.8 ml of distilled water (at a ratio of 1: 10) and then 0.2 ml of diluted effluent was poured into ready-to-use vials (0-15000 mg/l, Iran), and finally, the measurement was performed by a Lovibond spectrophotometer MD200 (Germany) according to ASTM D1252-00 standard.

To measure the concentration of anions and cations, 40 ml of the treated effluent sample was analyzed by ion chromatography (IC) and IGS-R-CH-056-1 (0) standard. In addition, 10 ml of the treated effluent sample was applied to measure the concentration of $RS^-$ and $S^{2-}$ using the KEM's AT-510 Automatic potentiometric titrator (Japan) in accordance with UOP 212 standard.

### *Characteristics of feed and treated spent caustics*

The spent caustic collected from the Bandar Abbas oil refinery was treated by CWAO method in the Batch reactor. The analytical characteristics of the feed and treated spent caustic effluents under the optimal conditions during the CWAO reaction are presented in Tables 2 and 3, respectively.

Table 2: Analytical characteristics of feed spent caustic collected from Bandar Abbas oil refinery

| Contents | Concentration (mg/l) |
|---|---|
| $Na_2S$ Sulfide $S^{2-}$ | 8212 |
| sulfur content in $RS^-$ mercaptide | 16733 |
| Chloride $Cl^-$ | 28873 ± 955 |
| $SO_3^{2-}$ Sulfite | 2892 ± 115 |
| $SO_4^{2-}$ Sulfate | <1 |
| $S_2O_3^{2-}$ Thiosulfate | 9527 ± 381 |
| $PO_4^{3-}$ Phosphate | <1 |
| Nitrate $NO_3^-$ | <1 |
| Nitrite $NO_2^-$ | 551± 14 |
| Thiocyanate | <1 |
| $NCO^-$ Cyanate | <1 |
| $CH3COO^-$ Acetate | 987 ± 39 |
| $HCOO^-$ Formate | 1477 ± 59 |
| $C_2O_4^{2-}$ Oxalate | <1 |
| (NaOH) $OH^-$ | < 5.5 wt% |

The spent caustic collected from Bandar Abbas oil refinery had a COD concentration of 64000 mg/l. In addition, the compound contained 8000 mg/l of sodium sulfide, 16700 mg/l of mercaptide, 2800 mg/l of sulfites, 9000 mg/l of thiosulfate, and 900 mg/l of acetic acid.

Table 3: Analytical characteristics of spent caustic after catalytic wet air oxidation at an optimal point

| Contents | Concentration (mg/l) |
|---|---|
| $Na_2S$ Sulfide $S^{2-}$ | <1 |
| sulfur content in $RS^-$mercaptide | <1 |
| Chloride $Cl^-$ | 8835 ± 353 |
| $SO_3^{2-}$ Sulfite | <1 |
| $SO_4^{2-}$ Sulfate | 19549 ± 776 |
| $S_2O_3^{2-}$ Thiosulfate | <1 |
| $PO_4^{3-}$ Phosphate | <1 |
| Nitrate $NO_3^-$ | <1 |
| Nitrite $NO_2^-$ | <1 |
| Thiocyanate | <1 |
| $NCO^-$ Cyanate | <1 |
| $CH3COO^-$ Acetate | 4341 ± 173 |
| $HCOO^-$ Formate | 762 ± 30 |
| $C_2O_4^{2-}$ Oxalate | <1 |
| (NaOH) $OH^-$ | <5.24 ± 0.20 wt% |
| COD | 37242 |

As can be seen, the values of some parameters have been reduced to less than 1 mg/l after the CWAO process. However, there is an increase in the amount of acetic acid due to the organic matter conversion. After acidification, these materials were removed from the system using the separation method.

Table 4 shows the characteristics of wastewater discharges of industrial units in accordance with the standards of the Environmental Protection Organization of Iran (Mohsenzadeh and Mirbagheri 2018).

Table 4: Characteristics of wastewater discharge of industrial units in accordance with the standards of the Environmental Protection Organization of Iran

| Parameters | Discharge into surface water (mg/l) | Discharge into absorbing well (mg/l) | Agricultural and irrigation uses (mg/l) |
|---|---|---|---|
| COD | 60 | 60 | 200 |
| TSS | 40 | - | 100 |
| pH | 6.5-8.5 | 5-9 | 6-8.5 |
| Turbidity | NTU 50 | - | NTU 50 |
| Color | 75 TCU | 75 TCU | 75 TCU |

*Experimental data and tests reactor system*

The spent caustic was treated by the CWAO method using a cylindrical reactor made of Grade 316 stainless steel with a volume of 500 ml, which was able to withstand pressures up to 20 Bar and was equipped with a pressure relief valve (PRV) and other accessories (Fig 1). Thus, 100 ml of spent caustic was weighed and poured into the reactor, according to the specified concentration of IVKAZ catalyst from VENIUSS (Russia); a stirrer magnet was used to mix feed and oxygen. Then, the reactor was placed on the heater; after the system reached a temperature of 50°C and a pressure of 8 Bar, the tests were performed. According to the test design, the feed containing different concentrations of catalyst (50, 100 and 150 mg/l) exposed to a certain amount of air flow (2, 4 and 6 l/h) established by the air mass flow controller is controlled for different contact times (1, 2 and 3 h); the time required to perform the reaction is the same as the residence time.

After the experiments, the COD concentration of the product sample was measured by spectrophotometery, and the concentrations of anions and cations were measured by ion chromatography (IC) methods.

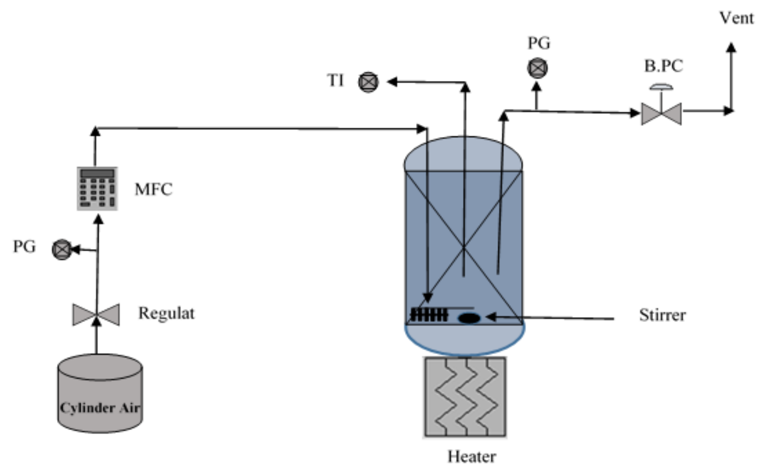


Fig. 1- Schematic of a laboratory reactor system for catalytic wet air oxidation; equipment: air cylinder, B.PC regulator, mass flow controller (MFC), batch reactor, heater, stirrer, pressure gauges (PG) and temperature indicator (TI) and controller

*Experimental design method - RSM for experimental data*

In the experiment design with full factorial method, since the possibility of examining all interactions leads to an increase in the number of experiments, longer duration of study and increased cost (Montes 2008), this bottleneck can be bypassed using the RSM for optimization studies by Box and Wilson (1992). Therefore, the experiments were designed by Design Expert 11 software to optimize CWAO bearing three variables. Moreover, the RSM being a set of statistical techniques and applied mathematics used to build experimental models (proposed by Box and Draper in 1987) was employed for design, mathematical modeling, and optimization. To this end, among the two methods of Box-Behnken design and central composite design, which are of the most accurate and efficient optimization subsets of the RSM method, the BBD method was chosen because it requires fewer optimal tests for modeling and examines the variable at only three levels, as well as the proposed model is designed in the range of the lower limit, the center and the upper limit of each variable and the space between the levels is equal.

*Experimental data of spent caustic treatment by CWAO process based on BBD method*

The test data are presented in Table 6, which is based on Box-Behnken design (BBD) method and experiments.
The BBD method was performed to determine the optimal conditions for reducing COD content and the factors affecting CWAO. Input variables used in this method are catalyst concentration, residence time and stoichiometric air flow. The effect of these three factors on spent caustic removal was evaluated as well. The design to reduce the number of experiments was carried out using Design Expert 11.0.3.0 software. The COD removal efficiency was considered as dependent variable (response). Table 5 shows the characteristics of the factors and the range of raw and modeled data of the independent variables at different levels of this experimental scheme.

Table 5: Characteristics of factors and range of raw and coded data of independent variables at different levels

| Factor | Name | Units | Type | Minimum | Maximum | Coded Low | Coded High | Mean |
|---|---|---|---|---|---|---|---|---|
| A | Catalyst concentration | ppm | Numeric | 50.00 | 150.00 | -1 ↔ 50.00 | +1 ↔ 150.00 | 100.00 |
| B | Stoichiometric air flow | l/h | Numeric | 2.00 | 6.00 | -1 ↔ 2.00 | +1 ↔ 6.00 | 4.00 |
| C | Residence time | h | Numeric | 1.0000 | 3.00 | -1 ↔ 1.00 | +1 ↔ 3.00 | 2.00 |

## 3. Results

*Chemical reactions and related mechanisms in the CWAO process of spent caustic effluent*

The CWAO reactions of spent caustic effluent in the batch reactor in the presence of IVKAZ catalyst were as follows (Karimi et al. 2016).

$NaOH + {}^{1}/_{2}Na_2S_2O_3 + O_2 \rightarrow Na_2SO_4 + {}^{1}/_{2}H_2O$ (1)
$NaSH + 2O_2 + NaOH \rightarrow Na_2SO_4 + H_2O$ (2)
$NaSH + 2O_2 \rightarrow {}^{1}/_{2}Na_2S_2O_3 + {}^{1}/_{2} H_2O$ (3)
$2RSNa + {}^{1}/_{2}O_2 + H_2O \rightarrow RSSR + 2NaOH$ (4)

*Test results and data analysis based on BBD statistical method*

The results obtained for spent caustic COD after each test are shown in Table 6.

Table 6: Experimental design to reduce spent caustic COD for independent input variables and dependent variables (response) by catalytic wet air oxidation using Box-Behnken design

| | | Factor 1 | Factor 2 | Factor 3 | Factor 1 | Factor 2 | Factor 3 | Response 1 |
|---|---|---|---|---|---|---|---|---|
| | | Coded level | | | Actual level of variables | | | |
| Std | Run | | | | A: Catalyst concentration( ppm) | B: Stoichiometric air flow(l/h) | C: Residence time (h) | COD(ppm) |
| 1 | 5 | -1 | -1 | 0 | 50 | 2 | 2 | 44150 |
| 2 | 9 | 1 | -1 | 0 | 150 | 2 | 2 | 41050 |
| 3 | 15 | -1 | 1 | 0 | 50 | 6 | 2 | 42250 |
| 4 | 10 | 1 | 1 | 0 | 150 | 6 | 2 | 40650 |
| 5 | 13 | -1 | 0 | -1 | 50 | 4 | 1 | 40850 |
| 6 | 4 | 1 | 0 | -1 | 150 | 4 | 1 | 38475 |
| 7 | 16 | -1 | 0 | 1 | 50 | 4 | 3 | 38525 |
| 8 | 3 | 1 | 0 | 1 | 150 | 4 | 3 | 37300 |
| 9 | 14 | 0 | -1 | -1 | 100 | 2 | 1 | 42700 |
| 10 | 11 | 0 | 1 | -1 | 100 | 6 | 1 | 40750 |
| 11 | 2 | 0 | -1 | 1 | 100 | 2 | 3 | 41100 |
| 12 | 8 | 0 | 1 | 1 | 100 | 6 | 3 | 39475 |
| 13 | 7 | 0 | 0 | 0 | 100 | 4 | 2 | 38350 |
| 14 | 12 | 0 | 0 | 0 | 100 | 4 | 2 | 38200 |
| 15 | 6 | 0 | 0 | 0 | 100 | 4 | 2 | 38800 |
| 16 | 1 | 0 | 0 | 0 | 100 | 4 | 2 | 38050 |

Table 7 shows the analysis of variance (ANOVA) test results, including the goodness of fit test, and the evaluation of the significant effects of process variables on the response performed. The significance of the fit test for a model indicates the proper distribution of points around the model; the model can be used to predict the values of function variables. The quadratic polynomial regression model, which is the most appropriate design model in this experiment, was employed to predict the magnitude of the response variable, encompassing both binary interactions and their power, in addition to the effect of individual variables

Table 7: Final analysis of variance of the fitted equations of reduced spent caustic COD by catalytic wet air oxidation on laboratory scale

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 5.612E+07 | 9 | 6.236E+06 | 52.09 | < 0.0001 | significant |
| A-Catalyst concentration | 8.611E+06 | 1 | 8.611E+06 | 71.93 | 0.0001 | |
| B-Stoichiometric air flow | 4.314E+06 | 1 | 4.314E+06 | 36.04 | 0.0010 | |
| C-Residence time | 5.080E+06 | 1 | 5.080E+06 | 42.44 | 0.0006 | |
| AB | 5.625E+05 | 1 | 5.625E+05 | 4.70 | 0.0733 | |
| AC | 3.306E+05 | 1 | 3.306E+05 | 2.76 | 0.1476 | |
| BC | 26406.25 | 1 | 26406.25 | 0.2206 | 0.6552 | |
| $A^2$ | 2.121E+06 | 1 | 2.121E+06 | 17.71 | 0.0056 | |
| $B^2$ | 3.474E+07 | 1 | 3.474E+07 | 290.16 | < 0.0001 | |
| $C^2$ | 3.379E+05 | 1 | 3.379E+05 | 2.82 | 0.1440 | |
| Residual | 7.183E+05 | 6 | 1.197E+05 | | | |
| Lack of Fit | 4.033E+05 | 3 | 1.344E+05 | 1.28 | 0.4220 | not significant |
| Pure Error | 3.150E+05 | 3 | 1.050E+05 | | | |
| Cor Total | 5.684E+07 | 15 | | | | |

*Fit Statistics table of experimental data in the process of spent caustic treatment by CWAO method*

According to Table 8, the Std. Dev. is equal to 346.00 which is insignificant digits relative to COD = 37300; therefore, the lower the Std. Dev., the better the result, obtained from the following equation.

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{n-1}} \qquad (5)$$

Where, *S* stands for sample standard deviation, ∑ for sum of…, *X* for each value, $\bar{x}$ for sample mean and *n* for number of values in the sample. *Mean* is the average of the data and *C.V.%* stands for the coefficient of variation that is obtained by dividing *Std. Dev.* by *Mean* multiplied by 100, indicating that if these experiments are repeated, there is a 0.86% chance of new data being obtained, which reveals the accuracy of this experiment.

$R^2$ and Adjusted $R^2$ are 0.9874 and 0.9684, respectively, indicating a high correlation between the predicted data and the obtained data. Since $R^2$ represents the change around the mean response and alone cannot explain the accuracy of the model, another coefficient called Adjusted $R^2$ is used, which is calculated from the following equations.

$$R^2 = 1 - \frac{SS_{residual}}{SS_{total}} \qquad (6)$$

$$R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{SS_{total}/(DF_{model} + DF_{residual})} \qquad (7)$$

Where, $SS_{residual}$ represents the residual sum of squares, *DF* represents the degree of freedom, and $SS_{total}$ represents the sum of the total squares of $SS_{residual}$ + $SS_{model}$. The difference between Adjusted $R^2$ and Predicted $R^2$ should not be more than 0.2.

Table 8: Statistical data of final analysis of variance of fitted equations for COD reduction by CWAO

| Std. Dev. | 346.00 | $R^2$ | 0.9874 |
|---|---|---|---|
| Mean | 40042.19 | Adjusted $R^2$ | 0.9684 |
| C.V. % | 0.8641 | Predicted $R^2$ | 0.8766 |
| | | Adeq Precision | 25.3396 |

*Actual and predicted values related to COD obtained from experimental data in the process of spent caustic treatment by CWAO*

Table 9 compares the actual values of the experiment with the predicted values, indicating the close correlation of these numbers. Fig 2 shows the actual test data with the predicted data ($R^2$), confirming the appropriate fit of the model with the test data.

Table 9: Comparison of actual values with predicted ones related to COD in the spent caustic treatment by CWAO method

| Run Order | Standard Order | Actual Value | Predicted Value |
|---|---|---|---|
| 1 | 16 | 38050.00 | 38350.00 |
| 2 | 11 | 41100.00 | 40862.50 |
| 3 | 8 | 37300.00 | 37240.63 |
| 4 | 6 | 38475.00 | 38259.38 |
| 5 | 1 | 44150.00 | 44171.88 |
| 6 | 15 | 38800.00 | 38350.00 |
| 7 | 13 | 38350.00 | 38350.00 |
| 8 | 12 | 39475.00 | 39556.25 |
| 9 | 2 | 41050.00 | 41346.88 |
| 10 | 4 | 40650.00 | 40628.13 |
| 11 | 10 | 40750.00 | 40987.50 |
| 12 | 14 | 38200.00 | 38350.00 |
| 13 | 5 | 40850.00 | 40909.38 |
| 14 | 9 | 42700.00 | 42618.75 |
| 15 | 3 | 42250.00 | 41953.13 |
| 16 | 7 | 38525.00 | 38740.63 |

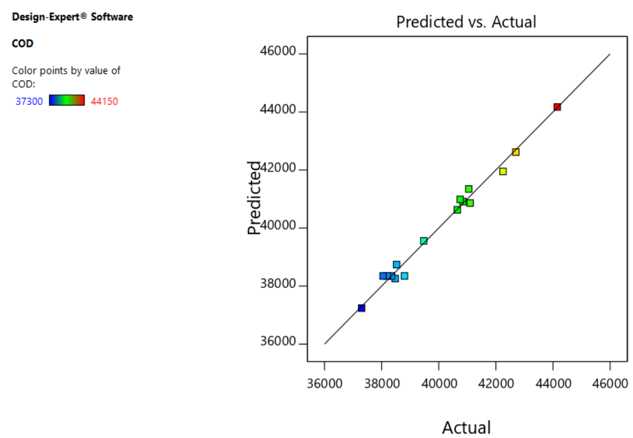


Fig. 2- Comparison of actual and predicted values related to reduction of spent caustic COD by CWAO method, (R2 = R-Squared = 0.9874)

*Extraction of data model of spent caustic COD changes due to CWAO on a laboratory scale*

Since the main objective of this study is the optimization of test parameters, the results were imported to Design Expert software in order to extract the governing model of the process. The final design equation of this research is the following mathematical model equation, which uses the attained data. Therefore, the parameters of A, B and C have a great impact on reducing spent caustic COD.

$$\text{Final COD} = +38204.7 - 1037.5 * A - 734.375 * B - 796.875 * C + 375 * AB + 728.125 * A^2 + 2946.88 * B^2 \quad (8)$$

In Equation (8), the parameters of A, B and C represent catalyst concentration, stoichiometric air flow and residence time, respectively.

*Plot of normal data distribution*

Fig 3 shows the statistical diagrams to evaluate the adequacy of residual plot model.

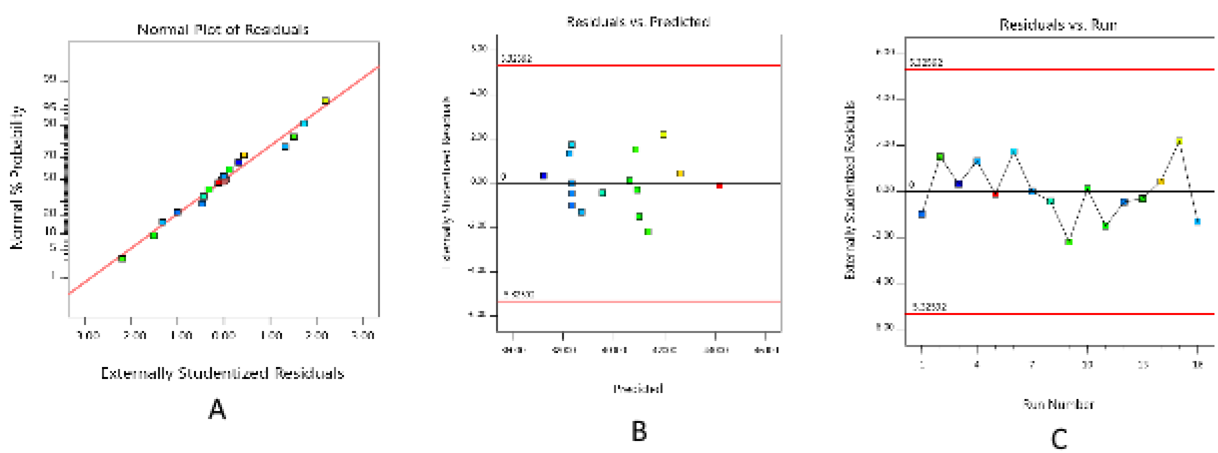


Fig. 3- Statistical diagrams to evaluate the adequacy of the proposed model;
(A) Normal Plot of Residuals; (B) Residuals vs. Predicted; (C) Residuals vs. Run

*Data deviation graph*

Fig 4 shows the data deviation graph. As seen, the catalyst concentration is inversely associated with the spent caustic COD.

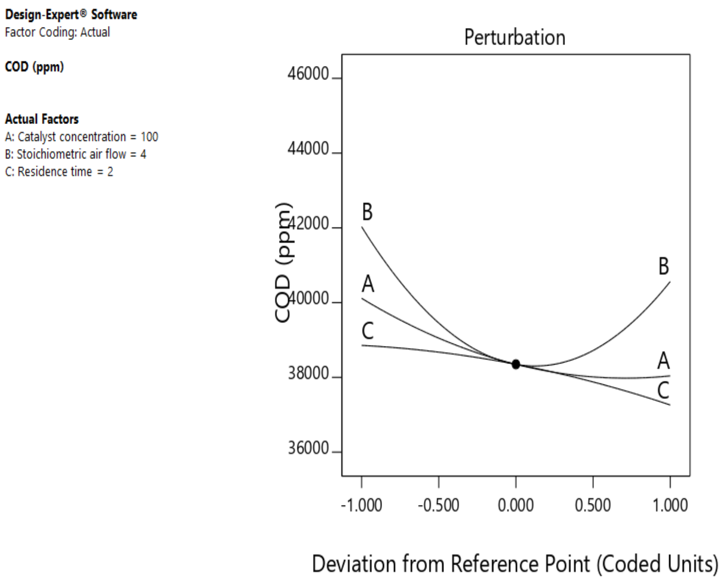


Fig. 4- Data deviation graph

*Investigating the co-effect of catalyst concentration and stoichiometric air flow on COD response*

Fig 5 and 6 show the 2D and 3D plots of the interaction between the catalyst concentration and the stoichiometric air flow at a residence time of 2 h.

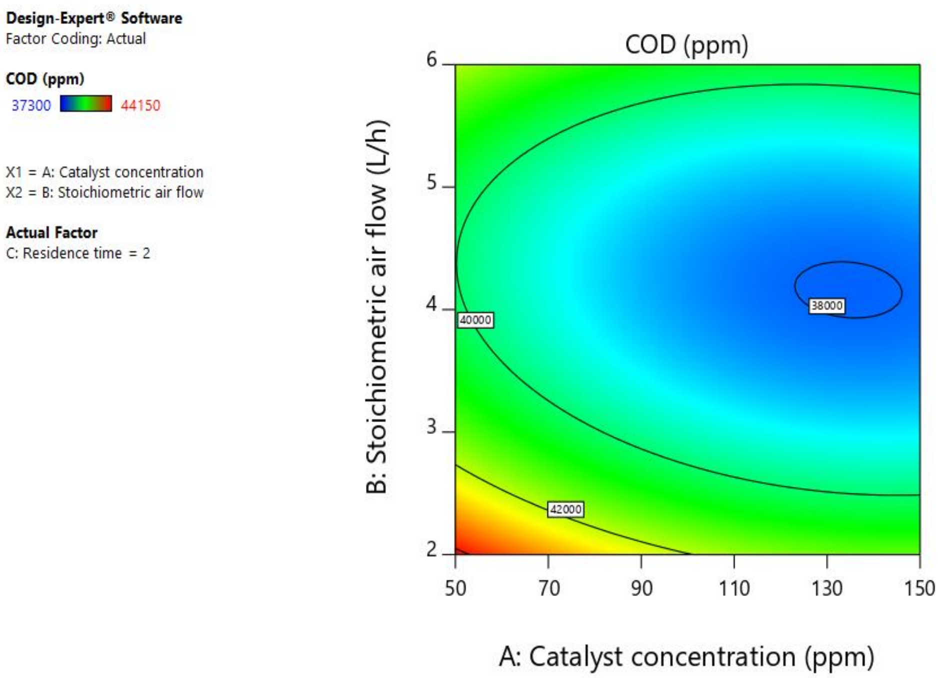


Fig. 5- Two-dimensional plot of the interaction between catalyst concentration and stoichiometric air flow on the COD response

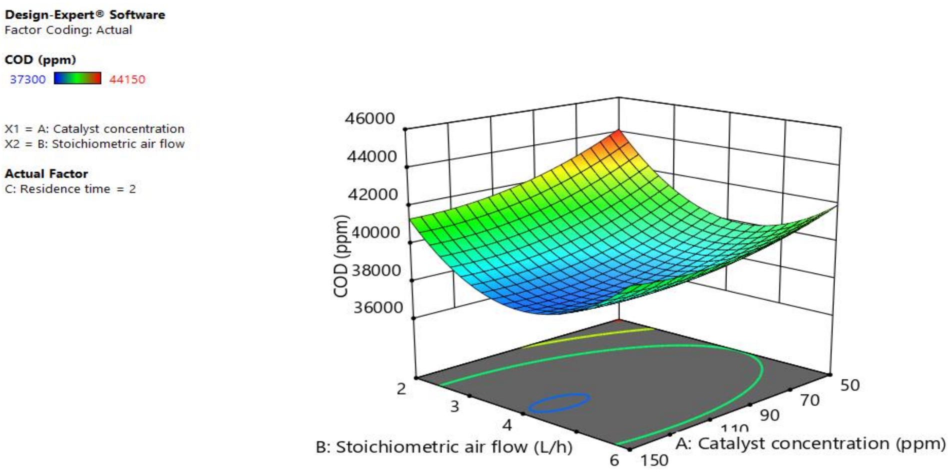


Fig. 6- Three-dimensional plot of the interaction between catalyst concentration and stoichiometric air flow on the COD response

*Optimization conditions for design method of catalytic wet air oxidation of spent caustic effluent*

Fig 7 shows the Ramp diagrams for optimal conditions; the higher the catalyst concentration and the stoichiometric airflow, the higher the residence time.

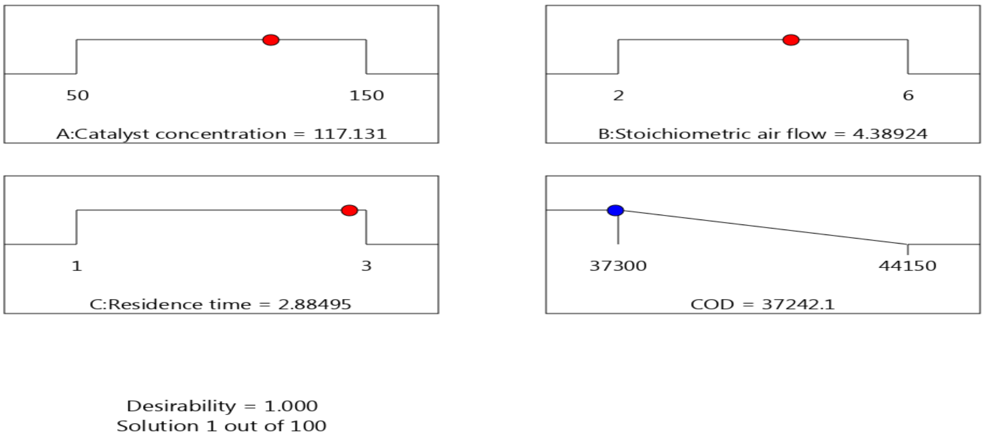


Fig.7- Ramp diagrams of optimal conditions to minimize the COD concentration by CWAO method

*Verification of the model*

To confirm the optimal point provided by the model and further validation, the optimal point was tested in triplicate (Table 10).

Table 10: Optimal point confirmation in the CWAO process

| Solution 1 of 10 Response | Predicted Mean | Predicted Median | Std Dev | n | SE Pred | 95% PI low | Data Mean | 95% PI high |
|---|---|---|---|---|---|---|---|---|
| COD | 37146.6 | 37146.6 | 345.996 | 3 | 288.86 | 36439.8 | 37225.7 | 37853.4 |

Two-sided Confidence = 95%

## 4. Discussion

The present study aimed to apply catalytic wet air oxidation method for the treatment of spent caustic effluent collected from the Bandar Abbas oil refinery and to optimize associated parameters. According to the results from the CWAO reactions of spent caustic effluent in the batch reactor in the exposure to IVKAZ catalyst, the catalysts accelerate thermodynamically feasible reactions. Among the catalysts, the heterogeneous catalysts possess the noble metals known as highly active catalysts for oxidation reactions and have been applying in industrial activities. Based on evidence, the level of Disulfide-S-oxide increases and further sulfate is produced as a result of catalytic oxidation and with increasing oxygen content. Therefore, the concentration of COD in the effluent also decreases with declining concentration of $S^{2-}$ ion. During this oxidation process, thiosulfates are converted to sulfates. As shown in Table 6, the number of experiments performed using BBD method with four repetitions of the central point was 16 and random.

According to Table 7, the F-Value of the catalyst concentration is 71.93, indicating that factors A, B, C, AB, $A^2$ and $B^2$ have the greatest effect on COD. As can be seen, the catalyst concentration and the stoichiometric air flow have a large effect on the CWAO, and the rate of sulfide removal enhances with increasing amount of inlet air.

P-values less than 0.05 indicate that the factors are significant and that these factors are 95% likely to influence the process. P-values less than 0.05 indicate that the factor is significant and P-values higher than 0.1 mean that the factor is insignificant. Therefore, P-values less than 0.05 to 0.1 are a confidence interval that affects the response by 90%. If considered, the P-value for this model is significant.

Based on the P-values and F-Values mentioned in Table 7, it is possible to understand the effect and importance of the parameters in the model. As seen, all parameters except the catalyst concentration and residence time interaction parameter are efficient in terms of COD removal efficiency. According to Table 7, the P-value for Lack of fit in this model is 0.4220. Therefore, the value of this parameter indicates that the factors fit together and the proposed model has sufficient fit. Therefore, p-value is considered to be significant for the model and not significant for Lack of Fit test; these two are essential in verifying the model. Table 8 shows the statistical data of final analysis of variance of fitted equations for COD reduction by CWAO. Moreover, Fig 2 presents the actual test data with the predicted data ($R^2$), confirming the appropriate fit of the model with the test data. Therefore, the closer the data distribution is to the regression line and the closer the slope of the graph is to the number one, the higher the accuracy and validity of the model, indicating a greater agreement between the predicted data and the actual data. Additionally, Fig 2 confirms an acceptable statistically correlation between experimental data and predicted values. The advantage of using a mathematical model equation is to examine the relationship of variables from their coefficients. A positive coefficient means a direct relationship and a negative coefficient means an inverse relationship; the larger the coefficient, the greater the effectiveness of that parameter.

One of the most important sampling distributions is the normal distribution. Because the condition of the sample varies as a result of the error caused by the experiments, the normal distribution plays a pivotal role in analyzing the data obtained from the designed experiments. In addition, the normal data distribution plot is also used to check the adequacy of the model provided by the software of the model. Based on the residual plot in Fig 3a, the more linear the data dispersion and the closer to the regression line, the more normal the data. Therefore, in this study, the data have a normal distribution. Uniform and linear distribution indicates the normal distribution of errors, indicating fewer errors and increased model validity. Fig 3b shows a graph of the residual values versus the predicted values; the dispersion is within the specified limits and indicates the accuracy of the tests. Fig 3c shows a graph of residual values versus run; the dispersion is within the specified limits.

According to Fig 4, it can be seen that the catalyst concentration is inversely related to the spent caustic COD. The COD removal efficacy of spent caustic was enhanced with increasing catalyst concentration. Moreover, increasing the stoichiometric air flow has a great impact on CWAO. Elevating the amount of inlet air increases the efficiency of sulfide removal and naturally reduces the concentration of COD. In general, the stoichiometric air flow is inversely related to values slightly above average and then directly related to the spent caustic COD. The residence time has no much effect on COD removal. However, increasing all three factors enhances sulfide removal, but the effect of catalyst concentration is greater than other factors.

In this study, the diagrams of the response procedure of spent caustic COD concentration were plotted. After confirming the final model, how to change the response with the relevant variables can be shown by a diagram. Graphs are as 2D contour plot and surface response. Contour plots and 3D surface plots provide the co-effect of two variables on the response. With the help of these diagrams, it is possible to evaluate the effectiveness of the response variable in relation to each of the operational variables in the presence of other variables. As shown in Fig 5 and 6, the catalyst concentration is significantly effective parameter in CWAO, the increase of which reduces the amount of COD; also, the higher the oxygen content, the better the oxidation reaction. Therefore, the minimum amount of COD was seen for catalysts with concentrations of 120-130 ppm and stoichiometric air flow of 4-4.5 l/h, and the highest amount of COD was observed with decreasing catalyst concentration below 120 mg/l and stoichiometric air flow below 4 l/h, indicating inverse relationship between catalyst concentration and stoichiometric air flow in the COD value.

As depicted in Fig 7, the significant reported values for F-value and P-value and high values for $R^2$ and adjusted $R^2$, as well as normal dispersion of data show the sufficient accuracy of the data. Therefore, to determine the optimal conditions for minimizing the amount of COD, the results of Design Expert software for the variables of catalyst concentration, stoichiometric air flow and residence time are 117.131 ppm, 4.38924 l/h and 2.88495 h, respectively. The results predict that if the COD value is obtained to be 37242.1 mg/l, the utility for this optimization will be 1.

Considering that the confidence interval is between 36439.8 and 37853.4, and due to the fact that the average optimal point is in this interval, the experimental data were confirmed with 95% probability, as seen in Table 10.

## 5. Conclusion

During the experiments for the treatment of spent caustic effluent of the Bandar Abbas oil refinery using the CWAO method, the following results were achieved:

A) The optimal conditions for the CWAO were as follows; the catalyst concentrations of 117.1 ppm, the stoichiometric air flow of 4.3 l/h and the residence time of 2.8 h resulted in a maximum spent caustic COD reduction of 42% (from 64100 to 37242 mg/l), as well as reduced concentration of most toxins to less than 1 mg/l.

B) The BBD method was employed to perform experiments and optimize the parameters of catalyst concentration, stoichiometric air flow and retention time (as independent variables), and finally the experiments were optimized using RSM. The obtained values for F-value, p-value, $R^2$ and Adjusted $R^2$, and normal data distribution diagram as well as 2D and 3D plots showed that the optimal operational conditions for catalyst concentration, stoichiometric air flow and retention time are 117.13 ppm, 4.38 l/h and 2.88 h, respectively.

C) The results of experiments showed that the catalyst concentration and the stoichiometric air flow have the greatest effect on reducing the pollutant rate (COD) of spent caustic by CWAO method. Therefore, the higher the oxygen content, the better the oxidation reaction and the higher the sulfide removal efficiency; moreover, the higher the catalyst concentration, the higher the conversion rate and the lower the COD. However, excessive increase in catalyst concentration is undesirable in this case, because firstly, the operating cost increases and secondly, since the catalyst is not separated from the wastewater, sending it to the environment through the wastewater is not desirable, so attempts are made to use low concentration. Additionally, increasing the residence time will partially reduce the COD of the effluent and will be ineffective to some extent. Furthermore, increasing the stoichiometric air flow has a great impact on CWAO. Elevating the amount of inlet air increases the efficiency of sulfide removal and naturally reduces the concentration of COD. In general, the stoichiometric air flow is inversely related to values slightly above average and then directly related to the spent caustic COD.

D) Considering that the WAO is the most appropriate and efficient commercial methods available for the disposal of industrial effluents and the performance of this method is at high temperature and pressure, therefore it increases the cost. Therefore, the wet air oxidation efficiency can be improved by adding homogeneous or heterogeneous catalysts with gentle temperature and pressure, which is a low operating cost and environmentally friendly method.

E) It is important to select appropriate catalysts used in environmental protection because proper catalysts prevent the production and the release of unwanted intermediate pollutants through a change in the process route. Furthermore, the main advantage of heterogeneous catalysts compared to homogeneous catalysts is that after oxidation, they are easily recovered, regenerated and reused, thus reducing operating costs.

F) It is impossible to compare the results of this study with other studies, because the compounds in different effluents are not the same. Researchers have studied different real and synthetic samples (Table 11). The current study analyzed the real samples of spent caustic effluent collected from the Bandar Abbas refinery, which is a wastewater with the worst possible conditions in terms of sulfidic, naphthenic and cresylic impurities. The treatment method of CWAO was performed in the presence of IVKAZ solid catalyst. According to the obtained results, the COD content was reduced to 42% under optimal conditions of catalyst concentration of 117.1 ppm, residence time of 2.8 h and the stoichiometric air flow of 4.3 l/h. Mohammadizadeh (2018) reported the elimination efficacy of COD (37.5%) for spent caustic effluent from phase 4 and 5 refineries of South Pars (Assaluyeh, Iran) with the catalyst concentration of 2000 ppm and the stoichiometric air flow of 9 l/h and the residence time of 2.37 h. Moreover, the air flow was 4.5 l/h, but with a longer residence time, the $S^{2-}$ level was decreased to less than 1 mg/l. Karimi et al. (2017) reported that the $S^{2-}$ level of refinery effluent was reduced to 362 mg/l at the airflow of 7 l/min and the reaction time of 30 min.

Table 11: Comparison of different research results on spent caustic effluent treatment using catalytic wet air oxidation method

| | Factor | Units | Minimum | Maximum | optimum condition | Catalyst used | Primary COD (mg/l) | Final COD(mg/l) | Remove COD(%) | Remove $S^{2-}$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|
| Chen C, Cheng T, 2013 | temperature | °C | 150 | 200 | 200 | MnOx-CeOx/γ-$Al_2O_3$ | 250,781 | | 95 | |
| | pressure | MPa | 0.2 | 2.5 | 2 | | | | | |
| Karimi et al. 2017 | temperature | °C | 90 | 110 | 90 | IVKAZ | 30000 | 5000 | 83 | 362 |
| | Reaction time | min | 20 | 30 | 30 | | | | | |
| | Air flow | l/min | 7 | 10 | 7 | | | | | |
| Mohammadizadeh 2018 | Catalyst concentration | ppm | 500 | 2000 | 2000 | liquid cobalt sulfonated phthalocyanine | 24000 | 15000 | 37.5 | 59.8 |
| | Stoichiometric air flow | l/h | 3 | 9 | 9 | | | | | |
| | Residence time | h | 1 | 3 | 2.37 | | | | | |
| Elmi et al. | Catalyst concentration | ppm | 50 | 150 | 117.1 | IVKAZ | 64100 | 37242 | 42 | <1 |
| | Stoichiometric air flow | l/h | 2 | 6 | 4.3 | | | | | |
| | Residence time | h | 1 | 3 | 2.8 | | | | | |

## 6. Abbreviations

COD= Chemical Oxygen Demand(mg/l)
TSS= Total suspension solid( mg/l)
WAO= Wet Air Oxidation
CWAO= Catalytic Wet Air Oxidation
AOP= Advanced Oxidation Processes
BBD= Box- Behnken Design
LPG= Liquefied Petroleum Gas
RCRA= Resource Conservation and Recovery Act
US EPA= United States Environmental Protection Agency
DAN = Direct Neutralization with Acid
RSM= Response Surface Methodology
CCD= Central Composite Design
IC= Ion Chromatography
ANOVA= Analysis of Variance
STD.DEV= Standard Deviation
C.V= Coefficient of Variation
PI= Prediction Interval
RPDM= Refinaria de Petroleos de Manguinhos S. A.
CPC= Chinese Petroleum Corporation
$R^2$ = Coefficient of Determination
SS= Sum of Squares
DF= Degrees of Freedom
NTU = Nephelometric Turbidity Unit
TCU= True Color Unit
FCC= Fluid Catalytic Cracking
ATF= Automatic Transmisson Fluid
AHP= Analytic Hierarchy Process
Adjusted $R^2$= Adjusted Coefficient of Determination
Predicted $R^2$= Predicted Coefficient of Determination
A= Catalyst Concentration Parameter
B= Stoichiometric Air Flow Parameter
C= Residence Time Parameter
S= Sample Standard Deviation
MEAN = Data Mean
IVKAZ = Cobal Phthlocyanine catalyst –this catalyst is synthesis in Russia.
PPM=Part Per Million ,mg/kg

## 7. Acknowledgments

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