International Journal of Multiphysics
Volume 18, No. 4, 2024
ISSN: 1750-9548

Separation and Removal of Hydrocarbon Compounds from Industrial Wastewater Using a Combined Approach of Oxidation, Adsorption, and Nanofiltration

Moslem Shahamatpour[1], Seyyed Mostafa Tabatabaei Ghomsheh[2*], Sarah Maghsoodi[2], Shima Azizi[2]

[1]PhD. Student, Dept. of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
[2]Assist. Prof., Dept. of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
*Corresponding author

Abstract

The purpose of this study is to use oxidation, adsorption, and nanofiltration in combination to separate and remove hydrocarbon compounds from industrial effluent. Initially, anthracite adsorption was used to remove hydrocarbon compounds from a refinery's wastewater. The refinery's wastewater was then subjected to advanced Fenton oxidation in order to eliminate hydrocarbon compounds. The oxidation process had a better removal percentage and a greater optimal hydrocarbon content than the adsorption method, according to a comparison of the results of the two processes (Fenton and adsorption). As a result, the oxidation process was started from the beginning of this series chain. However, in this round, the optimal parameters were determined as there was not any variation in the hydrocarbon concentration and the feed was the refinery's effluent, which had 40.2 mg/L of hydrocarbon compounds. 5.1 mg/L of hydrocarbon compounds existed in the Fenton process output, which was kept in the reservoir and used as feed for the adsorption process series. The feed from the Fenton stage's output was used to adjust the adsorption process's parameters. 2.16 mg/L of hydrocarbon compounds existed in the adsorption stage's output, which served as feedstock for the nanofiltration process. When all three of these steps were combined, the nanofiltration step produced water that could be used in the refinery's internal networks at a concentration of 0.4 mg/L of hydrocarbon compounds.

Keywords: Adsorption, Advanced Fenton Oxidation, Hydrocarbon Compounds, Nanofiltration, Wastewater Treatment.

Introduction

The growth of petrochemical and oil and gas refineries for producing a wide range of products has resulted in the production of wastewater and other dangerous pollutants. According to its operations, every industry generates a different type of effluent. Without considering environmental concerns seriously, lots of refining companies release their effluents, including fine particles, into the environment. A major global environmental concern today is an increase in wastewater generation from cities, industries, and farms brought on by population growth and economic expansion. The design of wastewater treatment plants and effluent management, with an emphasis on lowering output and improving water reuse, are essential for minimizing the environmental effects that emerge from it. In each production situation, protecting the environment and the land is a fundamental principle. For wastewater to be effectively treated, including caustic and other hazardous effluents, management and separation are essential [1].

Water is the most essential substance for living things [2]. Safe drinking water is critical for human health and well-being. Unfortunately, approximately two billion people do not have access to safe, clean drinking water [3].

Water contamination appears to be mostly caused by human activity, such as urban, industrial, and agricultural operations [4].

One of the most important challenges facing humanity in the twenty-first century is the preservation of the environment and natural resources, while raising the standard of living in every nation remains crucial [5]. A massive amount of wastewater is produced in urban, industrial, and environmental regions as a result of the recent changes in lifestyle and consumption patterns, particularly in emerging nations, as well as the growth of urbanization and industrialization [6]. The development and enhancement of wastewater's functional quality, as well as waste management, deal with things like production control, collection, transfer, and disposal [7]. A group can be useful and effective in raising the standard of health in the community when it takes the form of a set of comprehensive, well-coordinated guidelines and regulations and is founded on adequate knowledge and information about the circumstances that now exist in the target region [8]. Communities have expressed serious concerns about the potential negative impacts on their health and the environment that may result from pollutants released from nearby oil and gas facilities [9]. It is envisaged that senior industry managers will locate the components needed to build an industrial wastewater management collection system for wastewater evaluation and use it as a new management tool to maintain a clean environment [10].

Water quality degradation as a result of continuous discharge of contaminated water caused by global population increase, urbanization, and rapid industrialization has become a global concern [11-12]. More specifically, the frequent and continuous discharge of produced water from the oil and gas industry has become one of the world's most serious problems, with significant consequences for ecological balance, the environment, and the economy [13-15]. Produced water is mostly composed of dissolved oil, hydrocarbon gases, organic acids, phenols, metals, and different chemical additions. The dissolved oil pollutants include recalcitrant organic compounds like benzene, toluene, xylene, waxes, and surfactants [16]. Oil is one of several contaminants that can have major consequences for the ecosystem. Municipal and industrial institutions are frequently the primary sources of pollution [17]. Inorganic pollutants (such as nitrogen and nitrogen oxides, ammonia, heavy metals, phosphates) and organic pollutants (such as petroleum substances, hydrocarbons, pharmaceuticals, herbicides, pesticides) are the primary types of pollutants that end up in the soil and water environment [18-21].

Produced water remediation is an important task because improper disposal of produced water can interfere with the sustainability of the environment [22-23]. Various treatment technologies have been used for the removal of oil contaminants. For example, membranes and advanced oxidation are used for oily water treatment; however, their use is limited due to high capital and maintenance costs. Chemical flocculation achieves high removal efficiency and requires small floor space, but it consumes huge amounts of energy. Biological treatment is also used despite producing secondary pollution that requires further treatment and takes time [24-25].

Due to refineries have various processes units which operate together to produce different products, the result of these operations is the production of hazardous industrial effluents in addition to petroleum products. Depending on the type of effluent, the release of these pollutants into the atmosphere and environment will cause different pollutants to be released [26]. If adequate precautions and care are not taken while disposing of the waste generated by these industries, millions of cubic meters of polluted water will be released each year into receiving sources [27]. It is very difficult to remediate industrial effluent for reuse of water in industry without using membrane filtration techniques. As a membrane filtering technique that offers a high water flux rate, NF has generated more interest. By replacing nanofiltration membranes with RO membranes, you may increase flow rate while saving about 20% on electricity [28]. Compared to RO, the NF process requires a less initial investment since pumps, pipes, and tanks operate at lower pressures, which results in lower expenses. The NF process may easily replace the UF, RO, and electrodialysis processes in many of their applications because of their similarities [29]. The history of NF begins in the 1970s, and after that time, the method of filtering water of impurities has advanced significantly [30]. NF membrane technology is a well-liked technique for eliminating organic materials, residual disinfectant levels, color, odor, taste, and pesticide residues from water [31]. At suitable product flow rates and comparatively low pressures, reverse osmosis (RO) membranes were developed [32]. Among the many uses for the NF process, it's possible to note the softening process. They are sometimes referred to as "hardening membranes" even now [33]. It is now feasible to replace a membrane unit at various stages of the water purification process due to the simultaneous removal of inorganic and organic pollutants as well as hardness in a single step [34].

Chang and Chen extracted copper ions from aqueous solutions by attaching magnetite nanoparticles to chitosan. The outcomes demonstrated that Langmuir's adsorption isotherm is followed by copper adsorption onto nanoparticles. The Langmuir adsorption equilibrium constant was 0.0165 L/mg, and the highest adsorption capacity was 21.5 mg/g. In the pH range of 2 to 5, the adsorption capacity improved significantly with an increase in pH [35]. The effectiveness of the RO system in eliminating the heavy metal arsenic from drinking water was investigated by Vatanpour et al. The outcomes of the tests and measurements demonstrated that the RO membrane TE 2521's performance was influenced by variables such concentration, pH, solution temperature, and pressure. Performance and efficiency changed when any of these characteristics was increased or decreased [36]. Research on the production of NF membranes with excellent heavy metal ion removal efficiency over a broad acidic pH range was carried out by Jia et al. With a molecular weight cut-off of 300 Da, the NF membrane exhibited a comparatively high pure water permeability of 81.0 ± 7.0 $LMH.bar^{-1}$. In a broad range of acidic pH, this membrane effectively rejected the cations of heavy metals as Pb^{2+}, Cd^{2+}, and Ni^{2+} by over 93% [37]. Zhang et al. employed spectrum analysis to find structural alterations and electrocatalytic oxidation technology to break down DOM in NCLL. The results demonstrated that the removal rates of COD (chemical oxygen demand), TOC, and UV254 were 99.0%, 57.4%, and 99.3%, respectively, under optimal experimental factors (pH = 2.0, NaCl concentration = 0.7%, $Fe_2(SO_4)_3$ concentration = 0.8%, retention time = 6 hours). Analysis using UV-Vis spectroscopy showed that aromatic C=C bonds could be efficiently broken by electrocatalytic oxidation, which reduced the amount of aromatics and molecular weight in NCLL [38].

For the effective removal of PAH, Chen et al. suggested modifying the surface of a PES-PAA-ZrO_2 NF membrane to make it extremely wettable and durable. Chemical bonding created a ZrO_2 coating on the PES membrane surface, which led to the PES-PAA-ZrO_2 membrane's remarkable hydrophilicity, underwater oil repellency, and stability. The modified membrane's contact angle with water dropped dramatically from approximately 50 degrees to less than 10 degrees and quickly to 0 degrees in less than a second when compared to the original PES membrane. This resulted from the remarkably strong affinity for water, which required a lot less energy to permeate. Following adjustment, the efficacy of wastewater treatment rose by more than 90%, resulting in a removal rate of PAHs that was over four times higher. Under a variety of conditions, the PES-PAA-ZrO_2 membrane's exceptional strength was verified, demonstrating the membrane's usefulness for long-term operations [39]. Li et al. suggested a unique 3DET for treating wastewater that uses waste aluminum as the electrode particles. The findings show that coagulation by Al species and indirect oxidation by oxidative species (H_2O_2, $OH^{\bullet}$, and RCS), in addition to direct anodic oxidation, are essential for the elimination of pollutants. Experiments with continuous flow demonstrate that adding EC Fe as a post-treatment after 3DET Al treatment can successfully neutralize 3DET effluent and increase the effectiveness of pollutant removal. The combined process had an overall operational cost of USD/m^3 of 1.307. The 3DET-Fe EC technique is a promising approach for treating concentrated NF permeate, as this study shows [40].

It appears essential to use an ideal method of water purification due to the growing population, the depletion of drinking water supplies, the enforcement of stringent legislation, and the rise in operating expenses, such as energy [41]. To reach a given purity or to meet industry process goals, a single separation method is insufficient. As a result, hybrid procedures that combine several separation techniques ought to be employed [42]. In general, a hybrid process combines multiple devices and processes to best utilize each of their abilities. These components are then integrated to create an integrated system that boosts process productivity overall and can be employed as a tool in processes that involve various stages of separation [43]. Because these membranes are susceptible to high pollutant concentrations, most synthetic aqueous solutions and process fluids have clogging qualities that necessitate filtering the input feed to the nanofiltration process. Moreover, the quantity of organic chemicals in this kind of water can quickly clog the membrane, reducing both the membrane's lifespan and the amount of time it takes to purify. Consequently, it will be economical to remove organic matter clogs and solid particles prior to nanofiltration [44]. Since individual procedures may have disadvantages, a lot of recently completed research in this field focuses on the use of combined processes [45].

Several methods to treating industrial and municipal wastewater have been thoroughly investigated in the past, taking into account both the advantages and disadvantages of each technique. For this research, an adsorption, oxidation, and NF technique combination has been chosen.

Adsorption seems to be a successful approach because of its straightforward design [46]. Petroleum compounds have been absorbed using a variety of adsorbents. Some examples of these include the Fe_3O_4/Bentonite adsorbent for diesel [47], the Bentonite and Org-bentonite adsorbents for diesel [48], and the Fe_3O_4/Bent/rGO and Fe_3O_4/Bent/MWCNTs adsorbents for diesel [49]. Total petroleum hydrocarbon concentration, or TPH, is the environmental quality metric that is most frequently used to evaluate the degree of oil contamination. TPH contaminants are hydrophobic, refractory molecules that are a component of complex combinations of asphaltenes, resins, and aliphatic, aromatic hydrocarbons, according to Tran et al. Due to the operations of oil exploration, extraction, and refining as well as oil spills, underground oil storage tank leaks, and runoff, petroleum-contaminated places are prevalent around the world [50]. Sanches-Filho et al. [51] and Pinto et al. [52] in Brazil, Li et al. [53] and Zhou et al. [54] in China, Vane et al. [55] in the United States, and Ashok et al. [56] in various locations in the Persian Gulf in the Middle East have shown that Heavy metals and petroleum hydrocarbons readily settle in the estuary vegetation's silt, which keeps hydrocarbon films in place and prevents them from flowing through the water systems under study.

The present study aims to enhance the achieved efficiency by optimizing the adsorption process's process variables (pH, contact time, hydrocarbon concentration, and reactor flow rate) and by placing the adsorption process in a series arrangement. The placement of the oxidation process in this three-stage series process was determined after the optimization of process variables (pH, hydrocarbon concentration, reaction time, and hydrogen peroxide amount) for the advanced oxidation process. Now, depending on whether the adsorption or oxidation process comes first in this arrangement, the output of the first process is chosen as the input for the second process, and the variables of the second process have been adjusted to decrease the hydrocarbon concentration. The output of the second step is then used as input to the NF stage. Depending on whether the adsorption or oxidation process occurs first in this arrangement, the output of the first process is selected as the input for the second process, and the parameters of the second process have been modified to reduce the hydrocarbon concentration. The second stage's result is subsequently used as input for the NF stage.

Materials and Methods

There are several methods available for treating industrial wastewater, and this paper studies three of them: adsorption, nanofiltration, and advanced fenton oxidation.

Shaaban et al. determined the quantity of oil removed from wastewater using the following equation [57]:

$$\text{Removal Efficiency } (\%) = [(C_i - C_f) / C_i] \times 100$$

where C_i is the initial oil concentration before treatment and C_f is the final oil concentration after treatment.

One technique for experimental design is the response surface method, which is used to find the best parameters among various data in a process or processes. Within these various data, the factors we can control are referred to as independent variables, while the variables we are powerless to affect are referred to as dependent variables [58]. The response surface methodology (RSM) is a useful statistical technique that facilitates the economical and effective evaluation of the interactive impacts of several factors. The system can identify the optimal experimental parameters by observing the impact of changing parameters that are entered into it on the response [59]. In order to fit quadratic polynomials, the CCD (central composite design) design which is frequently used for quadratic model fitting combines a two-level factorial design with axial points, also known as star points, and at least one point in the center of the experimental region [60-61]. According to several studies, this design possesses certain features [62-65].

1. Adsorption

Due to its ease of use, simplicity, and high removal capability, adsorption is seen to be a promising technology when compared to the present state of produced water treatment technologies [66-67]. One method that has shown promise for dealing with many pollution issues, including oil pollution, is biosorption. In recent decades, sorbents have garnered significant interest for their demonstrated affordable and effective application in rectifying oil contamination. Over the years, a variety of sorbents have been developed with varying degrees of success, including vegetable and fruit waste [68], straw [69], tree bark [70], almond shells [71], coconut shells [72], sugarcane bagasse, soya beans [73], algae [74], tea waste [75], sawdust [76], and more [77]. Moi et al. employed corn cob carbon to remove emulsified oil from wastewater, with an effectiveness of 17.1 mg/g [78]. Anifah et al. found that using sewage sludge to manufacture activated carbon effectively removed oil and grease from restaurant wastewater, with an effectiveness of 63.75 mg/g [79]. Alatabe et al. employed sedge cane grass to remove oil from wastewater, with a maximum effectiveness of 137.40 mg/g [80].

These experiments focused on the adsorption of hydrocarbon compounds on a continuous column. Important design parameters such as fluid flow rate, duration, pH, and oil concentration in the feed were investigated. A glass column with a diameter of 4 cm and height of 90 cm was developed. This column had a 75 cm-long bed filled with anthracite. The wastewater solution was pumped onto the fixed bed, and the feed flow temperature was set at 25 degrees Celsius.

The variables and levels for optimization are computed using CCD principles and laboratory data. The reactor flow rate, sampling time, pH, and concentration of oil compounds in the feed are denoted by A, B, C, and D, respectively. Each variable was investigated at 5 distinct levels (-α, -1, 0, 1, α). The response is expressed as the percentage of hydrocarbons removed. α equals $(2^k)^{1/4}$, where k is the number of factors (Table 1).

2. Advanced Fenton Oxidation Process

In the presence of iron ions in aqueous solutions, hydrogen peroxide breaks down in water and oxygen to create $OH^{\bullet}$ stoichiometrically, which oxidizes Fe(II) to Fe(III) [81].

In this research all studies utilized the same volume of 250 milliliters of wastewater solution and 5 grams of iron salt, with all other variables remaining within the experimental ranges. The variables and levels for optimization are computed using CCD principles and laboratory data. The amount of hydrogen peroxide, reaction time, pH, and concentration of oil compounds in the feed are designated as A, B, C, and D, respectively. Table (1) shows the levels of the defined parameters in the Fenton process. Each variable is explored on five levels (Table 1). The percentage of hydrocarbon elimination is used as the response variable.

3. Fenton Process Experiments with Feed from Refinery Wastewater with Constant Oil Concentration

The variables and levels for optimization are computed using CCD principles and laboratory data. The values for hydrogen peroxide quantity, reaction duration, and pH are denoted by A, B, and C. Each variable is explored on five levels (Table 1). The percentage of hydrocarbon elimination is used as the response.

4. Adsorption Process Experiments Using Feed from the Fenton Process Output

In this situation, the Fenton process output is used to feed the adsorption process. The variables and levels for optimization are computed using CCD principles and laboratory data. The reactor flow rate, sample duration, and pH are denoted as A, B, and C, respectively. Each variable is explored on five levels (Table 1). The percentage of hydrocarbon elimination is used as the response.

5. Nanofiltration Process

The membrane used in the NF process is made of polyamide material, as shown in Figure 1. The specifications of this membrane are firm. Sepro model NF-1 has a thickness of 0.165 mm and a pore size of 0.003 µm. Process pH ranges from 3 to 10, with a P max of 8.4 MPa and a T max of 50 degrees Celsius.

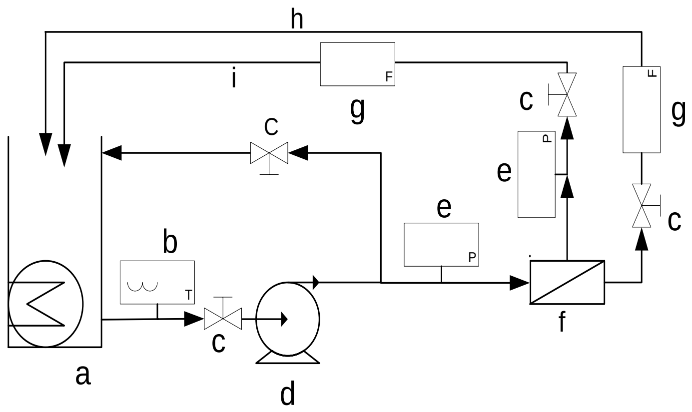

Fig. 1 The laboratory-scale NF process apparatus is shown schematically as follows: a- Feed tank with heater, b- Thermometer, c- Industrial valve, d- Pump, e- Pressure gauge, f- Membrane housing, g- Flow meter, h- Treated permeate flow, and i- Concentrated reject flow

The variables and levels for optimization are computed using CCD principles and laboratory data. Pressure, temperature, and pH are denoted as A, B, and C, respectively. Each variable is explored on five levels (Table 1).

Table 1 Variables and their levels for the CCD in processes

				Surface				
	Variable	**Unit**	**Sign**	**-α**	**-1**	**0**	**1**	**α**
adsorption process	Reactor flow rate	Lit/min	A	5	8.75	12.5	16.25	20
	Sampling time	min	B	5	21.75	38.5	55.25	72
	pH	-	C	4	5	6	7	8
	Concentration of Oil Substances	ppm	D	20	30	40	50	60
fenton process	hydrogen peroxide amount	mlit	A	55	67.5	80	92.5	105
	Reaction Time	min	B	10	17.5	25	32.5	40
	pH	-	C	3	3.75	4.5	5.25	6
	Concentration of Oil Substances	ppm	D	20	30	40	50	60
fenton process in series chain	hydrogen peroxide amount	mlit	A	55	65	80	95	105
	Reaction Time	min	B	10	16	25	34	40
	pH	-	C	3	3.6	4.5	5.4	6
adsorption process in series chain	Reactor flow rate	Lit/min	A	5	8.04	12.5	16.95	20
	Sampling time	min	B	25	92.9	192.5	292.1	360
	pH	-	C	4	4.81	6	7.19	8
NF process	Pressure	barg	A	4	5.4	7.5	9.6	11

	Temperature	C	B	15	18	22.5	27	30
	pH	-	C	4	4.6	5.5	6.4	7

The findings show that the Design Expert program, based on RSM and CCD principles, was used for data analysis, mathematical modeling, and optimization.

Results and Discussion

In this study, Design Expert software is employed in RSM based on CCD principles for data design, mathematical modelling, and optimization. A quadratic polynomial equation (Equation 1) is used to predict response behavior.

$$Y = a_0 + \sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k} a_{ii} {x_i}^2 + \sum^{k}_{i\ ,\ \ i<j} \sum_{j}^{k} a_{ij} x_i x_j + \varepsilon \qquad (1)$$

In this equation:

a_0: Constant

a_i:The i-th linear coefficient

a_{ii} : The i-th quadratic factor

a_{ij} : represents the i-th coefficient of interaction

x_i : represents the i-th independent variable

K : refers to the Number of variables

Ɛ : Companion error

1. Deriving the adsorption process's objective equation (when the refinery's effluent output serves as the process's input)

The relationship between the response and the variables has been obtained in coded forms.

$$\%\mathrm{Re} = +49.96 - 2.15 * A - 2.81 * B + 0.87 * C + 1.64 * D - 0.12 * A * B + 0.046 * A * C - 9.375E - 003 * A * D - 0.29 * B * C + 0.10 * B * D + 0.56 * C * D - 2.67 * A2 - 3.25 * B2 - 2.52 * C2 - 1.01 * D2 \quad (2)$$

The coefficients of each variable in equation 2 show that the influence of variables A and B is negative, D is positive, and the effect of variable C is slightly positive, with the following order of effects:

C<D<A<B

The three-dimensional response surface graphs show the interaction effect of two parameters on the removal percentage during the adsorption process (Figures 2a–2f).

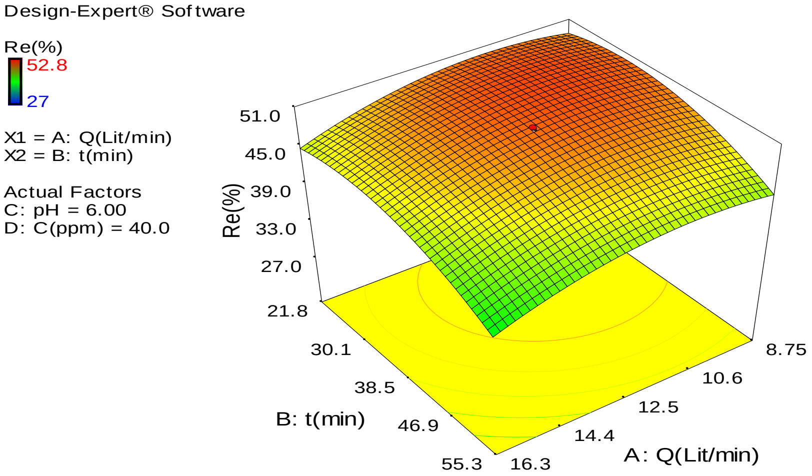

Fig. 2a Interaction effect of flow rate and time on removal percentage in the adsorption process

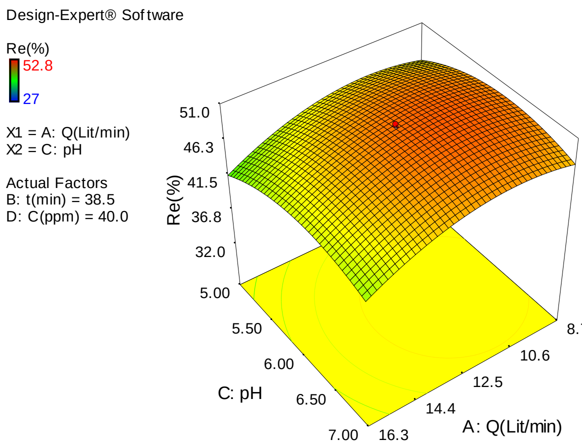

Fig. 2b Interaction effect of flow rate and pH on removal percentage in the adsorption process

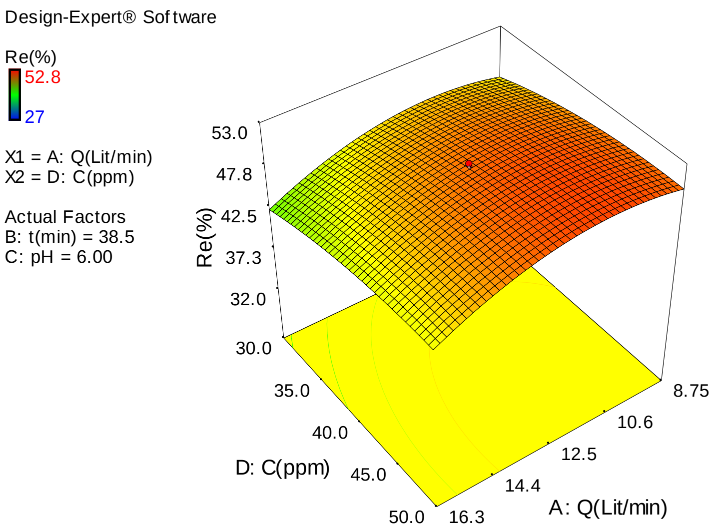

Fig. 2c Interaction effect of flow rate and concentration on removal percentage in the adsorption process

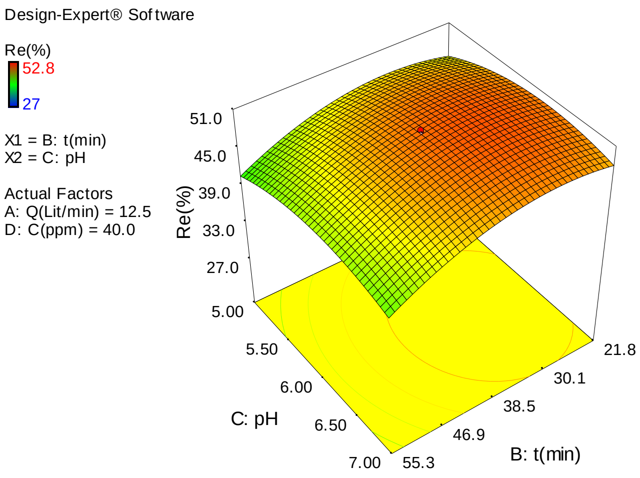

Fig. 2d Interaction effect of time and pH on removal percentage in the adsorption process

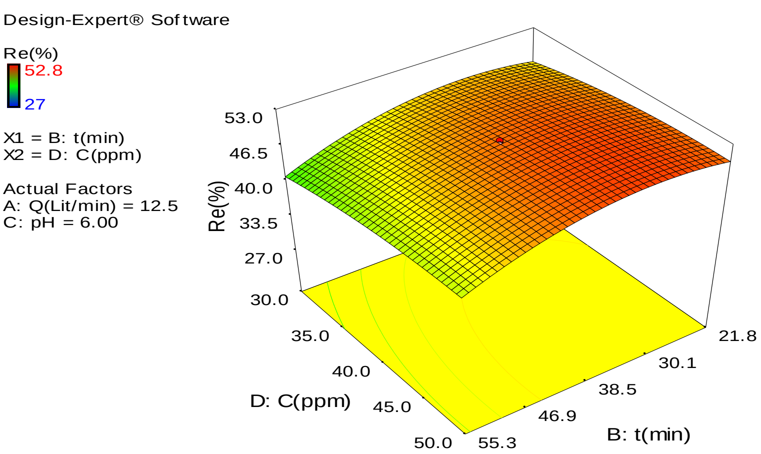

Fig. 2e Interaction effect of time and concentration on removal percentage in the adsorption process

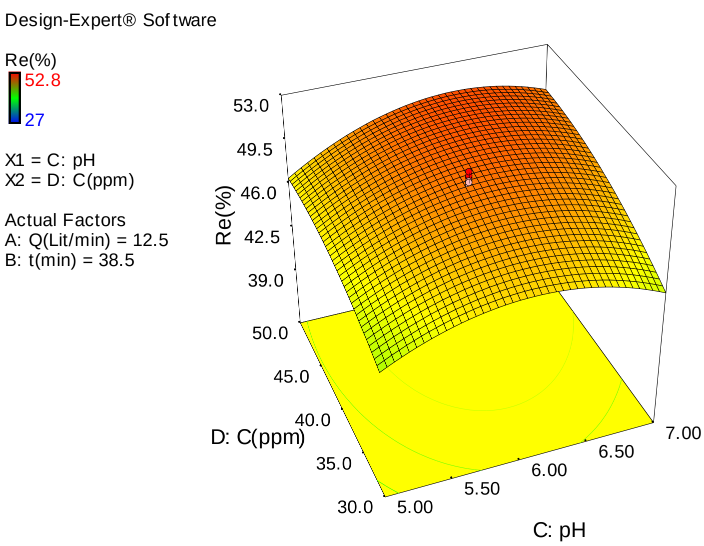

Fig. 2f Interaction effect of concentration and pH on removal percentage in the adsorption process

Figures (2a–2f) show the simultaneous effect of two variables on the removal percentage. The removal percentage decreases as the adsorbent's service period and the flow rate of the fluid passing through the bed rise. The more time passes, the more particles adsorb on the surface of the adsorbent. This process reduces the adsorbent's active surface over time, which decreases its adsorption capacity. The fluid in the adsorbent bed will move faster and spend less time there when its flow rate is increased through the bed. As a result, in this case, there is little opportunity for particles to be adsorbed on the adsorbent, which decreases the removal percentage [82]. The pH variable has a slight effect on the removal percentage within the experimental range. Because pH fluctuations create differences in ionization degree and adsorbent surface properties, pH influences adsorption effectiveness [83]. This is obvious in the shift in water clearance, which resulted in the detection of less oil in the solvent and reduced oil removal on the adsorbent. Destabilization of organic sorbent materials in neutral pH media has been associated to lower oil removal effectiveness than in acidic or alkaline solutions [84-85].

The initial adsorbate concentration has a substantial influence on the adsorption process, which is critical for the development of water treatment technology [86].

There are fewer adsorption sites available for rising pollutant concentrations when the adsorbate concentration rises because the adsorption sites, which are fixed on the adsorbent surface, gradually diminish over time. Consequently, the adsorption effectiveness falls [87]. When concentration is low, there is less material bound to the adsorption center, which means that more material is retained by the unit adsorbent. Adsorption reduces when concentration rises because of an increase in repulsive forces [88].

For the same amount of adsorbent, it is first noted that the oil removal increases as the starting oil concentration increases. This is because there are many more vacant active sites available than there is oil introduced. However, because there are fewer sites available for the oil to adsorb, the removal of oil reduces at increasing starting oil concentrations [89].

The Design Expert software estimates the best parameter values to maximize the removal percentage (Reactor flow rate: 11.03 Lit/min, sampling time: 31.39 min, pH: 6.29, Oil Substance Concentration: 48.73 ppm, Removal percentage: 51.82).

2. Obtaining the Objective Equation for the Advanced Fenton Oxidation Process (When the Input is the Output of Refinery Wastewater)

The relationship between the response value and the variables has been developed in coded forms.

$$\% \mathrm{Re} = +85.04 + 0.52 * A + 0.72 * B - 0.48 * C + 0.80 * D - 0.15 * A * B + 0.20 * A * C - 0.038 * A * D - 0.20 * B * C + 0.21 * B * D + 0.062 * C * D - 0.60 * A2 - 0.27 * B2 - 0.32 * C2 - 0.18 * D2 \quad (3)$$

The coefficients of each variable in equation 3 show that the influence of variable A is slightly positive, B and D are totally positive, and the effect of variable C is negative, with the following order of effects: C<A<B<D

The three-dimensional response surface graphs (Figures 3a-3f) show the interaction effect of the two factors on the removal percentage in the Fenton process.

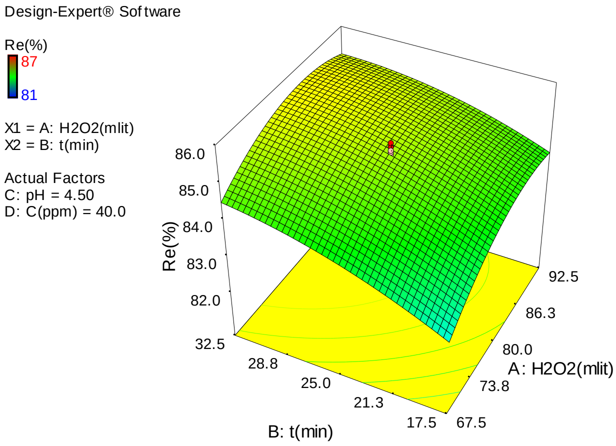

Fig. 3a Interaction effect of hydrogen peroxide amount and reaction time on removal percentage in the Fenton process

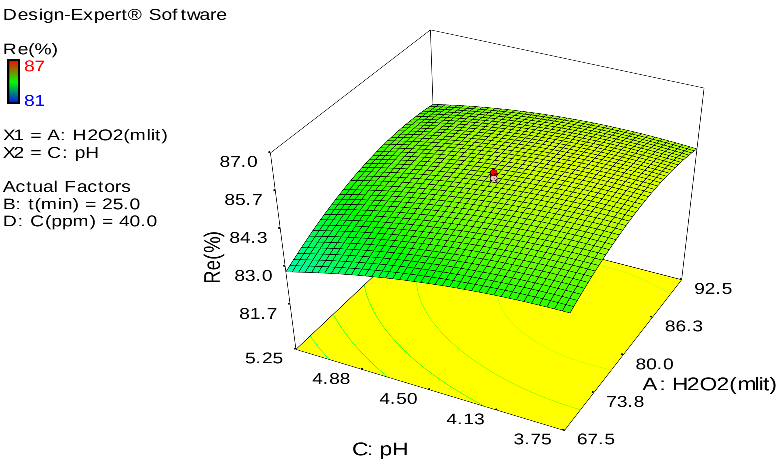

Fig. 3b Interaction effect of pH and hydrogen peroxide amount on removal percentage in the Fenton process

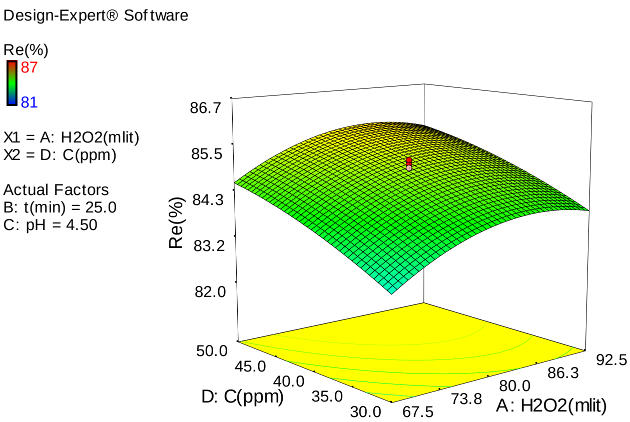

Fig. 3c Interaction effect of hydrogen peroxide amount and concentration on removal percentage in the Fenton process

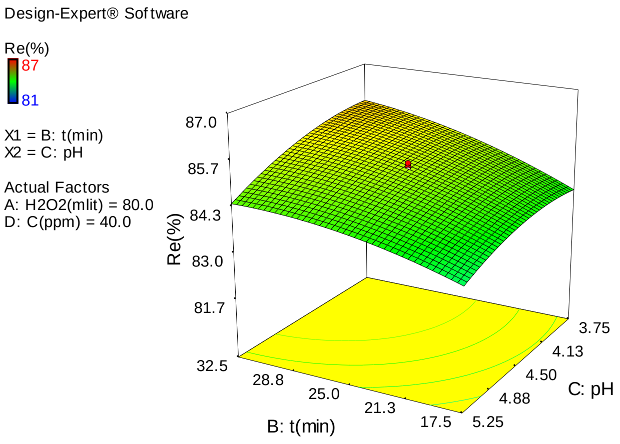

Fig. 3d Interaction effect of pH and reaction time on removal percentage in the Fenton process

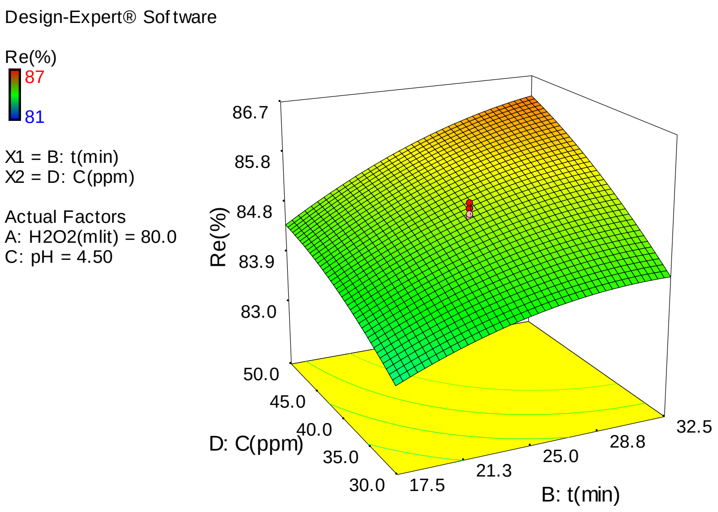

Fig. 3e Interaction effect of reaction time and concentration on removal percentage in the Fenton process

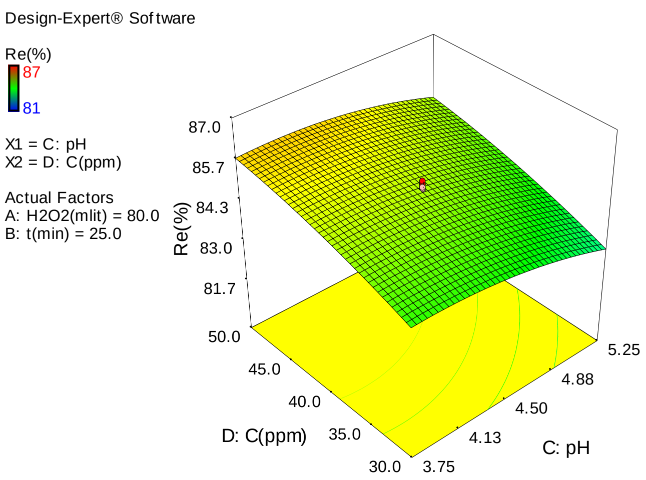

Fig. 3f Interaction effect of pH and concentration on removal percentage in the Fenton process

Figures 3a–3f show the simultaneous effect of two factors on the Fenton process's removal percentage. The percentage removal increases as reaction time increases because the reaction has more time to occur. However, for extremely long reaction durations within the experimental range, no substantial effect on the removal percentage is seen since the initial substance concentration has reduced and the reaction is virtually complete. Increasing the quantity of hydrogen peroxide while keeping the other factors constant results in a higher removal percentage. This is because an increase in hydrogen peroxide concentration accelerates the reaction rateHowever, at higher concentrations of hydrogen peroxide, no significant influence on the removal percentage is noticed since hydrogen peroxide up to a specific level is adequate. Reducing the pH raises the reaction rate, which improves the removal percentage.

The Design Expert program determines the best parameter values to maximize the presented removal percentage (hydrogen peroxide amount: 81.51mlit, reaction time: 32.5 min, pH: 3.8, concentration of oil substances: 50ppm, removal percentage: 86.6).

3. Obtaining the objective equation for the advanced Fenton oxidation process (where the input is the effluent output from the refinery with a constant hydrocarbon content)

The relationship between the response value and the variables has been developed in coded forms.

$$\%\,Re = +85.21 + 0.18 * A + 1.01 * B - 0.79 * C + 0.094 * A * B - 0.044 * A * C - 0.14 * B * C - 0.97 * A2 - 0.36 * B2 - 0.42 * C2 \quad (4)$$

The coefficients of each variable in equation 4 show the influence of variable A is somewhat positive, B is totally positive, and the effect of variable C is negative, with the order of these effects being as follows: A<C<B
The three-dimensional response surface graphs (Figures 4a-4c) show the interaction effect of the two factors on the removal percentage in the Fenton process.

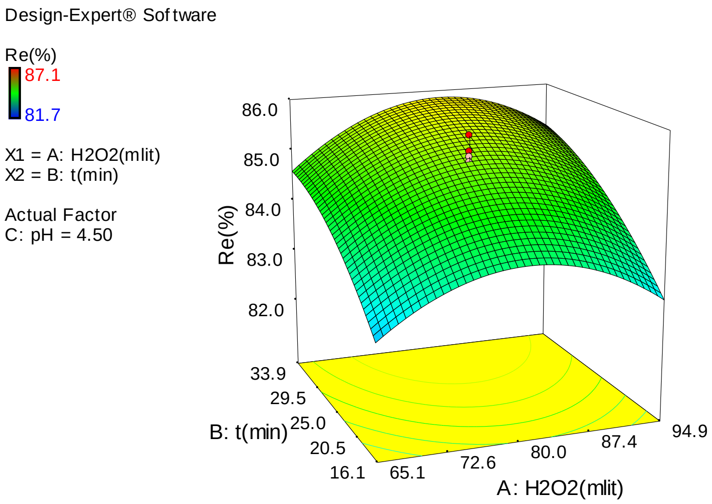

Fig. 4a Interaction effect of hydrogen peroxide amount and reaction time on removal percentage in the series Fenton process

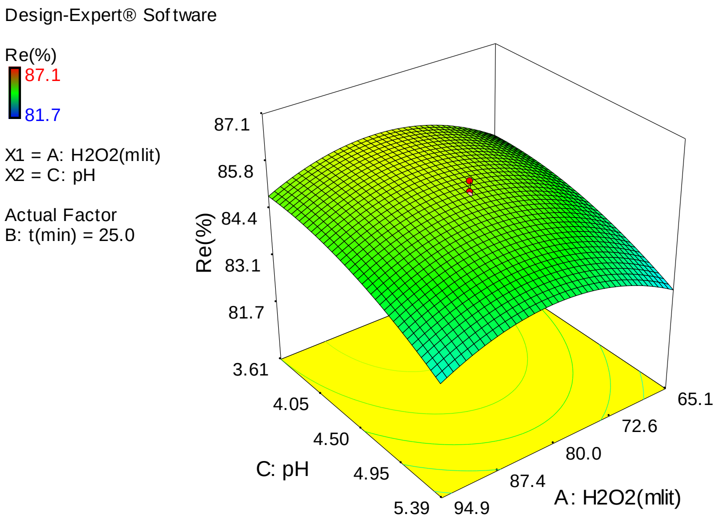

Fig. 4b Interaction effect of hydrogen peroxide amount and pH on removal percentage in the series Fenton process

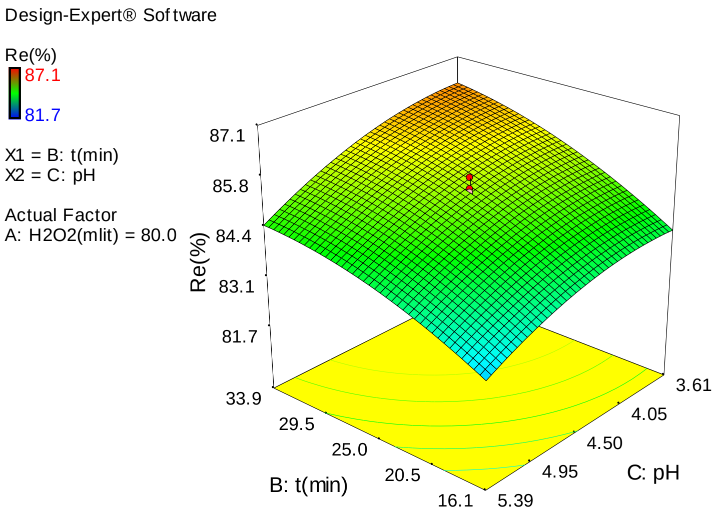

Fig. 4c Interaction effect of time and pH on removal percentage in the series Fenton process

Figures (4a–4c) show the simultaneous influence of two factors on the removal percentage in the Fenton process. As the response time grows, increases the removal percentage since the reaction has more time to occur. However, for extremely long durations within the experimental range, no substantial influence on the removal percentage is detected since the starting concentration of compounds has reduced and the reaction is almost complete. Increasing the hydrogen peroxide concentration while keeping the other variables constant results in a modest rise in removal percentage. This is because increasing the quantity of hydrogen peroxide increases the reaction rate, though a detectable effect is not found at higher hydrogen peroxide amounts, since hydrogen peroxide is required up to a specific level [90].

The Design Expert program estimates the best parameter values to optimize the removal percentage (hydrogen peroxide quantity: 78 mlit, reaction time: 33 minutes, pH: 3.61, removal percentage: 87.33).

4. Obtaining the objective equation of the adsorption process in a series arrangement (where the input is the output of the oxidation process)

The relationship between the response value and the variables has been developed in coded forms.

$$\%\mathrm{Re} = +50.06 - 3.87 * \mathrm{A} - 7.58 * \mathrm{B} + 1.57 * \mathrm{C} - 0.30 * \mathrm{A} * \mathrm{B} + 0.72 * \mathrm{A} * \mathrm{C} - 0.40 * \mathrm{B} * \mathrm{C} - 1.86 * \mathrm{A}^2 - 1.93 * \mathrm{B}^2 - 2.16 * \mathrm{C}^2 \quad (5)$$

The coefficients of each variable in equation 5 show that the influence of variables A and B is negative while the effect of variable C is virtually positive, with the following sequence of effects: C<A<B

Graphs of three-dimensional response surfaces show the interaction effect of two factors on the removal percentage in the series adsorption process (Figures 5a-5c).

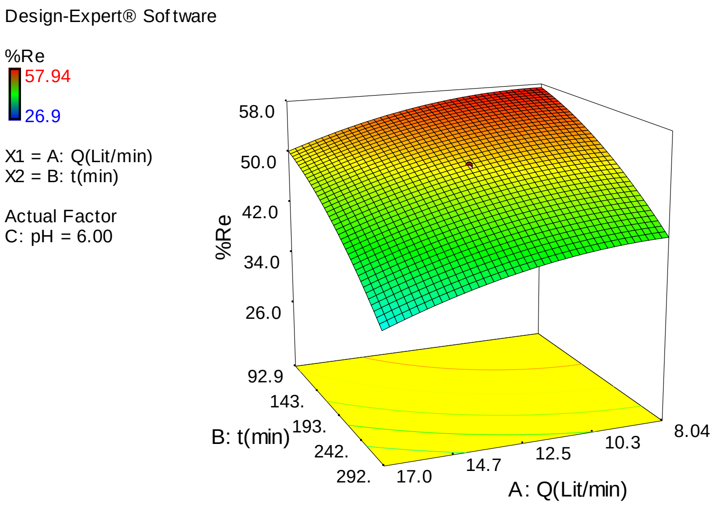

Fig. 5a Interaction effect of flow rate and time on removal percentage in the series adsorption process

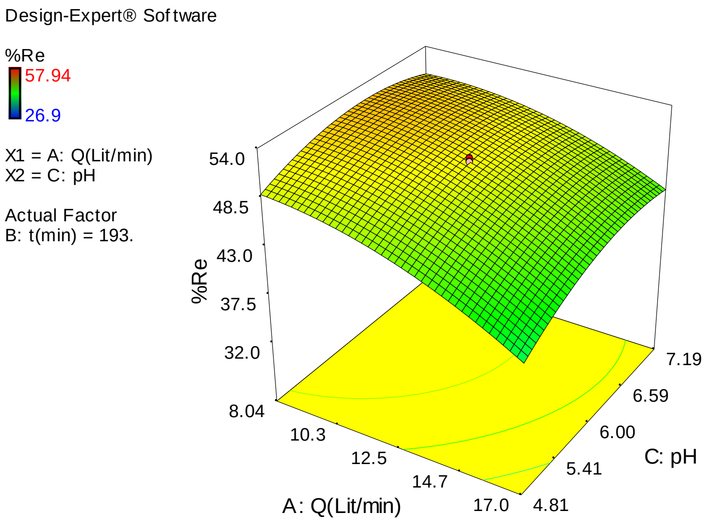

Fig. 5b Interaction effect of flow rate and pH on removal percentage in the series adsorption process

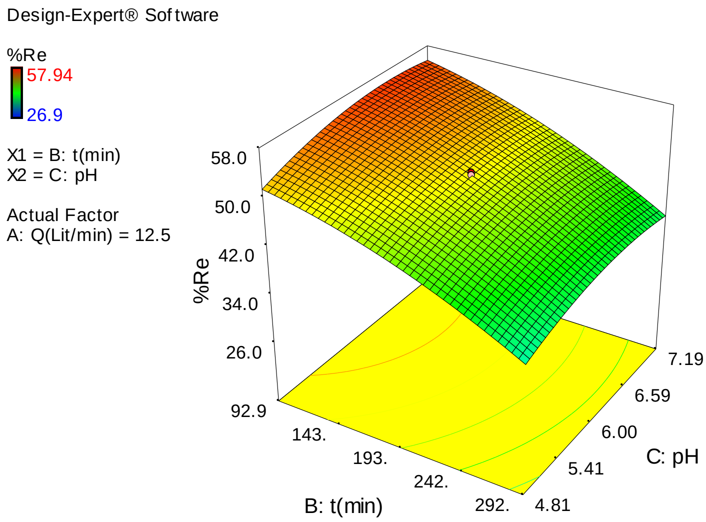

Fig. 5c Interaction effect of time and pH on removal percentage in the series adsorption process

Figures 5a–5c show the simultaneous influence of two variables on the removal percentage in the series adsorption process. The removal percentage falls as the adsorbent's service duration and fluid flow rate through the bed rise. As time passes, particles adsorb on the adsorbent's surface, resulting in a reduction in the adsorbent's active surface and a drop in adsorption capacity. When the fluid flow rate through the bed increases, the velocity increases while the fluid's residence time in the adsorbent bed decreases. As a result, in this case, particles do not have enough chance for adsorption on the adsorbent, resulting to a decrease in the removal percentage as the flow rate increases [91].

Due to de-emulsification and enhanced oil molecular interaction with the adsorbent surface, which facilitated oil penetration into its pores, the oil removal percentage first rose with time. This was only seen up to a certain point, after which it was discovered that the amount of oil removed decreased. The oil molecules that had previously been adsorbed leave the adsorbent's pores when equilibrium is reached because the rate of desorption outpaces the rate of sorption [92].

Solution pH is important in the adsorption process because it affects the ionization level of the pollutants and the surface charge of the adsorbent [93].

The amount of oil removed was found to be very high at the neutral pH value, however the amount of oil removed increased as the pH decreased. This is explained by the formation of a layer of positive charge on the anthracite's surface, which attracted the negatively charged ends of the oil molecules and caused the solution to de-emulsify, speeding up the sorption process. However, deliberate acidification of the emulsion was not required, and even a high pH drop did not significantly enhance the amount of oil removed [94-95].

The Design Expert program suggests the best parameter settings to optimize the predicted removal percentage (Reactor flow rate: 8.48 Lit/min, sampling time: 92.9 minutes, pH: 6.36, removal percentage: 57.62).

5. Obtaining the objective equation for the filtering process in a series arrangement (where the input into this process is the output of the adsorption process)

The relationship between the response value and the variables has been developed in coded forms:

$$\%\mathrm{Re} = +79.33 + 2.91 * \mathrm{A} - 0.063 * \mathrm{B} - 0.020 * \mathrm{C} + 3.750\mathrm{E}-003 * \mathrm{A} * \mathrm{B} - 1.250\mathrm{E}-003 * \mathrm{A} * \mathrm{C} - 6.250\mathrm{E}-003 * \mathrm{B} * \mathrm{C} - 1.07 * \mathrm{A2} + 0.077 * \mathrm{B2} + 0.033 * \mathrm{C2} \quad (6)$$

The coefficients of each variable in equation 6 show that variable A has a very strong and positive influence on the nanofiltration process, but variables B and C have essentially little effect. This is explicitly defined in the response equation.

The three-dimensional response surface graphs show the interaction effect of two factors on the removal percentage in the NF process (Figures 6a-6c).

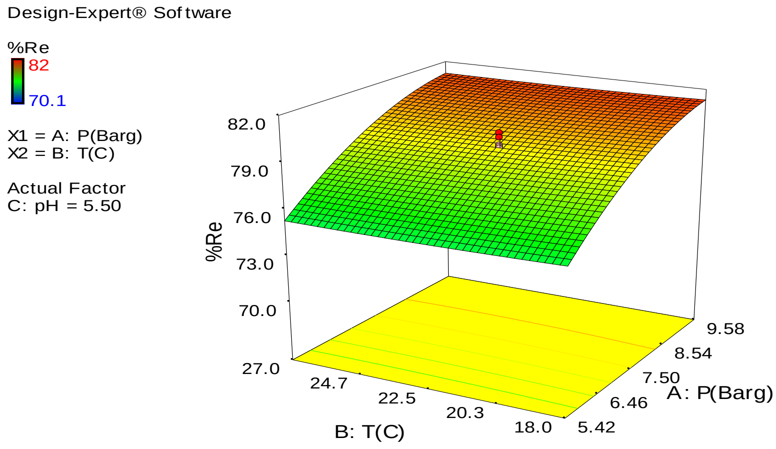

Fig. 6a Interaction effect of pressure and temperature on removal percentage in the NF process

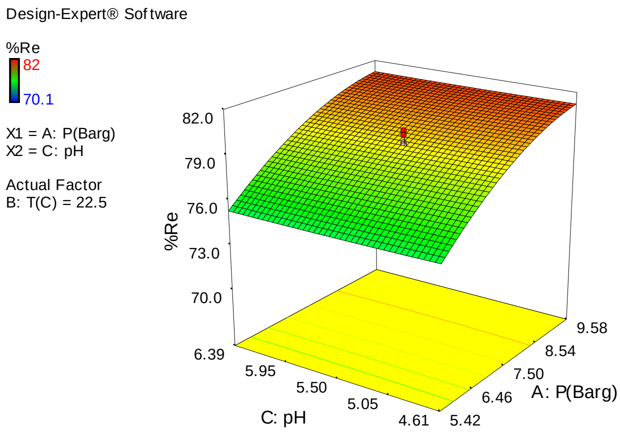

Fig. 6b Interaction effect of pressure and pH on removal percentage in the NF process

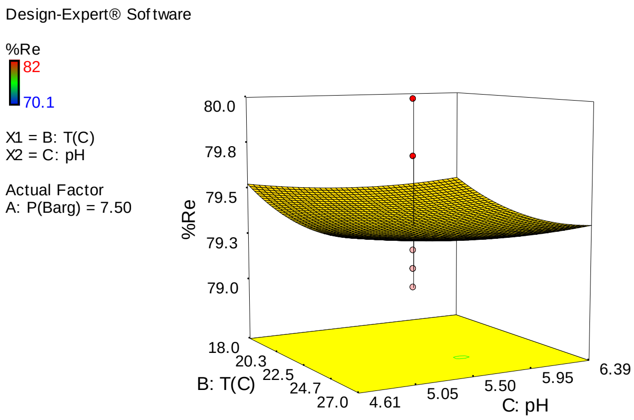

Fig. 6c Interaction effect of pH and temperature on removal percentage in the NF process

Figures 6a–6c show the simultaneous influence of two factors on the removal percentage. The factors pH and temperature have no significant influence on the removal percentage within the experimental range, and the removal percentage's dependency on these two variables is minimal. The pressure variable has a significant influence on the removal percentage, an increase in pressure results in a larger removal percentage. Increasing pressure while keeping other variables constant improves both the permeate flow and the removal efficiency. As pressure rises, particles inside membrane holes become stuck; nevertheless, at lower pressures, same particles can more readily flow through the membrane. The effect of membrane surface pressure on the removal percentage is positive [96].

The Design Expert software provides the best parameter settings to maximize the anticipated removal percentage (pressure: 9.58 barg, temperature: 18.04 C, pH: 4.62, removal percentage: 81.35).

Conclusion

This study focused on industrial wastewater treatment in order to reuse the water in industrial systems. The majority of previous research in the field of industrial wastewater treatment has focused on rectifying the properties of these wastewaters before discharging them into the environment. There has also been research done on how to utilize these wastes. Membrane clogging has been a major concern in studies on treating wastewater for reuse in industrial systems. This study evaluated the purification of industrial wastewater from the Abadan refinery, which included 40.2 mg/L of hydrocarbon compounds, utilizing a combination of three processes: fixed-bed adsorption, advanced Fenton oxidation, and NF.

Because the water entering the nanofiltration stage must contain less than 3 mg/liter of hydrocarbon compounds, the removal power of hydrocarbon compounds in the refinery's production effluent was first determined independently by two methods of surface absorption and Fenton, and then in combination with each other, and the addition of the nanofiltration step in this series chain, which was the main goal of the current project, was investigated. The goals of this research were defined in two levels: the first level was wastewater treatment to reduce hydrocarbon compounds to the permissible limit for discharge into the environment, and the second level was the reduction of hydrocarbon compounds to reuse the wastewater in the refinery's internal systems. This procedure successfully converted wastewater containing 40.2 hydrocarbon compounds into water containing 0.4 hydrocarbon compounds.

Acknowledgements This research was partially supported by Deptartment of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran.

Declarations

Conflict of interest All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

References:

[1] Ahmed, S. N., & Haider, W. (2018). Heterogeneous photocatalysis and its potential applications in water and wastewater treatment: a review. Nanotechnology, 29(34), 342001.

[2] Gundag O. (2017). Comparison of humic acid removal alternatives in water. Master's Thesis, Namik Kemal University, Institute of Science and Technology. 80.

[3] Everard, M. (2019). Meeting global drinking water needs. Nature Sustainability, 2, 360–361.

[4] Rashed, M. N., & Arfien, A. A. (2020). Adsorption of heavy metals on chemically modified muscovitE. Aswan University Journal of Environmental Studies, 1(2), 183–203.

[5] Ahmad, T., Aadil, R. M., Ahmed, H., ur Rahman, U., Soares, B. C., Souza, S. L., ... & Cruz, A. G. (2019). Treatment and utilization of dairy industrial waste: A review. Trends in Food Science & Technology, 88, 361-372.

[6] Gaur, V. K., Sharma, P., Sirohi, R., Awasthi, M. K., Dussap, C. G., & Pandey, A. (2020). Assessing the impact of industrial waste on environment and mitigation strategies: A comprehensive review. Journal of hazardous materials, 398, 123019.

[7] Mo, J., Yang, Q., Zhang, N., Zhang, W., Zheng, Y., & Zhang, Z. (2018). A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. Journal of environmental management, 227, 395-405.

[8] Gunatilake, S. K. (2015). Methods of removing heavy metals from industrial wastewater. Methods, 1(1), 14.
[9] Alipour, Z., & Azari, A. (2020). COD removal from industrial spent caustic wastewater: A review. Journal of Environmental Chemical Engineering, 8(3), 103678.
[10] Arshad, N., & Imran, S. (2020). Indigenous waste plant materials: An easy and cost-effective approach for the removal of heavy metals from water. Current Research in Green and Sustainable Chemistry, 3, 100040.
[11] Mahmud, N., Benamor, A., Nasser, M. S., Ba-Abbad, M. M., El-Naas, M. H., & Mohammad, A. W. (2021). Efective Heterogeneous Fenton-Like degradation of Malachite Green Dye Using the Core-Shell Fe3O4@SiO2 NanoCatalyst. Chemistry Select, 6, 865–875.
[12] Zamora-Ledezma, C., Negrete-Bolagay, D., Figueroa, F., Zamora-Ledezma, E., Ni, M., Alexis, F., & Guerrero, V. H. (2021). Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. Environmental Technology & Innovation, 22, 101504.
[13] Chao, W., Wang, S., Li, Y., Cao, G., Zhao, Y., Sun, X., Wang, C., & Ho, S.-H. (2020). Natural sponge-like wood-derived aerogel for solar-assisted adsorption and recovery of highviscous crude oil. Chemical Engineering Journal, 400, 125865.
[14] Mofokeng, M., Nthunya, L. N., Gutierrez, L., Matabola, P., Mishra, S., & Nxumalo, E. N. (2020). Perfurooctyltriethoxy silane and carbon nanotubes-modifed PVDF superoleophilic nanofbre membrane for oil-in-water adsorption and recovery. Journal of Environmental Chemical Engineering, 8, 104497.
[15] Ejeta, D. D., Tan, F.-H., Mathivathanan, A., Juang, T.-Y., Abu-Omar, M. M., Wang, C.-F., Lin, C.-H., & Lai, J.-Y. (2022). Preparation of fuorine- and nanoparticle-free superwetting polybenzoxazine/cellulose composites for efcient oil/water separations. Separation and Purifcation Technology, 288, 120675.
[16] Olajire, A. A. (2020). Recent advances on the treatment technology of oil and gas produced water for sustainable energy industry-mechanistic aspects and process chemistry perspectives. Chemical Engineering Journal Advances, 4, 100049.
[17] Bozdogan Sert, E., Turkmen, M., & Cetin, M. (2019). Heavy metal accumulation in rosemary leaves and stems exposed to traffic-related pollution near Adana-İskenderun Highway (Hatay, Turkey). Environmental Monitoring and Assessment, 191, 1–12.
[18] Adebiyi, F. M., & Ayeni, D. A. (2021). Chemical speciation, bioavailability and risk assessment of potentially toxic metals in soils around petroleum product marketing company as environmental degradation indicators. Petroleum Research (in Press).
[19] Bandura, L., Białoszewska, M., Malinowski, S., & Franus, W. (2021). Adsorptive performance of fly ash-derived zeolite modified by β-cyclodextrin for ibuprofen, bisphenol A and caffeine removal from aqueous solutions–equilibrium and kinetic study. Applied Surface Science, 562, 150160.
[20] Bernasconi, C., Demetrio, P. M., Alonso, L. L., Mac Loughlin, T. M., Cerda, E., Sarandon, S. J., & Marino, D. J. (2021). Evidence for soil pesticide contamination of an agroecological farm from a neighboring chemical-based production system. Agriculture, Ecosystems & Environment, 313, 107341.
[21] Long, Z., Zhu, H., Bing, H., Tian, X., Wang, Z., Wan, X., & Wu, Y. (2021). Contamination, sources and health risk of heavy metals in soil and dust from different functional areas in an industrial city of Panzhihua City, Southwest China. Journal of Hazardous Materials, 420, 126638.
[22] Liu, Q., Chen, Z., Huang, L., Mujtaba Munir, M. A., Wu, Y., Wang, Q., Ma, L., Xu, S., Wen, Z., & Feng, Y. (2021). The effects of a combined amendment on growth, cadmium adsorption by five fruit vegetables, and soil fertility in contaminated greenhouse under rotation system. Chemosphere, 285, 131499.
[23] Zhang, Z., Teng, C., Zhou, K., Peng, C., & Chen, W. (2020). Degradation characteristics of dissolved organic matter in nanofiltration concentrated landfill leachate during electrocatalytic oxidation. Chemosphere, 255, 127055.
[24] Deng, Y., Peng, C., Dai, M., Lin, D., Ali, I., Alhewairini, S. S., Zheng, X., Chen, G., Li, J., & Naz, I. (2020). Recent development of super-wettable materials and their applications in oil-water separation. Journal of Cleaner Production, 266, 121624.
[25] Ewis, D., Ismail, N. A., Hafz, M., Benamor, A. & Hawari, A. H. (2021). Nanoparticles functionalized ceramic membranes: fabrication, surface modifcation, and performance. Environmental Science and Pollution Research. 28, 12256–12281.
[26] Schiller, A. D. P., Gonçalves, A. C., Braccini, A. D. L., Schwantes, D., Campagnolo, M. A., Conradi, E., & Zimmermann, J. (2020). Potential of agricultural and agroindustrial wastes as adsorbent materials of toxic heavy metals: a review. Desalination and Water Treatment, 187, 203-218.
[27] Droste, R. L., & Gehr, R. L. (2018). Theory and practice of water and wastewater treatment. John Wiley & Sons.
[28] Tul Muntha, S., Kausar, A., & Siddiq, M. (2017). Advances in polymeric nanofiltration membrane: A review. Polymer Plastics Technology and Engineering, 56(8), 841-856.
[29] Van der Bruggen, B. (2009). Chemical modification of polyethersulfone nanofiltration membranes: a review. Journal of applied polymer science, 114(1), 630-642.
[30] Shon, H. K., Phuntsho, S., Chaudhary, D. S., Vigneswaran, S., & Cho, J. (2013). Nanofiltration for water and wastewater treatment–a mini review. Drinking Water Engineering and Science, 6(1), 47-53.

[31] Wang, Z., Ma, C., Xu, C., Sinquefield, S. A., Shofner, M. L., & Nair, S. (2021). Graphene oxide nanofiltration membranes for desalination under realistic conditions. Nature Sustainability, 4(5), 402-408.
[32] Johnson, D. J., & Hilal, N. (2022). Nanocomposite nanofiltration membranes: State of play and recent advances. Desalination, 524, 115480.
[33] Esfahani, M. R., Aktij, S. A., Dabaghian, Z., Firouzjaei, M. D., Rahimpour, A., Eke, J., ... & Koutahzadeh, N. (2019). Nanocomposite membranes for water separation and purification: Fabrication, modification, and applications. Separation and Purification Technology, 213, 465-499.
[34] Lau, W. J., & Ismail, A. F. (2009). Polymeric nanofiltration membranes for textile dye wastewater treatment: preparation, performance evaluation, transport modelling, and fouling control—a review. Desalination, 245(1-3), 321-348.
[35] Chang, Y. C., & Chen, D. H. (2005). Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu (II) ions. Journal of colloid and interface science, 283(2), 446-451.
[36] Vatanpour, V., Madaeni, S. S., Khataee, A. R., Salehi, E., Zinadini, S., & Monfared, H. A. (2012). TiO2 embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance. Desalination, 292, 19-29.
[37] Jia, T. Z., Lu, J. P., Cheng, X. Y., Xia, Q. C., Cao, X. L., Wang, Y., ... & Sun, S. P. (2019). Surface enriched sulfonated polyarylene ether benzonitrile (SPEB) that enhances heavy metal removal from polyacrylonitrile (PAN) thin-film composite nanofiltration membranes. Journal of membrane science, 580, 214-223.
[38] Zhang, T., Zhang, C., Zhao, G., Li, C., Liu, L., Yu, J., & Jiao, F. (2020). Electrospun composite membrane with superhydrophobic-superoleophilic for efcient water-in-oil emulsion separation and oil adsorption. Colloids and Surfaces a: Physicochemical and Engineering Aspects, 602, 125158.
[39] Chen, X., Huang, G., An, C., Feng, R., Wu, Y., & Huang, C. (2022). Superwetting polyethersulfone membrane functionalized with ZrO_2 nanoparticles for polycyclic aromatic hydrocarbon removal. Journal of Materials Science & Technology, 98, 14-25.
[40] Li, J., Wang, L., Lu, J., Peng, W., Chen, J., Jiang, G., & Liu, D. (2024). Treatment of landfill leachate nanofiltration concentrate by a three-dimensional electrochemical technology with waste aluminum scraps as particle electrodes: Efficacy, mechanisms, and enhancement effect of subsequent electrocoagulation. Waste Management, 173, 118-130.
[41] Lee, J., Shin, Y., Boo, C., & Hong, S. (2023). Performance, limitation, and opportunities of acid-resistant nanofiltration membranes for industrial wastewater treatment. Journal of Membrane Science, 666, 121142.
[42] Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., ... & Doumenq, P. (2017). From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review. Water research, 111, 297-317.
[43] Srivastava, A., Parida, V. K., Majumder, A., Gupta, B., & Gupta, A. K. (2021). Treatment of saline wastewater using physicochemical, biological, and hybrid processes: Insights into inhibition mechanisms, treatment efficiencies and performance enhancement. Journal of environmental chemical engineering, 9(4), 105775.
[44] Asaithambi, P., Yesuf, M. B., Govindarajan, R., Hariharan, N. M., Thangavelu, P., & Alemayehu, E. (2022). A review of hybrid process development based on electrochemical and advanced oxidation processes for the treatment of industrial wastewater. International Journal of Chemical Engineering, 2022.
[45] Costa, S. I., Ferreira, F. L., Weschenfelder, S. E., Fuck, J. V. R., Maria de Fátima, R., Marinho, B. A., ... & de Souza, A. A. U. (2023). Towards the removal of soluble organic compounds present in oilfield produced water by advanced oxidation processes: critical review and future directions. Process Safety and Environmental Protection.
[46] Dehghani, M. H., Dehghan, A., & Najafpoor, A. (2017). Removing reactive red 120 and 196 using chitosan/zeolite compositefrom aqueous solutions: Kinetics, isotherms, and process optimization. Journal of Industrial and Engineering Chemistry, 51, 185–195.
[47] Ewis, D., Benamor, A., Ba-Abbad, M. M., Nasser, M., El-Naas, M., & Qiblawey, H. (2020). Removal of Oil Content from Oil-Water Emulsions Using Iron Oxide/Bentonite Nano Adsorbents. Journal of Water Process Engineering, 38, 101583.
[48] Emam, E. (2013). Modifed Activated Carbon and Bentonite Used to Adsorb Petroleum Hydrocarbons Emulsifed in Aqueous Solution. American Journal of Environmental Protection, 2, 161.
[49] Ewis, D., Mahmud, N., Benamor, A., Ba-Abbad, M. M., Nasser, M., & M., El-Naas. (2022). Enhanced Removal of Diesel Oil Using New Magnetic Bentonite-Based Adsorbents Combined with Different Carbon Sources. Water Air Soil Pollut, 233, 195.
[50] Tran, H. T., Lin, C., Bui, X. T., Ngo, H. H., Cheruiyot, N. K., Hoang, H. G., & Vu, C. T. (2021). Aerobic composting remediation of petroleum hydrocarbon-contaminated soil. Current and future perspectives. Science of The Total Environment, 753, 142250.
[51] Sanches-Filho, P. J., Böhm, E. M., Böhm, G. M. B., Montenegro, G. O., Silveira, L. A., & Betemps, G. R. (2017). Determination of hydrocarbons transported by urban runoff in sediments of São Gonçalo Channel (Pelotas – RS, Brazil). Marine Pollution Bulletin, 114(2), 1088–1095.

[52] Pinto, A. B., Pagnocca, F. C., Pinheiro, M. A. A., Fontes, R. F. C., & de Oliveira, A. J. F. C. (2015). Heavy metals and TPH effects on microbial abundance and diversity in two estuarine areas of the southern-central coast of São Paulo State, Brazil. Marine Pollution Bulletin, 96(1-2), 410–417.

[53] Li, L., Shen, X., & Jiang, M. (2019). Characteristics of total petroleum hydrocarbon contamination in sediments in the Yangtze Estuary and adjacent sea areas. Continental Shelf Research, 175, 110–115.

[54] Zhou, R., Qin, X., Peng, S., & Deng, S. (2014). Total petroleum hydrocarbons and heavy metals in the surface sediments of Bohai Bay, China: Long-term variations in pollution status and adverse biological risk. Marine Pollution Bulletin, 83(1), 290–297.

[55] Vane, C. H., Kim, A. W., Moss-Hayes, V., Turner, G., Mills, K., Chenery, S. R., Barlow, T. S., Kemp, A. C., Engelhart, S. E., Hill, T. D., Horton, B. P., & Brain, M. (2020). Organic pollutants, heavy metals and toxicity in oil spill impacted salt marsh sediment cores, Staten Island, New York City, USA. Marine Pollution Bulletin, 151, 110721.

[56] Ashok, A., Cusack, M., Saderne, V., Krishnakumar, P. K., Rabaoui, L., Qurban, M. A., Duarte, C. M., & Agustí, S. (2019). Accelerated burial of petroleum hydrocarbons in Arabian Gulf blue carbon repositories. Science of the Total Environment, 669, 205–212.

[57] Shaaban, A. E. S. M., Badawy, R. K., Mansour, H. A., Abdel-Rahman, M. E., & Aboulsoud, Y. I. (2017). Competitive algal biosorption of Al3+, Fe3+, and Zn2+ and treatment application of some industrial effluents from Borg El-Arab region, Egypt. Journal of Applied Phycology, 29, 3221–3234.

[58] Rodrigues, D. S. C., Madeira, M., & L.& Boaventura, A. R. R. (2009). Optimization of the azo dye Procion Red H-EXL degradationby Fenton's reagent using experimental design. Journal of Hazardous Materials, 164(2–3), 987–994.

[59] Hilmioglu, N. (2022). Optimization of synthesis of ethyl acetate by response surface method and investigation of reactive sorption effect of hydrogel in synthesis. Avrupa Bilim ve Teknoloji Dergisi, 35, 94–101.

[60] Hibbert, D. B. (2012). Experimental design in chromatography: A tutorial review. Journal of Chromatography B, 910, 2–13.

[61] Stalikas, C., Fiamegos, Y., Sakkas, V., & Albanis, T. (2009). Developments on chemometric approaches to optimize and evaluate microextraction. Journal of Chromatography A, 1216(2), 175–189.

[62] Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta, 76(5), 965–977.

[63] Manousi, N., Vlachaki, A., Kika, F. S., Markopoulou, C. K., Tzanavaras, Paraskevas, D., & Zacharis, C. K. (2022). Saltingout homogeneous liquid liquid microextraction for the determination of azole drugs in human urine: Validation using total error concept. Journal of Separation Science.

[64] Tsanaktsidou, E., Markopoulou, C. K., Tzanavaras, P. D., & Zacharis, C. K. (2022). Homogeneous liquid phase microextraction using hydrophilic media for the determination of fluoroquinolones in human urine using HPLC-FLD. Microchemical Journal, 172(PA), 106906.

[65] Zacharis, C. K., & Vastardi, E. (2018). Application of analytical quality by design principles for the determination of alkyl p-toluenesulfonates impurities in Aprepitant by HPLC. Validation using total-error concept. Journal of Pharmaceutical and Biomedical Analysis, 150, 152–161.

[66] Elmobarak, W. F., & Almomani, F. (2021). Application of Fe3O4 magnetite nanoparticles grafted in silica (SiO2) for oil recovery from oil in water emulsions. Chemosphere, 265, 129054.

[67] Khan, S., Anjum, R., & Bilal, M. (2021). Revealing chemical speciation behaviors in aqueous solutions for uranium (VI) and europium (III) adsorption on zeolite. Environmental Technology & Innovation, 22, 101503.

[68] Liu, S., Wang, S., Wang, H., Lv, C., Miao, Y., Chen, L., & Yang, S. (2021). Gold nanoparticles modifed graphene foam with superhydrophobicity and superoleophilicity for oil-water separation. Science of the Total Environment, 758, 143660.

[69] Liu, Q., Li, Y., Chen, H., Lu, J., Yu, G., Moslang, M., & Zhou, Y. (2020). Superior adsorption capacity of functionalized straw adsorbent for dyes and heavy-metal ions. Journal of Hazardous Materials, 382, 121040.

[70] Ighalo, J. O., & Adeniyi, A. G. (2020). Adsorption of pollutants by plant bark derived adsorbents: An empirical review. Journal of Water Process Engineering, 35, 101228.

[71] Maaloul, N., Oulego, P., Rendueles, M., Ghorbal, A., & Diaz, M. (2017). Novel biosorbents from almond shells: Characterization and adsorption properties modeling for Cu(II) ions from aqueous solutions. Journal of Environmental Chemical Engineering, 5(3), 2944–2954.

[72] Islam, M. S., Ang, B. C., Gharehkhani, S., & Afifi, A. B. M. (2016). Adsorption capability of activated carbon synthesized from coconut shell. Carbon Letters, 20(1), 1–9.

[73] Raziq Rahimi Kooh, M., Khairud Dahri, M., Lim, L. L. B., Hoon Lim, L., Muhammad Raziq Rahimi Kooh, B., Darussalam, B., Tungku Link, J., Gadong, P., & Seri Begawan, B. B. (2015). Batch adsorption studies on the removal of acid blue 25 from aqueous solution using Azolla pinnata and soya bean waste. Arabian Journal for Science and Engineering, 41(7), 2453–2464.

[74] Roy, D., Greenlaw, P. N., & Shane, B. S. (2008). Adsorption of heavy metals by green algae and ground rice hulls. Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology, 28(1), 37–50.

[75] Amarasinghe, B. M. W. P. K., & Williams, R. A. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chemical Engineering Journal, 132(1–3), 299–309.
[76] Bulut, Y., & Tez, Z. (2007). Removal of heavy metals from aqueous solution by sawdust adsorption. Journal of Environmental Sciences, 19(2), 160–166.
[77] Mathew, B. B., Jaishankar, M., George Biju, V., & Beeregowda, K. N. (2016). Role of bioadsorbents in reducing toxic metals. Journal of Toxicology, 2016, 4369604.
[78] Moi, F. Y., Ghazi, R. M., & Alias, M. Z. M. (2020, August). Removal of emulsified oil in wastewater by corn cob carbon. In IOP Conference Series: Earth and Environmental Science (Vol. 549, No. 1, p. 012065). IOP Publishing.
[79] Anifah, E. M., Ariani, I. K., Hayati, R. N., & Nugraha, S. A. (2022, October). Adsorption of oil and grease in wastewater using activated carbon derived from sewage sludge. IOP Conference Series: Earth and Environmental Science (Vol. 1098, No. 1, p. 012043). IOP Publishing.
[80] Alatabe, M. J. A., Faris, H. A., & Husham, H. (2023). Natural biosorbent for oil adsorption from produced water by sedge cane. Journal of Ecological Engineering, 24(10).
[81] Malato, S., Fernandez-Ibanez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. Catalysis Today, 147(1), 1–59.
[82] Costa, E. P., Roccamante, M., Plaza-Bolaños, P., Oller, I., Agüera, A., Amorim, C. C., & Malato, S. (2021). Aluminized surface to improve solar light absorption in open reactors: Application for micropollutants removal in effluents from municipal wastewater treatment plants. Science of The Total Environment, 755, 142624.
[83] Jaber, W. S., & Alwared, A. I. (2019). Removal of oil emulsion from aqueous solution by using Ricinus communis leaves as adsorbent. SN Applied Sciences, 1(8), 1–12.
[84] Martini, S., Afroze, S., & Roni, K. A. (2020). Modified Eucalyptus bark as a sorbent for simultaneous removal of COD, oil, and Cr (III) from industrial wastewater. Alexandria Engineering Journal, 59(3), 1637–1648.
[85] Ahmad, A. L., Bhatia, S., Ibrahim, N., & Sumathi, S. (2005). Adsorption of residual oil from palm oil mill effluent using rubber powder. Brazilian Journal of Chemical Engineering, 22, 371–379.
[86] Afroze, S., Sen, T. K., & Ang, H. M. (2016). Adsorption removal of zinc (II) from aqueous phase by raw and base modified Eucalyptus sheathiana bark: Kinetics, mechanism and equilibrium study. Process Safety and Environmental Protection, 102, 336–352.
[87] Soleimani, H., Mahvi, A., Yaghmaeian, K., Abbasnia, A., Sharafi, K., Alimohammadi, M., & Zamanzadeh, M. (2019). Effect of modification by five different acids on pumice stone as natural and low-cost adsorbent for removal of humic acid from aqueous solutions-application of response surface methodology. Journal of Molecular Liquids, 290, 111–118.
[88] Dehghani, H. M., Zarei, A., Mesdaghinia, A., Nabizadeh, R., Alimohammadi, M., Afsharnia, M., & Mckay, G. (2018). Production and application of a treated bentonite–chitosan composite for the efficient removal of humic acid from aqueous solution. Chemical Engineering Research and Design, 140, 102–115.
[89] Kerrou, M., Bouslamti, N., Raada, A., Elanssari, A., Mrani, D., & Slimani, M. S. (2021). The use of sugarcane bagasse to remove the organic dyes from wastewater. International Journal of Analytical Chemistry, 2021, 5570806.
[90] Zhang, M. H., Dong, H., Zhao, L., Wang, D. X., & Meng, D. (2019). A review on Fenton process for organic wastewater treatment based on optimization perspective. Science of the Total Environment, 670, 110-121.
[91] Wang, J., & Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. Journal of Hazardous materials, 390, 122156.
[92] Olufemi, B. A., & Otolorin, F. (2017). Comparative adsorption of crude oil using mango (Mangnifera indica) shell and mango shell activated carbon. Environmental Engineering Research, 22(4), 384–392.
[93] Kuang, Y., Zhang, X., & Zhou, S. (2020). Adsorption of methylene blue in water onto activated carbon by surfactant modification. Water, 12(2), 587.
[94] Elanchezhiyan, S. S. D., Muthu Prabhu, S., & Meenakshi, S. (2018). Treatment of emulsified oil using biopolymer assisted materials. Polymer Composites, 39, E261– E270.
[95] Elanchezhiyan, S. S., Prabhu, S. M., & Meenakshi, S. (2018). Effective adsorption of oil droplets from oil-in-water emulsion using metal ions encapsulated biopolymers: Role of metal ions and their mechanism in oil removal. International Journal of Biological Macromolecules, 112, 294–305.
[96] Zhang, Z., Teng, C., Zhou, K., Peng, C., & Chen, W. (2020). Degradation characteristics of dissolved organic matter in nanofiltration concentrated landfill leachate during electrocatalytic oxidation. Chemosphere, 255, 127055.