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Determination of chemical oxygen demand for phenolic compounds from oil refinery wastewater implementing different methods

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ABSTRACT

In this study, the reduction of the chemical oxygen demand (COD) for the wastewater contaminated by phenolic compounds was investigated using three techniques: batch adsorption, electrochemical processing, and adding a granular third electrode (GTE) to an electrochemical process. The COD removal rate of the simulated phenolic wastewater with a phenol concentration range from 500 to 1,500 mg/L was measured. The actual samples from the Al-Daura Refinery (Iraq) oil refinery wastewater (ORW) were examined as a case study. Adsorption was conducted with either nanoparticle zero-valent iron (nFe^0) or silty clay-supported for nFe0 ($SC\text{-}nFe^0$) as an efficient adsorbent. The electrochemical process and electrochemical process with nFe^0 or $SC\text{-}nFe^0$ as a GTE were also investigated. The influences of various parameters (e.g., time, pH, nFe^0 and $SC\text{-}nFe^0$ dose, phenol concentration, temperature, current density, and electrode distance) were examined to determine the optimal operating conditions of each process. The maximum removal rate of the COD in adsorption with nFe^0 and $SC\text{-}nFe^0$ was 89.5% and 84.2%, respectively. When using the electrochemical process and GTE in an electrochemical process with nFe^0 or $SC\text{-}nFe^0$, the maximum removal rates were 79.8%, 93% and 94%, respectively. All of the proposed processes achieved an excellent COD removal rate when applied to actual petroleum refinery wastewater and rates higher than those attained in the refinery wastewater treatment plant.

Keywords: Chemical oxygen demand; Electrochemical process; Granular third electrode; Nanomaterials; Oil refinery wastewater; Phenol; Environmental pollution; Wastewater treatment; Adsorption; Nano zero-valent iron

1. Introduction

Treatment of water pollution is expensive and complex, with pollutants generally being difficult to eliminate. This pollution affects the life of organisms and may damage all ecosystems. The extreme abundance of organic materials in wastewater had recently made water pollution a serious concern because of the nondegradable nature, toxicity and semi-volatility of these materials [1]. Organic pollutants, especially phenolic compounds, polycyclic aromatic hydrocarbons and agricultural organic pollutants have adverse effects on aquatic systems, environmental degradation and human health [2].

The chemical oxygen demand (COD) value indicates the presence of all forms of organics (biodegradable and non-biodegradable). This makes the COD useful as an indicator of organic pollution in surface waters. COD is the oxygen magnitude (mg/L) required chemically in the organic and inorganic oxidation of oxidizable compounds [3]. Among the indicator parameters for water quality (i.e., COD, biochemical oxygen demand, carbon and nitrogen compounds), COD is the most important [4]. Also, in order not to have to add the theoretical balance between COD and phenolic compounds, studies focused on using such an analytical determination for the follow-up of recalcitrant organic

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compounds such as phenols [5]. Several techniques have been employed to reduce or completely remove COD from various types of wastewater [6], such as Fenton oxidation, coagulation and flocculation, reverse osmosis, electrochemical technique, adsorption and biological processes [7–18].

The composition of petroleum refinery wastewater is related to the crude oil properties and refining process conditions [19]. Petroleum refinery wastewater contains water from refining crude oil, surface runoff and sanitary wastewater as well as water that rises to the surface in oil wells during drilling operations. Petroleum refinery wastewater is characterized by high concentrations of COD, phenol and its derivatives [20,21]. Most studies have been concerned with the process of decomposition and removal of contaminants in oil refinery wastewater, such as organic substances, phenols, sulfides, and ammonia [19].

Nanomaterials have been employed in various forms as one of the most advanced processes for COD removal. The significant features of nano zero-valent iron (nFe^0), such as high specific surface area, surface energy and conductivity, provide great potential for treating wastewater and soil [22–24]. Many studies have proven that nFe^0 is an effective adsorbent and can be used for efficient COD removal with removal efficiency of 85% and 100% [25,26].

As a result of its quality, simplicity and ecofriendly nature, an electrochemical technique has recently gained considerable attention in wastewater remediation in the removal of refractory organic pollutants [27]. However, this conventional electrochemical technique is considered unworkable because of its low current density. Therefore, the addition of a granular electrode to the traditional electrochemical unit is deemed an excellent improvement to enhance efficiency and raise the current density of the electrochemical process [28].

The main target of this study is to determine the COD removal of phenolic compounds from wastewater. For this purpose, three techniques were investigated: (1) batch adsorption, with the effectiveness of the manufactured nFe^0 or SC-nFe^0 as an efficient adsorbent, (2) an electrochemical process, and (3) an electrochemical process with nFe^0 and SC-nFe^0 as a granular third electrode (GTE). This study investigated the maximum removal rate of the COD and the efficiency of each proposed process for COD removal from the actual samples from the Al-Daura Refinery (Iraq) oil refinery wastewater (ORW).

This work was performed to find an efficient ecofriendly method to remove COD of phenolic compound wastewater with excellent removal efficiency. This method will be a perfect candidate for the COD removal in petroleum refinery wastewater treatment plant (Al-Daura Refinery (Iraq) ORW). The novelty of this study is using SC-nFe0 as an efficient adsorbent for COD of phenolic compounds. Also, this is the first time that green nFe^0 and SC-nFe^0 are successfully used as GTEs in electrochemical system for COD removal from phenolic wastewater.

2. Chemicals and methods

2.1. Chemicals

The commercial Ahmed brand of green tea (biomaterial waste) was used in the synthesis of nFe^0 and SC-nFe^0. The following chemicals were also used: phenol crystal (C_6H_5OH) with 99.5% purity, ferric chloride anhydrous (FeC_{13}), sodium sulfate (Na_2SO_4), NaOH, H_2SO_4, and deionized water. These chemicals were bought from Thomas Baker Chemicals (India). The silty clay utilized in this work was brought from Mosul (Smehlla 36°31′25N, 43°53′52E), in northern Iraq. The preparation and characterization of the green tea waste extract, preparation of the silty clay, and synthesis and characterization of the nFe^0 and SC-nFe^0 were conducted according to our previous study [29] (for more detailed information about the physical and chemical properties of nFe^0 and SC-nFe^0).

2.2. Electrochemical cell

The electrochemical cell utilized in this study is demonstrated in Fig. 1a, in which a glass reaction tank with dimensions 10 × 6 × 5 cm and two parallel aluminum plates (2.5 × 3 × 0.1 cm) with good electrochemical stability were used as the anode and cathode electrodes, respectively. Also, a 60V 5A DC power supply (Maisheng MS-605D, China) and magnetic stirrer were used.

The same electrochemical cell was used in both the GTE and the electrochemical processes, as shown in Fig. 1b.

2.3. Batch experiments

The experimental work was carried out to determine the effectiveness of the manufactured nFe^0 and SC-nFe^0 as adsorbents as well as the efficiency of the electrochemical and three-dimensional electrode electrochemical processes with nFe^0 and SC-nFe^0 as third granular electrodes to remove COD from the phenolic wastewater. Abundance of effective parameters (e.g., pH, time, nFe^0 and SC-nFe^0 dose, phenol concentration, temperature, current density, and electrode distance) was examined to determine the optimum operating conditions of each process.

The COD measurement was based on “Standard Methods for the Examination of Water and Wastewater,” Method 5220 [30]. A COD apparatus (Lovibond (Germany)) was used to measure the COD. Adsorption experiments were performed in a 500 mL beaker, while all electrochemical and 3-D electrochemical experiments were performed in a 250 mL electrochemical cell.

2.3.1. Adsorption

The first group of batch experiments was conducted using adsorption techniques. A determined dose of nFe^0 or SC-nFe^0 was mixed with the prepared phenol solution (C_6H_5OH). The pH adjustment processes were conducted using 0.1 N NaOH or 0.1 N H_2SO_4. After that, a magnetic stirrer at 250 rpm was utilized to agitate the solution. A filtration process was performed using a 0.45 μm syringe filter.

The parameters that affected the adsorption using nFe^0 and SC-nFe^0 were examined to find the optimal conditions for the maximum COD removal rate. Over 90 min (sampled every 5 min), the pH ranged from 2 to 5, adsorbent doses (nFe^0 or SC-nFe^0) ranged from 0.75 to 2 g/L, phenol concentration ranged from 500 to 1,500 mg/L, and temperature ranged from 15°C to 45°C.

2.3.2. Electrochemical process

All experiments were performed with solutions of a specific concentration of phenol and 0.25 g/L of the electrolyte (Na_2SO_4). The pH adjustment was made using 0.1 N sodium hydroxide or 0.1 N sulfuric acid solutions. The COD was measured at zero and *t* times, and the removal rate was calculated.

As with the adsorption experiment above, the parameters affecting the electrochemical process were investigated to determine the optimum conditions for the maximum removal rate of COD. The same time interval was used (90 min, sampled every 5 min), with the pH varying from 2 to 5, current density from 20 to 60 mA/cm^2, electrode plate distance from 3 to 6 cm, phenol concentration from 500 to 1,500 mg/L, and temperature from 15°C to 45°C.

2.3.3. GTE in an electrochemical process

In all experiments, a particular weight of SC-nFe^0 or nFe^0 was added to the mixture of a measured concentration of phenol (C_6H_5OH) along with (Na_2SO_4) and deionized water. A magnetic stirrer at 250 rpm was employed to stir the prepared solution. A filtration process was applied to the samples using a 0.45 μm syringe filter. The COD was measured at zero and *t* times, and the removal rates were calculated.

As with the variables described above, the parameters affecting the GTE in an electrochemical process were examined, and the optimum conditions were found for the maximum COD removal rate. During a 90-min period (sampled every 5 min), the pH ranged from 2 to 5, granular electrode dose ranged from 0.75 to 2 g/L, phenol concentration ranged from 500 to 1,500 mg/L, and temperature ranged from 15°C to 45°C.

2.3.4. Real samples of ORW

Real samples from Al-Daura ORW were taken from two points in the treatment plant: (1) the effluent of the American Petroleum Institute (API) unit, and (2) the effluent from the plant prior to being discharged into the river. American Petroleum Institute (API) is the main separator tank, and it is the first station in Dura refinery wastewater treatment plant in Baghdad/Iraq. This strategy of sampling was employed to detect the efficiency of the manufactured nFe^0 and SC-nFe^0 and the proposed techniques in COD removal from a petroleum refinery.

3. Results and discussion

3.1. Batch adsorption

3.1.1. Effect of contact time

The effect of the contact time on the COD removal rate was investigated over 160 min at the following conditions: pH = 4, nFe^0 or SC-nFe^0 dosage = 1 g/L, phenol concentration = 500 mg/L, and temperature = 25°C. Fig. 2 illustrates the gradual increase in the removal rate of COD with time over 120 min. At this time, adsorption equilibrium was attained for both nFe^0 and SC-nFe^0, with COD removal efficiency rates of 47.5% and 54.8%, respectively. After 2 h, the

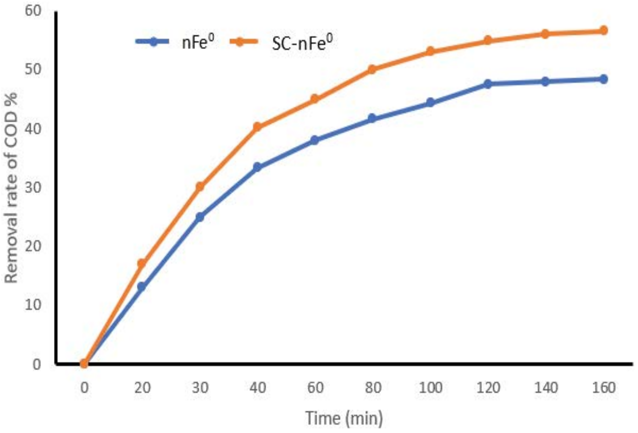

Fig. 2. Effect of contact time on the removal rate of COD (phenol concentration 500 mg/L, nFe^0 or SC-nFe^0 dose = 1 g/L, temperature = 25°C, pH = 4).

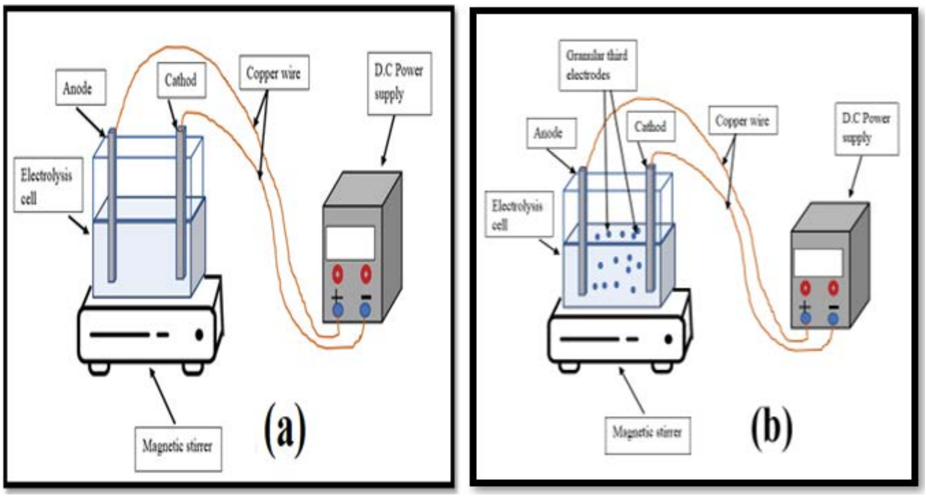

Fig. 1. Electrochemical cell; (a) electrochemical process, and (b) granular third electrode electrochemical cell.

adsorption of the phenol and its derivatives reached the minimum limit, possibly due to the severe decrease in the number of empty surface binding sites [31].

3.1.2. Effect of pH

Batch experiments were performed within a pH range of 2–5, using the value that optimally maximized the reaction rate of phenol [32,33]. These experiments were performed at 25°C, over 120 min, using 500 mg/L phenol, and 1 g/L nFe^0 or SC-nFe^0. At a low pH, oxonium ions will prevent the formation of surface acidic dissociation groups. These conditions generated H bonds and π-π reactions between phenol and nFe^0 or SC-nFe^0. Therefore, the adsorption capacity attained a maximum value [34]. The greatest removal of COD was 75.9% at pH = 2.5 for nFe^0 and also at 65% at pH = 3 for SC-nFe^0. The impact of the pH on the removal rate of COD is shown in Fig. 3.

3.1.3. Effect of adsorbent dose

The adsorbent dose effect was investigated within a range from 0.75 to 2 g/L, over 120 min, with a phenol concentration of 500 mg/L, temperature of 25°C, and a pH of 2.5 or 3 for nFe^0 and SC-nFe^0, respectively. As illustrated in Fig. 4, the COD removal rate increased with an increase in the adsorbent dose when nFe^0 and SC-nFe^0 measured less than 1 g/L, while a reverse reaction appeared when the dosage was greater than this value. One explanation is that using a high dose of the nano-adsorbent caused an agglomeration, which thereby decreased the specific surface area of the adsorbent and increased the path of the pollutants. A second explanation is that the unsaturated adsorption sites (which result from the low concentration of the adsorbate) in conjunction with the high dose of the adsorbent led to the oxidation of the excess nFe^0 to Fe_2O_3 and the excess SC-nFe^0 to Fe_3O_4. Therefore, the reduction capacity and equilibrium adsorption of the adsorbent decreased when their dose reached a specific value [35]. The highest removal rates of COD utilizing nFe^0 and SC-nFe^0 were 77.7% and 66.1%, respectively.

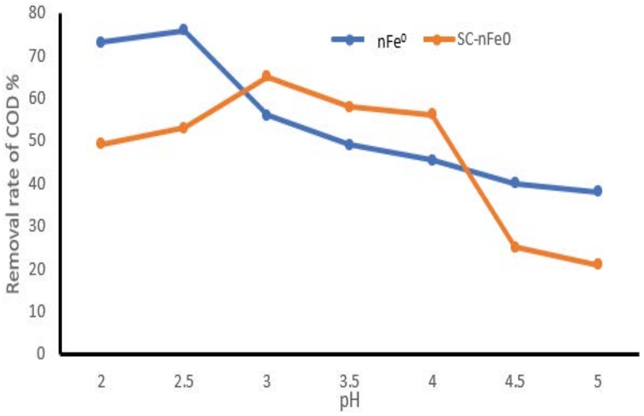

Fig. 3. Effect of pH on removal rate of COD (time = 120 min, adsorbent dose = 1 g/L, phenol concentration = 0.5 g/L, temperature = 25°C).

3.1.4. Effect of phenol

The concentration of phenol was adjusted from 500 to 1,500 mg/L to study the effect on the COD removal rate under the following conditions: nFe^0 or SC-nFe^0 dose = 1 g/L; temperature = 25°C; operation time = 120 min, and pH = 2.5 and 3 for nFe^0 and SC-nFe^0, respectively. As illustrated in Fig. 5, the COD removal efficiency decreased with an increase in the phenol concentration. This trend was caused by increased competition between the phenol ions and adsorption sites [36,37].

3.1.5. Effect of temperature

The effect of the temperature on the COD removal rate using nFe^0 and SC-nFe^0 as adsorbents was examined at 15°C, 25°C, 35°C and 45°C, contact time = 120 min, phenol concentration = 500 mg/L, nFe^0 and SC-nFe^0 dosage = 1 g/L, and pH = 2.5 and 3 for nFe^0 and SC-nFe^0, respectively. As displayed in Fig. 6, the COD removal rate increased as the temperature rose, demonstrating that the operation is endothermic. This result may have been caused by the increase in phenol mobility due to rising temperatures [38]. This increase in the COD removal resulted from the

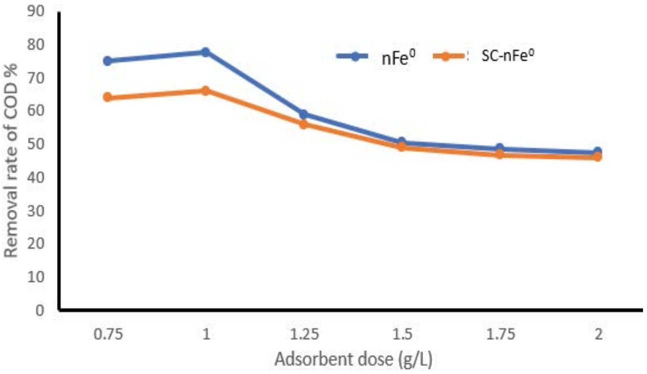

Fig. 4. Effect of the adsorbent dose on the removal rate of COD (phenol concentration 0.5 g/L, contact time = 120 min, temperature = 25°C, pH = 2.5 and 3 for nFe^0 and SC-nFe^0, respectively).

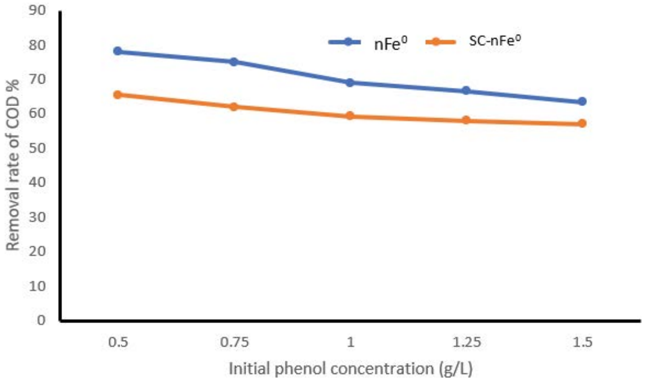

Fig. 5. Effect of initial phenol concentration on the removal rate of COD (contact time = 120 min; nFe^0 or SC-nFe^0 dose = 1 g/L; pH = 2.5 and 3 for nFe^0 and SC-nFe^0, respectively; temperature = 25°C).

increase in the adsorption of phenol with temperature and because of the increase in phenol oxidation caused by an increase in temperature [39]. The highest removal rates of COD occurred at 45°C, at 89.5% and 84.2% for nFe^0 and $SC\text{-}nFe^0$, respectively.

3.1.6. Optimum conditions

The optimum operational conditions for COD removal are (1) pH of 2.5 and 3 for nFe^0 and $SC\text{-}nFe^0$, respectively, (2) nFe^0 and $SC\text{-}nFe^0$ dosage of 1 g/L, (3) contact time of 120 min, (4) phenol concentration of 500 mg/L, and (5) temperature of 45°C. The highest removal rates of COD at these optimal conditions were 89.5% and 84.2% for nFe^0 and $SC\text{-}nFe^0$, respectively.

3.2. Electrochemical process

3.2.1. Effect of pH

The initial pH value considerably influences the electrochemical technique [40], and therefore, the COD removal rate. The impact of a pH value from 2 to 5 on the removal rate of COD was studied at current density = 40 mA/cm^2, plate distance = 4 cm, phenol concentration = 500 mg/L, (Na_2SO_4) = 0.25 g/L, and temperature = 45°C. As illustrated in Fig. 7, the minimum removal rates were both at a low and a high pH, while the maximum value was at pH of 4. This resulted from the highly acidic condition, where $Al(OH)_3$ does not precipitate due to its amphoteric property [41]. Also, at the higher pH value, $Al(OH)_4$ forms and prevents phenol adsorption [42].

3.2.2. Effect of time

The effect of the electrolysis time on the removal rate of COD was investigated over 1.5 h, at pH = 4, phenol concentration = 500 mg/L, Na_2SO_4 = 0.25 g/L, temperature = 45°C, current density (CD) = 40 mA/cm^2, and plate distance = 4 cm. As shown in Fig. 8, the removal rate of COD increased as the electrolysis time reached 50 min. After this time, there was no considerable increase in the removal rate. These results may be due to the decrease in the probability of contact between the contaminants and the electrode as a result of the decrease in the concentration of the contaminants during the electrochemical process. Another probable cause is the generation of intermediate recalcitrant compounds as a result of the insufficient oxidation of the organic materials [43].

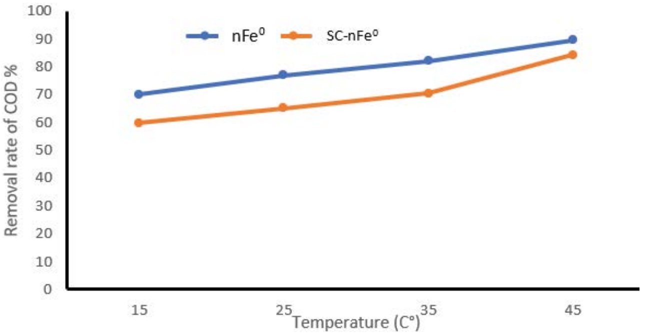

Fig. 6. Effect of temperature on the removal rate of COD (contact time = 120 min, phenol concentration = 0.5 g/L, NZVI or SC-NZVI dose = 1 g/L, pH = 2.5 and 3 for nFe^0 and $SC\text{-}nFe^0$, respectively).

3.2.3. Effect of current density (CD)

The effect of the CD on the COD removal rate was examined using current densities from 20 to 60 mA/cm^2, at the following initial conditions: pH = 4, electrolysis time = 50 min, phenol concentration = 500 mg/L, Na_2SO_4 = 0.25 g/L, plate distance = 4 cm, and temperature = 45°C. As displayed in Fig. 9, the increase in the current density was accompanied by a rise in the COD removal efficiency. This might have been caused by the promotion of the redox reactions of the contaminants on the electrodes, which resulted from an increase in the transmission of electrons (i.e., increase in current density) [44]. When the current density was more than 40 mA/cm^2, the increase in the COD removal became insignificant. This may be due to the excess quantity of oxygen and hydrogen bubbles that are formed due to the increase in the current density, which limit the contaminants' contact with the electrodes [45]. For adequate COD removal and greater energy savings, the optimum CD was 50 mA/cm^2.

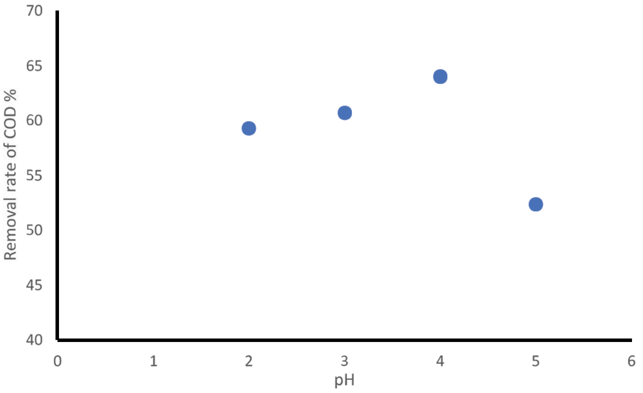

Fig. 7. pH effect on removal rate of COD (CD = 40 mA/cm^2, plate distance = 4 cm, phenol concentration = 0.5 g/L, (Na_2SO_4) = 0.25 g/L, and temperature = 45°C).

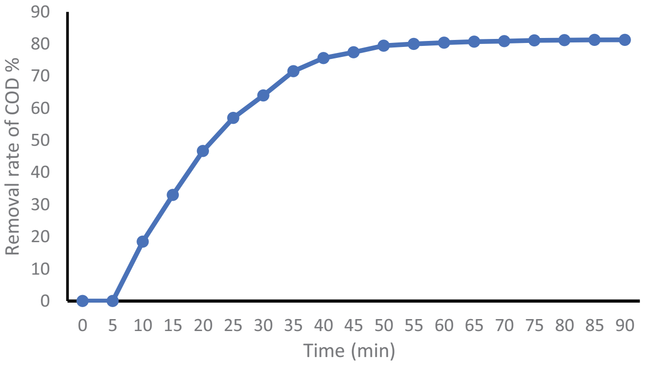

Fig. 8. Effect of electrolysis time on the removal rate of COD (phenol concentration of 500 mg/L and 0.25 g/L (Na_2SO_4), temperature of 45°C, pH of 4, CD of 40 mA/cm^2).

3.2.4. Effect of electrode distance

Electrochemical batch experiments were conducted using four electrode plate distances (i.e., 3, 4, 5, and 6 cm) under the following conditions: pH = 4, electrolysis time = 50 min, initial phenol concentration = 500 mg/L, 0.25 g/L Na_2SO_4, current density = 50 mA/cm^2, and temperature = 45°C. As demonstrated in Fig. 10, the maximum COD removal rate was at an electrode distance of 4 cm. At greater distances, there was a slight decrease in the removal rate. The probable cause of this decline was the decrease in the generation of Al cations due to the increase in the ohmic potential, which reduces the effectiveness of the electrochemical process [22].

3.2.5. Effect of initial phenol concentration

Electrochemical experiments were conducted using various phenol concentrations ranging from 500 to 1,500 g/L to investigate the effect of the phenol concentration on the COD removal rate. The experimental conditions included using 0.25 g/L Na_2SO_4, pH of 4, electrolysis time of 50 min, electrode plate distance of 4 cm, CD of 50 mA/cm^2, and temperature of 45°C. Fig. 11 reveals that the effectiveness of the electrochemical cell for COD removal was inversely related to the initial phenol concentration. This occurs because the number of aluminum ions that pass to the electrolyte is dependent on the current density value rather than on the phenol concentration. Thus, the extra amount of phenol did not coagulate when the phenol concentration was increased [40].

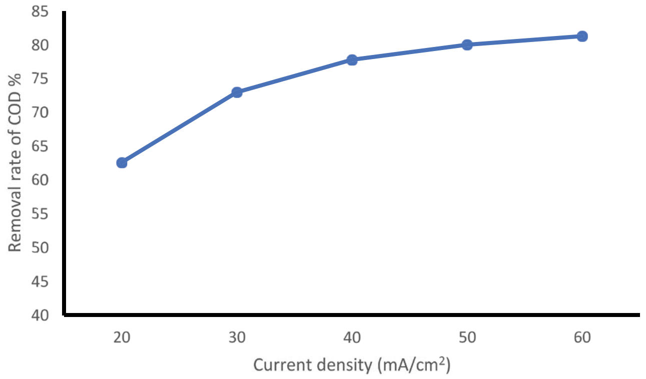

Fig. 9. Effect of current density on the removal rate of COD (phenol concentration of 0.5 g/L and 0.25 g/L Na_2SO_4, temperature of 45°C, pH of 4, electrolysis time of 50 min, and plate distance of 4 cm).

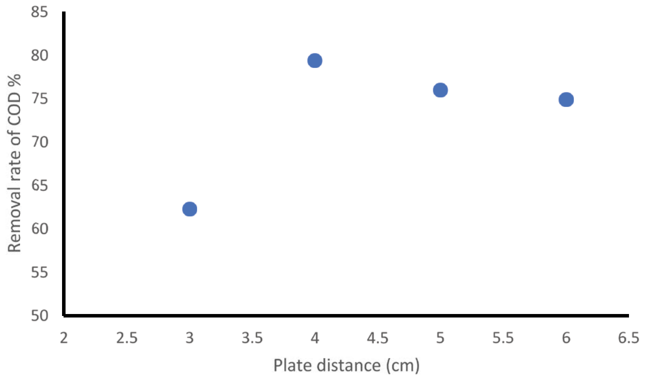

Fig. 10. Effect of electrode plate distance on COD removal (phenol concentration of 0.5 g/L and 0.25 g/L Na_2SO_4, temperature of 45°C, pH of 4, electrolysis time of 50 min, and current density of 50 mA /cm^2).

3.2.6. Optimum operating conditions

The optimal operating conditions were as follows: operating time = 50 min, pH = 4, CD = 50 mA/cm^2, electrode distance = 4 cm, and initial phenol concentration = 500 mg/L. The maximum COD removal rate at the optimum operating conditions was 79.8%.

3.3. GTE electrochemical experiments

3.3.1. Effect of time

Batch experiments were conducted over 1.5 h at the following conditions: pH of 3, initial phenol concentration of 500 mg/L, 0.25 g/L Na_2SO_4, granular electrodes (nFe^0 or SC-nFe^0) of 1 g/L, temperature of 45°C, plate distance of 4 cm, and CD of 40 mA/cm^2. As shown in Fig. 12, the increase in the operating time paralleled the rise in the COD removal rate for the first 35 min. After this period, there was no considerable increase in the removal rate. These results may be due to the decrease in the probability of contact between the contaminants and electrode as a result of the decrease in the concentration of contaminants during the electrochemical process. The other probable cause is the generation of intermediate recalcitrant compounds resulting from the insufficient oxidation of the organic materials [43,46].

3.3.2. Effect of pH

The influence of the pH on the COD removal rate was studied using values from 2 to 5, plate distance = 4 cm, CD = 50 mA/cm^2, phenol concentration = 500 mg/L, Na_2SO_4 = 0.25 g/L, granular electrodes (nFe0 or

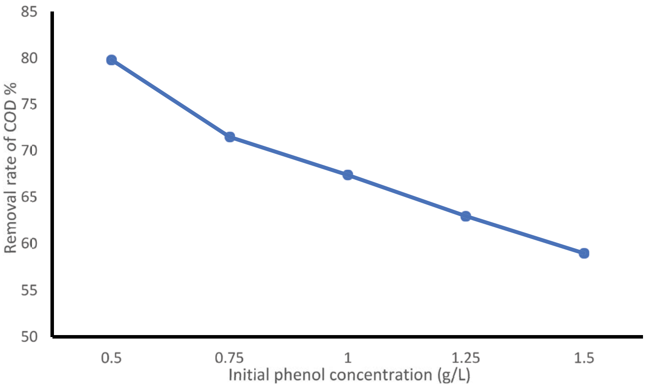

Fig. 11. Effect of initial phenol concentration on COD removal (0.25 g/L Na_2SO_4, pH of 4, electrolysis time of 50 min, electrodes plate distance of 4 cm, CD of 50 mA/cm^2, and temperature of 45°C).

SC-nFe^0) = 1 g/L, temperature = 45°C, and electrolysis time = 35 min. As shown in Fig. 13, the removal rate of COD decreased at the lowest pH value (i.e., 2) and with the increase of pH for both nFe0 and SC-nFe^0. During the electrolysis process, H_2O_2 was produced by the reduction of oxygen at a low pH. An indirect Fenton reaction occurs between nFe^0 and hydrogen peroxide, producing OH radicals [47]. In addition, a reduction of Fe^{3+} to Fe^{2+} on the cathode electrode occurs because the OH combines with the organic pollutants, thereby degrading them. At a very low pH (i.e., <2.5), the removal rate of phenol decreases because the saturated hydrogen ions supply a proton for hydrogen peroxide to form hydroxonium ions (Eq. (1)), thus decreasing the activity of the hydrogen peroxide [46]. Under these conditions, the strong scavenging action of H^+ to OH (Eq. (2)) is evident [48]. Thus, the optimum pH value is 2.5 for both nFe^0 and SC-nFe^0.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{1}$$

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \tag{2}$$

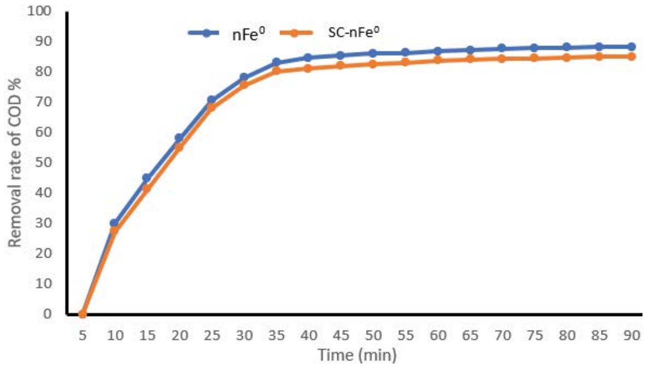

Fig. 12. Effect of time on COD removal (phenol concentration of 0.5 g/L and 0.25 g/L (Na_2SO_4), nFe^0 or SC-nFe^0 = 1 g/L, temperature of 45°C, pH of 3, CD of 40 mA/cm^2, and plate distance of 4 cm).

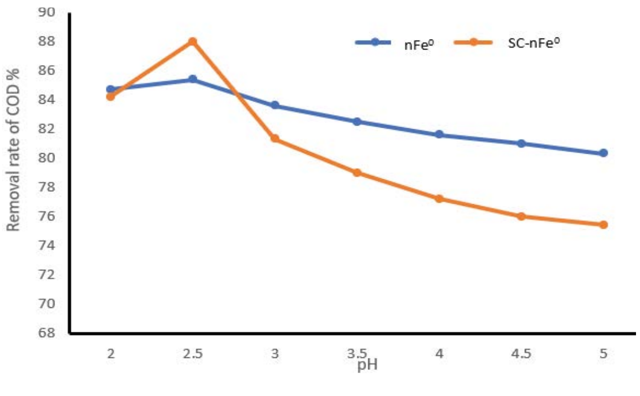

Fig. 13. Effect of pH on COD removal (plate distance = 4 cm, CD = 50 mA/cm^2, phenol concentration = 0.5 g/L, Na_2SO_4 = 0.25 g/L, nFe^0 or SC-nFe^0 = 1 g/L, temperature = 45°C, and electrolysis time = 35 min).

3.3.3. Effect of the GTE dose

The impact of the GTE dose was studied using nFe^0 or SC-nFe^0 = 0.75–2 g/L, plate distance = 4 cm, CD = 50 mA/cm^2, phenol concentration = 500 mg/L, Na_2SO_4 = 0.25 g/L, pH = 2.5, temperature = 45°C, and electrolysis time = 35 min, along with a magnetic stirrer. As demonstrated in Fig. 14, the COD removal rate rose with an increase in the dose of the granulated electrodes until the rate reached 1 g/L for nFe^0 and 1.25 g/L for SC-nFe^0. When the doses were larger, a downward trend occurred. The increase in the granular electrode doses causes an increase in the contact chance between the electrodes and the phenols molecules, which boosted the adsorption and reduction of the phenols and would support a Fenton reaction. This phenomenon might be caused by the aggregation of the granular electrodes due to the increase in their doses; that minimizes the specific surface area and elongates the diffusion pathway of the phenol molecules. Another probable cause is the high doses of the granulated electrodes, which lead to unsaturated adsorption sites and oxidation of the excessive doses of nFe^0 or SC-nFe^0 to Fe_2O_3 and Fe_3O_4. Therefore, when the granulated electrodes (nFe^0 and SC-nFe^0) reach specific values, their equilibrium adsorption and reduction capacity is reduced [49]. The highest removal rates of COD utilizing nFe^0 and SC-nFe^0 were 93% and 94.1%, respectively.

3.3.4. Effect of the initial phenol concentration

The effect of the initial phenol concentration was examined utilizing phenol concentrations ranging from 500 to 1500 mg/L, at the following conditions: Na_2SO_4 = 0.25 g/L, nFe^0 = 1 g/L, SC-nFe^0 = 1.25 g/L, pH = 2.5, plate distance = 4 cm, temperature = 45°C, and electrolysis time = 35 min. As illustrated in Fig. 15, the COD removal rate decreased gradually with an increase in the phenol concentration. This may have resulted from the number of generated aluminum oxides being too low to oxidize additional amounts of the phenol molecules [29].

3.3.5. Effect of temperature

The effect of temperature on the removal of COD was examined at 15°C, 25°C, 35°C and 45°C, Na_2SO_4 = 0.25 g/L,

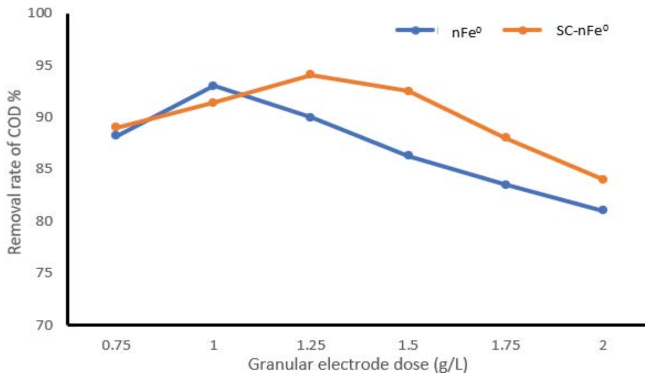

Fig. 14. Effect of the granular electrode dose on the removal rate of COD (plate distance = 4 cm, CD = 50 mA/cm^2, phenol concentration = 0.5 g/L, Na_2SO_4 = 0.25 g/L, pH = 2.5, temperature = 45°C, electrolysis time = 35 min).

pH = 2.5, phenol concentration = 500 mg/L, nFe^0 = 1 g/L or SC-nFe^0 = 1.25 g/L, plate distance = 4 cm, and electrolysis time = 35 min. As evident in Fig. 16, the COD removal rate increased gradually as the temperature rose, as was found in the literature [50,51]. Additionally, the increase in temperature raises the hydrolysis rate of Al^{3+} to Al $(OH)_3$ [52] and led to an increase in the diffusivity and rate of mass transfer of Al^{3+} [51].

3.3.6. Optimum operating conditions

In conclusion, the optimum operating conditions for COD removal are pH = 2.5, operating time = 35 min, CD = 50 mA/cm^2, granular electrode doses (nFe^0 = 1 g/L; SC-nFe^0 = 1.25 g/L), electrode plates distance = 4 cm, initial phenol concentration = 500 mg/L, and temperature = 45°C. The highest COD removal rates at optimal conditions were 93% and 94% for nFe^0 and SC-nFe^0, respectively.

4. Samples of the ORW

4.1. Characterization of the ORW

Table 1 demonstrates the characteristics of the Al-Daura ORW, representing the average value of three months, which were examined in the wastewater treatment plant laboratory according to standard methods [52].

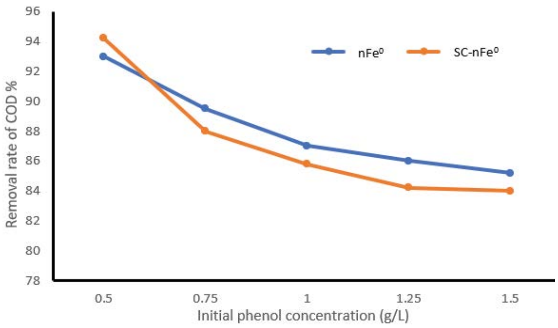

Fig. 15. Effect of the initial phenol concentration on the removal rate of COD (Na_2SO_4 = 0.25 g/L, nFe^0 = 1 g/L, SC-nFe^0 = 1.25 g/L, pH = 2.5, plate distance = 4 cm, temperature = 45°C, and electrolysis time = 35 min).

4.2. COD of the ORW

The three techniques proposed by this research, with the optimum operating conditions for each technique, were applied to samples from the API units at the Al-Daura refinery wastewater treatment plant in Baghdad/Iraq. The removal rates of COD were 83.7%, 84.1%, 85.2%, 89.7%, and 92.8%, respectively, when each of the following were tested: adsorption by nFe^0, adsorption by SC nFe^0, electrochemical, 3-D electrochemical with nFe^0, and 3-D with SC-nFe^0. All techniques achieved excellent COD removal rates, which were higher than those of the Al-Daura wastewater treatment plant (82.8%), and 3-D with SC-nFe^0 technique was of the highest removal efficiency, as displayed in Table 2.

5. Conclusions

In this study, the three proposed techniques (i.e., batch adsorption, an electrochemical process, and GTE in an

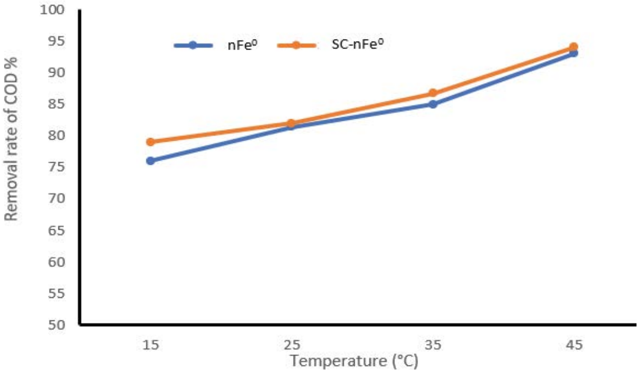

Fig. 16. Effect of temperature on the removal rate of COD (plate distance = 4 cm, nFe^0 = 1 g/L, SC-nFe^0 = 1.25 g/L, Na_2SO_4 = 0.25 g/L, pH = 2.5, phenol concentration = 0.5 g/L, and electrolysis time = 35 min).

Table 1
Characteristics of Al-Daura ORW

Item	Effluent from API	Effluent from plant	Iraq's treated wastewater standards
pH	7.2	7.1	6.5–8.5
T (°C)	26	22	–
TDS (mg/L)	835	838	–
Turbidity (NTU)	56.8	7.2	5
SO_4 (mg/L)	379	371	200 or more as naturally present
Sulfide (mg/L)	0.145	0.053	–
Suspended solid (mg/L)	176	45	60
BOD_5 (mg/L)	23	5	40
PO_4 (mg/L)	0.67	0.37	0.4
DO (mg/L)	0.0	7.1	5
CL^- (mg/L)	257	269	200 or more as naturally present
Phenol (mg/L)	2.3	0.039	0.05
COD (mg/L)	286	52	100

Table 2
COD removal rate for actual samples from Al-Daura ORW using three techniques

Techniques	Conditions	COD removal rate%
Adsorption with nFe^0 adsorbent	pH of 2.5, nFe^0 dosage of 1 g/L, contact time of 120 min, phenol concentration of 500 mg/L, and a temperature of 45°C.	83.7
Adsorption with SC-nFe^0 adsorbent	pH of 3, SC-nFe^0 dosage of 1 g/L, contact time of 120 min, phenol concentration of 500 mg/L, and a temperature of 45°C.	84.1
Electrochemical	Operating time = 50 min, pH = 4, CD = 50 mA/cm^2, electrode distance = 4 cm, and initial phenol concentration = 500 mg/L	85.2
nFe^0 GTE electrochemical	pH = 2.5, operating time = 35 min, CD = 50 mA/cm^2, granular electrode doses (nFe^0 = 1 g/L), electrode plates distance = 4 cm, initial phenol concentration = 500 mg/L, and temperature = 45°C.	89.7
SC-nFe^0 GTE electrochemical	pH = 2.5, operating time = 35 min, CD = 50 mA/cm^2, granular electrode doses (SC-nFe^0 = 1.25 g/L), electrode plates distance = 4 cm, initial phenol concentration = 500 mg/L, and temperature = 45°C.	92.8
Al-Daura ORW	Refinery wastewater treatment plant conditions	82.8

electrochemical process) were successfully applied to determine the amount of COD present in wastewater and to reduce this amount optimally. The green tea waste nFe^0 and silty clay supported nFe^0 were used as efficient adsorbents to remove COD from simulated phenolic wastewater. The maximum COD removal rates using these adsorption techniques were achieved at optimal operating conditions: 89.5% and 84.2% for nFe^0 and SC-nFe^0, respectively. This compares with the electrochemical process, GTE in an electrochemical process with nFe^0, and GTE in an electrochemical process with SC-nFe^0 at 79.8%, 93% and 94%, respectively. The electrochemical processes worked successfully with the addition of nFe^0 and SC-nFe^0 as GTEs. Using actual ORW samples and the three proposed techniques achieved COD removal rates higher than those obtained by the ORW treatment plant, and GTE of SC-nFe^0 in an electrochemical process achieved the highest removal efficiency.

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