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Research

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Phenolic wastewater remediation employing nano zerovalent iron as a granular third electrode in an electrochemical reactor

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Abstract

The rise in toxic industrial and domestic wastewater due to urbanization makes it necessary to pursue new, alternative routes for the removal of refractory pollutants. In this study, both unsupported nano zerovalent iron (NZVI) and silty clay-supported nano zerovalent iron (SC-NZVI) were employed as a granular third electrode (3-D) in an electrochemical reactor. The electrochemical system with two aluminum electrodes as anode and cathode was performed as a granular third electrode treatment process to degrade aqueous phenol. The maximum removal rate of phenol using the tow electrodes electrochemical process (2-D) was 82%. The optimum conditions in a 2-D electrode were as follows: pH = 4, electrolysis time = 30 min, current density = 50 mA/cm², electrode distance = 4 cm, and phenol concentration = 0.5 g/L. It was concluded that the 3-D electrode system exhibited high efficiency in removing phenolic wastewater in a third electrode system. The optimum conditions were as follows: pH = 2, electrolysis time = 30 min, current density = 50 mA/cm², electrode distance = 4 cm, and phenol concentration = 0.5 g/L. The maximum removal efficiencies of phenol in the presence of a 3-D electrode with doses of NZVI = 1 g/L or SC-NZVI = 1.25 g/L were 96.1 and 97.8%, respectively.

Keywords: Electrochemical technique; 3D electrode; Nano zerovalent iron; Phenol; Wastewater treatment.

1. Introduction

Phenol and its compounds exist in wastewater of various industries, including petroleum refineries, petrochemical industries, coking operations, pharmaceutical production and phenolic resins industries [1]. According to the US Environmental Protection Agency (EPA) and the National Pollutant Release Inventory (NPRI) of Canada, phenol is classified as a priority pollutant [2, 3]. People exposed to phenol acutely or chronically may suffer adverse health consequences, which may be quite serious depending on the degree of exposure [4]. Several techniques have been used to remove phenol from water and wastewater, including chemical oxidation [5, 6], microbial degradation [7, 8], membrane separation [9], photocatalytic degradation [10], solvent extraction [11], ultrasonic degradation [12], enzymatic polymerization [13], Fenton-like reactions [14], adsorption [15, 16], and electrochemical oxidation [17, 18].

In general, an electrooxidation system includes an oxidation process at the anode and a reduction process at the cathode (redox reaction). Additionally, the electrooxidation processes used for removing organic materials from wastewater depend upon the potential of gaining partial degradation or full mineralization by using anodic oxidation [19]. Electrooxidation processes can be divided into direct (anodic oxidation) and indirect (using intermediary redox reagents) pathways [20]. In recent years, the green synthesis of nano zerovalent iron (NZVI) and its potential as an adsorbent have gained considerable attention. This interest is due to their natural, eco-friendly, low cost, and efficiency as an adsorbent. The high surface energy, high conductivity, and large specific surface area of nano zerovalent iron make it a useful alternate as a granulated electrode in wastewater treatment [21]. Unfortunately, NZVI particles without any modification are inclined to aggregate and oxidize due to van der Waals and magnetic attraction forces [22], thus decreasing their performance in application. Also, employing bare NZVI in the wastewater treatment process will likely cause a rapid loss of nano zerovalent iron as well as a high concentration of iron ions [23]. Hence, it is necessary to support NZVI by applying it onto a material that can decrease iron leaching and elongate the lifespan of the NZVI [24].

Recently, the electrochemical technique has gained considerable attention in wastewater remediation as a result of its quality, simplicity, and eco-friendly character in the removal of refractory organic pollutants [25]. However, the 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

the efficiency and raise the current density of the electrochemical process [26]. The space between the granular electrodes in the electrochemical process that employed granular electrodes (3-D) systems was shorter, which allowed for more rapid electron transfer and treatment [25]. For these reasons, many researchers have been reporting excellent results using a 3-D electrochemical technique as a tertiary process in wastewater treatment [27, 28, 29].

In this study, NZVI and silty clay-supported nano zerovalent iron (SC-NZVI) synthesis and characterization are reported. Due to their large specific surface area, both NZVI and SC-NZVI have proved to be highly reactive and efficient adsorbents, which makes them both excellent candidates for use as a third electrode. Furthermore, the efficiency of NZVI and SC-NZVI as granular third electrodes for the removal of aqueous phenol was examined. Various significant operating conditions were optimized, such as pH, electrolysis time, current density, electrode plate distance, granular electrode dose, and phenol concentration.

2. Materials and Methods

2.1 Materials

The source of polyphenol used in this work was the commercial leaves of green tea. Ferric chloride anhydrous (FeCl_3), phenol crystal ($\text{C}_6\text{H}_5\text{OH}$), 0.01 M sodium hydroxide (NaOH), 0.01 M sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4) and deionized water were also used. All chemicals were purchased from Thomas Baker (India). The natural silty clay was obtained from Mosul, Iraq.

2.2 Synthesis of NZVI and SC-NZVI

In this study, NZVI and SC-NZVI were synthesized according to the methods used in our previous study, which has been submitted for publication. The synthesis methods are demonstrated in **Fig. 1**.

Fig. 1. Synthesis methods of (a) NZVI and (b) SC-NZVI.

2.3 Characterization of NZVI and SC-NZVI

The characterization of the prepared adsorbents NZVI and SC-NZVI was achieved using the following: X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform

infrared spectroscopy (FTIR), and zeta potential (ζ). A detailed characterization of NZVI and SC-NZVI is given in our previous study.

2.4 Electrolytic cell

The electrolytic cell used in this work is illustrated in **Fig. 2**. A reaction tank was made of a glass box, with dimensions 10 x 6 x 5 cm. Two parallel aluminum plates (2.5 x 3 x 0.1 cm) with good electrochemical stability were used as parallel anode and cathode electrodes. This study also used a 60V 5A DC power supply (Maisheng MS-605D) and magnetic stirrer.

Fig. 2. Electrochemical apparatus.

2.5 Batch experiments

The performance of the NZVI and SC-NZVI as granulated electrodes in an electrochemical reactor to remove an aqueous phenol was evaluated by two groups of batch experiments. The first group researched the electrochemical processes without any modification. The second group studied the electrochemical processes in the presence of a granulated electrode (i.e., NZVI or SC-NZVI). All experiments were performed with 250 ml of deionized water and 0.25 g/l of the electrolyte (Na_2SO_4). Experimental solutions were made by dissolving a specific weight of phenol in deionized water. The pH was adjusted using 0.1 N NaOH and 0.1 N H_2SO_4 solutions. For the second set of experiments, a specific weight of NZVI or SCNZVI was added to the prepared solution of the specific concentration of phenol ($\text{C}_6\text{H}_5\text{OH}$) along with (Na_2SO_4) and deionized water. The produced solution was agitated at 250 rpm using a magnetic stirrer. Samples were filtered using a 0.45- μm syringe filter. A calibration curve of the phenol was made by UV 9200 Biotech Engineering, with a maximum λ of 268 nm. Depending on the absorbance (measured by UV spectroscopy) and calibration curve, the concentration and removal rate of phenol were calculated.

$$\text{Removal rate } \% = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where C_o and C_t are the concentration of phenol (mg/L) at times zero and t, respectively.

3. Results and Discussion

3.1. Electrochemical experiments

3.1.1 Effect of pH

The initial pH value has a considerable influence on the removal rate of phenol [30]. The removal rates of phenol were determined in the pH range from 2-6 and at an initial phenol concentration of 0.5 g/L and 0.25 g/L (Na_2SO_4), temperature of 45°C , current density (CD) of 40 mA/cm^2 , and plate distance of 4 cm. **Fig. 3** shows the influence of the initial pH of the phenol solution on the removal rate of phenol. The removal rates of phenol had their lower value at both low and high pH values, while the maximum removal rate was at a pH of 4. These results occurred because at the lower pH value, $\text{Al}(\text{OH})_3$ does not precipitate due to its amphoteric property [31]. Additionally, at the higher pH value, $\text{Al}(\text{OH})_4$ forms, and this compound is ineffective for phenol adsorption [32].

Fig. 3. Effect of pH on the phenol removal percentage.

3.1.2 Effect of electrolysis time

The effect of the electrolysis time on the removal rate of phenol was investigated over 90 min and at an initial phenol concentration of 0.5 g/L and 0.25 g/L (Na_2SO_4), temperature of 45°C , pH of 4, CD of 40 mA/cm^2 , and plate distance of 4 cm as initial conditions, as illustrated in **Fig. 4**. The removal rates of phenol increased with the elongation of the electrolysis time until 30 min. However, there was no significant increase in the removal rate of phenol after this time. After a specific time within the electrochemical process, the reduction in the concentration of pollutants leads to a decrease in the chance of contact with the electrode, which reduces the removal rate. Another potential cause is the formation of intermediate recalcitrant compounds due to the insufficient oxidation of organics [33].

Fig. 4. Effect of the electrolysis time on the removal rate of phenol.

3.1.3 Effect of current density

The experiments were conducted with a current density (CD) from 20 to 60 mA/cm^2 and with an initial 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 30 min, and plate distance of 4 cm. As displayed in **Fig. 5**, the removal rate of phenol increased with a rise in the CD. The increase in the CD meant an increase in the transmission of electrons, which promoted the redox reactions of the pollutants on the electrodes [21]. However, when the CD surpassed 40 mA/cm^2 , the increase in the removal rate of phenol

was slight and insignificant. These results occurred because the increase in CD generated additional oxygen and hydrogen bubbles, which limited the contact of the pollutants with the electrodes [34]. For maximal energy savings and an appropriate removal rate of phenol, the optimum current density was 50 mA/cm². The consumption of electrical energy is represented in the following:

$$EC = \frac{VIt}{v} \quad (2)$$

where EC is the energy consumption (kWh/m³), V is the voltage (V), I is the applied current (A), t is the electrolysis time (min), and v is the volume of wastewater (m³). For a CD of 50 mA/cm² and an electrolysis time of 30 min, the energy consumption was 6.34 KW.h/m³.

Fig. 5. Effect of the current density on the removal rate of phenol.

3.1.4 Effect of electrode plate distance

The effect of the electrode plate distance was investigated using a 3-6-cm plate distance, phenol concentration = 0.5 g/L, Na₂SO₄ = 0.25 g/L, temperature = 45°C, pH = 4, CD = 50 mA/cm², and electrolysis time = 30 min, as illustrated in **Fig. 6**. The phenol removal rate increased when the distance between the plates was less than 4 cm. When the electrode distance exceeded 4 cm, the removal rate of phenol decreased slightly. This decrease was perhaps due to the decline in the formation of aluminum cations, which resulted from the increment in the ohmic potential. Hence, there was a decrease in the effectiveness of the electrochemical process [35]. The maximum removal rate of phenol was 82% at the optimum electrode distance of 4 cm.

Fig. 6. Effect of the electrode plate distance on phenol removal.

3.2. Third granulated electrode experiments

3.2.1 Effect of pH

The effect of the pH on the removal rate of phenol in the electrochemical cell in the presence of NZVI and SC-NZVI as granulated electrodes was studied at a plate distance = 4 cm, CD = 50 mA/cm², phenol concentration = 0.5 g/L, Na₂SO₄ = 0.25 g/L, NZVI or SC-NZVI = 1g/L, temperature = 45°C, and electrolysis time = 30 min. The pH was adjusted from 2-5, as shown in **Fig. 7**. The maximum removal rates of phenol decreased at a lower pH value (i.e., 2.5) and with

the increment of pH for both NZVI and SC-NZVI. During the electrolysis process, H_2O_2 was produced by the reduction of oxygen at a low pH. An indirect Fenton reaction will occur between ZVI and hydrogen peroxide, producing OH radicals [36]. In addition, a reduction of Fe^{3+} to Fe^{2+} on the cathode electrode will occur. The OH will combine with the organic pollutants, thereby degrading them. At a very low pH (i.e., < 2), the removal rate of phenol will decline because the saturated hydrogen ions will supply a proton for hydrogen peroxide to form hydroxonium ions (Eq. 3), thus decreasing the activity of the hydrogen peroxide [21]. Furthermore, the strong scavenging action of H^+ to OH (Eq. 4) will be evident [37]. Thus, the optimum pH value is 2 for both NZVI and SC-NZVI.

Fig. 7. Effect of the pH on the removal rate of phenol.

3.2.2 Effect of granular electrode dose

The influence of the granular electrode dose was investigated using 0.75-2 g/L of NZVI or SC-NZVI, plate distance = 4 cm, CD = 50 mA/cm², phenol concentration = 0.5 g/L, Na_2SO_4 = 0.25 g/L, pH = 2, temperature = 45°C, electrolysis time = 30 min, along with a magnetic stirrer. As demonstrated in **Fig. 8**, the phenol removal rate increased when the dose of NZVI was less than 1g/L and the dose of SC-NZVI was below 1.25 g/L. However, a downward trend took place when the doses were larger. The increase in NZVI and SC-NZVI doses led to an increase in the contact chance between the granular electrodes and the phenol molecule, which enhanced the adsorption and reduction of the latter. In addition, this increase in granular electrode doses can support a Fenton reaction. As for the decrease in the removal rate of phenol, there are two possibilities. First, the aggregation could be due to the increasing dose of the adsorbent leading to a decrease in the specific surface area and also a lengthening of the diffusion path of the organic pollutants. Second, because the concentration of phenol was low, the high dose of NZVI or SC-NZVI caused unsaturated adsorption sites and an increase in NZVI or SC-NZVI, which oxidized to Fe_2O_3 and Fe_3O_4 . As a result, the equilibrium adsorption and reduction capacity of NZVI and SC-NZVI decreased when the dosage reached a specific level [38]. The maximum removal rates of phenol using NZVI and SC-NZVI were 96.1% and 97.8%, respectively.

Fig. 8. Effect of the granular electrode dose on the removal rate of phenol.

3.2.3 Effect of phenol concentration

The influence of the initial phenol concentration was studied using phenol concentrations ranging from 0.5 to 1.5 g/L. The electrolysis process was conducted with a magnetic stirrer under the following conditions: plate distance = 4 cm, NZVI = 1 g/L, SC-NZVI = 1.25 g/L, Na_2SO_4 = 0.25 g/L, pH = 2, temperature = 45°C, and electrolysis time = 30 min. As illustrated in **Fig. 9**, the removal rate of phenol decreased gradually as the phenol concentration increased. A possible explanation for this result is that the aluminum oxides that formed during the electrolysis process were insufficient to oxidize all of the additional amounts of the phenol molecules [30].

Fig. 9. Effect of the phenol concentration on the removal rate of phenol.

3.3. Optimum operating conditions

The optimal operating circumstances for various examined parameters were obtained for the maximum removal rate of phenol in two cases, as shown in **Fig. 10**. First, when using only the electrolysis process, where pH = 4, electrolysis time = 30 min, $\text{CD} = 50 \text{ mA/cm}^2$, and electrode distance = 4 cm, the removal rate of phenol was 82%. Second, when using the electrolysis process in the presence of granular electrodes (i.e., NZVI or SC-NZVI), the optimum operating conditions were pH = 2, electrolysis time = 30 min, $\text{CD} = 50 \text{ mA/cm}^2$, electrode distance = 4 cm, granular electrode doses (NZVI = 1 g/L; SC-NZVI = 1.25 g/L), and phenol = 0.5 g/L. The second case provided removal rates of 96.1 and 97.8% using NZVI and SC-NZVI, respectively.

Fig. 10. Optimum operating conditions for phenol removal.

3.4. Three-dimensional electrochemical mechanism

The three-dimensional electrochemical process for organic materials removal is dependent on several parameters, such as the electrode material, current density, properties and concentrations of the pollutant, granular electrode type, and pH value. **Fig. 11** demonstrates a generalized mechanism of the processes (i.e., electrolysis, adsorption, and reduction) that occur in a hybrid

system and that assist NZVI and SC-NZVI as granular electrodes in an electrochemical reactor for phenol removal.

Due to the low pH value, the possible reason for phenol degradation was a Fenton-like reaction. The addition of a granular third electrode (i.e., NZVI or SC-NZVI) of a high specific surface area provides an excellent adsorbent for the organic pollutant (i.e., phenol). In addition to adsorption, NZVI or SC-NZVI will reduce the organic pollutant, and mineralization of organics to CO₂ and H₂O will occur.

Oxidation of NZVI or SC-NZVI by O₂ and the formation of Fe²⁺ will take place (Eq. 5) [39]. At strong acidic conditions, a Fenton reaction between either NZVI or SC-NZVI and hydrogen peroxide will occur. Generation of H₂O₂ due to the reduction of O₂ by H⁺ will take place near the cathode (Eq. 6). Therefore, as a result of the Fenton reaction of H₂O₂ with Fe²⁺, an abundance of •OH with a high oxidation capability is formed (Eq. 7) [40]. Also, the immediate reduction of the generated Fe³⁺ to Fe²⁺ creates a cycle of iron ion transformations that decrease NZVI or SC-NZVI exhaustion and oxidize organic pollutants effectively [33].

Fig. 11. Electrochemical processes for organics removal in a 3-D electrochemical reactor.

Comparative study

A comparative study between this research and the literature can be done by assessing the derived results of the removal rate of phenol using different granular electrodes in hybrid 3-D electrochemical systems, as shown in Table 1. This table illustrates that using nanoparticle zerovalent iron synthesized from modified green tea biowaste and supported on silty clay provides the highest removal rate of aqueous phenol as well as providing the benefit of using eco-friendly materials as a granular third electrode.

Table 1. Phenol removal rate by a 3-D electrochemical system using various granular electrodes

4. Conclusions

In this study, synthesized NZVI and SC-NZVI were successfully used as granular electrodes in an electrochemical reactor. This work revealed that the electrochemical treatment of aqueous phenol using aluminum as the anode and cathode electrodes is an effective method, which produces a maximum phenol removal rate of 82%. The following optimum conditions were determined: pH = 2, electrolysis time = 30 min, current density = 50 mA/cm², electrode distance = 4 cm, and phenol concentration = 0.5 g/L. It was proved that either NZVI or SC-NZVI improve the treatment process when they are employed as efficient and effective granular electrodes in hybrid systems. In the hybrid system, the removal rate of phenol increased to 96.1 and 97.8% using NZVI and SC-NZVI, respectively. This study demonstrated that a 3-D electrode system was an effective technology for the treatment of phenolic wastewater in an electrochemical reactor.

Data Availability Statement:

Raw data were generated at [University of Technology/ Chemical Engineering Department]. Derived data supporting the findings of this study are available from the corresponding author on request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contribution statement

Shaimaa T. Kadhum: Conceived and designed the experiments; Analyzed and interpreted the data.

Ghayda Y. Alkindi: Performed the experiments.

Talib M. Albayati: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Figures

Figure 1

Synthesis methods of (a) NZVI and (b) SC-NZVI.

Figure 2

Electrochemical apparatus.

Figure 3

Effect of pH on the phenol removal percentage.

Figure 4

Effect of the electrolysis time on the removal rate of phenol.

Figure 5

Effect of the current density on the removal rate of phenol.

Figure 6

Effect of the electrode plate distance on phenol removal.

Figure 7

Effect of the pH on the removal rate of phenol.

Figure 8

Effect of the granular electrode dose on the removal rate of phenol.

Figure 9

Effect of the phenol concentration on the removal rate of phenol.

Figure 10

Optimum operating conditions for phenol removal.

Figure 11

Electrochemical processes for organics removal in a 3-D electrochemical reactor.