Application and optimization of electro-Fenton technology in advanced treatment of petrochemical industry wastewater

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Abstract. Within this research endeavor, a refined electric-Fenton remediation protocol was put forth for the enhanced reconditioning of intensely polluted organic effluents originating from the petrochemical sector. Using DSA (Dimensionally Stable Anode) electrode material and ultraviolet (UV) catalysis, the wastewater treatment efficiency and the ability to degrade refractory organic compounds were significantly improved. By optimizing the reaction parameters, the mineralization speed and treatment efficiency of organic matter are significantly improved, the use of H2O2 is reduced, and the cost of chemicals and energy consumption are reduced. At the same time, the technology avoids the use of a large number of harmful chemicals and mitigates the peril of subsequent contamination, thus rendering it appropriate for a spectrum of petrochemical effluents. Moreover, it exhibits efficacious abatement on diverse categories of organic contaminants.

Keywords: Electro-Fenton; Petrochemical industry; wastewater.

1. Introduction

The core of the improved electro-Fenton process lies in its unique electrode material, Dimensionally Stable Anode (DSA), and the synergistic catalysis of ultraviolet (UV). With excellent electrochemical stability and conductivity, DSA electrodes are able to maintain stable performance in long-term operation, avoiding the corrosion and wear problems common to traditional electrode materials, thus significantly extending the service life of the equipment and reducing maintenance costs. At the same time, the introduction of ultraviolet light not only enhanced the efficiency of Fenton reaction, but also promoted the photolysis process of refractory organic matter, accelerated the mineralization rate of organic matter, and realized the deep purification of wastewater.

The improved electro-Fenton process shows extensive adaptability to a variety of petrochemical wastewater, whether it is light oil processing wastewater or heavy oil cracking wastewater, whether it is a single organic matter or complex mixture, it can achieve good treatment effect. This process can effectively remove benzene series, phenols, polycyclic aromatic hydrocarbons and other refractory organic pollutants in petrochemical wastewater, and the water quality after treatment is stable, meets the national discharge standards, and even better than the effluent quality of traditional treatment technology.

2. Wastewater treatment method

To avoid environmental and health hazards caused by petrochemical wastewater, such methods as physicochemical, biological, advanced oxidation, and electrochemical have been applied. Physicochemical interactions, for instance, the adsorption of soot and tea residue were able to remove up to 99% uranium from the effluent [1], and polyacrylonitrile nanofiltration distributed 87.093% nickel and 83.271% chromium [2]. Chemical precipitation was reported to be effective in reducing the concentration of arsenic and fluoride by over 93% [3]. However, this technique is quite expensive and it causes the production of sludge [4]. "The biological treatment there that could

reach a level of 80% COD removal under efficient aeration for printed circuit board wastewater" [5]. Waste water treatment processes usually convert pollutants in the environment to more environmentally friendly compounds, for example, ozone treatment unveiled 78.6% COD [6] and photofenton under solar irradiation got rid of 90.7% COD [7]. Fenton's method at pH=2, with Fe^{2+} at 500mg/L and H2O2 at 3000mg/L, met discharge standards within an hour [8]. While the use of Electroflocculation removed 80% nickel and 99.9% zinc [9] was completely eliminated by the process of combination oxidation-electrolysis with 94.9% COD removal [10]. Copper-EDTA complexes and copper ions are scattered as the main derivatives of degreasing reactions, which results in excessive species oxidation and leads to the precipitation of the metal compounds in the sludge or DAF [11].

3. Electronic Fenton technology

Electro-Fenton methodology is an electrochemical advanced oxidation technology rely upon Fenton reaction. The foundational principle of the reaction is to use Fe^{2+} and H_2O_2 existing in the solution as the source of Fenton reagent, The reaction process is as follows:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \#(1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \#(2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \#(3)$$

In electro-Fenton system, the generation of H_2O_2 and Fe^{2+} can be realized through a variety of ways, the reaction process is shown in Figure 1.

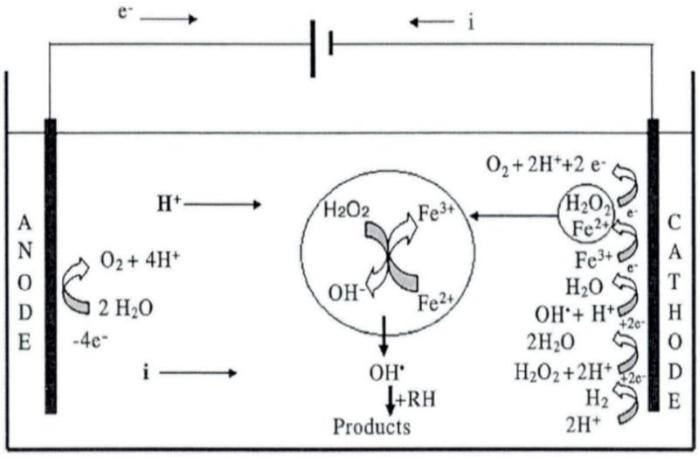

Figure 1. Schematic diagram of the main mechanism of the electro-Fenton reaction process.

Studies have shown that synergistic catalytic effects can be observed when metal ions are added to the electro-Fenton system. For example, Brillas found that the combination of copper ions (Cu^{2+}/Cu^+) and iron ions (Fe^{3+}/Fe^{2+}) showed enhanced catalytic performance [12]. Another study was carried out by Lin et al., who prepared a cobalt sulfide/graphytized carbon (Co_9S_8/PGC) composite through a synchronous carbonization process [13], the equation is as follows:

$$H_2O_2 + Cu^+ \rightarrow Cu^{2+} + \cdot OH + OH^- \#(4)$$

$$Cu^+ + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+} \#(5)$$

$$H_2O_2 + Co^{2+} \rightarrow Co^{3+} + \cdot OH + OH^- \#(6)$$

When transition metal Ce is used as catalyst, Assumpcao et al. [14] directly modify carbon materials with Ce metal particles. Due to the strong hydrophobicity of carbon felt and other materials, the loading capacity of CeO_2 is very low.

4. Experimental apparatus and analysis and test method

4.1 Experimental setup

A unique 15cm × 10cm × 18cm vessel, shown in Figure 2, made of engineered glass with a 2.6L capacity, was used. A 100mm × 80mm × 1mm conductor plate featured a DSA anode connected to the positive terminal and a Fe rod, acting as the cathode, linked to the negative terminal. The setup included a DC voltage regulator and a 15W UV lamp with 254nm wavelength, coupled with a ventilation system.

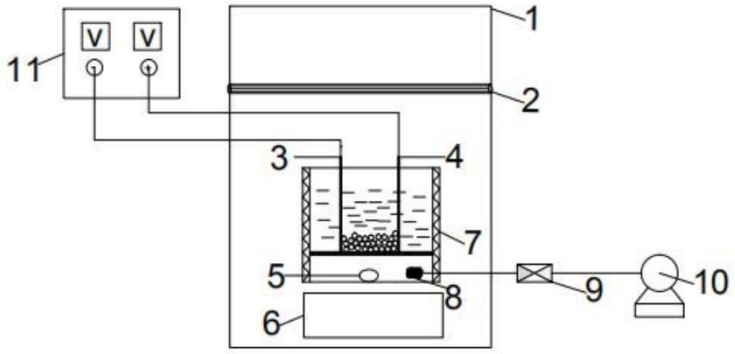

Figure 2. Schematic diagram of the experimental setup.

In Figure 2, 1 is the dark box; 2 is UV lamp; 3 is graphite plate electrode; 4 is titanium-ruthenium-iridium electrode; 5 is the rotor; 6 is magnetic stirrer; 7 is the reactor; 8 is the aeration head; 9 for air flow meter; 10 for air compressor; 11 is the power supply.

4.2 Water for experiment

To prepare the water sample, 0.08 g of crude oil was first accurately weighed in a reaction vessel and dissolved in 700 ml of water. Then 4 drops of surfactant were added and sonicated for 20 min using an ultrasonic cleaner to promote oil-water mixing and emulsification. After that, 5 grams of sodium sulfate (Na_2SO_4) powder and 2 drops of antifoaming agent were incorporated into the solution, and the acidity level of the solution was adjusted to 4 to complete the immediate configuration and use of water samples.

4.3 Laboratory equipment and reagents

Table 1. Test instrument

Serial number	instrument	Number
1	Dc regulated power supply	FPS-303D
2	Uv-vis spectrophotometer	UV-6000
3	Electronic analytical balance	PTX-FA120
4	Magnetic stirrer	MS-H280-Pro
5	Air compressor	ACO-318
6	PH meter	pHS-3E
7	254nm UV lamp	15W
8	Glass ware	several
9	eliminator	TC-100B
10	Drying oven	GZX-9846 MEB
11	Rotor flow meter	LZT-4T

Table 2. List of main reagents

Serial number	Reagent	Purity
1	Na_2SO_4	B
2	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	B
3	$C_{12}H_8N_2 \cdot H_2O$	B
4	CH_3COONa	B
5	H_2SO_4	A
6	$AgSO_4$	B
7	$K_2Cr_2O_7$	A
8	$FeSO_4 \cdot 7H_2O$	B
9	CH_3COONa	B

In Table 2, A represents purity as excellent grade purity and B represents purity as analytical purity.

4.4 Experimental analysis index

1.1.1. Determination of CODcr.

The calculation method is as shown in Equation 7, and the unit is mg/L.

$$\mathrm{COD_{cr}}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = \frac{\mathrm{C}(\mathrm{V_1} - \mathrm{V_2}) \times 8000}{\mathrm{V_0}} \#(7)$$

Amidst this scenario, C represents the potency of the ferrous ammonium sulfate benchmark amalgamation, V_1 signifies the intensity of the ferrous ammonium sulfate benchmark amalgamation dispensed within the pilot test, V_2 marks the vigor of the ferrous ammonium sulfate benchmark amalgamation employed in the hydrologic sample, whilst V epitomizes the volume of the hydrologic sample.

1.1.2. Oil removal rate was determined.

The oil content was determined by gravimetric analysis and calculated as in Equation 8.

$$\frac{\mathrm{W_1} - \mathrm{W_2}}{\mathrm{V}} \times 1000 \#(8)$$

Here, W_1 is the beaker refueling weight, W_2 is the beaker weight, and V is the water sample volume.

5. Experimental analysis

The distance between the plates was fixed at 9 cm, the reaction cycle lasted for 120 minutes, the stirring rate was maintained at 400 RPM, The acidity level was calibrated to a value of 4, and the introduction concentration of the conductive agent was set to 5 grams per liter.

5.1 Effect of different experiments on oil content

Figure 3 contrasts our device with a baseline electro-Fenton setup using a C anode, tracking oil content changes under varying aeration intensities in an identical solution.

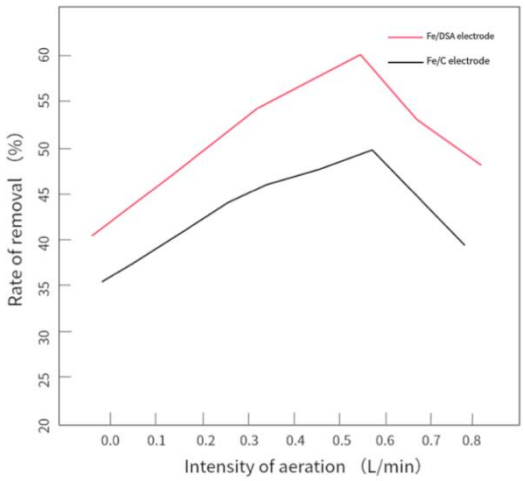

Figure 3. Effect of aeration intensity on oil removal of different electrodes.

In Figure 3, it's evident that moderate aeration boosts oil removal efficiency for both electrodes, yet excessive aeration reduces removal rates, possibly altering reaction dynamics. Notably, the DSA electrode exhibits superior performance, following an initial rise from 40% removal at no aeration to a peak of around 60% at 0.5 L/min. Post-peak, removal rates decline, settling at approximately 48% at 0.8 L/min aeration intensity.

The aeration volume was adjusted to 0.6L/min, the initial concentration was 50mg/L, 254nm UV light was used, 8 and 15W were used for reaction, and the reaction time was 60min. Figure 4 shows the effect of UV light with different power on the removal rate.

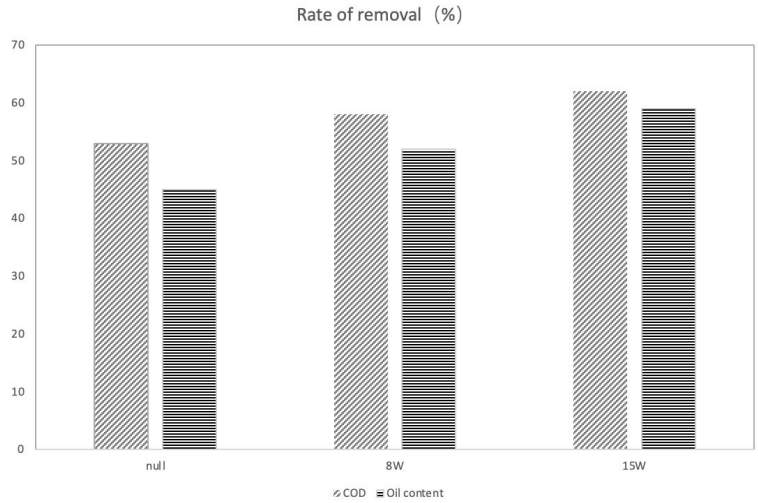

Figure 4. Comparison of removal rates under different UV intensities.

As observed in Figure 4, the abatement percentages of Chemical Oxygen Demand and grease concentration lie within a bracket of 40% to 50% when devoid of ultraviolet illumination. Under conditions featuring ultraviolet radiation, an augmentation in the ultraviolet luminosity corresponds to an elevation in the abatement percentage. Specifically, the diminishment ratio of COD and grease at an ultraviolet intensity of 8 watts spans from 50% to 60%. Moreover, the attenuation proportion of COD and grease escalates beyond 60% under a 15-watt ultraviolet intensity, this suggests that ultraviolet exposure serves to enhance the efficacy of effluent remediation.

6. Conclusion

The core innovation of this study lies in the selection of DSA electrodes and the integration of UV photocatalytic technology. Due to its excellent electrochemical stability and electrical conductivity, DSA electrode ensures the long-term reliability of the system, effectively avoids the

corrosion and loss of traditional electrode materials, greatly extends the life of the equipment and reduces maintenance costs. The introduction of UV light significantly improves the efficiency of Fenton reaction, accelerates the mineralization rate of refractory organic matter, ensures the effect of deep purification of wastewater, and significantly reduces the consumption of H_2O_2, diminishes the exploitation of energy and chemical substances, not merely curtailing the expenditure of processing, but also mitigating the latent peril of subsequent contamination, thereby enhancing the security and eco-friendliness of effluent remediation.

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