

Aniline removed from simulated wastewater by electro-Fenton process using electric energy from photovoltaic modules

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ABSTRACT

The novel electro-Fenton powered by photovoltaic modules, which is with double anodes and Pd/MWCNTs catalyst, is constructed to remove aniline from wastewater. The results show that when current density is 50 mA/cm², removal efficiency of aniline (REOA) is the highest and up to 95.1% in 15 min. REOA for electrode plate of 20 mm × 20 mm is the highest and 96.6% in 30 min. There is an optimal pH of 2. When current ratio between the Pt anode B and the iron anode A is 15:1, its REOA is the highest and 94% in 30 min, and a first order kinetics can be concluded. Aniline is removed obviously by the electrode reactions and H₂O₂ oxidation, and the strong oxidation of hydroxyl radical is also an important pathway. In the open, SII solar irradiation intensity of 460 W/M² is the largest, and REOA is the highest and 88.6% in 30 min. Surprisingly, although SIIA solar irradiation intensity of 670 W/M² is higher than SIII's, SIIA REOA for natural wastewater is lower than SIII's for simulated wastewater. The adopted process is feasible and aniline can be removed from wastewater in a safer and lower-cost way.

Keywords: Aniline wastewater; Electro-Fenton; Pd/MWCNTs catalyst; Double anodes; Photovoltaic modules

1. Introduction

Aromatic compounds are a kind of organic substances with benzene ring structure. They are stable in structure, highly toxic and difficult to decompose in nature [1]. Thereinto, aniline, a kind of aromatic compounds and an important organic intermediate, is widely used in chemical dyes, medicine, pesticides and national defense industries. However, aniline discharged into water body has the characteristics of long-term residue, bioaccumulation, carcinogenicity, teratogenicity and mutagenicity, which will bring great disasters to the ecological environment and seriously endanger peoples' health [2–11]. Therefore, aniline, like some aromatic compounds, is listed as one of the priority pollutants to be controlled in most countries [2–11].

In China, aniline, due to its severe hazard, is also listed in the blacklist of environmental priority control pollutants and is strictly restricted to discharge into wastewater [2–11].

At present, the main treatment technologies for refractory aniline can be divided into physical methods (e.g., adsorption, extraction, etc.), biological methods (e.g., activated sludge, A²O processes, etc.) and chemical methods (e.g., advanced oxidation processes, ozonation, etc.) [2–11]. However, aniline is difficult to degrade biologically due to its toxicity. The cost of adsorbent is high and its reproducibility is poor, which also prevents the adsorption process from spreading [5]. Fortunately, chemical methods, due to high effectiveness, are considered as promising processes and widely used. Among them, Fenton oxidation method, in which strongly oxidizing hydroxyl radical

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($\cdot\text{OH}$) is produced under the action of Fe^{2+} ion and H_2O_2 and then is used to oxidize the refractory organic matter in water [Eqs. (1) and (2)], is of good treatment effect, thorough reaction and no secondary pollution. Therefore, Fenton oxidation is widely used to treat refractory organic matter in wastewater [5–33]. When the process is used, H_2O_2 , Fe^{2+} and acid-base reagents generally need to be added. At present, their adding modes mainly include one-time adding and continuous adding. Thereinto, for one-time adding, a great deal of sludge will be generated and utilization efficiency of reagents is very low, too. Likewise, for continuous adding, the adding devices will lead to higher one-time investment and larger labor intensity [19]. In addition, the storage safety risk of H_2O_2 hinders its wide application, too. For that, many researchers have been trying their best to improve the above shortcomings [5–33]. In recent years, the emergence of electro-Fenton method has just made up for the above drawbacks [8–25]. When electro-Fenton is utilized, an appropriate concentration of H_2O_2 is generally in-situ produced by the electrochemistry processes [Eqs. (3)], which will decrease the cost and safety risk of H_2O_2 . However, O_2 , acid-base reagent and Fe^{2+} ion [Eqs. (1)–(3)] still need to be added externally. Thus, the labor intensity is still very high. In addition, excessive addition of iron salt will make iron content in the discharged water exceed the Emission Standard and affects the senses of water body. Moreover, the adopted electric energy is mainly provided by fossil fuels and needs to be transformed into a stable DC power. What's more, in some remote regions, this technology application is still restricted due to the operation cost and power supply.



Synthesis of hydrogen peroxide [25,34]:



Cathode:



Anode:



Oxidation of hydrogen to hydrogen peroxide [25,34]:



Electric dissolution of iron anode:



Therefore, in this paper, the photovoltaic modules are used to supply electric energy, O_2 and H_2 produced by water electrolysis are utilized to in-situ synthesize H_2O_2

under the action of Pd/MWCNTs catalyst [Eqs. (4)–(6)], and then strongly oxidizing hydroxyl radical ($\cdot\text{OH}$), which is produced by the reaction between H_2O_2 and Fe^{2+} from the electric dissolution of iron anode (provide Fe^{2+} in wastewater, Eq. (7)), is used to oxidize aniline in wastewater [Eqs. (1) and (2)]. Consequently, the process only requires renewing the catalyst and the iron anode regularly, both H_2O_2 and Fe^{2+} are in-situ generated and replenished gradually. Additionally, the renewable energy is used, and so the operating cost is reduced significantly. Therefore, the adopted process overcomes the drawbacks of Fenton and common electro-Fenton [19] and is very suitable for removal of aniline in slightly polluted water body. Based on this, in this paper, the novel electro-Fenton powered by photovoltaic modules, which is with double anodes and Pd/MWCNTs catalyst, is constructed to remove aniline from wastewater. The aim is to provide a new idea for removal of aniline from wastewater in a safer and lower-cost way.

2. Materials and methods

2.1. Preparation of simulated wastewater

Firstly, 0.1 mol/L K_2SO_4 (Sinopharm Chemical Reagent Co. Ltd., China) electrolyte solution is prepared using deionized water. Then, a certain amount of solution containing 1 g/L aniline is diluted by the above electrolyte solution to a desired concentration to prepare wastewater containing aniline. Finally, according to the experimental requirements, pH of wastewater is adjusted by dropwise adding 1 mol/L H_2SO_4 or NaOH (Sinopharm Chemical Reagent Co. Ltd., China) solution.

2.2. Experimental setup and procedure

The schematic diagram of experimental setup is shown in Fig. 1. Prior to a trial, Pd/MWCNTs (Suzhou Tanfeng Technology Inc., China) catalyst of 0.5g is put into the glass beaker, and then 100 mL simulated wastewater containing aniline is poured into the beaker. Meantime, the anode plate A (Iron nail, $\Phi 2.5$ mm \times 45 mm), the graphite cathode plate (75 mm \times 25 mm \times 1 mm) and the anode plate B (Pt, 20 mm \times 20 mm \times 0.1 mm) are inserted into the beaker in parallel, and their depths are adjusted according to the experimental requirements. When the setup is used in the room, the anode plate B is connected with the positive pole of DC power supply (KXN-305D, Zhaoxin, China) through the sliding rheostat and the ammeter B. Similarly, the anode plate A is connected with the power supply through the ammeter A and the sliding end of rheostat, and the cathode plate is directly connected with the negative pole of power supply through a wire. Next, the magnetic agitator is turned on and run at a proper speed. Afterwards, the power supply is switched on. Finally, after current throughout the anode plate A and anode plate B is adjusted to a proper value, the timer is run to start timing. During a trial, a certain amount of water sample is taken from the beaker at a desired time interval, and then an equal volume of wastewater is quickly replenished into the beaker. When the trial is finished, all the samples to be tested are sent to centrifuge at 4,000 rpm for 5 min and the

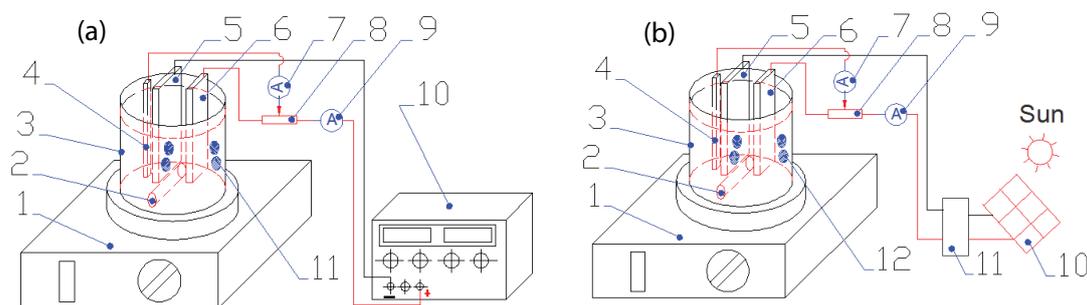


Fig. 1. Schematic diagram of the experimental setup (A: In the room; B: In the open). 1. Magnetic agitator; 2. Rotor; 3. Glass beaker; 4. Anode plate A; 5. Graphite plate cathode; 6. Anode plate B; 7. Ammeter A; 8. Sliding rheostat; 9. Ammeter B; 10. DC power supply (for A) or photovoltaic modules (for B); 11. Catalyst (for A) or Constant current controller (for B); 12. Catalyst (only for B).

supernatant is taken to analyze the relevant water quality parameters. Meantime, the precipitated Pd/MWCNTs catalyst is washed using distilled water and poured into a 100 mL plastic centrifuge tube. Next, it, together with the remaining water sample, is centrifuged at 3,000 rpm for 10 min. Finally, all the precipitated Pd/MWCNTs catalyst is dried in a vacuum drying oven for future use. Similarly, if a trial is carried out in the open, the anode plate B is connected with the positive pole of photovoltaic modules (Model XLY30M, Wuhan Solar Technology Co., Ltd, Hubei, China) through the sliding rheostat, the ammeter B and the constant current controller. Meantime, the anode plate A is connected with the photovoltaic modules through the ammeter A and the sliding end of rheostat, and the cathode plate is connected with the negative pole of photovoltaic modules through the constant current controller. After that, the operation procedures are similar to those in the room.

2.3. Analytical methods

Aniline concentration in wastewater is measured using a high performance liquid chromatography (HPLC) (Agilent 1260 Infinity, USA) equipped with a SB-C18 reverse-phase column (150 mm × 4.5 mm, 5 μm, Agilent, USA) at 30°C. pH value are measured by a pH meter (Hach 2000, Hach Company, USA). Current and voltage flowed throughout the electrodes are determined using a digital multi-meter (Model PROVA 803, Taiwan, China). Solar irradiation intensity is monitored by a digital solar power meter (TES-132, TES, China). Conductivity is analyzed using a conductivity meter (DDS-11C, INESA Scientific Instrument Co., Ltd, Shanghai, China).

3. Results and discussion

3.1. Feasibility of aniline removal

To verify the feasibility of aniline removed from wastewater by the novel electro-Fenton, the anode plate A in Fig. 1a is not inserted in wastewater temporarily. In addition, the experiments under different conditions are also carried out to explore the pathway of aniline removal when the process is adopted. During a run, initial concentration of aniline is 10 mg/L, pH is 2 and current density is 50 mA/cm². Additionally, Fe²⁺ ion is supplied temporarily by 0.09 mol/L FeSO₄ solution and its concentration is kept at 20 mg/L.

Fig. 2 demonstrates that for the adopted electro-Fenton system, when only catalyst and Fe²⁺ ion are added into wastewater, removal efficiency of aniline (REOA) is very low and is 17.4% in 30 min. As the power supply is turned off, oxygen and hydrogen in wastewater are very poor, and so the catalyst cannot fully exert its catalytic effect. However, due to a certain specific surface area of 233 M²/g, MWCNTs have a certain adsorption capacity. Therefore, the above results show that REOA is very low by the adsorption action of Pd/MWCNTs catalyst. When the power supply is turned on and Fe²⁺ ion is added, REOA increases gradually with time extending and it can attain to 64.7% in 30 min, which is mainly attributed to the electrode reactions of aniline. However, when the catalyst is added into wastewater and the power supply is turned on, REOA also improves progressively with time prolonging and efficiency of 84.7% can be achieved in 30 min. In addition, its efficiency is higher than that for the former two conditions. Apart from the action of electrode reactions, when the power supply is turned on, oxygen and hydrogen are produced due to water electrolysis, and subsequently H₂O₂ is in-situ synthesized in the presence of the catalyst [34]. Due to strong oxidation of H₂O₂, aniline in wastewater is further removed, which is perhaps a reason that its efficiency is higher than that for the former two conditions. Surprisingly, when the catalyst and Fe²⁺ ion are added together and the power supply is turned on (Namely electro-Fenton), aniline is quickly removed and its efficiency can reach 88.2% in 5 min, which indicates that the adopted process is efficient and feasible. Besides the fore-mentioned actions, more strongly oxidizing hydroxyl radical ([•]OH) is produced in the presence of Fe²⁺ ion and H₂O₂, and then aniline is thoroughly oxidized to be efficiently removed, which is another important pathway of aniline removal. Therefore, the pathway of aniline removal, when electro-Fenton process is used, can be considered as follows: aniline removal is very low by the adsorption action of Pd/MWCNTs catalyst, and the electrode reactions and H₂O₂ oxidation are obvious for aniline removal. Finally, the strong oxidation of hydroxyl radical is also an important pathway.

3.2. Effect of current density

Current density can reflect the migration situation of ions in wastewater, which not only affects the removal

efficiency of pollutants but also provides guidance for the current density distribution between the subsequent two anodes system. During a test, current density is adjusted by changing the output current of DC power supply. In addition, the other experimental conditions can be seen in Section 3.1 – Feasibility of aniline removal.

As can be seen from Fig. 3, for current density of 25, 37.5 and 50 mA/cm², aniline removal rate is very fast, their removal efficiency in 10 min can reach to more than 88%. However, when current density is 12.5 mA/cm², aniline removal rate is relatively slow, removal efficiency in 20 min increases all the time. In addition, Fig. 3 shows that at the same instant, REOA in 15 min increases with current density improving. For example, when current density is 50 mA/cm², REOA is the highest and up to 95.1% in 15 min. Conversely, while current density is 12.5 mA/cm², its efficiency is the lowest and 87.7%. In a certain range of current density, the greater current density is, the more H₂O₂ will be produced according to Eqs. (4)–(6) [34]. When concentration of Fe²⁺ ion is constant, the more strongly oxidizing hydroxyl radical will be generated [19,20,27], and then the more aniline will be removed, which is a possible reason that REOA in 15 min increases with current density improving.

3.3. Effect of anode plate size

The size of platinum electrode not only affects the space utilization ratio of the reactor but also does the operating cost. During a trial, the size of the adopted electrode is 10 mm × 10 mm, 15 mm × 15 mm, 20 mm × 20 mm, respectively. In order to slow down the reaction rate, initial concentration of aniline and current density are adjusted to 20 mg/L and 12.5 mA/cm², respectively. Additionally, the other experimental conditions can be seen in Section 3.1 – Feasibility of aniline removal.

Fig. 4 depicts that after initial concentration of aniline and current density are adjusted, aniline removal rate becomes slower than that of Section 3.2 – Effect of current density. For instance, in 20 min, all REOA always increases with time elapsing. Afterwards, REOA gradually becomes stable and 95% efficiency can be obtained. It is worth noting that at the same instant, REOA in 20 min increases with the size of electrode changing from 10 mm × 10 mm to 20 mm × 20 mm. Thereinto, REOA for 20 mm × 20 mm is the highest and 96.6% in 30 min. On the contrary, REOA for 10 mm × 10 mm is the lowest and 95.4%. The larger the size of electrode plate is, the greater the chance of collision with aniline in wastewater is, the more aniline is involved in the reaction [19,20,27], and so the higher REOA is, which may be a reason that removal efficiency for 20 mm × 20 mm is the highest.

3.4. Effect of pH

On the basis of the above researches, the experimental setup with two anodes (Fig. 1A) is run to explore removal of aniline when Fe²⁺ ion and H₂O₂ are simultaneously in-situ produced by an electrochemistry method. To provide a support for the subsequent application, the effect of pH on removal of aniline is studied. During the experiments, pH is changed by dropwise adding 1 mol/L H₂SO₄ or NaOH solution, the size of the adopted Pt electrode is 10 mm × 10 mm, initial concentration of aniline is 20 mg/L, and Fe²⁺ ion in solution is produced according to Eq. (7). In addition, current flowed through the Pt anode B is 0.15 A while current throughout the iron anode A, lasted only for 10 min, is 0.01 A.

As can be seen from Fig. 5 that for the same pH, when Fe²⁺ ion and H₂O₂ are simultaneously in-situ generated by the electrochemistry method, REOA all increases with time lengthening. Among them, when pH is 2, aniline removal rate is the fastest and efficiency of 88% can be gotten in

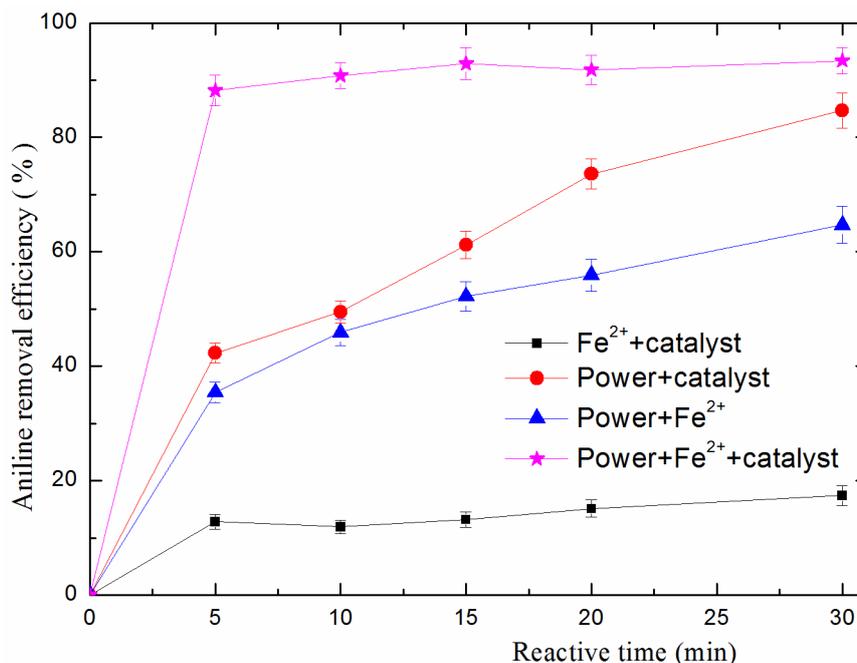


Fig. 2. Removal of aniline under different experimental conditions.

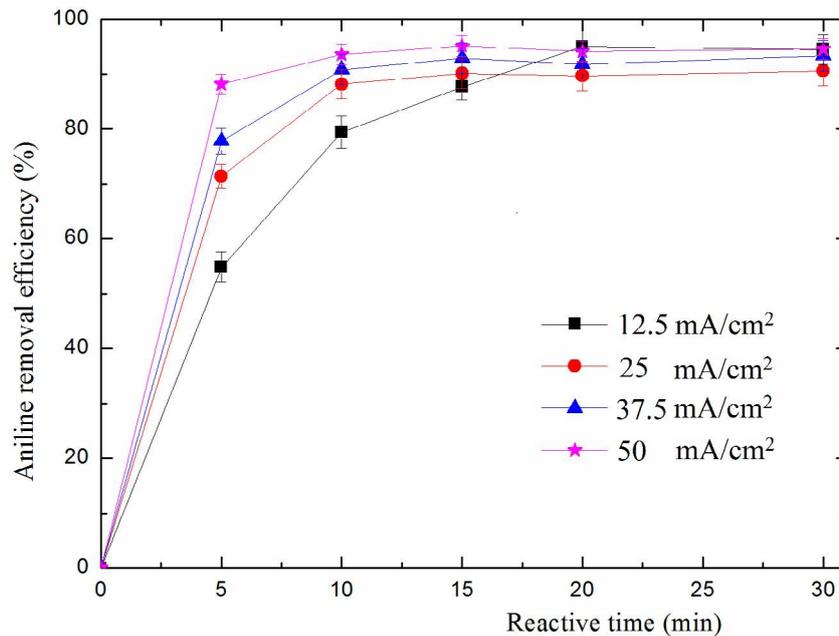


Fig. 3. Effect of current density on aniline removal.

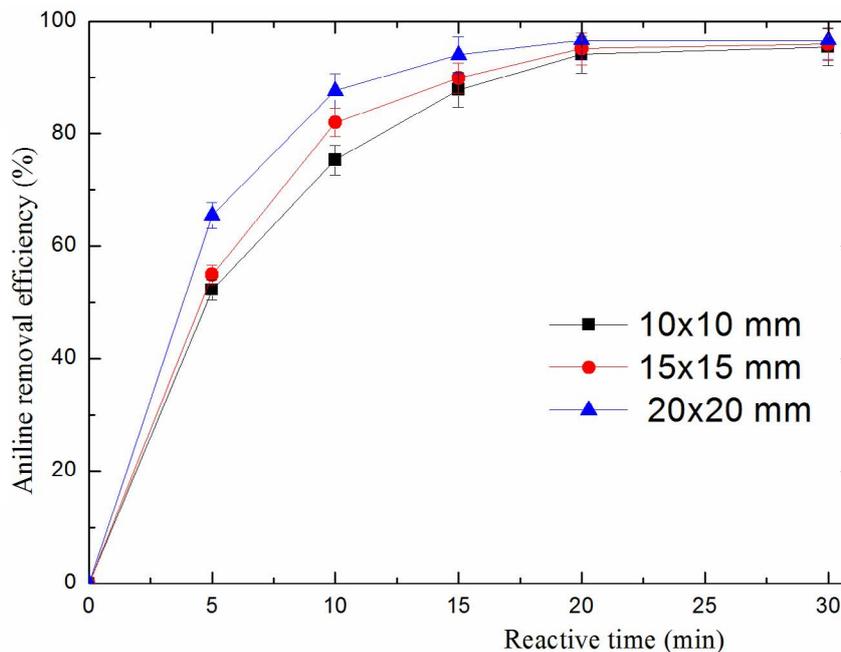


Fig. 4. Effect of electrode plate size on aniline removal.

15 min. Conversely, when pH is 7, aniline removal rate is the lowest and REOA is only 68.4% in 30 min. In addition, at the same instant, when pH varies from 1.5 to 2, REOA increases, too. However, when pH further climbs to 7, REOA shows a decreasing tendency, which suggests that there is an optimal pH of 2 where REOA is the highest and 92.1% in 30 min. It is reported that in an anodic oxidation reaction, there is always a competition phenomenon between oxygen evolution reaction and electrocatalytic degradation

of organic matter on the anodic surface. At the anode surface, acidic circumstance improves current efficiency for direct and indirect oxidation of organic pollutants by controlling oxygen evolution reaction [19,30,31]. According to Eqs. (3) and (6), oxygen evolution reaction further affects the yield of H_2O_2 and ultimately does the number of strongly oxidizing hydroxyl radical in-situ produced in wastewater. When pH is 2, the synergistic characteristic between hydroxyl radical oxidizing reaction and electrode reaction

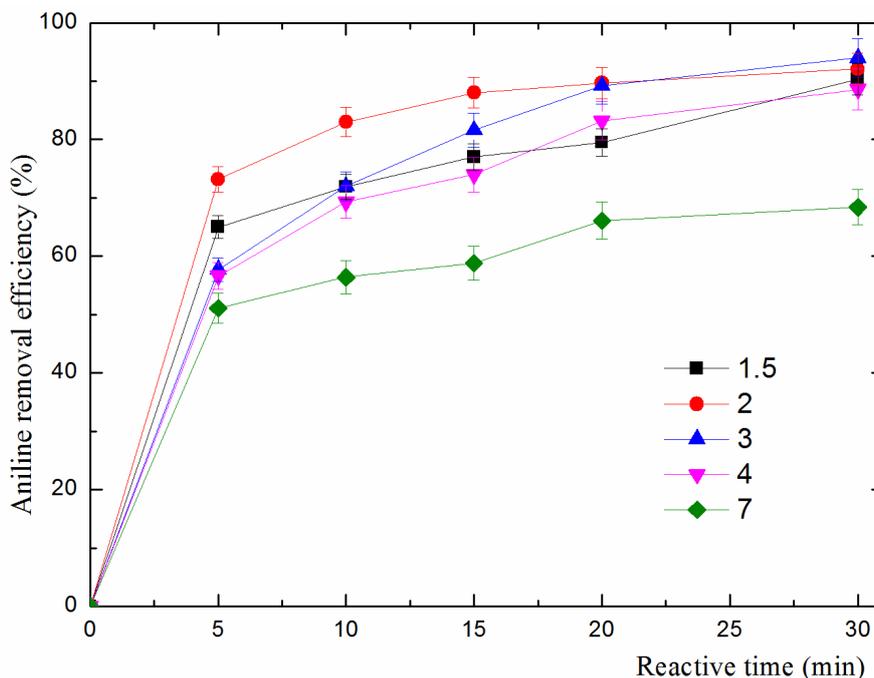


Fig. 5. Effect of pH on aniline removal.

may be optimal [19,30,31], and so REOA is the highest, which may be a reason that REOA for pH 2 is the highest.

3.5. Effect of current ratio between two anodes

As the constructed electro-Fenton setup has double anodes, the distribution of current flowed through the iron anode A and the Pt anode B is a very important parameter, which affects not only the in-situ yields of Fe^{2+} ion and H_2O_2 in wastewater but also the number of strongly oxidizing hydroxyl radical. Therefore, the effect of current ratio between the Pt anode B and the iron anode A on aniline removal is studied. During a run, current flowed through the Pt anode B is maintained at 0.15 A and current ratio is adjusted by changing current through the iron anode A. Meantime, current through the iron anode A is only lasted for 10 min. In addition, initial pH in wastewater is 2, and the other experimental conditions can be seen in Section 3.4 – Effect of pH.

Fig. 6 indicates that for the same current ratio, REOA all increases in 30 min with time extending. Thereinto, aniline removal rate for current ratio of 15:1 is the fastest while one for 15:4 is the slowest. Additionally, at the same time point, REOA for 15:1 is the highest and can attain to 94% in 30 min. Remarkably, when the current ratio is 15:3, a relatively higher removal efficiency can be also obtained. However, when the current ratio is 15:4, REOA is the lowest and is only 72% in 30 min, which implies that there may be two or more key factors affecting aniline removal and the specific reasons are worth further exploring. In addition, it is also noticeable in the experiments that the smaller the current ratio is, that is, the larger current of iron electrode is, the shorter the service life

of Pd/MWCNTs catalyst is and the catalyst precipitation performance is also significantly deteriorative.

In addition, Fig. 7 shows that for the above experimental conditions, the plots of $(-\ln C/C_0)$ vs. time (t) all demonstrate a linear relationship and a first order kinetics on aniline removal can be concluded. Thus, the model on aniline removal can be presented by the following equation:

$$\frac{dC}{dt} = KC \quad (8)$$

where C is the concentration of aniline, t is reactive time, and K is the removal rate constant and is represented by the slope in the plot of $(-\ln C/C_0)$ vs. time (t). It can be seen from Fig. 7 that correlation coefficients (R^2) are all high and more than 0.96, which shows that the above kinetics model can depict successfully aniline removal.

Meantime, Table 1 represents aniline removal efficiency for various treatment methods. Seen from Table 1, many methods have been implemented for aniline removed from wastewater. Moreover, as the reactive conditions are different, aniline removal efficiency and time required to reach efficiency are slightly different among the various processes. According to removal efficiency and time, the adopted process in this study can be considered as an alternative method for aniline removed from wastewater.

3.6. Effect of solar irradiation intensity in the open

When the constructed electro-Fenton setup (Fig. 1B) is utilized in the open, solar irradiation intensity has great influence on the output current and voltage of photovoltaic

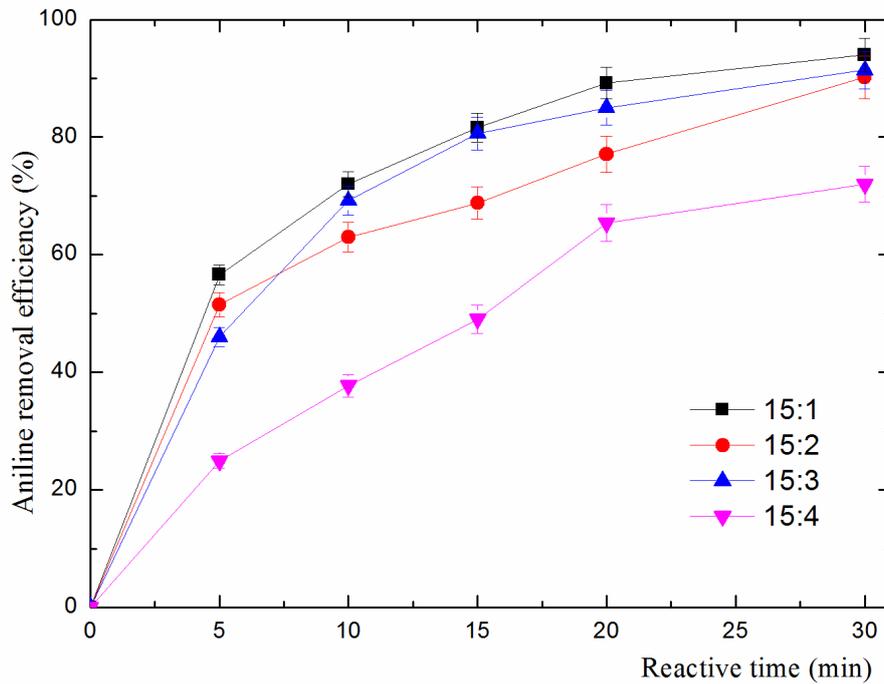


Fig. 6. Effect of current ratio between two anodes on aniline removal.

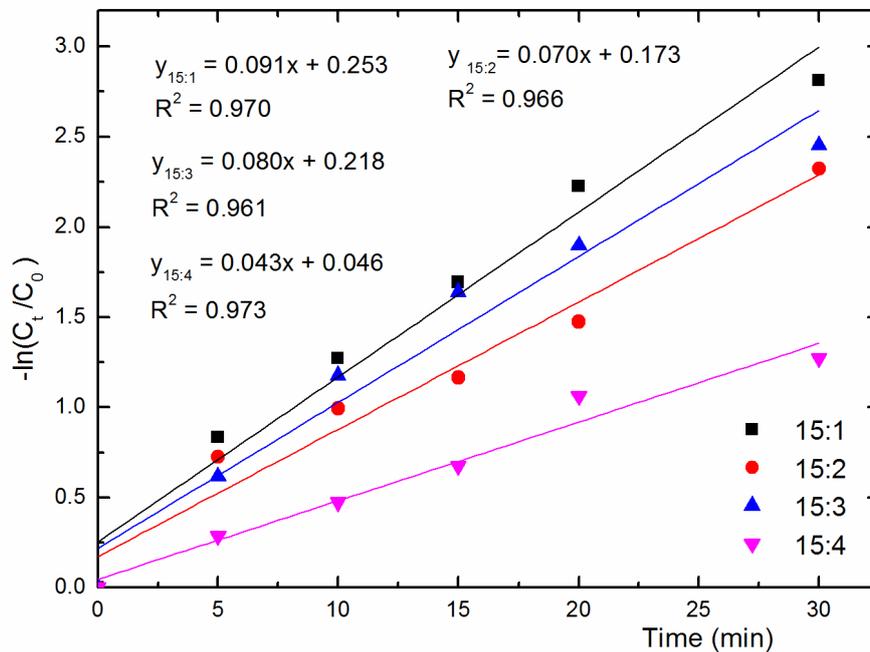


Fig. 7. Plot of $-\ln(C_t/C_0)$ vs. electrolysis time (t). C_0 : initial aniline concentration, mg/L; C_t : aniline concentration at the time of t , mg/L.

modules [19,35–38]. Meantime, it is also a prerequisite for deciding whether the adopted process can be popularized and used in the field of wastewater treatment. For this reason, the experiments are conducted. During a test, the photovoltaic modules provide the electric energy and the current ratio between two anodes is set at 15:1. Moreover, the

other experimental conditions can be seen in Section 3.5 – Effect of current ratio between two anodes.

As can be seen from Fig. 8, solar irradiation intensity of SII1 fluctuates between 400 and 530 W/M², and its average is 460 W/M², which is of typical solar irradiation feature on a cloudy day. For SII2 with an average of 215 W/M², solar

Table 1
Removal efficiencies of aniline using various treatment methods

Treatment method	Initial concentration	Reactive conditions	Efficiency and time	References
UV/CaO ₂ and UV/H ₂ O ₂	20 mg/L	[CaO ₂] ₀ = 1.0 g/L, [H ₂ O ₂] ₀ = 14 mM, pH = 7	90.1% in 2 h	[3]
Ozone/Zn(0)	10 mg/L	Initial pH range of 4–10, ozone of 4.80 mg/min, Zn(0) of 1.0 g/L	Almost 100% in 20 min	[4]
O ₃ /Fenton process	200 mg/L	Gravity factor of 100, initial pH of 5, Fe(II) of 0.8 mmol/L, H ₂ O ₂ of 2.5 mL	100% in 10 min	[5]
Heterogeneous Fenton	20 mg/L	293 K, initial pH of 5.4, catalyst dosage of 0.2 g/L, H ₂ O ₂ concentration of 4 mmol/L	100% in 35 min	[7]
Electro-Fenton	5 mg/L	Current density of 1.25 mA/cm ² , initial pH of 5.0, aeration flow rate of 0.10 m ³ /h, and Fe ²⁺ concentration of 0.20 mmol/L	99% in 60 min	[11]
Electro-Fenton	20 mg/L	pH of 2, current ratio between the two anodes of 15:1, catalyst dosage of 0.5 g	94% in 30 min	This study

irradiation intensity can be held stable in a small range of 190–230 W/M², which can stand for a sunny day with a weak solar irradiation. Similarly, for SII3, solar irradiation intensity is very steady with an average of 65 W/M², which is thought to be an overcast day with a weak solar irradiation.

Fig. 8 also shows that REOA in 15 min increases with solar irradiation intensity improving. Thereinto, for SII1, solar irradiation intensity is the largest and removal efficiency is always the highest in 30 min and can reach to 88.6%. Similarly, for SII3, solar irradiation intensity is the lowest and efficiency in 15 min is the lowest, too. However, REOA can also achieve about 66.2% in 30 min, which greatly exceeds our expectations. Remarkably, during the experiments, the current tests show that for SII1, current passing through the Pt anode B and the iron

anode A can be stabilized at 0.15 A and 0.01 A, respectively. Likewise, the voltage tests show that voltage between the anode and cathode only fluctuates slightly, which is similar to the characteristics of the used DC power supply. The above results also indicate that for high solar irradiation intensity of SII1, the output power of the adopted photovoltaic modules can fully meet the energy requirement of reaction. Similarly, for SII2, current through the anodes sometimes fluctuates. Moreover, voltage between the electrodes fluctuates evidently, which suggests that for low solar irradiation intensity of SII2, the output power of the photovoltaic modules is occasionally insufficient. In addition, for SII3, current through the anodes is very small and cannot be kept at the preset value, and voltage between the electrodes also

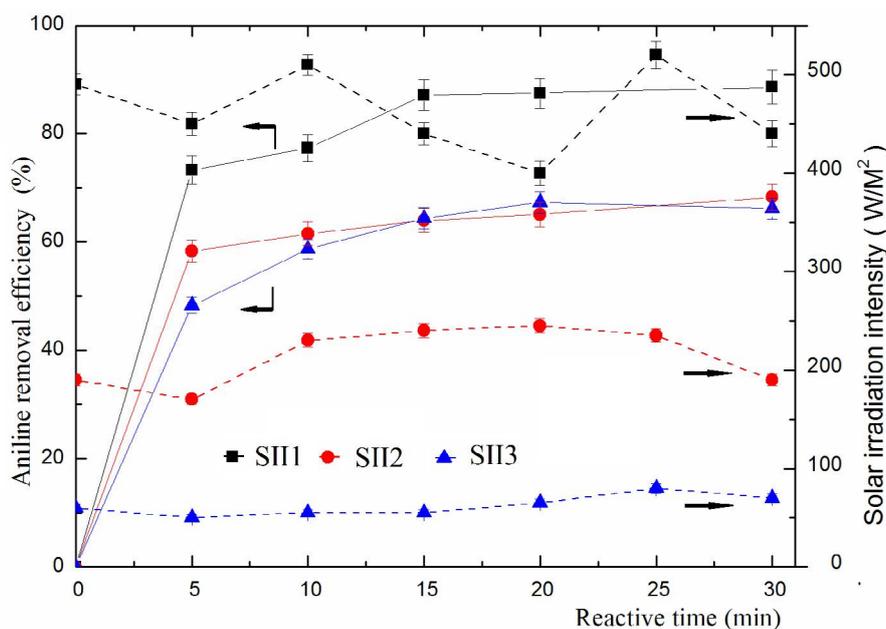


Fig. 8. Effect of solar irradiation intensity on aniline removal.

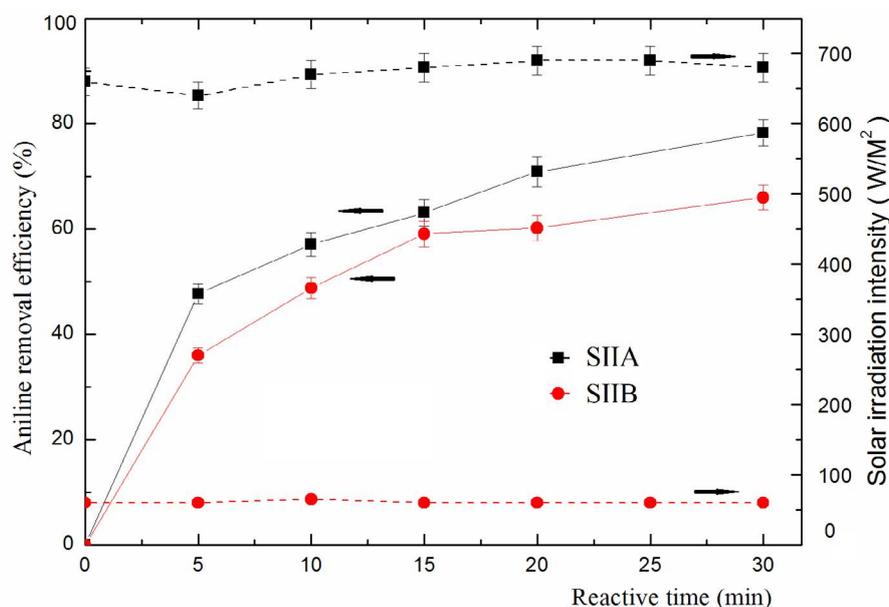


Fig. 9. Aniline removed from natural water body.

gradually drops, which implies that for very low solar irradiation intensity of SII3, the output power of the photovoltaic modules is seriously insufficient. Consequently, it is reasonable to consider that solar irradiation intensity has a direct impact on the output power of photovoltaic modules and further affects current through the anodes, which is perhaps a reason for the above results.

3.7. Aniline removed from natural water body

Aniline is added into natural water, which is taken from a pool near our campus, to prepare natural wastewater containing aniline of 20 mg/L. Meantime, pH value of wastewater is adjusted to 2 by dropwise adding 1 mol/L H_2SO_4 solution. Additionally, the other experimental conditions can be seen in Section 3.6 – Effect of solar irradiation intensity in the open.

Fig. 9 presents that solar irradiation intensity of SIIA is very high and can almost be stabilized at 670 W/M^2 . In contrast, solar irradiation intensity of SIIB is very low and can be kept steady at about 60 W/M^2 , too. In addition, for SIIA, REOA always increases with time prolonging and efficiency of 78.3% can be obtained in 30 min. Surprisingly, for SIIB, even if solar irradiation intensity is very low, high removal efficiency of 66% can be achieved in 30 min. However, for natural wastewater, although SIIA solar irradiation intensity of 670 W/M^2 is higher than SIII irradiation intensity of 460 W/M^2 (Section 3.6 – Effect of solar irradiation intensity in the open), SIIA removal efficiency is lower than SIII's, which is in contradict with the results in Section 3.6 – Effect of solar irradiation intensity in the open. Meantime, the current tests show that for SIIA and SIIB, current passing through the Pt anode is all only 0.11 A while current through the iron electrode is 1–2 mA, which are all lower than the corresponding values in Section 3.6 – Effect of solar

irradiation intensity in the open. In order to understand the above phenomena, the conductivity of the adopted natural wastewater and the fore-mentioned simulated wastewater is measured. It is found that the conductivity of the natural wastewater is only 800 $\mu S/cm$ while the conductivity of the simulated wastewater is 37000 $\mu S/cm$. Therefore, for the same voltage, current through high conductivity wastewater is generally larger. However, for a photovoltaic power supply, its output voltage is generally not more than the open-circuit voltage of 21.6 V [19,35–38], which is difficult to output larger current for low conductivity wastewater. Thus, current ratio between the Pt anode B and the iron anode A is difficult to reach the desired value, which may be a main reason that although SIIA solar irradiation intensity is higher than SIII's, SIIA removal efficiency for natural wastewater is lower than SIII's for simulated wastewater. Of course, for natural wastewater, even if solar irradiation intensity is very low, REOA of 66% can be obtained in 30 min. Therefore, it can be predicted that if the reactive time is extended, aniline can completely be removed, which shows once again that the adopted process is feasible.

3.8. Analysis on operating cost

The operating cost is a key factor to be considered when the adopted electro-Fenton process is used to remove aniline. During a trial, the operating cost mainly includes electrode consumption and energy consumption. For that, the operating cost on Section 3.6 – Effect of solar irradiation intensity in the open is estimated.

During each analysis, electrode consumption (C_{Fe}), which is used to remove aniline per mass unit, is calculated in accordance with literatures [33,35,37]. In addition, energy consumption (C_E), which is used to remove aniline per mass unit, is evaluated according to literatures [33,35,37].

Table 2
Analysis on operating cost for different solar irradiation intensity

	Solar irradiation intensity		
	SII1	SII2	SII3
C_{Fe} (kg/kg)	0.982	1.274	1.314
C_t (RMB/yuan kg)	12.77	16.56	17.08

However, as the photovoltaic modules are applied, the cost of energy consumption is neglected. Consequently, the theoretical operating cost (C_t) required removing aniline per mass unit is calculated in accordance with the following Eq. (9):

$$C_t = xC_{Fe} \quad (9)$$

where x is the price of electrode plate. During a test, the iron electrode plate is easily consumed. Consequently, the consumption of iron electrode determines the operating cost. At present, x is 13.00 RMB yuan/kg in China market.

Table 2 shows that when current flowing throughout the iron electrode is identical and the photovoltaic modules are adopted, the operating cost for SII1 is the lowest and 12.77 RMB yuan/kg and the running cost for SII3 is on the contrary and 17.08 RMB yuan/kg.

4. Conclusion

In this paper, the novel electro-Fenton powered by photovoltaic modules, which is with double anodes and Pd/MWCNTs catalyst, is successfully used to remove aniline from wastewater. REOA for current density of 50 mA/cm² is the highest and up to 95.1% in 15 min. REOA for electrode plate of 20 mm × 20 mm is the highest and 96.6% in 30 min. There is an optimal pH of 2. When current ratio between the Pt anode B and the iron anode A is 15:1, REOA is the highest and 94% in 30 min. Additionally, a first order kinetics can be concluded. Study on the pathway of aniline removal shows that the strong oxidation of hydroxyl radical ($\cdot\text{OH}$) is also an important pathway. In the open, for SII1, solar irradiation intensity with average of 460 W/M² is the largest, and removal efficiency is always the highest and 88.6% in 30 min. Surprisingly, although SIIA solar irradiation intensity of 670 W/M² is higher than SII1's, SIIA removal efficiency for natural wastewater is lower than SII1's for simulated wastewater. The adopted process is feasible.

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