A Novel Method for Efficient Electrochemical Treatment of Actual Dyeing Wastewater With Energy Saving

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A novel method for efficient electrochemical treatment of actual dyeing wastewater with energy saving

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Abstract: Electro-oxidation is a promising technology for wastewater treatment with bio-refractory organic and nitrogen pollutants; however, the high energy-demanding hinders its wide application. In this study, a novel method by regulating the significant parameter during electro-oxidation process timely for actual dyeing wastewater treatment with energy saving was studied. Operating factors (i.e., flow rate, initial pH value, electrode distance, and current density) were investigated for chemical oxygen demand (COD) and ammonia removal, and results indicated that current density was the key factor which obviously influenced the electrochemical performance. Indirect oxidation by active chlorine was then confirmed as the main reaction pathway for pollutants oxidation, and the relationship between the current density and the generation of active chlorine was established, suggesting that a large part of the generated active chlorine was not utilized effectively. Subsequently, a novel method by variation of current density timely based on the reaction mechanism was proposed; results indicated that, with similar pollutant removal efficiency, energy consumption could be reduced from 31.6 kWh/m^3 to 20.5 kWh/m^3. Additionally, the novel system was further optimized by Box-Behnken design: COD and ammonia removal efficiencies could reach 71.8% and 100% respectively, and energy-demanding could be reduced by 45.6%.

Keywords: Novel method; Parameter optimization; Removal efficiency; Energy saving; Box-Behnken design

1. Introduction

Textile industry is a traditional pillar industry in developing countries and has greatly contributed to the development of economy (Tang et al., 2021). However, the dyeing wastewater from textile production usually contains large amounts of residual dyestuffs, additives and inorganic salts (Aghili et al., 2021). The incompletely treated dyeing wastewater will pose a direct hazard to environmental safety and public health due to its highly toxic, mutagenic, and carcinogenic compositions (Patel et al., 2021). Biological treatment has been considered as one of the most cost-effective technologies for biodegradation of organic and nitrogen pollutants (Paz et al., 2017); but some non-biodegradable dyes impede biological activity, even causing the death of microorganism (Chen et al., 2019). Other techniques such as Fenton (Esteves et al., 2016), ozone oxidation (Xin et al., 2020), and membrane filtration (Cao et al., 2020), are also proposed for treating such wastewater; however, the potential secondary by-products hinder their wide applications (Bae et al., 2015; Yao et al., 2016a).

Nowadays, electro-oxidation has presented as a favorable approach for environmental remediation, especially for the treatment of bio-refractory wastewater (Meng et al., 2020; Chung et al., 2020). Ma et al. (2018) summarized that, compared with traditional physico-chemical methods, electro-oxidation is much suitable for the degradation of persistent color and pollutants from dyeing wastewater. Nippatla and Philip (2020) investigated the electrochemical performance for dyeing wastewater treatment; results indicated that 98.3% chemical oxygen demand (COD) removal

efficiency along with complete decolourization could be achieved under optimal conditions.

Although electro-oxidation has received great attention due to its advantages of environmental compatibility, easy handling, and no sludge production, it is a highly energy-demanding method which hinders its extensive application (Adeogun et al., 2021; Ozturk and Yilmaz, 2019). In recent decades, intensive attentions have focused on the electrode preparation (Xia et al., 2020), reactor design (Dória et al., 2020), multi-technology combination (Bustos-Terrones et al., 2021), and parameter operation (Aquino et al., 2014). Hamous et al. (2021) developed a carbon textiles electrode modified with Pt nanoparticles for electrochemical treatment of Orange G (OG) azo dyeing wastewater; results indicated that the removal efficiency of OG reached 91.8%, and energy saving could be up to 37.2%. Wang et al. (2020a) investigated the effects of frequency, pulse duty cycle, and current density on the electrochemical treatment of indigo carmine wastewater using a pulse power supply; after parameters operated, energy consumption of 35.5% was saved. In our previous work (Yao et al., 2021), a process control, namely stepping control of key parameter, was developed for the treatment of simulated wastewater with known contaminants by direct oxidation. Firstly, the degradation pathway of target pollutant was measured, i.e., intermediate products were detected. Then, the oxidation potentials of the target pollutant and its intermediate products were determined by the linear sweep voltammetry. Finally, stepping control of oxidation potential was performed timely to oxide the contaminants selectively based

on the degradation pathway of the target pollutant. The results indicated that pollutants could be efficiently removed, and energy saving could be up to 33.8%, i.e., it proved that operating key parameter regularly could achieve high contaminants removal and low energy consumption. However, the composition of actual wastewater is usually complex so that it is difficult to determine the type of pollutants (Ye et al., 2021; Liu et al., 2021). Thus, it is necessary to find a way to achieve non-selective oxidation of pollutants. Generally, in-situ electrochemical generation of excessive active radical is proposed as a promising method (Yang et al., 2019; Wang et al., 2020b). As reported by Díaz et al. (2011) and Wang et al. (2021), compared with the traditional method, pollutants elimination by the in-situ produced oxidants via parameter regulation seemed to be one of the most convenient methods to achieve the purpose. Though this method can promote the pollutant removal so as to save energy, a part of energy is still wasted on maintaining the active radical excess (da Costa et al., 2021). Herein, it's time to propose an applicable way to regulate the formation of oxidants regularly for efficient electrochemical wastewater treatment and reduce its energy-demanding.

In this study, a novel method, i.e., regulating key parameter timely, was developed for the treatment of actual dyeing wastewater. Firstly, the effects of flow rate, initial pH value, electrode distance, and current density on COD and ammonia removal were investigated, and a significant parameter was determined. Secondly, the reaction mechanism of the electro-oxidation process was studied to confirm the types of the active radicals which provided contributions to the pollutant removal, and the

relationship between the significant parameter and the generation of the dominated active radical was established. Then, the novel method by regulating the selected significant parameter was operated and validated to evaluate its efficiency and energy consumption. Finally, Box-Behnken design was applied to optimize the novel system for maximizing pollutant removal and minimizing energy consumption.

2. Materials and methods

2.1 Wastewater characteristics

The actual dyeing wastewater was provided by a dyeing factory located in Shaoxing (Zhejiang, China). The main characteristics of the actual wastewater were as follows: the COD concentration was 285±20 mg/L; the ammonia concentration was 35±2 mg-N/L; the pH value was 8.0±0.1; and the concentration of chloride ion was 1530±26 mg/L.

2.2 Electro-oxidation experiments

Electro-oxidation experiments were carried out in a self-made electrochemical cell equipped with a Ti/PbO_2 anode and two Ti cathodes. The anode was placed in the middle of the two cathodes, and each electrode has an effective area of 9 cm^2. A reservoir was connected with the electrochemical cell. During the experiments, the actual dyeing wastewater (250 mL) could be recirculated in the electrochemical system with a set flow rate by a peristaltic pump. An electrolysis time of 180 min was selected for each electro-oxidation experiment.

2.3 Analysis and calculation methods

COD and ammonia were measured by the dichromate method and Nessler reagent spectrophotometry, respectively. Active chlorine and chloramines were measured using the DPD standard method (Yao et al., 2021).

The current efficiency *CE* (%) was estimated as:

$$CE = \frac{[COD]_0 - [COD]_t}{8It} FV + \frac{3([NH_4^+]_0 - [NH_4^+]_t)}{14It} FV \quad (1)$$

where $[COD]_0/[NH_4^+]_0$ and $[COD]_t/[NH_4^+]_t$ are the COD/ammonia concentrations at time *0* and *t*, respectively; *I* is the applied current; *F* is the Faraday constant (96 485 C/mol); *8* is the oxygen equivalent mass (g/eq); *14* is the atomic mass of N; *3* is the electron transfer number from ammonia to N_2; *V* is the solution volume; *t* is the reaction time.

The energy consumption *E* (kWh/m^3) was calculated as follows:

$$E = \frac{UIt}{V} \quad (2)$$

where *U* is the voltage.

Response surface methodology based on Box-Behnken design (BBD) was selected as an experimental design to investigate the effect of significant parameter on pollutant removal and energy consumption. The three current densities were set as explanatory variables in BBD, and the pollutant removal and energy consumption were set as responses.

3. Results and discussion

3.1 Effect of the main parameters

The effect of flow rate, initial pH value, electrode distance, and current density on

electrochemical performance were investigated individually to determine the optimal conditions. **Fig. 1a** shows that, with the increase of flow rate, pollutant removal increased gradually at the beginning of the experiment, and then reached a maximum value with a flow rate of 150 mL/min. This finding implies that mass transfer limitation of pollutants existed at flow rate lower than 150 mL/min, and then reaction limitation hindered increasing pollutants degradation with further increase of flow rate (Huang et al., 2016). The effect of initial pH value is illustrated in **Fig. 1b**. The increase of initial pH value had a negative effect on COD removal. Such results might be related to the existence form of active chlorine, that is, HClO (E^0=1.49 V vs. SHE) mainly exists in the pH range from 3 to 8, and ClO^- (E^0=0.89 V vs. SHE) at pH > 8 (Zou et al., 2017). Although excellent ammonia removal efficiency was also obtained in acidic condition, initial pH value of 9 was also favorable for ammonia removal; the explanation was connected with the direct electron transfer which had been reported in our previous work (Yao et al., 2016b). **Fig. 1c** displays that an apex existed for the COD and ammonia removal efficiencies at electrode distance of 1 cm. Shortening the electrode distance can not only increase the potential between the solution phase and the electrode, but also reduce the mass transfer resistance; however, too small distance may cause electrode breakdown or short circuit, resulting in reduction of electro-oxidation performance (Kahraman and Şimşek, 2020). Additionally, **Fig. 1d** indicates that there was always an upward trend for COD removal with the increase of current density. The same phenomenon was observed on ammonia oxidation: it was completely removed as

158 current density of 20 mA/cm^2 was applied. These results were consistent with other
159 studies: high current density could accelerate the generation of active radicals and thus
160 promote the pollutant removal (Li et al., 2020).

161 According to the results shown in **Fig. 1**, an inflection point always existed for the
162 pollutant removal with flow rate, initial pH value, and electrode distance, that is, these
163 parameters could be easily optimized. However, the optimization of current density
164 would be further investigated combining reaction mechanism, current efficiency,
165 energy consumption, etc.

166 **3.2 Reaction mechanism**

167 Base on the results of optimization process, current density was selected as the key
168 factor to illustrate the oxidation mechanism during the electrochemical wastewater
169 treatment. As reported by many scholars (Ken and Sinha, 2021; Iskurt et al., 2020),
170 COD and ammonia are usually oxidized by direct (i.e., electron transfer) and indirect
171 (mainly by hydroxyl radical and active chlorine) oxidation. In order to reveal the
172 electrochemical performance of different oxidation pathways, several comparative
173 experiments were carried out. In the first group, *p*-chlorobenzoic acid (*p*CBA), which
174 could react with hydroxyl radicals (•OH) extremely fast but slowly by other oxidants
175 and direct electro-oxidation, was selected as the scavenger to measure the function of
176 •OH radicals (Yao et al., 2016b; Rosal et al., 2008). In the second group, Cl^- was
177 removed in advance by the chemical precipitation to avoid the disturbance of active
178 chlorine during the experiments. The third group combined the above mentioned

179 methods by utilizing the *p*CBA and silver ion to measure the electrochemical
180 performance by electron transfer. In sight of this, a comparison of the oxidation
181 pathways of COD/ammonia during the electro-oxidation process were investigated and
182 the results are shown in **Fig. 2**.

183 **Fig. 2a** presents that the COD removal was contributed by electron transfer, •OH,
184 and active chlorine. The order of dominance of these three pathways was active
185 chlorine > •OH > electron transfer. Moreover, with the increase of current density, the
186 function of active chlorine became more and more obvious, while the role of electron
187 transfer decreased gradually. This phenomenon might be in connection with the
188 chlorine evolution reaction (**Eq. (3)**): more electron was consumed to generate active
189 chlorine. Additionally, similar results were observed for ammonia removal, as shown
190 in **Fig. 2b**. All the results indicated that the COD and ammonia were mainly removed
191 by active chlorine in this case.

192 $$2Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

193 Because of the importance of active chlorine, the variations of its concentration
194 with different current densities are measured and displayed in **Fig. 3**. The results
195 indicated that the generation of active chlorine increased with electrolysis time, and it
196 was positively correlated with current density. As the current density ranging from 10
197 mA/cm^2 to 25 mA/cm^2, the production of active chlorine increased exponentially.
198 However, compared with the phenomenon in **Fig. 2**, the COD/ammonia removal rate
199 contributed by active chlorine increased slowly with respect to the current density. Such

200 results suggested that the produced active chlorine was excessive, and a large part was
201 not utilized effectively in the electro-oxidation process. Thus, it seems that a feasible
202 way to enhance the electrochemical performance and reduce the energy consumption is
203 to conduct the chlorine evolution reaction and improve the utilization ratio of active
204 chlorine.

205 **3.3 A novel method for wastewater treatment**

206 Based on the above investigation, current density was undoubtedly determined as
207 the key factor to achieve the aims of high efficiency and low energy consumption for
208 wastewater treatment. A novel method by variation of current density (VCD) timely
209 was conducted, that is, the current density was controlled and decreased from 20 to 15,
210 and 10 mA/cm^2 gradually for each electrolysis time of 60 min. As shown in **Fig. 4a**, the
211 removal efficiencies of 73.0% and 100% were achieved in the VCD system for COD
212 and ammonia, respectively, which were higher than the efficiencies obtained by current
213 density of 15 mA/cm^2 (66.3% COD; 97.4% ammonia) and close to 20 mA/cm^2 (75.1%
214 COD; 100% ammonia). Besides, the current efficiency of VCD was compared with the
215 traditional electrochemical system as displayed in **Fig. 4b**. It indicated that the current
216 efficiencies decreased from 34.6% to 25.6%, and 21.2% with the increase of current
217 density from 10 mA/cm^2 to 20 mA/cm^2, respectively. Fortunately, 27.7% current
218 efficiency was obtained by VCD. More significantly, the VCD system also had an
219 advantage in energy saving: the energy consumption was calculated as 20.5 kWh/m^3
220 which was approximately equal to the required energy with current density of 15

221 mA/cm^2 (20.2 kWh/m^3) and much lower than that of 20 mA/cm^2 (31.6 kWh/m^3).

222 The variation of active chlorine generation in electrolysis is shown in **Fig. 5a**. A
223 linear relationship between the concentration of active chlorine and electrolysis time
224 could be observed during the VCD, which was different with the situation in traditional
225 electrochemical process (**Fig. 3**). It indicated that the stable growth of active chlorine
226 concentration could ensure the efficient oxidation of pollutants, rather than to oxidize
227 pollutants by generating excessive active chlorine, suggesting that the energy utilization
228 efficiency could be greatly improved. **Fig. 5b** displays the concentration profiles of
229 chloramines with different current densities in electrolysis. Fortunately, after 180 min
230 electrolysis, the generated chloramine concentration in all cases was negligible,
231 especially for current density of 20 mA/cm^2 and VCD. **Fig. 5c** shows that the pH value
232 decreased obviously in electrolysis as the current density increased, which was in
233 accordance with the above results of chlorine evolution reaction (**Eqs. (4)** and **(5)**). For
234 the VCD system, the pH variation was relatively stable compared with the traditional
235 electrolysis.

236 $$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (4)$$

237 $$HClO \rightarrow ClO^- + H^+ \quad (5)$$

238 **3.4 Optimization of the novel method using BBD**

239 Box-Behnken design was selected to provide an advisable way to regulate the
240 interactions between pollutant removal efficiency and energy consumption (Sharma
241 and Simsek, 2020; Tak et al., 2015). Herein, three current densities (A, B, C) were
242 chosen as the explanatory variables of BBD. The detailed levels of the current densities

are listed in **Table S1**, where the range for current density A is 15−20 mA/cm^2, for current density B is 12.5−17.5 mA/cm^2, and for current density C is 10−15 mA/cm^2. An electrolysis time of 60 min was arranged for each stage. And the current density was set to decrease gradually from A to C. Besides, the above results indicated that ammonia could be efficiently removed in this electrochemical system; thus, COD removal efficiency was selected as the evaluation indicator of pollutant degradation. Subsequently, seventeen runs of individual experiments with different current densities were required to fit the three-factor BBD (**Table S2**). Moreover, normality of data was estimated by means of normal probability plot (**Fig. S1**) which showed that residuals generally fell near the straight line. Such results supported normal distribution and confirmed the applicability of the model for well-fitting of the data. The response contour diagrams for the interactive effect of three current densities on the corresponding experimental results are shown in **Fig. 6**, and their related 3D surface diagrams are shown in **Fig. S2**. For the effect of the current densities on the COD removal, the A-B plot indicated that the contour values increased obviously when the B increased, and it was also highly linked with A; the A-C plot showed that A is the significant factor for the COD removal over C; besides, the B-C plot also depicted that the increase of current density B was beneficial to the COD removal. When it came to the impact on energy consumptions, similar results could be observed. Such results obtained from the BBD were consistent with the phenomena as mentioned in **Figs 1** and **4**.

By regulating the effect of each explanatory variable in a reasonable operating range, the optimal operating parameters of A, B and C were predicted as 18.1, 14.7, and 11.6 mA/cm^2, respectively. After optimization, the model values of the pollutant removal efficiencies and the energy consumptions were experimentally verified. **Table 1** shows that the experimental results were in good agreement with the model results. As shown, actual removal efficiencies of 71.8% and 100% were obtained for COD and ammonia respectively, and energy consumption of 17.2 kWh/m^3 was calculated. Compared with the traditional electrolysis (20 mA/cm^2), though the COD removal efficiency decreased slightly from 75.1% to 71.8%, the energy consumption was saved by 45.6%.

4. Conclusion

A novel method for efficient treatment of dyeing wastewater by electro-oxidation was investigated. Main factors, such as flow rate, initial pH value, electrode distance, and current density, were studied to reveal their impacts on the pollutant removal, and the results of electrochemical performance indicated that the current density was the dominant factor. The reaction mechanism was then explored, suggesting that COD and ammonia were mainly oxidized by active chlorine. Simultaneously, the relationship between the current density and active chlorine generation was established; results indicated that improving the utilization ratio of active chlorine was favorable for pollutant degradation and energy reducing. A novel method by variation of current density timely to conduct the chlorine evolution reaction was thus presented, suggesting

that energy-demanding could decrease from 31.6 kWh/m^3 to 20.5 kWh/m^3. Further investigation of the interactive effect of current densities on energy saving was predicted by BBD; results indicated that the energy efficiency could be enhanced: with a high level of pollutant removal efficiency, the energy saving could be up to 45.6%.

Ethical Approval Not applicable

Consent to Participate Not applicable

Consent to Publish Not applicable

Authors Contributions

Jiachao Yao: formal analysis, investigation & writing;

Sini Lv: formal analysis & investigation;

Zeyu Wang: validation & data curation;

Liyong Hu: review & methodology;

Jun Chen: resources, writing & review

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Competing Interests

The authors declare that they have no competing interests.

Availability of data and materials

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

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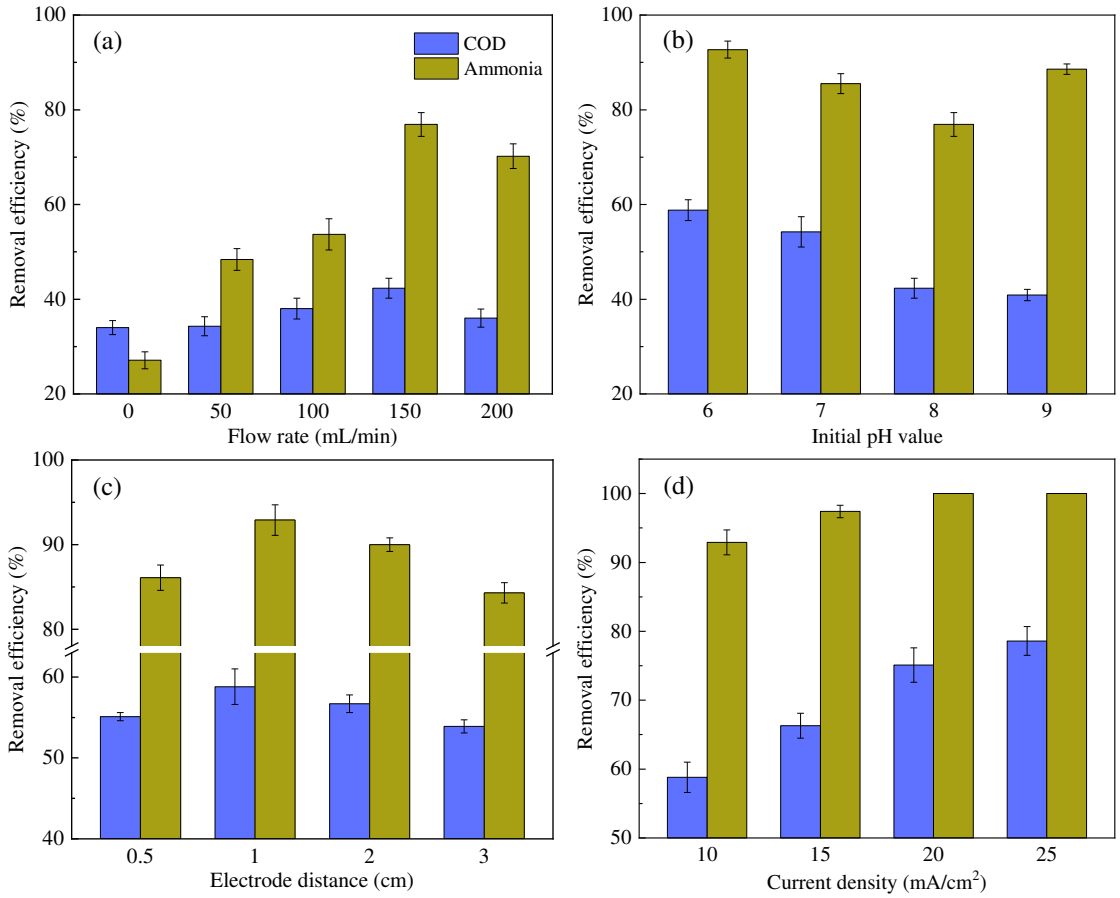
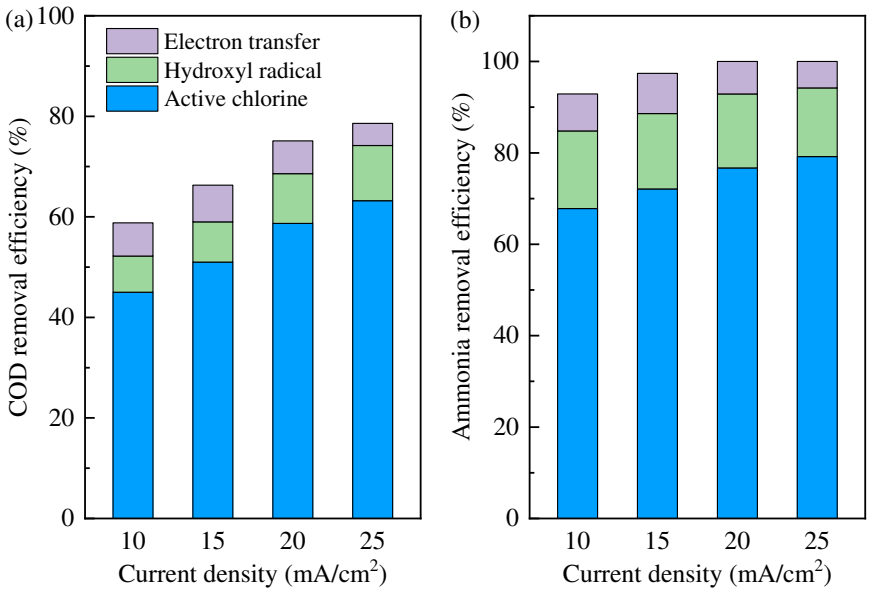


Fig. 1. The effect of (a) flow rate, (b) initial pH value, (c) electrode distance, and (d) current density on COD/ammonia removal.



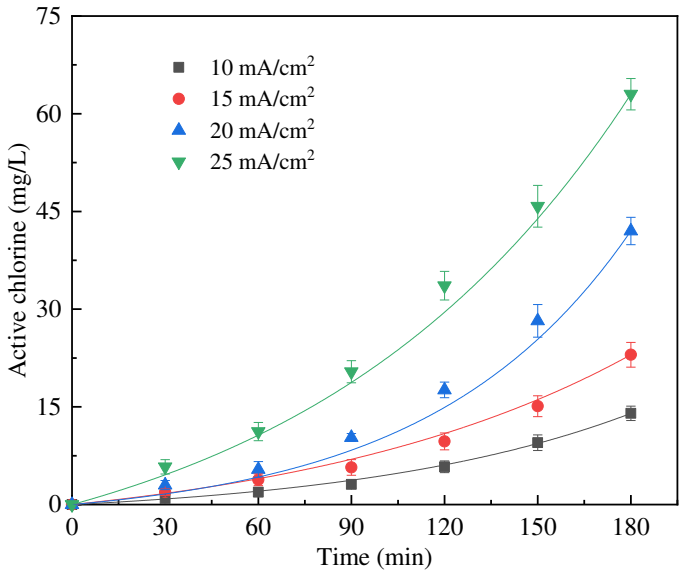
448

449 **Fig. 2.** Reaction mechanism for (a) COD and (b) ammonia oxidation with different

450 current densities. (Flow rate of 150 mL/min, initial pH value of 6, electrode distance of

451 1 cm)

452

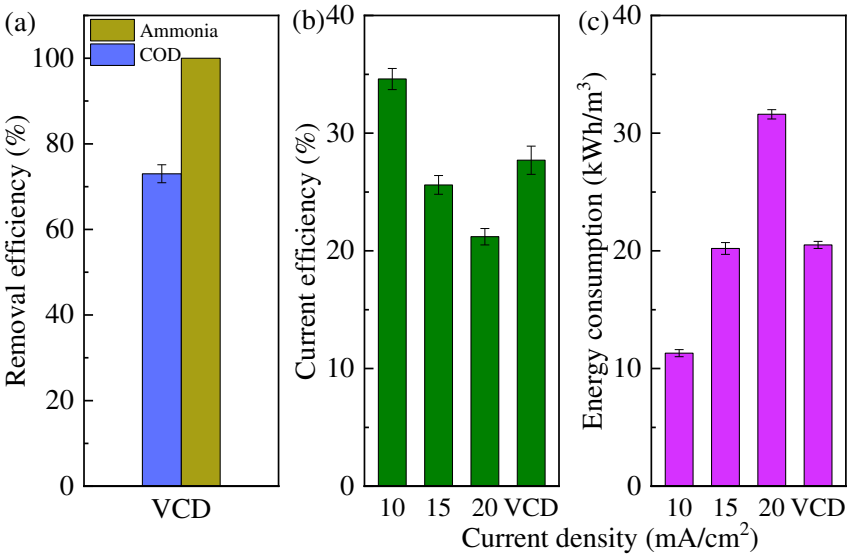


453

454 **Fig. 3.** The effect of current density on active chlorine generation. (Flow rate of 150

455 mL/min, initial pH value of 6, electrode distance of 1 cm)

456



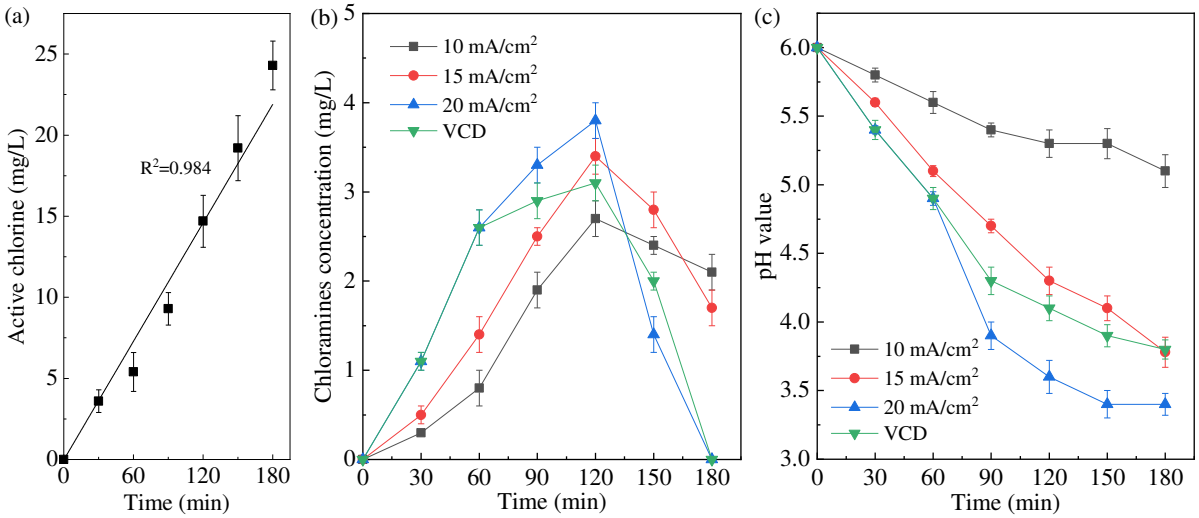
457

458 **Fig. 4.** The effect of current density variation on (a) removal efficiency, (b) current

459 efficiency, and (c) energy consumption. (Flow rate of 150 mL/min, initial pH value of

460 6, electrode distance of 1 cm)

461



462

463 **Fig. 5.** The variation of (a) active chlorine concentration, (b) chloramines concentration,

464 and (c) pH value. (Flow rate of 150 mL/min, initial pH value of 6, electrode distance of

465 1 cm)

466

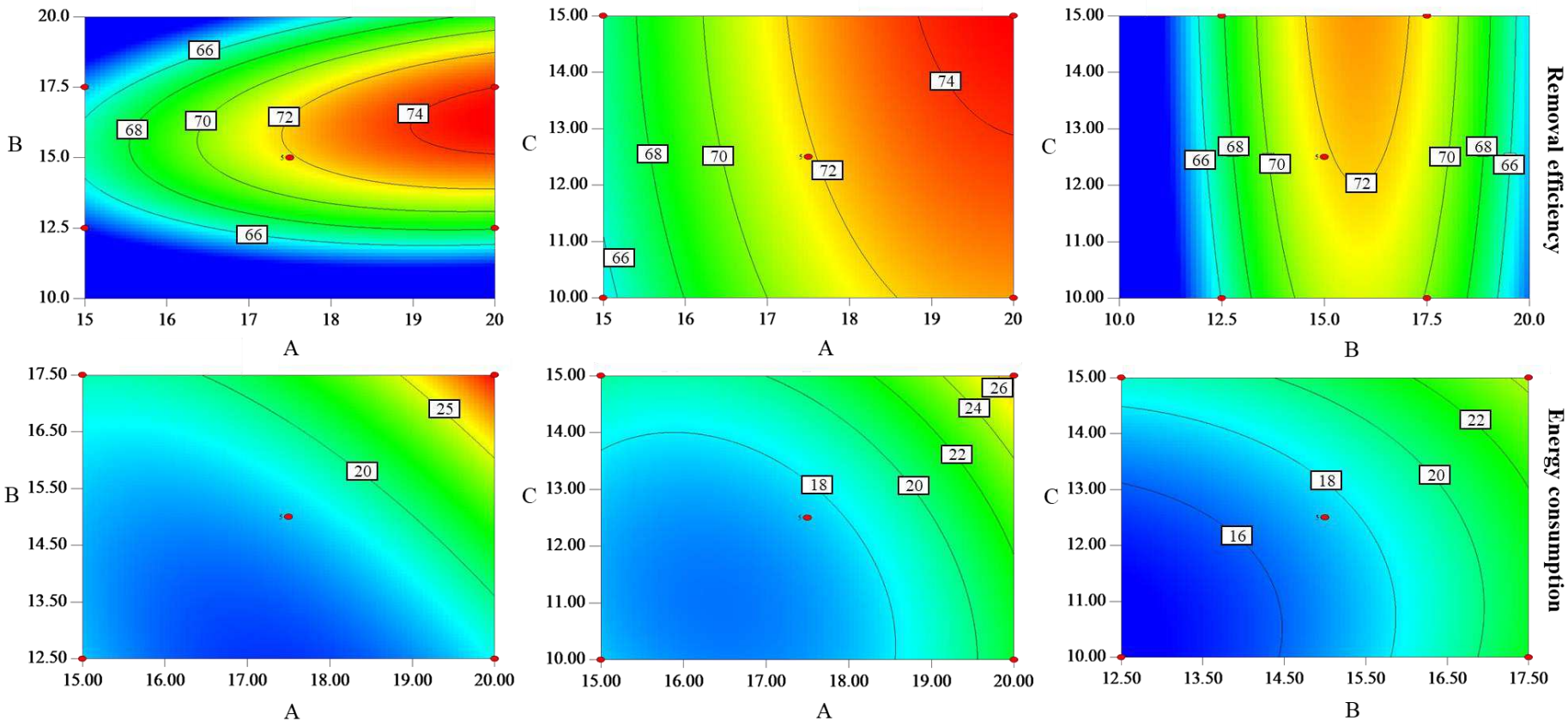


Fig. 6. Response contour diagrams of Box-Behnken designs for the variation of current density (A, B, and C) on the COD removal and energy consumption. The first and second row in the figure refer to the removal efficiency and energy consumption, respectively. The change of color from blue to red represents an increase of removal efficiency/energy consumption.

471 **Table 1**. The determination and verification of BBD for maximizing removal efficiency and minimizing energy-demanding.

Condition	A (mA/cm^2)	B (mA/cm^2)	C (mA/cm^2)	COD removal (%)	Ammonia removal (%)	Energy consumption (kWh/m^3)
Predicted	18.1	14.7	11.6	72%	/	17.1
Actual	18.1	14.7	11.6	71.8%	100%	17.2
Traditional	20	20	20	75.1%	100%	31.6

472

Supplementary Files

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- Supportinginformation.docx