

Electrochemical Oxidation Combined with Adsorption: A Novel Route for Low Concentration Organic Wastewater Treatment

Xu Hao^{1,*}, Guo Hua¹, Feng Jiangtao¹, Wang Dan¹, Liao Zhengwei², Wang Yu², Wei Yan¹

¹ Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an, 710049, China

² Water Affair Science and Technology Research Institute, Shaanxi Water Affair Group, Xi'an, 710021, China

*E-mail: xuhao@xjtu.edu.cn

Received: 8 April 2019 / Accepted: 27 May 2019 / Published: 30 June 2019

Electrochemical oxidation treatment is an efficient method for the mineralization of bio-refractory organics, but not an economic method for its high energy consumption. The results of electrochemical degradation of Acid Red G in aqueous solution showed that high organic concentration was beneficial for reducing the average energy consumption. Adsorption method has good enrichment effect on low concentration organic wastewater, but it has no degradation ability. In order to overcome the weakness of these two methods, a novel route which use the adsorption method as the pretreatment method for electrocatalytic treatment, was proposed for resolving the high energy consumption issue, especially for the low concentration organic wastewater. The results of by using the Acid Red G, Acid Red 6B and Methyl orange as the target indicated that the combined process would be a good alternative for the organic wastewater treatment, especially when the organic concentration was low. After electrochemical treatment, the biotoxicity of the concentrated solution is reduced and the biodegradability is improved. These indicated that the treated solution could be returned to the biochemical treatment system and be further treated by the biochemical method.

Keywords: electrochemical oxidation treatment; adsorption; energy consumption; combined process

1. INTRODUCTION

Electrochemical oxidation treatment (EOT) has been developed for decades and reached a promising stage in degrading toxic or bio-refractory organic pollutants efficiently because of its versatility, high energy efficiency, environmental compatibility, and high cost effectiveness [1-3]. However, the EOT is not an economic method for completely organic mineralization due to the high energy consumption (*EC*). For instance, the *EC* was 45.6 kWh·kgCOD⁻¹ for the degradation of cationic red X-GRL (500 mg·L⁻¹) by PbO₂ electrode under the constant current density (4.8 mA·cm⁻²) [4].

Similarly, PbO_2 electrode consumed $26.13 \text{ kWh}\cdot\text{kgCOD}^{-1}$ to reach 95% COD removal of auramine-O dye degradation under the constant current density ($50 \text{ mA}\cdot\text{cm}^{-2}$) [5]. Therefore, Yao [6] and Shao [7] pointed out that the EOT should be served as a pretreatment of the toxic pollutant for subsequent treatment.

It is well known that hydroxyl radicals ($\cdot\text{OH}$), which are responsible for the oxidation of organic matters and oxygen evolution, are generated during EOT reaction [8]. When the EOT process is under mass transport control, the formed $\cdot\text{OH}$ is not responsive for the degradation process but for the oxygen evolution side reaction. This would decrease the current efficiency and increase the *EC*. Thus, the primary reason for the high *EC* is due to the mass transport control during the degradation process, which is typical for low concentration of reactants. It is necessary to develop new methods to enhance the mass transport process of the EOT, especially for the situation under low concentration of reactants.

Adsorption has a long history of enriching organic matter [9-11]. Its basic principle is to fix organic matter on its surface by physical or chemical means through the specific structure or functional groups of adsorbents. The greatest advantage of the method is that the process can be used to concentrate the organic pollution of the wastewater and reduce the wastewater volume. The biggest disadvantage of this method is that it only realizes the phase transfer of organic matter, which means the concentrated organic pollution can not be mineralized by the adsorption process. It needs to be connected with methods that can thoroughly treat organic matter, such as electrocatalytic oxidation process.

In order to overcome the weakness of these two methods, we attempted to combine the electrochemical oxidation with adsorption processes. The adsorption process is expected to concentrate the organic matters and reduce the volume of the wastewater for further treatment. Then, the electrochemical oxidation is used to treat the desorption solution which is concentrated compared with the original wastewater.

In this work, the PANi- TiO_2 composite which was synthetic by our group, was used as the adsorbents [10, 11]. The PbO_2 electrode was served as the anode in the electrochemical oxidation. First, Acid Red G (ARG) was chosen as the model compound for the adsorption-EOT method. Then, Acid Red 6B (AR6B) and Methyl orange (MO) were used as the organic target. Finally, an actual low concentration wastewater from a biochemical treatment system was used to demonstrate the feasibility of the combined process in real wastewater treatment.

2. MATERIALS AND EXPERIMENTS

2.1 Materials

All chemical agents used in this paper were analytical reagent grade or higher and were used without further purification. The preparation method of PbO_2 electrode was described in Ref [12-14]. The preparation method of PANi- TiO_2 composite adsorbent was described in Ref [10, 11].

2.2 Electrochemical oxidation

The electrochemical oxidation tests for simulation wastewater were conducted in batch using an undivided electrolytic cell under galvanostatic condition. The active volume for the electrolytic cell was 130 mL. The solution was cycled by a peristaltic pump between the electrolytic cell and the tank. The current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ was supplied by a WYK-303B potentiostat/galvanostat. The PbO_2 electrode ($2\text{cm}\times 4.5\text{cm}$) served as the anode and the cathode was copper sheet (the same size with the anode), with a distance of 2.0 cm between the electrodes. The experiments were carried out at room temperature. During the experiments, liquid samples were withdrawn from the electrolytic cell every 10 min for the UV-vis spectrophotometer (Agilent 8453) and COD analysis (ET 125 SC, CSB/COD Reactor). The maximum adsorption wavelength of ARG, AR6B and MO molecular is 503 nm, 466 nm and 464 nm, respectively. The 5 days BOD were determined according to the Standard Methods (A. D. Eaton et al., APHA, AWWA, WEF, Baltimore, 2005).

The electrochemical oxidation tests for actual wastewater were conducted in an undivided electrolytic cell without circulation system. The applied current density was $100 \text{ mA}\cdot\text{cm}^{-2}$. The electrode group combined by the PbO_2 electrode and titanium sheet was used for the oxidation. The actual area for the PbO_2 electrode was 360 cm^2 . The experiments were carried out at room temperature. During the experiments, liquid samples were withdrawn from the electrolytic cell every 1 h for the UV-vis and COD analysis.

2.3 Adsorption and desorption experiment

All adsorption and desorption experiments were carried out in the dark condition at room temperature. The suspension containing $10 \text{ mg}\cdot\text{L}^{-1}$ of dye solution (10 L) and $2 \text{ g}\cdot\text{L}^{-1}$ of PANI- TiO_2 adsorbent was stirred for 1 h. Then the suspension was separated into treated solution and used adsorbent. The desorbed processes were carried out by dipping the exhausted PANI- TiO_2 adsorbent in 0.1 mol/L NaOH solution for 60 min and solid-liquid separation by vacuum filtration. The filtrate was as the desorbed solution. Then the desorbed solution was degraded by electrochemical oxidation process mentioned in Section 2.2.

2.4 Data analysis

The color removal efficiency of organic solution in electrochemical oxidation can be calculated as follow:

$$\eta_{color} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where η_{color} is the color removal efficiency at t , A_0 is the UV-vis absorbance value in maximum adsorption wavelength of initial wastewater sample and A_t is the absorbance value in maximum adsorption wavelength of the wastewater samples at the given time t .

The COD removal efficiency of organic solution in electrochemical oxidation can be calculated as follow:

$$\eta_{COD} = \frac{COD_0 - COD_t}{COD_0} \times 100\% \quad (2)$$

Where η_{COD} is the COD removal efficiency at t , COD_0 is the COD value of initial wastewater sample ($\text{mg}\cdot\text{L}^{-1}$) and COD_t is the COD value of the wastewater samples at the given time t ($\text{mg}\cdot\text{L}^{-1}$).

The average energy consumption per gram (EC , $\text{kWh}\cdot\text{g}^{-1}$) of organic solution in electrochemical oxidation can be calculated as follow:

$$EC = \frac{50}{3} \cdot \frac{U_{cell} \cdot I \cdot t}{c_0 \cdot \eta \cdot V} \quad (3)$$

Where U_{cell} is the average cell voltage (V), I is the current during the reaction (A), t is the electrolysis time (min) and V is the volume of the treated solution (mL). When the η in formula (3) was η_{color} , EC was the average energy consumption per gram organic. When the η in formula (3) was η_{COD} , EC was the average energy consumption per gram COD.

The average current efficiency (CE, %) of organic solution in electrochemical oxidation can be calculated as follow:

$$CE = \frac{COD_0 - COD_t}{8It} \times FV \quad (4)$$

where F the Faraday constant ($96487 \text{ C}\cdot\text{mol}^{-1}$)

2.5 Luminous bacteria bioassay

For the acute toxicity test, *Photobacterium phosphoreum* T3 (China General Microbiological Culture Collection Center, China) was cultured in enriched medium overnight at 20 °C while shaking at 120 r/min. The test was carried out according to an improved method which derived from the national standard method of China (Water quality—Determination of the acute toxicity - Luminescent bacteria test. GB/T 15441-1995). Luminescence inhibition assay was performed in test tubes using a Modulus™ Single Tube Multimode Reader (Turner Biosystems, America). For each test, 434 μL and 867 μL of the bacterial suspension and water sample was added into each tube, respectively. Each sample was conducted in triplicate. 0.3% of NaCl solution was used instead of water sample in control. After 15 min of exposure at 20° C, the relative light unit (RLU) of *P. phosphoreum* T3 was measured on the Modulus™, and the acute toxicity of the sample on *P. phosphoreum* T3 was expressed as the relative luminosity (X%).

$$X\% = \frac{\bar{LU}}{LU_0} \times 100\%$$

where LU_0 is the RLU of *P. phosphoreum* T3 exposed to the blank control, and \bar{LU} is the RLU to the average of triplicate samples. The larger X% value means the smaller toxicity.

3. RESULTS AND DISCUSSION

3.1 Different initial ARG concentration

The color removal efficiency and energy consumption of ARG degradation for different initial

concentration ($10\text{-}100\text{ mg}\cdot\text{L}^{-1}$) are presented in Fig. 1. Almost complete color removal can be achieved even at high ARG concentration. As shown in Fig. 1a, it would take more time to achieve the complete decolorization for higher concentration solution. Meanwhile, the pseudo-first-order rate constant (k) decreased with the increase of initial ARG concentration, as shown in the Fig. 1b. These results confirmed that higher organic concentration led to lower η_{color} and k . This is consistent with our previous work [13, 15, 16] and other researchers' reports [17-20]. However, the tendency of EC_{ARG} was opposite to that of the η_{color} . Fig. 1c shows the EC_{ARG} for different initial ARG concentration during the electrochemical degradation. EC_{ARG} decreased with the increase of initial ARG concentration. For instance, the EC_{ARG} after 30 min electrolysis is 0.201, 0.108, 0.0694, 0.0592, 0.0551 and 0.0452 $\text{kWh}\cdot\text{gARG}^{-1}$ when the initial ARG concentration are 10, 20, 40, 60, 80 and 100 $\text{mg}\cdot\text{L}^{-1}$, respectively. These results indicated that EOT process consumes less energy consumption for high-concentration wastewater than for low-concentration wastewater [16]. This phenomenon was probably explained in terms of diffusion control.

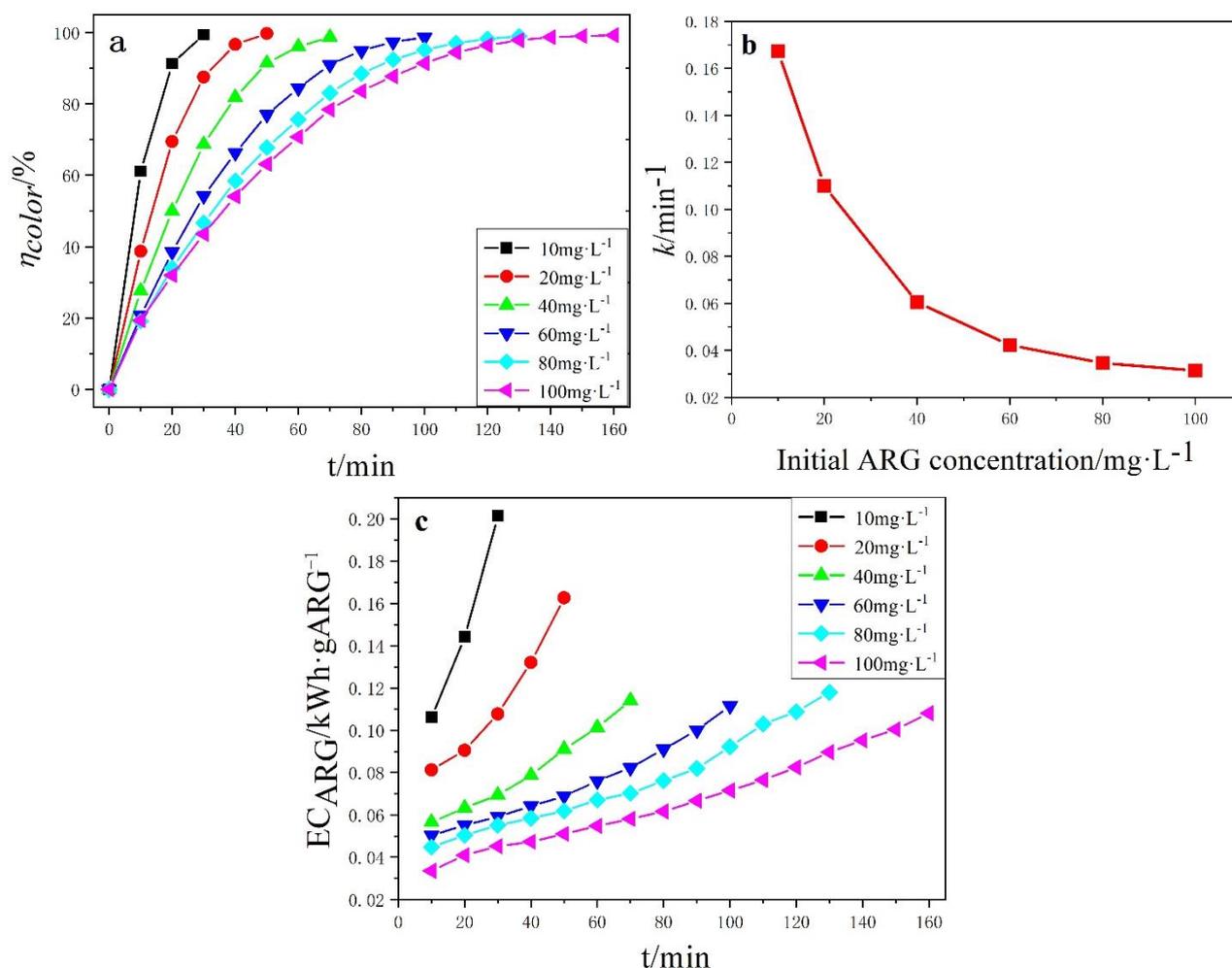
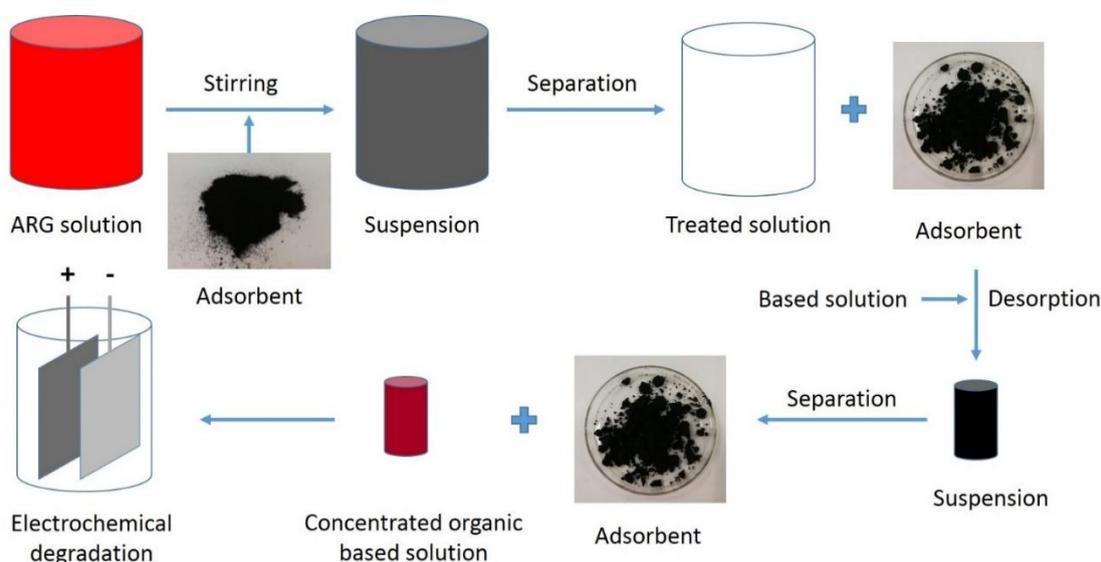


Figure 1. Color removal efficiency of ARG (a), the pseudo-first-order rate constant (b) and average energy consumption per gram ARG (c) under different initial concentration

According to the literature [19], the electrocatalytic oxidation process is controlled by mass transfer. At low initial ARG concentrations, the electrochemical reaction is faster than the diffusion process. The dye molecule was expected to be degraded completely at the electrode-solution interface. When the initial ARG concentrations increased, the amount of ARG molecule achieved the anode surface was larger than that in the low concentration solution. Thus, there were more ARG molecules reacting with the $\cdot\text{OH}$ on the anode surface in the high concentration solution [21, 22]. As a matter of fact, the amount of $\cdot\text{OH}$ generated on the surface of PbO_2 anode at a given current density was fixed. Active free radicals generated on the electrode surface are insufficient for pollutant degradation with increasing ARG concentration. Then the η_{color} and k decreased with the increase of the initial ARG concentrations, while EC_{ARG} decreased with the increase of the initial ARG concentrations. These results confirm that an adsorption pretreatment, which can be used to concentrate the organic pollution of the wastewater, would be beneficial for reducing the energy consumption of the EOT.

3.2 Combined method for low concentration ARG solution

In order to figure out whether the adsorption-EOT process is efficient than the single EOT process, more experiments were carried out. The scheme for the adsorption-EOT process was shown in Scheme 1. For the first step of the combined process, the initial dye wastewater ($10 \text{ mg}\cdot\text{L}^{-1}$, 10 L) was treated by the PANI-TiO₂ adsorbent as shown in Scheme 1. Then the separated adsorbent was treated by desorption solution and the azo dye desorbed and entered into the desorption solution. In order to simulate different concentration multiple, different NaOH solution volume was used (2 L, 1 L and 500 mL). The desorption efficiency of all the process was 100%. Thus, the concentration multiple was 5, 10 and 20 when the used NaOH solution volume was 2 L, 1 L and 500 mL, respectively. Finally, the desorption solution with higher azo dye concentration was treated by the electrochemical oxidation process. For the single EOT process, the treatment process was directly carried out in the 10-L dye wastewater.



Scheme 1. The adsorption-desorption-EOT method flow chart for low concentration ARG wastewater treatment

Fig. 2 shows the results of the η and EC for different concentration multiple. From Fig. 2a and 2b, one can easily find that the combined process showed better color removal and COD removal performance than the single EOT. The η_{color} at 6 h was 47.2%, 86.9%, 97.8% and 100% when the concentration multiple was 1, 5, 10 and 20. The η_{COD} at 6 h was 22.4%, 25%, 54.6% and 63.5% when the concentration multiple was 1, 5, 10 and 20. The removal efficiency increased as the concentration multiple increased. At the same time, the EC of the combined process was less than that of the single EOT, as shown in Fig. 2c and 2d. All these results confirmed that the adsorption-EOT process in ARG solution treatment showed a more-efficiency and less-energy-consumption than the single EOT process. The adsorption process was acted as a pretreatment of the EOT process, which reduced the mass control limitation during the EOT process, as mention above in Section 3.1.

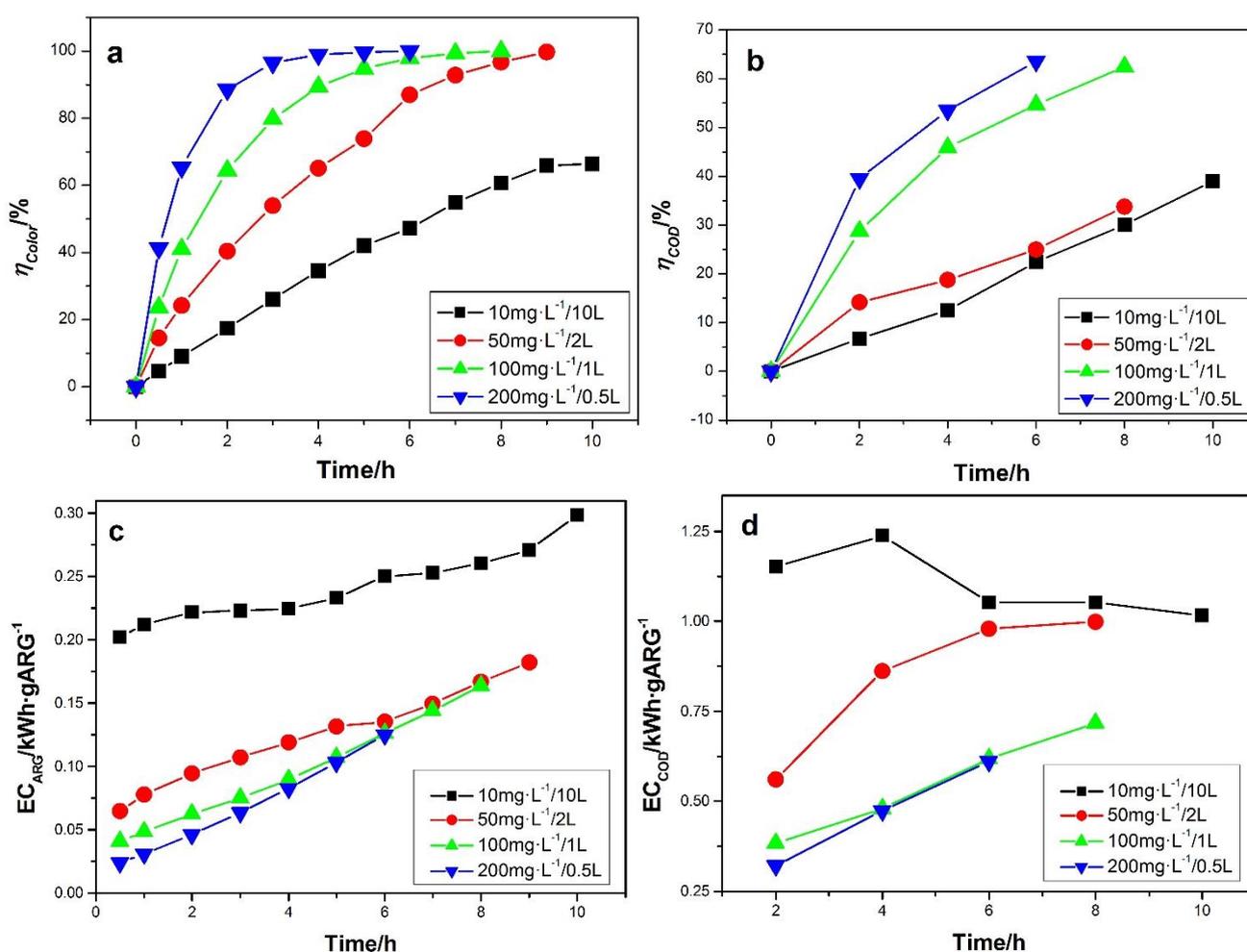


Figure 2. ARG Color removal efficiency (a), COD removal efficiency (b) and the average energy consumption per gram ARG (c) and per gram COD (d) under different concentration multiple

3.3 Combined method for other organic materials

To prove the general applicability for the adsorption-EOT method, Acid Red 6B (AR6B) and

Methyl orange (MO) were used as the organic target. The concentration multiple for both target was 20. The experimentation was in keeping with Scheme 1. The desorption efficiency of all the process was 100%. Fig. 3 shows the results of the η_{color} and η_{COD} for AR6B and MO. In Fig. 3a, one can find that the AR6B color removal efficiency was 49.1% and 99.6% at 6 h for the $10 \text{ mg}\cdot\text{L}^{-1}$ -10L sample and $200 \text{ mg}\cdot\text{L}^{-1}$ -0.5 L sample. Similarly, the AR6B COD removal efficiency was 37.2% and 67.4% at 6 h for the $10 \text{ mg}\cdot\text{L}^{-1}$ -10 L sample and $200 \text{ mg}\cdot\text{L}^{-1}$ -0.5 L sample. When the electrochemical oxidation time is extended to 10 h, the AR6B color removal efficiency and COD removal efficiency were only 67.3% and 58.0% for the $10 \text{ mg}\cdot\text{L}^{-1}$ -10 L sample. The values were still lower than that of the $200 \text{ mg}\cdot\text{L}^{-1}$ -0.5 L sample at 6 h. The results shown in Fig. 3b for MO was similar with that of AR6B. The reason for this phenomenon was the concentration process weakened the diffusion control during the electrochemical oxidation process and enhanced the hydroxyl radical utilization efficiency [22]. This result further confirms the adsorption-EOT combined method was useful for the low concentration organic wastewater.

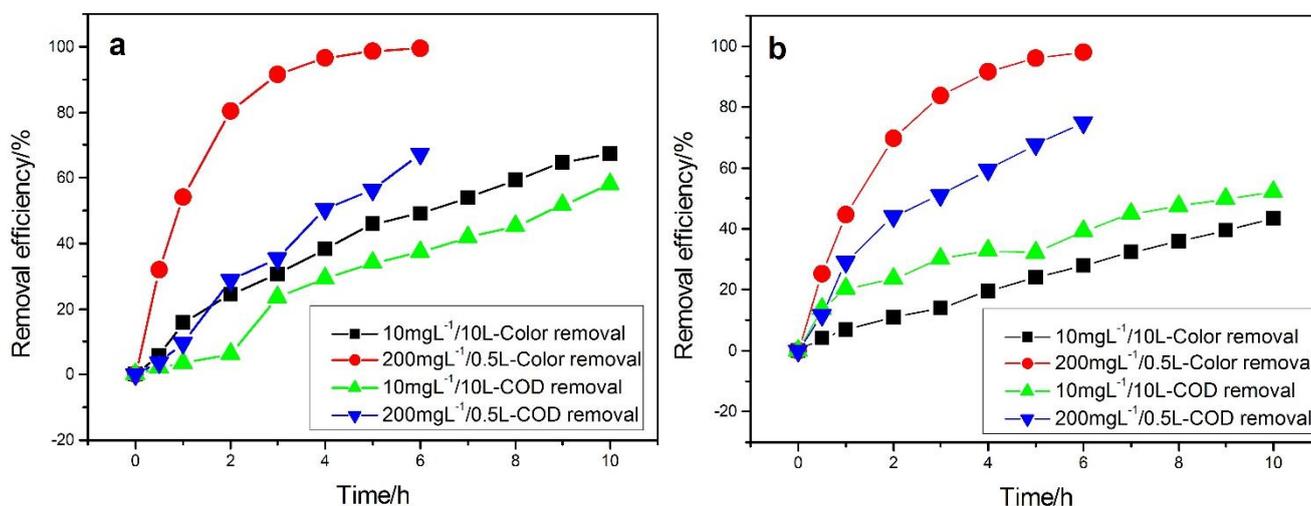


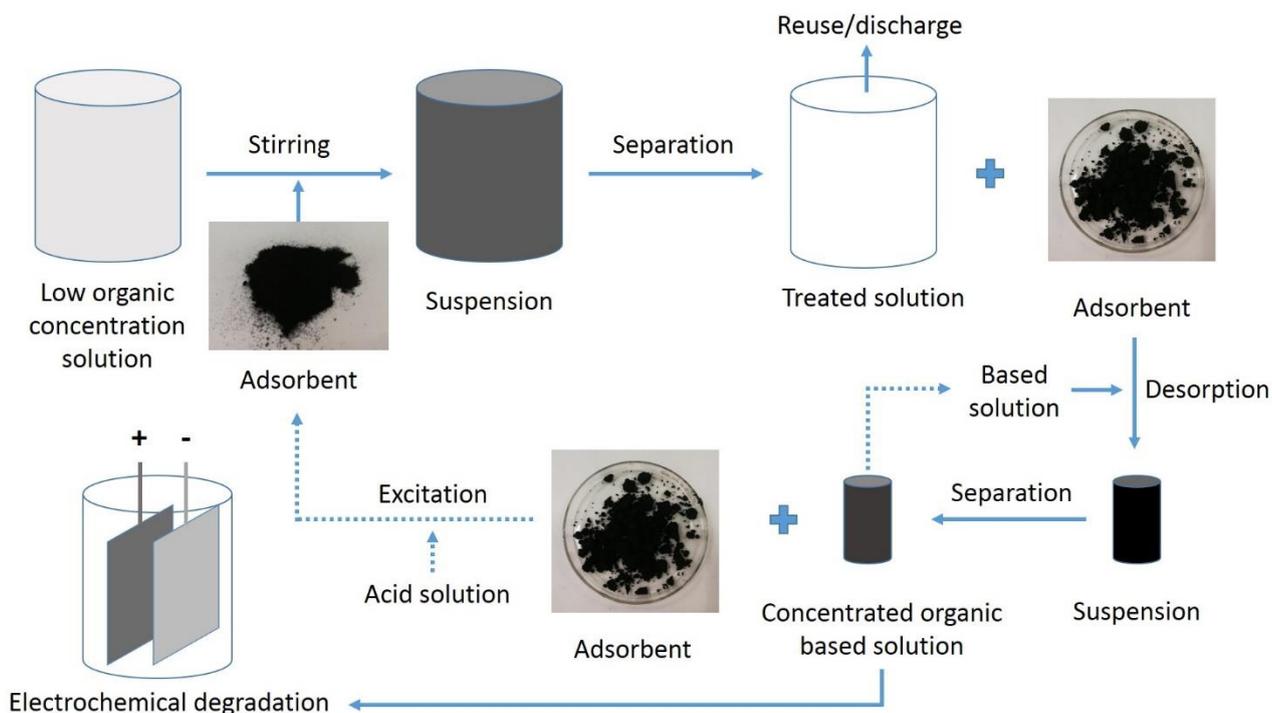
Figure 3. Color removal efficiency and COD removal efficiency for AR6B (a) and MO (b) when the concentration multiple was 20

3.4 Combined method used in actual wastewater

To further extend the concentration multiple, the real adsorption process was used in the real environment. The scheme for the real adsorption process was shown in Scheme 2. The low organic concentration solution is the effluent from a biochemical treatment system of a chemical industrial park sewage treatment plant in Xi'an City, Shaanxi Province. Different from Scheme 1, the adsorbent used in the real environment was excited by the acid solution when the adsorbent reach adsorption saturation.

The average COD value of the effluent was $150 \text{ mg}\cdot\text{L}^{-1}$. After the adsorption process, the average COD value of the effluent was under $60 \text{ mg}\cdot\text{L}^{-1}$. The different COD value before and after the adsorption process was $90 \text{ mg}\cdot\text{L}^{-1}$. When the adsorbent reach adsorption saturation, the based solution was used to desorb the organic materials in the adsorbent. The average COD value for the concentrated organic based solution was $22000 \text{ mg}\cdot\text{L}^{-1}$, which mean the concentration multiple was more than 240. This means that

the volume of effluent requiring electrochemical treatment is greatly reduced.



Scheme 2. The adsorption-desorption-EOT method flow chart for low concentration organic wastewater in real environment

It is awfully difficult to use EOT as the deep-treatment method for the low organic concentration solution from the biochemical treatment system, due to the very poor electrical conductivity of the effluent. Fortunately, the desorption solution used in the real action was $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution, which mean the electrical conductivity was not an obstacle for EOT process. For instance, when the same current (1.204 A) is used for electrolytic treatment, the cell voltage for treating effluent from biological system is 11.45 V, which is much higher than the cell pressure of 6.7V for treating desorption concentrated solution under the same condition.

The electrochemical oxidation tests for the concentrated organic based solution were conducted in an undivided electrolytic cell using PbO_2 electrode as the anode and the applied current density was $100 \text{ mA}\cdot\text{cm}^{-2}$. The results were shown in Fig. 4. It can be found that all the absorption peak for the initial concentrated organic solution was in ultraviolet region as shown in Fig. 4a. These mean that the organic in the concentrated organic solution was all cyclic compound.

The intensity of the absorption peak was decreased with the electrolysis time increased, which indicated that the organic ring was broken by the attack of $\cdot\text{OH}$. This is similar to the degradation pathway of organic substances proposed in some reports [16-18]. With the decrease of the intensity, the solution color became shallow as shown in the inset of Fig. 4a. The η_{COD} increased with the electrolysis time and was 70.07% after 6h electrolysis. During EOT process, the CE was between 54%-85% as shown in Fig. 4b, which was at a higher lever for the conventional electrochemical oxidation method. After 6h

electrolysis, the EC_{COD} was $35.5 \text{ kWh}\cdot\text{kgCOD}^{-1}$ within acceptable limits.

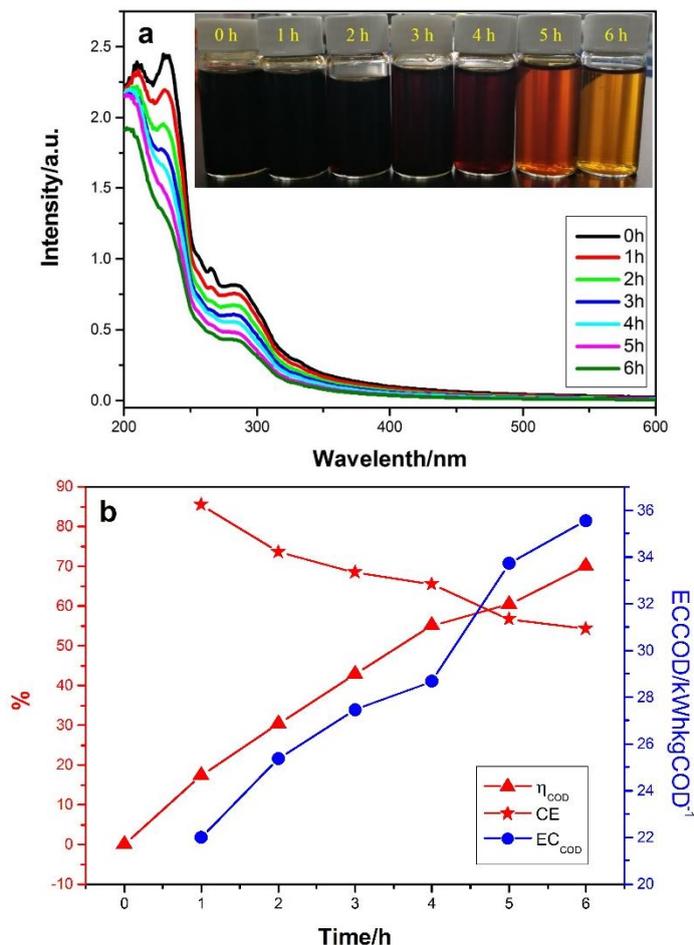


Figure 4. UV-vis spectrogram (a) and η_{COD} , CE, EC_{COD} (b) for the desorbed dconcentrated organic solution during the EOT process

The COD value of the desorption solution decreased from $22000 \text{ mg}\cdot\text{L}^{-1}$ to $6625 \text{ mg}\cdot\text{L}^{-1}$ after 6 h electrolysis. Although the majority of COD was removed by electrolysis process, the remaining COD value in the solution was still very high. It is not economical to treat the desorbed concentrate by electrolysis until the discharges are up to standard. Biological treatment of the remaining solution may be considered after a period of electrolysis [16].

The BOD_5/COD value and the the relative luminosity of the untreated concentrated solution was 0.066 and 0.020%. Both results indicate that the untreated concentrated solution was un-biodegradable. However, the BOD_5/COD value and the the relative luminosity of the EOT-treated solution was 0.63 and 4.34%. Both results show that after electrochemical treatment, the biotoxicity of the solution is reduced and the biodegradability is improved. These indicated that the treated solution could be returned to the biochemical treatment system and be further treated by the biochemical method.

4. CONCLUSIONS

A novel route, electrochemical oxidation combined with adsorption, was proposed for resolving the high energy consumption problem. The adsorption process was acted as a pretreatment of the EOT process, which reduced the mass control limitation during the EOT process. The results of the comparative experiment showed that the combined process removal the color more efficiently and consumed less energy. The combined process would be a good alternative for the organic wastewater treatment, especially for the low organic concentration wastewater.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Key R&D Programs in Shaanxi Province (Program No. 2018SF-372) and Water Science and Technology Projects Foundation of SWAG (Program No. 2018SWAG0203).

References

1. C.M. Dominguez, N. Oturan, A. Romero¹, A. Santos¹ and M.A. Oturan, *Environ. Sci. Pollut. R.*, 25 (2018) 34985
2. M. Panizza and G. Cerisola, *Chem. Rev.*, 109 (2009) 6541.
3. C.A. Martínez-Huitle and E. Brillas, *Appl. Catal., B*, 87 (2009) 105.
4. M.H. Zhou and J.J. He, *J. Hazard. Mater.*, 153 (2008) 357.
5. E. Hmani, Y. Samet and R. Abdelhedi, *Diam. Relat. Mater.*, 30 (2012) 1.
6. Y.W. Yao, C. Zhao, M. Zhao and X. Wang, *J. Hazard. Mater.*, 263 (2013) 726.
7. D. Shao, J.D. Liang, X.M. Cui, H. Xu and W. Yan, *Chem. Eng. J.*, 244 (2014) 288.
8. S. Chai, G. Zhao, Y. Wang, Y. Zhang, Y. Wang, Y. Jin and X. Huang, *Appl. Catal., B*, 147 (2014) 275.
9. J.T. Feng, J.J. Li, W. Lv, H. Xu, H.H. Yang and W. Yan, *Synthetic Met.*, 191 (2014) 66.
10. J.J. Li, J.T. Feng and W. Yan, *Appl. Surf. Sci.*, 279 (2013) 400.
11. J.J. Li, Q. Zhang, J.T. Feng and W. Yan, *Chem. Eng. J.*, 225 (2013) 766-775.
12. H. Xu, D. Shao, Q. Zhang, H.H. Yang and W. Yan, *RSC Adv.*, 4 (2014) 25011.
13. J. Wu, K. Zhu, H. Xu and W. Yan, *Chinese J. Catal.*, 40 (2019) 917.
14. X.L. Li, H. Xu and W. Yan, *J. Alloy Compd.*, 718 (2017) 386.
15. X.L. Li, H. Xu and W. Yan, *Chinese J. Catal.*, 37 (2016) 1860.
16. J. Wu, H. Xu and W. Yan, *RSC Adv.*, 5 (2015) 19284.
17. R. Kaur, J.P. Kushwaha and N. Singh, *Chemosphere*, 193 (2018) 685.
18. R. Kaur, J.P. Kushwaha and N. Singh, *Electrochim. Acta*, 296 (2019) 856.
19. R.Z. Xie, X.Y. Meng, P.Z. Sun, J.F. Niu, W.J. Jiang, L. Bottomley, D. Li, Y.S. Chen and J. Crittenden, *Appl. Catal., B*, 203 (2017) 515.
20. Y.W. Yao, G.G. Teng, Y. Yang, C.J. Huang, B.C. Liu and L. Guo, *Sep. Purif. Technol.*, 211 (2019) 456.
21. Y.W. Yao, B.L. Ren, Y. Yang, C.J. Huang and M.Y. Li, *J. Hazard. Mater.*, 361 (2019) 141.
22. P.Z. Duan, X. Hu, Z.Y. Ji, X.M. Yang and Z.R. Sun, *Chemosphere*, 212 (2018) 594.