

### King Saud University

# Arabian Journal of Chemistry

www.ksu.edu.sa



## **ORIGINAL ARTICLE**

# Influencing factors of venlafaxine degradation at boron-doped diamond anode



Boping Yu<sup>a,b</sup>, Qi Han<sup>a,b</sup>, Chaolin Li<sup>c,\*</sup>, Yuying Zhu<sup>c,\*</sup>, Xingliang Jin<sup>a,b</sup>, Zhiguang Dai<sup>a,b</sup>

<sup>a</sup> Shenzhen Research Academy of Environmental Sciences, Shenzhen 518001, China

<sup>b</sup> Guangdong Provincial Environmental Protection Wastewater Quality Utilization Engineering Technology R&D Center, Shenzhen 518001, China

<sup>c</sup> School of Civil and Environmental Engineering, Harbin Institute of Technology, Shenzhen 518055, China

Received 9 July 2021; accepted 27 September 2021 Available online 05 October 2021

#### **KEYWORDS**

Boron-doped diamond electrode; Anode; Venlafaxine; Influencing factors Abstract Degradation of the antidepressant venlafaxine by an effective electrocatalytic process, boron-doped diamond (BDD) electrode, was study. The BDD electrode was selected as the anode, and the degradation efficiency of venlafaxine under different influencing factors was systematically investigated. The preliminary grasp of the degradation law of venlafaxine by anodic electrodegradation using BDD electrode was obtained. The experimental results showed that the electrochemical oxidation technology using BDD anode can effectively degrade venlafaxine and remove total organic carbon (TOC) from the solution, complete venlafaxine degradation and TOC elimination could be achieved within 30 and 120 min of BDD oxidation process, respectively, and it has good stability and reusability. Increasing the electrolyte concentration ( $\leq 0.1 \text{ mol/L}$ ) and current density ( $\leq 100 \text{ mA/cm}^2$ ) within a certain range could accelerate the degradation of venlafaxine. HCO<sub>3</sub><sup>--</sup> and PO<sub>4</sub><sup>3--</sup> could inhibit the degradation efficiency of venlafaxine through of competing for free radicals. It is interesting that the presence of Cl<sup>--</sup> significantly promoted the degradation efficiency of venlafaxine. The results of this study suggest that the Electro-degradation treatment may provide a promising way to treat venlafaxine contaminated water.

© 2021 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

\* Corresponding author.

E-mail addresses: 371465514@qq.com (B. Yu), 469071317@qq.com (Q. Han), lichaolin@hit.edu.cn (C. Li), Zhuyuying361@163.com (Y. Zhu), xingl.jin@qq.com (X. Jin), szdai168@VIP.163.com (Z. Dai). Peer review under responsibility of King Saud University.



Venlafaxine is one of the most widely used antidepressants due to its outstanding antidepressant effect. However, venlafaxine cannot be completely absorbed by human body after ingestion, and is often eventually enters the water environment (Stadler, 2015). As a result, venlafaxine has been detected in wastewater treatment plants (González Alonso et al., 2010; Rua-Gomez and Puettmann, 2012), urban rivers (Writer et al., 2013), ocean

https://doi.org/10.1016/j.arabjc.2021.103463

1878-5352 © 2021 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). (Chabenat et al., 2019) and other water environments, with concentrations as high as  $(2010 \pm 50)$  ng/L. In addition, the detected concentration of venlafaxine in the effluent of some pharmaceutical factories was as high as (15  $\pm$  0.02) µg/L, which was much higher than that of other drugs (Papageorgiou, 2016). Venlafaxine is difficult to be degraded in natural water, and it is easy to bioaccumulate in water, causing potential risks to the environment (Painter et al., 2009). Studies have shown that venlafaxine can affect the gene expression of salmon (Hodkovicova et al., 2020), isolate the feet of freshwater snails, conches and other mollusks (Fong and Molnar, 2013), significantly reduce the serotonin concentration in the brain of hybrid striped bass then reduce its hunting ability (Bisesi et al., 2014) and cause serious harm to aquatic organisms. However, traditional biological treatment technologies (such as activated sludge process and biofilm process) cannot effectively remove venlafaxine (Gros et al., 2010). Therefore, it is necessary to study how to efficiently remove venlafaxine from water.

To date, the relevant technologies for the degradation of venlafaxine include electro-peroxone and UV photochemical degradation. Electro-peroxone can get a preferable effect on the removal of venlafaxine and its intermediate products, but the cost is too expensive. Besides, the effective utilization rate is low and it is easy to cause secondary pollution to the environment (Li et al., 2015). UV photochemical degradation of venlafaxine is inefficiency, and the dosage of hydrogen peroxide and illumination time must be increased to achieve high efficiency. Therefore, how to remove venlafaxine efficiently, cheaply, safely and environmentally friendly is still worth studying.

Electrochemistry advanced oxidation technology has been proved to be able to generate a variety of oxidizing active substances, such as hydroxyl radical (•OH), singlet oxygen radical ( $^{1}O_{2}$ ), sulfate radical ( $SO_{4}^{\bullet-}$ ), etc. The technology has a wide range of application scenarios, low reaction conditions, higher stability and good reusability, which enable it to have incomparable advantages over other advanced oxidation technologies (Thiam et al., 2016). Boron-doped diamond (BDD) film electrode has excellent electrochemistry characteristics, such as high hydrogen and oxygen evolution potential, wide electrochemical window, very small background current and comparatively stable physical and chemical characteristics (Serrano et al., 2002). It has been reported that BDD electrode has a good effect on the degradation of bisphenol A, phenol, ibuprofen and other chemicals (Serrano et al., 2002). Therefore, it is an effective electrode for the degradation of pollutants by electrochemistry oxidation technology. However, there are few relevant researches on electrochemical oxidation of venlafaxine using BDD anode (Li et al., 2015).

It was explored the degradation of venlafaxine in water by BDD electrode in this study. Firstly, the removal performance of venlafaxine and total organic carbon (TOC) was preliminarily evaluated, and then the influencing factors were systematically studied, including electrolyte concentration, current density, initial pH value of solution, anion species (such as  $HCO_3^-$ ,  $PO_4^{3-}$ ,  $Cl^-$ ), to explore the degradation efficiency and law of venlafaxine by BDD electrode.

#### 2. Materials and methods

#### 2.1. Reagent and chemicals

All chemical solutions were prepared using analytical grade chemicals and deionized water. Venlafaxine, sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), formic, methanol at HPLC grade were obtained from Aladdin. BDD electrode (50 mm  $\times$  100 mm  $\times$  1 mm, bipolar) was purchased from NeoCoat, Switzerland. Graphite electrode (50 mm  $\times$  100 mm  $\times$  1 mm), Pt (20 mm  $\times$  200 mm  $\times$  1 mm) and Ru-Ir (20 mm  $\times$  200 mm  $\times$  1 mm) electrodes were supplied by Shanxi Kaida Chemical Ltd, China.

#### 2.2. Experimental procedures

In this study, BDD electrode was used as the anode, graphite electrode as the cathode, and support electrolyte was a mixture of Na<sub>2</sub>SO<sub>4</sub> and venlafaxine with known concentrations. The reaction took place in a special electrolytic cell. All support electrolytes were prepared with ultrapure water. BDD and graphite electrodes were directly immersed in the electrolyte with a cation exchange membrane (Nafion-117) as the membrane. A constant current density was applied to the electrode surface through a direct current (DC) power supply to initiate a chemical reaction. A sample of 1 mL was taken at regular intervals, and then 20  $\mu$ L methanol was added to the sample to terminate the reaction. The sample was stored at 4°C for subsequent analysis. The schematic diagram of the experimental device is shown in Fig. 1.

#### 2.3. Analytical methods

Venlafaxine was determined by ultra-performance liquid chromatography with ultraviolet detector (UPLC-UV) equipped with a Waters Symmetry C18 column ( $4.6 \times 100$  mm). The column oven temperature was set at 30 °C. The mobile phase was a mixture of methanol and ultrapure water (with 0.01% formic acid and 2 mM ammonium acetate) at a ratio of 60:40 with a flow rate of 0.2 mL min<sup>-1</sup>. The wavelength of UV detection



1-anode; 2-anode tank; 3-cation exchange membrane; 4-cathode; 5- cathode tank

Fig. 1 Schematic diagram of experimental device.

was set at 226 nm. The injection volume was 1  $\mu$ L. The concentration range of the standard curve is 0–1 mg/L, and the concentration of the sample needs to be controlled within this range.

Cyclic voltammetry (CV) was performed using an electrochemical workstation (CHI-660e, Shanghai Chenhua, China) with a three electrode arrangement and the counter and reference electrodes was a Pt plate and an Ag/AgCl electrode. Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, Japan). TOC sample preparation: Take 10 mL of filtered sample to the sample bottle, and was stored at 4°C for subsequent analysis

#### 3. Results and discussion

#### 3.1. Electrochemical performance of electrode

In this section, Ru-Ir electrode and Pt electrode were used as reference electrodes, which are common electrocatalytic electrodes used in water treatment (Zhang, 2018). The potential window and background current of BDD electrode, Ru-Ir electrode and Pt electrode were investigated to evaluate the electrochemical performance of BDD electrode. The background current of Pt electrode and BDD electrode in the potential window was almost 0, while that of Ru-Ir electrode was higher (Fig. 2. The potential windows of BDD electrode, Ru-Ir electrode and Pt electrode were -1.6-1.8 V, -0.6-1.0 V, -0.8-1.2 V, respectively. BDD electrode has a wider potential window, indicating that oxygen evolution, hydrogen evolution and other side reactions are more difficult to occur. BDD electrode will produce more •OH, when the same current density is applied. The application of electrode materials in the degradation of pollutants is mainly through the oxidation of pollutants by •OH or other oxidizing substances (such as active chlorine,  $SO_4 \bullet^-$ , *etc.*) generated on the electrode surface. BDD has a relatively high oxygen evolution potential, which means oxygen evolution reaction is difficult to occur, thus ensuring a comparatively high current efficiency. On the other hand, it can be seen that there is an oxidation peak on the



Fig. 2 The cyclic voltammograms recorded on different anodic electrodes. Conditions:  $Na_2SO_4 = 0.1$  M, scan rate = 20 mV s<sup>-1</sup>, initial potentials = -2.5 V, venlafaxine = 25 mg/L, the reference electrode is Ag/AgCl.

BDD curve, which may be the corresponding peak produced by the oxidation of venlafaxine. In general, BDD has good electrochemical performance and shows good degradation potential

#### 3.2. Degradation of venlafaxine at BDD anode

Transformation products generated during venlafaxine degradation may also pose potential risks to the environment. It is desirable to consider the degradation of venlafaxine and TOC. As shown in Fig. 3 (a) and (b), the concentration of venlafaxine and TOC were no changed when no current was applied. In sharp contrast, venlafaxine was completely degraded in 30 min when a current of 100 mA/cm<sup>2</sup> was applied, and the apparent degradation rate constant was  $k_{app} = 1.93 \times 10^{-3} \text{ s}^{-1}$ . The degradation of TOC had the same performance. The TOC removal efficiency at the current of 100 mA/cm<sup>2</sup> reaches ~ 80%. The results showed that the removal of venlafaxine and TOC were mainly due to the electrochemistry degradation.

BDD anode can produce a variety of oxidizing free radicals in sulfate electrolyte, such as hydroxyl radical ( $\bullet$ OH), and sulfate radical (SO<sub>4</sub><sup>-</sup>) (Eqs. (1)-(4)).  $\bullet$ OH ( $E_0 = 2.80$  V vs SHE) and SO<sub>4</sub><sup>-</sup> ( $E_0 = 2.5-3.1$  V vs SHE) are strong oxidizing agent, could non-selectively oxidizes most organic compounds until the total mineralization. These active species played an important role in the degradation of venlafaxine and its intermediate products (Thiam et al., 2016).

$$H_2 O \rightarrow \bullet O H + H^+ + e^-$$
(1)

$$HSO_4^- + \bullet OH \rightarrow SO_4^{\bullet -} + 2H^+$$
(2)

$$SO_4^{2-} \rightarrow SO_4^{\bullet-} + e^-$$
 (3)

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$
 (4)

After five cycles of experiments, the degradation rate of venlafaxine by electro-oxidation using BDD anode did not decrease, and the removal of venlafaxine was still efficient, showing good stability and reusability of BBD electrode (Fig. 3c).

#### 3.3. Impact of factors on venlafaxine degradation by BDD anode

To get more insight on the degradation of venlafaxine by BDD anode, important factors such as electrolyte concentration, current, solution pH, and anions coexistence were evaluated systematically.

#### 3.3.1. Effect of electrolyte concentration

Electrolyte concentration not only affects the conductivity of the solution, but also affects the yield of the active substance (Liu et al., 2018). In this section, the efficiency of the concentration (0.05–0.6 mol/L) of support electrolyte, on the degradation of venlafaxine was studied (Fig. 4 (a)). The apparent degradation rate constants were  $1.8 \times 10^{-3} \text{ s}^{-1}$ ,  $2.41 \times 10^{-3} \text{ s}^{-1}$ ,  $2.3 \times 10^{-3} \text{ s}^{-1}$ ,  $1.75 \times 10^{-3} \text{ s}^{-1}$ ,  $1.6 \times 10^{-3} \text{ s}^{-1}$ , respectively. The results showed that excessive SO<sub>4</sub><sup>2–</sup> could not effectively promote the degradation efficiency of venlafaxine. When the concentration of SO<sub>4</sub><sup>2–</sup> increases, the proportion of •OH



Fig. 3 Electrochemical oxidation by BDD of (a) venlafaxine and (b) TOC; (c) The cycling test for the degradation of venlafaxine by the BDD. Conditions: current density =  $100 \text{ mA/cm}^2$ ,  $\text{Na}_2\text{SO}_4 = 0.2 \text{ M}$ , venlafaxine = 25 mg/L, initial pH =  $6.5 \pm 0.2$ .



Fig. 4 Effect of (a) electrolyte concentration, (b) current and (c) solution pH. Conditions: current density = 100 mA/cm<sup>2</sup>, Na<sub>2</sub>-SO<sub>4</sub> = 0.1 M, venlafaxine = 25 mg/L, initial pH =  $6.5 \pm 0.2$  (except for otherwise specified).

participating in the reaction with  $SO_4^{2-}$  to produce other active substances such as  $SO_4^{--}$  will increase. There will be a variety of strong oxidants in the system to degrade venlafaxine, thus improving the degradation efficiency. However, if the concentration of  $SO_4^{2-}$  is too high (>0.1 mol/L), •OH will be consumed by  $H_2SO_4$  or  $HSO_4^{--}$  to form  $S_2O_8^{2--}$  (Serrano et al., 2002), and the oxidation activity of  $S_2O_8^{2--}$  (Serrano et al., 2012), and the oxidation activity of  $S_2O_8^{2--}$  ( $E_0 = 2.01 \text{ V } vs$ SHE) is weaker than that of •OH ( $E_0 = 2.80 \text{ V } vs$  SHE) and  $SO_4^{--}$  ( $E_0 = 2.5-3.1 \text{ V } vs$  SHE), resulting in the degradation efficiency of venlafaxine decreased. The optimum electrolyte concentration is 0.1 M.

#### 3.3.2. Effect of current density

Current density is an important factor affecting the electrochemical reaction rate (Yao, 2019). As shown in Fig. 4 (b), the degradation efficiency of venlafaxine at currents density of 60, 80, 100 and 120 mA/cm<sup>2</sup> was studied.

The apparent degradation rate constants  $k_{app}$  of venlafaxine at the currents density of 60, 80, 100 and 120 mA/cm<sup>2</sup> were  $1.4 \times 10^{-3} \text{ s}^{-1}$ ,  $1.75 \times 10^{-3} \text{ s}^{-1}$ ,  $2.78 \times 10^{-3} \text{ s}^{-1}$  and  $2.36 \times 10^{-3} \text{ s}^{-1}$ , respectively. The degradation rate of venlafaxine increased with the increase of current density. However, when the current density exceeds 100 mA/cm<sup>2</sup>, the high voltage causes oxygen evolution reaction on the anode, which is unfavorable to venlafaxine degradation.

Theoretically, increasing the current density can accelerate the degradation of venlafaxine by promoting the generation of various free radical substances on the surface of BDD electrode. Higher current density means faster electron transfer, which can enhance the production of free radicals. However, with the removal of venlafaxine, the concentration of venlafaxine gradually decreases. When there is no enough venlafaxine in the solution to react with free radicals and the free radicals lost their activity without oxidizing venlafaxine. Therefore, blindly increasing the current density in the reaction process is not conducive to improving the current efficiency.

#### 3.3.3. Effect of solution pH

The corresponding removal rates of venlafaxine at pH of 3.5, 6.5 and 10.5 were ~86.1%, ~75.7% and ~40.9%, respectively, in 5 min (Fig. 4 (c)). The degradation rate of venlafaxine increased slightly under an acidic condition while it decreased under an alkaline condition. Venlafaxine contains a tertiary amine group with pKa = 9.24. When pH = 10.5, it mainly exists in an ionic state. However, when the solution pH is 3.5 and 6.5, •OH is more likely to attack protonated amines. In addition, acidic condition accelerated the production of •OH and S<sub>2</sub>O<sub>8</sub>2- (Tang et al., 2020), thus promoting the degradation of venlafaxine.

#### 3.3.4. Effect of anion coexistence

The common anions in natural water, will react with free radicals (Zhang et al., 2014); thus affecting the degradation of pollutants. In this section, the effects of common anions (i.e.,



Fig. 5 Effect of (a)  $HCO_3^-$ , (b)  $PO_4^{3-}$ , and (c)  $CI^-$  on venlafaxine degradation. Conditions: current density = 100 mA/cm<sup>2</sup>, Na<sub>2</sub>-SO<sub>4</sub> = 0.1 M, venlafaxine = 25 mg/L, initial pH = 6.5 ± 0.2.

HCO<sub>3</sub>, PO<sub>4</sub><sup>3-</sup>and Cl<sup>-</sup>) on the degradation of venlafaxine in wastewater were studied and the results are shown in Fig. 5. The degradation rate of venlafaxine decreased with the increase of the concentration of  $HCO_3^-$  (Fig. 5 (a)). The removal rate of venlafaxine was ~93.5% without the addition of  $HCO_3^-$  while the corresponding removal rates were 86.5%, 74.5% and 58.5% when the concentration of  $HCO_3^-$  was 5 mmol/L, 10 mmol/L and 20 mmol/L, respectively in 10 min, which means that the presence of  $HCO_3^-$  significantly inhibited the degradation of venlafaxine. And this is because bicarbonates (HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) are scavengers for  $\bullet$ OH and  $SO_4^{\bullet-}$  (Yan et al., 2019). They can completely with pollutants for free radicals  $\bullet$ OH and SO<sub>4</sub><sup> $\bullet$ -</sup> and react with them to generate  $CO_3^{\bullet-}$  (Eqs. (5)-(6)) (Canonica et al., 2005). The oxidation ability of  $CO_3^{\bullet-}$  ( $E_0 = 1.57$  V vs SHE) is significantly weaker than that of  $\bullet OH$  and  $SO_4^{\bullet-}$ , which results in the decrease of the degradation rate of venlafaxine.

$$\mathrm{SO}_4^{\bullet-} + \mathrm{HCO}_3^{-} \rightarrow \mathrm{H}^+ + \mathrm{SO}_4^{2-} + \mathrm{CO}_3^{\bullet-}$$
(5)

$$\bullet OH + HCO_3^{-} \rightarrow H_2O + CO_3^{\bullet -}$$
(6)

As shown in Fig. 5 (b), the degradation rate of venlafaxine decreased under the addition of  $PO_4^{3-}$  with different concentrations. After 20 min of reaction, the removal rate of venlafaxine decreased from 100% to 85% when the addition of  $PO_4^{3-}$  increased from 0 to 20 mmol/L. This is because negatively charged  $PO_4^{3-}$  is easily adsorbed on the surface of anode electrode, which affects the generation of active substances. In addition, similar to  $HCO_3^{-}$ ,  $PO_4^{3-}$  also reacts with •OH and  $SO_4^{4-}$ , but its ability to compete for free radicals is weaker than that of venlafaxine, so  $PO_4^{3-}$  has a weaker effect on reducing the degradation rate of venlafaxine than that of  $HCO_3^{-}$ .

As shown in Fig. 5 (c), different from the results of adding  $HCO_3^-$  and  $PO_4^{3-}$ , the addition of different concentrations of  $Cl^-$  promoted the degradation of venlafaxine, and the higher the concentration, the greater the promotion effect. After 5 min of reaction, the removal rate of venlafaxine with 20 mmol/L of  $Cl^-$  solution added reached 98.5% while the removal rate of venlafaxine without adding  $Cl^-$  was only 75.7%.  $Cl^-$  accelerated the degradation of venlafaxine mainly for two reasons: First, the BDD anode can convert  $Cl^-$  to strong oxidizing substances such as  $ClO_3^-$ . In addition,  $Cl^-$  is easy to react with •OH and  $SO_4^-$  to generate  $Cl_{\bullet}$  (Eqs. (7) and (8)), and  $Cl_{\bullet}$  will attack the electron-rich group amino

group and benzene ring on venlafaxine, thus accelerating its electro-oxidation degradation efficiency (Yang et al., 2014).

$$SO_4 \bullet^- + Cl^- \to SO_4^{2-} + Cl \bullet \tag{7}$$

$$\bullet OH + Cl^{-} \rightarrow OH^{-} + Cl \bullet \tag{8}$$

#### 4. Conclusion

In this study, BDD anode can effectively degraded venlafaxine and TOC from the solution. After repeated recycling, the degradation effect of venlafaxine did not decrease, and showing stability and reusability. Increasing the concentration of electrolyte can promote the degradation of venlafaxine. But when the concentration of electrolyte exceeded 0.1 mol/L, the  $\bullet$ OH and SO<sub>4</sub> $\bullet$ <sup>-</sup> in the system would be consumed to produce  $S_2O_8^{2-}$  (oxidation is weaker than the former), which cannot effectively degrade venlafaxine. Increasing the current density can significantly accelerate the degradation of venlafaxine, but blindly increase of current density is not conducive to the efficient utilization of current, and the comparatively optimal current density is 100 mA/cm<sup>2</sup>. The optimal reaction conditions were be found, study the degradation law of typical antidepressant venlafaxine at BDD, providing basic data for scientific evaluation of the feasibility the degradation of antidepressants at BDD, and providing technical support for the practical application of this system to degrade antidepressants. In general, this work suggest that the BDD anode treatment may offer a promising alternative to treat antidepressants.

#### **Declaration of Competing Interest**

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

#### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51678182) and the Basic Research Project, Natural Science Foundation of Shenzhen.

#### References

- Bisesi, J.H., Bridges, W., Klaine, S.J., 2014. Effects of the antidepressant venlafaxine on fish brain serotonin and predation behavior. Aquat. Toxicol. 148 (4), 130–138. https://doi.org/10.1016/j. aquatox.2013.12.033.
- Canonica, S., Kohn, T., Mac, M., Real, F.J., Wirz, J., von Gunten, U., 2005. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. Environ. Sci. Technol. 39 (23), 9182–9188. https://doi.org/10.1021/ es051236b10.1021/es051236b.s001.
- Chabenat, A., Bellanger, C., Jozet-Alves, C., Knigge, T., 2019. Hidden in the sand: alteration of burying behaviour in shore crabs and cuttlefish by antidepressant exposure. Ecotoxicol. Environ. Saf. 186, 109738. https://doi.org/10.1016/j.ecoenv.2019.109738.
- Fong, P.P., Molnar, N., 2013. Antidepressants cause foot detachment from substrate in five species of marine snail. Mar. Environ. Res. 84 (38), 24–30. https://doi.org/10.1016/j.marenvres.2012.11.004.
- González Alonso, S., Catalá, M., Maroto, R.R., Gil, J.L.R., de Miguel, Á.G., Valcárcel, Y., 2010. Pollution by psychoactive pharmaceuticals in the rivers of Madrid metropolitan area (Spain). Environ. Int. 36 (2), 195–201. https://doi.org/10.1016/j. envint.2009.11.004.
- Gros, M., Petrović, M., Ginebreda, A., Barceló, D., 2010. Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. Environ. Int. 36 (1), 15–26. https://doi.org/10.1016/j.envint.2009.09.002.
- Hodkovicova, N., Sehonova, P., Blahova, J., Faldyna, M., Marsalek, P., Mikula, P., Chloupek, P., Dobsikova, R., Vecerek, V., Vicenova, M., Vosmerova, P., Svobodova, Z., 2020. The effect of the antidepressant venlafaxine on gene expression of biotransformation enzymes in zebrafish (Danio Rerio) embryos. Environ. Sci. Pollut. Res. 27 (2), 1686–1696. https://doi.org/10.1007/s11356-019-06726-2.
- Li, X., Wang, Y., Zhao, J., Wang, H., Wang, B., Huang, J., Deng, S., Yu, G., 2015. Electro-peroxone treatment of the antidepressant venlafaxine: operational parameters and mechanism. J. Hazard. Mater. 300, 298–306. https://doi.org/10.1016/j. jhazmat.2015.07.004.
- Liu, J., Zhong, S., Song, Y., Wang, B., Zhang, F., 2018. Degradation of tetracycline hydrochloride by electro-activated persulfate oxidation. J. Electroanal. Chem. 809, 74–79. https://doi.org/10.1016/ j.jelechem.2017.12.033.
- Painter, M.M., Buerkley, M.A., Julius, M.L., Vajda, A.M., Norris, D. O., Barber, L.B., Furlong, E.T., Schultz, M.M., Schoenfuss, H.L., 2009. Antidepressants at environmentally relevant concentrations affect predator avoidance behavior of larval fathead minnows (Pimephales Promelas). Environ. Toxicol. Chem. 28 (12), 2677. https://doi.org/10.1897/08-556.1.
- Papageorgiou, M. et al, 2016. Mass loading and environmental risk assessment of 55 pharmaceuticals and personal care products in a

municipal wastewater treatment plant in central Greece. Sci. Total Environ. 543 (2), 547–569. https://doi.org/10.1016/j. scitotenv.2015.11.047.

- Rua-Gomez, P.C., Puettmann, W., 2012. Occurrence and removal of lidocaine, tramadol, venlafaxine, and metabolites in German wastewater treatment plants. Environ. Sci. Pollut. Res. 19 (3), 689–699. https://doi.org/10.1007/s11356-011-0614-1.
- Serrano, K., Michaud, P.A., Comninellis, C., Savall, A., 2002. Electrochemical preparation of peroxodisulfuric acid using boron doped diamond thin film electrodes. Electrochim. Acta. 48 (4), 431– 436. https://doi.org/10.1016/S0013-4686(02)00688-6.
- Stadler, L.B. et al, 2015. Effect of redox conditions on pharmaceutical loss during biological wastewater treatment using sequencing batch reactors. J. Hazard. Mater. 282 (3), 106–115. https://doi.org/ 10.1016/j.heliyon.2018.e00205.
- Tang, Y., He, D., Guo, Y., Qu, W., Shang, J., Zhou, L., Pan, R., Dong, W., 2020. Electrochemical oxidative degradation of X-6g dye by boron-doped diamond anodes: effect of operating parameters. Chemosphere 258, 127368. https://doi.org/10.1016/j. chemosphere.2020.127368.
- Thiam, A., Brillas, E., Garrido, J.A., Rodríguez, R.M., Sirés, I., 2016. Routes for the electrochemical degradation of the artificial food azo-colour ponceau 4r by advanced oxidation processes. Appl. Catal. B. 180, 227–236. https://doi.org/10.1016/j. apcatb.2015.06.039.
- Writer, J.H., Ferrer, I., Barber, L.B., Thurman, E.M., 2013. Widespread occurrence of neuro-active pharmaceuticals and metabolites in 24 Minnesota rivers and wastewaters. Sci. Total Environ. 461-462, 519–527. https://doi.org/10.1016/j.scitotenv.2013.04.099.
- Yan, S., Liu, Y., Lian, L., Li, R., Ma, J., Zhou, H., Song, W., 2019. Photochemical formation of carbonate radical and its reaction with dissolved organic matters. Water Res. 161, 288–296. https://doi. org/10.1016/j.watres.2019.06.002.
- Yang, Y.i., Pignatello, J.J., Ma, J., Mitch, W.A., 2014. Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs). Environ. Sci. Technol. 48 (4), 2344–2351. https://doi.org/ 10.1021/es404118q.
- Yao, J.C. et al, 2019. Different control of anode/cathode potentials of paired electrolysis for simultaneous removal of chemical oxygen demand and total nitrogen. Sci. Total Environ. 687, 1998–2205. https://doi.org/10.1016/j.scitotenv.2019.06.106.
- Zhang, T. et al, 2018. Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation. Environ. Sci. Technol. 156, 12–18. https://doi.org/10.1016/j. est.2018.03.035.
- Zhang, T., Chen, Y., Wang, Y., Le Roux, J., Yang, Y., Croué, J.-P., 2014. Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation. Environ. Sci. Technol. 48 (10), 5868–5875. https://doi.org/10.1021/ es501218f.