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Study on Removal of Endocrine Disruptors in Water Bodies by Advanced Persulfate Oxidation Technology: A Review

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Abstract. Endocrine disruptors (EDCs), as emerging micro-contaminants, interfere with hormones secretion and are harmful to human reproductive system when entering human body. Derived from industry pollution, municipal sewage or agricultural irrigation and run-off, they are able to penetrate to groundwater or gather into surface water that finally supply humans' daily use. Water quality is closely related to human health, especially drinking water, so it is necessary to remove EDCs from polluted water bodies before water is treated and put into use. It is how to efficiently and maximally remove such substances in water bodies that has been a hot issue recently, which has stirred wide attention both at home and abroad. This paper reviews the previous research achievements in this field, simply expounds the mechanism of the reaction between persulfate and EDCs, discusses the characteristics and drawbacks of different activation methods, and finally gives suggestions on how advanced persulfate oxidation technology will develop to an optimization in the future when considering low cost, high removal efficiency and zero secondary pollution.

Keywords: Persulfate advanced oxidation technology, Free radicals, Endocrine disruptors, Activation.

1. Introduction

Although the content in the environment is very small and the mass concentration is at the level of ng/L, EDCs are persistent and pervasive in water bodies [1-3], which means that it is difficult to remove them, so they can cause damage to the reproductive system by interfering with the endocrine system of humans. Thus, the removal of EDCs in water becomes a top priority now. Conventional process of drinking water treatment includes four steps, coagulation, sedimentation, filtration and disinfection, however, the removal rate of organic substances in these processes is only 20%-30%, and is likely to produce degradation by-products with greater disrupt effects and toxicity than the parent substances[4]. Persulfate advanced oxidation technology is a good choice for removing endocrine disruptors in water.

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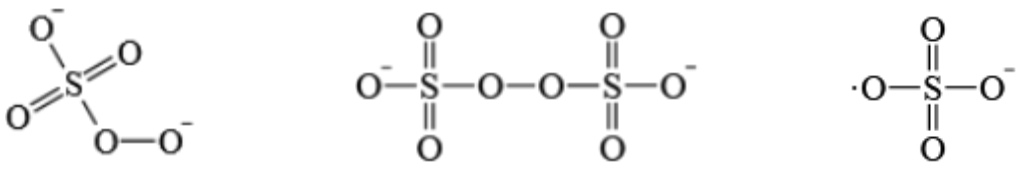
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1.1. Basic processes of degrading EDCs by persulfate oxidation

Add persulfate to the water containing EDCs, then activate persulfate to generate sulfate free radicals, which are used to degrade EDCs in a higher efficiency. Sulfate free radicals react with organics to form sulfates (SO_4^{2-}), which need to be removed in the end, and these organics are degraded into non-toxic or low-toxic products by this free radical.

1.2. Structures of persulfate and its product sulfate free radical

In this paper, the oxidation mechanism mainly focuses on the reaction between persulfate and EDCs organic compounds. Persulfates (PMS or PS) are structurally similar to H_2O_2, that is, they have O-O bonds and they will be broken after being activated and then produce sulfate free radicals (1c). In the process of persulfate oxidation, what really works is the double oxygen bond.



(a) (b) (c)

Figure 1. (a)Structures of PMS, (b)PS ions. (c)Sulfate free radical.

There are three main ways for sulfate free radicals to oxidate EDCs: addition reaction, hydrogen extraction reaction and electron transfer reaction. These three reactions are applicable to certain types of organic pollutants. For instance, organics that contain C=C functional group tend to be the easiest and first to be degraded through addition reaction, whereas aromatic compounds such as PCBs, bisphenol A are the second easily to be degraded by electron transfer reaction.

The second part of this paper will review the "activation" step in the process of persulfate advanced oxidation.

2. REVIEW

EDCs and is a hot research field in recent years. Many researchers in this field have explored the advanced oxidation technology of persulfate through unremitting efforts, and on this basis have also continuously optimized the method of activating and catalyzing persulfate. However, many methods cannot take into account multiple advantages, so they can only be reasonably selected according to the conditions of researchers and the aspects they wish to focus on.

2.1. Activation methods already known

Here several common methods already known to publics towards activating persulfate are listed, both of them have advantages and limitations.

One of these methods is thermal activation. It is to break the O-O bonds under thermal radiation. The higher the temperature within a certain range, the more complete the activation. Different types of organic matters have different optimum temperatures for this activation. However, this method also has detriments like high energy consumption, difficulty on controlling reaction temperature.

Another is UV light activation, which is using the excitation energy of ultraviolet light to break the O-O bonds. This method has several disadvantages, for example, this method costs much for advanced UV light source equipment and UV light is easily absorbed by water compounds during the activation process, resulting in reduced amount of sulfate free radicals [5].

Sometimes there is also transition metal ion activation, in this method, persulfate absorbs an electron from the transition metal like Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+} etc. to break O-O bonds. Being considered as simple and efficient chemical reaction, this method saves energy and can occur at room

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temperature that is easy to operate and reach. But what matters is that in this method, pH is required to be controlled to avoid the precipitation of transition metals.

Having combined with other methods or substances, these common methods may have better activation effect and may produce more free radicals.

Surprisingly, many researchers have explored many new methods of activating persulfate on the basis of common living methods through unremitting efforts (mentioned in 2.2). These methods all have advantages in one or more aspects of energy consumption, efficiency, cost, reaction conditions, no secondary pollution, recyclable materials etc.

2.2. Emerging methods of activating persulfate

There is a method corresponds to zero-valent metals, such as iron, which can slowly and continuously release metal ions of different valence states to break O-O bonds. Zero-valent metal activation is improved by the activation of transition metal ions. Controlling the amount of iron is extremely important. For instance, if Fe^{2+} is too low, the activation ability is limited; if Fe^{2+} is too high, the excess Fe^{2+} will be oxidized to Fe^{3+} by sulfate radicals that produced from activation, resulting in the reduction of available sulfate radicals. Furthermore, not only the ions cannot be utilized to the greatest extent, but also the reaction speed will be too fast, resulting in low activation efficiency and uncomplete activation to produce sulfate free radicals. Fortunately, releasing ions slowly in this method can alleviate this situation. In addition to this, this activation can be performed over a wide pH range because of the different valence states of the ions. Another metal-related activation method mainly makes sense by metal-containing minerals. Taking iron as an example, iron-containing minerals (such as magnetite, hematite) become Fe^{2+} under neutral conditions, which can control the amount of Fe^{2+} in the system and increase the utilization of Fe^{2+} and sulfate free radicals.

Carbon-based materials such as activated carbon, carbon nanotubes, biochar, etc., have huge specific surface area and well-developed pore structures on the surface, which provides good condition for persulfate oxidation. The oxygen-containing functional group in activated carbon is the activator of electron transfer medium, and electron transfer may cause the decomposition of persulfate. Adding activated carbon to the activation system, for example, some scholars found that in the compatible system of activated carbon and persulfate, the activation energy is low, and the activated carbon can still maintain a high level of activation capacity after 4 times of repeated use, indicating that this composite system can regenerate the activation performance of activated carbon.[6-7]

There are also other methods, such as microwave activation at the molecular heating level, ultrasonic activation using cavitation and activation method of strong oxidant with synergistic effect of various strong oxidants and persulfate, etc.

2.3. Discussions about some new technologies of advanced persulfate oxidation

What is worth to mention is the combinations of multiple methods. But to a certain extent, these technologies are limited by high costs. In fact, researchers around the world are constantly pursuing technologies that are recyclable and consume less energy, even at some extra cost. A new finding is shown in Table 1, it focuses on the degradation efficiency of BPA with different catalysts.

Table 1. The relationship between catalyst and BPA degradation efficiency.

Persulfate	Catalyst	Effect
Peroxymonosulfate (PMS)	none	Almost no BPA is removed
	MMT	13.3% of BPA are removed by oxidation in 60 mins
	Fe-MMT	96.4% of BPA are removed by oxidation in 60 mins

Comparing the three treatment methods in Table 1, it can be easily seen that the appropriate catalyst can promote the removal reaction. The effect of using montmorillonite (MMT) alone as a catalyst is not good, while the oxidation removal efficiency of BPA after using molysite modified

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montmorillonite (Fe-MMT) is close to 100%, indicating that Fe-MMT is a catalyst with high efficiency. According to the further analysis of the spectroscopic technology, it can be seen that in the PMS activated by Fe-MMT, the superposition of two free radicals, i.e HO • and SO_4 • $^-$, appeared in the beginning of the reaction, and then HO • will be continuously converted to SO_4 • $^-$, and the system will finally change to SO_4 • $^-$ dominated oxidative removal reaction[8].

The use of advanced materials effectively shortens the reaction time, improves the reaction efficiency, and broadens the reaction conditions, but may be limited by high costs.

3. Conclusion

3.1. Reaction conditions that need to control

Many factors influence final effects, such as reaction optimum temperature, catalyst concentration, pH at the beginning of the reaction and during the reaction, as well as the concentration of sulfate free radicals and EDCs. In order to achieve a good reaction effect, the reaction conditions should be strictly controlled. That is, different optimum temperatures, catalysts, and pH ranges are continuously required for different types of activation and pollutants.

3.2. Final comprehensive treatment

On one hand, if the target substance contains amino-group or nitro-group, nitric acid or/and nitrous acid may be produced during the treatment process, causing a certain degree of pollution to the outlet water. In this case, subsequent denitrification treatments are required. On the other, as mentioned in 1.1, SO_4 • $^-$ will be converted into sulfate (SO_4^{2-}) by EDCs and flows out from the effluent. Although SO_4^{2-} is non-toxic and does not directly harm the environment, its potential danger cannot be ignored (shown in Table 2). Thus, removing them before they flow out is important. Common methods include adsorption, ion exchange, precipitation, crystallization, coagulation, etc.

Table 2. Potential harms to the environment by sulfate

Water (effluent) environment in the system after the reaction to remove EDCs	Possible influences on the environment
High sulfate content	Some sulfate is reduced to S^{2-}, others lead to a low pH condition, which makes the water corrosive
pH is too low	Metals that were previously absorbed in the soil will precipitate and migrate, then cause water pollution
S^{2-} in system	Aquatic plants lack necessary trace metals by reacting with S^{2-}

3.3. Prediction of the development trend of new technologies

Due to their low cost and good characteristics like long-lasting catalytic efficiency, easy recycling, transition metals as catalytic activators are the most commonly studied methods in recent years, but transition single-metal catalysis has limitations in some aspects, so double-metal composite catalysis can be used. It can not only ensure the enhanced catalytic performance, but also the two metals can complement each other, exert their own chemical properties, and may generate new properties.

References

[1] Wee S Y, Aris A Z. Endocrine disrupting compounds in drinking water supply system and human health risk implication[J]. Environment international, 2017, 106:207-233. DOI: https://doi.org/10.1016/j.envint.2017.05.004

[2] Omar T F T, Ahmad A, Aris A Z, et al. Endocrine disrupting compounds (EDCs) in environmental matrices: Review of analytical strategies for pharmaceuticals, estrogenic

hormones, and alkylphenol compounds[J]. TrAC Trends in Analytical Chemistry, 2016, 85: 241-259. DOI: https://doi.org/10.1016/j.trac.2016.08.004

[3] Ahmed M B, Zhou J L, Ngo H H, et al. Sorptive removal of phenolic endocrine disruptors by functionalized biochar: Competitive interaction mechanism, removal efficacy and application in wastewater[J]. Chemical Engineering Journal, 2018, 335:801-811. DOI: https://doi.org/10.1016/j.cej.2017.11.041

[4] Ruoyu Li, et al. Research progress on removal of endocrine disruptors from drinking water in China[J].China water & Wastewater, 2006, 22:1-3.

[5] Lee Y M, Lee G, Zoh K D. Benzophenone-3 degradation via UV/H2O2 and UV/persulfate reactions[J]. Journal of hazardous materials, 2021, 403: 123591. DOI: https://doi.org/10.1016/j.jhazmat.2020.123591

[6] ZHANG Jun, SHAO Xueting, SHI Chao, et al. Decolorization of AcidOrange 7 with peroxymonosulfate oxidation catalyzed by granularactivated carbon[J]. Chemical Engineering Journal, 2013, 232:259-265. DOI: https://doi.org/10.1016/j.cej.2013.07.108

[7] YANG Shiying, ZHANG Ao, REN Tengfei, et al. Surface mechanism ofcarbon-based materials for catalyzing peroxide degradation of organicpollutant[J]. Progress in Chemistry, 2017, 29(5): 539-552. DOI: https:// doi.org/10.7536/PC170310

[8] Wang P P, Zhao B. Catalytic degradation performance and mechanism of bisphenol A by peroxymonosulfate activation through Fe (III)-modified montmorillonite[J]. Journal of Harbin Institute of Technology, 2022, 5:19-23. DOI: 10.11918/202106031