

Study on Fenton-like degradation of bisphenol A by α -MnO₂ and α -MnO₂/AC (1:1, w/w)

Junqing You (✉ 2910308680@qq.com)

Hebei University of Technology

Xihui Zhang

Hebei University of Technology

Jinglei Chen

Hebei University of Technology

Research Article

Keywords: manganese oxide, activated carbon, degradation of bisphenol A, no pH adjustment

Posted Date: May 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-528294/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Bisphenol A is used in various industrial productions and large amounts of industrial wastewater containing bisphenol A is produced. Heterogeneous Fenton-like process in advanced oxidation technology can oxidize and degrade most organic compounds non-selectively, and it has become an effective method to treat bisphenol A. The aim is to overcome the shortcomings of the traditional Fenton method and synthesize catalysts by a simple method, which can help to degrade bisphenol A effectively under neutral conditions, with less catalyst and less H₂O₂ consumption. In this experiment, α-MnO₂ and α-MnO₂/AC (1:1, w/w) were synthesized by a simple method, and the degradation rate of bisphenol A by α-MnO₂ and α-MnO₂/AC (1:1, w/w) under different conditions were studied. The optimal conditions for the degradation of bisphenol A by the two materials were determined by single factor and orthogonal experiments. When the dosage of α-MnO₂ catalyst is 6.5g/L and the concentration of H₂O₂ is 200 mg/L with pH = 4.5 at 328K, the degradation rate of 50mg/L bisphenol A can reach 91.02% within 70 minutes. When α-MnO₂/AC (1:1, w/w) has a catalyst dosage of 1.5g/L, at 298K with no pH adjustment, the degradation rate of 50 mg/L of bisphenol A within 70 minutes can be reached 94.17%.

1 Introduction

With the continuous development of the industrialization process of human society, a large amount of industrial waste water is produced, which poses a serious threat to human health and survival. Organic sewage is the main part of industrial wastewater. Its composition is complex, toxic, and difficult to degrade, which is a difficult point in environmental governance.

Bisphenol A is an important chemical raw material for the production of polycarbonate and epoxy resins with a wide range of uses (such as plastic bottles, pipes, toys, medical equipment and electronic products) and other polymer materials¹. It can also be used in fine chemical products such as plasticizers, flame retardants, heat stabilizers, antioxidants, and pesticide coatings.

Bisphenol A is also a hormone disruptor, which can cause disorders of the endocrine system², and be exposed to the human body through diet or non-dietary, causing harm to human health³. After bisphenol A enters the human body, it produces estrogen-like or anti-estrogen effects through a variety of reaction mechanisms, thereby affecting the endocrine, reproductive and nervous systems, and producing adverse effects such as cancer promotion. Toyohira, Y used animal experiments to prove that bisphenol A can affect the secretion of hormone levels in the body and affect the normal metabolism of animals⁴.

In addition, bisphenol A also has certain embryo toxicity and teratogenicity. Animal and cell tests have confirmed that bisphenol A can increase the incidence of breast, prostate, and ovarian cancer in the body⁵⁻⁷.

Since the 1980s, Advanced Oxidation Process (AOPs), which is marked by the generation of hydroxyl radicals (•OH), has attracted wide attention because of its advantages such as fast reaction rate,

complete treatment, no pollution, and wide application range.

The Fenton method is one of the classic AOPs processes, and the $\cdot\text{OH}$ generated by the Fenton system has a higher redox potential⁸, which can perform non-selective oxidative degradation of organic pollutants. Once hydroxyl radicals are formed, they will induce a series of free radical chain reactions, attack various organic pollutants in water, and finally mineralize them into H_2O , CO_2 and inorganic salts⁹. Fenton process has the advantages of high pollutant removal efficiency, mild reaction conditions, simple operation and low cost¹⁰, and has been widely used in sewage treatment in recent years. However, there are some problems in the traditional Fenton process, including the difficulty in separating and recovering the catalyst, and prone to secondary pollution and so on. In addition, the traditional Fenton reaction can be applied to a very narrow pH range, generally from 3 to 5. When treating organic wastewater, the wastewater needs to be pre-acidified. Therefore, reducing the cost of polluting wastewater treatment and simplifying the treatment process while ensuring that the water quality treatment requirements meet the standards have become an important direction for the development of industrial wastewater treatment technology.

In recent years, there have been many studies on the degradation of bisphenol A, Matz Dietrich¹¹ et al. used a low frequency (24 kHz) ultrasonic horn and two boron-doped diamond electrodes to study the degradation of bisphenol A by a electrochemical hybrid system. It is found that under the synergistic effect of ultrasound and electrochemical oxidation, the degradation rate of bisphenol A with an initial concentration of 1 mg/L can reach 90% within 30 minutes. Anakovai et al.¹² had studied the degradation of bisphenol A from lab-scale to pilot-scale, in which the degradation rate of bisphenol A can reach 90% under certain conditions.

Cai et al.¹³ proposed an effective method to remove bisphenol A from water using HP- β -CD polymer, which can quickly remove bisphenol A. Yiguang Qian¹⁴ et al. used the activated sludge biodegradation method to treat bisphenol A and achieved good results.

In the past, many researches on the removal of bisphenol A also have some shortcomings, such as the high cost of material synthesis, some need to add more acid to adjust the pH, the treatment process is complicated, and the treatment time is long and so on.

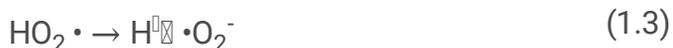
In this experiment, the configured bisphenol A solution was used to simulate organic wastewater. This paper aims to overcome the shortcomings of the traditional Fenton method. A simple method is used to synthesize a green and pollution-free catalyst, and under neutral conditions, can achieve a good treatment effect on bisphenol A with less amount of catalyst and H_2O_2 . In this way, the treatment time and treatment cost is reduced, and the organic wastewater treatment process is simplified.

MnO_2 is one of the most effective transition metal oxides to degrade organic pollutants, and it is also favored because of its low cost and environmental friendliness¹⁵. MnO_2 has a good adsorption and degradation effect on phenolic organic matter in water. Among the many crystal phases of MnO_2 , $\alpha\text{-MnO}_2$

has better catalytic activity than other crystal phases. The catalytic activity in the many crystal phases of MnO_2 has the following order: $\alpha\text{-MnO}_2 > \gamma\text{-MnO}_2 > \lambda\text{-MnO}_2 > \beta\text{-MnO}_2$ ¹⁶. Saputra et al. tested the catalytic activity of different MnO_2 crystals ($\alpha\text{-MnO}_2$, $\beta\text{-MnO}_2$, $\gamma\text{-MnO}_2$) in PMS solution, and found that $\alpha\text{-MnO}_2$ nanowires presented the highest activity, which was attributed to its high surface area and better crystal structure¹⁷.

Coconut shell activated carbon has a good adsorption effect due to its large specific surface area. Combining the advantages of $\alpha\text{-MnO}_2$ and coconut shell activated carbon to prepare a composite catalyst $\alpha\text{-MnO}_2/\text{AC}$ can better catalyze the degradation of bisphenol A. Activated carbon can adsorb bisphenol A on the surface of the catalyst, then the effective component $\alpha\text{-MnO}_2$ on the surface of the catalyst degrades bisphenol A to achieve the purpose of rapid degradation of bisphenol A.

This experiment used bisphenol A as the target pollutant, the $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2/\text{AC}$ were synthesized by a simple method, the degradation efficiency of $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2/\text{AC}$ on bisphenol A was studied. The mechanism of degradation of bisphenol A by $\alpha\text{-MnO}_2$ is seen in Fig. 1 and possible reaction is as follows :



Abdul et al.¹⁸ took a certain solution during the degradation of bisphenol A and analyzed the intermediate products of bisphenol A degradation by LC-MS. From the LC-MS results, several products were identified, including *p*-isopropenylphenol, 4-isopropylphenol, benzophenone, dihydroxylated bisphenol A and formic acid. In conjunction with other papers¹⁹⁻²¹, possible pathways for the degradation of bisphenol A have been proposed, as shown in Fig. 2.

2 Preparation And Characterization Of Materials

All chemicals were purchased from the chemical management platform in HEBUT. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was distributed by Shanghai Maikelin Biochemical Technology Company and the coconut shell activated carbon (AC) by Chengde Huajing Activated Carbon Company. KMnO_4 , Na_2CO_3 , HCl (36%-38%), Bisphenol A were sold by Tianjin Komiou Chemical Reagent Company. All chemicals are analytical purity and were used as received without further purification. Deionized water was used throughout the work.

2.1 Preparation of α -MnO₂ and α -MnO₂/AC (1:1, w/w)

A volume of 100ml solution of 0.2M KMnO₄ and 0.2M Na₂CO₃ was slowly introduced to a round-bottom flask with 100mL solution of 0.3M MnCl₂, and stirred at 303K for 5h. After filtering and washing, the residues (α -MnO₂) were dried for 24h at 353K, and then calcined at 673K for 3h.

For α -MnO₂/AC (1:1, w/w), the active manganese was supported on coconut shell activated carbon by incipient wetness impregnation of the solution of 0.3M MnCl₂, and then prepared by alkaline solution of 0.2M KMnO₄ and solution of 0.3M MnCl₂ as above.

2.2 Characterization

2.2.1 FTIR analysis

The FTIR diagram of α -MnO₂ is shown in Fig. 3. The characteristic peaks at the wavenumbers of 3410 cm⁻¹ and 1636 cm⁻¹ correspond to the O-H asymmetric stretching vibration peak and the O-H bending vibration peak in the water, respectively. 724 cm⁻¹ and 586 cm⁻¹ correspond to the stretching vibration of Mn-O-Mn, 520 cm⁻¹ corresponds to the stretching vibration of Mn-O. It shows that the material obtained is manganese oxide.

In Fig. 4, 492 cm⁻¹ is the stretching vibration peak of Mn-O-Mn, and 609 cm⁻¹ is the stretching vibration peak of Mn-O²². It shows that the production of manganese oxide was not affected during the material preparation process.

2.2.2 XRD analysis

The instrument model used is Broker D8 Discover, the test condition is Cu target, Wavelength 1.5418 Å, Scan range 10-80°, the scanning speed is 6°/min.

According to Fig. 5, the diffraction peaks of the synthesized α -MnO₂ on the crystal planes of (110), (200), (310), (400), (211), (301), (411), (600), (521), (002) and (541) are basically consistent with the standard α -MnO₂ spectra (the PDF standard card of jade software, PDF#44-0141). The figure shows that the prepared α -MnO₂ has good crystal shape, high purity and does not contain other impurities. The diffraction peaks of the synthesized α -MnO₂(1:1, w/w) on the (110), (200), (310) and (521) crystal planes are consistent with those of the standard α -MnO₂ spectra, the diffraction peaks on other crystal planes are slightly shifted compared with the standard spectrum of α -MnO₂. It shows that adding coconut shell activated carbon did not affect the formation of α -MnO₂, but some diffraction peaks were shifted.

2.2.3 SEM and TEM images of α -MnO₂ and α -MnO₂/AC (1:1, w/w)

It can be seen from the SEM image of α -MnO₂ (Fig. 6) that the synthesized material has a rich pore structure. From the TEM image of α -MnO₂, it can be seen that the material has a sheet structure of tens to

300 nm.

From the SEM image of $\alpha\text{-MnO}_2/\text{AC}$ (1:1, w/w)(Fig. 7), it can be seen that the structure of $\alpha\text{-MnO}_2/\text{AC}$ (1:1, w/w) composite material is looser and more porous than the single $\alpha\text{-MnO}_2$, and then it has a larger specific surface area than $\alpha\text{-MnO}_2$. From the TEM image of $\alpha\text{-MnO}_2/\text{AC}$ (1:1, w/w), it can be seen that the prepared material is 30nm small spherical particles while the single $\alpha\text{-MnO}_2$ has a sheet structure of tens to 300 nm.

2.2.4 UV-Vis analysis

It can be seen from Fig. 8 and Fig. 9 that the two materials have better absorption in the ultraviolet wavelength range. In the catalysis process of this experiment, a 365nm UV lamp was selected as the illumination source. At the same time, UV radiation can also directly promote the production of $\cdot\text{OH}$ from H_2O_2 .

3 Results And Discussion Of Degradation Of Bisphenol A By $\alpha\text{-mno}_2$

The experiments were carried out in a magnetically stirred batch reactor with a certain amount of 50 mg/L bisphenol A aqueous solution. The temperature was controlled by immersed in a thermostatic bath. After a certain amount of $\alpha\text{-MnO}_2$ was added, the solution would be stirred for 30min in the dark to reach the equilibrium of adsorption and desorption. The solution pH was adjusted with 0.1mol/L and 0.01mol/L HCl, then we turned on the 365nm UV lamp, magnetically stirred, took a sample every 10 minutes, and filter it with a 0.22 μm PTFE needle filter. The absorbance of the filtered filtrate was measured with the ultraviolet-visible spectrophotometer, and the degradation rate was calculated as follows:

$$w\% = \frac{A_0 - A}{A_0} \times 100\% \quad (3-1)$$

A_0 is the initial concentration of bisphenol A before degradation, A is the concentration of bisphenol A after degradation.

3.1 Single factor experiment

3.1.1 The effect of the amount of catalyst on the degradation rate

Fig. 10 shows the degradation rate of bisphenol A in 70 minutes under different catalyst amounts (other conditions are the same). It can be seen from the figure that as the amount of catalyst increases, the degradation rate of bisphenol A gradually increases. When the amount of catalyst is increased to 6g/L, increasing the amount of catalyst does not significantly improve the degradation rate of bisphenol A, the

reason may be that when the concentration of the catalyst is low, the number of active sites is small and the degradation rate is not high. When the concentration of the catalyst is high, the absorption of light is affected, and the utilization rate of light is reduced, resulting in low degradation efficiency²³. The optimal amount of catalyst is 6g/L

3.1.2 The effect of temperature on degradation rate

Fig. 11 shows the degradation rate of α -MnO₂ to bisphenol A within 70 min at different temperatures (other conditions being the same). It can be seen from the figure that the degradation effect is best when the temperature is 323K. Too high or low temperature will affect the degradation efficiency, the reason may be that when the temperature is low, it is unable to provide sufficient energy for α -MnO₂ to catalyze the degradation of H₂O₂ to produce \cdot OH, this leads to a low degradation rate. When the temperature is high, part of the H₂O₂ is decomposed during the degradation process, the reduced utilization of H₂O₂ leads to low degradation rate.

3.1.3 The effect of pH on degradation rate

Fig. 12 shows the degradation rate within 70 min under different pH conditions (other conditions are the same), it can be seen from the figure that within a certain pH range, when pH=3, the degradation effect of bisphenol A is the best, but the degradation rate is not much different from that at pH=5. Considering the cost and requirements of equipment, choose pH=5 as the best condition. At pH=5, the degradation rate within 70 minutes is 85.23%.

3.1.4 The effect of the amount of H₂O₂ on the degradation rate

Fig. 13 shows the degradation rate in 70 min under different concentrations of H₂O₂ (other conditions are the same), it can be seen from the figure that the degradation effect is the best when the concentration of H₂O₂ is 0 mg/L. When the concentration of H₂O₂ is 0 mg/L, the degradation rate within 70 minutes is 88.41%. Excessive H₂O₂ concentration will affect the degradation efficiency, the reason may be that H₂O₂ decomposes at this temperature. In addition, when the concentration of H₂O₂ is high, a large amount of H₂O₂ chemically reacts with \cdot OH, and consumption of a certain amount of \cdot OH leads to a decrease in the degradation rate.

3.2 Orthogonal experiment

According to the above single factor experiment results, we determined the level of several factors in the orthogonal experiment. The amount of catalyst selected is 5g/L, 5.5g/L, 6g/L, 6.5g/L. The temperature selection is 298K, 308K, 318K, 328K. Choose pH 4.5, 5, 5.5, no HCl. The amount of H₂O₂ is selected as 0mg/L, 100mg/L, 200mg/L, 300mg/L. Then we used Orthogonal Design Assistant to design orthogonal experiments, the following Table 1 is the result of orthogonal experiment design.

Table 1. Orthogonal experimental design and result table

Factor Serial number	The amount of catalyst/g/L	Temperature [K]	pH	The amount of H ₂ O ₂ /mg/L	Degradation rate/%
1	5	298	4.5	0	88.28
2	5	308	5	100	83.06
3	5	318	5.5	200	87.2
4	5	328	6	300	81.41
5	5.5	298	5	200	79.81
6	5.5	308	4.5	300	85.35
7	5.5	318	6	0	79.78
8	5.5	328	5.5	100	87.73
9	6	298	5.5	300	87.43
10	6	308	6	200	78.15
11	6	318	4.5	100	86.29
12	6	328	5	0	84.01
13	6.5	298	6	100	75.85
14	6.5	308	5.5	0	89.35
15	6.5	318	5	300	89.38
16	6.5	328	4.5	200	91.02
Mean 1	84.988	82.843	87.735	85.355	
Mean 2	83.168	83.977	84.065	83.233	
Mean 3	83.970	85.663	87.928	84.045	
Mean 4	86.400	86.042	78.797	85.892	
Range	3.232	3.199	9.131	2.659	

The above Table 1 is the analysis of the results of orthogonal experiments. The analysis result is analyzed by the orthogonal design assistant, it can be seen that the range of the orthogonal experiment is: $R_3 > R_1 > R_2 > R_4$. The influencing factors from large to small are: $pH > \text{the amount of catalyst} > \text{temperature} > \text{the amount of H}_2\text{O}_2$, the best experimental conditions are the amount of catalyst 6.5g/L, the temperature is 328K, the pH is 4.5, and the concentration of H₂O₂ is 200 mg/L. Under these conditions, the degradation rate of bisphenol A can reach 91.02% within 70 minutes.

4 Results And Discussion Of Degradation Of Bisphenol A By

The experiments were carried out in the same conditions as part 3, but with AC supported catalyst of $\alpha\text{-MnO}_2 / \text{AC}$ (1:1, w/w).

4.1 Single factor experiment

4.1.1 The effect of the amount of catalyst on the degradation rate

Fig. 14 shows the degradation rate in 70 min under the condition of different amounts of catalyst (other conditions are the same), it can be seen from the figure that the degradation effect is best when the amount of catalyst is 2 g/L, the degradation rate reaches 93.71% within 70 minutes, the reason may be that when the concentration of the catalyst is low, the number of active sites is small and the degradation rate is not high. When the concentration of the catalyst is high, the absorption of light is affected, and the

utilization rate of light is reduced, resulting in low degradation efficiency. We choose 2 g/L as the best condition.

4.1.2 The effect of temperature on degradation rate

Fig. 15 shows the degradation rate within 70 min under different temperature conditions (other conditions are the same). It can be seen from the picture that the degradation effect is better when the temperature is 303K. The reason may be that when the temperature is low, it is unable to provide sufficient energy for $\alpha\text{-MnO}_2$ /AC (1:1, w/w) to catalyze the degradation of H_2O_2 to produce $\cdot\text{OH}$, this leads to a low degradation rate. When the temperature is high, part of the H_2O_2 is decomposed during the degradation process, the reduced utilization of H_2O_2 leads to low degradation rate.

4.1.3 The influence of the amount of H_2O_2 on the degradation rate

Fig. 16 shows the degradation rate within 70 min under different concentrations of H_2O_2 (other conditions are the same), it can be seen from the figure that the degradation effect is the best when the concentration of H_2O_2 is 750 mg/L. However, the H_2O_2 concentration of 250 mg/L and the H_2O_2 concentration of 750 mg/L have little difference in the degradation rate of bisphenol A. From the point of view of energy saving, we choose 250 mg/L of H_2O_2 as the best condition. If the concentration of H_2O_2 is too high or too low, it will affect the degradation efficiency, the reason may be that when the concentration of H_2O_2 is low, sufficient $\cdot\text{OH}$ cannot be provided. When the concentration of H_2O_2 is high, a large amount of H_2O_2 reacts with $\cdot\text{OH}$, which consumes a certain amount of $\cdot\text{OH}$ and reduces the degradation rate.

4.2 Orthogonal experiment

According to the above single-factor experiment results, the levels of several factors in the orthogonal experiment are determined as the amount of catalyst is 1g/L, 1.5g/L, 2g/L, 2.5g/L, and the temperature is 293K, 298K, 303K and 308K, the amount of H_2O_2 is selected as 0mg/L, 100mg/L, 200mg/L, 300mg/L. we used the Orthogonal Design Assistant to design the orthogonal experiment, the following Table 2 shows the results of the orthogonal experiment design.

Table 2. Orthogonal experimental design and result table

Factor Serial number	The amount of catalyst [g/L]	Temperature [K]	The amount of H ₂ O ₂ [mg/L]	Degradation rate[%]
1	1	293	0	93.51
2	1	298	100	93.62
3	1	303	200	93.76
4	1	308	300	93.35
5	1.5	293	100	93.62
6	1.5	298	0	94.17
7	1.5	303	300	94.17
8	1.5	308	200	93.49
9	2	293	200	93.49
10	2	298	300	92.98
11	2	303	0	92.57
12	2	308	100	93.26
13	2.5	293	300	93.12
14	2.5	298	200	93.12
15	2.5	303	100	94.09
16	2.5	308	0	93.95
Mean 1	93.560	93.435	93.550	
Mean 2	93.863	93.473	93.648	
Mean 3	93.075	93.648	93.465	
Mean 4	93.570	93.512	93.405	
Range	0.788	0.213	0.243	

Table 2 is the analysis of the results of the orthogonal experiment, and the analysis results are obtained by the analysis of the orthogonal design assistant. It can be seen that the range of the orthogonal experiment is: $R_1 > R_3 > R_2$, The influencing factors from large to small are: the amount of catalyst > the amount of H₂O₂ > temperature, under the two conditions of 1.5g/L of catalyst, temperature of 298K, concentration of H₂O₂ of 0 mg/L and catalyst dose of 1.5g/L, temperature of 303K, concentration of H₂O₂ of 300 mg/L, the degradation rate of bisphenol A can reach 94.17% in 70 minutes. From the perspective of energy saving, the optimal conditions are selected as the catalyst dosage 1.5g/L, the temperature is 298K, and the H₂O₂ concentration is 0 mg/L.

5 Conclusions

The α -MnO₂ and α -MnO₂/AC (1:1, w/w) were synthesized by a simple method, and the degradation rate of bisphenol A under different conditions was explored through single factor and orthogonal experiments. In order to achieve a higher degradation rate of bisphenol A, it needs to be under acidic conditions, and a larger amount of α -MnO₂ need to be added. The modified α -MnO₂/AC (w/w 1:1) can reach a higher degradation rate under neutral conditions, and only a small amount of α -MnO₂/AC (1:1, w/w) was added to achieve a higher degradation rate.

The optimal experimental conditions for the catalytic degradation of bisphenol A by α -MnO₂/AC (w/w 1:1) are as follows: neutral pH, 298K, 1.5g/L catalyst and no H₂O₂. The results show that the degradation rate of 50 mg/L bisphenol A can reach 94.17% . Under neutral conditions, without adding H₂O₂, and only

adding a small amount of catalyst, and it don't need too high temperature, the degradation rate of 50 mg/L bisphenol A can reach 94.17%. Compared with the traditional Fenton method, which requires pre-acidification of the solution and the need to add a large amount of H₂O₂, it has been greatly improved.

The synthesis method of the materials in this experiment is very simple, and the synthesis reagents are cheap and easy to obtain. The modified α -MnO₂/AC (1:1, w/w) can achieve a higher degradation rate under neutral conditions resulting to low equipment requirements. It can be a good process for treating bisphenol A wastewater and has certain application prospects.

Declarations

Acknowledgements This work was supported by Natural Science Foundation of Hebei Province (B2016202290)

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

Declarations The content of this manuscript has not been published, there is no conflict of interest, and there is no multiple submission of one manuscript.

References

1. Wang, L. *et al.* Deriving the freshwater quality criteria of BPA, BPF and BPAF for protecting aquatic life. *Ecotoxicology and environmental safety* **164**, 713-721 (2018).
2. Zhang, C. *et al.* Construction of luffa sponge-based magnetic carbon nanocarriers for laccase immobilization and its application in the removal of bisphenol A. *Bioresource technology* **305**, 123085 (2020).
3. Li, A. *et al.* Serum concentration of bisphenol analogues in pregnant women in China. *Science of The Total Environment* **707**, 136100 (2020).
4. Toyohira, Y. *et al.* Inhibition of the norepinephrine transporter function in cultured bovine adrenal medullary cells by bisphenol A. *Biochemical pharmacology* **65** (12), 2049-2054 (2003).
5. Segovia-Mendoza, M. *et al.* The chemical environmental pollutants BPA and BPS induce alterations of the proteomic profile of different phenotypes of human breast cancer cells: A proposed interactome. *Environmental Research* **191**, 109960 (2020).

6. Di Donato, M. *et al.* Recent advances on bisphenol-A and endocrine disruptor effects on human prostate cancer. *Molecular and cellular endocrinology* **457**, 35-42 (2017).
7. Guo, Y. *et al.* Bisphenol A and polychlorinated biphenyls enhance the cancer stem cell properties of human ovarian cancer cells by activating the WNT signaling pathway. *Chemosphere* **246**, 125775 (2020).
8. Lv, H. *et al.* Efficient degradation of high concentration azo-dye wastewater by heterogeneous Fenton process with iron-based metal-organic framework. *Journal of Molecular Catalysis A: Chemical* **400**, 81-89 (2015).
9. Dindarsafa, M. *et al.* Heterogeneous sono-Fenton-like process using martite nanocatalyst prepared by high energy planetary ball milling for treatment of a textile dye. *Ultrasonics sonochemistry* **34**, 389-399 (2017).
10. Nguyen, T. D., Phan, N. H., Do, M. H. & Ngo, K. T. Magnetic Fe₂MO₄ (M: Fe, Mn) activated carbons: fabrication, characterization and heterogeneous Fenton oxidation of methyl orange. *Journal of Hazardous Materials* **185**, 653-661 (2011).
11. 1 Dietrich, M., Franke, M., Stelter, M. & Braeutigam, P. Degradation of endocrine disruptor bisphenol A by ultrasound-assisted electrochemical oxidation in water. *Ultrasonics sonochemistry* **39**, 741-749 (2017).
12. 1 Kovačič, A. *et al.* The removal of bisphenols and other contaminants of emerging concern by hydrodynamic cavitation: From lab-scale to pilot-scale. *Science of The Total Environment* **743**, 140724 (2020).
13. 1 Cai, J., Zhang, P., Kang, S., Xu, W. & Tang, K. Fast and efficient adsorption of bisphenols pollutants from water by using Hydroxypropyl-β-cyclodextrin polymer. *Reactive and Functional Polymers* **154**, 104678 (2020).
14. 1 Qian, Y. *et al.* Occurrence and removal of bisphenol analogues in wastewater treatment plants and activated sludge bioreactor. *Science of The Total Environment* **758**, 143606 (2021).
15. 1 Boyom-Tatchemo, F. W., Devred, F., Ndiffo-Yemeli, G., Laminsi, S. & Gaigneaux, E. M. Plasma-induced redox reactions synthesis of nanosized α-, γ- and δ-MnO₂ catalysts for dye degradation. *Applied Catalysis B: Environmental* **260**, 118159 (2020).
16. 1 Cao, Y., Yang, H., Ai, X. & Xiao, L. The mechanism of oxygen reduction on MnO₂-catalyzed air cathode in alkaline solution. *Journal of Electroanalytical Chemistry* **557**, 127-134 (2003).
17. 1 Saputra, E. *et al.* Different crystallographic one-dimensional MnO₂ nanomaterials and their superior performance in catalytic phenol degradation. *Environmental science & technology* **47**(11), 5882-5887 (2013).
18. 1 Abdul, L., Si, X., Sun, K. & Si, Y. Degradation of bisphenol A in aqueous environment using peroxymonosulfate activated with carbonate: Performance, possible pathway, and mechanism. *Journal of Environmental Chemical Engineering*, 105419 (2021).

19. 1 Bai, X., Lyu, L., Ma, W. & Ye, Z. Heterogeneous UV/Fenton degradation of bisphenol A catalyzed by synergistic effects of $\text{FeCo}_2\text{O}_4/\text{TiO}_2/\text{GO}$. *Environmental Science and Pollution Research* **23** (22), 22734-22743 (2016).
20. Liu, Z. *et al.* Degradation of bisphenol A by combining ozone with UV and H_2O_2 in aqueous solutions: mechanism and optimization. *Clean Technologies and Environmental Policy* **20** (9), 2109-2118 (2018).
21. Wang, J.-W., Qiu, F.-G., Wang, P., Ge, C. & Wang, C.-C. Boosted bisphenol A and Cr (VI) cleanup over Z-scheme $\text{WO}_3/\text{MIL-100}$ (Fe) composites under visible light. *Journal of Cleaner Production* **279**, 123408 (2021).
22. Palsaniya, S., Nemade, H. B. & Dasmahapatra, A. K. Graphene based PANI/ MnO_2 nanocomposites with enhanced dielectric properties for high energy density materials. *Carbon* **150**, 179-190 (2019).
23. Davari, N., Farhadian, M., Nazar, A. R. S. & Homayoonfal, M. Degradation of diphenhydramine by the photocatalysts of $\text{ZnO}/\text{Fe}_2\text{O}_3$ and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ based on clinoptilolite: Structural and operational comparison. *Journal of environmental chemical engineering* **5**(6), 5707-5720 (2017).

Figures

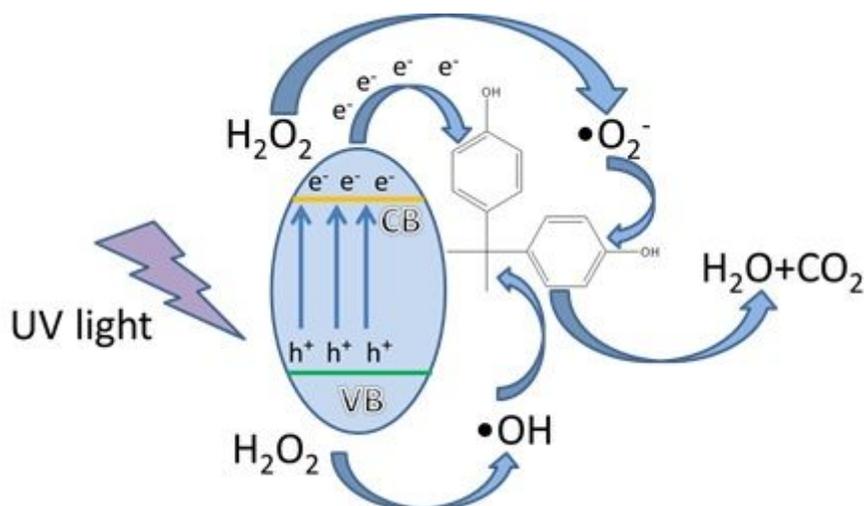


Figure 1

Mechanism of degradation of bisphenol A by $\alpha\text{-MnO}_2$

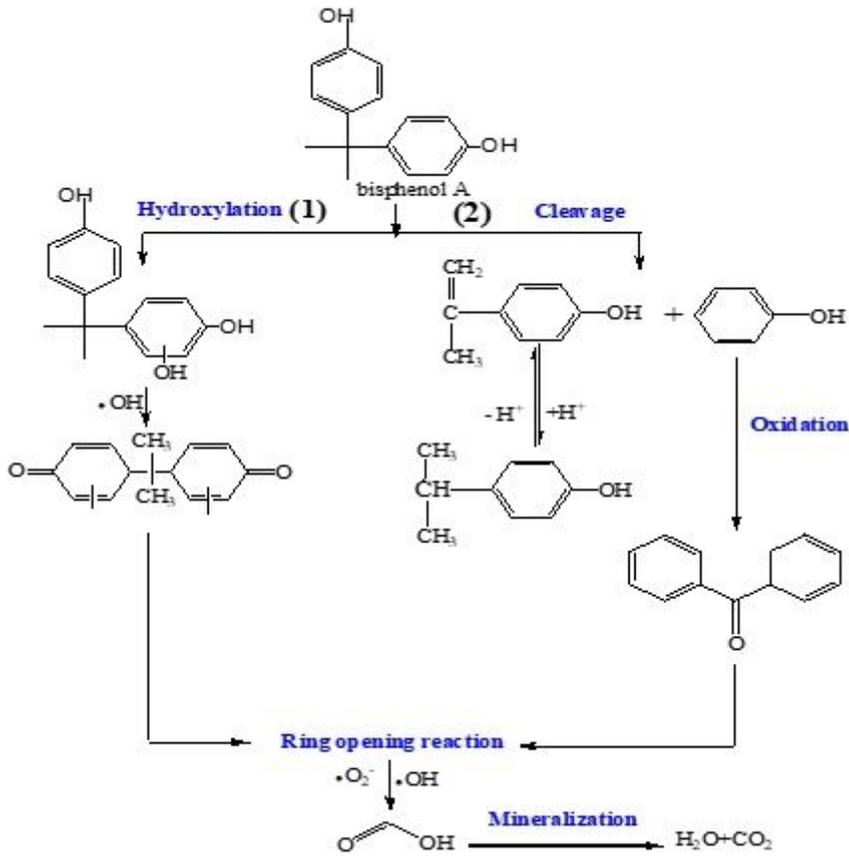


Figure 2

Possible pathways to degrade bisphenol A 18

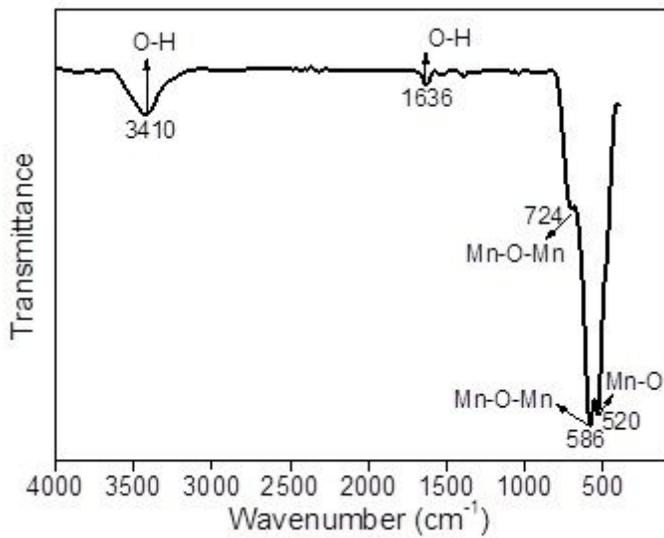


Figure 3

FTIR diagram of α - MnO_2

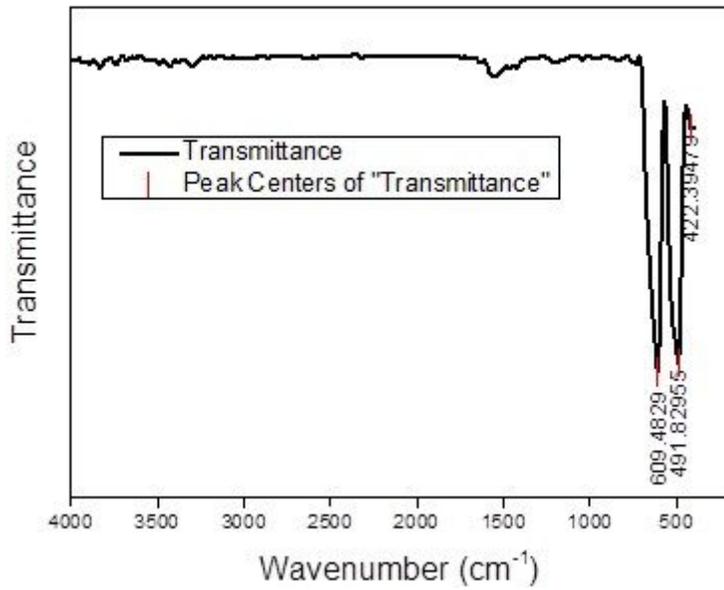


Figure 4

FTIR diagram of $\alpha\text{-MnO}_2/\text{AC}$ (1:1, w/w)

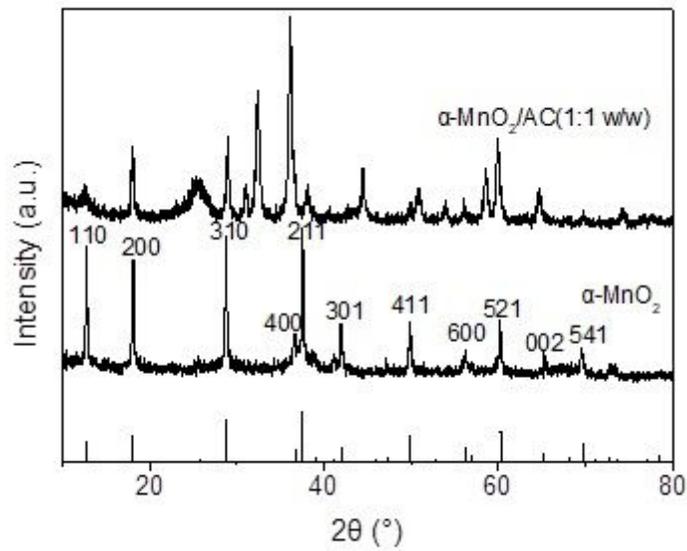


Figure 5

XRD patterns of $\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2/\text{AC}$ (1:1, w/w)

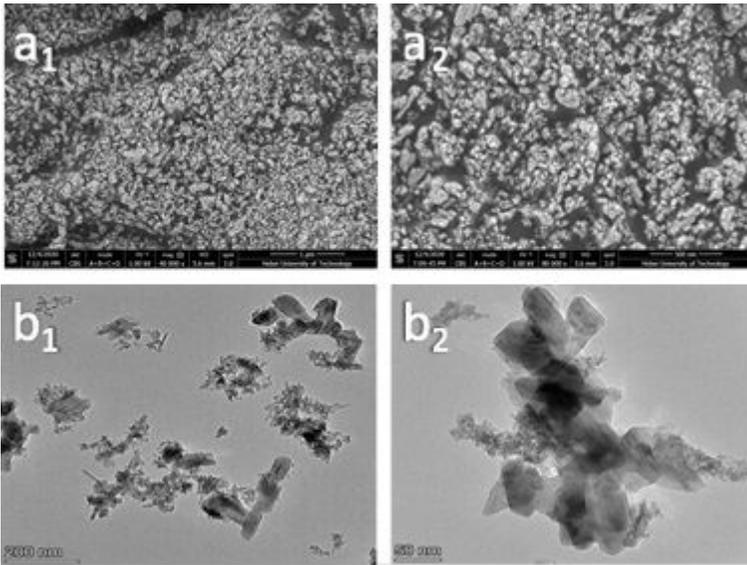


Figure 6

SEM and TEM images of α -MnO₂ (a1 and a2 are SEM images of α -MnO₂, b1 and b2 are TEM images of α -MnO₂)

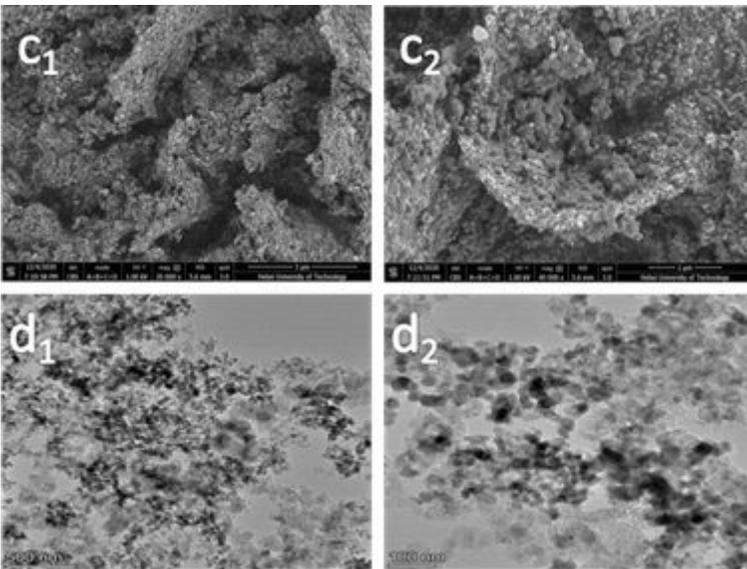


Figure 7

SEM and TEM images of α -MnO₂/AC (1:1, w/w) (c1 and c2 are the SEM images of α -MnO₂/AC (1:1, w/w), d1 and d2 are the TEM images of α -MnO₂/AC (1:1, w/w))

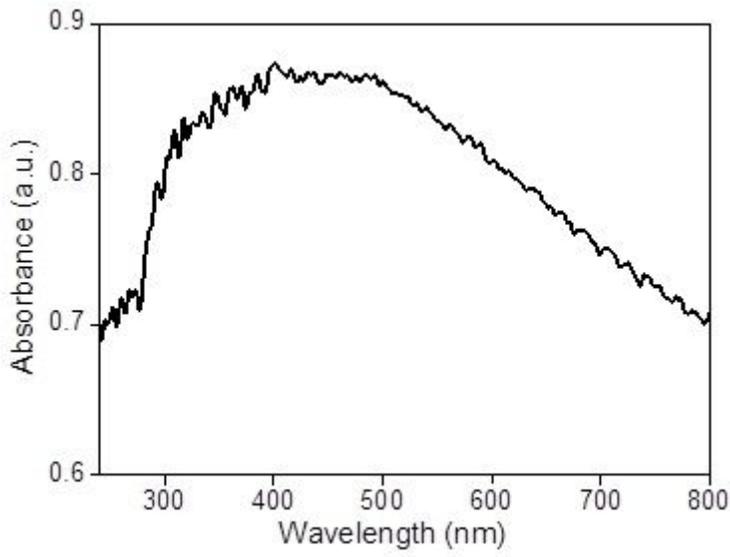


Figure 8

UV-Vis image of α -MnO₂

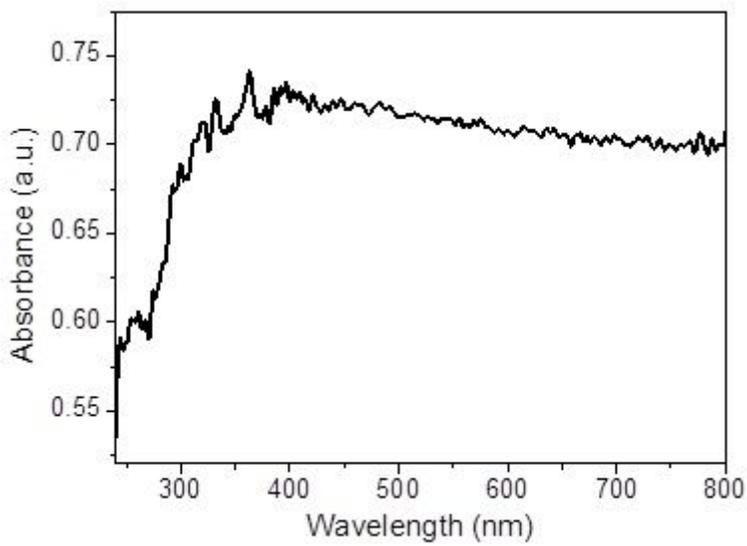


Figure 9

UV-Vis diagram of α -MnO₂/AC (1:1, w/w)

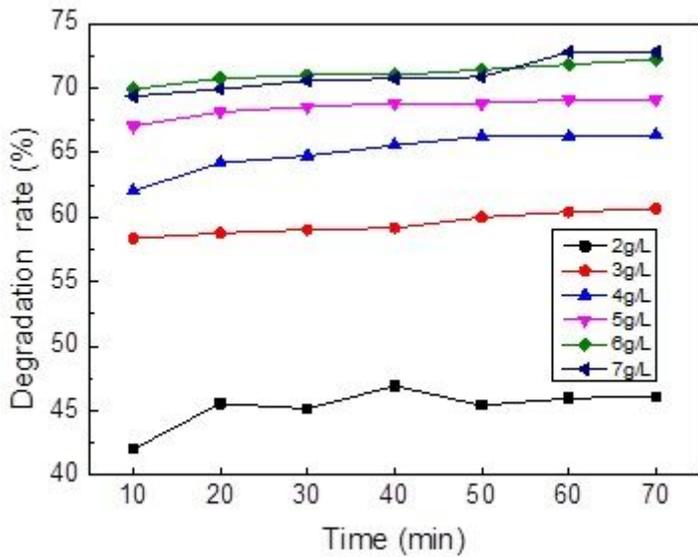


Figure 10

The degradation rate of bisphenol A with different catalyst amounts in 70 minutes (Other reaction conditions: T=303K; [H₂O₂] =500mg/L; 365nm; no pH adjustment)

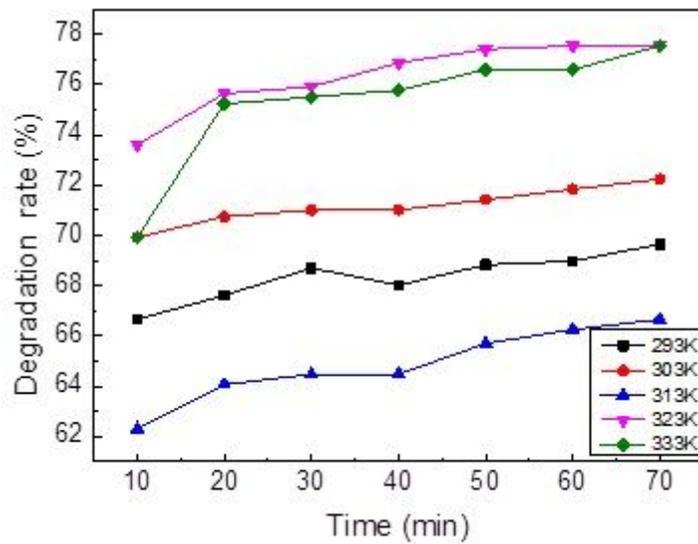


Figure 11

Degradation rate of bisphenol A at different temperatures within 70 minutes (Other reaction conditions: [α-MnO₂] =6 g/L; [H₂O₂] =500mg/L; 365nm; no pH adjustment)

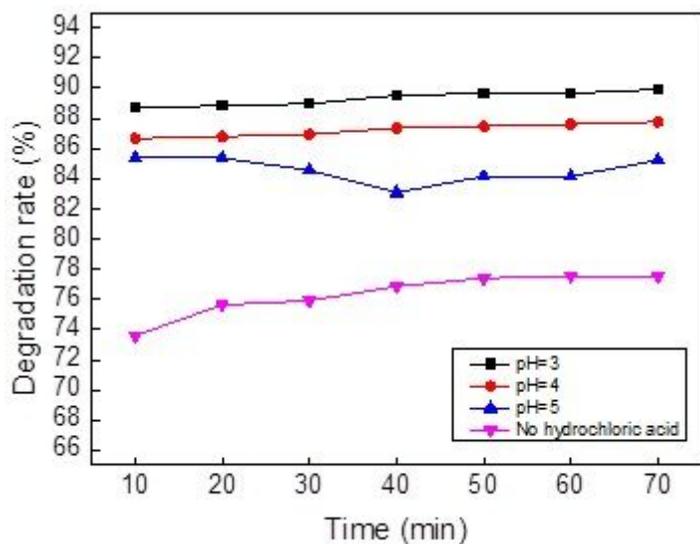


Figure 12

Degradation rates of bisphenol A within 70min under different pH conditions (Other reaction conditions: $[\alpha\text{-MnO}_2] = 6 \text{ g/L}$; $T = 323\text{K}$; $[\text{H}_2\text{O}_2] = 500\text{mg/L}$; 365nm)

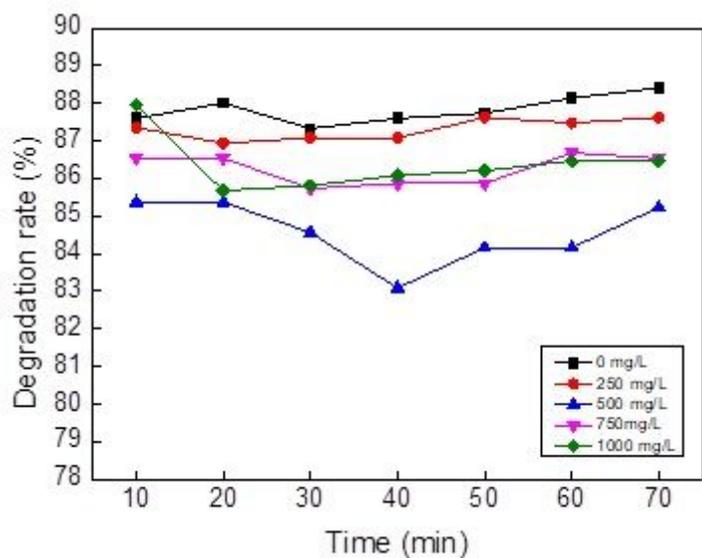


Figure 13

The degradation rate of different amounts of H_2O_2 within 70 minutes (Other reaction conditions: $[\alpha\text{-MnO}_2] = 6\text{g/L}$; $T = 323\text{K}$; $\text{pH} = 5$; 365nm)

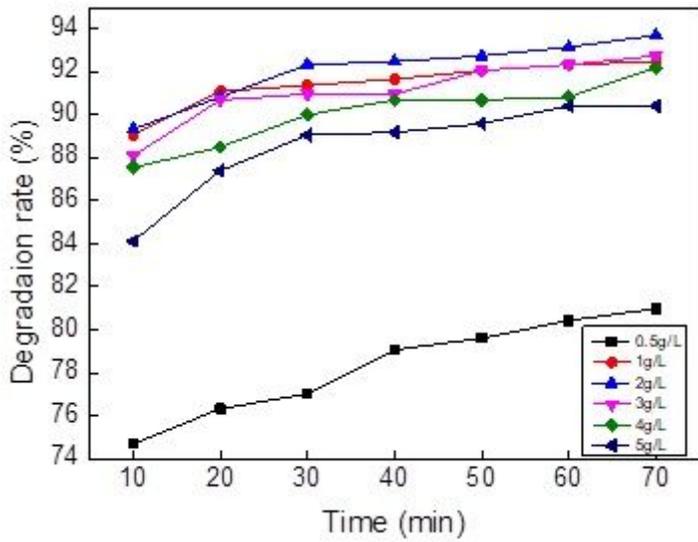


Figure 14

Degradation rate of different catalyst amounts within 70 minutes (Other reaction conditions: T=303K; [H₂O₂] =250mg/L; 365nm)

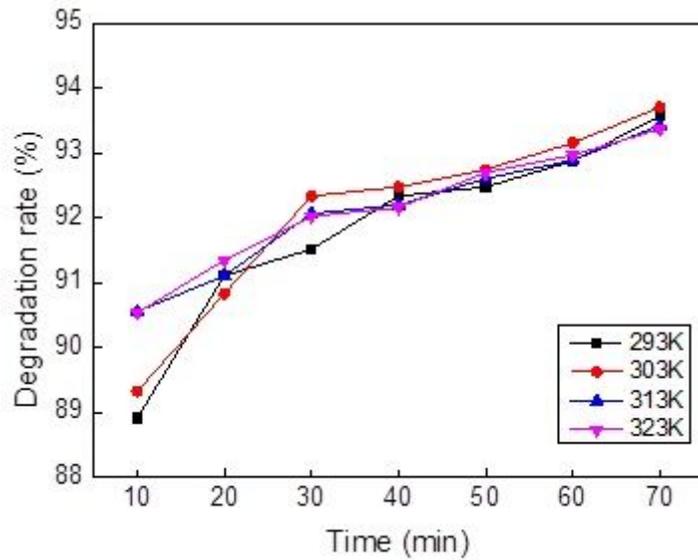


Figure 15

Degradation rate within 70 min under different temperature conditions (Other reaction conditions: [α-MnO₂/AC] =2 g/L; [H₂O₂] =250 mg/L; 365nm)

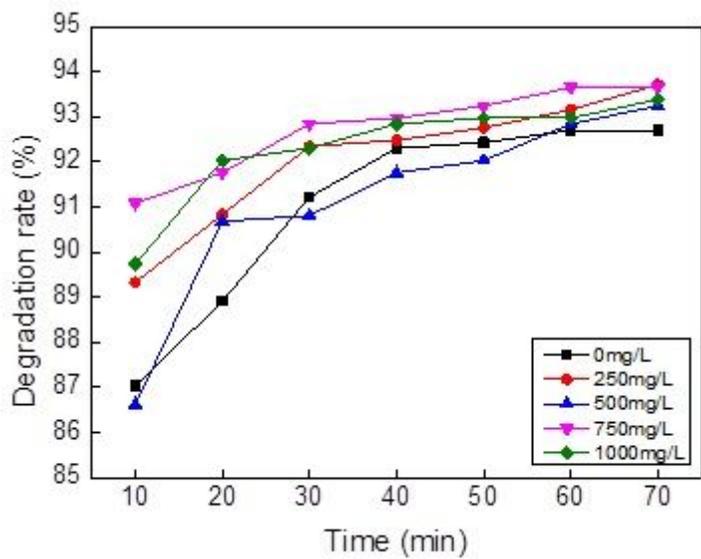


Figure 16

The degradation rate of different amounts of H₂O₂ within 70 minutes (Other reaction conditions: [α-MnO₂/AC] = 2g/L; T=303K; 365nm)