

Study on Adsorption Properties of Activated Carbon for Advanced Treatment of Chemical Wastewater

Yuetong Bie *

The Williston Northampton School, Easthampton MA, USA

* Corresponding author: tbie@williston.com

Abstract. The discharge of untreated or inadequately treated wastewater from chemical factories can lead to severe environmental degradation, posing threats to aquatic ecosystems and human health. Initially, the fine chemical factory in Inner Mongolia relied on a conventional method, primarily based on electrochemical oxidation coupled with electro-Fenton oxidation, resulting in chemical oxygen demand (COD) concentrations of approximately 12,000 mg/L. This research contrasts the enhanced wastewater treatment process incorporating electrochemical oxidation with the method of electrochemical oxidation and chemical additives integrated with activated carbon adsorption. The integration of activated carbon led to a substantial improvement in wastewater treatment efficiency. After treatment with the introduction of activated carbon, COD concentrations were reduced to values ranging from 322 mg/L to 622 mg/L across different batches, indicating a reduction of up to 95% compared to the original method. The stark contrast between the two methods underscores the transformative potential of integrating activated carbon adsorption, positioning it as a pivotal solution for chemical factories in Inner Mongolia.

Keywords: Wastewater treatment, chemical oxygen demand (COD).

1. Introduction

From the 19th century onwards, industrial activities have been a major contributor to environmental pollution, with the release of various organic pollutants into the environment. This intensification, particularly during the 20th century, can be attributed to extended durations of unregulated waste disposal and the lack of effective treatment technologies. Addressing this issue has become a top priority for the international community [1]. Many of these pollutants are toxic, endocrine-disrupting, mutagenic, or even carcinogenic, posing threats to humans, animals, and aquatic life even at minimal concentrations [2, 3].

The inherent challenge is the treatment of these organic pollutants, which are characterized by their bio-refractory nature, making them resistant to conventional treatment methods. Traditional oxidation methods, such as those using ozone or chlorine dioxide, often prove insufficient. Moreover, the transportation and storage of these reactants' present safety concerns [4]. While biological processes are traditional treatment methods, they often fall short of addressing these stubborn contaminants [2,3]. Consequently, oxidation processes have become more prominent as an effective approach to degrade such organics. While direct oxidation techniques have shown promise, they are hampered by challenges such as stringent operating conditions and the need for specific reactants [5-7].

Recent studies have emphasized the potential of integrating (AOPs) with traditional treatment methods, such as biological processes. This combination can lead to synergistic effects, significantly enhancing the efficiency of pollutant removal and expanding the spectrum of treatable contaminants. Particularly, AOPs based on electrochemical methods have demonstrated remarkable efficacy in degrading a diverse array of organic pollutants, even those present in trace amounts. The Fenton process, a notable AOP, involves the reaction of peroxides with iron ions to produce active oxygen species that can oxidize various compounds. Introduced in 1894 by H.J.H. Fenton, this reaction has been widely used for wastewater treatment, effectively removing numerous hazardous organics [8]. AOPs primarily generate hydroxyl radicals, which are highly reactive and can swiftly attack most organic molecules [9, 10]. Their versatility is evident from their adaptability to different treatment

requirements and diverse methods of hydroxyl radical production. However, it's essential to note that while AOPs like photo-electro-Fenton and sono-electro-Fenton are becoming popular, some methods, especially those dependent on solar energy, might be less effective in regions with limited sunlight [11, 12].

The coupling technology addresses the stagnation issues of Fenton oxidation and the inefficiencies of electrochemical oxidation, achieving a stable COD_{Cr} removal rate of 60% to 90%. This is an improvement of 2-5 times compared to traditional Fenton oxidation techniques. Additionally, sludge production is reduced by 80%, operational costs decrease by two-thirds, and there's a realization of iron recycling and continuous COD degradation [13, 14].

While advanced oxidation processes (AOPs) and the Fenton process are effective in degrading organic compounds, they sometimes face challenges in completely removing certain persistent pollutants. Activated carbon, on the other hand, a form of carbon processed to have small, low-volume pores, is renowned for its high adsorptive capacity. In wastewater treatment, it serves as an efficient method for removing organic pollutants due to its vast surface area and chemical stability. When combined with AOPs, activated carbon can act as an adsorbent, capturing those pollutants that might not be fully degraded by the oxidation processes. Moreover, activated carbon can serve as a catalyst or catalyst support in some AOPs, enhancing the generation of reactive species and improving the overall efficiency of the treatment. Therefore, the integration of activated carbon into AOPs provides a synergistic effect, ensuring a more comprehensive and efficient wastewater treatment.

A specific fine chemical company in Inner Mongolia, China, produces wastewater laden with a significant number of organic pollutants, inorganic salts, and peroxides. This unique composition makes the wastewater highly toxic and challenging to degrade. Notably, the chemical oxygen demand (COD) of wastewater from this chemical company reaches alarming levels of 12,000 mg/L, far exceeding many standard thresholds. This high concentration underscores the presence of abundant organic substances in the wastewater, which, if untreated, can pose severe environmental threats. While the original treatment method employed by the company was based on AOPs, it was found to be insufficient in meeting the required standards, leading to excessive pollutant levels. This study introduces an innovative approach that integrates activated carbon adsorption with electrochemical oxidation, coupled with electro-Fenton oxidation techniques. By leveraging this combined method, we aim to significantly enhance the removal efficiency of organic pollutants, ensuring that the treated water meets environmental safety standards in terms of pollutant concentration, pH balance, and overall water quality.

2. Experimental methods

2.1. Materials

The activated carbon used in this study was procured from Zhongchuang, located in Henan, China, under the model number ZC 102820 with a high purity level of 99.99%. Originating from high-quality coal, activated carbon is processed to possess a uniform particle size of 6 mm. Such a size is optimal for ensuring efficient adsorption of organic pollutants from wastewater, given its extensive surface area and the inherent porosity of the carbon particles.

2.2. Wastewater Treatment Process with Electrochemical Oxidation

The chemical factory has implemented a solution based on electrochemical oxidation coupled with electro-Fenton oxidation, rooted in the Fenton reaction. A hallmark of this technique is the synergistic action between the anode and cathode in electrocatalytic Fenton oxidation. The oxygen molecules/atoms generated at the anode become supersaturated and are strongly urged to diffuse to the cathode, realizing in-situ oxygen utilization in electro-Fenton oxidation. This results in an oxidation efficiency increase by 6.58 times. Figure 1 illustrates the electrocatalytic wastewater treatment process. The process begins with wastewater inflow, followed by two stages of electrocatalytic treatment, each accompanied by the addition of sulfuric acid/hydrogen peroxide.

Subsequent flocculation sedimentation processes, with the addition of alkaline solutions, ensure the effective removal of contaminants. The final step involves water outflow, ensuring the treated water meets the desired quality standards.

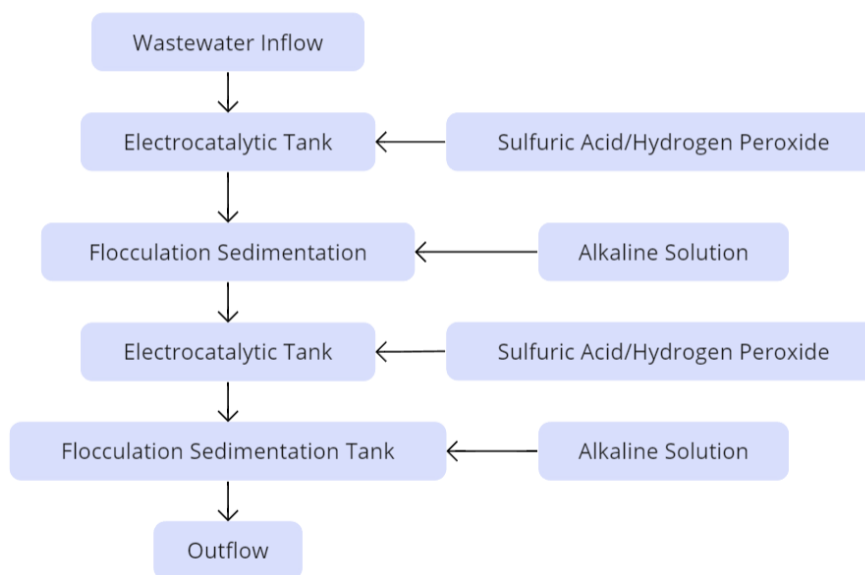


Figure 1. Enhanced wastewater treatment process incorporating electrochemical oxidation and chemical additives.

2.3. Wastewater Treatment Process with Electrochemical Oxidation and Activated Carbon Adsorption

Building on the processes previously described, Figure 2 delves deeper into the enhanced wastewater treatment process. It particularly highlights the sequence where the activated carbon adsorption phase is introduced after the primary electrocatalytic oxidation phase. This incorporation of activated carbon adsorption, which lasts approximately 2 hours, plays a pivotal role in amplifying the overall treatment efficiency.

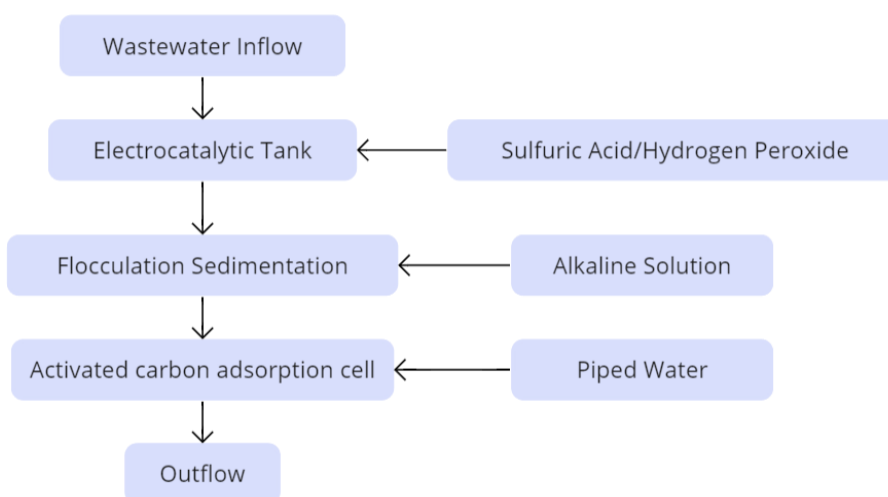


Figure 2. Enhanced wastewater treatment process incorporating electrochemical oxidation and chemical additives with integrated activated carbon adsorption.

2.4. COD Analyzer

To ensure the reliability of our findings, especially concerning the COD concentration, we utilized the HACH CODMAXIII online COD analyzer. This instrument, equipped with an LED light source at 620 nm, provided us with precise and reliable COD measurements within a range of 10.0 to 5,000

mg/L. In terms of accuracy. For concentrations between 10.0 to 39.9 mg/L, the accuracy is $\pm 10\%$. For concentrations between 40.0 to 99.9 mg/L, the accuracy is $\pm 6\%$. For concentrations between 100.0 to 5,000 mg/L, the accuracy is $\pm 3\%$. Furthermore, the precision is $\leq 5\%$ for concentrations between 10.0 to 39.9 mg/L and $\leq 3\%$ for concentrations between 40.0 to 5,000 mg/L. The instrument also boasts built-in sample verification features and can automatically calibrate based on verification results. An expandable quality control module allows for sample verification at any specified concentration and spike recovery functions.

3. Result and Discussion

3.1. Wastewater Quality Indicators of This Project

The wastewater from the original chemical factory exhibited high concentrations of several pollutants. Among these, the Chemical Oxygen Demand (COD) stands out as a primary concern due to its high initial concentration. This study primarily focuses on the COD indicator, aiming to align with the data presented in the subsequent sections.

Ammonia nitrogen is another crucial parameter to consider. A concentration exceeding 1.5 mg/L is known to be detrimental to aquatic life [10]. Our sample revealed an ammonia nitrogen concentration of 30 mg/L, which is twenty times the recommended threshold, signifying a substantial ammonia presence. However, given our study's emphasis on COD, we will limit our discussion to ammonia nitrogen. Additionally, the wastewater contained a chloride concentration of 27,000 mg/L. Such elevated levels can lead to salinity pollution, posing threats to aquatic ecosystems.

Referring to Table 1, the desired water quality standards necessitate reducing the COD to below 400 mg/L. This translates to a reduction of the original wastewater's COD concentration by nearly 30 times. Concurrently, the target for BOD5 (Biochemical Oxygen Demand) is set below 10 mg/L. BOD5 serves as an indicator of the biodegradability of organic matter in wastewater. A diminished BOD5 value indicates effective degradation of the organic content.

Table 1. Wastewater discharge volume and quality indicators of this project (unit: mg/L, except pH)

	COD	Ammonia Nitrogen	SS	TDS	pH	Chloride	Volume
Value	12000	30	112	55000	14	27000	100t/d

Table 2. Target water quality indicators (unit: mg/L, except pH)

	COD	BOD5	SS	TDS	pH	Chloride
Value	≤ 400	≤ 10	≤ 30	57000	6~9	35000

3.2. AOP with Activated Carbon

To ensure the accuracy of COD measurements in this study, we employed the HACH CODMAXIII online COD analyzer. This device consistently delivered precise and trustworthy results, bolstering the reliability of our experimental data. For the experiment, we randomly selected three batches. Each batch underwent identical electrocatalytic treatment for the initial 12 hours, leading to comparable COD concentrations across the batches at the 0, 6, and 12-hour intervals. Table 3 provides a comprehensive overview of these COD concentrations. Following the 12-hour treatment, the batches took different treatment routes. While the first batch persisted with the electrocatalytic treatment, the second and third batches transitioned to the activated carbon adsorption process. This shift resulted in a notable decline in COD concentrations, emphasizing the efficacy of integrating activated carbon into the treatment process.

Table 3. COD concentrations before activated carbon adsorption.

Reaction Duration	Batch 1 (mg/L)	Batch 2 (mg/L)	Batch 3 (mg/L)
0h	12415	11235	10135
6h	433	4362	3834
12h	2408	3200	2120
15h	1980	2532	1859
18h	1360	1603	1202

After 12 hours of treatment, the treatment paths for each batch were divided. For every batch, a portion continued with the electrocatalytic treatment, while another portion began the activated carbon adsorption process. According to factory technical standards, the activated carbon adsorption process requires adsorption of 1 kg of activated carbon per ton of water. The replacement frequency of the activated carbon is determined by its saturation level, which is contingent on the scale of the operation. The activated carbon can be regenerated stably, with an adsorption time of approximately 2 hours.

Table 4. COD concentrations after activated carbon adsorption

Reaction Duration	Batch 1 (mg/L)	Batch 2 (mg/L)	Batch 3 (mg/L)
0h	12415	11235	10135
6h	4333	4362	3834
12h	2408	3200	2120
After Adsorption(2h)	374	662	322

The post-adsorption results are evident in Table 4. There's a marked reduction in COD concentrations across all batches after introducing activated carbon adsorption. Specifically, after the adsorption process, for Batch 1, COD reduced from 2,408 mg/L at 12 hours to 374 mg/L, achieving an approximate 84.5% removal rate. For Batch 2, COD dropped from 3,200 mg/L at 12 hours to 662 mg/L, resulting in a removal rate of around 79.3%. For Batch 3, COD declined from 2,120 mg/L at 12 hours to 322 mg/L, marking a removal rate of about 84.8%.

In conclusion, the AOP with activated carbon method proves more effective for the deep treatment of chemical wastewater compared to other methods. With an activated carbon dosage of 1kg per ton of water and a reaction time of about 2 hours, the effluent's average COD value saw a significant decrease.

4. Conclusion

In this research, we conducted a comprehensive assessment of the wastewater treatment techniques utilized by a specific chemical factory in Inner Mongolia. By comparing the conventional electrochemical oxidation and electro-Fenton oxidation methods with a novel strategy that integrates activated carbon adsorption, we observed marked differences in their performance. The integration of activated carbon adsorption led to a significant decrease in COD concentrations. Specifically, values dropped to 374 mg/L, 662 mg/L, and 322 mg/L across various batches. In relative terms, this represents a remarkable reduction, with some batches showing a decrease of up to 95%. The advantages of this integrated method are manifold. Firstly, the use of activated carbon enhances the overall efficiency of the treatment process due to its high adsorptive capacity, which effectively captures pollutants that might not be fully degraded by oxidation processes. Secondly, the method offers a sustainable and environmentally friendly solution, reducing the need for chemical reactants and minimizing secondary pollution. Lastly, from an economic standpoint, the reduced operational costs and potential for reusing the activated carbon make it a cost-effective alternative. These results highlight the importance of incorporating activated carbon adsorption into wastewater treatment strategies. Furthermore, our study underscores the sustainability and economic benefits of this

approach, positioning activated carbon adsorption as a game-changing solution in the realm of wastewater treatment.

References

- [1] S. E. Manahan, *Environmental Chemistry*. Lewis Publishers, Boca Raton, USA, 1994, 223 – 240.
- [2] A. Garg, I.M. Mishra, S. Chand, Oxidative phenol degradation using non-noble metal-based catalysts. *CLEAN*, 2010, 38: 27 – 34.
- [3] L.A. Bernal-Martinez, C. Barrera-Diaz, C. Solis-Morelos, N. Reyna. Synergy of electrochemical and ozonation processes in industrial wastewater treatment. *Chem. Eng. J.*, 2010, 165: 71 – 77.
- [4] K. Rajeshwar, J. G. Ibañez, G. M. Swain. *J. Appl. Electrochem*, 1994, 24: 1077 – 1091.
- [5] A. Cybulski. Catalytic wet air oxidation: are monolithic catalyst and reactors feasible? *Ind. Eng. Chem. Res.*, 2007, 46: 4007 – 4033.
- [6] P. Kritzer, E. Dinjus. An assessment of supercritical water oxidation (SCWO): existing problems, possible solutions and new reactor concepts. *Chem. Eng. J.*, 2001, 83: 207 – 214.
- [7] S.T. Kolaczowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh. Wet air oxidation: a review of process technologies and aspects in reactor design. *Chem. Eng. J.*, 1999, 73: 143 – 160.
- [8] E. Neyens, J. Baeyens. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.*, 2003, 98: 33 – 50.
- [9] W.H. Glaze, J.W. Kang, D.H. Chapin. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. Eng.*, 1987, 9: 335 – 352.
- [10] J. Hoigne. Inter-calibration of OH radical sources and water quality parameters. *Water Sci. Technol.*, 1997, 35: 1 – 8.
- [11] M. Klavarioti, D. Mantzavinos, D. Kassinos. Removal of residual pharmaceutical from aqueous systems by advanced oxidation processes. *Environ. Int.*, 2009, 35: 402 – 417.
- [12] J.V. Anderson, H. Link, M. Bohn, B. Gupta. Development of solar detoxification technology in the USA: an introduction. *Sol. Energy Mater.*, 1991, 24: 538 – 549.
- [13] Alexandro M.M., Vargas A.L., Cazetta M.H., et al. Adsorption of methylene blue on activated carbon produced from flamboyant pods: Study of adsorption isotherms and kinetic models. *Journal of Chemical Engineering*, 2011, 67: 2 - 10.
- [14] Wang L.W., Tamainot Z.T., Thorpe R., et al. Study of thermal conductivity, permeability, and adsorption performance of consolidated composite activated carbon adsorbent for refrigeration. *Water Research*, 2011, 36: 2062-2066.
- [15] Zhang, L., & Tan, P. Coupling technologies for efficient wastewater treatment. *Journal of Water Resources*, 2020, 40 (3): 234 - 245.
- [16] Yang, M., & Li, Z. Traditional vs. modern Fenton oxidation techniques. *Journal of Oxidation Processes*, 2018, 29 (2): 112 - 120.
- [17] Mohajerani, M., Mehrvar, M., & Ein-Mozaffari, F. An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment. *International Journal of Engineering*, 3 (2), 120.