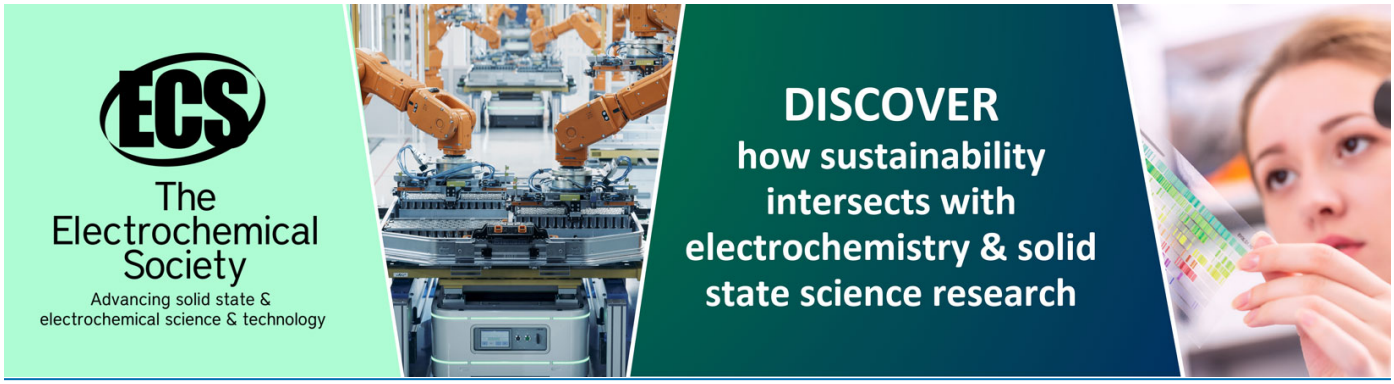
A new water treatment technology—Hybrid ozonation-coagulation process: A review



A new water treatment technology—Hybrid ozonation-coagulation process: A review

Lelan Wei [1a*]

[1]XAUAT UniSA An De College, Xi' an University of Architecture and Technology, Xi'an 710311, China

[a*]weilelan@xauat.edu.cn

Abstract—Hybrid ozonation-coagulation (HOC) process is an integrated water treatment process of simultaneous ozone and coagulation processes. This paper introduces the origin, performance, reaction mechanism and influence of coagulant in HOC system. Compared with traditional air flotation and pre-ozone-coagulation, HOC system shows more advantages in removal of organic pollutants. It is attributed to abundant pathways for reactive oxygen species (ROS) generation in HOC process, which not only transfers pollutants to flocs but also synchronously degrades some organic pollutants.

1. Introduction

Hybrid ozonation-coagulation (HOC) process is proposed for the purpose of shortening the water treatment process and improving the removal efficiency of organic pollutants, in which ozone oxidation and coagulation process is simultaneously placed in the one system (Jin, Jin et al. 2017).

The inspiration of hybrid ozonation-coagulation (HOC) comes from integrated reactor of dissolved ozone flotation (DOF) (Jin, Wang et al. 2006). DOF is an intensified technology integrating ozonation and dissolved air flotation (DAF) together. By replacing air with ozone as the air source of flotation could not only achieve separation of flocculated particulates but also decolorizing, disinfection and degradation of organic matters, making up for the limited degradation ability of DAF (Wilinski, Marcinowski et al. 2017). Through the aid of coagulation and the microbubbles generated by the air floatation process, DOF could also improve the ozonation effect (Coward, Tribe et al. 2018, Wang, Wang et al. 2021), hence intensify the removal of pollutants and achieve smaller footprint and lower cost (Jin, Wang et al. 2006, Yao, Jin et al. 2021).

HOC achieves the simultaneous coagulation and ozonation by aerating ozone into the reactor while the coagulation reaction is going on (Jin, Jin et al. 2017). Based on electric flocculation and DOF, electro-hybrid ozonation-coagulation (E-HOC) is proposed, which as the derivative of HOC, is realized by injecting high concentration of ozone reserve water in an electric coagulation reactor (Jin, Xie et al. 2020).

This work summarizes application and advantages of HOC system, and differences of effect and mechanism based on different coagulants and reaction conditions of HOC system. The purpose of this paper is to provide a theoretical basis for the application of HOC in a wider range of wastewater treatment.

2. Performance and advantages of HOC system

HOC based on both aluminum coagulants and ferric coagulants can effectively remove organic compounds and ibuprofen from effluent from sewage treatment plants and removal efficiency of DOC were 39%~58% at pH 6~8, much higher than pre-ozonation coagulation (Jin, Liu et al. 2020).

Based on electric flocculation and HOC, Jin Xin et al. further proposed that electro-hybrid Ozonation-coagulation (E-HOC) for wastewater treatment plant effluent and ibuprofen treatment. At pH 5~9, the performance of E-HOC (DOC removal efficiency 41%~59%) is better than that of single electric flocculation (32%~39%), ozonation (11%~17%) and pre-ozonation electric flocculation (20%~39%) (Jin, Xie et al. 2020).

Furthermore, the effects of electrode including metal cation type and configuration of connection and were studied. Bipolar E-HOC (BE-HOC) configuration demonstrate better removal performance and cost less energy than monopolar E-HOC process (ME-HOC), and dual-coagulant (released by Al electrode and Fe electrode) pattern is more efficient than single coagulant pattern (Al or Fe) (Jin, Xie et al. 2021).

In HOC system, the ozone aerated flocs are formed by flocs wrapping and adsorbing bubbles. The dynamic characteristic (Wang, Jin et al. 2021), changes in chemical composition (Jin, Wang et al. 2019, Jin, Xie et al. 2020) and morphological structure (Liu, Jin et al. 2018) of aerated flocs generated in HOC system were studied. According to these results, it is inferred that each piece of ozone aerated floc as a micro unit which carries ozone microbubble, coagulant hydrolysate, particulates and organic matter is important in degradation and separation of pollutants in HOC.

3. Interactions of ozone and coagulation

According to previous studies, ozone aerated floc with complex composition and interface may be the reaction centre. Ozone on it oxidizes organic matter and improves its coagulation capacity after modification. Meanwhile, the hydrolysed coagulant catalyses the ozonation process.

3.1. Modification of organic matter by ozone may promote coagulation

Ozone significantly affects the properties of organic functional groups. It was found that with the increase of ozone concentration, the aromaticity of hydrophobic organic compounds in effluent water of municipal sewage treatment plants decreases significantly, while aliphatic and ketone (C=O) components increase when ozone concentration is low (Jin, Jin et al. 2016).

In addition, the oxidation modification of organic functional groups by ozone molecules is also selective. Ozone preferentially oxidizes the electron-giving groups such as phenolic hydroxyl, amino and olefin on the benzene ring, increasing the amount of oxygen-containing functional groups such as hydroxyl and carboxyl in the organic matter (Jin, Jin et al. 2016). Carboxyl and hydroxyl groups are important in complexation and coagulation between coagulant and organic matters (Song, Jin et al. 2019).

By modification of the local structure of organic pollutants through oxidation, the existence of ozone increases the content of polar and hydrophilic components (Liu, Wang et al. 2006) and particle instability (rise in zeta potential), which improves the flocculation of water, enhances the removal of DOC and reduces the consumption of coagulants (Sadrnourmohamadi and Gorczyca 2015). It is enriched on the surface of the flocs and combined with the hydroxyl complex in the flocs, so as to realize the rapid transfer and separation of pollutants (Jarvis, Jefferson et al. 2005).

It was reported that pre-ozonation could destabilize the microalgae particles, reduce the surface charge and benefit coagulation/flocculation (Oliveira, Machado et al. 2020).

Due to the existence of ozone, functional groups on organic matters are changed, potentially affecting the coagulability of pollutants and enabling promotion of coagulation

3.2. Hydrolysed coagulant may catalyse ozonation

There are abundant research bases for promoting ozonation by using aluminum oxide as catalyst. For example, nano-aluminum oxide degrades carboxylic acid and ciprofloxacin (Nemati Sani, Navaei

fezabady et al. 2019), catalytic ozonation of ibuprofen on mesoporous SBA-15 supported by Al_2O_3 (Bing, Hu et al. 2015), and mineralization of sulfamethoxazole, phenytoin, diphenhyramine, diclofenac sodium and acyclovir in aqueous solution by mesoporous γ -Ti-Al_2O_3 (Bing, Hu et al. 2017).

Considering that the complex surface of ozone aerated flocs contains both aluminum or iron coagulant hydrolysates and organic matter, a reaction mechanism similar to heterogeneous catalytic ozonation may exist.

4. Mechanism of hybrid ozonation-coagulation

In hybrid ozonation-coagulation system, reactive oxygen species (ROS) eg. •OH, $•O_2^-$, $•HO_3$, $•HO_2^-$ are detected, revealing that advantage ozonation process takes place (Jin, Jin et al. 2017). The surface hydroxyl groups bond to Al were determined to be the active reaction sites for the HOC process (Jin, Jin et al. 2017, Jin, Wang et al. 2019).

There are four proposed pathways for ROS generation in HOC as shown in Table 1.

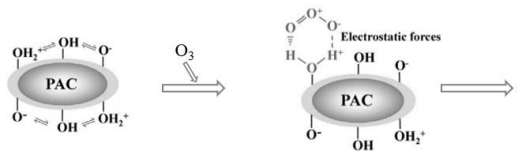
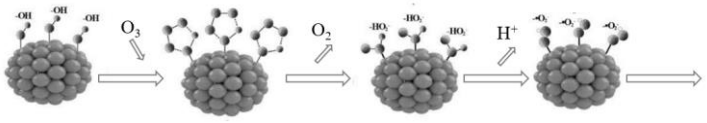
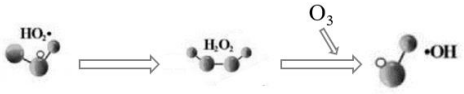
1) Direct decomposition of ozone produces reactive oxygen species (ROS) by electron transfer.

2) O_3 could be absorbed on hydrolyzed aluminum and bond to surface hydroperoxyl anion (HO_2^-) to form a ring, then the ring could decompose to ROS.

3) O_3 could be absorbed on hydrolyzed aluminum and ferric coagulant and bond to surface hydroxyl (HO^-) with Al-OH-O_3 or Fe-OH-O_3 to form a ring, then the ring opens and release O_2, and leave surface HO_2^-, to react with O_3 to form one $•HO_3$ and one surface adsorbed superoxide anion radical ($•O_2^-$). Both$•HO_3$ and $•O_2^-$ can initiate chain reactions to generate more •OH.

4) Peroxone reaction takes place in the HOC process where H_2O_2 was generated and then react with O_3 to form •OH.

Table 1. Proposed mechanism of HOC

	Pathway	ROS products	Conditions	Reference
Pathway 1	O_3 decompose directly.	•OH, $•O_2^-$, $•HO_3$, $•HO_2^-$	pH=5, 7, 9	(Jin, Jin et al. 2017, Jin, Xie et al. 2020)
Pathway 2		•OH, $•O_2^-$, $•HO_3$, $•HO_2^-$	pH=5, 7, 9	(Jin, Jin et al. 2017)
Pathway 3		•OH, $•O_2^-$, $•HO_3$, $•HO_2^-$	pH=6, 7, 8	(Jin, Liu et al. 2020)
Pathway 4		•OH	pH=5, 6, 7, 8	(Jin, Liu et al. 2020, Jin, Xie et al. 2020)

Type of coagulants have influence on HOC process and the removal efficiency.

$AlCl_3•6H_2O$ and preformed Al_{13} are both aluminum salt coagulants, but their treatment effects are obviously different. $AlCl_3•6H_2O$ and preformed Al_{13} both can generate •OH in situ, however preformed Al_{13} with higher proportion of surface hydroxyl groups to generate •OH showed a higher removal performance of ibuprofen in the HOC process. than that with $AlCl_3•6H_2O$ as the coagulant (Jin, Wang et al. 2019).

Aluminum and ferric coagulant are also compared in treatment of wastewater treatment plant (WWTP) effluent and ibuprofen (IBP). Fe-HOC (ferric salt as coagulant in HOC) exhibit better

performance than Al-HOC (aluminum salt as coagulant in HOC), because higher content of surface hydroxyl groups was detected on hydrolyzed ferric coagulant than the hydrolyzed aluminum salt. Moreover, higher H_2O_2 and $\bullet O_2^-$ detected in Fe-HOC implies more contribution of peroxone process (Liu, Jin et al. 2018).

Crystal morphology of aluminum evolves in HOC process – proportion of tetrahedral Al decreases and octahedral Al increases. The reason is that tetrahedral Al is stronger Lewis acid site than octahedral Al and Lewis acid sites are considered to be important active components in catalytic ozonation (Bing, Hu et al. 2017, Yu, Li et al. 2019).

5. Future trends in study of HOC

The studies of mechanism of HOC and chemical composition changes of ozone aerated floc are relatively thorough, but the study of hydrodynamics in the process needs to be strengthened, which is related to the design optimization of HOC reaction device.

6. Conclusions

HOC is superior to traditional air flotation and pre-ozone coagulation in removing organic pollutants. EHOC has advantages over electric flocculation alone and pre-ozone-electric flocculation. Abundant ROS has been detected in HOC process, and four pathways to generate free radicals have been found. Surface hydroxyl groups on ozone aerated floc are key to free radical generation. Different kinds of coagulants show differences in HOC system due to different surface hydroxyl content and aluminium crystal morphology. For E-HOC, the type and configuration of electrodes also affect the generation of active free radicals in the system.

Acknowledgments

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