Ultraviolet-activated sodium perborate process (UV/SPB) for removing humic acid from water

Ahmed Jaber Ibrahim [a],*
[a] *Scientific Research Center, Al-Ayen University, ThiQar 64011, Iraq*

ABSTRACT

Humic acid (HA) has a complex chemical composition and the ability to chelate, adsorb, and exchange ions with organic and inorganic contaminants in bodies of water, which worsens water quality and poses a threat to human health and the environment. In this research, an Ultraviolet-activated sodium perborate (UV/SPB) symbiotic method (UV/SPB) was developed to eliminate humic acid in water. The major synergistic and degradative processes of the humic acid were investigated, as well as the impact of the starting humic acid concentration, sodium perborate dose, and primary pH value on the humic acid elimination. Results indicate that just 0.5 % and 1.5 % of humic acid were eliminated mostly by sole UV and sole sodium perborate (SPB) methods, respectively. More effectively than other methods, UV/SPB removed humic acid with an efficiency of 88.83%. An experiment using free radicals to mask them revealed that the primary catalyst for humic acid removal is the hydroxyl radical generated by sodium perborate activation. The excitation-emission matrix spectroscopy, Ultraviolet-visible absorption (UV-Vis) spectrum, absorbance ratio values, specific Ultraviolet-visible absorbance values (SUVA), and UV/SPB method performance findings demonstrated the UV/SPB method's capability to degrade and mineralize humic acid.

1. Introduction

Humic acid, a non-regular macromolecular polymer formed over a long period by the polymerization of various biological remnants, is the principal component of natural organic matter (NOM) [1]. The complex chemical composition of humic acid and the presence of numerous organic functional groups, including hydroxyl(-OH), carboxyl(-COOH), carbonyl(C=O), methoxy(-O-CH3), and quinone groups (–(C(=O)–), make it able to chemically adsorb, exchange ions, and physical chelation with contaminants in bodies of water that are both organic and inorganic. This compromises the water quality and endangers the ecosystem and public health [2]. Environmental studies now have one goal figuring out how to eliminate humic acid from water properly and effectively. Physical and chemical oxidation techniques are the primary means of regulating humic acid in water. The coagulation method [3], flocculation method [4], and adsorption method [5] are physical techniques for removing humic acid. However, these techniques transport humic acid into the solid phase; further solid waste processing is still necessary. Due to the rapid degradation and mineralization of humic acid, chemical oxidation is of major interest [6]. Commonly used chemical

*Corresponding Author: Ahmed Jaber Ibrahim
Email: ahmed.jibrahim@alayen.edu.iq
https://doi.org/10.24200/amecj.v5.i03.191

oxidation processes for treating organic wastewater include the photocatalysis method [7-9], The Fenton oxidation method [10], and the electrochemical oxidation method [11]. Despite this, each of these processes has drawbacks, including difficult reaction conditions and complicated operations. The in situ oxidizing agent sodium perborate (SPB, $NaBO_3$) is frequently employed. In contrast to sodium percarbonate, cyclic perborate ions ($B_2O_8H_4^{-2}$), which are made up of two peroxide chains lacking BO_3^- anions, are present in sodium perborate instead of being associated with inorganic salt and hydrogen peroxide [12]. After being dissolved in water, sodium perborate creates hydrogen peroxide steadily, making it an effective hydrogen peroxide alternative [13]. Solid sodium perborate is safer, simpler to carry, and easier to store than liquid hydrogen peroxide. The formation of hydroxyl radicals (·OH) can occur during sodium perborate activation across a broad range, which is crucial. The primary methods for sodium perborate activating are ultraviolet light [14] and transitional metal ions [15]. Scientists have utilized UV-activated perborate to remove organic pollutants [13]. Furthermore, the perborate is often used as an oxidant in homogeneous photo-Fenton and heterogeneous Fenton-like reactions to remove colorant and phenolic compounds [12,16]. Of these, the UV-activated process is simple to use, secure, and free of other pollutants, allowing it to effectively stimulate hydrogen peroxide to break down organics in sewage [17,18]. Though UV-activated peroxide as well as the UV-activated sodium perborate (UV/SPB) approach has been used to eliminate organics from water, reports of the elimination of HA using UV-activated SPB are infrequent. To reduce humic acid in an aqueous solution, it was important for this research to construct a UV/SPB symbiotic system (UV/SPB). The influences of the primary humic acid concentration, sodium perborate concentration, and starting pH value on humic acid cleansing were investigated using the practical and effective spectrophotometric approach [19]. Using a free radical masking test, the primary compounds

produced in the symbiotic system for removing humic acid were identified. The degradation process was carefully investigated using UV spectrum, total organic carbon, and 3-dimensional excitation-emission matrix spectroscopic (3D-EEM).

2. Material and Methods
2.1. Chemicals
Every chemical was obtained with the highest level of purity, including humic acid (M.wt 2485 dalton, CAS1415-93-6, Merck Millipore Co., USA), Sodium perborate ($NaBO_3$, SPB, CAS10486-00-7, Weifang Haizhiyuan Chemistry and Industry Co., China), Sodium sulfate (Na_2SO_4, CAS7757-82-6, Tokyo Chemical Industry Co., Japan), Sodium hydroxide (NaOH, CAS1310-73-2, Weifang Haizhiyuan Chemistry and Industry Co., China), Sulfuric acid (H_2SO_4, CAS7664-93-9, Merck Millipore Co., USA), Sodium carbonate (Na_2CO_3, CAS497-19-8, Merck Millipore Co., USA), Sodium dihydrogen phosphate (NaH_2PO_4, CAS7558-80-7, Tokyo Chemical Industry Co., Japan), Sodium nitrate ($NaNO_3$, CAS7631-99-4, Merck Millipore Co., USA), Sodium bicarbonate ($NaHCO_3$, CAS144-55-8, Weifang Haizhiyuan Chemistry and Industry Co., China), Sodium chloride (NaCl, CAS7440-23-5, Weifang Haizhiyuan Chemistry and Industry Co., China), and Tertiary butanol (TBA, CAS75-65-0, Merck Millipore Co., USA).

2.2. Experiment
The humic acid removal studies were carried out at 25°C. The UV led (16 W, 254 nm) was positioned above the beaker at a length of 3.5 cm. The magnetic stirrer held the beaker, which served as the chemical reactor. In this study, the UV irradiation was estimated to be 35.2 $Jm\,cm^{-2}$ for an hour. A certain amount of the humic acid solution was diluted to 100 mL before the experiment. The sodium perborate was then added to the HA-imitated wastewater, and light irradiation started the reaction. 2.5 mL aliquots were taken out at predetermined intervals to measure the absorbance. Every experiment was run at least twice. Tertiary butanol was utilized as the scavenger to confirm the

creation of hydroxyl radicals.

2.3. Analysis and Procedure

To determine the effectiveness of the humic acid removal process, the solution's absorbance was measured using a UV-vis spectrophotometer and an external reference technique at a wavelength of 254 nm [20]. The mathematics formula read in Equation 1 as follows:

$$\text{HA elimination efficiency} = (C_0 - C_t / C_0) \times 100 \%$$
$$\text{(Eq.1)}$$

where C_t represents the humic acid quantity at the time of treatment t, and C_0 represents the initial humic acid quantity.

A variety of distinct UV-vis adsorption patterns were used to determine the change in the humic acid molecule structure. absorbance values were determined by spectrophotometer at wavelengths (nm) at 203, 250, 253, 254, 365, 436, 465, and 665, respectively [21]. To characterize the changes in the humic acid molecule structure, continuous variations in the solution's absorbance range (200-800 nm) were also examined (Schema 1). A TOC tester was used to measure total organic carbon (TOC). Ax (sample absorbance at x nm) and TOC were used to determine specific UV absorbance (SUVAx) which was shown in (Equation 2) [22].

$$\text{(SUVAx)} = (Ax / TOC) \times 100\%$$
$$\text{(Eq.2)}$$

The mechanism of the humic acid degradation was investigated using the 3D-EEM spectrum. The corresponding apertures were 10 and 5 nm, respectively, while the wavelength limits for the emission and stimulation ranges were (280-550 nm) and (200-400 nm), respectively.
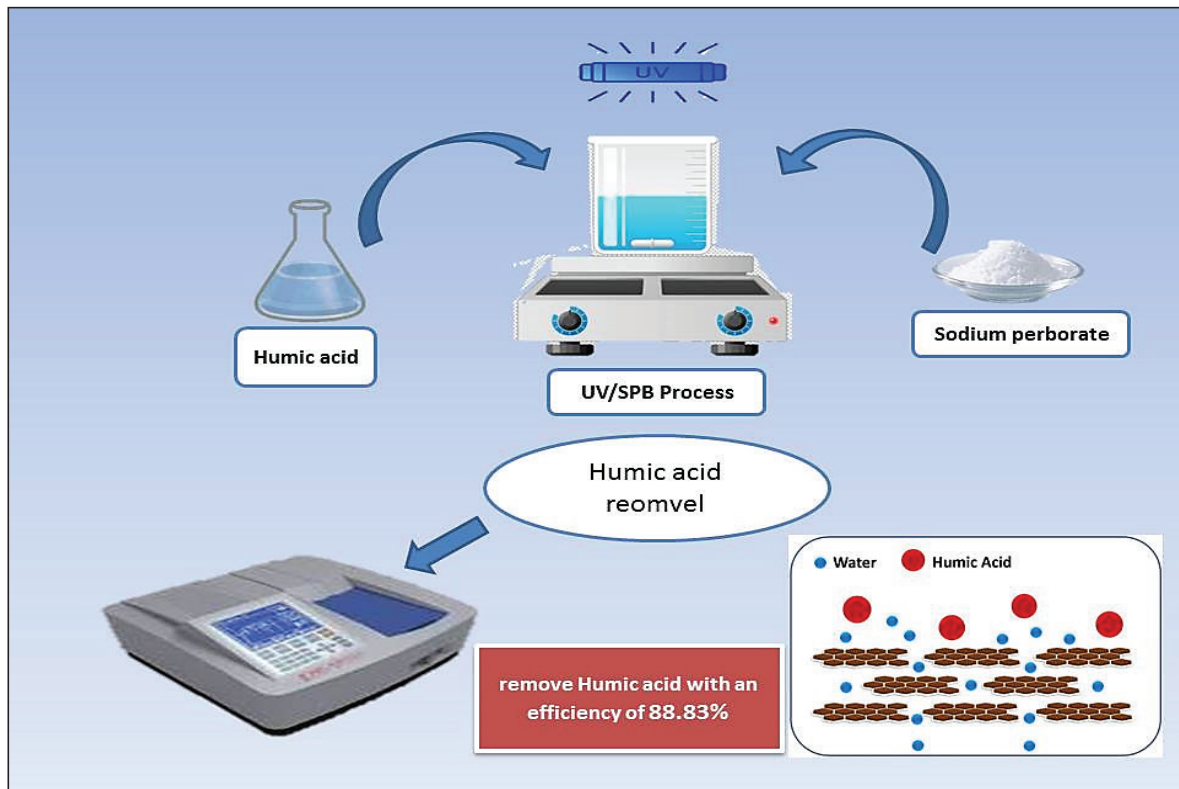
Schema 1. Removal procedure for the humic acid and determined by the UV-Vis spectrophotometer

3. Results and discussion

3.1. Study of the humic acid elimination by UV/SPB process

3.1.1. Performance comparison of the humic acid elimination in various systems

First, three processes—UV, SPB, and UV/SPB—were examined for their ability to remove the humic acid, as shown in Figure 1 The following were the experimental parameters: starting pH 3, 10 mg L^{-1} of the humic acid, 1 mmol L^{-1} of Sodium perborate, and 10 mg L^{-1} of the humic acid.

The single UV treatment took 1 hour to remove 0.5 % of the humic acid, which was barely eliminated. The single sodium perborate treatment had a negligible effect on the removal of the humic acid, with a decolorization ratio of 1.5% after an hour. The UV/SPB process had a higher decontamination efficiency of 88.83 % than the other two processes, which rose by a smaller amount. In addition, when the humic acid was removed using UV light and hydrogen peroxide with the same molecular weight, the elimination ratio was only 40.2 % after 1 hour (60 min). It has the same effect as hydrogen peroxide when Sodium perborate is dissolved in water (Equation 3) [12], which is why it is frequently employed for in situ chemical oxidation. Hydrogen peroxide was produced in the only Sodium perborate system, but because it cannot be activated to produce hydroxyl radicals, very little humic acid was eliminated. In the UV/SPB system, hydrogen peroxide produced from Sodium perborate can generate hydroxyl radicals after being exposed to UV (Equation 4) [14], This might oxidize and damage the functional groups in the structure of the molecule of the humic acid.
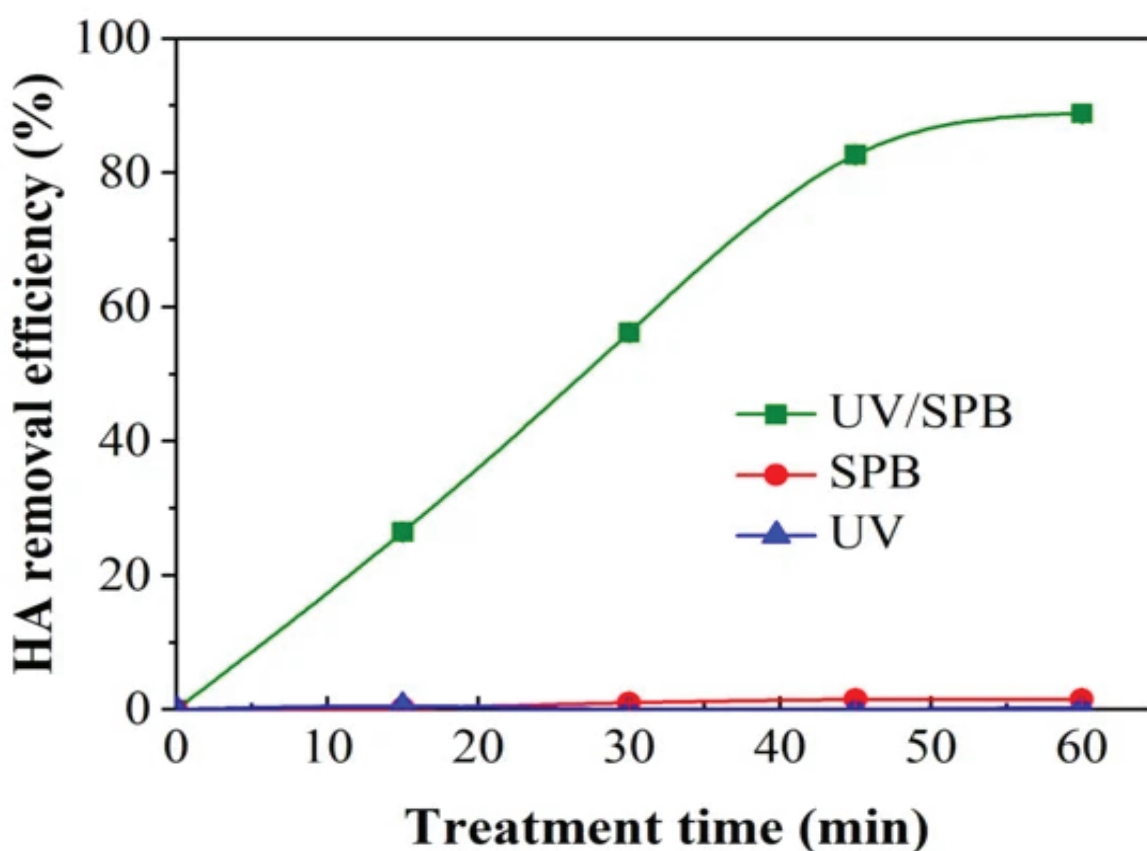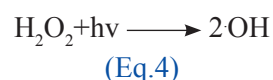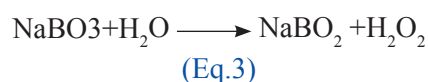
$$NaBO3 + H_2O \longrightarrow NaBO_2 + H_2O_2$$
(Eq.3)

$$H_2O_2 + hv \longrightarrow 2 \cdot OH$$
(Eq.4)

Fig. 1. Performance comparative of humic acid elimination in various systems
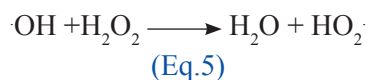
3.1.2. Humic acid concentration effect

Figure 2a illustrates the impact of the humic acid concentration on the humic acid elimination by the UV/SPB system. The optimized parameters were the sodium perborate concentration of 1 mmol L-1 and primary pH of 3. The elimination ratio dropped as the humic acid primary concentration raised. After 1 hour, the elimination ratio dropped from 89.81% to 70.81% when the humic acid content increased from 5 to 15 mg L^{-1}.

Because there weren't enough oxygen radicals generated by the system to completely oxidize all of the pollutants in the solution, it proved that the oxygen radicals generated during the UV/SPB system were continually used. Additionally, as humic acid concentration gradually increased, the competition between humic acid molecules and oxygen radicals grew more intense. Further, the increased humic acid content would absorb more UV rays [23], preventing hydrogen peroxide activation and the subsequent generation of hydroxyl radicals ($\cdot$OH), which resulted in a decrease in the elimination of the humic acid.
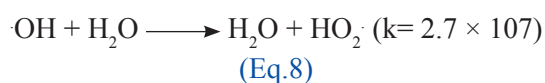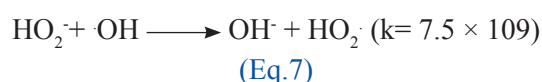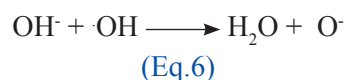
3.1.3. Effect of sodium perborate concentration

Reactive radicals are produced by the Sodium perborate (SPB), which is important for the symbiotic mechanism. Investigations were done on the effect of Sodium perborate concentration on humic acid removal (Figure 2b). A concentration of humic acid of 10 mg L^{-1} and a pH of 3 was used in the test. After 1 hour, the Sodium perborate concentration was increased from 0.25 to 1.0 mmol L^{-1}, and the humic acid elimination ratio increased from 53.0 to 88.83 %. The number of active oxygen radicals in the system was increased with an increase in Sodium perborate concentration, which aided in the elimination of humic acid. Nevertheless, In excess, Sodium perborate would hunt the hydroxyl radical and produce the peroxy hydroxyl radical ($HO_2\cdot$) (Equation 5) [24]. peroxy hydroxyl radical has a weaker redox potential than hydroxyl radical. Consequently, the reduction in humic acid elimination was caused by the excess Sodium perborate (2 mmol L^{-1}).

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot$$
$$(Eq.5)$$

3.1.4. Primary pH effect

Figure 2c illustrates the impact of various initial pH levels on the elimination of humic acid following UV/SPB processing. The Sodium perborate concentration was 1 mmol L^{-1} and the humic acid concentration was 10 mg L^{-1} during the experiment. After 1 hour, the pH value increased from 3 to 11, while the humic acid elimination fell from 88.83% to 58.4%. Strongly acidic conditions render the humic acid molecule neutral, resulting in more photochemical activity than under neutral or basic conditions. The pH has an impact on the redox potential Energy$_{(OH, H2O)}$ as well. The redox of Energy$_{(OH, H2O)}$ decreases from 2.61 V to 2.14 V as pH rises from 3 to 11 [25]. The alkaline state would cause the hydroxyl radical to undergo a reaction (Equation 6-8) that would change it into O$^-$ (E = 1.78 V), which had a lower oxidation capability than the hydroxyl radical. When the pH reaches 11, the main form of hydrogen peroxide changes to HO_2^-, which reacts with hydroxyl radical ($\cdot$OH) at a faster rate than hydrogen peroxide does [27], therefore going to lead using more hydroxyl radical in the process.

$$OH^- + \cdot OH \longrightarrow H_2O + O^-$$
$$(Eq.6)$$

$$HO_2^- + \cdot OH \longrightarrow OH^- + HO_2\cdot \ (k= 7.5 \times 109)$$
$$(Eq.7)$$

$$\cdot OH + H_2O \longrightarrow H_2O + HO_2\cdot \ (k= 2.7 \times 107)$$
$$(Eq.8)$$

### 3.1.5. Elimination of humic acid in various water bodies

Figure 2d shows how the UV/SPB system removes humic acid from various water bodies. Following a one-hour reaction, the amounts of humic acid removed from tap water, lake water, and DI (deionized water) were 88.83%, 59.63%, and 47.53 %, respectively. It shows that both tap water and lake water prevented humic acid from being eliminated. These were the underlying causes. First, the hydroxyl

radical produced by the UV/SPB process would face competition from other naturally occurring organic substances in the lake. Second, the attendance of several anions in both tap water and lake water may limit the action of the oxidizing agents, decreasing the effectiveness of removing humic acid.

3.1.6. Common anions' influence on water

Figure 3a illustrates how common anions including HCO_3^-, CO_3^{-2}, NO_3^-, SO_4^{-2}, Cl^-, and $H_2PO_4^-$ affect the removal of humic acid by the UV/SPB process. When the Carbonate anion (CO_3^{-2}) concentration was dropped from 1 to 10 mmol L^{-1}, as shown in Figure 3a, the elimination efficiency dropped from 63.7 to 44.9 %. The cause of the decline in humic acid elimination was that the hydroxyl radical produced by the process was used by Carbonate anion (CO_3^{-2}) to create CO_3^- with a low oxidation capability (Equation 9) [28].

$$\cdot OH + CO_3^{-2} \longrightarrow CO_3^- + OH^- \ (k= 4.2\times 10^8) \ (Eq.9)$$

According to Figure 3b, the humic acid elimination efficiency rapidly declined from 74.2 to 53.5 % during 1 hour when the HCO_3^- concentration rose from 1 to1 to 10 mmol L^{-1}. The system also converted hydroxyl radicals into HCO_3^- (Equation 10). In addition, the HCO_3^- addition would result in a rise in the pH of the solution [29].

$$\cdot OH + HCO_3^- \longrightarrow CO_3^- + H_2O \ \ (k= 4.2\times 10^8)$$
$$(Eq.10)$$
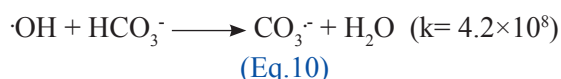
In Figure 3c, the elimination of humic acid reduced from 84.1 % to 79.9 % as the chlorine anion (Cl^-) was increased from 1 to 30 mmol L^{-1}. more excess chlorine anion would use more hydroxyl radicals and create more chlorine radicals (Equation 11,12). Therefore, the decrease in humic acid elimination was caused by the loss in oxidation capability [30].
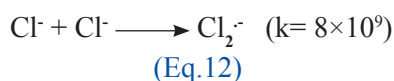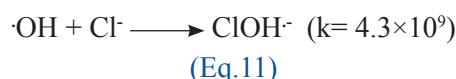
$$\cdot OH + Cl^- \longrightarrow ClOH^- \ \ (k= 4.3\times 10^9)$$
$$(Eq.11)$$

$$Cl^- + Cl^- \longrightarrow Cl_2^- \ \ (k= 8\times 10^9)$$
$$(Eq.12)$$

Figure 3d shows that the humic acid elimination ratio decreased with increasing Nitrate anion (NO_3^-) addition. The humic acid elimination was reduced to 33.4 % when 20 mmol L^{-1} of Nitrate anion was introduced. Reactive nitrogen species ($NO_2\cdot$) ($E_0 = 0.867$ V), can be produced when UV ray activated Nitrate anion which has reduced oxidation capability and also would be damaged through the UV/SPB process (Equation 13-15) [31]. Additionally, Nitrate anion could use hydroxyl radical immediately (Equation 16) [32].
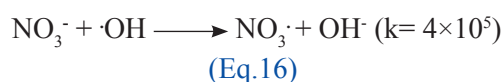
$$NO_3^- + hv \longrightarrow NO_2\cdot + O^-$$
$$(Eq.13)$$

$$NO_3^- + hv \longrightarrow NO_2^- + O$$
$$(Eq.14)$$

$$2NO_2\cdot + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+$$
$$(Eq.15)$$

$$NO_3^- + \cdot OH \longrightarrow NO_3\cdot + OH^- \ (k= 4\times 10^5)$$
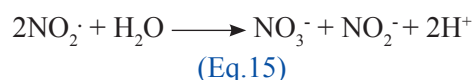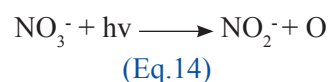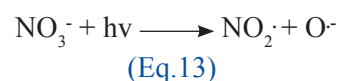$$(Eq.16)$$

Figure 3e demonstrates that the humic acid elimination activity was unaffected by the rise in sulfate anion ($SO4^{-2}$) quantity. The sulfate anion concentration was increased to 20 mmol L^{-1}, which resulted in an 88.0 % increase in humic acid elimination effectiveness. The literature claims that sulfate anion does not interact with the reactive species produced in the system [33,34]; hence it has no impact on eliminating humic acid. As shown in Figure 3f, the increase of $H_2PO_4^-$ anion little affected the humic acid elimination. The humic acid removal efficiency decreased from 86.3 % to 82.4 % as the Dihydrogenphosphate anion ($H_2PO_4^-$) level increased from 10 to 30 mmol L^{-1}. Although Dihydrogenphosphate anion and hydroxyl radical can combine to generate the hydrogen phosphate radical ($HPO_4\cdot$) (Equation 17) [35], The elimination of humic acid wouldn't be impacted because of the highly sluggish reaction rate.

$$H_2PO_4^- + \cdot OH \longrightarrow HPO_4\cdot + H_2O \ (k= 2\times 10^4)$$
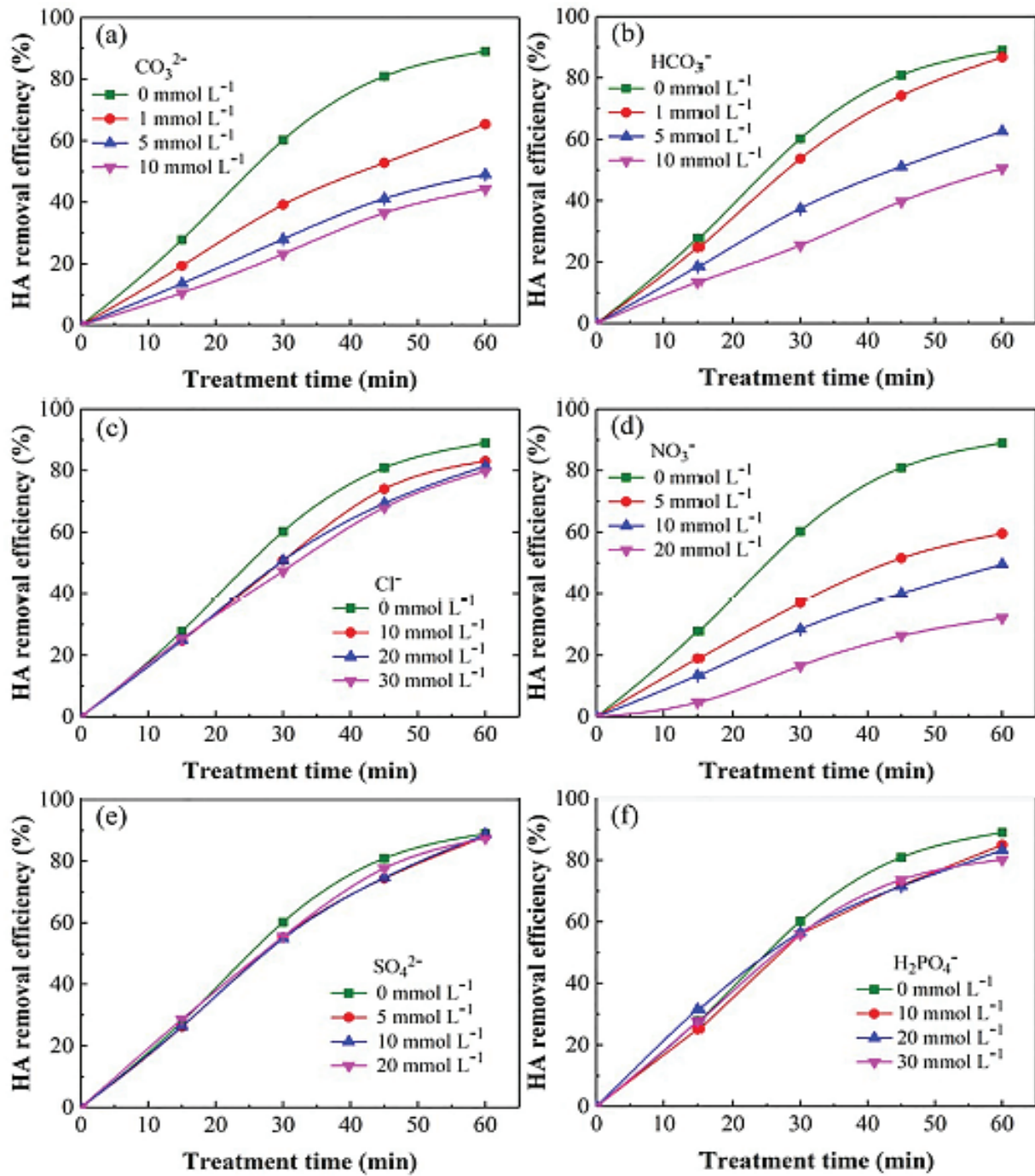$$(Eq.17)$$
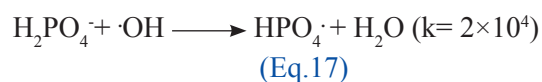
Fig. 2. Effect of several factors during UV/SPB system on Humic acid elimination:
a) Humic acid concentration, b) Sodium perborate concentration,
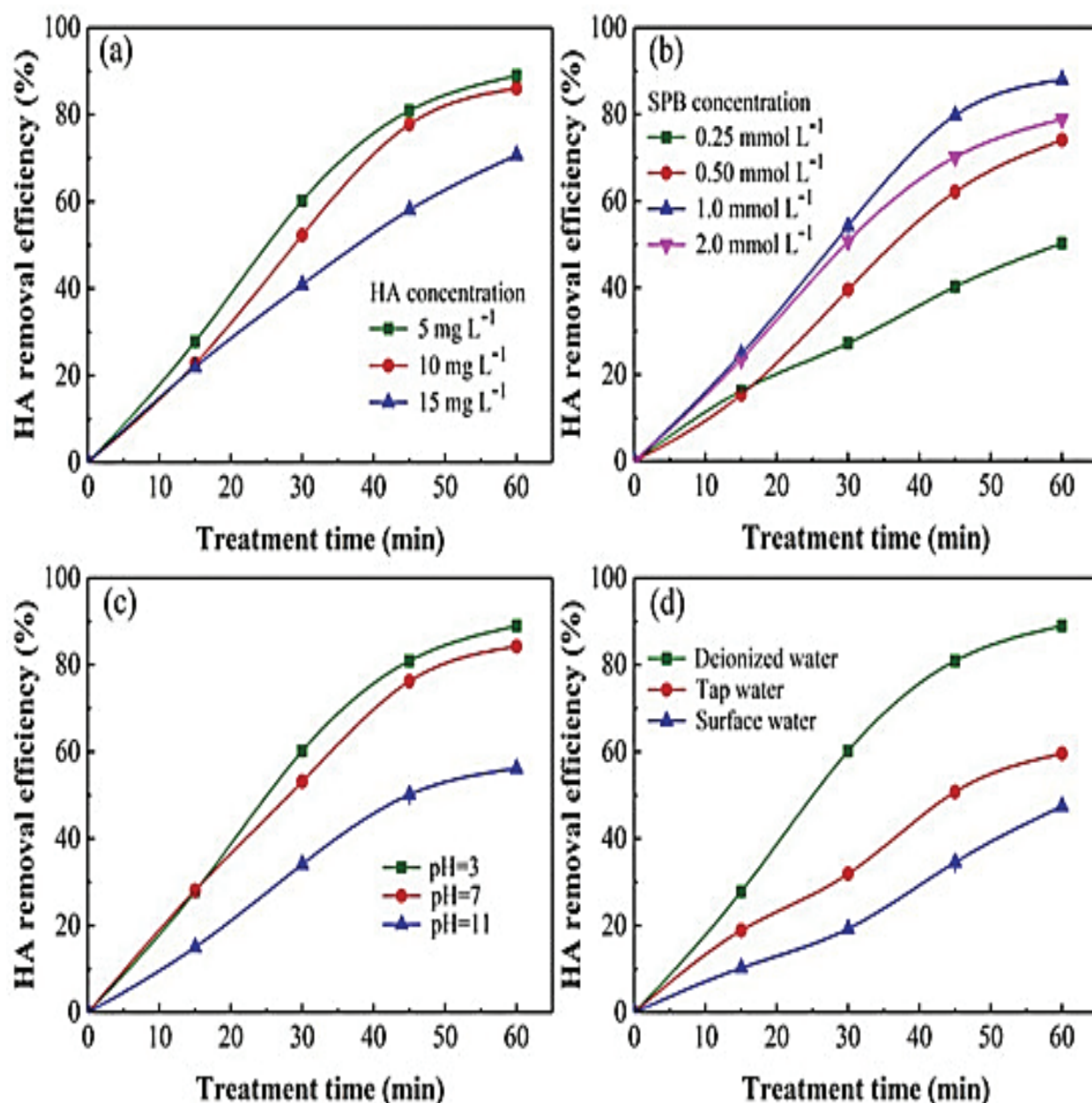c) primary pH, d) UV/SPB elimination of Humic acid in various waterbodies

Fig. 3. Common anions' effects on the elimination of humic acid in UV/SPB process
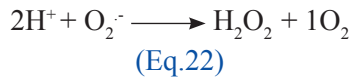
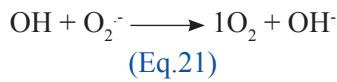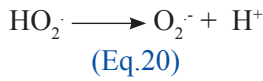### 3.2. Mechanism of UV/SPB humic acid elimination

3.2.1. Examining Scavenging

Tertiary butanol (TBA) had the ability to remove hydroxyl radical from the process of oxidation ($k_{TBA, OH}$ = 3.8-7.6×10⁸) [36]. The effect of Tertiary butanol adding on the elimination of humic acid in the UV/SPB process is shown in Figure 4. The

empirical parameters were starting pH 3, humic acid concentration of 10 mg L⁻¹, and Sodium perborate dosage of 1.0 mmol L⁻¹. The humic acid elimination was constrained by the addition of Tertiary butanol, as shown in the figure, which decreased from 16.5 to 11.5 % with the addition of Tertiary butanol and increased from 0.05 to 0.5 mol L⁻¹.

According to its testimony, hydroxyl radical may

be the primary oxidizing agent in the symbiotic system. After the addition of Tertiary butanol, the removal of humic acid was not entirely inhibited, which may be because the HO_2 generated by the breakdown of hydrogen peroxide (H_2O_2) could likewise produce other activated particles, including superoxide anion radicals (O_2^{-}) and singlet oxygen ($1O_2$) (Equation 18-22) [37,38], which also have some oxidation ability and cannot be entirely repressed by Tertiary butanol.

$$H_2O_2 \longrightarrow 2\,{}^{\cdot}OH$$
(Eq.18)

$${}^{\cdot}OH + H_2O_2 \longrightarrow HO_2^{\cdot} + H_2O$$
(Eq.19)

$$HO_2^{\cdot} \longrightarrow O_2^{\cdot-} + H^+$$
(Eq.20)

$${}^{\cdot}OH + O_2^{\cdot-} \longrightarrow 1O_2 + OH^-$$
(Eq.21)

$$2H^+ + O_2^{\cdot-} \longrightarrow H_2O_2 + 1O_2$$
(Eq.22)
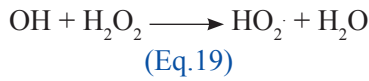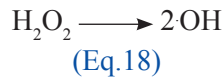
3.2.2. Mechanism of humic acid degradation

The humic acid molecule structure changes may be reflected in the absorbance ratios [39]. Figure 5a depicts the development of these ratios in the UV/SPB mechanism. The value of absorbance ratio (253/203) declined from 0.98 to 0.44 with a rise in reaction time, showing the durability of functional groups (such as carboxyl [-COOH] and carbonyl groups [-C=O]) in humic acid aromatic structure gradually decreased. The absorbance ratio (250/365) increased from 2.42 to 3.20, which indicated that the humic acid molecular weight had been reduced. The humic acid chromophore was damaged by the absorbance ratio (254/436) rising from 4.63 to 5.60. The absorbance ratio (465/665) dropped from 3.5 to 1.0, demonstrating the loss of aromaticity in humic acid.

The humic acid molecule's structural differences can also be seen in the UV-visible absorption spectra. Figure 5b depicts the evolution of the humic acid absorption spectrum in the UV/SPB process over time. Implies that hydroxyl radical produced in the UV/SPB process damaged the chromophore groups and double bond structure (C=C) of humic acid, as well as oxidizing the
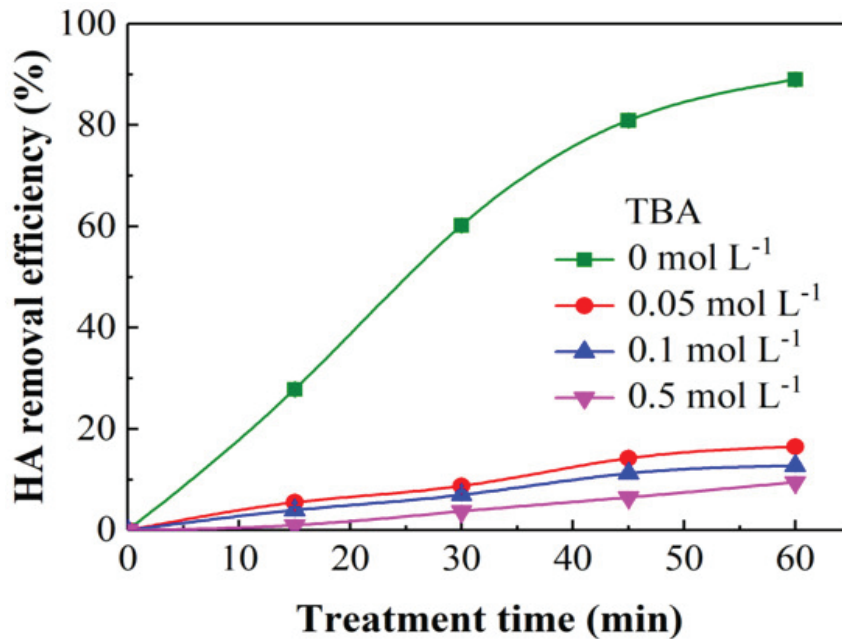

Fig. 4. Tertiary butanol addition's effect on humic acid removal

unsaturated ketone, the absorption edge of humic acid at 200-250 nm, becomes weaker with time. Additionally, the absorption edge shifted to the region of short wavelengths, a phenomenon known as blue shift. This proved that the carbon atom substitution process took place in the carbonylic group (C=O) of the humic acid chromophore [40]. Linearly expanded quinone groups and unsaturated carbons make up humic acid and fulvic acid. When specific substituent groups were used to replace the carbon atom of a chromophore, such as a carbonyl group (C=O), the absorption edge would shift to a low amplitude. In general, specific ultraviolet absorbances (SUVA) (254, 280, 365, and 436) were chosen to describe the mineralization and decomposition of natural organic matter. Where SUVA-365 nm denotes the molecular volume, SUVA-436 nm denotes the chromophore situation in natural organic matter, SUVA-280 nm denotes the stability of the aromatic system, and SUVA-254 nm denotes the molar mass [39].

After one hour of UV/SPB treatment, Figure 5c demonstrates that the SUVA-254 and SUVA-280 values decreased with time, indicating that the molar mass of organic compounds decreased and the basic aromatic framework was destroyed. The decrease in SUVA-365 showed that as the process developed, the volume of organic molecules dropped. The lowering value of SUVA-436 demonstrated that different oxidizing agents

destroyed the functional groups and chromophores. Additionally, the total organic carbon (TOC) in the process decreased from 7.139 to 2.440 mg L^{-1} and the mineralization efficiency increased to 65.81 %, showing that the majority of humic acid had been converted into water (H_2O) and carbon dioxide (CO_2). UV spectrum and total organic carbon findings demonstrated that the UV/SPB symbiotic therapy could successfully break down the intricate chemical composition of humic acid.

Figure 6 displays the outcomes of further investigating the humic acid degradation process in the UV/SPB process using 3D-EEM. The intricacy of the spectral reaction and the scanning sample led to the division of the scanning spectrum into five sections. According to the structure of heterocyclic amino acids in natural organic matter, the I and II range can indicate aromatic proteins in organic molecules [40]. The III region in the humus structure denotes fulminate-like compounds connected to hydroxyl (-OH) and carboxyl (-COOH) groups. Region IV's coverage area reflects the tiny molecular structure of organic materials [35]. A humic-like fluorescence is shown by the V area. The fluorescence density of the five locations whole decreased and slowly vanished from 0 to 15 minutes (Fig. 6a and 6b) and 1 hour (Fig. 6c), moreover demonstrating that the humic acid molecular formula was broken down and mineralized in this cooperative system.
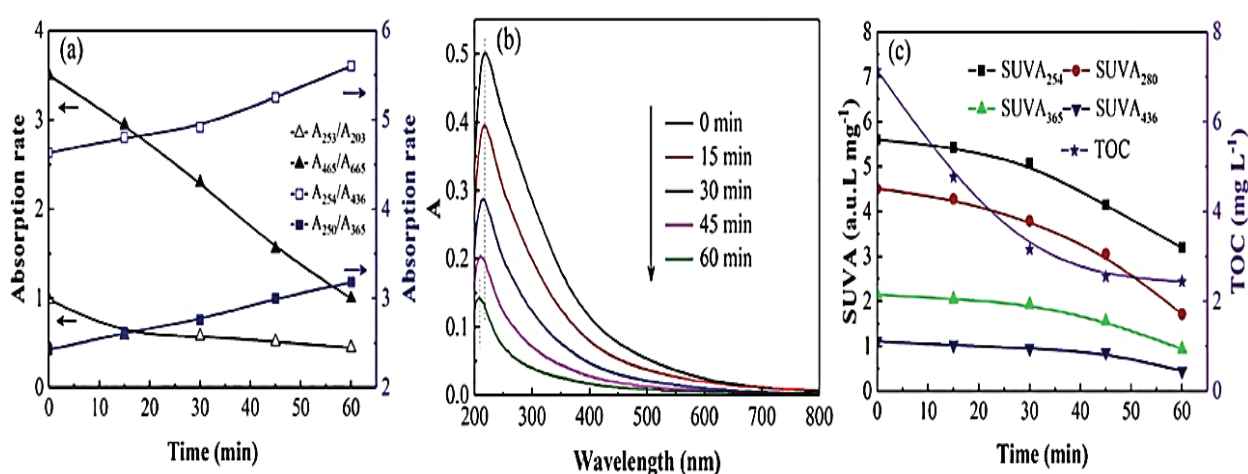

Fig. 5. (a)Ultraviolet absorption level, (b) Ultraviolet-visible spectrum, (c) SUVAx and TOC content for humic acid degradation
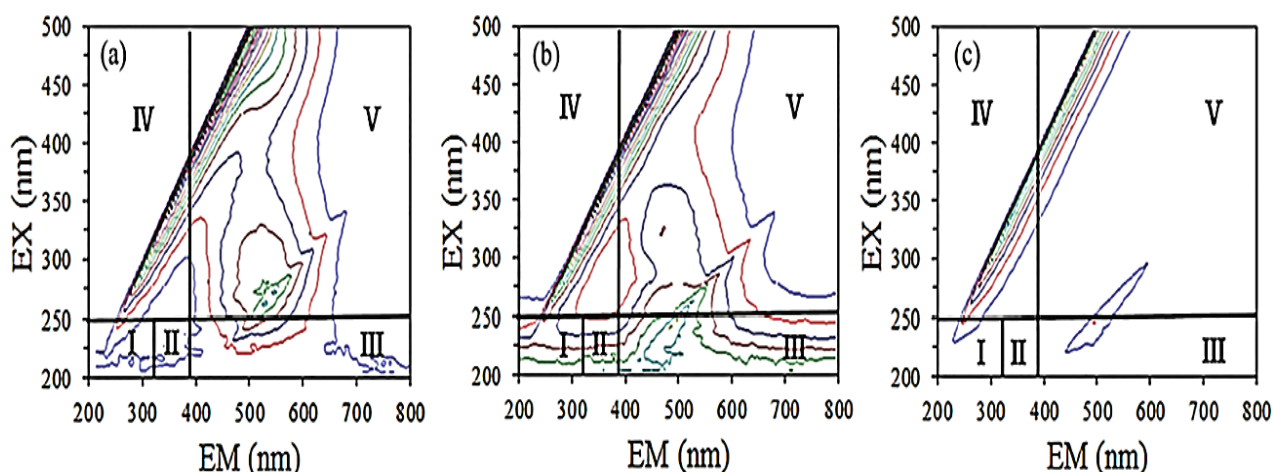
Fig. 6. humic acid's time-changing 3D-EEM spectra in the UV/SPB mechanism
(a) 0 min, (b) 15 min, (c) 1 hour (60 min)

4. Conclusions

The UV/SPB synergistic technique was developed in this work to eliminate humic acid from water, and the experimental findings showed that the procedure could efficiently degrade humic acid. The humic acid elimination effectiveness was 88.83 % after 1 hour of therapy under the experimental parameters of 10 mg L^{-1} humic acid concentration, 1 mmol L^{-1} Sodium perborate dose, and initial pH 3. When compared to DI (deionized water), the humic acid was eliminated far less effectively In tap and lakes water. The anion effect studies proved that, aside from SO_4^{-2}, Cl^-, and $H_2PO_4^-$. the carbonate anion (CO_3^{-2}), bicarbonate anion (HCO_3^-), and nitrate anion (NO_3^-) exhibited varying degrees of humic acid elimination inhibition. By using masking tests, it was determined that the primary chemical responsible for removing humic acid was the hydroxyl radical produced by Sodium perborate activation. Results from the UV-vis spectrum, absorbance ratio, specific UV absorbance (SUVA), and 3D-EEM together demonstrated that the symbiotic mechanism could decompose and mineralize humic acid in water effectively.

5. Acknowledgements

6. References

[1] J. Ryu, J. Jung, K. Park, W. Song, B. Choi, J. Kweon, Humic acid removal and microbial community function in membrane bioreactor, J. Hazard. Mater., 417 (2021) 126088. https://doi.org/10.1016/j.jhazmat.2021.126088.

[2] L. Cui, Y. Zhang, K. He, M. Sun, Z. Zhang, Ti4O7 reactive electrochemical membrane for humic acid removal: Insights of electrosorption and electrooxidation, Separ. Purif. Tech., 293 (2022) 121112. https://doi.org/10.1016/j.seppur.2022.121112.

[3] Y. Yue, G. An, L. Lin, H. Demissie, X. Yang, R. Jiao, D. Wang, Design and coagulation mechanism of a new functional composite coagulant in removing humic acid, Separ. Purif. Tech., 292 (2022) 121016. https://doi.org/10.1016/j.seppur.2022.121016.

[4] X. Huang, Y. Wan, B. Shi, J. Shi, Effects of powdered activated carbon on the coagulation-flocculation process in humic acid and humic acid-kaolin water treatment, Chemosphere, 238 (2019) 124637. https://doi.org/10.1016/j.chemosphere.2019.124637.

[5]   Y. Chen, Y. Qian, J. Ma, M. Mao, L. Qian, D. An, New insights into the cooperative adsorption behavior of Cr(VI) and humic acid in water by powdered activated carbon, Sci. Total Environ., 817 (2022) 153081. https://doi.org/10.1016/j.scitotenv.2022.153081.

[6]   S.Lee, Y. Roh, D.-C. Koh, Oxidation and reduction of redox-sensitive elements in the presence of humic substances in subsurface environments: A review, Chemosphere, 220 (2018) 86–97. https://doi.org/10.1016/j.chemosphere.2018.11.143.

[7]   V. Oskoei, M. H. Dehghani, S. Nazmara, B. Heibati, M. Asif, I. Tyagi, S. Agarwal, V. K. Gupta, Removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption, J. Mol. Liq., 213 (2016) 374–380. https://doi.org/10.1016/j.molliq.2015.07.052.

[8]   E. Doustkhah, M. Esmat, N. Fukata, Y. Ide, D. A. Hanaor, M. H. N. Assadi, MOF-derived nanocrystalline ZnO with controlled orientation and photocatalytic activity, Chemosphere, 303 (2022) 124932. https://doi.org/10.1016/j.chemosphere.2022.134932.

[9]   B. Hashemzadeh, H. Alamgholiloo, N.N. Pesyan, E. Asgari, S A. heikhmohammadi, J. Yeganeh, H. Hashemzadeh, Degradation of ciprofloxacin using hematite/MOF nanocomposite as a heterogeneous Fenton-like catalyst: A comparison of composite and core-shell structures, Chemosphere, 281 (2021) 130970. https://doi.org/10.1016/j.chemosphere.2021.130970.

[10]   B. Huang, C. Qi, Z. Yang, Q. Guo, W. Chen, G. Zeng, C. Lei, Pd/Fe3O4 nanocatalysts for highly effective and simultaneous removal of humic acids and Cr(VI) by electro-Fenton with H2O2 in situ electro generated on the catalyst surface, J. Catal., 352 (2017) 337–350. https://doi.org/10.1016/j.jcat.2017.06.004.

[11]   T. Maqbool, Q.V. Ly, K. He, L. Cui, Y. Zhang, M. Sun, Z. Zhang, Reactive electrochemical ceramic membrane for effective removal of high concentration humic acid: Insights of different performance and mechanisms, J. Membr. Sci., 651 (2022) 120460. https://doi.org/10.1016/j.memsci.2022.120460.

[12]   C. Zhang, Y. Dong, B. Li, F. Li, Comparative study of three solid oxidants as substitutes of H_2O_2 used in Fe (III)-oxalate complex mediated Fenton system for photocatalytic elimination of reactive azo dye, J. Clean. Prod., 177 (2018) 245–253. https://doi.org/10.1016/j.jclepro.2017.12.211.

[13]   H.R. Sindelar, M.T. Brown,; T.H. Boyer, Evaluating UV/H2O2, UV/percarbonate, and UV/perborate for natural organic matter reduction from alternative water sources, Chemosphere, 105 (2014) 112–118. https://doi.org/10.1016/j.chemosphere.2013.12.040.

[14]   J. Gao, J. Song, J. Ye, X. Duan, D.D. Dionysiou, J.S. Yadav, M.N. Nadagouda, L. Yang, S. Luo, Comparative toxicity reduction potential of UV/sodium percarbonate and UV/hydrogen peroxide treatments for bisphenol A in water: An integrated analysis using chemical, computational, biological, and metabolomic approaches, Water Res., 190 (2021) 116755. https://doi.org/10.1016/j.watres.2020.116755.

[15]   D. Habibi, M.A. Zolfigol, M. Safaiee, A. Shamsian, A. Ghorbani Choghamarani, Catalytic oxidation of sulfides to sulfoxides using sodium perborate and/or sodium percarbonate and silica sulfuric acid in the presence of KBr, Catal. Comm., 10 (2009) 1257–1260. https://doi.org/10.1016/j.catcom.2008.12.066.

[16]   F. LACSA, Oxidative degradation of phenol via heterogeneous Fenton-Like reaction over Fe-ZSM5 catalyst using sodium perborate and sodium percarbonate as oxidants, Ph.D. Thesis, Ateneo de Manila University, Metro Manila, Philippines (2017). https://archium.ateneo.edu/theses-dissertations/30

[17]   X. Chang, T. Lin, J. Mo, H. Xu, H. Tao, W. Liu, Coagulation combined with ultraviolet irradiation activated sodium percarbonate as pretreatment prior to ultrafiltration: Analysis

of free radical oxidation mechanism and membrane fouling control, Chemosphere, 287 (2022) 132049. https://doi.org/10.1016/j.chemosphere.2021.132049.

[18] J. Gao, R.F. Nunes, K. O'Shea, G.L. Saylor, L. Bu, Y.-G. Kang, X. Duan, D.D. Dionysiou, S. Luo, UV/Sodium percarbonate for bisphenol A treatment in water: Impact of water quality parameters on the formation of reactive radicals, Water Res., 219 (2022) 118457. https://doi.org/10.1016/j.watres.2022.118457.

[19] A.H. Alminshid, H.A. Alalwan, H.A. Abdulghani, M.M. Mohammed, Spectrophotometric study of ephedrine hydrochloride in drug using molecular absorption UV–Visible, Spectrochim. Acta. Mol. Biomol. Spectros., 270 (2022) 120828. https://doi.org/10.1016/j.saa.2021.120828.

[20] X.-F. Zhou, J.-P. Liang, Z Z.-L. hao, H. Yuan, J.-J. Qiao, Q.-N. Xu, H.-L. Wang, W W.-C. ang, D.-Z. Yang, Ultra-high synergetic intensity for humic acid removal by coupling bubble discharge with activated carbon, J. Hazard. Mater., 403 (2021) 123626. https://doi.org/10.1016/j.jhazmat.2020.123626.

[21] Y. Cui, J. Yu, M. Su, Z. Jia, T. Liu, G. Oinuma, T. Yamauchi, Humic acid removal by gas–liquid interface discharge plasma: Performance, mechanism and comparison to ozonation, Environ. Sci. Water Res. Tech., 5 (2019) 152–160. https://doi.org/10.1039/C8EW00520F.

[22] D. Yuan, J. Tang, Z. Nie, S. Tang, Study on humic acid removal in water by ultraviolet activated sodium percarbonate, J. Yanshan Univ., 45 (2021) 220–226. https://doi.org/10.3390/coatings12070885

[23] X. Li, B. Wu, Q. Zhang, D. Xu, Y. Liu, F. Ma, Q. Gu, F. Li, Mechanisms on the impacts of humic acids on persulfate/Fe2+-based groundwater remediation, Chem. Eng. J., 378 (2019) 122142. https://doi.org/10.1016/j.cej.2019.122142.

[24] C. Tan, N. Gao, Y. Deng, Y. Zhang, M. Sui,

J. Deng, S. Zhou, Degradation of antipyrine by UV, UV/H2O2 and UV/PS, J. Hazard. Mater., 260 (2013) 1008–1016. https://doi.org/10.1016/j.jhazmat.2013.06.060.

[25] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O) in Aqueous Solution, J. Phys. Chem. Ref. Data., 17 (1988) 513–886. https://doi.org/10.1063/1.555805.

[26] S. Tang, D. Yuan, Y. Rao, M. Li, G. Shi, J. Gu, T. Zhang, Percarbonate promoted antibiotic decomposition in dielectric barrier discharge plasma, J. Hazard. Mater., 366 (2019) 669–676. https://doi.org/10.1016/j.jhazmat.2018.12.056.

[27] D. Das, A. Bordoloi, M.P. Achary, D.J. Caldwell, R.P. Suri, Degradation and inactivation of chromosomal and plasmid encoded resistance genes/ARBs and the impact of different matrices on UV and UV/H2O2 based advanced oxidation process, Sci. Total Environ., 833 (2022) 155205. https://doi.org/10.1016/j.scitotenv.2022.155205.

[28] D. Yuan, C. Zhang, S. Tang, Z. Wang, Q. Sun, X. Zhang, T.Jiao, Q. Zhang, Ferric ion-ascorbic acid complex catalyzed calcium peroxide for organic wastewater treatment: Optimized by response surface method, Chin. Chem. Lett., 32 (2021) 3387–3392. https://doi.org/10.1016/j.cclet.2021.04.050.

[29] J. Fang, Y. Fu, C. Shang, The Roles of Reactive Species in Micropollutant Degradation in the UV/Free Chlorine System, Environ. Sci. Tech., 48 (2014) 1859–1868. https://doi.org/10.1021/es4036094.

[30] L. Cai, L. Li, S. Yu, J. Guo, S. Kuppers, L. Dong, Formation of odorous by-products during chlorination of major amino acids in East Taihu Lake: Impacts of UV, UV/PS and UV/H2O2 pre-treatments, Water Res., 162 (2019) 427–436. https://doi.org/10.1016/j.watres.2019.07.010.

[31] Y. Ji, C. Zeng, C. Ferronato, J.-M. Chovelon,

X. Yang, Nitrate induced photodegradation of atenolol in aqueous solution: Kinetics, toxicity and degradation pathways, Chemosphere, 88 (2012) 644–649. https://doi.org/10.1016/j.chemosphere.2012.03.050.

[32] Z. Xu, C. Shan, B. Xie, Y. Liu, B. Pan, Decomplexation of Cu(II) EDTA by UV/persulfate and UV/H2O2: Efficiency and mechanism, Appl. Catal. B Environ., 200 (2017) 439–447. https://doi.org/10.1016/j.apcatb.2016.07.023.

[33] S. Tang, Z. Wang, D. Yuan, C. Zhang, Y. Rao, Z. Wang, K. Yin, Ferrous ion-tartaric acid chelation promoted calcium peroxide fenton-like reactions for simulated organic wastewater treatment, J. Clean. Prod., 268 (2020) 122253. https://doi.org/10.1016/j.jclepro.2020.122253.

[34] D. Yuan, K. Yang, E. Zhu, X. Li, M. Sun, L. Xiao, Q. Hari, S. Tang, Peracetic acid activated with electro-Fe2+process for dye removal in water, Coatings, 12 (2022) 466. https://doi.org/10.3390/coatings12040466.

[35] S. Tang, J. Tang, D. Yuan, Z. Wang, Y. Zhang, Y. Rao, Elimination of humic acid in water: Comparison of UV/PDS and UV/PMS, RSC Adv., 10 (2020) 17627–17634. https://doi.org/10.1039/D0RA01787F.

[36] M. Zhao, Y. Xiang, X. Jiao, B. Cao, S. Tang, Z. Zheng, X. Zhang, T. Jiao, D. Yuan, MoS2 co-catalysis promoted CaO2 Fenton-like process: performance and mechanism, Separ. Purif. Tech., 276 (2021) 119289. https://doi.org/10.1016/j.seppur.2021.119289.

[37] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review, Chem. Eng. J., 284 (2016) 582–598. https://doi.org/10.1016/j.cej.2015.09.001.

[38] Y. Xiang, H. Liu, E. Zhu, K. Yang, D. Yuan, T. Jiao, Q. Zhang, S. Tang, Application of inorganic materials as heterogeneous cocatalyst in Fenton/Fenton-like processes for wastewater treatment, Separ. Purif. Tech., 295 (2022) 121293. https://doi.org/10.1016/j.seppur.2022.121293.

[39] T. Wang, G. Qu, J. Ren, Q. Yan, Q. Sun, D. Liang, S.Hu, Evaluation of the potentials of humic acid removal in water by gas phase surface discharge plasma, Water Res., 89 (2016) 28–38. https://doi.org/10.1016/j.watres.2015.11.039.

[40] Y. Li, G. Qu, L. Zhang, T. Wang, Q. Sun, D. Liang, S.Hu, Humic acid removal from micro-polluted source water using gas phase surface discharge plasma at different grounding modes, Separ. Purif. Tech., 180 (2017) 36–43. https://doi.org/10.1016/j.seppur.2017.02.046.