Review

Recent Advancements in the Treatment of Emerging Contaminants Using Activated Persulfate Oxidation Process

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Abstract: Emerging contaminants (ECs) usually refer to pesticides, polycyclic aromatic hydrocarbons (PAHs), dioxins, personal care products, cosmetics, and medications. Due to the strong demand and quick growth of these businesses, the ECs have continuously been found in alarming amounts in groundwater, surface water, and wastewater. These ECs provide a significant non-esthetic threat to the ecosystem as a whole and can cause significant non-esthetic contamination when released into the aquatic environment. The conventional wastewater treatment techniques such as activated sludge, membrane filtration, coagulation, adsorption, and ozonation showed ECs removal performance to a certain extent. In turn, numerous emerging advanced oxidation processes (AOPs), especially activated persulfate oxidation, have garnered a huge amount attention due to their outstanding performance in the remediation of ECs. This article presents a systematic and critical review of electro, sono and thermal activation of persulfate for the treatment of ECs. The effect of key parameters such as electrode materials, solution pH, persulfate concentration, current density, and temperature on electro, sono- and thermal-activated degradation of ECs was discussed. The possible reaction mechanism of ECs degradation was also elucidated in detail. It was closed with a note on the situation now and the future course of electro, sono and thermal activation in ECs degradation applications. Experiments performed in recent studies show that with the aid of persulfate in electro activation, the removal efficiency of chemical oxygen demand can be achieved up to 72.8%. Persulfate activated by sono shows 100% removal efficiency of 1,1,1-trichloroethane and sulfamethoxazole. While for thermal activation of persulfate, 100% removal efficiency of carbamazepine, atrazine and sulfamethazine was achieved. All these vital shreds of evidence are substantial enough to picture the negative impact of ECs on the environment.

Keywords: wastewater treatment; emerging contaminants; persulfate oxidation; elector degradation; ultrasonication

1. Introduction

One of the most crucial resources for maintaining life on Earth is water. The aquatic environment is polluted by a variety of activities, including farming, industry, the production of cosmetics and other goods, the operation of healthcare facilities, etc. Such human-made activities exacerbate the issue of freshwater supply that exists today [1,2]. Personal care products, pharmaceuticals, pesticides, artificial sweeteners, endocrine-disrupting chemicals, etc., have been progressively identified in the aqueous bodies over the past decade [3].

These chemicals are collectively categorized as emerging contaminants (ECs) because there are not yet any comprehensive recommendations or toxicological evidence surrounding them. Previously, most of these pollutants were incorrectly classified as toxins with

potential environmental risks, unidentified and even unknown [4]. These harmful compounds are universal and might enter the water stream via numerous wastewater streams through agricultural runoff, hospital wastewater, industrial wastewater stream, wastewater treatment plants effluents, etc. [5,6]. Figure 1 illustrates a few key sources and the high concerns of ECs.
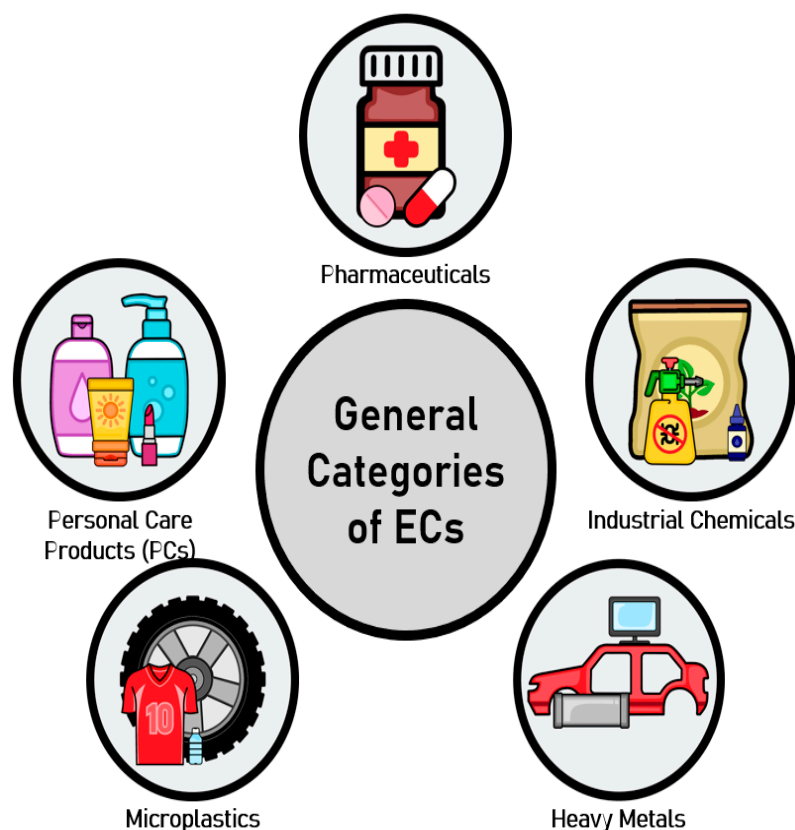

Figure 1. The sources and high concerns of ECs.

The concentrations of these ECs in the aqueous environment depend on the water consumption, usage pattern, sewer conditions, catchment properties (e.g., population density, land use) and environment persistence [7,8]. Although the concentration of the ECs is relatively lower (ranging from ng/L to µg/L), discharging it directly into water bodies can cause a substantial detrimental impact on environmental sustainability and human health [9]. Recent reports revealed that the unregulated discharge of ECs into the aqueous environment can lead to a huge risk to the whole ecosystem [10,11]. The absence of stringent legislation and insufficient toxicological data on these ECs causing the pollution remains unregulated. However, the development of temporary aqueous guidelines is developed as an awareness. Additionally, a list of contaminants along with their permitted discharge levels have been published by the US Environmental Protection Agency, the European Union, and the World Health Organization (USEPA) organizations, and numerous other international regulatory authorities. All these new legislations showed the importance of treating these ECs before discharging into the environment.

Among various wastewater treatment techniques, advanced oxidation processes (AOPs) demonstrate effective ECs elimination, and the mechanisms involved mostly depend on the production of hydroxyl radicals ($\bullet$OH) [12]. Additionally, with redox potential of 2.8 V, $\bullet$OH radical is a non-selective powerful oxidant that can both partially mineralize and damage the structure of organic molecules [13]. In comparison with the $\bullet$OH radicals, sulfate radicals (SO_4^-) may own equal or even higher redox potential (2.5–3.1 V). In addition, it also has a higher selectivity as well as longer half-life than $\bullet$OH radicals in some situations [14]. A radical precursor for instance potassium persulfate ($K_2S_2O_8$) needs

activation to produce $SO_4^{\bullet-}$ radicals. Persulfate (PDS) has the $[O_3S\text{-}O\text{-}O\text{-}SO_3]^{2-}$ chemical structure. The essence of PDS activation is to break the –O–O– bond and produce $SO_4^{\bullet-}$ radicals. The degradation of ECs without the activation of PDS is possible. However, the oxidation potential of PDS−generated anion is around three times (3X) lower than the $SO_4^{\bullet-}$ radicals [15,16]. PDS activation resulted in the $SO_4^{\bullet-}$ radicals generation, which accelerates the degradation of ECs compounds. Sonolytic (ultrasonic), electrocatalytic and thermal (high temperature) are among the most prominent persulfate activation techniques.

Wang and Zhou, et al. [17], reported that the addition of $S_2O_8^{2-}$ anions and the increase of ultrasonic power could favorably stimulate the degradation of carbamazepine in an aqueous solution due to the production of the $SO_4^{\bullet-}$ radicals from the decomposition of $S_2O_8^{2-}$ activated by ultrasounds. Lee et al. [18] added that the persulfate activation by sono using a mechanical mixing system is a cost-effective technique and a promising strategy to degrade ibuprofen or other residual organic pollutants in wastewater.

According to Acero et al. [19], persulfate ion (PS, SO_4^{2-}) is the most widely used oxidant for the production of $SO_4^{\bullet-}$ as it is generally stable under typical wastewater treatment conditions and it can be activated by inducing heat or thermal activation. They stated that the ECs degradation using direct UV photolysis or dark PS alone was almost the same. However, upon the addition of PS, the photodegradation efficiency significantly increased due to the generation of $SO_4^{\bullet-}$ and $\bullet OH$. Chekem et al. [20] stated that ECs in water can be effectively degraded under advanced oxidation reactions.

On the other hand, in electrochemically-activated persulfate (EC/PS) systems, the generation of $SO_4^{\bullet-}$ and $\bullet OH$ by the activation of persulfate is due to the production of ferrous ions (Fe^{2+}) from iron electrodes [20]. Miao et al. [21] reported that BDD electro-activated persulfate technology possess the advantages of low energy consumption and high efficiency in a wide pH range and concluded that the technology is appropriate for practical refractory wastewater treatment.

In the ever-growing number of published papers on persulfate activation and applications in recent years, sulfate radical-based advanced oxidation processes (AOPs) have been widely investigated [22]. Kang et al. [23], investigated the activation of persulfate in sulfachloropyridazine removal and obtained results in oxidation efficiency and efficient adsorption capacity.

In recent years, Wang et al. [24] has compiled studies on metal organic frameworks-based materials catalysts for catalytical removal of ECs in the perspective of Fenton-like and photo-Fenton systems. Persulfate activation by biochar-based materials has been discussed widely due to its ability to remove the organic contaminant and pharmaceutical pollutants through adsorption and persulfate-based AOPs [25,26]. However, there is no recent review combining electro-, thermal- and sono-activated persulfate in the degradation of ECs. Thus, this review focuses on the recent 10 years of published work on the degrading performance of ECs using various persulfate activation methods including electro, thermal and sono activations. Effectiveness, limitations, and future perspective are analyzed and highlighted.

2. ECs Treatment Technologies

There are currently many technologies available for the elimination of ECs, which can be broadly separated into conventional, advanced, and natural attenuation procedures [27]. The easy and inexpensive biological natural attenuation mechanisms include dilution, volatilization, photolysis, sorption, and biodegradation. Barbosa et al. [28], showed that ECs accumulations were accelerated during the sorption process, which makes processes such as volatilization less successful because suspended particles interfere with the removal efficiency.

Conventional treatment methods that effectively remove ECs include ozonation, membrane filtering, and activated carbon-mediated adsorption [29]. Despite this, Rizzo et al. [30] disapprove and assert that oxidation byproducts may be produced as a result of ozonation, in addition to the fact that adsorption by activated carbon is ineffective at killing bacteria. The study also suggests that because membrane filtration requires a lot of energy to run,

concentrate disposal can be difficult. In the recent decades, a number of cutting-edge treatment technologies, including AOPs, artificial wetlands, bioelectrical systems, and enzymatic treatment, have been presented [27].

AOPs can be categorized as chemical, photochemical, electrochemical, sonochemical and hydrochemical processes, depending on how the HO• are generated, or as homogeneous and heterogeneous process it depends on the quantity of phases involved during the transport and reaction of species [31]. Technologies on AOPs such as Fenton oxidation, ozonation, photocatalysis and persulfate oxidation are well-known to be effective treatment approaches for ECs [32].

The conventional Fenton process utilizes the "Fenton's reagent", a mixture of Fe^{2+} and H_2O_2 that yields HO• and Fe^{3+} as reaction products. This reagent is environmentally compatible and low toxicity with the oxidant H_2O_2, which self-decomposition leads to non-toxic products (H_2O and O_2). However, the regeneration of Fe^{2+} under darkness in the conventional Fenton process is very slow [33].

Ozonation take place at both the gas-liquid interface and in the bulk liquid, depending on the concentration of the reactants given that the influence of O_3 as disinfection and oxidant has been applied for the purification of drinking water [34]. The conversion of organic substances by ozonation is a result from decomposition of O_3 at neutral and alkaline pH which occurs by either reaction with less selective HO• or reaction with molecular O_3 [31]. The limited rate of dissolved organic carbon mineralization and consequent accumulation of toxic oxidation by-products include nitrosamines, bromate and formaldehyde due to the incomplete oxidation of the targeted compounds and from reaction with the water matrix constituents has become the main drawback of the ozonation process [35].

Huang et al. [36] introduced an engineered catalyst of self-doped iron/carbon nanocomposite derived from waste toner product to degrade persistent organic pollutants. The fabricated nanocomposite as a heterogeneous catalyst by facile carbonization consists of Fe_3O_4, polymers and carbon black. The catalytic mechanism of the fabricated engineered catalyst consists of radical and non-radical pathways and has favorable environmental and energy metrics compared to other reported catalyst.

Heterogeneous photocatalysis is based on the application of wide band-gap semiconductors, which produce conduction band electrons and valence band holes, under irradiation with light energy (*hν*) equal to or higher than the semiconductor band-gap energy [31]. The study added that in the last decades the most common photocatalyst has been TiO_2 favorably to its relatively high photoactivity, high mineralization efficiency, low cost and toxicity, high photochemical stability and suitable band-gap energy in either bulk or supported on a substrate. However, even this process has major shortcomings, including a relatively high rate of electron-hole pairs recombination which reduces the available charges for redox reactions and limited absorption of natural sunlight.

Activated persulfates are at the top of the list containing advanced treatment processes investigated against ECs removal in the recent years [30], due to their strong oxidative capabilities and wide pH tolerance [37]. Unlike the conventional AOPs in which hydroxyl radicals (OH•) serve as the main oxidant, persulfate-based AOPs utilize highly reactive sulfate radical to degrade organic contaminant [38]. Not just that, sulfate radical has greater redox potential (2.60~3.10 V vs. NHE) and longer half-time (30~40 µs) compared to hydroxyl radical (1.90~2.70 V vs. NHE and ~20 ns) [39].

Therefore, activated persulfate oxidation treatment technologies will be the center of focus for this review study. PDS directly reacts with the organic contaminants at a low reaction rate, albeit a strong oxidizer, thus a relevant activation is essential to generate a strong oxidizer [14].

Devi et al. [40] listed the vital parameters of different approaches adopted for persulfate activation based on in situ chemical oxidation, which were alkali, transition metals, thermal, radiation, and activated carbon. Given of all the aforementioned methods of activation, only the sono, thermal and electro activation methods of persulfate will be discussed as shown in Figure 2.
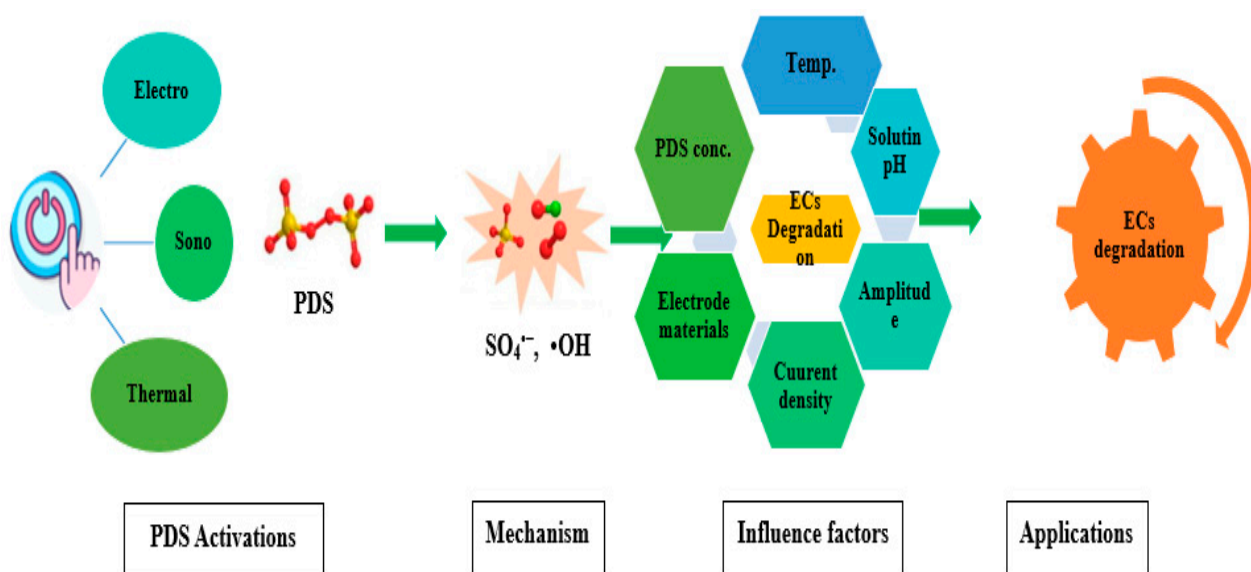
Figure 2. Activations methods of persulfate for ECs degradation.
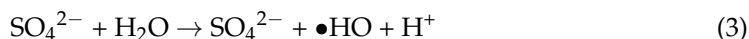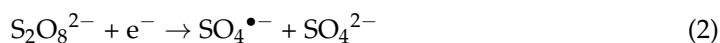
3. Persulfate Oxidation Process

There are two main precursors including peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate or PDS ($S_2O_8^{2-}$) that are used in producing sulfate radicals in aqueous medium [41]. It is a well reported fact that the PDS salt is further stable, ecologically friendly, and cheaper compared to PMS salt, being favorably used in sulfate radical-based AOPs [42]. Hence, PDS will be the key focus of discussion in the current review. PDS has high stability, and it is a colorless or white crystal. It has a solubility of 730 g L^{-1} making it easily dissolved in water and its solution pH lies in the acidic range.

Sodium PDS ($Na_2S_2O_8$) and potassium PDS ($K_2S_2O_8$) are the most frequent PDS types employed. Moreover, persulfate is known as a strong oxidizing reagent (E0 = 2.01 V, SHE) that is close to ozone (E0 = 2.07 V, SHE) and it is moderately steady at room temperature [21]. The oxidizing ability of $SO_4^{\bullet-}$ radical is greater than •OH radical in both neutral and alkaline environments. Moreover, $SO_4^{\bullet-}$ has a longer half-life and it can react with organic matters much easier in bulk solution [43]. In order to obtain optimum performance of PDS, it needs to be activated under specific external conditions such as thermal, ultraviolet light, transition metal, ultrasound, heat and electricity to produce sulfate radicals [40].

3.1. Electrochemically Activated Persulfate

PDS is a strong oxidant that has a redox potential in the range of 2.5–3.1 V and will generate $SO_4^{\bullet-}$ radical by electrochemical activation, which is stronger than •OH radical [44]. According to Yu et al. [45], due to its great efficiency, the electrochemically-activated PDS method has been given consideration as a viable solution for water treatment. It has garnered increased attention since, in contrast to other common activators including heat, photo, metal, chelated metal, quinone, phenols, and hydrogen peroxide activated PDS, it is less expensive, non-toxic, and extremely effective. Iron ion (Fe^{2+}), termed as the coactivator, has been intensively discussed in relation to electrochemically-activated PDS with iron as the sacrificial anode. However, iron indication on the anode and cathode was not necessary for PDS activation [46]. PDS can be created electrochemically in a sulfate-containing solution by the oxidation of SO_4^{2-} (Equation (1)) or it can be introduced externally to the system, which is electrochemically cleaved by the reaction with an electron to form $SO_4^{\bullet-}$ (Equation (2)) due to the peroxide bond (−O–O−) of PDS [47]. According to Zhang et al. [48], in a commercial setting, PDS is often made by electrolyzing sulfuric acid/sulfuric solution (>2 mol L^{-1}) at low temperature and high current density, which is ≥500 mA cm^{-2} with a Ti-based platinum electrode (Ti/Pt) or a polished Pt electrode as the anode. At pH < 7, •OH and sulfate radicals contribute equally to reactions with

sulfate radical being the dominants reactive and the reaction of sulfate radical with water (Equation (3)) will generate a secondary radical, i.e., •OH radical, which will enhance the removal efficiency in pollution [49].

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \tag{1}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \tag{2}$$

$$SO_4^{2-} + H_2O \rightarrow SO_4^{2-} + \bullet HO + H^+ \tag{3}$$

A diagram of the primary electrochemical reactions involved in the generation and activation of PDS is shown in Figure 3. Given that PDS may be produced electrochemically from sulphate ions, it has been proposed that PDS can be renewed at the anode following the conclusion of sulphate radical reactions with water, organics, etc., allowing for a constant source of sulphate radicals [49]. The summary of prior research findings for persulfate electrochemical activation is summarized in Table 1.
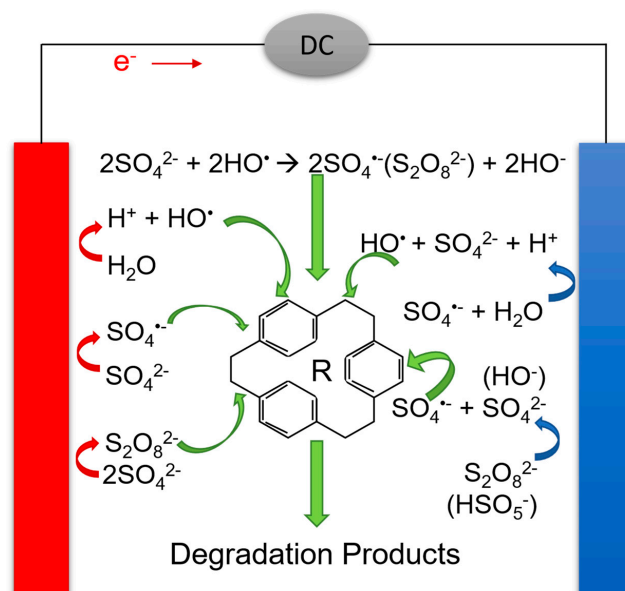

Figure 3. Scheme of the main reactions involved in the persulfate electrochemical production and activation (modified based on [47]).

Table 1. Summary of research results previously reported for persulfate electrochemical activation.

Type of Effluent	Anode/Cathode	PS Added	Applied Current	Electrolysis Time/Min	pH	Pollutant	Removal (%)	Reference
Landfill Leachate	Al/Al	0.88 g/L	44.66 mA cm^{-2}	68.30	4.00	COD	45.70	[50]
Landfill Leachate	Fe/Fe	PS/COD Ratio 2.50	1.80 A	35.90	6.40	COD	84.20	[51]
Landfill Leachate	Fe/Fe	PS/COD Ratio 1.90 PDS/COD Ratio 1.72	2.10 A 1.26 A	34.80	5.00	COD	72.60	[44]
Stock solution	Fe/Fe	0.50 mM	30 mA	15.00	7.00	Diuron	>77	[45]
Stock solution	BDD/Stainless steel	0.02 M	1.70 mA/cm^2	30.00	4.40	Malachite Green (MG)	>95	[21]
Stock solution	Pt/Pt	12.60 mM	13.33 mA/cm^2	240.00	4.42	Tetracycline Hydrochloride (TCH)	81.10	[52]
Landfill Leachate	BDD/BDD Dimension Stable Anode (DSA)	1.00 mM	5.00 mA/cm^{-2}	10.00	NA	Bisphenol A	85.00 60.00	[46]

Table 1. *Cont.*

Type of Effluent	Anode/Cathode	PS Added	Applied Current	Electrolysis Time/Min	pH	Pollutant	Removal (%)	Reference
Paper industry wastewater	Fe	PDS/COD Ratio 1.25	4.14 A	5.00	6.00	COD	53.50	[51]
	Al	PDS/COD Ratio 0.50	4.25	25.00	7.25		72.80	

3.2. Thermally Activated Persulfate

The PDS can be activated successfully using heat [13]. Recent research has demonstrated that PDS can be triggered at room temperature (22 °C), although with poor benzoic acid elimination efficiency [53]. Additionally, thermally-activated PDS has been investigated for the elimination of organic pollutions and is regarded as a greener source of sulphate radicals than other activation technologies [54]. The O-O bond fission in the PDS structure is the primary mechanism of PDS activation. According to estimates, O-bond O's energy ranges from 140 to 213.3 kJ/mol. When heat is activated, the energy from a high temperature (>50 °C) can result in the O-O bond breaking, releasing sulphate radicals as shown in Equation (4).

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{\bullet-} \tag{4}$$

According to the Equation (5), sulphate radicals swiftly converted into $\bullet$OH radicals during the heat process, as shown by the fact that $\bullet$OH radicals are the predominant radicals during the heat activation of the PDS process [55].

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO\bullet + H^+ \tag{5}$$
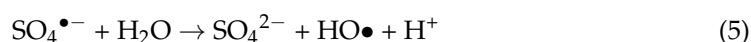
Additionally, a rise in temperature might hasten side reactions, e.g., the recombination of sulphate radicals or $\bullet$OH radicals, which can improve the effectiveness of impurities being removed [56]. Ji et al. [57] stated that thermally activation of PDS has the ability to increase the solubility of organic contaminants, enhancing the reaction rates and treatment efficiency. Jorfi et al. [58] investigated the efficiency of thermally activated PDS towards the treatment of a recalcitrant high total dissolved solid (TDS) petrochemical wastewater. The study has successfully proven that thermally-activated persulfate can be a practical remedy used for treatment as it has obtained 94.3% and 82.8% removal efficiency for COD and TOC, respectively. Sakulthaew et al. [59], reported a successful treatment of 17β-estradiol (E2), which is most frequently found in animal farm wastewater. E2 can be treated by UV/heat-activation PDS. Only 35 °C was required to completely remove the E2 and activate a high PDS concentration (>100 mg/L). The experimental setup for the UV/heat-activated persulfate oxidation of E2 is shown in Figure 4. The summary of persulfate thermal activation for emerging pollutant degradation is shown in Table 2.
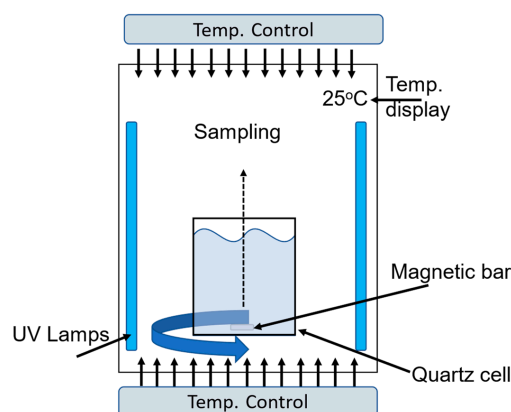

Figure 4. Experimental setup for the UV/heat activated PDS oxidation (adopted and modified from Sakulthaew et al. [59]).

Table 2. Thermal activation of persulfate for degradation of ECs.

| Pollutant	Pollutant Concentration	Oxidant Concentration	Temperature (°C)	pH	Reaction Time (h)	Degradation (%)	References
Acid orange 7	20.00 mg L^{-1}	0.57 PS	80.00	6.50	3.00	99.00	[60]
Antipyrine	0.0265 mM	0.125 mM PS	60.00	4.50	2.00	73.00	[61]
Carbamazepine	0.04 mM	1.00 mM PS	70.00	5.10	2.00	~100.00	[62]
Chloramphenicol	0.20 mM	16.00 mM PS	70.00	5.40	2.70	96.30	[63]
Atrazine	0.05 mM	1.00 mM PS	60.00	7.00	2.00	100.00	[57]
Sulfamethazine	0.03 mM	2.00 mM PS	60.00	7.00	6.00	100.00	[64]
Sulfachloropyridazine	1.00 μM	140.00 μM	40.00	3.00	1.10	85.00	[65]
Azole Fungicide Fluconazole	10.00 mg L^{-1}	20.00 mM	60.00	3.00	4.00	87.00	[66]
Benzene, toluene, ethylbenzene, xylenes (BTEX)	0.10 mM	20.00 mM	50.00	3.50	6.00	>90.00	[67]
Sulfamethoxazole	40.00 μM	2.40 mM	60.00	7.00	2.00	>80.00	[68]
Sulfanilic Acid	50.00 mg/L	20.00 mmol/L	60.00	7.00	4.00	57.40	[69]

3.3. Sono Activated Persulfate

Studies have demonstrated that using oxidants such as persulfate in conjunction with ultrasonic and UV radiation increased the efficacy of oxidation processes [70,71]. The production of radical hydroxyl and oxygen by ultrasound is caused by the development of cavities during the cavitation phenomena in the solution. Ultrasound is any wave with frequency greater than that of human hearing (20–40 kHz). The benefits of ultrasound include its absence of generation of intermediate pollutants, generation of free radicals, and activation of the persulfate ion, among other benefits. Due to the breakdown of persulfate ions, ultrasonic vibrations produce sulphate radicals with an oxidation power of 2.56 V (Equation (6)) [72].

$$S_2O_8{}^{2-} + US \rightarrow 2SO_4{}^{\bullet-} \tag{6}$$

A key element in defining the activation of PDS is quantum yield. The quantum yields are significantly influenced by the UV wavelength. Quantum yields of sulphate radicals in the UV spectrum between 248 and 351 nm decreased with increasing UV wavelength [14]. At 248 nm and 253.7 nm, the maximum quantum yield was around 1.4. The typical radiation wavelength for persulfate is 254 nm. Two processes may be implicated in the activation of PDS by UV light. One is the fission of the O-O bond by UV radiation input, as shown in the Equation (7).

$$S_2O_8{}^{2-} \rightarrow 2SO_4{}^{\bullet-} \tag{7}$$

As shown in Equations (8) and (9) by the water molecule's ability to create an electron when exposed to ultraviolet light, persulfate is activated (9).

$$H_2O \rightarrow H\bullet + HO\bullet \tag{8}$$

$$S_2O_8{}^{2-} + H\bullet \rightarrow SO_4{}^{\bullet-} + SO_4{}^{2-} + H \tag{9}$$
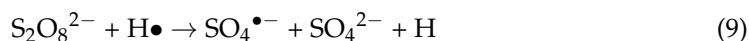
According to Ferkous et al. [73], treating water with ultrasound can produce HO• while producing other reactive oxygen species as $HO_2{}^{\bullet}$, H• or $O_2{}^{\bullet-}$. They added that PDS triggered with ultrasound mostly produces •OH and $SO_4{}^{\bullet-}$, enhancing the performance of organic compound breakdown. An examination on the degradation of a diclofenac (DCF) utilizing ultrasonicated persulfate anions was conducted by Monteagudo et al. [74] and the study successfully removed 95% of the DCF. In Figure 5 the experimental setup used in the investigation is schematically illustrated. Table 3 displays the ultraviolet and ultrasound activated persulfate for the degradation of ECs.
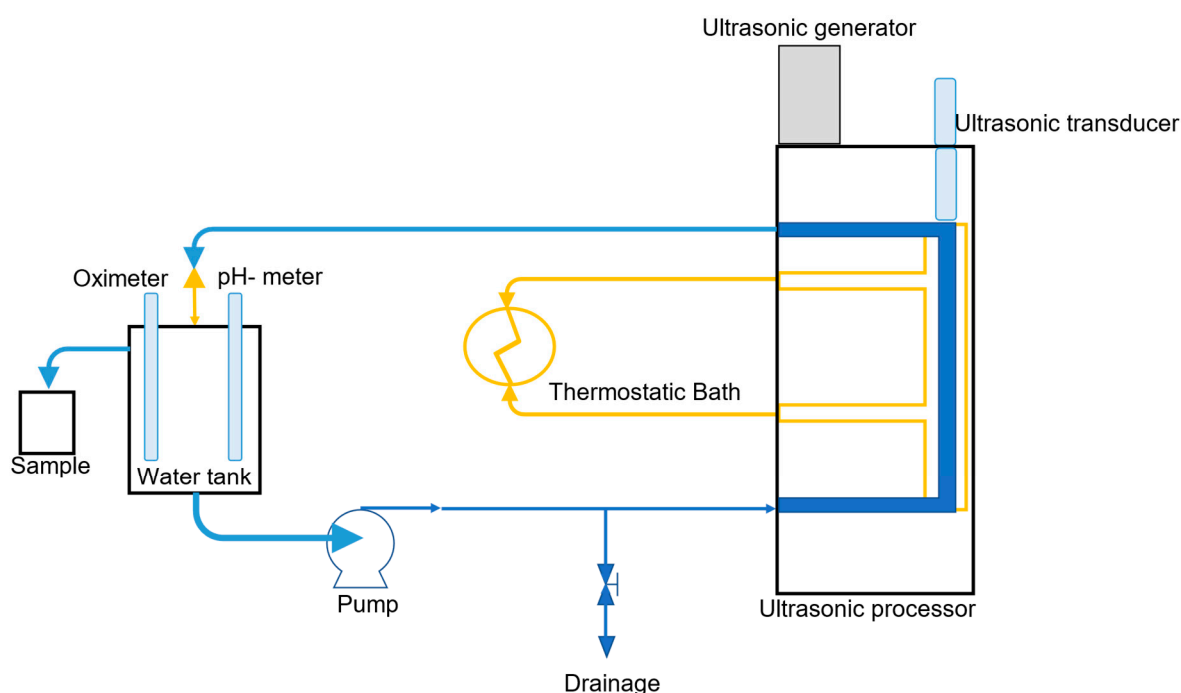
Figure 5. Schematic illustration of ultrasonic/persulfate process (adopted from Monteagudo et al. [74].

Table 3. Ultraviolet and ultrasound activated persulfate for the degradation of ECs.

[Ultraviolet Activated Persulfate]							
Pollutant	**Pollutant Concentration**	**Oxidant Concentration**	**Wavelength (nm)**	**pH**	**Reaction Time (h)**	**Degradation (%)**	**References**
Perfluorooctanoic Acid	0.15 mM	15.00 mM PS	254.00	7.10	8.00	>80.00	[75]
2-methylisoborneol	0.238 μM	10.00 μM PS	254.00	7.00	0.14	>90.00	[76]
Sulfamethoxazole	20.00 μM	1.00 mM PS	254.00	8.00	2.00	100.00	[66]
Sucralose	0.126 mM	3.78 mM PMS	254.00	7.00	1.00	>95.00 (TOC)	[77]
[Ultrasonic activated persulfate]							
Pollutant	**Pollutant concentration**	**Oxidant concentration**	**Frequency (kHz)**	**pH**	**Reaction time (h)**	**Degradation (%)**	**References**
1,1,1-trichloroethane	50.00 mg L^{-1}	0.94 mM	400.00 (bath)	6.90	2.00	100.00	[78]
Carbamazepine	0.025 mmol/L	1.00 mmol/L	40.00 (bath)	5.00	2.00	89.40	[17]
Naphthol	5.00 mg L^{-1}	9.00 mg L^{-1} PDS	585.00 (probe)	6.00	0.33	>90.00	[73]
Azorubine	20.00 mg L^{-1}	4.00 mM PDS	40.00 (bath)	3.50	1.00	66.54	[79]
COD	720.00 mg/L	500.00 mg/L	130.00	3.00	1.00	74.50	[80]
Diclofenac	5.00 mg/L	120.00 mg/L	1. 3.50 W/cm^2 acoustic intensity 2. 30 °C temperature	6.00	4.00	95.00	[74]
Ibuprofen	24.00 μm	0.80 mM	35	4.90	1.00	Tap–90.40 River–85.30	[18]
Carbamazepine	2.50 mmol/L	5.00 mmol/L	(1) 200.00 W ultrasonic power (2) 50 °C temperature	5.00	2.00	89.40	[17]

4. Important Factors Affecting the Electro, Sono and Thermal Activated Persulfate

To achieve the optimum performance of each of the activation methods, important factors such as pH, reaction time, PDS concentration, current density and electrode material need to be taken into consideration.

4.1. Electrochemically Activated PDS

Numerous electrode materials such as Ti/RuO_2-IrO_2, Pt, Fe and BDD have been prepared and work as electrochemical-activated PDS for ECs degradation [81]. Zhi et al. [82] reported that significant interest has been shown in the electrochemical activation of persulfate using a sacrificial iron electrode due to the anodic oxidation reaction, where iron electrode forms Fe^{2+} to activate PDS. This method uses less energy while improving the usage of ferrous and persulfate ions. Different anode/cathode pairings can improve the efficiency of persulfate electrochemical activation. Matzek et al. [83], stated that a combination of Pt/Gr, BDD/Pt and BDD/Gr in a single cell rotating disk electrode system resulted into the reaction of PDS activation, the BDD/Gr anode exhibited higher performance than that of the BDD/Pt. According to Matzek and Carter [49], a crucial component of the electro-activated persulfate is current density, which is regulated easily by the operator. According to Frontistis et al. [84], who made a further addition, the electrochemical oxidation reaction is not kinetically constrained by the mass transport of the organic pollutant onto the anode, hence the main way to speed up the reaction rate is to increase the current density. The degradation of pollutants may critically also be affected by the pH of the electro activated PDS even in various circumstances, where the pH value is below the value needed for activating alkalis [82].

According to Chen et al. [81], utilizing electrochemically activated PDS to remove 2,4-dichlorophenol resulted in a greater persulfate production in acidic solutions. Using ferrous ions as the homogeneous catalyst, electro-activated PDS is being investigated at various level of pH from 3.0 to 11.0. It was found that found that the diuron elimination rate changed from 0.154 to 0.008 min^{-1}. At a pH of 2.5, $FeOH^{2+}$ and $Fe(OH)^3$ predominated over Fe^{2+}, and that their production decreased the concentration of free Fe^{2+} and hence the activation of $SO_4^{\bullet-}$.

According to Song et al. [13], the concentration of persulfate used directly correlates with the effectiveness of contaminants being removed. The study also revealed that, while PDS alone was unable to efficiently degrade carbamazepine, electrochemical activation of PDS at Ti/Pt anode increased carbamazepine degradation upon an increase in PDS rate from 1 mmol/L to 5 mmol/L. Matzek and Carter [49] reported that based on the analyte and persulfate concentration, the pace at which activated persulfate degraded organic chemicals adhered to second order kinetics. The effect of temperature on electrochemically activated persulfate should not be neglected as the temperature rose, the PDS output and current efficiency fell [48]. According to the study, the rationale for this conclusion is that under the circumstances of thermal augmentation (≥ 40 °C), $S_2O_8^{2-}$ may homogenize and disintegrate into $SO_4^{\bullet-}$ with significant heat activation-induced oxidation (Equation (4)), leading to a reduction in PDS concentration.

4.2. Thermally Activated PDS

It was reported by Chekem et al. [20] that as the temperature of the treated solution rises, the removal rate of the pollutants becomes significant as well. The study also suggests that temperature affects the heat activation-induced oxidation of PDS to produce free radical species. However, it does not prove that the removal efficiency increases with temperature. According to Wang et al. [85], there is an ideal temperature for the degradation of PAH since the effectiveness of PAH degradation reduced at activation temperatures higher than 60 °C. A study by Bashir et al. [4] also reported that the elimination of color by thermally-activated persulfate oxidation shows the biggest changes, increasing from 40% at 25 °C to 80% at 60 °C and then increasing to 100% at 80 °C.

It should be mentioned that pH has an impact on the conversion of sulphate radicals to •OH radicals at a specific temperature. According to Chekem et al. [20], $SO_4^{•−}$ was the main radical at pH 7, $SO_4^{•−}$ and •OH radicals were both present at pH = 9, and •OH was the dominant radical at pH = 12; according to their research, Jorfi et al. [58] stated that quick change of $SO_4^{•−}$ to •OH radicals attributed to the experimental conditions and the acidic pH favored the most COD removal efficiency of 87%, 86.67% and 86.02% for pH 3, 4 and 5, respectively. Park et al. [86], asserted that through acid catalysis, more sulphate radicals could be produced under acidic conditions. The presence of oxidant effectuates the significant reduction of pollutant, hence promoting the degradation of pollutants in the solution, as increasing oxidant concentration is constructive to organic removal, which compliments the available sulfate radicals for oxidation [20]. Ahmadi et al. [87] supported this finding which demonstrates how important and influential persulfate concentration is for thermally-activated persulfate since it directly affects the equilibrium of the sulphate radicals. A higher persulfate concentration leads to the diffusion of more sulphate radicals, functioning as a scavenger that effectively breaks down the contaminants [88].

4.3. Sono Activated PDS

Temperature plays a crucial role in the oxidation process because it influences the activation energy and the behavior of the pollutants. The rate constants at 10, 25, and 40 °C were 3.63×10^{-2} min^{-1} (R2 = 0.99), 5.86×10^{-2} min^{-1} (R2 = 0.99), and 7.8×10^{-2} min^{-1} (R2 = 0.98), respectively. According to Lee et al. [18], the rate constant increases with temperature. The physical and chemical characteristics of a solution, which affect the oxidation kinetic constant, are also influenced by pH in addition to temperature [18]. The pH value could be lowered in accordance with Equations (10) and (11) to promote the formation of sulphate radicals from persulfate anion [74].

$$S_2O_8^{2−} + H^+ \rightarrow HS_2O_8^{−} \tag{10}$$

$$HS_2O_8^{−} + e^{−} \rightarrow SO_4^{•−} + SO_4^{2−} + H^+ \tag{11}$$
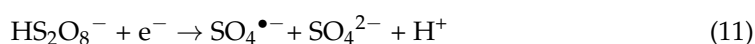
An investigation by Monteagudo et al. [74] on sono-activated persulfate oxidation of diclofenac stated that the maximal concentration of •OH and $SO_4^{2−}$ achieved at pH 3 were higher than those at pH 8 under similar conditions. The finding was further confirmed in another study of the sono−activated PDS process for the remediation of dairy wastewater by Hossein et al. [80]; they show that the highest removal COD efficiency was achieved in acidic pH (pH 3) and the removal percentage of organic matter for the same time were 62.9% and 68.3%, respectively. Because persulfate ions are one of the oxidants that directly form sulphate radical to breakdown organic compounds and indirectly react with hydroxyl ions and water molecules, persulfate concentration is one of the most crucial parameters in the degradation of pollutants [80]. They claimed that the early phases of the procedure saw an increase in organic matter degradation due to an increase in persulfate concentration and reaction time. The process efficiency was reduced, nonetheless, due to an excessive rise of persulfate ions. This is due to the fact that extra $S_2O_8^{2−}$ anions in solution act as radical scavengers and impede the effectiveness of removal while also increasing the risk of radicals annihilating themselves [17].

Ultrasound intensity or amplitude is another effective parameter in sono-activated PDS processes. Higher ultrasonic amplitudes led to the formation of extra radicals, and sonication might unintentionally have a significant mechanical impact on a homogeneous system, enhancing the mass transfer reaction in solution [74]. An increase in DCF removal from 88% to 98% was recoded after a 240 min reaction with the intensification of acoustic intensity from 2.5 to 4.5 W/cm. According to Wang et al. [17], who implemented this theory, there are two factors that contribute to the improved elimination effectiveness with upgraded ultrasonic power: (1) augmented ultrasonic power caused further cavitation bubbles, which provided additional energy to produced radical, resulting in a higher rate of radical generation; and (2) mass transfer resistances could be removed because of the

turbulent flow produced by ultrasonic irradiation. Other than that, a single ultraviolet ray can efficiently break down some organic contaminants, but it had a limited ability to remove other organic contaminants. Nitrosodimethylamine, for instance, is susceptible to direct photolysis [89]. As a result, UV photolysis is easily able to break it down. The use of UV-activated PS was severely hampered by the ultraviolet's low penetration of the water and viability in the subsurface [74]. Table 4 summarizes the important factor affecting the PDS activation method.

Table 4. Summarization of the important factor affecting the persulfate activation method.

Influencing Factor	Electrochemically-Activated Persulfate	Thermally-Activated Persulfate	Sono-Activated Persulfate
Electrode Material	• Example of electrode material being use in the industry: $Ti/RuO_2\text{-}IrO_2$, Pt, Fe, Al, carbon and BDD • Electrochemical activation of persulfate with sacrificial iron electrode has attracted huge attention due to the anodic oxidation reaction where iron electrode forms Fe^{2+} to activates PDS • This process demands lower energy yet improves the utilization of persulfate and ferrous ions • Various anode/cathode combination can contribute to the effectiveness of electrochemical activation of persulfates, e.g., combinations of Pt/Gr, BDD/Pt and BDD/Gr	No electrode involved	No electrode involved
Current Density/amplitude	• Easy-controlled properties by operators • The reaction rate can be accelerated if the current density is kinetically restricted by the mass transport of the organic pollutant onto the surface of the anode	No current density/amplitude involved	• Higher ultrasonic amplitudes produced high generation of radicals • The turbulent flow achieved with ultrasonic irradiation eliminating the mass transfer resistances
pH	Formation of persulfate was higher in acid solution than in alkaline solution	• Rapid conversion of $SO_4^\bullet$ to $OH^\bullet$ attributed at basic condition • Acidic pH favored the most COD removal efficiency • More sulfate radicals could be generated through acid catalyzation in acidic condition	• pH determines the physical and chemical properties of a solution which affect the oxidation kinetic constant • The generation of sulfate radicals from persulfate anion could be increased by decreasing the pH value

Table 4. *Cont.*

Influencing Factor	Electrochemically-Activated Persulfate	Thermally-Activated Persulfate	Sono-Activated Persulfate
Persulfate Concentration	Reaction rates are directly proportional to the concentration of persulfate	• Persulfate concentration is vital and influential factor for thermally activated persulfate due to its direct impact on the sulfate radical equilibrium. • Higher concentration of persulfate causes extra sulfate radicals' diffusion, thus acting as a scavenger that was effective in decomposing the pollutants	• Excessive increase in persulfate ions resulted in reduction in the efficiency of the process • Excess $S_2O_8^{2-}$ anions in solution act as radical scavenger
Temperature	PDS output and current efficiency decreased with the increase of temperature	• Thermal activation of persulfate for generation of free radical species is temperature dependent • The degradation efficiency is dependable to the temperature, but not necessarily the increment of temperature leads to higher degradation efficiency as optimum temperature needs to be addressed	• Temperature affects the activation energy and pollutant behavior • The rate constant increase with the temperature

5. Limitation and Future Perspective of Persulfate Activation by Electro, Sono and Thermal

In the study literature, AOPs are portrayed as effective at degrading ECs. There is, nevertheless, a sizable knowledge vacuum in relation to their industrialization or process scalability. Only a small number of studies have been conducted on this issue [90]. Despite being the top list studies for ECs removal in recent years, the application of AOPs at full scale is yet to be discovered [30], leaving a space for future research. Another limitation for this technique is the electricity or energy consumption during the operation in a larger scale, which is mostly a case in industrial settings [91]. This is a future perspective that can be investigated for researchers to consider the feasibility of incorporating economical and renewable resources.

Moreover, similar to the treatment of any pollutants, the main issue is surrounding the power supply, or the energy needed to operate the overall process, which is directly proportional to the cost of operation [92,93]. Chekem et al. [20] stated that the energy balance optimization and process competitiveness for treating micropollutants in wastewater will be the next critical step. Considering transforming energy source from a solar system can be adaptable. However, the initial investment should give the treatment plant operator a cause to ponder. The starting concentration of organic compounds strongly influences the PDS concentration needed [92], showing that the PDS concentration needed to degrade organic compounds varies depending on the kind and initial concentration of the organic compounds. Thus, real wastewater presents a significant difficulty for treatment [94,95], and it is important to establish the best PDS concentration [14]. The excessive addition of persulfate in electro-activated persulfate processes leads to a significant concentration, which will cause problems in the treated effluent, albeit its ability for a persulfate regeneration [47]. The sulfate concentration in the treated effluents must comply to the quality

standard to accomplish proper industrial requirement discharge. Hence, the dosage of PDS required for the effective treatment of the effluent must be well understood.

This creates another restriction for application optimization because different contaminants require different reaction rates of activated persulfate degradation [82]. Matzek and Carter [49] claimed that by better understanding the second order reaction rates with reference to analyte and persulfate, the optimization of persulfate utilization in certain systems is conceivable. This opens a knowledge gap to exclusively study PDS activation for the degradation of specific pollutants.

Single treatment technology applications in achieving significant ECs removal can be challenging. Therefore, as suggested by [27], using an integrated system to opt the limitation of the individual treatment technologies can be bridged, and it could be broadened up as a potential alternative in the future for efficient ECs removal from the environment.

6. Conclusions

Recently, with the emergence of new contaminants, effective wastewater treatment has become highly important. PDS-based AOPs, especially, electro, sono and thermal activation have been successful for various types of ECs contaminates. This paper provides an inclusive collection of evaluations on the application of PDS activation methodology (sono, thermal and electro) for ECs degradation covering its mechanisms, efficiency, limitation, and future perspectives. The important factor affecting each of the methods is discussed and compared with each other to bring out the comprehensive understanding, not only on the importance but as also on the dependency between the factors. Plus, the currently existed limitations and future directions were also critically reviewed. It can be concluded that with the aid of PDS, the degradation of pollutants can be improved up to 100%. However, different fragments of pollutants need different reaction rates of activated persulfate due to the variance in application optimization. This provides a gap of knowledge for future researchers to explore. Other than that, larger scale applications have fewer approaches, which could be because of the consumption of high-power supply which contributes to the high cost of operation, however, this can be slowly avoided by comprehending the potential uses of solar power systems.

Author Contributions: M.J.K.B. came up with the concept; writing by F.J., M.J.K.B. and Z.H.J.; S.S. revised the manuscript and collude it. Revision and editing were carried out by J.W.C.W. and J.Z. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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