

UV/periodate and UV/chlorine for dye degradation and real wastewater treatment: a comparative study

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ABSTRACT

The discharge of synthetic dyes into the environment poses a significant threat to both human health and the ecosystem, necessitating the treatment of contaminated water. To generate free radicals for the elimination of Direct Blue 71 (DB71) dye from aqueous solutions, periodate (PI) and chlorine (Cl₂) have been employed. In this study, separate activation of PI and Cl₂ was achieved using ultraviolet (UV) light. The impact of various operational parameters was investigated, resulting in the complete degradation of the dye within 12 min. The presence of ferrous and copper ions had a minor enhancing effect on the degradation rate in both systems. Scavenging experiments confirmed that HO[•] and IO₃⁻ were the primary agents responsible for DB71 degradation in the UV/PI system, while reactive chlorine radicals played a dominant role in the UV/Cl₂ process. In terms of mineralization, application for real wastewater and energy efficiency, the UV/PI system exhibited slightly superior performance compared to the UV/Cl₂ system.

Key words: advanced oxidation processes, chlorine, Direct Blue 71, periodate, textile wastewater

HIGHLIGHTS

- UV/chlorine and UV/periodate were compared together for the first time.
- A complete degradation of DB71 was achieved in at short time for both processes.
- The carboxylic evolution of DB71 degradation was monitored.
- A practical study was conducted on real wastewater.

1. INTRODUCTION

Various contaminants, such as organic pollutants, nutrients, bacteria, metals and micro-pollutants, can be found in water resources (Al-Hazmi *et al.* 2022). In recent years, an increase in the production of colored products has been observed. In fact, to enhance the attractiveness of products, various dyes are added to raw materials since color is the biggest issue for customers. The variety of colors increases the extended production of various dyes in different industries (Yousefi *et al.* 2017). Azo dyes account for around 60–70% of all dyes used in manufacturers containing one or more azo bonds (–N = N–). Among azo dyes, Direct Blue 71 (DB71) is widely used as blue color for various products. It is known as Direct Fast Blue and structurally has eight aromatic rings (Lu *et al.* 2017; Yousefi *et al.* 2017). Due to its complicated molecular structure, it is highly resistant to bio-degradation in natural environments leading to the acute toxicity of the ecosystem. There is a severe concern when high concentrations of synthetic dyes enter the water bodies (Matouq *et al.* 2014). Recently, synthetic dyes have demonstrated a genotoxicity property and also it has been reported long-term carcinogenicity synthetic dyes (Ganiyu *et al.* 2019). The water contaminated with dyes and wastewater generated from manufacture-producing dye should be treated since these effluents become an earnest threat to aquatic life (Thiam *et al.* 2015). Several physicochemical processes have been employed for dye degradation in recent decades. Most of them are inefficient for complete dye degradation in the water environment. Moreover, some limitations such as long reaction time and sludge generation stimulate researchers to apply new methods for water and wastewater treatment (Al-Hazmi *et al.* 2023). Advanced oxidation processes (AOPs) are effective technologies for decontamination

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using the generation of reactive species (Khavari Kashani *et al.* 2022; Hassani *et al.* 2023). Classically, hydroxyl radicals (HO[•]) have been considered as the main species for AOPs that are produced through various methods at room temperature and atmospheric pressure (Khiehm *et al.* 2023). Recently, a variety of reactive species has been examined for the degradation of organic pollutants (Ghanbari *et al.* 2021; Eslami *et al.* 2023a). In this way, different and new oxidants have been applied for the generation of various reactive species such as sulfate radicals, chlorine radicals, singlet oxygen, periodate radicals and organic radicals (Afify *et al.* 2023; Eslami *et al.* 2023b). In such a manner, chlorine (Cl₂) and periodate (IO₄⁻) have been used in AOPs for the generation of different free radicals. To activate Cl₂ and IO₄⁻, various methods have been used including UV irradiation (Yaghoot-Nezhad *et al.* 2023), ultrasound (US) (Eslami *et al.* 2023b), transition metals (Mao *et al.* 2021; Yaghoot-Nezhad *et al.* 2023), carbon catalysts (He *et al.* 2022) and alkaline (Bokare & Choi 2015). UV-based activation of oxidants is an effective, practical and chemical-less method which has been widely investigated for the degradation of organic pollutants. UV/chlorine and UV/periodate are new AOPs which are able to produce powerful free radicals based on the following equations (Ghanbari *et al.* 2021; Yaghoot-Nezhad *et al.* 2023).



As above-mentioned, besides HO[•] generation, several reactive species are generated in UV/periodate and UV/chlorine which may enhance the degradation process. UV/chlorine and UV/periodate have been separately examined on the various pollutants. Accordingly, UV/chlorine have been used for acetaminophen (Ghanbari *et al.* 2021), sulphiride (Zhang *et al.* 2023), 1,4-dioxane (Masjoudi & Mohseni 2023), Bisphenol A (Cao *et al.* 2023) and dyes (Rafiei *et al.* 2021), while few contaminants including ciprofloxacin (Zhang *et al.* 2022), 2,4-dichlorophenol (Zhang *et al.* 2021), para-nitrophenol (Eslami *et al.* 2023b) and dye (Bendjama *et al.* 2018) have been considered for UV/periodate.

Although both methods (UV/periodate and UV/chlorine) have been separately used for different pollutants, there is no study to show the comparison of both methods for the degradation of a sample of pollutants. Moreover, there are various unknown aspects of both processes including the mechanism, application for real wastewater and promotional factors that their studies are necessary.

In this work, UV/periodate and UV/chlorine were investigated on the dye degradation. The decolorization of the dye was studied under different conditions and several variables were scrutinized. Moreover, the mineralization degree and the formation of carboxylic acids were vindicated. Finally, the application of UV/periodate and UV/chlorine processes was tested on real wastewater.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Sodium periodate (NaIO₄⁻, 99.8%), phenol and tert-butyl alcohol (TBA) were purchased from Samchun company. NaOCl (10%) was purchased from Merck. Sodium chloride (NaCl, >99%), sodium bicarbonate (NaHCO₃, >99%), potassium nitrate (KNO₃, >99%), sodium sulfate (Na₂SO₄, 99%) and ferrous sulfate (FeSO₄) were supplied from Chem-Lab company. Furfuryl alcohol (FFA), 2-Propanol anhydrous (99.5%), 1,4-Benzoquinone (BQ) (98%) were purchased from Acros-organic Company. Real textile wastewater was collected from a manufacturer in Zanjan City (Iran). The characteristics of real wastewater are presented in Table 1.

Table 1 | Characteristics of real textile wastewater

Parameter	Unit	Value
COD (Chemical Oxygen Demand)	mg/L	870
Color	ADMI	2,330
TDS (Total Dissolved Solids)	mg/L	560
TOC	mg/L	290
pH	–	6.4

2.2. Oxidative experiments

Experiments were conducted to degrade the DB71 dye solution within a glass cylinder. The reactor (a 250 mL flat beaker) contained 100 mL of synthetic dye solution, and then a precise amount of oxidant was introduced. The pH of the solution was adjusted using H₂SO₄ and NaOH. To initiate the degradation process, a UVC lamp (Osram 4 W, 254 nm) was employed, placed at a distance of 30 mm from the solution while the UV lamp was placed above the reactor (UV intensity = 1.01 mW/cm²). The UV light intensity was measured by A radiometer (Lux-UV-IR meter, Leybold Didactic GMBH-666-230). Throughout the experiment, the dye solution was constantly mixed using a magnetic stirrer while maintaining a temperature range of 23–25 °C. A known amount of sodium periodate and sodium hypochlorite was separately added to the solution. Once the UVC lamps were activated, the oxidative process commenced to remove the DB71 compound. At specific time intervals, 2.5 mL samples were extracted from the solution for subsequent determination of the DB71 concentration. To identify the reactive species, some quencher agents (TBA, BQ, phenol, FFA, HCO₃⁻ and 2-Propanol) were added to the dye solution before the oxidation process. Moreover, some experiments using some anions and humic acids were conducted to determine the effect of the water matrix. All experiments were conducted in triplicate and their average was reported.

2.3. Analytical methods

For analytical purposes, the concentrations of DB71 were assessed using a UV-vis spectrophotometer at a wavelength of 587 nm. The total organic carbon (TOC) value was measured using a Shimadzu-VCSH model TOC analyzer. Furthermore, the carboxylic acid by-products were identified using a Waters model high-performance liquid chromatography at a wavelength of 220 nm. The color of real textile wastewater was measured by the American Dye Manufacture Institute (ADMI) method by a spectrophotometer (HACH, DR5000).

3. RESULTS AND DISCUSSION

3.1. Comparison of DB71 elimination by multiple decontamination procedures

Figure 1(a) evinces the DB71 decomposition in aqueous media adopting several oxidation methods. As displayed, the UV, PI and Cl₂ sole processes had unsatisfactory decontamination efficacies of roughly 5, 8 and 10%, respectively. It can be deduced that the individual use of these processes is incapable of decomposing organic pollutants owing to the inability to produce reactive oxygen species (ROS). Nonetheless, hybridizing UV with PI and Cl₂ resulted in a remarkable DB71 elimination percentage of 100%. The complete decontamination efficiency of the target pollutant utilizing these processes is attributed to the formation of ROS and reactive chlorine species (RCS) due to the direct photolysis of PI and Cl₂. The oxidizing radical agents responsible for the promoted DB71 removal rate are recognized to be IO₃[•] and [•]OH in the UV/PI procedure and integration of chlorine-based radicals and [•]OH in the UV/Cl₂ procedure. To further investigate the capability of the UV/PI and UV/Cl₂ systems in eliminating DB71, the reaction rate constant (*k*_{obs}) of whole treatment systems is elicited in Figure 1(b). As noted, the computed values of *k*_{obs} for UV, PI, Cl₂, UV/PI and UV/Cl₂ decontamination procedures accounted for 0.0081, 0.0159, 0.0167, 0.5174 and 0.4847 min⁻¹, respectively. Based on these results, it can be clarified that coupling ultraviolet irradiation with chemical oxidation systems leads to a strong synergistic impact.

3.2. The effect of operating parameters

Figure 2(a) illustrates the elimination of DB71 using the UV/PI process with a PI concentration of 0.75 mM at various pH levels (3–9). The utmost efficacy was achieved at pH = 3, resulting in a 99.9% removal of DB71.

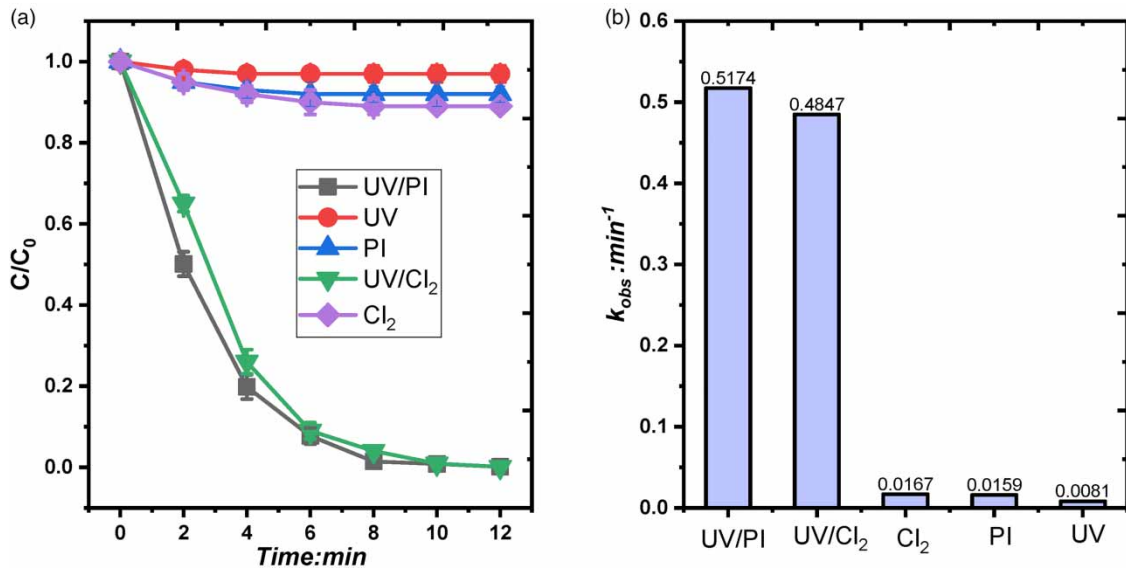


Figure 1 | (a) DB71 degradation by UV/PI and UV/Cl₂ and (b) the rate constant of DB71 degradation (pH = 3, DB71 = 20 mg/L, PI = Cl₂ = 0.75 mM).

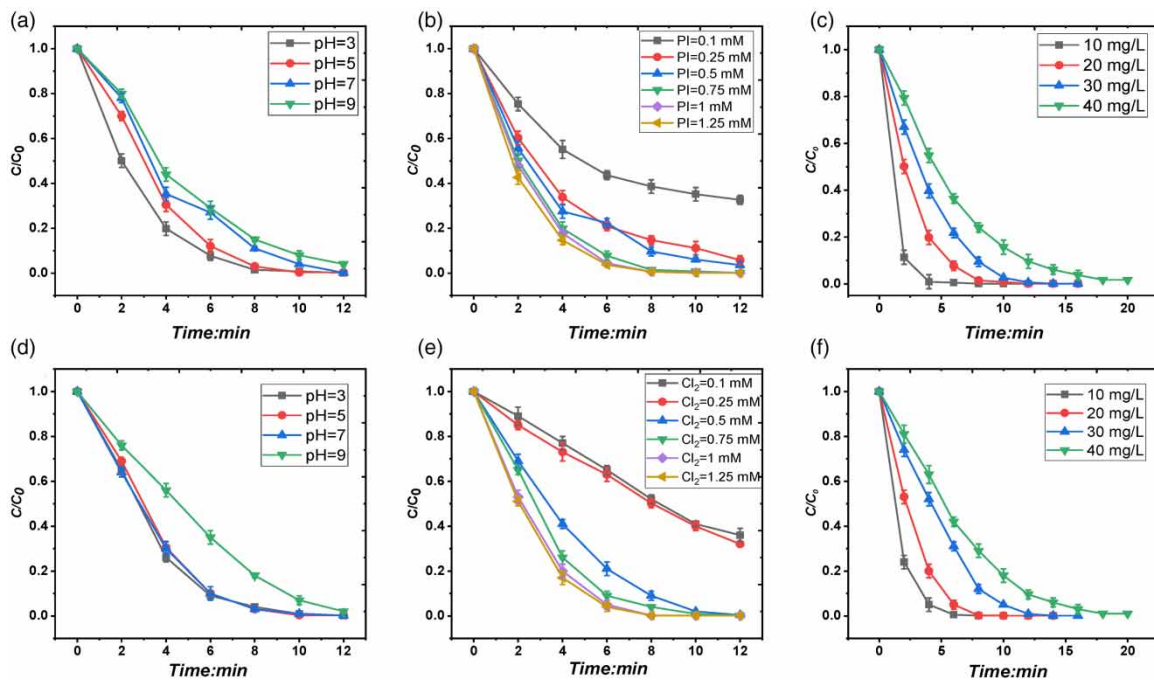
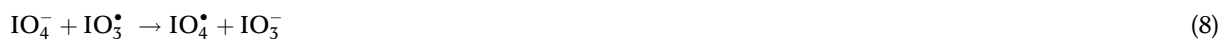


Figure 2 | The effect of operating parameters on UV/PI process: (a) pH, (b) PI dosage, and (c) DB71 concentration; the effect of operating parameters on UV/Cl₂ process, (d) pH, (e) Cl₂ dosage, and (f) DB71 concentration.

Whereas, as the solution's pH was further increased to 9, a minor decline in the rate constant for dye degradation was detected. Long *et al.* (2022) documented a notable decrease in removal efficiency under neutral and alkaline conditions. It is worth noting that at pH < 8, IO₄⁻ predominates as the primary species, which readily decomposes into free reactive radicals (Eslami *et al.* 2023b). This explains the better performance of the UV/PI process in acidic conditions.

The amount of oxidizing agent used in chemical oxidation plays a critical role in the generation of free radicals. Therefore, an increase in oxidant dosage promotes the production of HO[•], RCS and iodine radicals, leading to enhanced dye degradation in UV/PI. In this study, a considerable improvement in DB71 degradation was

observed when the PI concentration was raised to 0.5 mM, due to the increased amount of radicals present in the solution (Figure 2(b)). The degradation rate was further increased as oxidant dosage was raised to 1.25 mM, however, the DB71 removal was only slightly improved as dosage was increased from 0.75 to 1.25 mM in UV/PI. It can be deduced that excess IO_4^- can quench the generated IO_3^\bullet radicals at a very fast rate (Equation (8)). Moreover, the recombination of iodine radicals due to reacting with one another at higher periodate concentrations could also result in lower DB71 removal rates (Equations (9) and (10)). Hence, 0.75 mM was chosen as the optimum oxidant dose in other experiments.



The effect of the initial dye concentration on the removal rate for UV/PI has been investigated and the results are presented in Figure 2(c). It is apparent that increasing the dye concentration leads to much lower removal rates. This can be explained by considering that at a fixed oxidant dosage, a specific amount of radicals is produced. Hence, by increasing the target pollutants present in the reaction media, lower removal rates are expected.

In the UV/ Cl_2 process, the presence of ClO^- and HOCl species can be influenced by the pH of the solution. Figure 2(d) illustrates the elimination of DB71 by UV/ Cl_2 process with a chlorine concentration of 0.75 mM at various pH levels. The results indicate that as pH was increased, the DB71 removal rate was reduced. Moreover, the highest removal rate was achieved at pH = 3–7, while the lowest rate was achieved at pH = 9. Further, the elimination of DB71 was observed to be satisfactory in acidic to neutral conditions (pH levels of 3–7), where the removal rates are very close in value. In acidic solutions (pH < 6.5), HOCl dominates, as the pK_a of HOCl/OCl^- is 7.5, whereas OCl^- dominates at pH > 8.5 (Yaghoot-Nezhad *et al.* 2023). Previous studies have suggested a higher quantum yield for HOCl (0.62) compared to OCl^- (0.55) under 254 nm UV irradiation (Zhao *et al.* 2019). Consequently, it can be inferred that HOCl photolysis yields higher efficiency in comparison to OCl^- (Watts & Linden 2007). Therefore, considering that the $\text{HOCl}:\text{OCl}^-$ ratio is reduced as pH is increased (Wang *et al.* 2016), indicating that more hydroxyl and chlorine radicals are produced in acidic conditions. It is also important to note that OCl^- exhibits higher reactivity than HOCl in scavenging HO^\bullet and Cl^\bullet radicals (Equations (11)–(14)) (Lu *et al.* 2018), which further explains the lower rates observed at higher pH levels.

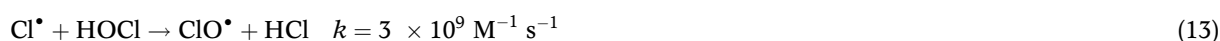
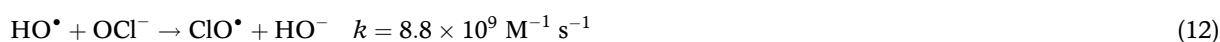


Figure 2(e) shows the effect of chlorine dosage on DB71 removal. A dramatic enhancement was observed in DB71 removal when chlorine dosage was increased from 0.1 to 0.75 mM. After that, insignificant decolorization was observed when chlorine dosage was increased to 1.25 mM. It has been reported that oxidant dosage should be at the optimum amount and its excess dosage leads to negative results. This can be attributed to the scavenging of radicals by excess HOCl and OCl^- in higher chlorine dosage of the UV/ Cl_2 process, as described in Equations (11)–(14) (Huang *et al.* 2019). The primary product of this scavenging effect in cases of chlorine overdose is ClO^\bullet , which is known to act as a weak oxidizing agent.

Figure 2(f) depicts DB71 removal by UV/ Cl_2 under various DB71 concentrations. Complete degradation took place at 8, 12, 14 and 20 min for initial DB71 concentrations of 10, 20, 30 and 40 mg/L, respectively. In fact, an increase in the dye concentration needs more ROS and RCS or more reaction time.

3.3. The determination of reactive species

Mounting recent studies have shown multiple ROS, such as IO_3^\bullet , HO^\bullet , $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ in UV/PI process and HO^\bullet and reactive chlorine agents in the UV/ Cl_2 , could be formed in the oxidation system. To clearly understand the impact of ROS responsible for the decontamination of DB71 via UV/ Cl_2 and UV/PI processes, quenching experiments were conducted in the presence of multiple chemical probes at optimized operating circumstances. The

FFA (a rate constant of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and BQ (a rate constant of $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) were employed in UV/PI as scavengers to trap $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$, respectively (Gao *et al.* 2022). The findings from Figure 3(a) illustrate that the elimination rate of DB71 was not declined with the increase in the concentration of BQ and FFA. The phenomenon revealed that the contribution of $^1\text{O}_2$ and $\text{O}_2^{\cdot-}$ radicals is insignificant during the decontamination of DB71. TBA and 2-Propanol were utilized as quenchers of HO^{\cdot} and $\text{O}(^3\text{P})/\text{HO}^{\cdot}$ over the degradation of DB71 in the UV/PI system, respectively (Bendjama *et al.* 2018). Indeed, the difference between DB71 degradation in the presence of TBA and 2-Propanol indicates the contribution of $\text{O}(^3\text{P})$. Accordingly, the role of $\text{O}(^3\text{P})$ in the degradation of DB71 was scant. As displayed in Figure 3(a), the decontamination rate of DB71 in the presence of TBA was considerably reduced. These findings showed that HO^{\cdot} radicals played a major role in the decomposition of DB71 over the UV/PI system. Phenol has a good scavenging feature for $\text{IO}_3^{\cdot}/\text{IO}_4^{\cdot}$ and HO^{\cdot} radicals (Bendjama *et al.* 2018). As it can be observed in Figure 3(a), in the presence of phenol, the DB71 decontamination was significantly inhibited, which illustrated that $\text{IO}_3^{\cdot}/\text{IO}_4^{\cdot}$ was also a major oxidative agent in DB71 elimination. This was confirmed by monitoring IO_3^- concentration over 12 min of operating time, as shown in Figure 3(b). The content of iodate was improved after 12 min of oxidation time and it reached 0.37 mM, revealing that PI was degraded and converted into HO^{\cdot} and IO_3^{\cdot} radicals as the major oxidation agents responsible for the degradation of DB71. Regarding the results obtained, the IO_3^{\cdot} and HO^{\cdot} were the main ROS for the degradation of DB71 in which the electron transfer (from HO^{\cdot} and IO_3^{\cdot} to DB71), H-abstraction and radical addition using HO^{\cdot} are three possible mechanisms for the degradation of DB71.

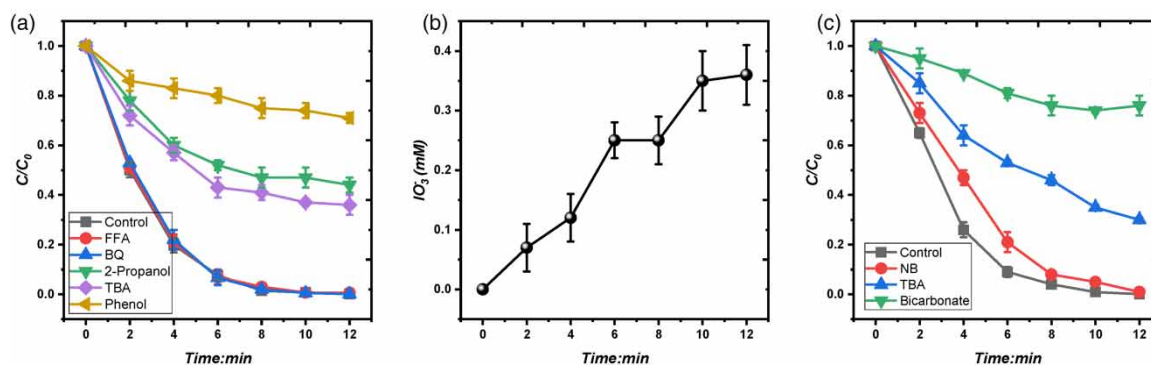


Figure 3 | (a) The effect of scavengers on UV/PI (BQ = FFA = 2 mM, 2-propanol = TBA = phenol = 50 mM, PI = 0.75 mM, pH = 3 and DB71 = 20 mg/L), (b) iodate concentration during UV/PI process, and (c) The effect of scavengers on UV/Cl₂ (TBA = NB = HCO₃⁻ = 50 mM, Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).

Three different quenchers nitrobenzene (NB), TBA and bicarbonate were deployed to capture the produced radicals in UV/Cl₂ system. Herein, 50 mM of bicarbonate, TBA and NB was employed to quench $\text{HO}^{\cdot}/\text{Cl}^{\cdot}/\text{Cl}_2^{\cdot-}$ and $\text{HO}^{\cdot}/\text{Cl}^{\cdot}/\text{ClO}^{\cdot}$ and HO^{\cdot} , respectively. As displayed in Figure 3(c), all scavengers had significant inhibitory impacts on the decontamination efficiency of DB71 except for NB. The order of inhibitory impact of scavengers is bicarbonate > TBA > NB. Considering that NB is a strong scavenger of hydroxyl radicals (a rate constant of $3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Remucal & Manley 2016), it can be concluded that HO^{\cdot} had a lower impact on DB71 removal in the UV/Cl₂ system than that of UV/PI. Furthermore, all radicals can be quenched by bicarbonate and TBA except for ClO^{\cdot} and $\text{Cl}_2^{\cdot-}$, respectively (Wu *et al.* 2017; Gao *et al.* 2020). Therefore, it is apparent that RCS has played a major role in DB71 removal in the UV/Cl₂ system. Indeed, it can be concluded that $\text{Cl}_2^{\cdot-}$, ClO^{\cdot} and Cl^{\cdot} were corresponding agents for DB71 degradation. These radicals can degrade DB71 through dehydrogenation, single electron transfer and addition to unsaturated bonds. It should be stated that the higher contribution of HO^{\cdot} in UV/PI resulted in a better performance in DB71 degradation since HO^{\cdot} is non-selective compared to RCS in UV/Cl₂.

3.4. The impact of co-existing anions

Practically, the existence of natural water constituents can have quenching impacts on the contaminant degradation potential. In view of this, the impact exerted by the HCO₃⁻, CO₃²⁻, SO₄²⁻, NO₃⁻ and Cl⁻ on the potential of DB71 decomposition utilizing UV/PI and UV/Cl₂ systems were scrutinized under optimized circumstances and the outcomes are illustrated in Figure 4(a) and 4(b). It is apparent that the addition of SO₄²⁻, NO₃⁻ and

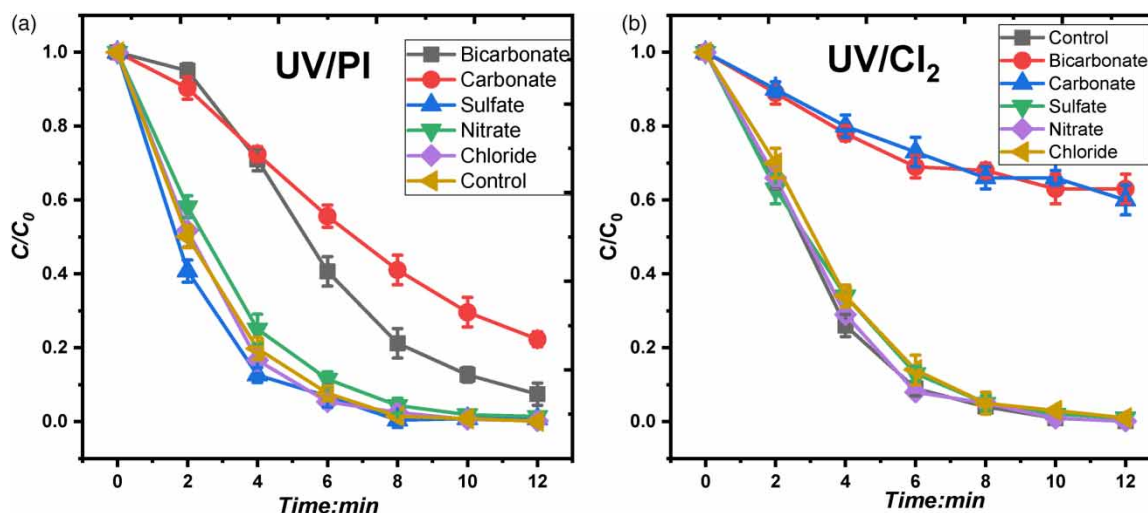
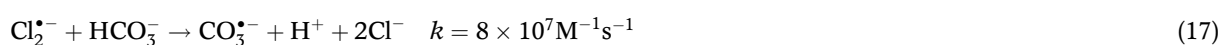


Figure 4 | The effect of anions on DB71 degradation using (a) UV/PI (b) UV/Cl₂ (anions⁻ = 5 mM, PI = Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).

Cl⁻ did not have a significant influence on DB71 decomposition efficiency over the UV/PI and UV/Cl₂ processes after 12 min of operating time. It should be noted that Cl⁻ anions have different influences on the degradation potential of AOPs, including quenching, elevating and neutral impact (Huang *et al.* 2019). In this study, Cl⁻ ions had a neutral impact on the degradation efficiency of DB71, owing to the resultant of both quenching and promoting effects of Cl⁻ in aqueous media. Furthermore, SO₄²⁻ and NO₃⁻ anions did not have noticeable impacts on the performance of UV/PI and UV/Cl₂ processes, as the DB71 degradation efficiency was similar to controlled circumstances. Although it is proven that SO₄²⁻ and NO₃⁻ can alter the capability of AOPs (De Laat & Le 2005; Huang *et al.* 2019), the current study showed that the aforementioned anions did not have an inhibitory impact on the decomposition efficiency of DB71 during Cl₂ and PI-based AOPs. In contrast, HCO₃⁻ and CO₃²⁻ anions are acknowledged as strong quenchers affecting the performance of AOPs. As can be seen, the decomposition efficiency of DB71 was significantly reduced in the presence of HCO₃⁻ and CO₃²⁻. Note that HCO₃⁻ and CO₃²⁻ had the greatest quenching effect over the UV/Cl₂ and UV/PI processes, respectively. According to Equations (15) and (16), IO₃[•] and Cl[•] may be quenched by HCO₃⁻ and formed CO₃^{•-}. Moreover, the aforementioned anion is able to scavenge Cl₂⁻ (Equation (17)).



Also, CO₃²⁻ can react with IO₃[•] and Cl[•] and produce CO₃^{•-} (Equations (18) and (19)).



The as-mentioned relations illustrate that HCO₃⁻ and CO₃²⁻ anions could easily react with various reactive species and scavenge all the major radicals generated during the UV/PI and UV/Cl₂ processes. Hence, the addition of HCO₃⁻ and CO₃²⁻ resulted in the reduction of DB71 degradation potential in both systems.

3.5. Effect of HA on DB71 degradation

The DB71 degradation rate was decreased in the presence of humic acid (HA). As can be seen in Figure 5(a) and 5(b), with the addition of HA, the removal rates related to the UV/PI and UV/Cl₂ processes were reduced. To elucidate the adverse influence of HA on the removal of DB71 during UV-based oxidation methods, the subsequent explanations are put forth:

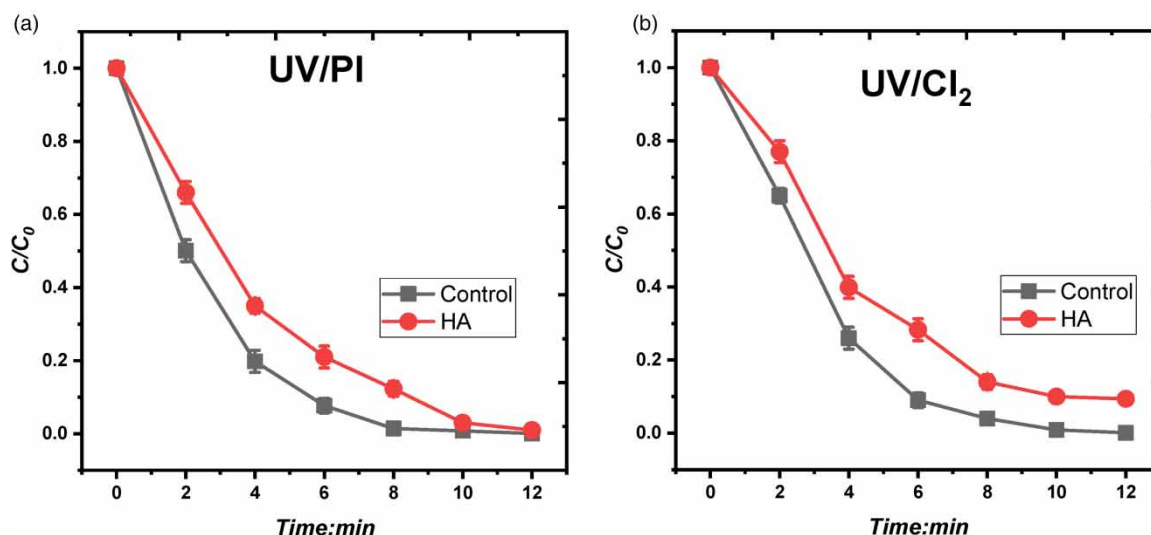


Figure 5 | The effect of humic acid on DB71 degradation using (a) UV/PI and (b) UV/Cl₂ (HA = 2 mg/L, PI = Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).

- (1) HA functions as a UV barrier that hinders the absorption of photons by periodate and chlorine. Therefore, the initiation of oxidative radicals (IO₃[•], IO₄[•], HO[•] and RCS) generation for DB71 elimination is impeded in both UV/PI and UV/Cl₂ processes. In fact, natural organic matter absorbs UV light at 254 nm and its extinction coefficient is 3.15. Hence, it acts as an inner filter to decrease PI and Cl₂ (Fang *et al.* 2014).
- (2) HA additionally suppresses the activity of the oxidative radicals generated during each process. HA is capable of effectively scavenging the produced hydroxyl and chlorine radicals. The reaction between HO[•] and Cl[•] radicals with HA occurs at rate constants of 2.5×10^4 and 1.3×10^4 (mg C/L)⁻¹ s⁻¹, respectively (Fang *et al.* 2014). Therefore, HA can significantly affect DB71 degradation through the competition with DB71 for the reaction with HO[•] and Cl[•] radicals.

3.6. Effect of transition metals on DB71 degradation

Transition metals have been extensively employed in UV/oxidant-based systems for pollutant degradation. In the chlorine/Fe(II) process, HOCl reacts with ferrous ions, and as a result, hydroxyl and chlorine radicals are produced (Equations (20) and (21)) (Zohra Meghlaoui *et al.* 2019).



Compared to other UV/oxidant systems, photo-Fenton-like processes have shown superior effectiveness in removing contaminants. In these processes, the Fe-complex decomposes into •OH and ferrous ions (Equation (22)) (Liu *et al.* 2018). The limitation in the rate of ferrous ion regeneration in Fenton-based processes is successfully overcome by UV irradiation. This results in the rapid conversion of Fe³⁺ to ferrous ions and the simultaneous generation of HO[•] (Equation (23)) (Khavari Kashani *et al.* 2023).



Similar to ferrous ions, copper ions can also catalyze HOCl to produce hydroxyl and chlorine radicals in the UV/Cl₂ process. It should be noted that in contrast with Fe²⁺, Cu²⁺ is at a higher state (Cu(II)/Cu(I)), hence, there is likely a mediated reaction prior to the formation of Cl[•] and HO[•] in Equations (20) and (21). In fact, first, Cu²⁺ is reduced into Cu⁺ and then hypochlorous acid is broken down into hydroxyl and chlorine radicals. Based on the Fenton chemistry, the formation of speculative reactions is probable in the chlorine/Cu(II) process

according to the following equations.



According to Figure 6(a), PI can also be activated with ferrous and copper ions, considering that the DB71 degradation rate using the UV/PI process was slightly improved in the presence of these transition metals. The following equations present the reactions between PI and the aforementioned ions, resulting in the formation of IO_3^\bullet and IO_4^\bullet radicals.

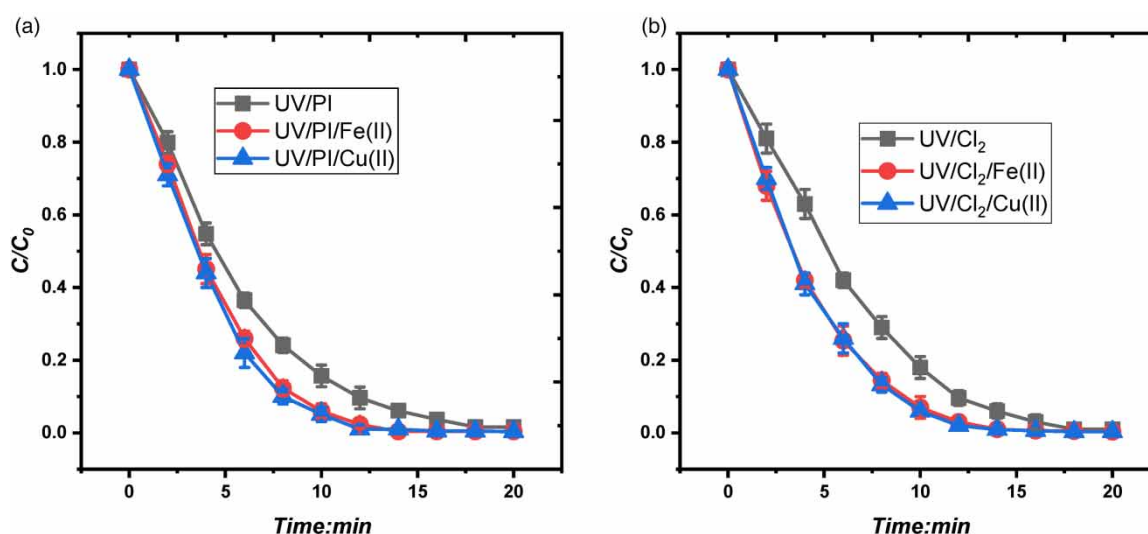


Figure 6 | The effect of transition metals on DB71 degradation using (a) UV/PI and (b) UV/Cl₂ (Cu(II) = Fe(II) = 0.5 mM, PI = Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).



As can be seen in Figure 6(b), a slight enhancement was observed in the degradation rate of DB71 using UV/Cl₂ process when Fe²⁺ and Cu²⁺ were added to the solution, due to the generation of oxidative radicals.

Moreover, UV irradiation plays a major role in DB71 degradation through not only ferrous ions regeneration (Equations (22) and (23)) but also the photolysis of HOCl (Equation (5)), OCl⁻ (Equation (6)) and PI (Equations (1) and (2)), which leads to the production of further reactive radicals.

Hence, the presence of transition metals has proven beneficial for DB71 degradation in the UV/Cl₂ and UV/PI processes.

3.7. Mineralization extent

Investigations were carried out to analyze the DB71 mineralization degree through the employment of UV/Cl₂ and UV/PI processes, and the results are depicted in Figure 7. Extensive research supports that a satisfactory level of mineralization can be accomplished by utilizing UV-based methods in combination with oxidants, thanks to the presence of UV irradiation (Li *et al.* 2016; Deng *et al.* 2019). It is apparent that around 39% of DB71 was mineralized within a 30-min reaction time using the UV/Cl₂ system. Conversely, the UV/PI system exhibited a higher degree of mineralization, reaching 48% within the same duration. Previous studies have indicated that hydroxyl radicals play a significant role in the mineralization of organic pollutants (Lin *et al.* 2016; Wu *et al.* 2016). Thus, the disparity in mineralization levels between the UV/PI and UV/Cl₂ systems can be explained

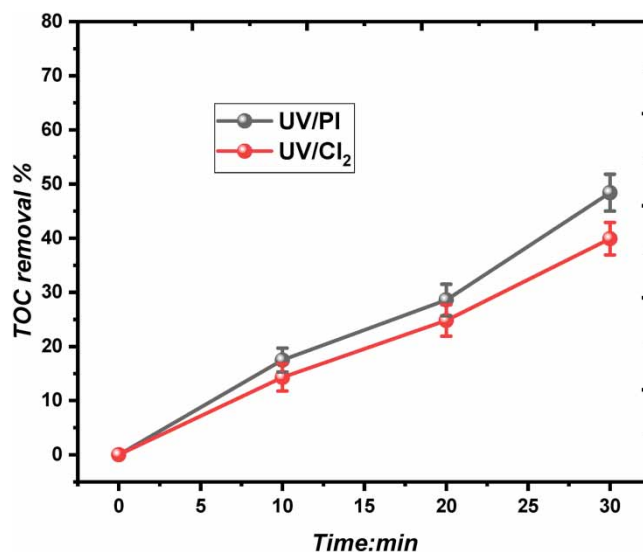


Figure 7 | TOC removal from DB71 solution by UV/PI and UV/Cl₂ (PI = Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).

by the greater contribution of hydroxyl radicals in the former process. It should be noted that the chlorinated substances generated in chlorine-based processes exhibited the highest resistance to mineralization (Huang *et al.* 2017). Consequently, a lower degree of mineralization should be expected from the UV/Cl₂ process compared to UV/PI. Additionally, the degradation of organic pollutants can be a challenging process, often involving the formation of various intermediates before the parent compound can be completely reduced to CO₂. Hence, the limited mineralization of DB71 can be attributed to the extended and intricate reactions involved in the complete removal of this compound.

3.8. Carboxylic acids evolution

Four carboxylic acids including oxalic acid, malic acid, formic acid and tartronic acid were monitored during DB71 degradation by UV/PI and UV/Cl₂ processes, in which these compounds correspond to the ring opening products of DB71 deriving from the attack of reactive radicals. The aryl groups of the aromatic dye are anticipated to undergo cleavage, resulting in the production of tartronic and malic acids (Diagne *et al.* 2007; Brillas *et al.* 2009). These acids, in turn, undergo separate transformations and are converted into oxalic and formic acids, respectively. Figure 8(a) and 8(b) depict the concentration of these carboxylic acids during DB71 degradation.

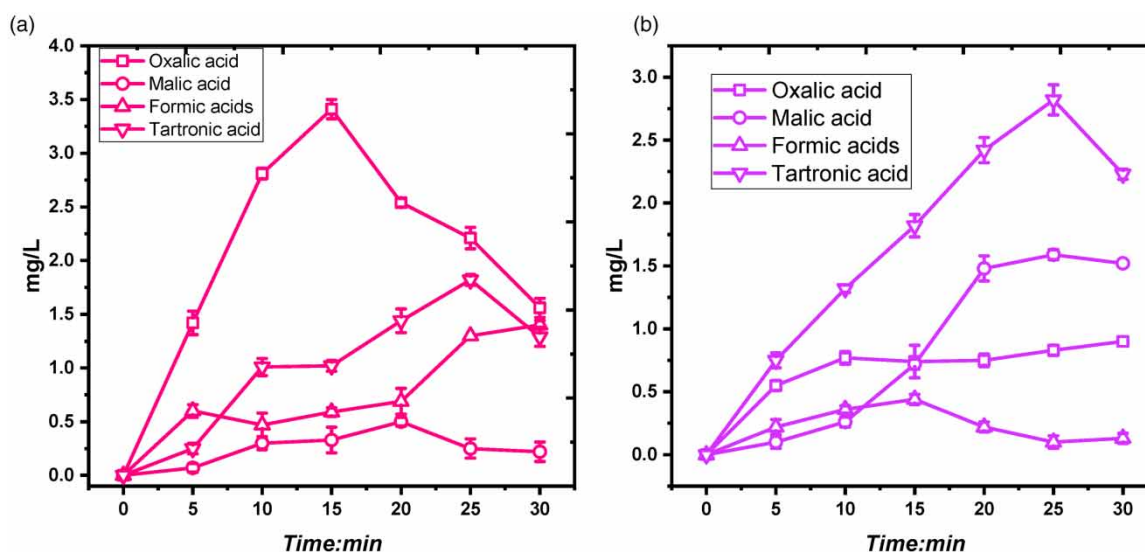


Figure 8 | Evolution of the concentration of the carboxylic acids within DB71 degradation: (a) UV/PI and (b) UV/Cl₂ (PI = Cl₂ = 0.75 mM, pH = 3 and DB71 = 20 mg/L).

The detected concentrations for UV/PI and UV/Cl₂ processes are as follows, respectively: Malic acid (0.3 and 1.6 mg/L), tartronic acid (1.2 and 2.3 mg/L), oxalic acid (1.5 and 0.8 mg/L) and formic acid (1.4 and 0.2 mg/L). First, considering the overall increase in concentration of oxalic acids over a 30-min reaction time, the successful oxidation of DB71 compound is vindicated by both processes utilized. Further, it is evident that the measured concentrations of malic and tartronic acids are higher in the UV/Cl₂ process compared to UV/PI, whereas the concentrations of oxalic and formic acids are higher in the UV/PI process. Note that the oxidation of malic and tartronic leads to the production of oxalic and formic acids, which are the final acids that undergo direct mineralization into CO₂ (Garcia-Segura *et al.* 2011). Therefore, considering that higher amounts of oxalic and formic acids are formed in the UV/PI process and the concentrations of malic and tartronic acids are considerably lower, it is more efficient in mineralizing DB71 than UV/Cl₂. These findings are in agreement with the results of Figure 7.

3.9. EE/O analysis

From an economic standpoint, this study compared the UV/PI and UV/Cl₂ processes employed for DB71 removal by assessing the expenses associated with the amount of electricity used. The electrical energy per order (EE/O) is a metric that quantifies the amount of electric energy, measured in kWh, needed to reduce the contaminant concentration by one order of magnitude in one cubic meter of effluent. This evaluation is performed using the following equation (Bolton *et al.* 2001).

$$\frac{EE}{O} = \frac{P.t.1,000}{V.\log\left(\frac{C_0}{C_t}\right)} \quad (29)$$

where P represents the total electrical power in kilowatts (kW) of UV lamps used, V indicates the volume in liters (L) of DB71 solution, t in hours (h) represents the reaction period, and C_0 and C_t , respectively, denote the initial and final measured DB71 concentrations. Figure 9 illustrates the EE/O values for the elimination of DB71. The results demonstrate significantly higher EE/O values for the mineralization of DB71 (34.74 and 63.42 kWhm⁻³order⁻¹) in comparison to its removal (1.67 and 11.97 kWhm⁻³order⁻¹) when utilizing the UV/PI and UV/Cl₂ systems, respectively. Based on the findings, the UV/PI method proves to be a more cost-efficient approach for degrading DB71. This suggests that a more favorable outcome can be attained while utilizing fewer resources. Furthermore, the UV/Cl₂ method requires a higher energy input compared to UV/PI when it comes to mineralizing DB71. This is likely due to the potential formation of more complex by-products that present greater challenges in the oxidation process.

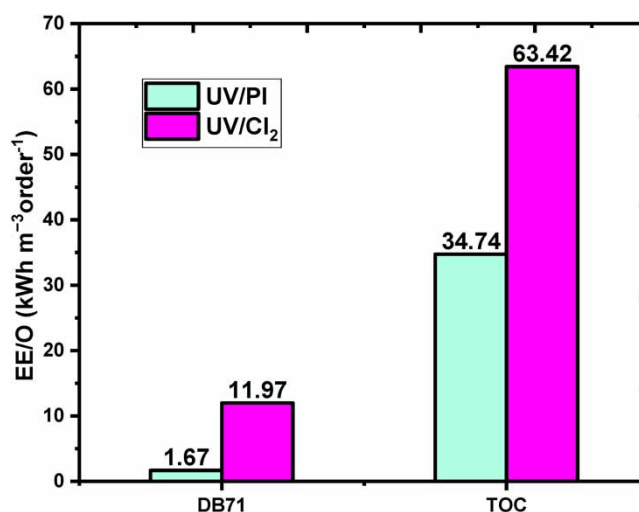


Figure 9 | EE/O for UV/PI and UV/Cl₂ for the removal of DB71 and TOC.

3.10. Application for real matrix

AOPs are usually under the influence of real conditions in which several anions, cations and organic compounds can compete with the reactive species for the reaction with the target pollutant. In this way, UV/PI and UV/Cl₂

were tested on a real textile wastewater and the results are presented in Figure 10. Compared to synthetic solution, a long reaction time is needed to decolorize the wastewater in a way that 78 and 64.8% of color were removed by UV/PI and UV/Cl₂ systems during 30 min reaction time, respectively. At the same time, 38 and 22.1% of TOC were also eliminated by UV/PI and UV/Cl₂ systems, respectively. The results showed that PI was more effective than chlorine in the generation of reactive species to destroy organic pollutants. In comparison with synthetic solution, UV/PI and UV/Cl₂ had lower efficiency. It can be attributed to several factors. First, the natural pH of the real wastewater is close to neutral conditions in which the power of hydroxyl radicals is reduced. Second, the presence of various anions and cations (TDS = 560 mg/L) can affect the free radicals and oxidants (IO₄⁻ and HOCl) and reduce the degradation rate of organic compounds. Third, colloidal solids can absorb UV irradiation and reduce PI or Cl₂ activation. Nevertheless, some strategies should be considered in real wastewater treatment like the use of pre-treatment and increase of oxidant dosage to obtain an acceptable result.

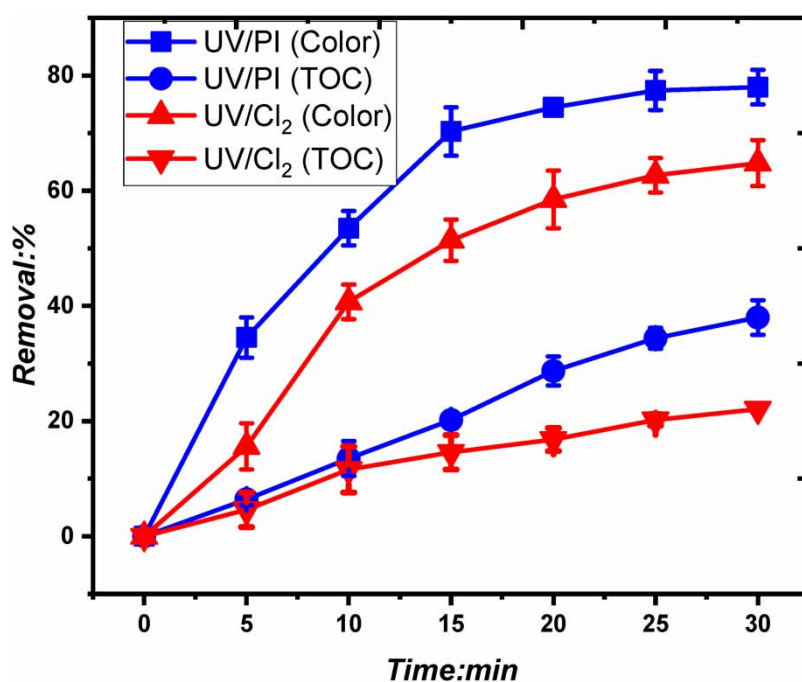


Figure 10 | The performance of UV/PI and UV/Cl₂ on TOC and color removals from real wastewater (PI = Cl₂ = 2 mM and pH = 6.9).

3.11. Comparison with other advanced processes

There are several processes for the removal/degradation of DB71 in the literature. In this way, current work was compared to advanced processes and the advantages and disadvantages of processes were explained (Table 2). Electro-coagulation-flotation (ECF) exhibited a high efficiency for DB71 removal under mild conditions. Although ECF is an effective method for the removal of organic pollutants, the generation of sludge is the most important challenge for this work (Ahangarnokolaei *et al.* 2021). The same problem was also observed in Fenton oxidation where both oxidation and coagulation occurred simultaneously (Ertugay & Acar 2017). H₂O₂/Zero Valent Iron (ZVI) as Fenton-like the process could remove DB71 effectively and it has lower sludge compared to classic Fenton. However, homogenous Fenton oxidation suffers from the operation under acid conditions (Ertugay & Acar 2022). US/H₂O₂ degraded only ~65% of DB71 during 20 min sonolysis time. In spite of low performance, the application of US-based processes on a large scale is difficult and costly. Anodic oxidation (AO) is a promising process for the degradation of organic pollutants in which reactive species are generated through water discharge. Hence, it reduces the cost of chemical oxidants. However, AO needed a longer time (120 min) for the oxidation of DB71, it increased the electrical energy consumption consequently (Xu *et al.* 2022). The photocatalysis process is probably the most popular AOP among advanced processes in which it can be operated by solar irradiation. However, escaping and the deactivation of nanoparticles during the operation are problematic issues. In this way, ZrO₂/persulfate/UV could completely remove DB71 under 40 min

Table 2 | Comparison of advanced processes for DB71 removal

Treatment method	Experimental conditions	DB71 (mg/L)	Removal efficiency (%)	Ref.
ECF	Electrical conductivity = 6.7 mS/cm, current = 0.6 A, pH = 8 and time = 40 min	200	99	Ahangarnokolaei <i>et al.</i> (2021)
Fenton	pH = 3, Fe(II) = 3 mg/L, H ₂ O ₂ = 125 mg/L and time = 20 min	100	94	Ertugay & Acar (2017)
AO(boron-doped diamond anode)	Na ₂ SO ₄ = 2 mM, flow rate = 600 mL/min, current density = 7.75 mA/cm ² and time = 120 min	50	100	Xu <i>et al.</i> (2022)
ZrO ₂ /Persulfate/UV	pH = 7, ZrO ₂ = 0.4 g/L, persulfate = 0.75 mM and time = 40 min	50	100	Moradi <i>et al.</i> (2016)
ZVI/H ₂ O ₂	pH = 2.5, ZVI = 0.2 g/L, H ₂ O ₂ = 100 mg/L and time = 20 min	100	100	Ertugay & Acar (2022)
BWO/g-C ₃ N ₄ /visible light	BWO/g-C ₃ N ₄ = 1 g/L and time = 50 min	10	78	Shende <i>et al.</i> (2019)
H ₂ O ₂ /Ultrasound	pH = 2.5, H ₂ O ₂ = 74 mg/L, US power = 95W and time = 20 min	50	64.1	Ertugay & Acar (2013)
UV/Cl ₂	pH = 3, Cl ₂ = 0.75 mM and time = 12 min	20	100	This work
UV/PI	pH = 3, PI = 0.75 mM and time = 12 min	20	100	This work

irradiation. On the other hand, 78% of DB71 was eliminated using BWO/g-C₃N₄/visible light during 50 min reaction time. Compared to other works, the current work was an effective process in at short time (12 min) indicating that the DB71 degradation rate is very high by UV/Cl₂ and UV/PI processes. However, there are some issues with these processes. First, the possibility of the halogenation of organic compounds during oxidation of the dyes produces persistent organic compounds as by-products. Second, residual iodates in PI/UV may affect the effluent quality. Third, UV-based processes need a pre-treatment for the removal of suspended solids since they can absorb light and reduce activation of Cl₂ and PI. In general, all processes have some disadvantages, it is important that they are applied in a suitable position and time and employed for the proper quality of the effluent. PI-based AOPs are promising processes and there are several unknown aspects for scientists to conduct further studies especially their application on real wastewater, the toxicity of the effluent and the use of other enhanced methods for the activation of PI. Moreover, further basic research should be studied on the interaction of PI and its related radicals with water constituents like anions, cations and organic compounds.

4. CONCLUSION

Complete degradation of DB71 was achieved within a 12-min timeframe at pH 3 and a concentration of 0.75 mM of oxidant (PI and Cl₂). The primary oxidation agents responsible for the elimination of DB71 in the UV/PI process were identified as HO[•] and IO₃[•], RCS were recognized as primary reactive radicals in the UV/Cl₂ process. The presence of transition metals contributed to an increased rate of dye removal by enhancing the activation of PI and Cl₂. These processes demonstrated high efficiency in the presence of various anions, except for bicarbonate ions. However, the presence of HA hindered the degradation rate as it competed with the target contaminant for reactive radical reactions. The PI-based process proved to be a more cost-effective route for DB71 removal compared to the chlorine-based process. Further, the evolution of carboxylic acids showed that higher amounts of oxalic and formic acids are formed in the UV/PI process and the concentrations of malic and tartronic acids are considerably lower, indicating that UV/PI is more effective in the mineralization of DB71. PI/UV exhibited an acceptable result for real wastewater treatment in terms of decolorization. However, its application of new oxidants such as PI should be carefully conducted on a large scale for actual wastewater due to unknown effects of by-products and residual PI.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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