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Sulfite excitation by photolysis to produce reducing species for 4-chloro-2-methylphenoxyacetic acid photo-reduction

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Abstract:
The photo-reduction of MCPA by UV/Sulfite reduction process is the subject of this study. The optimal pH was (MCPA: Sulfite molar ratio of 3:1 and pH 11) after 20 min reaction time. The Impact of In UV/Sulfite process, the pseudo-first-order reaction constant decreases as concentration rises from 50 to 200 mg L\textsuperscript{-1}, $K_{\text{obs}}$ and $r_{\text{obs}}$ decreased and reached from 0.299 to 0.029 min\textsuperscript{-1} and 14.95 to 5.80 mg L\textsuperscript{-1} respectively. Also, the analysis of energy consumption using the kinetic model and IUPAC shows that with the increase in the concentration of MCPA from 50 to 200 mg L\textsuperscript{-1}, the amount of $E_{\text{EO}}$ from 0.821 to 6.54 kwh.m\textsuperscript{-3} in the kinetic model and from 0.91 increases to 6.29 kwh.m\textsuperscript{-3} in the IUPAC model. In the decomposition of MCPA such as 2-prop-1-en-1-yloxyacetic acid (C\textsubscript{5}H\textsubscript{8}O\textsubscript{3}) and 1-ethoxyprop-1-ene (C\textsubscript{5}H\textsubscript{10}O) and hexa-1,3,5 -triene (C\textsubscript{6}H\textsubscript{8}), converted. These simple compounds have a high potential to become water and carbon dioxide. The improvement of biodegradability was investigated at 30 min reaction time and the amount of photo-reduction of MCPA, COD and TOC were 100%, 35% and 24%, respectively. In order to evaluate the toxicity of UV/Sulfite process effluent, the acute toxicity test by Kirby-Bauer disc was used, results showed that the zone of inhibition surrounding the disk reduced from 31 mm (without treatment) to 5 mm after treatment. As a Conclusion Sulfite/UV process had a good performance in converting toxic materials into degradable organic materials and the effluent toxicity to the environment was very low.

Keywords: Iodide; Photo- reductive; IUPAC; Toxicology; Biological treatment
Introduction:

4-chloro-2-methylphenoxyacetic acid (MCPA) is a herbicide belonging to the chlorophenoxy acid group, which is widely used in agricultural lands to increase crop production and generally to control all kinds of weeds. MCPA is relatively toxic to mammals, aquatic organisms and is less toxic to birds. Also, this herbicide is harmful to the eyes, skin, and respiratory tract, and consumption of high concentrations causes abdominal pain, bleeding, blood pressure, hepatotoxicity, tachycardia, and kidney dysfunction. The MCPA is in category 2 of the World Health Organization (WHO) and is considered a relatively dangerous poison. World Health Organization set standard for the amount of this herbicide in drinking water is 0.1 μg L$^{-1}$ and the standard of the Environmental Protection Agency is equal to 9 x 10$^{-6}$ mg L$^{-1}$. Adsorption, filtration, membrane separation, biological photo-reduction, and chemical coagulation processes lead to incomplete pollutant removal and only transfer the pollutant from one phase to another and produce secondary toxic pollutants.

Advanced oxidation and reduction reactions are suitable methods for complete removal of pollutants and improve treatment processes. Some mineral anions, such as iodide, sulfite, and carboxylate, produce electrons and reducing species when stimulated by a UV activator. Sulfite is a reductant for use in advanced reduction processes. The term "sulfite" is used to describe a group consisting of sulfuric acid (H$_2$SO$_3$), bisulfite (HSO$_3^-$), and sulfite (SO$_3^{2-}$).

The UV absorption spectrum (ε$_i$) of sulfite at neutral pH, ε$_i$ was 220 M$^{-1}$ cm$^{-1}$ and the e$_{aq}^{-}$ production per photon was 0.286 mol E$^{-1}$ at 253.7 nm wavelength. According to Eq (1-4), sulfite produces electrons and reducing species:

\[
\begin{align*}
\text{(1)} & \quad \text{SO}_3^{2-} + h\nu \rightarrow \text{SO}_3^{-} + e_{aq}^{-} \\
\text{(2)} & \quad \text{SO}_3^{2-} + e_{aq}^{-} \rightarrow \text{H}^+ + \text{SO}_3^{-} \\
\text{(3)} & \quad \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + e_{aq}^{-} \\
\text{(4)} & \quad \text{H}^+ + e_{aq}^{-} \rightarrow \text{H}^+ 
\end{align*}
\]

The hydrated electron e$_{aq}^{-}$ can be used as a very strong reducing agent (with a reduction potential of -2.9 volts). Hydrogen radical (H$^+$) also has a high standard reduction potential (-
2.3 volts). The advantages of using sulfite anion as an advanced regeneration method are high ability to produce reactive species, cheapness, non-toxicity. The aim of this study is to improve the biodegradability of MCPA with an advanced reduction method, and then use the biological treatment process to mineralize intermediate compounds. The main objectives of this study are (1) to investigate the influence parameters in the photo-reduction (2) to investigate the reaction kinetics (3) to identify and determine the intermediate products of MCPA in UV/Sulfite wastewater and the possible reaction pathway (4) to measure the toxicity of UV/Sulfite ARP wastewater by diffusion test Disk (5) to investigate the improvement of biodegradability.

Martials and methods

Chemicals

Analytical grade 4-chloro-2-methylphenoxyacetic acid herbicide (C₉H₅ClO₃, 98%), Sodium sulfite (Na₂SO₃, ≥99%), Sulfuric Acid (H₂SO₄, >99.8%), sodium hydroxide (NaOH, >97%), Sodium nitrate (NaNO₃, 99%), sodium chloride (NaCl, 98%), Sodium bicarbonate (NaHCO₃, 98%), Potassium sulfate (K₂SO₄, 99%), Potassium dihydrogen phosphate (KH₂PO₄, 98%), were supplied from the Merk Company. Methanol HPLC Grade (CH₃OH, >99.8%), Acetonitrile HPLC Grade (CH₃CN, >99.8%), were prepared from the Samchun Company.

Reactor configuration

The laboratory-scale pilot used in this study consisted of an ultraviolet lamp (power:16 W, ʎₘₐₓ = 254 nm) coated with a quartz sleeve with high transmission and excellent purity and fixed in the center of a glass cylinder. The contaminants
were located between the quartz sleeve and the glass cylinder as the reaction space. Water was constantly circulated around the cylinder to keep steady temperature on the reaction. Fig 1 is a view of the pilot used:

Fig 1. Schematic of photo-reduction reactor

Analytical methods

In examination, a stock arrangement of MCPA at 1000 mg L\(^{-1}\) was ready. The factors and their comparing ranges were as per the following: Molar ratio of sulfite: MCPA (1:3 -1:2 -1:1 - 2:1 - 3:1), pH (3 to 11) and MCPA concentration (5 to 25 mg L\(^{-1}\)). Diluted H\(_2\)SO\(_4\), NaOH solutions were utilized to change the pH of the solutions. A CECILCE-4100 HPLC with UV detector (CE-4900) and C18 column (250 mm × 4.6 mm × 5 µm) was used to quantify MCPA concentration. For for MCPA acetonitrile: acidic water (acetic acid 0.1 wt.%) (50:50, v/v) at 280 nm at a flow rate of 1.0 mL/min.

The MCPA removal was calculated from the following equation:

\[
\text{MCPA removal} = \frac{C_0 - C_t}{C_0}
\]  

Kinetic model and energy consumption estimate

According to Equations 6-7, the Pseudo-first-order (PFO) model was used to estimate of the kinetic model.
\[ \ln \frac{C_t}{C_0} = -K_{obs} t \]  \hspace{1cm} (6)

\[ r_{obs} = -k_{obs} C \]  \hspace{1cm} (7)

The International Union of Pure and Applied Chemistry (IUPAC) has introduced the \( E_{EO} \) parameter (Electrical Energy pet order 20,21).

\[ IUPAC \ E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log \frac{C_i}{C_f}} \]  \hspace{1cm} (8)

By planting the kinetic model in the energy consumption equation, energy consumption can be evaluated by the \( E_{EO} \) kinetic method. 9,22.

\[ Kinetic \ E_{EOk} = \frac{P \times 38.4}{V \times K_{obs}} \]  \hspace{1cm} (9)

**Determination some of intermediates product formed in optimal conditions using GC-MS device**

In order to determine the intermediate substances formed in optimal conditions using a GC-MS device. In the UV/\( SO_3^2- \) process was sampled, then the samples were analyzed to determine the intermediate substances formed in optimal conditions using a gas chromatograph mass spectrometry (GC-MS) detector with HP-5 column, i.d. = 0.12 mm, length = 25 m and measured, and finally the side products were determined according to the encyclopedia of the device(Agilent Technologies 7890a).

**Investigating the improvement of biodegradability and mineralization**

TOC analysis (Multi N/C 3100) were used to determine the degree of mineralization. Also, Sampling was done to determine the amount of COD in optimal conditions. Then, the COD in the wastewater was measured by Closed Reflux, calorimetric method based on No. 5220C presented in book of standard methods 23.
Toxicity test

The antibacterial activity of the effluent produced in the photo-reduction process and the intermediate products formed were evaluated using the Kirby & Bauer method according to CLSI guidelines. To identify the microbial inhibition of wastewater and intermediate products, the diameter of marginated circle of bacterial growth around the disk was measured at the beginning of the process and at the optimal point of the photoreduction process.

Results and discussion

Impact of pH on MCPA photo-reduction

Figure 1 shows the impact of pH on the MCPA photo-reduction using the UV/SO$_3^-$ process in the pH range, 3 to 11, Molar ratio of sulfite: MCPA 1: 1. Changes in the pH of the solution cause a significant increase in the photo-reduction rate of MCPA pollutant. At a reaction time of 20 minutes, the MCPA photo-reduction in 20 minutes increased with increasing pH, and at pH 11 no amount of MCPA was detected. At pH 3.0, after 20 minutes, the minimum photo-reduction occurred under acidic conditions about 20.68%. However, the removal efficiency of MCPA in neutral and alkaline pH conditions was higher than the acidic pH, so the highest and lowest removal efficiencies were observed at pH 11 and 3. In general, higher removal efficiencies were obtained for both contaminants in alkaline and neutral conditions than in the acidic state. The reason for the high removal efficiency of MCPA at alkaline pH can be stated that the production of hydrated electrons (e$_{aq}^-$) as the strongest reducing agent (E = -2.9 V) of the UV/sulfite process compared to the solution pH is very is sensitive. Under acidic conditions, e$_{aq}^-$ reacts rapidly with a proton to form a radical H$^+$ (Equation 10). On the other hand, sulfite has a good efficiency for producing of reactive species (e$_{aq}^-$, H$^+$ and SO$_3^{2-}$) at higher pH and also the quantum efficiency of hydrated electrons under alkaline conditions with radical
reaction of hydrogen $H^-$ and $OH^-$ increases greatly. However, at high pH (higher than 10), producing oxidizing radicals disrupts the process $^{18,25}$.

$$e_{aq}^- + H^+ \rightarrow H^+ \quad k = 2.3 \times 10^{10} \text{ M}^{-1}\text{S}^{-1} \quad (10)$$

$$H^+ + OH^- \rightarrow H_2O \quad k = 2.2 \times 10^{7} \text{ M}^{-1}\text{S}^{-1} \quad (11)$$

Sulfite species are relate of pH, and that’s including sulfuric acid ($H_2SO_3$), bisulfite ($HSO_3^-$) and sulfite ($SO_3^{2-}$) in solution $^{17,26}$. The results study of Tan et al. In 2021 showed that the rate of nitrate removal by UV/Sulfite process was clearly improved by increasing the pH from 1.5 to 9.2 and further increasing the pH from 9.2 to 11.1 led to a slight increase. By increasing the pH from 1.5 to 9.2, the amount of $r_{obs}$ increased from 0.0023 to 0.05 min$^{-1}$. They concluded that $e_{aq}^-$ are important role in the denitrification process under alkaline conditions. At pH 1.5, $HSO_3^-$ is the predominant component in solution and the contribution of $HSO_3^-$ to nitrate removal may not be considered due to poor UV absorption as well as low light activity. With increasing pH, the molar fraction of $SO_3^{2-}$ increased and at pH above 9 reached more than 98%, which led to the formation of more $e_{aq}^-$. As a result, it can greatly increase nitrate removal and prevent nitrite accumulation, thus accelerating the removal of dissolved nitrogen$^{27}$.
Fig 2. pH impact on MCPA photo-reduction by UV/Sulfite process

Molar ratio impact

As shown in Figure 3, the highest yield of 3:1 was obtained at about 100% at the MCPA:Sulfite molar ratio of 3:1 and after 30 minutes. The increase in efficiency strongly depends on the ratio of linkages the target compound and depends bands on pollutant structure. A MCPA:Sulfite molar ratio 3:1 was chosen as the best molar ratio. In 2015, Butlagodoro et al. showed that neutral and alkaline pH yield better results for the advanced UV/Sulfite reduction process than acidic pH. They stated that pH affects the relative concentrations of sulfuric acid \((H_2SO_3)\), bisulfite \((HSO_3^-)\) and sulfite \((SO_3^{2-})\) in solution, and in acidic conditions, bisulfite predominates, and at higher pH, sulfite is the main species. Rasulundi et al. showed that dexamethasone phosphate removal by UV/sulfite ARP was highest at pH 9.0.
Impact of UV lamp intensity on photo-reduction of MCPA by UV/Sulfite ARP

UV lamp intensity impact was investigated in ideal condition and is shown in Figure 4. When lamp intensity increased from 2 to 4 mWcm$^{-2}$ (6 to 11 W), the photo-reduction rate of MCPA increased from 63.21 to 100%. Also, when UV lamp was used alone MCPA photo-reduction increased from 41.26 to 76.44% respectively. Sun et al. reported that in the photo-reduction of N-nitrosodimethylamine by a 9 W lamp at pH 8 in 10 minutes, the photo-reduction efficiency reached 99.2% $^{29}$. Rasulundi et al. reported that 100% efficiency was reached in dexamethasone phosphate decomposition under optimal conditions and with an 11-watt lamp $^{20}$. In studies by Yazdanbakhsh et al. In 2018, by increasing the sulfite dose further, they prevented the rate of photo-reduction, citing the impact of reduction and radical inhibitors $^{30}$.
MCPA concentration impact, kinetics and energy consumption

MCPA initial concentration impact in range of 50 to 200 mg L$^{-1}$ and in time range of 0 to 30 minutes investigated and the results are presented in Table 1 and Figure 5. As the concentration increased from 50 to 200 mg L$^{-1}$ after 30 minutes of reaction time, MCPA photo-reduction decreased from 100 to 70.47%.
Fig 5. MCPA concentration impact on photo-reduction by UV/Sulfite ARP

the reaction kinetics were investigated and the constant ($K_{obs}$) of the reaction, reaction rate ($r_{obs}$) and the values of R2 are given in the table 1. The analysis of the obtained data shows that by increasing the concentration from 50 to 200 mg L$^{-1}$, $K_{obs}$ and $r_{obs}$ decreased and reached from 0.299 to 0.029 min$^{-1}$ and 14.95 to 5.80 mg L$^{-1}$ respectively. Also, the analysis of energy consumption using the kinetic model and IUPAC shows that with the increase in the concentration of MCPA from 50 to 200 mg L$^{-1}$, the amount of $E_{EO}$ from 0.821 to 6.54 kwh.m$^{-3}$ in the kinetic model and from 0.91 increases to 6.29 kwh.m$^{-3}$ in the IUPAC model. In the study of Azarpira et al., in the removal of diazinon (DIZ) by an advanced method of UV/Iodide reduction, the $k_{obs}$ increased from 0.065 to 0.137 min$^{-1}$. Also, with the increase of DIZ concentration from 5 to 15 mg L$^{-1}$, the $r_{obs}$ increased from 0.324 to 2.06 min$^{-1}$ and the energy consumption decreased from 8.61 to 5.37 kWh.m$^{-3}$. In 2022, Karimi et al., in the study of two-step removal of arsenic by advanced UV/Sulfite reduction process and adsorption on MnO$_2$, concluded that the removal follows the pseudo-first-order kinetic model and with increasing arsenic concentration from 50 to 250 The mg L$^{-1}$, $k_{obs}$ increased from 0.07 to 0.12
min\(^{-1}\) and the reaction rate \((r_{obs})\) increased from 3.74 to 24.36 mg L\(^{-1}\) min\(^{-1}\). Also, the energy consumption decreased from 15.23 to 5.37 kwh.m\(^{-3}\).

Table 1. Kinetic and energy consumption at different MCPA concentration

<table>
<thead>
<tr>
<th>MCPA (mg L(^{-1}))</th>
<th>(R^2)</th>
<th>(K_{obs}) (min(^{-1}))</th>
<th>(r_{obs}) (mg/L.min)</th>
<th>Kinetic (E_{EO}(\text{kwh/m}^3))</th>
<th>figure-of-merit (E_{EO}(\text{kwh/m}^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.99</td>
<td>0.299</td>
<td>14.95</td>
<td>0.821</td>
<td>0.91</td>
</tr>
<tr>
<td>100</td>
<td>0.978</td>
<td>0.108</td>
<td>10.80</td>
<td>2.60</td>
<td>2.42</td>
</tr>
<tr>
<td>150</td>
<td>0.976</td>
<td>0.058</td>
<td>8.775</td>
<td>4.81</td>
<td>4.05</td>
</tr>
<tr>
<td>200</td>
<td>0.995</td>
<td>0.029</td>
<td>5.80</td>
<td>6.54</td>
<td>6.29</td>
</tr>
</tbody>
</table>

The Impact of interfering anions

Real and syntactic waters was applied to better understand of unions impact in the efficiency of the UV/SO\(_3\)\(^{2-}\) process on photo-reduction of MCPA, phosphate, sulfate, bicarbonate, chloride and nitrate (concentration 1 and 5 mM) was investigated. The efficiency of UV/SO\(_3\)\(^{2-}\) advanced reduction process in pollutant photo-reduction was almost 100% in optimal conditions. the results in Fig 6 demonstrates that the investigated anions have the photo-reduction performance in the presence of nitrate, bicarbonate, sulfate, chloride was reduced to the 28.92 %, 23.58 %, 20.30 % and 17.92 %, respectively. With the addition of more ions, the process of photo-reduction efficiency slowly weakens, so it can be concluded that additional anions have inhibitory effect on pollutant photo-reduction. The reaction of anions and reactive species that produces weaker species and also the absorption of UV rays reduces the efficiency\(^{33,34}\). Possible reactions between anions and \(e_{aq}^-\) are as follows:

\[
\text{HCO}_3^- + e_{aq}^- \rightarrow \text{HCO}_3^{2-} \]  \hspace{1cm} (17)

\[
\text{Cl}^- + e_{aq}^- + \text{H}^+ \rightarrow \text{HCl} \]  \hspace{1cm} (18)

\[
\text{NO}_3^- + e_{aq}^- \rightarrow \text{NO}_3^{2-} \]  \hspace{1cm} (19)

\[
\text{SO}_4^{2-} + e_{aq}^- \rightarrow \text{SO}_4^{3-} \]  \hspace{1cm} (20)

\[
\text{PO}_4^{3-} + e_{aq}^- \rightarrow \text{PO}_4^{4-} \]  \hspace{1cm} (21)
The acid dissociation constant ($k_a$) may be the primary cause of most negative effect of nitrates.

Scavengers impact of reducing and oxidizing species

By sealing the species reducing carbon disulfide and carbon tetrachloride, the effects of reducing agents were investigated. As reducing species scavengers, the addition of CCl$_4$ and CS$_2$ inhibits photo-reduction efficiency by 61.19% and 59.79% respectively, as shown in Fig. 7. As a result, decreasing species are crucial to the photo-reduction of MCPA. Tert-butyl alcohol (an oxidative species scavenger) was also added to the reaction medium to identify the potential impact of oxidizing species, which decreased the yield by up to 6%. This implies that photocatalytic reduction is the reaction's mechanism.
According to the findings of Azizi et al. in codeine phosphate removal by UV/Iodide/ZnO, the photo-reduction efficiency decreased from 100% to 65.5% and 77% when CS₂ and CCl₄ were added.  

Intermediate products and photo-reduction pathways MCPA

The possible pathways and modifications to the MCPA bands during its transformation into intermediate are depicted in Fig. 8. At first, chlorine is separated from the structure of MCPA. Then the remaining substance that has a benzene ring is broken. After that the benzene ring is converted into a linear compound by electron or UV rays. The formed linear compounds turn into simple compounds with lower molecular weight and higher biodegradability. In the decomposition of 4-chloro-2-methylphenoxyacetic acid such as 2-prop-1-en-1-yloxyacetic acid (C₅H₈O₃) and 1-ethoxyprop-1-ene (C₅H₁₀O) and hexa-1,3,5 -triene (C₆H₈), converted. These simple compounds have a high potential to become water and carbon dioxide.
Fig 8. Possible pathways and modifications to the MCPA bands during its transformation into intermediate

**Toxicology test**

Samples were taken at various periods to test the toxicity of the MCPA's UV/iodide process' treatment effluent (0 to 30 min). Escherichia coli sensitivity to MCPA and that's intermediate were evaluated using the Kirby-Bauer test, which was used to study to determine the sensitivity or resistance of Escherichia coli (E.coli). As shown in Fig. 9, the inhibition diameter when bacteria culture without treatment was 31 mm and reached to 5 mm of resistance isolates, which indicates a significant decrease in sensitivity or resistance of E.coli in treated effluents.
Fig 9. Result of toxicology test

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Data availability: All data generated or analyzed during this study are included in this article.

Declaration

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Consent of Participant Not applicable
Conflict of Interest: The authors declare that they have no conflict of interest

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