Evaluation of Removal Performance of Triamcinolone Acetate by Typical Water Treatment Agents

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Abstract. In this paper, the removal performance of Triamcinolone acetonide (TA) by ClO₂, NaClO, O₃, K₂FeO₄, and KMnO₄ oxidation was assessed. The effects of pH value and humic acid (HA) on TA removal during KMnO₄ oxidation process were also investigated. The results showed that ClO₂, NaClO, and O₃ were not sufficient for TA elimination. However, K₂FeO₄ can capable of removing TA effectively, and the removal rate of TA can be achieved 84.6% at 60 min while K₂FeO₄ dosing at 10 mg/L. However, the removal effect of TA in water was inhibited as the concentration of K₂FeO₄ overdosed. KMnO₄ can degradate TA effectivly. TA can be completely removed after 90 minutes while the initial concentration of TA is 250μg/L and the KMnO₄ dosage at 50mg/L.Weakly acidic and neutral conditions can promote TA removal, the effect of Humid acid (HA) on TA removal was based on the HA dosage, an inhibitory effect was obsearved when the dosage of HA from 1mg/L to 5mg /L, however when C_HA≥7mg/L, HA can accelerate TA removal.

1. Introduction
Triamcinolone acetonide (TA) is a typical type of PPCPs. It will pose a threat to the health of organisms when it accumulates in a certain amount in the water environment, such as malformation and carcinogenesis of reproductive organs[1]. Triamcinolone acetonide chemical formula is C₂₆H₃₃FO₇. Up to now, the removal control technology of PPCPs mainly includes photodegradation and advanced oxidation [2,3,4]. However, in domestic water treatment technology, there is no in-depth removal of TA technology. At present, ClO₂, NaClO, KMnO₄, K₂FeO₄ and O₃ are commonly used as water treatment agents. Therefore, it is neccessary to evaluated the removal performance of TA by typical water treatment agents in order to provide scientific basis for PPCPs controlment.

2. Materials and methods
2.1. Experimental reagents and instruments
TA (Toronto Research Chemicals, Canada, >95%). Acetonitrile (Merck, Germany, HPLC). Humic acid(Sigma-Aldrich, America, Tech, 10g). NaClO (Sinopharm Group, China, HPLC). HCl (Sinopharm Group, China, AR, 36%~38%). Na₂S₂O₃·5H₂O (Sinopharm Group, China, AR, ≥99.5%). NaOH (Tianjin komeio, China, AR, ≥96.0%). CH₃OH (Shanghai Ann spectrum, China, HPLC). KMnO₄ (Shantou West Long, China, ≥99.5%). K₂FeO₄ (Tianjin weiyi chemical co, China, 90%). The water used in the laboratory was Mili-Q Ultrapure water (≤18.2MΩ).
LC-20A high performance liquid chromatography (Shimadzu, Japan), Automatic sampler (SIL-20A), detector (SPD-M20A); pH meter (Eutech, America); HJ-6A magnetic constant temperature agitator (jiangsu jintan outstanding Instrument).

2.2. Experimental method
This experiment was carried out in a beaker with added magnetic stirring at room temperature, a certain amount of TA was dissolved with ultra-pure water as the stock solution. During the experiment, a certain amount of TA stock solution was diluted to 250µg/L, and a certain amount of oxidant reagents was added and then start the reaction. A series of 10 mL of samples were taken out periodically, and the residual oxidation agent was quenched immediately by excess sodium thiosulfate, the water sample was filtered through a 0.45µm glass fibre filter membrane and analyzed. Except for the experiment to investigate the influence of pH, the pH of all other experiments was stable at about 6.82.

2.3. Analysis method
HPLC conditions: Chromatographic column for Inertsil®C18 (4.6×250mm,5μm). The mobile phase consisted of acetonitrile and water (40:60) at a flow rate of 1.0 mL/min. The UV wavelengths for the measurement of TA were set at 278nm.

3. Results and analysis

3.1. TA remove by typical water treatment agents
The degradation of TA by ClO₂, NaClO and O₃ oxidation processes are shown in Figure 1.

![Figure 1](image)

**Figure 1.** TA removal by ClO₂, NaClO and O₃ ([C_TA]=220µg/L)

As shown in Figure 1, the removal rate of TA was less than 10% during ClO₂ oxidation for 30min, ClO₂ had no significant effect on the removal of TA. The reason may be attributed to that TA can degraded by ClO₂ at a slower rate. NaClO can degrade TA by 20.6% within 30 min. It was observed that the removal efficiency by NaClO was higher than that of ClO₂ during TA degradation process. The removal of TA by NaClO is mainly due to the oxidation of NaClO and the strong oxidation of O₃ which is generated from NaClO[5]. The results also showed that O₃ can degrade TA by 55.8% at 120s. It was observed that TA cannot completely removed.
3.2. TA remove by K$_2$FeO$_4$

The Effect of K$_2$FeO$_4$ dosages on TA removal are shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** Effect of K$_2$FeO$_4$ dosages on TA removal ([C$_{TA}$]$_0$=194µg/L)

As shown in Figure 2, the removal rate reached by 84.6%, 35.5%, and 22.8%, respectively, while the dosage of K$_2$FeO$_4$ ranged from 10 to 50 mg/L.

\[
\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O} \quad (1)
\]

\[
\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{Fe(OH)}_3 + 5\text{OH}^- \quad (2)
\]

K$_2$FeO$_4$ is not stable enough under acidic conditions, and can be easily decomposes. With the increase of K2FeO4 dosages, its stability decreases with the increase of concentration, and the self-decomposition ability is enhanced. The reaction equation is as follows: (1), (2). Thus, the increasing of K2FeO4 addition result in the decrease of TA removal.[6]

3.3. TA remove by KMnO$_4$

The degradation of TA by different dosages of KMnO$_4$ are shown in Figure 3.

![Figure 3](image_url)

**Figure 3.** Effect of KMnO$_4$ dosages on TA removal ([C$_{TA}$]$_0$=250µg/L)
As shown in Figure 3, KMnO₄ has an obvious effect on the removal of TA. When the addition of KMnO₄ was 50mg/L, the removal rate reached 78.8% at 60 min, and TA was completely removed at 90 min. When the dosage of KMnO₄ was increased to 70mg/L, the removal rate reached 100% at 60 min. TA was totally removed at 40 min when the dosage of KMnO₄ was 100mg/L.

Yongpeng XU et al. found that the main reason for the removal of PPCPs by KMnO₄ is that KMnO₄ molecules collide with the PPCPs molecules in the liquid, and then leading to oxidation reaction. In fact, increasing the concentration of KMnO₄ is to increases the number of molecules in the unit volume of the reaction, thus increasing the reaction rate[7].

3.4. Factors affecting removal of TA by KMnO₄

3.4.1. Effect of pH on removal of TA by KMnO₄ As shown in Figure 4, the removal rate for TA degradation in the pH range of 4.0 to 10.0 during KMnO₄ oxidation.

The acidity and alkalinity of the solution will change the redox potential of KMnO₄[8], so pH is an important factor that affecting the oxidation capacity of KMnO₄. As show in Figure 4, increasing pH can reduce the removal rate of TA. The TA removal rates reached 84.9% and 75.4% at 20 min, respectively, when pH was 4 and 5. TA removal rates at 20min were 72.3%, 69.3%, and 64.5% when at 8, 9 and 10, respectively.

![Figure 4. Effect of pH on TA removal ([C_TA]=250µg/L, [KMnO₄]=100mg/L)](image)

Studies have found that the standard redox potential of KMnO₄ in acidic solution is 1.5 ev[9], which higher than that of neutral solution and alkaline solution. As a result, the TA degradation efficiency was higher in acidic conditions. KMnO₄ reacts to produce MnO₂ under weak acidic and neutral conditions. MnO₂ possessd good catalytic and adsorptive properties[10], so KMnO₄ can still show better removal ability under weak acidic and neutral conditions. It is better for TA degradation during a weak acidic environment. TA degradation decreased as the alkalinity increases.

3.4.2. Effect of humic acid (HA) on removal of TA by KMnO₄ The presence of natural organic compounds in different water sources can affect the quality of drinking water. Therefore, Humic acid was used to simulate natural organic matter in actual water sources. The results were shown in the Figure 5.
As shown in Figure 5, when the dosage of HA from 1mg/L to 5mg/L, the removal rates reached 82.5%, 75.5% and 66.5% at 40 min, respectively. Increasing the dosage decreased the removal effect of TA. However, when the dosage of HA was increased to 7mg/L, HA had a significant effect on promoting TA degradation. The reason why the low concentration of HA reduces the degradation rate of TA may be that the minimum HA relative atomic mass is 1358, which is greater than the relative atomic mass of TA (476) [8]. Therefore, HA can preferentially react with KMnO4 and its intermediate product (MnO2). On the other hand, the reason may be that KMnO4 is oxidized into MnO2•2H2O during the reaction process, and its adsorbability increase as the HA dosages increase. A large amount of HA is adsorbed on the surface of the metal oxide, so that the pollutant cannot be transferred from the liquid phase to the solid phase [8]. TA has a large reaction surface in the liquid phase, thus promoting the oxidation of TA [6]. HA has a good removal effect on TA due to this characteristic.

4. Result

(1) ClO2, NaClO and O3 in typical water treatment agents can not eliminate TA in water effectivey.

(2) The removal effect of TA was decreased with the increase of the K2FeO4 dosage. KMnO4 has a good effect on TA removal. the removal rate of TA was increased with the increase of KMnO4 concentration , .

(3) The weakly acidic water environment is favourable for KMnO4 to remove TA. the removal rate of TA is weakened with the increase of pH value.

(4) HA can have significant effect on TA degradation in water by KMnO4. 1mg/L ≤ C_HA≤5mg/L inhibited the removal of TA from water by KMnO4, C_HA≥7mg/L can promote the removal of TA.

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