Overview of Ecological Toxicity of Potassium Chlorate Pollution

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Abstract Potassium chlorate ($KClO_3$), as regulation medicament for longan production period, has been widely used in industrial application and enters the global ecological and environmental system. Its strong oxidation leads to certain pollution to ecological environment. In recent years, researches about ecological toxicity of $KClO_3$ have realized considerable progress, so it is necessary to make proper summarization. This paper makes an overview of researches about ecological toxicity of $KClO_3$ to land plants, longan, aquatic organism, animals, and human beings. Finally, it comes up with recommendations and prospects including further studying precise detection and degradation technologies for strong oxidation ClO_3^- and its residue, strengthening biological monitoring and recovery technology of $KClO_3$, and implementing wide science popularization.

Key words $KClO_3$, Pollution, Ecological toxicity, Research prospects

1 Introduction

In 1998, Taiwan horticulture scholars occasionally derived inspiration from promoting burning firecrackers nearby longan trees to bloom and successfully took $KClO_3$ as plant growth regulator for longan. Later, in longan production areas, such as Fujian, Guangxi, Guangdong, and Hainan in China and Thailand, similar researches and technical extension have been carried out, and chemical regulation of $KClO_3$ to longan production period gets constantly mature and widely applied[1-2]. Researches of Manochai *et al.*[3] indicate that $KClO_3$ can promote longan to realize year-round production and multiple planting of three crops two years. Besides, Subhadrabandhu *et al.*[4] found that $KClO_3$ also promotes flowering and fruit bearing for tropical fruit trees such as litchi and mango apart from exerting regulation effect on the longan production period. With extension of technology of $KClO_3$ in regulating longan flowering period, secondary pollution of ClO_3^- toxicity and its residue exerts adverse impact on agricultural ecological environment. This receives wide and wide concern. Combining current domestic and foreign researches about pollution of $KClO_3$ to ecological environment, we make overview of progress in researches about $KClO_3$ toxicity, to make clear environmental risk of $KClO_3$ and provide reference for $KClO_3$ application.

2 Overview of ecological toxicity of $KClO_3$ pollution

2.1 Effects of $KClO_3$ on land plants Strong oxidation of $KClO_3$ exerts significant toxic effect on plant growth. According to researches, except the moss, ClO_3^- is toxic to growth of green plants for 3 to 6 months. Its toxicity exerts excellent control effect on herbs such as *Pharbitis nil* (Linn.) Choisy, Canada thistle, and Sorghum halepense; it can remove leaves of cotton, maize, flax, and soybean; therefore, $KClO_3$ has been used as non-selective herbicide, defoliant, or even soil fungicide in the 1930s and 1940s[5]. It is reported that $KClO_3$ has obvious concentration gradient toxic effect on rice, wheat seedlings, tomato at normal temperature because after ClO_3^- enters into soil and gets absorbed by root system of plants to organs, its strong oxidization exerts direct toxic effect on plants[6]. Besides, accumulation of ClO_3^- and ClO_2^- within plant body will increase the content of catalase within plant body, leading to falling of leaves ahead of time and early aging of plants[7]. In addition, root system of plants does not have selection for absorption of ClO_3^- and NO_3^-, therefore, absorption of ClO_3^- will inhibit absorption and delivery of plant cells to NO_3^-, leading to lack of nitrogen and consequently influencing nutrition within plant and growth of plant[8-9].

2.2 Effects of $KClO_3$ on longan Taiwan scholar Yan Changrui[10] successfully promoting langan flowering using $KClO_3$. Later, the production period regulation technology realized breakthrough and rapid development, and Thailand, Malaysia, Guangdong, Fujian, and Guangxi carried out similar experiments, researches and extension[11-13]. At present, Thailand has realized annual batch production and export of off-season longan[14]. Chen Qingxi *et al*[15] studied off-season longan and found that after application of $KClO_3$, parent branches of longan trees have lower starch content, while total sugar, chlorophyll, endogenous ethylene, abscisic acid, trans – Zeatin – riboside, and catalase gradually increase in physiological differentiation period. However, residue of ClO_3^-, ClO_2^-, and ClO^- in longan leaves and fruit is lower than the detection limit obtained from ordinary ion chromatography, and there is no significant difference in corresponding quality indicators such as fruit color, size, and soluble solids between ordinary longan[13-14].

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2.3 Effects of $KClO_3$ on aquatic organisms DolfJVW *et al.*[16-17] found that the toxicity of $KClO_3$ on aquatic organisms is closely related with living species. The effects of $KClO_3$ on diversity of fishes and large invertebrate aquatic organisms are not high, the acute toxicity concentration is 2442 mg/L and 3815 mg/L respectively, but the effects on algae are greater, especially on brown alga. Generally, acute toxicity concentration of $KClO_3$ in sea water to brown alga is lower than 0.1 mg/L, EC50 is lower than 0.105 mg/L, and chronic toxicity concentration is lower than 0.005 mg/L. Also, experiment has proved that the toxic effect of $KClO_3$ on alga is restricted by NO_3^- in water, higher concentration NO_3^- will weaken the toxicity of $KClO_3$ to algae. Researches of Stauber. J. L[18] indicate that when KNO_3 concentration is lower than 0.005 mg/L, 72h EC_{50} of $KClO_3$ to Nitzschia and Dunaliella algae is 1.9 mg/L and 11 mg/L; in water with high concentration of NO_3^-, 72h EC_{50} of $KClO_3$ to Nitzschia and Dunaliella algae exceeds 500 mg/L and 1000 mg/L respectively; in the range of concentration of ClO_3^- inhibiting division of Nitzschia cell, it exerts no infuence on photosynthesis and ATP content.

2.4 Effects of $KClO_3$ on animals and human beings Since $KClO_3$ has the taste of salt, animals may take it as salt and get poisoned[18]; once polluted by $KClO_3$, green plants will be stained with salt taste, herbivore may eat and get poisoned[20-21]. Germgard U[22] found that after animal absorbs $KClO_3$, strong oxidization of ClO_3^- may lead to methemoglobinemia, hemolytic anemia, and kidney poisoning; if birds eat $KClO_3$ by mistake, it will reduce ability and quantity of egg production, but there is still no obvious toxic effect on bees; Wang Li *et al.*[23] found that 800 mg/L ClO_3^- water solution is negative on mouse bone-marrow micronucleus test, indicating that ClO_3^- does not have induction effect on mouse bone-marrow micronucleus in this range of concentration. The mechanism of $KClO_3$ toxicity to animals is that ClO_3^- damages their metabolism, leading to abnormal life activities. The lethal concentration (LC) of $KClO_3$ for dog is 1200 mg/L, for mouse, it is 1870 mg/L, and for rabbit, it is 2000 mg/L[24].

Phongtape *et al*[25] surveyed 40 fruit growers producing off-season longan in Lumphun Province of Thailand (57.5% are male and the average age is 47 years old), and found that in the process of applying $KClO_3$, 80.0% fruit growers do not wear gloves, 82.5% fruit growers do not wear mouth mask, and only 60.0% fruit growers wear long sleeve clothes, and daily average working hours are 2.3 hours. Before exposing to $KClO_3$, the average denatured hemoglobin of fruit growers is 1.16%; after exposing to $KClO_3$, the average denatured hemoglobin of fruit growers rises to 1.36%, and 20.0% fruit growers get methemoglobin, indicating $KClO_3$ will induce denature of hemoglobin. Therefore, without labor protection measures, fruit growers exposing to $KClO_3$ for a long time will have risk of getting methemoglobin. They also surveyed health condition of local workers engaged in off-season longan production and exposing to $KClO_3$ for a long time, and found that 64% workers process off-season longan in three steps, peeling, rinsing, and classification, the average daily working hours are up to 10.6 hours; 68% workers do not wear gloves during working, leading to 66% workers getting allergic skin, 35.2% workers getting methemoglobin, 31.2% getting anemia, 6.5% workers getting leukaemia. Also, they found 22.0% workers have hematuria, 20.5% workers have pyuria, and 7.5% workers have both hematuria and pyuria. No doubt, backward safety and protection measures pose great threat to longan production workers.

Therefore, to avoid poisoning and explosion of $KClO_3$, it is required to prevent animals and human beings from eating $KClO_3$ by mistake, strictly prohibit grazing in grassland with spraying of $KClO_3$, strictly separate foods and feeds, promptly clean vessels containing $KClO_3$, and strictly forbid pouring $KClO_3$ residue, and strictly prohibit storage of phosphorus, sulphur, carbon, organic matters, ammonium compound, cyanide, metal powders together with $KClO_3$. Government organs and legal institutions should formulate and improve relevant laws and regulations, to standardize production, storage, and use of $KClO_3$, implement excellent health and sanitation planning, and take effective labor protection measures, to protect health of relevant people exposing to or applying $KClO_3$ in actual work. At present, foreign scholars have carried out extensive researches on migration and conversion and ecological toxicity of ClO_2^- and ClO^- in water environment focusing on ClO_2 disinfection and bleaching agent. Animal toxicity experiment indicates that there is close relation between ClO_3^- and ClO_2^- in high level of in drinking water and anemia of animals, thus these two ions are suspected as factors inducing anemia. Both foreign and domestic scholars pay close attention to disinfection by-products (DBPs) ClO_2^- and ClO^-. In Sanitary Standard for Drinking Water Quality for Drinking Water issued by Ministry of Public Health of China in 2001, it specifies that the maximum mass concentration of ClO_2^- is 200 μg/L; in the latest *Guidelines for Drinking Water Quality* issued by the World Health Organization (WHO), it stipulates that the ClO_3^- concentration of should be as low as possible. Research data of American and Canadian environmental protection departments indicate that too high ClO_3^- concentration in drinking water or foods will damage thyroid gland and consequently influence normal secretion of hormone. Both ClO_3^- and ClO_2^- are included into list of preferred disinfectant and disinfection by-products of drinking water in Code of Federal Regulations, USEPA(2002), and the recommended total residue concentration of ClO_2, ClO_3^- and ClO_2^- should not exceed 10 mg/L. In the United States, due to emission of chlorate in military industry like fuel for rocket propulsion, pollution of ClO_3^- to underground water has greatly threatened health of surrounding residents. Government of California State reduces the standard of ClO_3^- in drinking water from 18 ppb to 4 ppb, but the Environmental Protection Agency detected local foods and found that the average content of ClO_3^- in milk and lettuce is up to 5.76 ppb, exceeding the specified 4 ppb; Food and Drug Administration (FDA) detected long-leaf lettuce and ice cream of California, Arizona, Florida, Texas and New Jersey states and found that the average content of ClO_3^- in these foods is as high as 10.49 ppb;

NAS reported that in 35 states of America, 93% lettuce and milk and 97% breast milk contain excessive ClO_3^-; according to estimation of EPA, drinking water of about 15 million people is influenced by ClO_3^- in the United States[26].

3 Research prospects

Each molecule of $KClO_3$ contains 3 oxygen atoms, and structure of ClO^{3-} is SP3 hybrid type, so $KClO_3$ has strong oxidation. With wide application of $KClO_3$ in industrial and agricultural production, secondary pollution resulted from its strong oxidation and residue will inevitably bring adverse effect on water and soil environment which are essential factor for human beings. Therefore, how to precisely detect and accelerate degradation of ClO^{3-} and its residue will become a leading direction of the research in this field. In the past, ecological toxicity researches of chlorate are restricted by detection technique and means[27]. Now, with improvement and application of Ion Chromatography (IC) and High Performance Liquid Chromatography (HPLC) and other techniques, detection means and methods of toxic substances gradually become mature. For example, the upper limit of detection for ClO^{3-} and ClO^{2-} in water by Ion Chromatography has reached 1.6 mg/L and 3.5 μg/L respectively[28]; Capillary Electrophoresis (CE) is also widely applied in detection of many types of anions including ClO^{3-}[29]. All of these provide assistance for in-depth study of ecological toxicity of chlorate. Besides, with the development of ecological toxicology, broad bean and mouse micronucleus detection methods have been widely applied in chlorate detection[1, 2, 15]. Strengthening the impact evaluation of environmental indication like earthworm and monitoring of soil pollution due to chlorate will be favorable for lifting chlorate monitoring and soil remediation to a new level. In sum, considering that the public are still not aware the ecological toxicity of chlorate, it is required to strengthen science popularization of chlorate, actively carry out pollution detection, and strengthen researches on control over pollution of chlorate to water and soil, so as to completely eliminate and solve the ecological and environmental problem resulted from $KClO_3$ and its residue.

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