THE ENVIRONMENTAL, HUMAN AND ANIMAL EFFECTS OF USING POTASSIUM BROMATE IN BREAD INDUSTRY AND CHEMICAL ANALYTICAL METHODS

Salem Irhema S. Irhema*[1], Salem M. El-Nakeib[2]

[1]*Environmental Sciences Department, Faculty of Sciences, University of Al-Zintan, Libya.*

[2]*Department of Chemistry, Faculty of Science, Al-Asmaryia Islamic University, Zliten, Libya.*

**Corresponding author: Email: s.irhema@uoz.edu.ly, salemerhima@yahoo.com*

ABSTRACT

Bread is a staple food for many nations globally. It is prepared by mixing wheat or barley flour with water and other additives. Potassium bromate ($KBrO_3$) is the most used additive in bread industry, because of its efficiency to make the bread cost-effective and favorable to consume. However, $KBrO_3$ is toxic to human and animals due to its ability to affect several body organs, e.g., liver, bones, blood, renal and hepatic, therefore $KBrO_3$ is classified as a carcinogenic chemical and banned for using in the bread industries in most countries. Even though, this material is still in use as bread improver in several countries, nevertheless several oxidising agents was suggested to use as replacements instead of $KBrO_3$ that doesn't have harmful effects to the consumers. Many technologies have been developed and applied to evaluate the residues of $KBrO_3$ in bakery products. This review paper explored the use of potassium bromate as a flour additive, and its effect on human, animal and environment, and the chemical methods to assess its remains in bread industries.

Keywords: Bread, Potassium bromate, Toxicity, Health.

1. INTRODUCTION

In most countries globally bread is a staple food in daily meals [1,2]. Bread contains high levels of nutrients including carbohydrate, fibre, vitamins, and several other minerals such as phosphorus (P), magnesium (Mg), potassium (K), calcium (Ca) and negligible concentrations of iodine (I), iron (Fe) and sodium (Na) [3-5]. Bread is made from barley or wheat flour mixed with water, yeast, salt and negligible amount of flour improvers. The presence of gluten in flour can improve the dough elasticity and ability to hold the produced gases can cause dough swelling which may improve the quality of bread. Before baking, the dough bread needs time for oxidation. The oxidation processes are responsible to obtain the preferable bread features [5,6]. In the past, the oxidation was done by exposing the bread dough to the air for days or weeks, however due to the increasing demand of bread and to produce in a short time, several oxidizing chemicals (e.g., Potassium bromate ($KBrO_3$) are used to reduce the oxidation period [4,7]. $KBrO_3$ was the main compound utilized as an oxidizing agent in making bread for several decades, because of its several features that make the bread desirable to consume such as softness and good appearance [8,9] and cost-effective material [10]. This compound is converted to KBr under superior baking conditions, which is nontoxic and safe. The breakdown phenomenon of $KBrO_3$ depends on the oven temperature, baking duration and quality of used $KBrO_3$ [7,11,12]. However, under a worst baking condition, $KBrO_3$ may not degraded completely as a result the produced loaf can be contain remains of this material which will cause several health effects to the consumers of beard. These health effects mainly are abdomen pain, diarrhoea, vomiting, damaging liver and may cause cancer. Also, $KBrO_3$ can breakdown several vitamins, e.g., niacin, A_2, B and B_2 in the produced bread [13]. Therefore, in 1993, world health organisation (WHO) and American food and drug administration (FAD) decided that the baseline of added $KBrO_3$ to flour should not exceeded 75mg/kg in the countries where $KBrO_3$ still under used, e.g., United States. In Japan and China, it should not be exceeded 10 mg/kg and 50 mg/kg, respectively [8], but in many other countries it is banned to use as food additive since 1990 such as UK, Canada, Nigeria, European union and Brazil [9,14]. The Libyan ministry of Economic and Tread have been banned the use of $KBrO_3$ as a bread improver since 2005, unfortunately this material is still used to make bread [15].Therefore, the objectives of current review to address this issue are: (1) discuss the use of $KBrO_3$ in bread industry ;(2) address its effect on human health and animal; (3) discover the environmental effect and fate of $KBrO_3$; (4) demonstrate the $KBrO_3$ replacers and current situation of use it in some countries; and (5) conclude the most use determination techniques of $KBrO_3$ residues in bread products.

2. METHODOLOGY

In this review, several consulted literatures were found on some scientific search engines including Google scholar, ResearchGate, Web of Science and Sci-Hub by using combined key subjects that are bread improver, Potassium bromate, the health effects of potassium bromate and methods to estimate potassium bromate in bread. In order to achieve the objectives of current review, the obtained published reviews and experimental studies was revised, analysed critically, and concluded as follows.

3. CHEMISTRY AND USES

$KBrO_3$ is a tasteless and inodorous white crystalline solid substance highly soluble in water [16], it decomposes at 370℃ and melts at 350℃. But, in the bread dough the decomposition point is lower, because of the presented of several minerals in the flour (e.g., Fe, Mg, Al) that may be responsible for this reduction [17]. In the dough medium it can be reduced to potassium bromide (KBr) and oxygen during the heating process in the oven. As mentioned earlier it used as a maturing agent for flour and bread improver, and utilized to improve the quality of fish paste production, especially in Japan for short period and later banned to use in this industry [12].

4. TOXICITY OF $KBrO_3$

The toxicity of $KBrO_3$ is the main reason led to prohibit the use of this material in most countries as it classified in chemical group 1.B, but the international cancer research center put it in group 2.B as a potential human carcinogen [17]. Likewise, several studies have classified it as cariogenic and toxic material to the environmental content [12,18,19].

4.1 Toxicity of $KBrO_3$ in humans

According to Chauhan and Jain [20], $KBrO_3$ may cause human carcinogen, however, the possible effects of this chemical only experimented and investigated in a laboratory trail on mouse and rats. The $KBrO_3$ toxicity on human health should be accountable. More recently, Ncheuveu et al., [8] found that several investigated bakeries in Cameroon have suffered from various symptoms of bromate toxicity that are purple eyes, shore throat, cough, and diarrhoea due to working in bakeries that are still dealing with $KBrO_3$. It has been noted that the death dosage ranging between 5-500 mg$KBrO_3$/kg of body mass. Several cases have recorded that due to the $KBrO_3$ contamination directly through intestine, 9 out of 24 people have died within 5 days, and the rest have found with poisoning symptoms, e.g., vomiting, hypotension, diarrhoea, anuria, oliguria, thrombocytopenia, vertigo depression and acute abdominal pain [21]. Chauhan and Jain [20] referred several laboratorial studies using human tissue that $KBrO_3$ can damage the cell DNA.

4.2 Toxicity of $KBrO_3$ in animals

The first observation of $KBrO_3$ toxicity detected in Japan in 1978 from the suffering of one type of mice which posed several toxic indicators due to the exposure to poisonous dosage of $KBrO_3$ [22]. Additionally, the effect of injecting single dose of 700-900 mg $KBrO_3$/kg of animal to Syrian golden hamsters, F344 rats and B6C3F1 male and female were studied by Kurokawa *et al*. [22]. They observed that approximately 66% of investigated animals died within first 3 hours of trial. And nearly 34% of tested animals severally suffered from ataxic gait, tachypnoea, hypothermia, diarrhoea, lacrimation, piloerection, lying in a prone position and suppression of locomotor movement within two days of experiment. Gibreel [23] reported that 100% of goats received doges of 90 mg_{KBrO3}/kg of animal and 60% of other group of goats received 60 mg_{KBrO3}/kg of animal have died after suffering from severe symptoms of dullness, nasal discharge, weakness, decreased appetite, diarrheal and lacrimation and the intensity of these symptoms is in direct proration with the $KBrO_3$ dosages, and all the goats received 30mg_{KBrO3}/kg of animal suffered of diarrheal discharge only. The residues of bromate ion (BrO_3^-) have detected in kidney (87.4 μg/g), pancreas (32.1 μg/g), stomach (113.5 μg/g), intestines (62.5 μg/g), red blood cells (289 $\mu g/g_{tissue}$) and in plasma (187.1 $\mu g/g_{tissue}$) after the exposure of mice male (*wistar*) to dosage of 100 mg_{KBrO3}/kg of animal , which gives an indicator about the ability of this ion to distribute in different body organs. In their review, Shanmugavel *et al.* [7] reported that several studies have discovered the effect of accumulated levels of $KBrO_3$ in some animal organs (table 1).

Table 1. The effects of accumulated potassium bromated in several organs of animals [7].

Experimented animal	Effected organ
Swiss albino rats	Altered liver function
Wistar rats	Liver
Adult mice	Changes in cerebellum
Swiss mice	Renal and hepatic tissues
Adult male albino rat	Liver
Swiss mice	Neuro behavioural changes
Adult mice	Bone and Blood
Adult male albino rat	Cardiac toxicity
Male F344 rats	Cardiac toxicity

The studies mentioned above, and more other toxicological investigations have proved additional information about the harmful effect of animal exposure to $KBrO_3$, suggesting that $KBrO_3$ is carcinogenic, mutagenic and cytotoxic for various animals by production of several oxygen spices intracellular of animals [24].

5. THE FATE AND EFFECT OF POTASSIUM BROMATE IN THE ENVIRONMENT

The use of $KBrO_3$ is not only in bread making industries, but also in cosmetic and textiles dyeing industries resulting to discharge various amount of this substance into terrestrial and aquatic ecosystems [25]. Soil and sediments have low adsorption potential for BrO_3^- and BrO_3^- is not volatile material, also it can react with soil or/and water organic compounds forming bromide ion (Br^-). Bromate ion can leach into groundwater via soil profile and may form Br^- due to its high-water solubility [26]. In addition, the ozonation process of drinking water may be form bromate when Br^- presented in pre-treated potable water and may happen in natural water bodies where the ozone occurs to following equations [27]:

$$O_3 + Br^- \rightarrow O_2 + BrO^- \quad (1)$$

$$2O_3 + BrO^- \rightarrow 2O_2 + BrO_3^- \quad (2)$$

Soils rich with carbon and microbial communities may lead to minimize the bromate concentration by reducing it to Br^- (equation 3) resulting to diminish BrO_3^- naturally [28].

$$CH_2O + 4BrO_3^- \rightarrow 6H_2O + 6CO_2 + 4Br^- \quad (3)$$

Because of the presence of this material in different environments, the safe concentration BrO_3^- in natural water suggested to be lower than 3.0 mg/L depending on the data concluded that the doses of 31-2258 mg/L of bromate can affect the newly born several species of fish, algae and crustaceans [27]. WHO recommended that the acceptable level of bromate ion in drinking water should be less than 0.01 mg/L [19].

6. POTASSIUM BROMATE REPLACERS

Due to the harmful effect of using $KBrO_3$ in bread industry that mentioned earlier in this paper, various replacers have been suggested to use rather than using $KBrO_3$ as flour addictive. Several substances may allow to use in bread making without any side effects to the consumers of bread [21] such as ascorbic acid, hemicelluloses, glutathione, glucose oxides, phospholipase, xylanase, and α-amylase were used as a food addictive instate of $KBrO_3$ [29,30]. Moreover, some other substance, e.g., soybean flour, KIO_3, azodicarbonamide, fava bean, ammonium chloride and ammonium persulphate, can also be used to replace KBrO3 in bread production [6,31].

7. POTASSIUM BROMATE DETERMINATION

After increasing the concern about the possible negative health effects due to the presence of $KBrO_3$ in bakery products several analytical technologies have been developed to determine the residues of $KBrO_3$in bread [16,32]. These techniques are summarized in table (2). The techniques used to determine the residues of $KBrO_3$ in bakery products have several disadvantages such as low sensitivity, high cost and unfeasibility of some methods. However, Yan *et al*. [33] concluded that the chemiluminescence and flow injection (FIA) analyses showed better sensitivity, low cost and short operation period that make them the popular technologies use to determine the residues of $KBrO_3$ fate in bread products.

Table 2: Potassium bromate determination methods (modified from Okolie and Osarenren [34]*; Shanmugavel *et al*. [7]).

Technique	Reagent	Reaction	Colour	Wavelength
Spectrophotometer by dyes oxidation	Congo red dye and crystal violet dye	Congo red and crystal violet dyes oxidation in HCl medium	Congo red dye: red to blue, Crystal violet: purple in weak acid, green in strong acid and ultimately changes to yellow	485 nm (crystalviolet) 452 nm (congo red dye)
Low injection analysis (FIA)	Thiocyanate and 2-(3,5-dibromo-2-pyridylazo)-5-diethyleminol(3,5-dibromo-PADAP)	Bromate reaction with acidified potassium iodine and	Unstable violet product	602 nm

	(colour reagent)	starch		
spectrophotometer	0.01 M Promethazine (PTZ)	Redox reaction between bromate and promethazine in acidic solution by HCl	Light pink to dark pink	515 nm
Photometric and Fluorometric technique	Benzyl 2-pyridyl ketone 2-quinolylhydrazone (BPKQH)	_	BPKQH produces fluorescent	374 nm (photometric) 343 nm (fluorimetric)
Chemiluminescence and FIA	$KBrO_3$-Na_2SO_3-quinine sulphate	$KBrO_3$-Na_2SO_3-quinine sulphate system in acidic solution	Produces luminescent	
UV–Visible spectrophotometer	0.5% KI in 0.1 N HCl	-	Light yellow to purple	620 nm
Iodometric titration*	For extracting $KBrO_3$: 2g portions: 1M $ZnSO_4$, 0.4 M NaOH, For titration: 4M H_2SO_4, 1.88M KI, 3% (w/v) ammonium molybdite, 0.00359M Na_2SO_3 1% starch solution and 0.00359M KIO_3.	Extracting the residues of $KBrO_3$ and reducing it to iodide by excess solution of Na_2SO_3 then Oxidising the excess of Na_2SO_3 by KIO_3 (back titration).	Appearing the Purple tinge	-

8. CURRENT PERSPECTIVE

Despite all the mentioned harmful effects, $KBrO_3$ as a bread improver is still uses by several nations, especially in developing countries [2]. For instance, in bread samples collected from different bakeries in Jos metropolis, Nigeria, the levels of potassium bromate were higher than the recommended concentration of this material by WHO (0.025 mg/kg) by 100-folds [35]. Ncheuveu *et al.* [8] recorded higher level of $KBrO_3$ ranging from 48.50 to 10148.50 mg/kg in mostly consumed bread brands in Bamerda town, Camerron. Additionally, 67% of bread samples collected from shops and bakeries in and around Dhaka, Bangladesh recorded elevate concentrations of $KBrO_3$ which exceeded the recommended amount of potassium bromate in bread by WHO [4]. Hama *et al.* [36] concluded that, all the bread brands collected from selected bakeries located on Sulaimani city- Iraq cotain levels of $KBrO_3$ above the recommended concentrations (0.02 mg/kg) set by FAD. In Libya, a study conducted by Alhanash *et al.* [15] found that all collected bread samples from several bakeries in Tajoura city contain very high level of $KBrO_3$ than the recommended level (0.02 mg/kg) of this martial suggested by FDA. Therefore, the local and national authorities should implement specific policies to ensure effective monitoring to the treading, handling, and using of $KBrO_3$. In this sense, the Libyan Government has issued an instruction (number 258, year 2021) to ban importing, using and dealing $KBrO_3$ as a bread improver in addition to 2005 instruction [15]. Therefore, having public and private sector concern to these instructions, we can ensure that Libyan bread products will be free of this harmful material.

9. CONCLUSION

Potassium bromate have been used as a bread improver for a long time, and later not recommended to use in bakery industries due to its several major toxic effects on human, animal and environment. As an alternative, several replacers have been recommended to use as food additives instead of $KBrO_3$. Even though, this harmful material is still in used by several nations, various technologies were recommended to monitor the $KBrO_3$ residues in bread products. Many challenges in terms of legacy improvements particularly in developing countries need to address for current and future trade and usage of $KBrO_3$. Policy support to the use of potassium bromate replacers would be effective to stop utilizing $KBrO_3$ in bread industries.

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