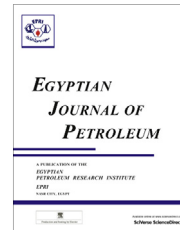


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FULL LENGTH ARTICLE

# Algae personification toxicity by GC–MASS and treatment by using material potassium permanganate in exposed basin

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## KEYWORDS

Algal toxins;  
 Potassium permanganate;  
 Treatment;  
 Biomass;  
 Chlorophyll

**Abstract** This study was conducted to address algal toxins using potassium permanganate through the control of biomass growth of algae under following conditions value  $25 \pm 1$  °C illumination intensity value 245 microeinstein/m<sup>2</sup>/s, using the culture media Chu-10 Modified for the purpose of development algae. We treated algal toxins belonging to groups of Neurotoxins, Hepatotoxins, Pyriproxyfen, Emodin, Brevetoxins-10 (A) and Cytotoxins using concentrations of potassium permanganate represented by 2, 4, 8 and 16 mg/l with alum concentration for each concentration of 30 mg/l, as the removal rate reached to 100% of the toxin blooms in concentrations of 8 and 16 mg/l respectively, through the examination of algal toxins mediated by GC–MASS compared to the standard, which diagnosed a range of algal toxins with C<sub>2</sub>H<sub>3</sub>C<sub>12</sub>NO formulas of synthetic C<sub>9</sub>H<sub>13</sub>NO<sub>2</sub>, C<sub>18</sub>H<sub>27</sub>NO<sub>3</sub>, C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>, C<sub>11</sub>H<sub>17</sub>N<sub>3</sub>O, C<sub>10</sub>H<sub>17</sub>N<sub>3</sub>O, C<sub>9</sub>H<sub>15</sub>Br<sub>2</sub>NO, CH<sub>4</sub>N<sub>2</sub>O<sub>2</sub>, C<sub>11</sub>H<sub>17</sub>NO<sub>2</sub>, C<sub>13</sub>H<sub>9</sub>BrN<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>H<sub>7</sub>NO<sub>4</sub>S, C<sub>20</sub>H<sub>29</sub>NO<sub>3</sub>, C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>C<sub>13</sub>NO the concentrations 2 and 4 mg/l turned toxic compounds into non-toxic compounds represented by C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O, C<sub>12</sub>H<sub>11</sub>ClO<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>, C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>, C<sub>10</sub>H<sub>17</sub>N, C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> and C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O. The results showed reduced primary productivity of algae chlorophyll a result of substance to stop chloroplast for vital activity through the influence of the concentration of potassium permanganate values 0.571, 1.142, 0.583 and 1.713 mg/l respectively, compared to the standard of 114.2 mg/l. As diagnosed types of Algae producing toxins are represented by *Microcystis aeruginosa*, *Microcystis flosaquae*, *Oscillatoria amoena*, *Oscillatoria amphibian*, *Oscillatoria boryana*, *Oscillatoria limnetica*, *Oscillatoria perornata*, *Phormidium ambiguum*, *Lyngbya digueti*, *Lyngbya major*, *Lyngbya nordgaa-*

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*dii*, *Lyngbya spirulinoides*, *Nostoc carneum*, *Nostoc spongiforme*, *Anabaena augstumalis*, *Chroococcus indicus* and *Chroococcus minor*, as the dry weight of live Algae producing toxins is 17.342 g/l.

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## 1. Introduction

Algae are very different and can be found everywhere on the earth. They play a necessary role in many of ecosystems levels, including providing the basis for the hydrous food supply chains supporting all fisher men in the seas, oceans and inland, as well as making about 70% of all the air we breathe [1]. The word Algae represents a big large group of different creatures from different phylogenetic groups, representing many systematic divisions. In general Algae can be referred to as plant-like organisms that are usually photosynthetic and hydrous, but do not have true leaves, roots, trunk, vascular tissue and have simple reproductive formation [2].

Algae are distributed worldwide in the sea, in freshwater and in wet situations on land. Most are microscopic algae, but some of them are so large, also some marine seaweeds that can exceed 50 m in length. The algae have chlorophyll and can make their own food through the steps of photosynthesis.

Recently they are classified in the kingdom of protiste, which include a variety of unicellular and some basic multinuclear and multicellular eukaryotic organisms that have cells with a diaphragm-bound nucleus. Algal poisoning is an intense, often lethal condition caused by high concentrations of toxic blue-green algae (more commonly known as cyanobacteria—literally blue-green bacteria) in drinking water as well as in water used for recreation, agriculture and aquaculture. Severe illness of livestock and Fatalities, birds, pets, fish and wildlife from high growths of cyanobacteria water blooms occur almost in all of the countries in the world. Severe deadly poisonings have also been notarized in people. Poisoning usually comes during warm seasons when the water blossom are more acute and of longer duration. Almost poisonings come among animals drinking cyanobacteria-infested freshwater, but aquatic animals, mostly mariculture fish and prawn, are also affected. The toxins of cyanobacteria comprise six special chemical classes collectively called cyanotoxins [3]. Toxic algae, micro-algal blooms, phytoplankton blooms, red tides, or harmful algae, are all terms for normally occurring phenomena. Around 300 species of micro algae are notify at times to form mass appearance, so called blooms. About one fourth of these species are recognized to produce toxins. The scientific society points out to these events with a generic term, ‘Harmful Algal Bloom’ (HAB), understanding that, because a wide range of organisms are implicated and some species have toxic impacts at low cell intensity, not all HABs are ‘algal’ and not all occur as ‘blooms’ [4]. Many of the organisms in charge for red tides are closely distributed and, in recent years, the organisms appear to be markedly spreading. Natural events such as hurricanes can spread over organisms, and it is doubtful that some organisms may be moved long distances in ship ballast waters. Another factor that may motivate algal proliferation in both freshwater and marine systems is augmentation nutrient loading. Certain algae occur more usually in some areas than others and it is

useful to know which ones are problems in particular locations. Good sources of information about algal blooms are the State public health department or the State division of marine resources or marine fisheries [5]. Studies have confirmed the use of UV for removal of all types of microbiology but it is expensive, making it difficult to use on an ongoing basis, while potassium permanganate are a sterile material and removes the microorganisms in addition to not hurting the outer wall of the algae or stopping the process of photosynthesis, causing the need to hold the vital events of moss energy disabled blastids of them, including the reduction in the productivity of material chlorophyll and all pigments in addition to this, it prevents algae toxins out to the outside center [8,6]. So study aims to address the algal toxins using material Potassium Permanganate in the open docks.

## 2. Materials and methods

### 2.1. Diagnosis of algae

The non-diatom algae were isolated and diagnosed by microscopic examination, depending on the number of references to classify of non-diatom algae [7–9].

### 2.2. Method of extract algae toxins Depending on the Reference of WHO [10]

For dried field algae samples certain amount of dry algae powder was added into extracting solution.

### 2.3. Method of chlorophyll extraction Depending on the Reference of Vollenweider [12]

In order to quantify the amount of chlorophyll in a particular species, the intracellular chlorophyll must first be extracted.

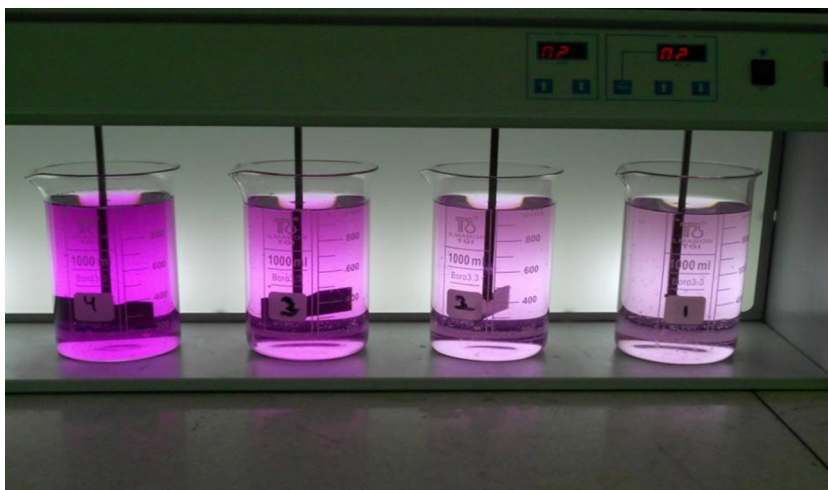
### 2.4. Examination of algal toxins using GC–MASS Depending on the Reference of Toshihiro et al. [11]

Examination of toxin algal is carried out using Shimadzu-2010 GC–MS.

- Column: 30 m length and 0.25 mm ID.
- Initial temperature: 85 °C.
- Post time: 2 min.
- Ramp: 10 °C/min.
- Final temperature: 340 °C.

### 2.5. Preparation of potassium permanganate and alum

The proper concentration of potassium permanganate was carried out by dissolving 1 g high purity  $\text{KMnO}_4$  (99.5% purity)



**Fig. 1** Streaming device mixer.

in 100 mL distilled water. 2, 4, 8 and 16 mg/l with 30 mg/l of alum solution ( $\text{AlSO}_4 \cdot 18\text{H}_2\text{O}$ ), perfect dose and Coagulant.

**Table 1** Numbers of algae toxin-producing, through chlorophyll value of 114.2 mg/l, and dry weight of 17.342 g/L for 100 mL of algal colonies of 100 mL.

Types of algae producing toxins	Numbers of algae (cells/l)	%
<i>Anabaena augstumalis</i>	32	8.48
<i>Chroococcus indicus</i>	26	6.89
<i>C. minor</i>	12	3.18
<i>Microcystis aeruginosa</i>	23	6.10
<i>M. flosaquae</i>	13	3.44
<i>Oscillatoria amoena</i>	24	6.36
<i>O. amphibian</i>	18	4.77
<i>O. boryana</i>	20	5.30
<i>O. limnetica</i>	22	5.83
<i>O. perornata</i>	14	3.71
<i>Phormidium ambiguum</i>	25	6.63
<i>Lyngbya digueti</i>	23	6.10
<i>L. major</i>	17	4.50
<i>L. nordgaardii</i>	27	7.16
<i>L. spirulinoides</i>	16	4.24
<i>Nostoc carneum</i>	18	4.77
<i>N. spongiforme</i>	26	6.89
<i>Westiellopsis prolifica</i>	21	5.57
Total	377	100

### 2.6. Measuring pH

pH measurement of water samples was directly measured using Boston EXTECH model m 62, calibrated by 4, 7 and 9 pH buffer solutions.

### 2.7. Mixing potassium permanganate and alum

This process is carried out according to Liang et al. [13] as shown in Fig. 1.

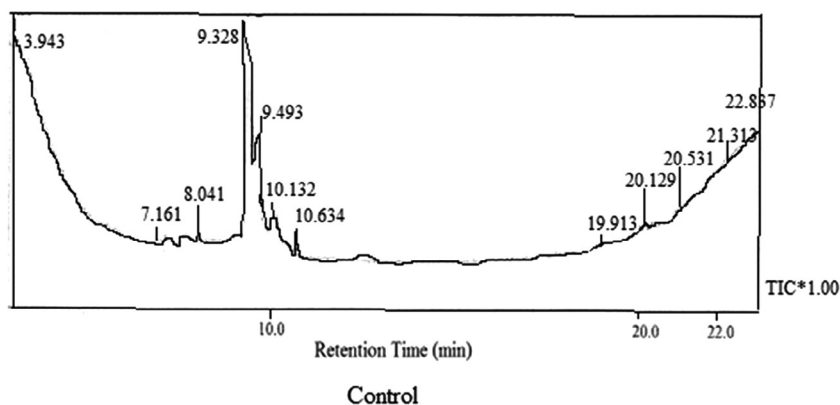
## 3. Results and discussion

100 mL liquid density of algae growth is spread over all the concentrations of the treated material (potassium permanganate) in addition to the basin control without the impact of any material processing with productivity knowledge Preliminary her through chlorophyll value 114.2 mg/l for the basin control and dry weight of 17.342 g/l. Algae were diagnosed to produce poisons and toxins (see Table 1).

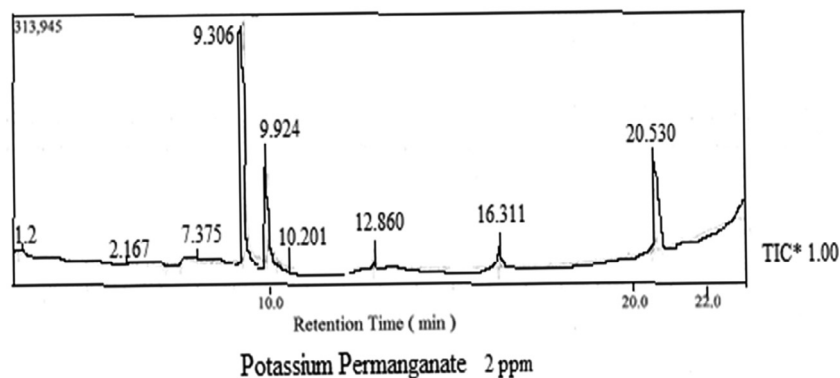
Many researchers used materials to damage growth rates of algae, such as substance use copper sulfate, which led to the rupture of the outer wall of the algae without toxic substance environmental center without affecting the use and this is very dangerous through the algae that carry genes to secrete those toxins including algae blue-greens Division, but for the use of material potassium permanganate, chlorine dioxide and ozone, which are sterile material for many of the germs, we

**Table 2** Low initial production of chlorophyll concentration of algae through using of material potassium permanganate and alum solution.

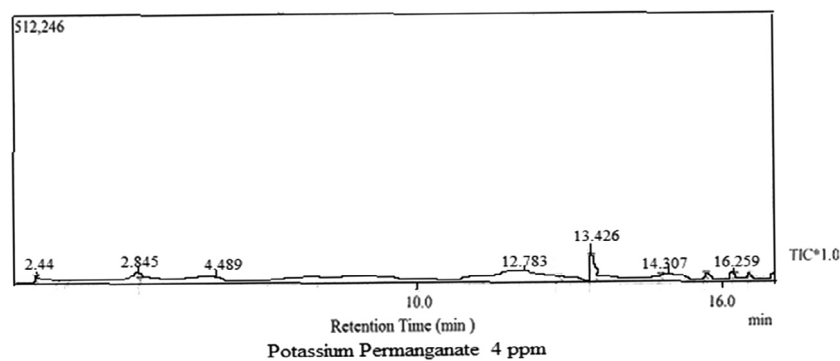
Concentrations (mg/l)	After 5 h	After 24 h	After 48 h	After 72 h
Standard	4.284	44.268	57.1	114.2
2	1.428	31.416	5.285	2.571
4	23.990	21.42	2.426	1.142
8	23.133	1.428	1.142	0.583
16	25.989	7.14	1.713	0.0713



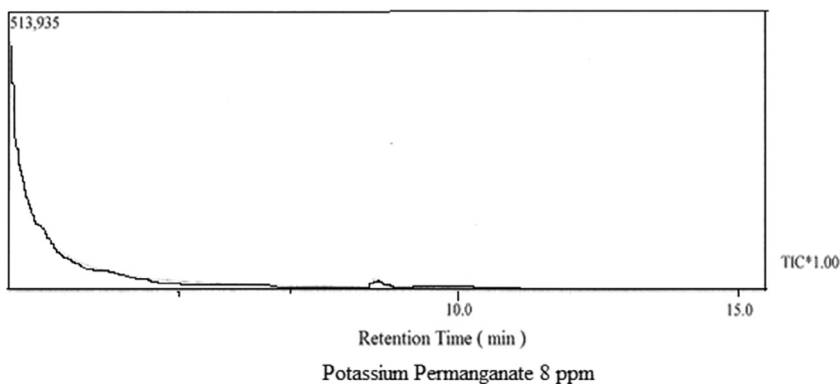
**Fig. 2** GC-MASS of algal toxins within the treated standard.



**Fig. 3** GC-MASS of algal toxins treated with concentration of 2 mg/l.



**Fig. 4** GC-MASS of algal toxins treated with concentration of 4 mg/l.



**Fig. 5** GC-MASS of algal toxins treated with concentration of 8 mg/l.

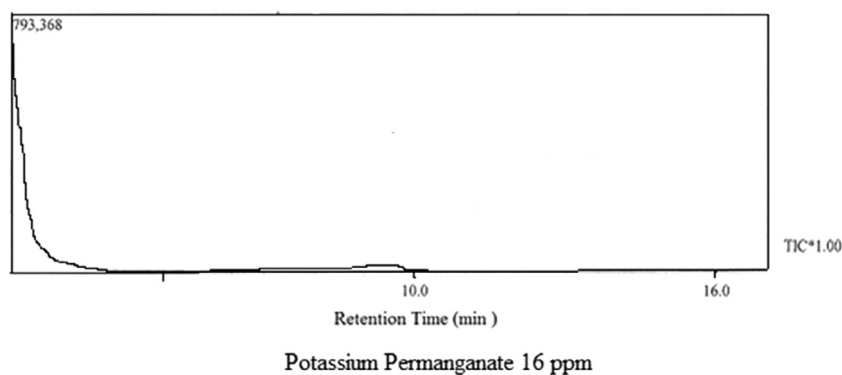


Fig. 6 GC-MASS of algal toxins treated with concentration of 16 mg/l.

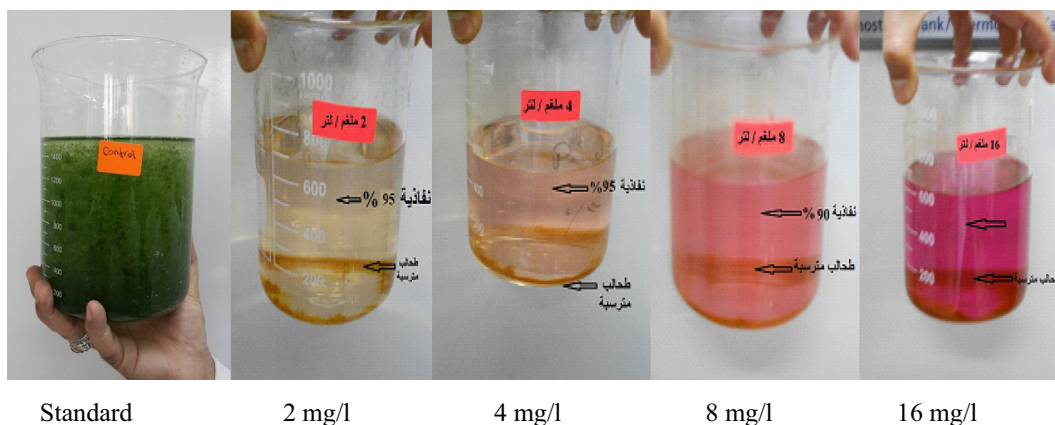


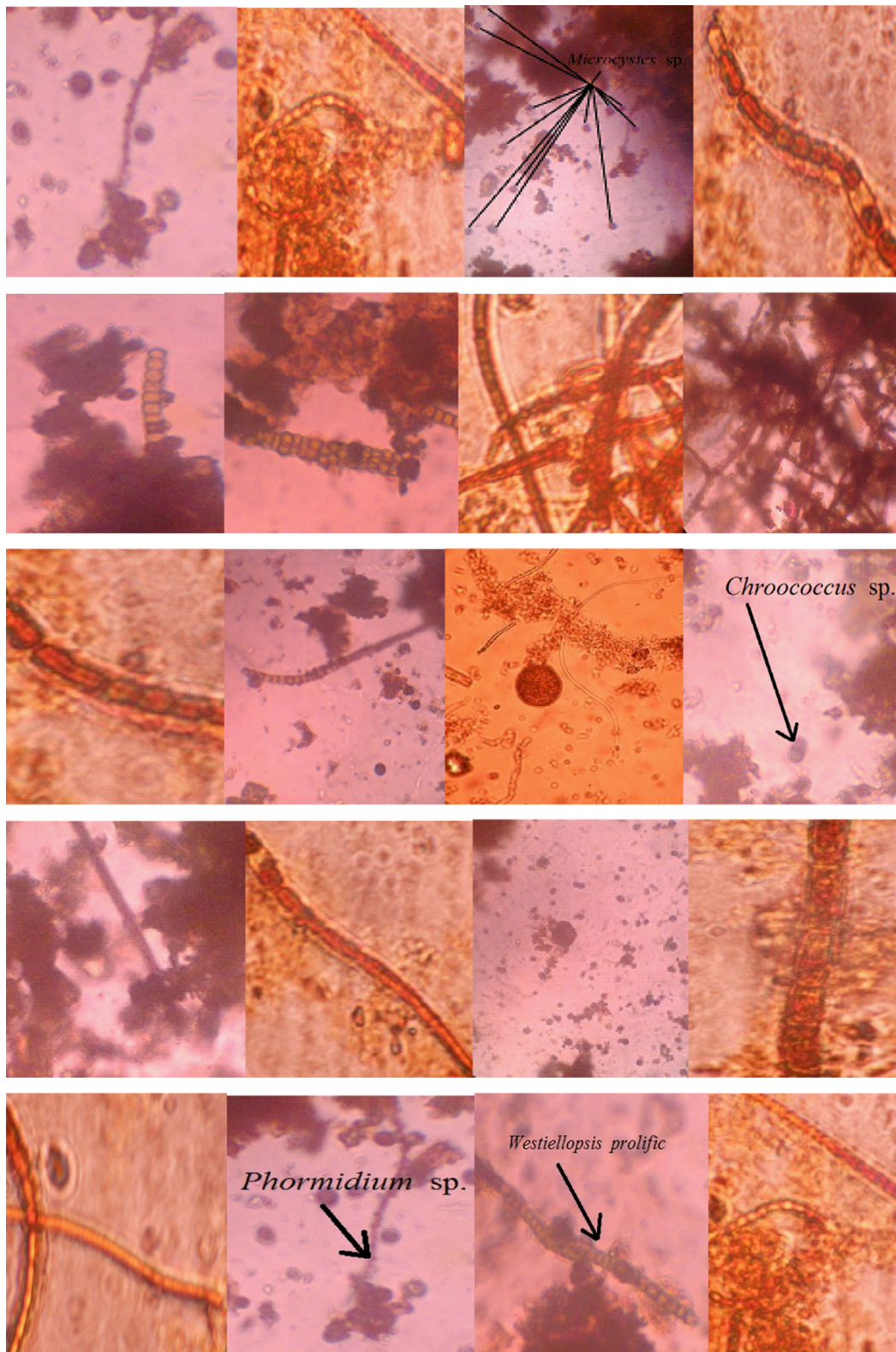
Fig. 7 Concentrations of potassium permanganate and its impact on algae society compared to standard.

**Table 3** Treatment of algal toxins of different concentrations of potassium permanganate with chemical formulations statement mediated by GC-MASS.

Algal Toxins	Synthetic version of the toxin	Standard	Concentrations (mg/l)			
			2	4	8	16
1-Neurotoxins						
Antoxin-a	$C_2H_3C_{12}NO$	*	-	-	-	-
	$C_9H_{13}NO_2$	*	-	-	-	-
	$C_{18}H_{27}NO_3$	*	-	-	-	-
	$C_{11}H_{12}N_2O_6$	*	-	-	-	-
	$C_{11}H_{17}N_3O$	*	-	-	-	-
	$C_{10}H_{17}N_3O$	*	-	-	-	-
	$C_9H_{15}Br_2NO$	*	-	-	-	-
Homoanatoxin-a	$CH_4N_2O_2$	*	-	-	-	-
	$C_{11}H_{17}NO_2$	*	-	-	-	-
	$C_{13}H_9BrN_2O_3$	*	-	-	-	-
2- Hepatotoxins						
Microcystin-LA	$C_3H_7NO_4S$	*	-	-	-	-
3-Pyriproxyfen	$C_{20}H_{29}NO_3$	*	-	-	-	-
4-Emodin	$C_{15}H_{10}O_5$	*	-	-	-	-
5-Brevetoxins-10 (A)	$C_4H_8O_2$	*	-	-	-	-
6-Cytotoxins	$C_2H_2Cl_3NO$	*	-	-	-	-

-, Absence of toxins.

\* The presence of toxins.



**Fig. 8** Algae treated with different concentrations of potassium permanganate without affecting the exterior of the algal cells.

have to be careful to use them in appropriate concentrations in the case of water treatment for human consumption [14].

Tests showed a low concentration of chlorophyll processor permanganate and the use of potassium permanganate blended alum within specific concentrations does not cause

any damage through the process of photosynthesis which stops and disables their activity with the presence of alum [14,15], which leads to the deposition of floating masses of algae to the bottom through a stop Productivity initial algae of reducing the concentration of chlorophyll; this means there is

decomposition of toxins located inside moss producer of toxins without tearing the outer wall, and Table 2 shows details of the results.

#### 4. Treatment of algal toxins

After decreasing number of algae that causes food to enrich the (excessive growth) using different concentrations of a substance potassium permanganate mixture a concentration of 30 mg/l textured alum as coagulate.

In addition to reducing productivity of initial algae by reducing the concentrations of chlorophyll algal toxins per transaction were examined and compared to standard at the end of the experiment, which lasted for 72 h mediated by GC/MS device. Results showed the presence of toxins' algal belonging to the group Neurotoxins, Hepatotoxins, Pyriproxifen, Emodin, Brevetoxins-10 (A) and Cytotoxins within the standard treatment, with a note detoxification algal 100% concentrations 8 and 16 mg/l, respectively textured potassium permanganate in comparison with standard, which contained a lot of belonging to the chemical compounds to algal toxins (Fig. 2).

A result of the cessation of photovoltaic installation process stops the outer wall systems (systems enzymatic) to withdraw nutrients that enter into the composition of the algal toxin combination the non-arrival of light to stop light receptors [15], and the concentrations of 2 and 4 mg/l for the same article have some toxic compounds converted into non-toxic compounds and Figs. 3–7 describe them.

Were treated toxins algal belonging to the group Neurotoxins a Besnfein Anatoxin-a, Homoanatoxin-a and the various toxins which is alkaline compounds Alkaloids with effect very quickly called and can be fatal in most cases where the cause muscle surrounding paralysis followed by a respiratory muscle paralysis, which leads to an inability to breathe then death.

As observed in Hepatotoxins group Class Microcystin-LA, these toxins are the most common among toxins Cyanobacteria and have a severe impact, but it takes longer than nerve toxins for death to occur during a period ranging from 5 min to a few days depending on several factors, including weight of the animal and the type of poison and the dosage and others.

Other types of toxins such as Pyriproxifen, Emodin and Brevetoxins-10 appeared (A) as to remove algal toxins that have emerged within the standard of treatment with 8 and 16 mg/l of potassium permanganate, and Table 3 shows the same.

The concentration of 2 and 4 mg/l of the same material has been converted into non-toxic compounds and toxic compounds as shown in Table 3.

The current study also points to the possibility of potassium permanganate within the concentration of 8 and 16 mg/l, respectively, in the treatment of algal cells by stopping the process of photosynthesis and disables all vital events without tearing the outer wall of moss and then deposition blocs blooms to the pelvic floor and a rise in turbidity levels in the water column compared to the standard that shows a rise in the value of biomass and low turbidity, Fig. 7.

Moreover, all potassium permanganate concentrations 2, 4, 8 and 16 mg/l did not affect the outer wall of the algae within the current study, it did not rupture the out of the cell walls.

This is because of potassium permanganate mixture specific concentration of alum led to not tear the outer wall of the algae, which preserves not outer toxins blooms.

It stops the process of photosynthesis, and this contributes to the reduction of primary productivity of algae of chlorophyll, solution Alum is essential for potassium permanganate and it helps the process of sintering and coagulation and sedimentation [17], as shown in Fig. 8.

Additionally, the potassium permanganate affects some algal toxins and do not affect others, as it affects the toxins Anatoxin-a, Cyndrospermopsin and Microcystin and analyses have valued the final removal, while not affecting Saxitoxin toxin, although it is produced by algae greens blue—this is what is confirmed by the organization [16].

#### 5. Conclusions

1. Detection of algal toxins using GC–MS system.
2. Knowledge of the chemical compositions of algal toxins derived from local algae toxin-producing.
3. Algal toxin treatment using potassium permanganate through the use concentrations does not affect the aquatic environment at the same time, a sterile material against germs.
4. Algae die without tearing the outer wall and the preservation of the internal contents without causing environmental pollution in the case of the center, out of their contents to the outside.
5. Photosynthesis of algae process stops and stops the enzymes responsible for the production of algal toxins.
6. Classification of toxic chemical compounds presents in algae extract to the basic varieties of groups toxic algae.

#### References

- [1] Algae Biomass Organization (ABO), 2013. All about algae.com. <http://allaboutalgae.com/algae-basics/>.
- [2] B.V. Lenntech, Algae Description and Types Rotterdamseweg 402 M, 2629 HH Delft, 2014, <http://www.lenntech.com/eutrophication-water-bodies/algae.htm>.
- [3] Wayne W. Carmichael, Overview of Algae Poisoning. Merck Manuals, 2013, [http://www.merckvetmanual.com/mvm/toxicology/algal\\_poisoning/overview\\_of\\_algal\\_poisoning.html](http://www.merckvetmanual.com/mvm/toxicology/algal_poisoning/overview_of_algal_poisoning.html).
- [4] UNESCO, IOC, Intergovernmental Oceanographic Commission of UNESCO, Harmful Algal Bloom Programme, Project Office for IODE, Oostende, Belgium, 2015, [http://hab.ioc-unesco.org/index.php?option=com\\_content&view=article&id=5&Itemid=16](http://hab.ioc-unesco.org/index.php?option=com_content&view=article&id=5&Itemid=16).
- [5] Lynn H. Creekmore, Field Manual of Wildlife Diseases: General Field Procedures and Diseases of Birds. USGS science for a changing world. Funded by the U.S. Fish and Wildlife Service, Division of Federal Aid, Administrative Grant No. AP95-017, 2013. [http://www.nwhc.usgs.gov/publications/field\\_manual/chapter\\_36.pdf](http://www.nwhc.usgs.gov/publications/field_manual/chapter_36.pdf).
- [6] J. Rositano, B. Nicholson, P. Pieronne, *Ozone Sci. Eng.* 20 (1998) 223–238.
- [7] T.V. Desikachary, *Cyanophyta*, Indian Council of Agricultural Research, New Delhi, 1959, p. 686.
- [8] Edward G. Bellinger, David C. Sigeo, *Freshwater Algae Identification and Use as Bioindicators Printed in Great Britain by Antony Rowe, Ltd. Chippenham, Wilts*, 2010, p. 285.

- [9] S.A. Felisberto, L. Rodrigues, *Braz. J. Biol.* 64 (1) (2004) 1–2.
- [10] WHO, in: J. Chorus, Bartram (Eds.), *Toxic Cyanobacteria in Water*, E & FN Spon, an imprint of Toutledge, London, 1999, p. 416.
- [11] O. Toshihiro, S. Steffi, K. Ina, B. Susan, S. André, Alisdair R. Fernie, *J. Metabolites* 3 (2013) 168–184.
- [12] R.A. Vollenweider, *A Manual on Methods for Measuring Primary Production in Aquatic Environments*. Int. Biol. Program Handbook, 12, Black Well Scientific Publication Ltd., Oxford, 1969, p. 225.
- [13] Liang Heng, Yang Yanling, Gong Weijia, Li Xing, Li Guibai, *Desalination* 222 (2008) 74–80.
- [14] R.P. Liu, X. Li, Y.L. Yang, H. Liang, G.B. Li, *High Technol. Lett.* 14 (2004) 90–93.
- [15] Ohio Section Technology Committee, *White Paper on Algal Toxin Treatment*, Environmental Protection Agency, 2011, pp. 1–6.
- [16] Ohio Section Technology Committee, *Draft White Paper on Cyano Toxin Treatment*, Environmental Protection Agency, American Water Works Association Ohio Section Technology Committee, 2015, pp. 1–15.
- [17] Ahmed Aidan Al-Hussieny, Elaf Sameer, Reweda Fahim, Zainab Hani, *J. Ministry Sci. Technol.* 5 (2) (2014) 62–71.
- [18] Ahmed Aidan Al-Hussieny, Ahmed Ibrahim Jassim, Haider Y. Lafta, *J. Mod. Sci. Heritage* 162 (2013) 152 (2)1, [www.jmsh.eu](http://www.jmsh.eu).