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Effect of pre-oxidation by chlorine/permanganate on surface water characteristics and algal toxins

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ABSTRACT

Previous studies on water treatment processes confirmed that pre-oxidation of the surface water improves the coagulation and filtration processes. However, only few studies focused on its effects on algae and their toxins. In this study, the variability of microcystins through conventional treatment processes was investigated within a full-scale plant, which is challenged with a high level of cyanotoxins and where surface water is pre-chlorinated. Treatment trials were conducted with and without pre-chlorination. The water characteristics, algal count, and microcystins were compared. The results revealed that pre-chlorination causes lysis of Cyanophyta cells, consequently releasing cell-bound toxins and other compounds that lead to the formation of harmful disinfection byproducts (DBPs). Laboratory jar tests were performed to evaluate potassium permanganate effectiveness as an alternative preoxidant. Unlike pre-chlorination, permanganate preserved the algal cells integrity, allowing for the removal of intact cells with their toxins and provided better controls of DBPs.

Keywords: Drinking water purification; Pretreatment; Chlorine; Permanganate; Algal toxins; Microcystins

1. Introduction

Pre-oxidation has been one of the principle means for improving the coagulation process in water treatment plants. It is generally used for destroying the organic coating attached to the surface of the particles [1]. In addition, it is used to control tastes and odors, algal growth, and oxidation of iron and manganese.

A continuing worldwide problem for the drinking water treatment industry is the presence of algae in the water supply source. Algae alter taste and odor, produce disinfection byproducts (DBPs), cause filter clogging, distress coagulation, and assimilable organic carbon for the growth of biofilm [2,3]. Algae removal by conventional treatment is more difficult than inorganic particles, due to their low specific density, motility, morphological characteristics, and negative surface charge [4]. Some preoxidants may cause physiological stress or cell membrane damage, resulting in releasing of taste and odor causing compounds or intracellular organic matter (IOM) into the bulk water [2]. Such IOMs may be precursors of DBPs. The effect of preoxidants on algae during water treatment may vary due to their type and dosages.

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Traditionally, pre-chlorination has been found to be an effective method to aid the coagulation of water with high organic content or algal blooms. Sukenik et al. [5] found that chlorine had a distinct effect on the algal cell surface architecture, which resulted in the release of cellular organic compounds. Therefore, the use of chlorine causes the formation of trihalomethanes (THMs) and haloacetic acids, which are harmful byproducts. This fact has limited the use of chlorine in many countries [6,7]. According to Plummer and Edzwald [8], ozone as an alternative to chlorine, causes the release of extracellular organic matters, which makes the coagulation easier but causes the increase in THMs precursors.

A primary use of permanganate is the removal of iron and manganese. The use of permanganate was found to be more effective for oxidizing manganese than aeration or chlorination [9]. Permanganate preoxidation obviously enhanced the coagulation of several kinds of surface water [10]. Its reducing product, manganese dioxide (MnO_2), incorporates into the algal floc and increases its specific gravity, consequently its settling velocity. Knappe et al. [11] studied the effect of permanganate concentration (C) and the contact time (T) on the removal efficiency of algae. They reported that the algal removals improved with increasing CT, under the same alum dose (40 mg/L). Pretreatments with 0.5 and 3 mg of $KMnO_4$/L resulted in 75 and 96% algal removal, respectively, with 3 h contact time. To avoid the formation of DBPs from chlorination and ozonation, potassium permanganate ($KMnO_4$) may be introduced as an alternative preoxidant when treating eutrophic source water [3].

Prokaryotic organisms (identified by a variety of names including, Cyanophyta, cyanobacteria, and blue-green algae) are ubiquitous in most fresh water bodies. If Cyanophyta blooms occur in surface water used as a drinking water source, the water utility may face several water quality problems. Taste and odor compounds may be produced by many species of cyanobacteria and are difficult to be removed by settling. The greatest concern in terms of human health is the production of low molecular weight metabolites, often referred to as cyanotoxins. At least 3 of 50 known genera of cyanobacteria are capable of producing toxins, and that between 50 and 70% of cyanobacteria blooms are toxic [12,13]. Cyanotoxins can be found either inside (intracellular) or outside (extracellular) the cell.

The cyanotoxins have a variety of toxic properties that are categorized according to their modes of action in mammalian test systems. These categories include neurotoxins (e.g. saxitoxin and anatoxin), hepatotoxins (e.g. microcystins and nodularins), and lipopolysaccharides. The hepatotoxins have the widest distribution in natural waters; of these liver toxins, microcystins (MCs) are the most commonly encountered. Several Cyanophyta genera including, *Mycrocystis*, *Anabaenopsis*, *Anabaena*, *Nostoc*, and *Oscillatoria* produce MCs. Since there are over 70 variants of MCs, a short list of four variants, LR, YR, LA, and RR, referring to changes in the amino acids, has been recommended based on their prevalence and toxicity [14]. Microcystin-LR (MC-LR) is the most common variant of these cyclic peptide hepatotoxins [15]. Its toxicity has prompted the World Health Organization [16,17] to publish a guideline value of 1.0 μg of MC-LR/L for drinking water.

Conventional treatment processes involving settling or air flotation followed by filtration can be effective for removing the intact Cyanophyta cells including their intracellular toxins. The removal of the dissolved or extracellular toxins cannot be achieved with this conventional treatment. They can be removed by adsorption onto granular or powdered activated carbon, or by chemical oxidation using chlorine, ozone, or potassium permanganate [18]. The effectiveness of granular or powdered is a water quality specific, carbon specific, and toxin specific. Although several oxidants inactivate some cyanotoxins, it is important to remember that not one oxidant inactivates all cyanotoxins. Drikas et al. [19] found that the chlorination process was effective for destroying MCs and cylindrospermopsin at pH < 8. It was ineffective against anatoxin-a at pH 6–7. They reported that ozone effectively inactivates MCs and anatoxin-a. The saxitoxins were not effectively oxidized to low levels. Drikas et al. [19] evaluated the effectiveness of $KMnO_4$ in destroying MC-LR; they found that it is more effective than chlorine for destroying the soluble MC-LR.

Numerous studies have shown that preoxidants such as ozone, chlorine, or permanganate can improve the algal removal by coagulation and filtration processes [3,8]. However, there is a little information available concerning the occurrence and evolution of the cyanotoxins within the treatment plants that use preoxidants as a preliminary treatment strategy. A reliable method for the removal of the commonly occurring cyanotoxins in a wide range of water would be of a great value to the international water industry [13]. The most desirable way to remove cyanotoxins from the water body is by removing Cyanophyta cells with the toxin intact.

This research aims mainly to study the behavior of the intracellular and extracellular microcystins within a full-scale conventional treatment plant where the surface water is pre-chlorinated and to gain a better

understanding on the effect of the various treatment stages on the fate of these cyanotoxins. In addition, laboratory jar tests were implemented to assess the direct effect of different doses of potassium permanganate as an alternative preoxidant on the water characteristics, algal count, and microcystins concentration.

2. Materials and methods

To investigate the effect of pre-chlorination process on the surface water characteristics, algal count, and cyanotoxins, two treatment scenarios (with and without pre-chlorination) were performed on a full-scale plant. Because of their chemical analogy with the common operating conditions, they were allowed by the water authorities. As it is not allowed to try new chemical preoxidants on full-scale plants, laboratory jar tests were performed on permanganate pre-oxidation in a trial to find a suitable substitute to chlorine pretreatment due to its harmful byproducts. The significance of all measurements was evaluated by statistical analyses, error bars are illustrated on the graphs, and standard errors are presented.

2.1. Field investigations

2.1.1. The full-scale plant

Assiut University hydro-compact drinking water treatment plant (HC-DWTP) was selected in this study. The plant purifies surface water of El-Ebrahemia canal, which is branched from the Nile River. In particular, it uses pre-chlorination as the first treatment stage and it is challenged with a high level of cyanotoxins. Mohamed [20] revealed the presence of toxic cyanobacteria in some surface water bodies in Egypt. Increased eutrophication due to the agricultural, municipal, and industrial run-off has contributed to the growth of toxin producing cyanobacteria in Egypt [21].

HC-DWTPs are complete containerized plants with a capacity of 2,400 m^3/d. The normal operating procedure of such type of plants is based on conventional processes, namely primary sedimentation, pre-chlorination, coagulation–flocculation–clarification, filtration, and post-chlorination as shown in Fig. 1 and can be described as follows:

(1) The raw surface water is delivered into the interspaces of tilted plates within a primary sedimentation tank, where the coarse impurities are settled.

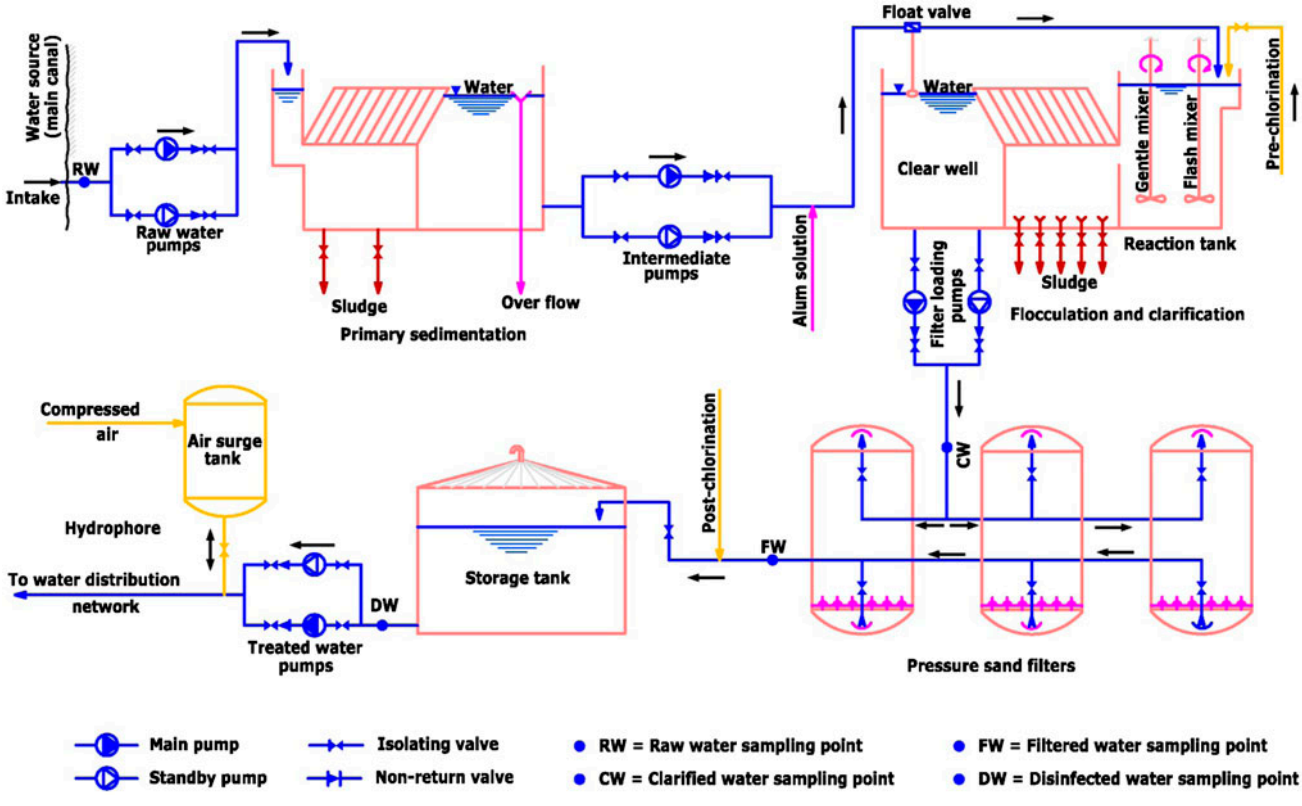

Fig. 1. A schematic flow diagram of the processes within the HC-DWTP of Assiut University.

(2) The pretreated raw water (RW) is pumped to the clarifier. A flocculation agent, an alum solution with a dosage of 40 mg/L is added and pre-chlorination is applied too. The pretreated water enters the reaction tank for both flash and gentle mixing and then settled in a tilted plates sedimentation tank.
(3) Filter-loading pumps deliver the clarified water (CW) to downward pressure sand filters to eliminate the residual small flocs.
(4) The filtered water (FW) is post-chlorinated, collected in a storage tank, and then pressurized to the water distribution network. A hydrophore unit is installed to keep a constant pressure within the network.

Two treatment scenarios, with and without pre-chlorination were conducted on the full-scale plant, HC-DWTP of Assiut University. The difference between the two scenarios is whether a pre-chlorination dose was added to the RW or not. In the first scenario, the normal operating procedure, a pre-chlorination dose was injected at the entrance of the flash mixing tank in addition to a second post-chlorination dose, which is fed ahead of the storage tank as presented in Fig. 1. However, in the exceptional without pre-chlorination study case, a unique chlorine dose was added at the entrance of the storage tank. Comparison tests between the two treatment scenarios were made for some of the physicochemical characteristics of the water, algal count, and MCs concentration. In the two cases, the produced water from the treatment plant under study was pumped into the drinking water distribution network of Assiut University campus.

2.1.2. Field tests

The effects of chlorine pretreatment as well as the conventional treatment processes on some of the surface water characteristics (pH value, turbidity, apparent, and true colors), algal count, and microcystins were investigated. Two treatment trials, with and without pre-chlorination were conducted on a full-scale plant, HC-DWTP of Assiut University. In the pre-chlorination case, a chlorine dose of 2 mg/L was injected at the entrance of the flash mixing tank, in addition to another post-chlorination dose of 2 mg/L at the entrance of the storage tank as presented in Fig. 1. However, in the case of without pre-chlorination, a unique chlorine dose of 4 mg/L was applied at the entrance of the storage tank, that is, where post-chlorination normally goes in. A post-chlorination dose of 4 mg/L was chosen to equalize the dose with the sum of the injected doses in the other treatment case. To collect data, four sampling points were established on the treatment line as shown in Fig. 1. The first point represents the RW; the second point picks samples from the CW after coagulation, flocculation, and sedimentation; the third point represents the FW; finally, the fourth point is located at the outlet of the storage tank to represent the disinfected water (DW).

2.2. Laboratory tests

2.2.1. The algal culturing

For jar tests, 3 L of water sample was collected from a fishpond where Cyanophyta grow in abundance. To enhance the growth of Cyanophyta group in the collected sample, it was enriched with a blue green (BG11) media to a volume of 6 L and kept at 25 ± 2°C under a continuous light intensity of 24 μmol m^{-2} s^{-1} for 3 weeks [22].

2.2.2. Jar tests

Water treatment operators have used jar tests for decades to optimize the dosing of the coagulants and preoxidants. Jar tests are intended to imitate, in 1-L jars in the laboratory, the processes of coagulation, flocculation, and sedimentation in full-scale plants. The studied full-scale water treatment plant covers the demands of around 12,000 consumers; therefore, the authorities do not allow trying a new preoxidant such as permanganate on such full-scale plant. Therefore, laboratory jar tests were carried out on the enriched water sample to study the effect of the permanganate pretreatment followed by alum coagulation on some of its physicochemical characteristics, algal count, and MCs concentration.

Basiouny et al. [7] found that the best alum coagulant dose for the Nile River water ranges between 40 and 60 mg/L. The laboratory experiments were carried out with a six-beaker standard jar test apparatus. The volume of each water sample in the beakers was fixed at 1 L. The test procedure was performed as described by Heng et al. [6] for permanganate preoxidation. At first, different weights of permanganate (0, 0.3, 0.5, 1, 1.5, 2 mg) were mixed at 200 rpm with the water sample in each beaker for 1 min. Then, all of the water samples were subjected to 40 mg/L alum coagulant and mixed at 120 rpm for 1 min. Thereafter, the samples were slowly stirred for 18 min at 30 rpm, and then settled for 30 min. The supernatant was siphoned at 1 cm below the water surface to examine its characteristics.

2.2.3. The algal count

Both the collected water samples from the full-scale plant of Assiut University and the siphoned water from jar tests were investigated for their algal counts. Sedge wick-Rafter cell, 1 cm^3 was used for counting. Firstly, the total number of cells for 30 units of filaments or colonies was counted and the mean number per filament or colony was calculated. Then after, the total number of cells per unit volume of the studied sample could be determined. The mean count of three replicates was taken into consideration and the data were given as cells/L algal suspension.

2.2.4. The analysis of microcystins

The MCs of the collected water samples from both field and laboratory jar tests were differentiated into intracellular and extracellular by filtration, assuming that the algal cells would be retained on 0.45-μm glass fiber filters. Thus, the detected MCs in the filtrate were termed as extracellular and the detected in the filter residue were considered to be cell bound or intracellular [23].

To measure the intracellular MCs, the filter paper of each sample was torn into small pieces and its retained phytoplankton were extracted in 5 mL of methanol (95%) at a temperature of 25 ± 2˚C and dim light for 24 h with shaking. After that, the extract was filtered through GF/C filter paper, the filtrate was evaporated until dryness, and the residue was redissolved in 1 mL of distilled water for detecting the cell-bound MCs. To measure the extracellular MCs, the filtrate of each sample was pre-concentrated on C18 cartridge and eluted with 80% methanol. C18 columns were obtained from Cole-Parmer Instrument Company, USA. The eluted fraction was evaporated to dryness and the residue was redissolved in 1 mL of distilled water for detecting the extracellular MCs.

The concentrations of both intracellular and extracellular MCs were determined as the means of two replicates by enzyme-linked immunosorbent assays (ELISA) according to Carmichael and An [24]. The microtiter plate and MCs reagent kit were obtained from Abraxis LLC, USA. This assay uses antibodies against MC-LR, the most common MC, and detects the presence of other MC variants to differing degrees [25]. The test is an indirect competitive ELISA that allows the congener-independent detection of MCs. It is based on the recognition of MCs and their congeners by specific polyclonal antibodies. They are stronger than monoclonal antibodies, as they provide overestimation of the total sum of MC congeners in the samples due to the recognition of the free ADDA group in MCs. The microcystins and their congeners when present in a sample and MCs-protein analog immobilized on the plate compete for the binding sites of antibodies in solution. After a washing step, a second antibody label is added. After another washing step and the addition of the substrate solution, a color signal is generated. The intensity of the blue color is inversely proportional to the concentration of MCs present in the sample. The color reaction is stopped after a specified time and the color is evaluated by TECAN® sunrise absorbance ELISA reader at 450 nm. The concentration of the sample was determined using a standard curve. The range of MCs standard solutions that were provided with the kit was from 0 to 5 μg/L. Samples showed concentrations greater than the upper limit of the available MCs standard solutions were diluted to a certain degree to come within the range.

2.2.5. Measurements of the water physicochemical characteristics

Some of the physicochemical characteristics of the collected water samples from the full-scale treatment plant of Assiut University and the siphoned water from jar tests were measured as means of three replicates. The Oyster pH meter was used for measuring pH value. The water turbidity was measured in Formazin Turbidity Unit by DR/2000 spectrophotometer (absorptiometry method). The samples were filtered through 0.45-μm glass fiber before measuring the true color. The apparent and true watercolors were measured in Platinum Cobalt Units (PCU) based on a platinum-cobalt standard by HI 83,200 multi-parameters bench photometer. The residual manganese concentration was determined by HI 83,200 multi-parameters bench photometer with citrate and sodium periodate kit reagent.

2.3. The statistical analysis

In the present study, the measured values of the water physicochemical parameters and algal counts were determined as the means of three replicates; however, values of the microcystins concentration were calculated as the means of two replicates. The statistical analysis was performed by one-way analysis of variance (ANOVA, SPSS 10.0 software for Windows). The differences were considered significant at $p < 0.05$. The means were compared using Duncan multiple range tests at 5% level of probability.

3. Results and discussion

3.1. Full-scale investigations on the effects of pre-chlorination

3.1.1. Pre-chlorination effects on the water characteristics

The measured pH value, water turbidity, and apparent and true colors of the collected samples from the HC-DWTP of Assiut University along the treatment line are plotted as shown in Fig. 2 with the two scenarios, with and without pre-chlorination. In both cases, the water temperature was approximately the same with a value of around 29˚C and did not exhibit significant changes through the treatment processes. Fig. 2(a) indicates that there was a little reduction in the measured pH value through the treatment processes in the two cases, which can be attributed to the effect of the alum coagulation. From Fig. 2(b) with the two cases of treatment, the water turbidity decreased along the treatment processes, although it slightly increased after the disinfection process in the case of without pre-chlorination due to the greater dose of the post-chlorination. Commonly, the water turbidity was found to be less in the case of pre-chlorination due to the effect of chlorine pre-oxidation in enhancing coagulation.

From Fig. 2(c) and (d), the apparent and true colors of the water decreased along the water treatment line, although the apparent color increased after the disinfection process in the case of without pre-chlorination due to the greater dose of the added post-chlorine.

3.1.2. Pre-chlorination effects on the algal counts

The algal count at different treatment stages in the full-scale plant of Assiut University was estimated for two scenarios, with and without pre-chlorination. As shown in Tables 1 and 2, the raw surface water of the branched canal that feeds the plant showed high algal counts with various phytoplankton structures belonging to the main four groups of algae, namely Chlorophyta (green algae), Bacillariophyta (diatoms), Dinophyta (dinoflagellates), and Cyanophyta (blue-green algae). In addition, Table 1 illustrates that the pre-chlorination process followed by alum coagulation and sedimentation decreased the total algal count to be 29.1% of that of the RW. The algal count still

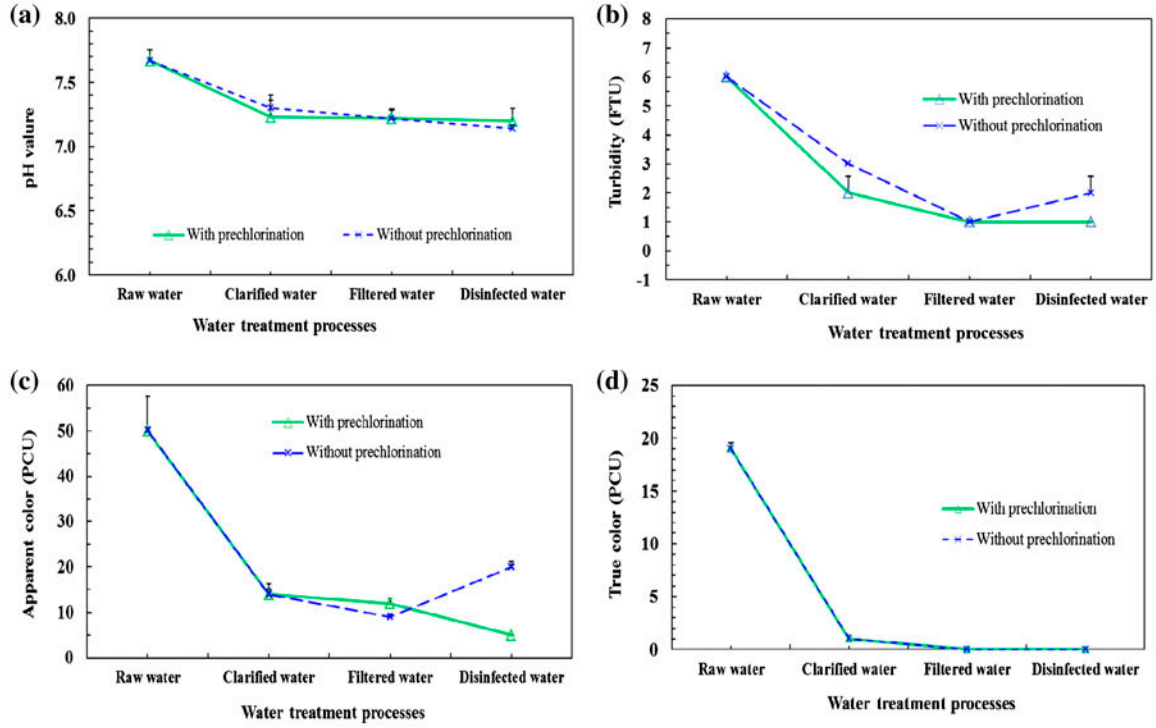

Fig. 2. The measured characteristics of the water through two treatment scenarios within the full-scale plant, with and without pre-chlorination; (a) pH value, (b) turbidity, (c) apparent color, and (d) true color. The error bars indicate standard errors. The data represent the means ± SE, $n = 3$.

Table 1
The algal counts through the treatment processes within the full-scale plant in the treatment line, with pre-chlorination

	Algal count (cells × 10^5/L)				
	Algal group				
Samples location	Chlorophyta	Bacillariophyta	Dinophyta	Cyanophyta	Total count
RW	23.0 ± 1.15^c	75.5 ± 2.02^c	1.0 ± 0.28	2.0 ± 0.50^a	101.5 ± 3.00^c
CW	9.0 ± 1.15^b	18.5 ± 0.86^b	0.0	2.0 ± 0.28^a	29.5 ± 0.50^b
FW	3.0 ± 0.50^a	8.5 ± 1.44^a	0.0	1.0 ± 0.32^a	12.5 ± 1.02^a
DW	3.0 ± 1.32^a	20.0 ± 1.73^b	0.0	1.0 ± 0.00^a	24.0 ± 1.80^b

Notes: RW = raw water, CW = clarified water, FW = filtered water, and DW = disinfected water. The means denoted by the same letter indicate a non-significant difference according to Duncan's test at $p < 0.05$. The data represent the means ± SE, $n = 3$.

Table 2
The algal counts through the treatment processes within the full-scale plant in the treatment line, without pre-chlorination

	Algal count (cells × 10^5/L)				
	Algal group				
Samples location	Chlorophyta	Bacillariophyta	Dinophyta	Cyanophyta	Total count
RW	23.0 ± 1.15^c	75.5 ± 2.02^b	1.0 ± 0.28	2.0 ± 0.50^a	101.5 ± 3.00^c
CW	13.0 ± 1.73^b	25.5 ± 0.87^a	0.0	1.5 ± 0.29^a	40.0 ± 1.53^b
FW	6.5 ± 0.87^a	21.0 ± 1.15^a	0.0	1.0 ± 0.29^a	28.5 ± 1.89^a
DW	6.5 ± 0.29^a	24.0 ± 3.51^a	0.0	3.0 ± 1.15^a	33.5 ± 2.57^a

Notes: RW = raw water, CW = clarified water, FW = filtered water, and DW = disinfected water. The means denoted by the same letter indicate a non-significant difference according to Duncan's test at $p < 0.05$. The data represent the means ± SE, $n = 3$.

decreased after the filtration process to be 12.3% of the RW count; however, it increased and the ratio reached to 23.6% after the disinfection process.

In the case of without pre-chlorination, the total algal counts of the treated water relative to that of the feeding water were found to be 39.4, 28.1, and 33.0% for the clarified, filtered, and DWs, respectively, as presented in Table 2. In the two scenarios, the observed increase in the algal count even with the disinfection process can be relayed on the presence of some stuck algal cultures on the internal wall surface of the storage tank. It is expected that some of these cultures were separated and resuspended in the DW due to the fluctuations of the water level in the tank in correspondence with the unbalance between the plant production and the community consumption. The impact of the fluctuated water surface in the reservoir on the algal count is upwardly when the water level rises due to the addition of the adherent algal cultures and vice versa.

In the case of pre-chlorination, the statistical analysis indicated significant differences in the algal counts between the raw and the treated water in both Chlorophyta and Bacillariophyta groups at $p = 0.092$, while the Cyanophyta group showed non-significant differences through the whole treatment line. The total algal count differed significantly through the stages of the treatment line (Table 1). With the scenario of without pre-chlorination, the algal counts of the Chlorophyta group expressed significant differences between the raw, clarified, and FW but the DW had a non-significant difference ($p = 1$) from the FW. In Bacillariophyta, the algal count of the RW differed significantly from those of the other treatment processes as given in Table 2. Cyanophyta had non-significant differences along the pass of the treatment line.

In general, the treatment with pre-chlorination proved more efficiency in the algal removal than without pre-chlorination. Although, the higher chlorine dosages could get better results, the risk of the DBPs limits its usage in high concentrations. From the given algal counts presented in Tables 1 and 2, it is observed that both the clarification and the down-flow filtration processes have little effects on Cyanophyta counts compared with the other algal groups. This observation results from the inherent buoyancy of

Cyanophyta that defects their removal by settling and downward filtration.

3.1.3. Pre-chlorination effects on the microcystins

Investigation of the cell-bound microcystins (intracellular MCs) and the water-released microcystins (extracellular MCs) is required for the assessment of the total MCs in water bodies. The effect of the treatment processes on the concentration of MCs was studied within the HC-DWTP of Assiut University in two cases, with and without pre-chlorination followed by alum coagulation, sedimentation, filtration, and post-chlorination. Intracellular and extracellular MCs in the collected samples were detected and measured.

Fig. 3 shows the variance of the measured MCs concentration (cell bound and released) through the water treatment line in the case of chlorine pretreatment. The total MCs of the RW reveals that the plant was challenged with a high concentration of 10.47 μg/L. One-way ANOVA statistical analysis on the measured MCs indicated significant differences between groups. A Duncan post hoc test revealed that the measured MCs in the RW differed significantly from those measured in the clarified, filtered, and DWs ($p < 0.05$), while it did not change significantly among the treatment processes.

According to Fig. 3, the measured concentrations of the intracellular and extracellular MCs were decreased dramatically through the clarification stage. The great destruction of the intracellular MCs from 5.32 to 0.14 μg/L through the clarification stage can be related to the pre-chlorination role in the algal removal. In addition, this reduction might support the concept that pre-chlorination causes algal cells membrane damage that resulted in releasing of cell-bound MCs and cellular organic matters to the surrounding water where the intracellular MCs were oxidized by chlorine. Such cellular organic compounds may present precursors of DBPs. The extracellular MCs reduction through the clarification stage (from 5.15 to 0.31 μg/L) can be attributed to the direct oxidation effect of pre-chlorination. In addition, the figure demonstrates that the chlorine pre-oxidation, alum coagulation, and clarification (before filtration) destructed the total MCs from 10.47 to 0.45 μg/L (95.7% removal efficiency) that complies with the WHO guideline (1.0 μg MC-LR/L). As shown in the figure, the intracellular MCs of the DW were decreased from 5.32 to 0.05 μg/L, through the treatment processes. On the other hand, the extracellular MCs were reduced from 5.15 to 0.30 μg/L. The slight increase in the total MCs in the DW over the FW can be interpreted by the effect of the accumulated algae on the internal wall surface of the storage tank.

Fig. 4 illustrates changes of the MCs concentration, both intracellular and extracellular through the treatment line in the case of without pre-chlorination. A solely chlorine dose was added after the filtration process for the post-disinfection. In this scenario, the statistical analysis showed significant changes in the total MCs through the water treatment line as $F = 74.658$ and $p < 0.05$. A Duncan post hoc test revealed that the MCs concentration in the raw and clarified water differed significantly from those in the filtered and disinfected water ($p < 0.05$).

Fig. 4 proves that the concentrations of the intracellular and extracellular MCs were slightly decreased through the water clarification stage (coagulation and sedimentation). The total MCs concentration was reduced from 10.47 to 9.74 μg/L (only 7.0% removal efficiency). However, the total MCs concentration was reduced after filtration to a value of 0.34 μg/L (96.8% overall removal efficiency) that is lower than the

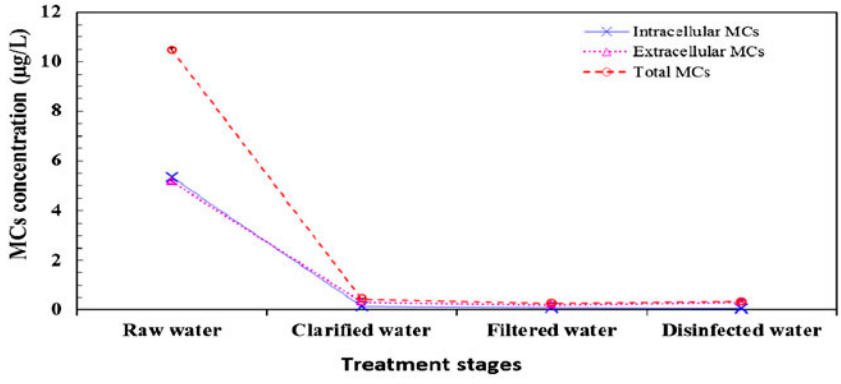

Fig. 3. The measured MCs concentration within the full-scale plant through the treatment line, with pre-chlorination. The error bars indicate standard errors. The data represent the means ± SE, $n = 2$.

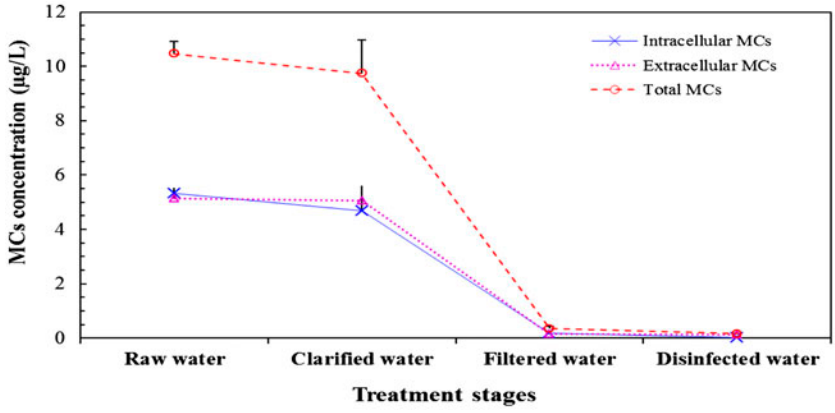

Fig. 4. The measured MCs concentration within the full-scale plant through the treatment line, without pre-chlorination. The error bars indicate standard errors. The data represent the means ± SE, $n = 2$.

WHO guideline (1.0 µg MC-LR/L). Both, the cell-bound and released MCs were effectively decreased through the filtration process. As the pressure sand filters were able to remove most of the intact algal cells, the intracellular MCs could be effectively removed too. On the other hand, the reduction of the extracellular MCs through the filtration process can be attributed to the biodegradation in the biofilm of the down-flow filter. Furthermore, the total MCs concentration was decreased to be 0.16 µg/L after the post-disinfection process, which is lower than the output MCs concentration of the pre-chlorination scenario (0.35 µg/L).

Finally, the full-scale treatment plant under study was able to remove MCs to levels below the WHO guideline in the two cases of treatment, with and without pre-chlorination. The case of without pre-chlorination has a distinct advantage over its higher overall removal efficiency of MCs as it removes the intact algal cells without ruptures, which reduces the precursors of DBPs. This means, by delaying the chlorination process to an application point after filtration, the releases of the cell-bound toxins and the formation of the chlorinated DBPs could be controlled. This change in the location of the chlorination point must be coupled with a good coagulation to remove the precursors and enhance the removal of the water turbidity and algae. Therefore, an alternative chemical preoxidant in the conventional water treatments is advisable with taking into consideration the removal of algae intact without cell rupture.

3.2. Laboratory investigations on permanganate pretreatment

To avoid the formation of the chlorinated DBPs, potassium permanganate ($KMnO_4$) was introduced as a substitute for chlorine to achieve pre-oxidation of eutrophic surface waters. In this study, a fishpond water sample was collected to clarify the effect of permanganate pretreatment followed by alum coagulation on some of the water physicochemical characteristics, algal count, and MCs concentration. The sample was enriched with BG11 media and jar tests were conducted at different permanganate doses, 0–2.0 mg $KMnO_4$/L followed by a constant coagulant concentration of aluminum sulfate (40 mg/L).

3.2.1. Effects of permanganate pretreatment on the water characters

Fig. 5 illustrates results of the jar tests for the effects of $KMnO_4$ doses as an alternative preoxidant followed by alum (aluminum sulfate) coagulation on some of the physicochemical characteristics of the enriched water sample (pH value, turbidity, apparent and true colors, and manganese residual). Fig. 5(a) shows that the dose of $KMnO_4$ pretreatment slightly affects pH values of the CW sample, as the value of pH changed from 8.4 at control (without permanganate pretreatment) to a minimum value of 8.2 at a dose of 0.50 mg/L after that, it mildly increased for the higher doses. Optimizing $KMnO_4$ dosage is also important for minimizing the residual turbidity after the clarification process. Fig. 5(b) demonstrates that at low $KMnO_4$ dosages (up to 0.5 mg/L), permanganate pre-oxidation effectively decreased the settled water turbidity. However, the higher doses of permanganate resulted in a steady increase in the residual turbidity. This increase can be interpreted as the higher $KMnO_4$ concentrations may change the polarity of the organic materials in the water sample, making them more hydrophilic and due to changes in the water color.

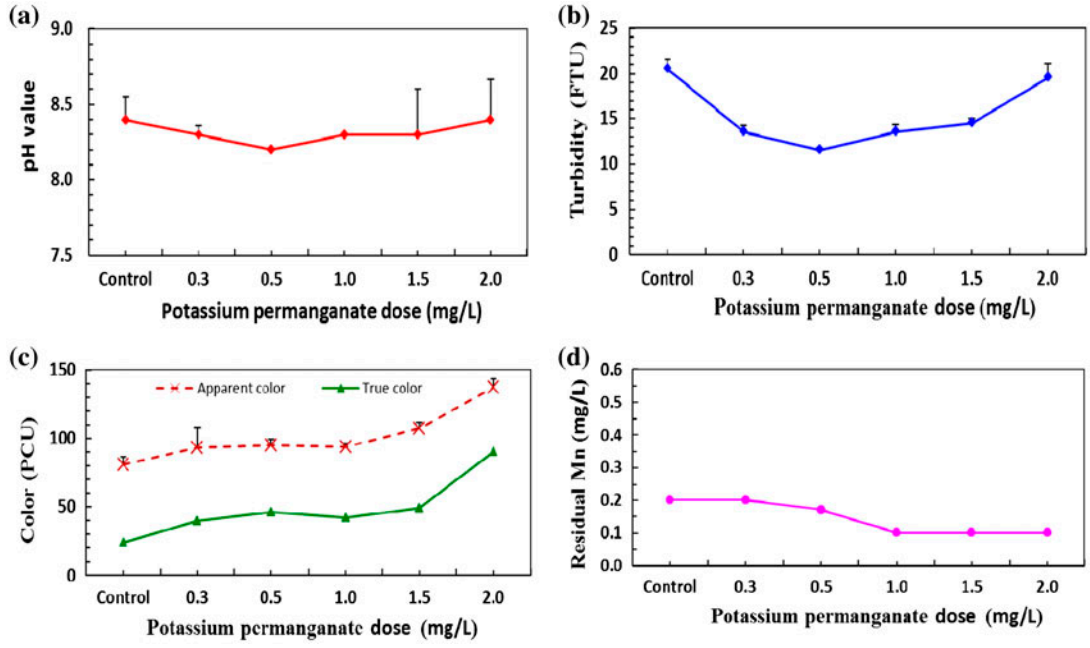

Fig. 5. Jar test results for the effects of permanganate pretreatment doses on the water characters of the enriched water sample; (a) pH value, (b) turbidity, (c) apparent and true colors, and (d) residual manganese (Mn). The error bars indicate standard errors. The data represent the means ± SE, $n = 3$.

When $KMnO_4$ reacts and manganese dioxide is formed, the inherent pink color of the permanganate solution changes to yellow or brown depending on the concentration. Fig. 5(c) illustrates that there was a significant increase in the apparent color of the CW sample from 81 PCU at control to 137 PCU with a dose of 2.0 mg $KMnO_4$/L. Similarly, the true color rose from 24 PCU at control to 90 PCU at a dose of 2.0 mg $KMnO_4$/L. The rate of increase in both apparent and true colors against the doses of $KMnO_4$ becomes disturbing beyond a concentration of 1.0 mg/L. Therefore, permanganate should be used with care, as an overdose can cause a pink color in water.

Fig. 5(d) shows that the residual manganese (Mn) concentration of the CW samples decreased from 0.2 mg/L at control to 0.1 mg/L at a dose of 1.0 mg $KMnO_4$/L. Further increasing in $KMnO_4$ dosages up to 2.0 mg/L did not achieve further enhancement in the residual Mn. These results agree with Ma and Liu [1] who found that the residual Mn in the FW of a full-scale plant that used $KMnO_4$ at a dosage of 0.50 mg/L was lower than the case of without permanganate pre-oxidation. Moreover, in consistent with the observations of this study, Ma and Liu [1] showed that the residual Mn concentration in the FW was very low for permanganate pre-oxidation followed by coagulation at pH values over 5.5, which presents in this study (pH ≥ 8.2) and is commonly employed in water treatment practices.

According to the United States Environmental Protection Agency, $KMnO_4$ removes the metal iron and manganese as well as decomposing plant materials. Permanganate oxidizes iron and manganese by converting ferrous (2+) iron into the ferric (3+) state and manganese (2+) to manganese (4+) state. The oxidized forms will precipitate as a ferric hydroxide and manganese hydroxide [26] and it is considered as another advantage of permanganate pre-oxidation. Finally, a dose of 0.50–1.0 mg $KMnO_4$/L is found to be the most suitable for clarifying the used water sample with respect to its physicochemical characters. More highly contaminated water may need higher dosages.

3.2.2. *Effects of permanganate pretreatment on the algal count*

The occurrence of the algal blooms and the possibility of producing cyanotoxins have become a major concern for the drinking water providers worldwide. Laboratory jar tests were used to study the effect of different effective doses of $KMnO_4$ (0 at control to 2.0 mg/L) pretreatment followed by 40 mg/L alum coagulation on the algal count of the enriched water sample. It was found that the total algal count of the settled water sample decreased from 15.1×10^6 cells/L at control to 3.0×10^6 cells/L at a dose of 2.0 mg

Table 3
Jar test results for the effect of permanganate pretreatment doses on the algal counts of the enriched water sample

Permanganate dose (mg/L)	Algal count (cells × 10^6/L)			Total count (cells × 10^6/L)
	Chlorophyta	Bacillariophyta	Cyanophyta	
C (control sample)	12.2 ± 1.19^{a}	1.5 ± 0.70^{a}	1.4 ± 0.15^{b}	15.1 ± 1.97^{d}
0.3	8.4 ± 0.83^{c}	1.4 ± 0.21^{a}	1.3 ± 0.17^{b}	11.1 ± 0.86^{c}
0.5	4.1 ± 0.67^{b}	1.2 ± 0.20^{a}	1.2 ± 0.20^{b}	6.5 ± 1.04^{b}
1.0	3.5 ± 0.29^{a,b}	1.2 ± 0.12^{a}	1.1 ± 0.07^{b}	5.8 ± 0.46^{a,b}
1.5	2.0 ± 0.44^{a,b}	1.1 ± 0.10^{a}	0.3 ± 0.06^{a}	3.4 ± 0.48^{a,b}
2.0	1.8 ± 0.15^{a}	1.0 ± 0.00^{a}	0.2 ± 0.05^{a}	3.0 ± 0.19^{a}

Notes: The means denoted by the same letter indicate a non-significant difference according to Duncan's test at $p < 0.05$. The data represent the means ± SE, $n = 3$.

$KMnO_4$/L and Cyanophyta count decreased from 1.4×10^6 to 0.2×10^6 cells/L as presented in Table 3. In this study, the overall removal efficiencies of the total algal count with doses of 0.3 and 2.0 mg $KMnO_4$/L were found to be 26.5 and 80.1%, respectively. Although higher $KMnO_4$ dosages could get a better effect on the algal count, they have adverse effects on the water turbidity and color. The results of the statistical analysis of the counted numbers of algae are given in Table 3.

3.2.3. Effects of permanganate pretreatment on the microcystins

Jar tests were performed on the enriched water sample to evaluate the effects of permanganate pre-oxidation at different doses followed by alum coagulation on the concentrations of both intracellular and extracellular MCs. Results of the control sample showed high concentrations of the intracellular and extracellular MCs as 1.62 and 10.08 μg/L, respectively. Duncan *post hoc* tests indicated that, the concentrations of MCs at control and 0.3 mg $KMnO_4$/L differed significantly from concentrations at 0.5 mg $KMnO_4$/L and shown very significant differences from those at 1, 1.5, and 2 mg $KMnO_4$/L ($p < 0.05$). From Fig. 6, it is observed that by increasing the dose of $KMnO_4$ in the effective range from 0 to 2 mg/L, the intracellular MCs of the clarified sample were decreased gradually from 1.62 to 0.14 μg/L and the extracellular MCs were destructed significantly from 10.08 to 0.40 μg/L. Consequently, the total MCs concentration was reduced from 11.7 to 0.54 μg/L. The most effective dose for removing the extracellular MCs from the used water sample was found to be 1.0 mg/L.

As shown in Fig. 6, the reduction rates of the intracellular and extracellular MCs in response to increasing the dose of $KMnO_4$ are completely different, which proves that the reduction was produced in different manners. There was a great reduction in the extracellular MCs concentration against the increase in $KMnO_4$ doses, which proves permanganate efficiency

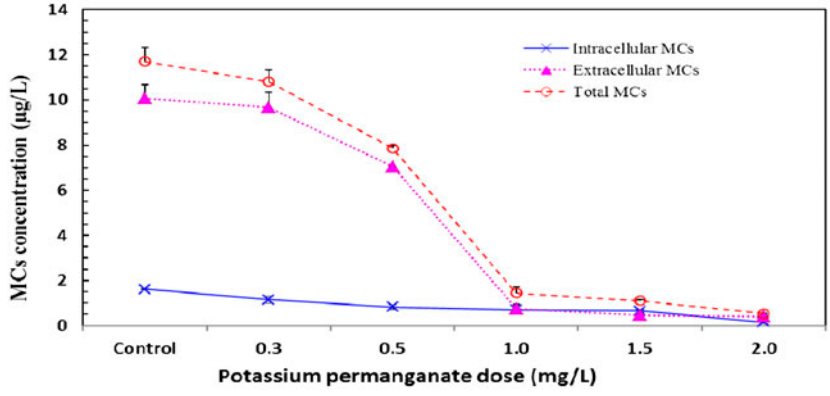

Fig. 6. Jar test results for the effect of permanganate pretreatment doses on the measured MCs concentration of the enriched water sample. The error bars indicate standard errors. The data represent the means ± SE, $n = 2$.

in oxidizing the extracellular MCs. The best $KMnO_4$ dosage for removing the extracellular MCs from the used water sample was found to be 1.0 mg/L. On the other hand, the mild reduction of the intracellular MCs versus $KMnO_4$ doses demonstrates that $KMnO_4$ does not affect the algal cells integrity and this reduction may be attributed to its enhancing effect on the clarification process. Consequently, the algal cells were removed intact, including their intracellular MCs. Accordingly, permanganate pre-oxidation is expected to reduce the precursors of DBPs. These results are in concomitant with those found by Xie et al. [27].

4. Conclusions

One of the most important needs of a society is a clean and secure drinking water supply. The effects of pre-chlorination and conventional treatment processes on some of the surface water characteristics, algal count, and MCs within a full-scale plant were investigated. The studied plant treats surface water that has a high level of MCs (10.47 μg/L). The validity of potassium permanganate ($KMnO_4$) for pre-oxidation as a substitute of chlorine has been studied by running jar tests on an enriched fishpond water sample. The most important findings are:

(1) A comparison between two treatment scenarios, with and without pre-chlorination, on a full-scale water treatment plant proved that the pre-chlorination case is relatively more efficient in removing the water turbidity and algae.
(2) Pre-chlorination followed by alum coagulation, sedimentation, filtration, and post-chlorination was found to be adequate for destructing the total MCs (intracellular and extracellular) concentration to a level lower than the WHO guideline (1.0 μg MC-LR/L). However, pre-chlorination causes lysis of the algal cells and releasing of bound toxins and cellular compounds that may present precursors of harmful DBPs.
(3) In the case of without pre-chlorination, the pressure rapid sand filters following alum coagulation and sedimentation processes within the studied plant removed significantly the intracellular and extracellular MCs to levels lower than the pre-chlorination case and comply with the WHO guideline.
(4) The case of without pre-chlorination was found to have a distinct advantage of preserving the algal cells integrity, which reduces the precursors of DBPs. Nevertheless, an alternative preoxidant other than chlorine should be used to ensure a good coagulation with keeping the algal cells integrity, removing the precursors of DBPs, and improving the removal of both water turbidity and algae.
(5) The performed jar tests on the used water sample showed that the residual manganese (Mn) was lower in the case of using $KMnO_4$ pretreatment than without permanganate pre-oxidation within the used concentration range (up to 2.0 mg $KMnO_4$/L). The best dosage of $KMnO_4$ for the used sample regarding to its physicochemical characteristics was found to be ranged from 0.50 to 1.0 mg/L.
(6) Pre-oxidation by $KMnO_4$ followed by alum coagulation for the used water sample could promote the aggregation of the algal cells to be removed by the following sedimentation process, intact without cell rupture and including their intracellular MCs and cellular compounds. The extracellular MCs were directly oxidized by $KMnO_4$. The most efficient permanganate dose for the used sample was found to be 1.0 mg/L.
(7) $KMnO_4$ improved the water physicochemical properties and the algal removal efficiency, decreased the algal toxins, and provided a better control of DBPs. Therefore, $KMnO_4$ could provide a suitable substitute for chlorine in water pretreatment processes.

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