Desalination and Water Treatment
www.deswater.com

1 (2009) 289–298

Removal of polycyclic aromatic hydrocarbons from Ismailia Canal water by chlorine, chlorine dioxide and ozone

O.A. Ali, S.J. Tarek*

National Research Center, El Buhouth Street, P.O. Box 12311, Dokki, Cairo, Egypt
Tel. +20 (12) 376-3699; Fax +20 (2) 3337-1479; email: omaytarek73@yahoo.com

Received 29 February 2008; accepted revised 28 July 2008

ABSTRACT

Survey and analysis for Ismailia Canal water indicated normal conditions for physicochemical parameters but high concentrations of organic compounds such as alkanes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and chlorinated hydrocarbons. Different doses of chlorine (2, 4 mg/L), chlorine dioxide (0.5, 2 mg/L), and ozone (0.5, 2 mg/L) were applied for treatment of raw Ismailia Canal water. The oxidation step was followed by coagulation with 30 mg/L alum, flocculation, and sedimentation. The removal percents with each oxidant were detected and 0.5 mg/L ozone showed better results in removal of PAH than 0.5 mg/L chlorine dioxide or 4 mg/L chlorine.

Keywords: Ismailia Canal water; PAH; Chlorine; Chlorine dioxide; Ozone

---

1. Introduction

Drinking water sources in Egypt are the River Nile and canals derived from the River Nile in addition to groundwater. Egypt consumes nearly 60 billion m^3 of water per year. Fifty-five billion m^3 of water are supplied by the River Nile which is considered the main source of water in Egypt while 5 billion m^3/y of water are supplied by underground water sources [1].

Ismailia Canal is one of drinking water sources in Egypt. It is used as drinking water source for Canal cities: Ismailia, Port Said, and Suez [2]. The system applied for drinking water treatment in Egypt includes prechlorination, coagulation using aluminum sulfate, flocculation, sedimentation, filtration, and postchlorination [3]. Several local and international studies revealed that conventional treatment processes do not remove organic compounds such as pesticide residues, hydrocarbons, chlorinated hydrocarbons, and polycyclic aromatic compounds. In addition, chlorination leads to the formation of halogenated organic compounds in raw water, such as trihalomethanes, haloacetic acids and many chloro-organics which have carcinogenic and mutagenic properties [4]. Accordingly, advanced oxidants such as ozone and chlorine dioxide replaced chlorine in disinfection. These oxidants have higher effect in removal of organic compounds in drinking water owing to their powerful oxidizing properties [5,6].

Polycyclic aromatic hydrocarbons (PAH) are formed by any kind of incomplete combustion of organic material in natural and anthropogenic processes (such as volcano activity, pyrolysis). Hence they are distributed ubiquitously. Concerning their mutagenic and carcinogenic potential, the United States Environmental Protection Agency (EPA) listed 16 PAH as priority pollutants [7]. Their genotoxicity rises with increasing number of condensed aromatic rings, while water solubility decreases drastically. Due to their hydrophobicity, PAHs are often dissolved in the dispersed phases of oil/water-emulsions or in hydrophobic organic materials. As a constituent of

---

* Corresponding author.

coal tar and its distillates, PAH occur at hazardous waste sites associated with fuel, gas, and wood-impregnation facilities, in contaminations by mineral oil and water from soil washing. Furthermore, they can be found in several industrial wastewaters especially from hydrocarbon production, coke plants, and metal processing industry. This wastewater showed concentrations of four-ring condensed pyrene (Pyr) and both five-ring condensed benzo(e)pyrene (BeP) and benzo(a) pyrene (BaP) in oily media. While PAH with less than five rings are usually biodegradable under aerobic conditions, the use of highly condensed PAH (X5 rings) by bacteria as sole carbon and energy source has not been proved yet. Therefore, a pretreatment by ozonation is necessary for a partial oxidation of highly condensed PAH, which is followed by a biological treatment of the formed oxidation products and the accompanying oil. Due to their low water solubility, the ozonation experiments presented in literature are conducted at low PAH-concentrations in water, by dissolution of PAH in pure solvents and in water-solvent mixtures or even in their crystalline state. Obviously, the disadvantage of using dissolved PAH in water is the high specific ozone dose in relation to the small PAH-concentrations [8].

One of the disinfecting options that show promising future is the use of chlorine dioxide. It has been in use since 1930s and was applied to water treatment in the United States in the 1940s. Primarily, it was used to control tastes and odors as well as to oxidize manganese and iron. Conventional treatment system, such as filtration and sedimentation are not adequate to remove organic compounds. Accordingly, chlorine dioxide is used mainly as preoxidant and disinfectant [9,10]. It is a very strong oxidant that suppresses chlorine in its ability to destroy pathogenic organisms. Reaction of chlorine dioxide with organics did not result in the formation of trihalomethanes. Consequently, it replaces chlorine to avoid the formation of organochlorine derivatives because it works as an oxidating agent and not a chlorinating one [11].

The final products of macromolecular aromatic compounds oxidation by chlorine dioxide are quinones and mono- and dicarboxylic acids, formed due to aromatic ring opening reaction [12]. During this process, odorous chlorophenols are not formed [13].

PAH-ozonation was performed in solvents to study the formed oxidation products like ozonides [14]. Another study showed that very different oxidation products are formed and the reaction pathway depends on the kind of solvent used [7].

2. Materials and methods

2.1. Extraction of organic compounds

Two liters of water samples were collected in glass bottles from Ismailia Canal (8 times during a year) for organic analysis. The glass containers were previously washed with dichloromethane. Organic compounds were extracted from water samples by liquid–liquid extraction technique using dichloromethane. The solvent layers were separated from the aqueous layers and passed through glass column containing anhydrous sodium sulfate. The extracts were cleaned up using alumina columns, and concentrated to 1 ml for injection into Hp 6890 gas chromatography.

The oxidized water was coagulated using 30 mg/L alum and then sedimented and filtered.

Different oxidants with different doses were used in oxidation as follows: chlorine (2 and 4 mg/L), chlorine dioxide (0.5 and 2 mg/L), and ozone (0.5 and 2 mg/L).

2.2. Preparation of chlorine dioxide

A pure solution of chlorine dioxide is prepared by slowly adding dilute sulfuric acid (H_2SO_4) to sodium chlorite ($NaClO_2$) solutions. Contaminants such as chlorine are removed by passing the gas through sodium chlorite ($NaClO_2$) scrubber and then into distilled water in steady stream of air [15].

2.3. Reaction between chlorine dioxide and organic compounds

Organic compounds mixture was prepared in 5-L glass bottle. Chlorine dioxide was added at concentrations of 0.5 mg/L and 2 mg/L. Two-liter sample was taken and analyzed after 30 min contact time.

2.4. Preparation of ozone

Ozone was prepared using ozone product plant for laboratories OL 0.5/50 A (Adolf Ireek, Germany).

2.5. Reaction between ozone and organic compounds

Reactions were carried out in homogenous batch system at 25°C. Ozone solution was prepared by passing an ozone–oxygen mixture through a sintered glass dispersed to 5000 ml distilled water. The ozone concentration was determined by the iodometric method. One-liter samples were withdrawn after 15 min for analysis.

2.6. Reproducibility and recovery

The recovery % of the studied PAHs varied between 85% and 110% (Table 1). The reproducibility was calculated and the standard division was varied between 0.7 and 3.2 (Table 2).

3. Results and discussion

3.1. Removal of PAHs by chlorine

The most chemical reactions of chlorine with organic matters in aqueous solution may be grouped into three

Table 1
Recovery % for the studied PAHs

Polycyclic aromatic hydrocarbons	Added concentration (μg/l)	Actual concentration (μg/l)	Recovery (%)
Naphthalene	40	38.840	97.10
Acenaphthylene	40	37.378	93.45
Acenaphthelene	40	44.701	111.75
Fluorene	40	35.170	87.93
Phenanthrene	40	42.140	105.35
Anthracene	40	42.742	106.85
Fluoranthene	40	42.278	105.70
Benzo (k) fluorancene	40	41.947	104.87
Pyrene	40	35.250	88.13
Chrysene	40	32.851	82.13
Benzo (a) anthracene	40	35.574	88.94
Benzo (b) fluoranthracene	40	45.521	113.80
Benzo (a) pyrene	40	45.647	114.12
Indeno (1,2,3-cd) pyrene	40	44.920	112.30
Dibenzo (a,h) anthracene	40	45.354	113.39
Benzo (ghi) perylene	40	39.694	99.24
1-methyl naphthalene	40	33.733	84.33
2-methyl naphthalene	40	35.833	89.58
Total concentration	720	719.574	99.94

Table 2
Reproducibility experiment for PAHs

Chlorinated hydrocarbons	Added concentration (μg/l)	First actual concentration (μg/l)	Second actual concentration (μg/l)	Third actual concentration (μg/l)	Mean	Standard division
Naphthalene	40	38.840	40.245	39.654	39.580	0.705
Acenaphthylene	40	37.378	39.235	36.988	37.867	1.201
Acenaphthelene	40	44.701	40.238	41.623	42.187	2.284
Fluorene	40	35.170	38.247	36.835	36.751	1.540
Phenanthrene	40	42.140	37.983	40.221	40.115	2.081
Anthracene	40	42.742	39.678	38.912	40.444	2.027
Fluoranthene	40	42.278	40.346	41.002	41.209	0.982
Benzo (k) fluorancene	40	41.947	43.237	40.223	41.802	1.512
Pyrene	40	35.250	39.004	37.223	37.159	1.878
Chrysene	40	32.851	38.224	36.001	35.692	2.700
Benzo (a) anthracene	40	35.574	40.112	36.998	37.561	2.321
Benzo (b) fluoranthracene	40	45.521	43.998	42.223	43.914	1.651
Benzo (a) pyrene	40	45.647	42.998	41.005	43.217	2.329
Indeno (1,2,3-cd) pyrene	40	44.920	45.112	41.009	43.680	2.315
Dibenzo (a,h) anthracene	40	45.354	39.004	41.298	41.885	3.215
Benzo (ghi) perylene	40	39.694	41.234	39.004	39.977	1.142
1-methyl naphthalene	40	33.733	39.124	36.667	36.508	2.699
2-methyl naphthalene	40	35.833	37.129	37.990	36.984	1.086
Total concentration	720	719.573	725.148	704.876	716.532	8.55

general types, namely, oxidation, substitution, and addition. Carbohydrates and related compounds are examples of compounds to be found in natural waters, and are subject only to oxidative reaction [3]. The second reaction type of interest is substitution in aromatic or heterocyclic compounds, and the haloform reactions. Aromatic compounds such as phenols and aromatic acids are readily chlorinated in aqueous solutions by HOCl and OCl^- to yield their chlorinated analogs [16]. The reaction consists of alternative halogenation and hydrolysis steps. The last type of organic reactions with chlorine addition occurs with organics containing reactive double ponds such as unsaturated compounds, which are found in natural waters [3].

The removal of PAHs using 2 mg/L and 4 mg/L chlorine doses was studied. The total removals of PAHs using 2 mg/L chlorine ranged between 11.9% and 46.4%, while their total removals using 4 mg/L chlorine ranged between 46.4% and 67.7%.

The removal of PAHs depends on their concentration in raw water. The removal % decreased with increasing the total concentration of PAHs in raw water.

The removal % of naphthalene were less than its derivatives (2-methyl naphthalene, acenaphthalene, and acenaphthylene). The removal % of 2-methyl naphthalene, acenaphthalene, and acenaphthylene were 93.9%, 32.9% and 36.5%, respectively, using 2 mg/L chlorine and they were 98.1%, 65.1%, and 63%, respectively, using 4 mg/L chlorine, while the removal % of naphthalene itself were 27.4% and 60.8% with 2 mg/L and 4 mg/L chlorine doses, respectively. This was attributed to presence of double bond in the cyclopentene ring in the case of acenaphthylene which was easily attacked by chlorine molecule to form dichloro acenaphthylene which was hydrolyzed to form acenaphthelene diol and the probability of ring rupture was too high to form 1,8-naphthalene dimethanol which was oxidized finally to form 1,8-naphthalene dicarboxylic acid as shown in Fig. 1 [16] and the presence of methyl group in the case of methyl naphthalene which was easily substituted to form the mixture of alcohol, aldehyde and carboxylic acid as shown in Fig. 2, the intermediates and the final byproducts were identified by GC/MS (Varian 4000).

Accordingly, the removal % for acenaphthylene (2 benzene rings and 1 pentene ring) were higher than those of acenaphthelene (2 benzene rings and 1 pentane ring) due to the presence of double bond which enhanced the addition reaction [3] to form the dichloro derivatives which easily hydrolyzed to form diol derivatives. On the other hand, 1-methyl naphthalene was not detected in Ismailia Canal water during this study (March–December 2004).

Increasing the number of benzene rings leads to decrease in the removal % due to difficulty of chlorine to react with macromolecules of high molecular weight and high number of benzene rings. The removal % for anthracene (three benzene rings) were higher than those for benzo (a) anthracene (four benzene rings) and their removal % were 33.1% and 26.8%, respectively using 2 mg/L chlorine and they were 63.9% and 61.4%, respectively, using 4 mg/L chlorine dose (Table 3).

Indeno (1,2,3-cd) pyrene, that has the highest molecular weight (5 benzene rings and 1 cyclopentane ring), had the lowest removal % (22.9% and 33.3%) using 2 mg/L chlorine and 4 mg/L chlorine doses, respectively. As well, pyrene (4 aromatic benzene rings) had low removal %

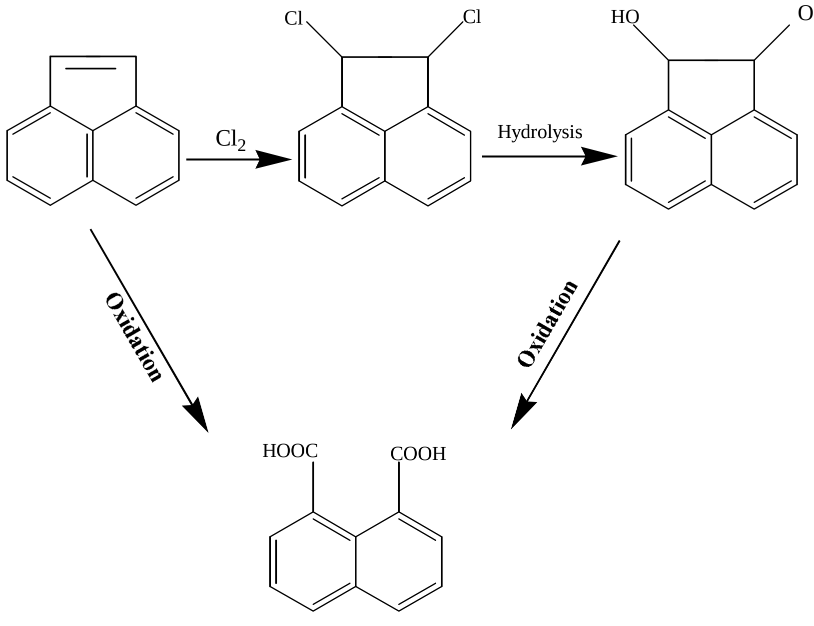

Fig. 1. Oxidation of acenaphthylene by chlorine and the by-products formed.

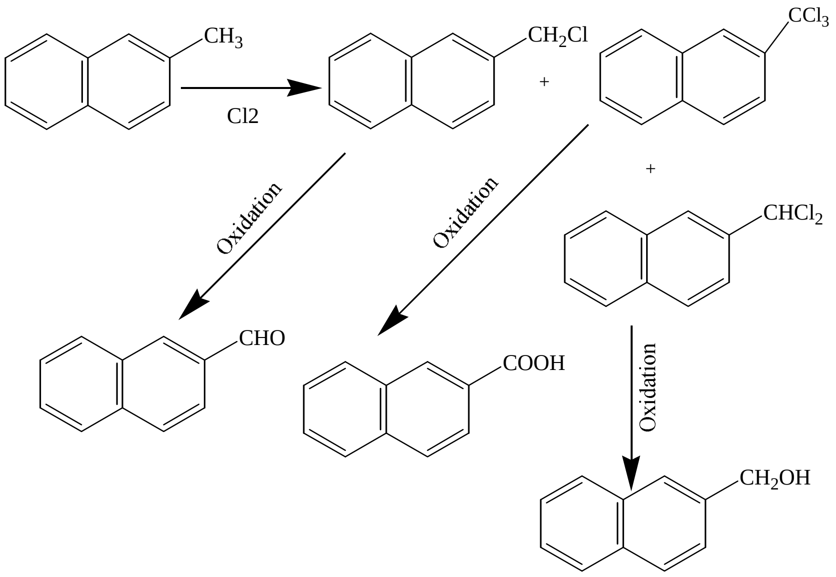

Fig. 2. Oxidation of 2- methyl naphthalene by chlorine and the by-products formed.

Table 3
Treatment of Ismailia Canal raw water with chlorine

Organic compounds	Raw	2 mg/L chlorine	% removal	4 mg/L chlorine	% removal
Naphthalene	1.838	1.335	27.38	0.720	60.81
Acenaphthylene	0.230	0.146	36.5	0.085	63.04
Acenaphthelene	0.586	0.393	32.91	0.225	61.60
Fluorene	2.110	1.091	48.32	0.769	63.56
Phenanthrene	2.688	1.723	35.90	0.839	68.77
Anthracene	1.532	1.025	33.10	0.553	63.90
Fluoranthene	6.066	4.254	29.87	3.012	50.34
Benzo (k) fluorancene	ND*	ND*	ND*	ND*	ND*
Pyrene	3.278	2.511	23.39	1.782	45.63
Chrysene	4.831	3.189	33.98	1.589	67.11
Benzo (a) anthracene	0.288	0.212	26.63	0.111	61.36
Benzo (b) fluoranthracene	9.520	5.917	37.84	3.380	64.49
Benzo (a) pyrene	ND*	ND*	ND*	ND*	ND*
Indeno (1,2,3-cd) pyrene	14.593	11.254	22.88	9.731	33.32
Dibenzo (a,h) anthracene	ND*	ND*	ND*	ND*	ND*
Benzo (ghi) perylene	ND*	ND*	ND*	ND*	ND*
1-methyl naphthalene	ND*	ND*	ND*	ND*	ND*
2- methyl naphthalene	1.967	0.120	93.92	0.038	98.06
Total	48.208	33.978	29.52	21.285	55.85

*ND = not detected

(23.4% and 45.6%) using 2 mg/L chlorine and 4 mg/L chlorine doses, respectively, due to its chemical structure. Benzo (a) pyrene (5 benzene rings) was not detected in Ismailia Canal raw water during this study as shown in Table 1.

The removal % of fluorancene were 29.9% and 50.3% using 2 mg/L and 4 mg/L chlorine, respectively. On the other hand, its benzo derivatives (benzo (a) fluorancene and benzo (k) fluorancene) were not detected in raw water during this study.

As shown in Table 1, the removal % of other PAHs ranged between 34–48.3% and 63.6–68.8% using 2 mg/L chlorine and 4 mg/L chlorine doses, respectively.

3.2. Removal of PAHs by chlorine dioxide

Chlorine dioxide reacts with PAHs via two mechanisms which are:

i) Substitution of hydrogen atoms in the benzene rings or in its substituents to form halogenated derivatives [16–18] which are hydrolyzed to form hydroxylated derivatives.
ii) Oxidation which may lead to ring rupture [13,18] by removal of electron from PAHs by chlorine dioxide to form radical and chlorite ion followed by attack of another chlorine dioxide molecule to form quinones or alcohols and by successive oxidation ring rupture takes place [19].

The final products of macromolecular aromatic compounds (PAHs) oxidation by chlorine dioxide are quinones and mono- and dicarboxylic acids, formed due to aromatic ring opening reaction. During this process odorous chlorophenols are not formed. Chlorine dioxide is able to oxidize macromolecular organic compounds' methoxy groups to aliphatic hydroxylic groups.

The removal of PAHs depends on their concentration in raw water since maximum removal % of PAHs were detected in August where concentration of PAHs in raw water was 43.9 μg/l and the removal % were 69.6% and 90.6% using 0.5 mg/L and 2 mg/L chlorine dioxide doses, respectively. While the minimum removal % were 42.12% and 69.92% in March with 0.5 mg/L chlorine dioxide and 2 mg/L chlorine dioxide, respectively, when the concentration of PAHs was 48.6 mg/L because with lower concentrations of PAHs successive oxidation with chlorine dioxide will take place since, more than chlorine dioxide molecule can attack one molecule of alkanes due to low concentration.

As shown in Table 2, the removal % of naphthalene was less than its derivatives. The removal % of acenaphthylene, acenaphthelene, and 2-methyl naphthalene were 69.1%, 93.3% and 96.3%, respectively, using 0.5 mg/L chlorine dioxide dose for oxidation and they were almost totally removed using 2 mg/L chlorine dioxide. On the other hand, the removal % of naphthalene itself were 36.7% and 71.6% using 0.5 mg/L and 2 mg/L chlorine dioxide doses for oxidation. As well, 1-methyl naphthalene was not detected during the period of this study. Acenaphthylene had the high removal. This was attributed to the presence of double bond in the cyclopentane ring in the case of acenaphthylene and this was easily attacked by chlorine molecule to form dichloro acenaphthylene which was hydrolyzed to form acenapthylene diol. The probability of ring rupture is too high to form 1,8-naphthalene dimethanol which oxidized finally to form 1,8-naphthalene dicarboxylic acid which was cleaved to form tartaric acid, glyoxalic acid and glyoxal as shown in Fig. 3 [12], the intermediates and the final byproducts were identified by GC/MS (Varian 4000).

On the other hand, 2-methyl naphthalene had the highest removal as mentioned due to presence of two possibilities for chlorine dioxide to react with it either substitution on methyl group or addition to the benzene ring which leads to ring rupture to form many by-products as mentioned in Fig. 4. The intermediates and the final byproducts were identified by GC/MS (Varian 4000).

Increasing the number of benzene rings leads to decrease in removal %. The removal % for anthracene (three aromatic benzene rings) were higher than those for benzo (a) anthracene (four aromatic benzene rings) and their removal % were 50.8% and 47.7% respectively, using 0.5 and 2 mg/L chlorine dioxide doses. Dibenzo (a,h) anthracene (5 aromatic benzene rings) was not detected in Ismailia Canal raw water during the period of this study.

Indeno (1,2,3-cd) pyrene (5 aromatic benzene rings and 1 pentane ring) and benzo (b) fluoranthene had low removal % (54.2% and 44.5% using 0.5 mg/L chlorine dioxide and they were 73.4% and 72.9% using 2 mg/L chlorine dioxide). On the other hand, pyrene (4 aromatic benzene rings) had higher removal % (83.9% and 95.3% using 0.5 and 2 mg/L chlorine dioxide dose, respectively, while benzo (a) pyrene was not detected in Ismailia Canal raw water during the period of this study. The removal of fluorancene was 65.4% using 4 mg/L chlorine dioxide.

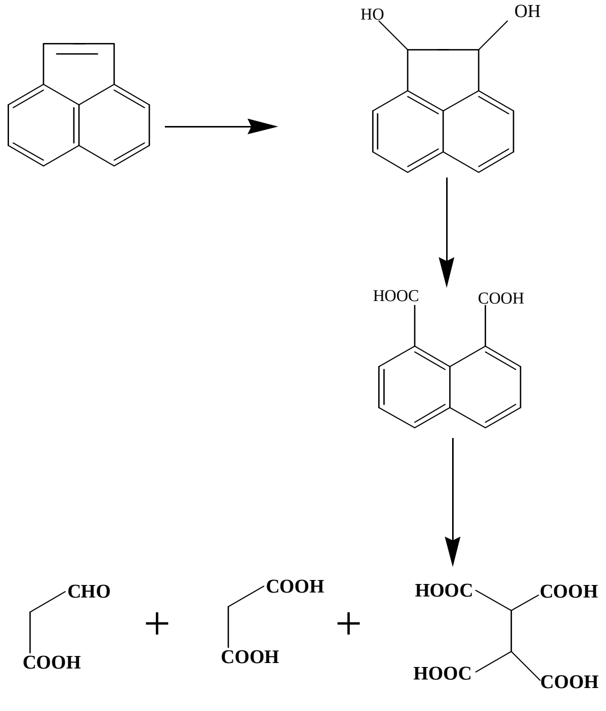

Fig. 3. Oxidation of acenaphthylene by chlorine dioxide and the by-products formed.

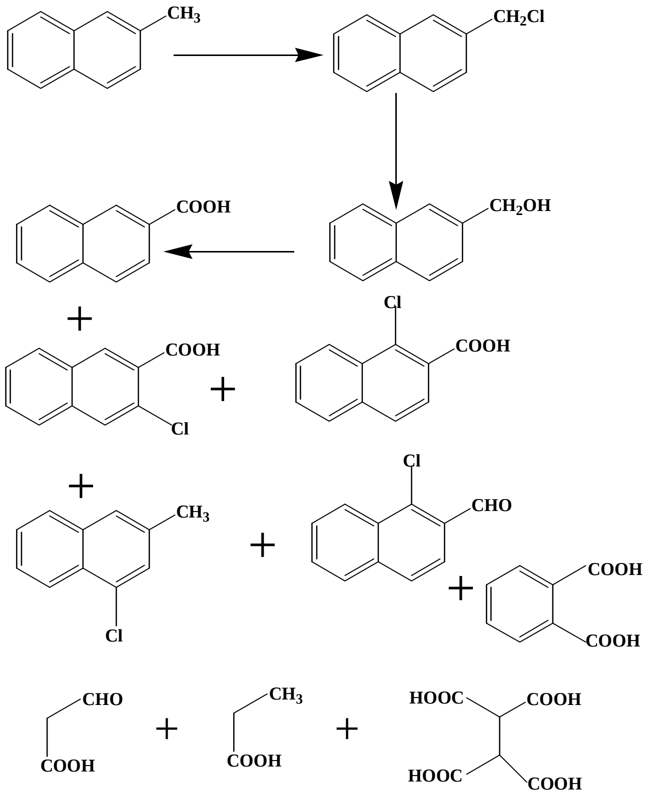

Fig. 4. Oxidation of 2-methylnaphthalene by chlorine dioxide and the by-products formed.

As shown in Table 4, the removal % of other PAHs ranged between 46.2% and 56.9% using 0.5 mg/L chlorine dioxide dose.

The higher removal showed with chlorine dioxide regarding chlorine was attributed to the high oxidation ability of chlorine dioxide and the variation in results was attributed to the competition between molecules during oxidation process.

3.3. Removal of PAHs by ozone

PAH-ozonation was performed in solvents to study the formed oxidation products like ozonides. Chen et al. [14] showed that very different oxidation products are formed and the reaction pathway depends on the kind of solvent used. Only a few studies focus on systems containing oil, like that of Kornmuller and Wiesmann [7] who observed a selective ozone attack on aromatic naphthalene derivatives (two rings) as opposed to aliphates during the ozonation of kerosene films floating on buffer solutions.

PAH ozonation leads to formation of polyhydroxylated aromatics, quinonoids both saturated and unsaturated oxygenated aliphatic compounds. Degradation goes finally to formation of carbon dioxide and water [17,18]. Ozonation of PAH such as pyrene (which is mutagenic and carcinogenic) results in formation of short chain polar aliphatic compounds as the major products [8].

Table 4
Treatment of Ismailia Canal raw water with chlorine dioxide

Organic compounds	Raw	0.5 mg/L ClO_2	% removal	2 mg/L ClO_2	% removal
Naphthalene	1.838	1.164	36.65	0.522	71.62
Acenaphthylene	0.230	0.071	69.13	0.000	100
Acenaphthelene	0.586	0.039	93.32	0.024	95.90
Fluorene	2.110	0.960	54.53	0.539	74.47
Phenanthrene	2.688	1.159	56.87	0.659	75.47
Anthracene	1.532	0.754	50.76	0.368	76.00
Fluoranthene	6.066	3.737	38.39	2.097	65.43
Benzo (k) fluorancene	ND*	ND*	ND*	ND*	ND*
Pyrene	3.278	0.526	83.94	0.154	95.31
Chrysene	4.831	2.601	46.16	0.755	84.38
Benzo (a) anthracene	0.288	0.151	47.66	0.074	74.46
Benzo (b) fluoranthracene	9.520	5.280	44.54	2.530	73.42
Benzo (a) pyrene	ND*	ND*	ND*	ND*	ND*
Indeno (1,2,3-cd) pyrene	14.593	6.678	54.24	3.958	72.88
Dibenzo (a,h) anthracene	ND*	ND*	ND*	ND*	ND*
Benzo (ghi) perylene	ND*	ND*	ND*	ND*	ND*
1-methyl naphthalene	ND*	ND*	ND*	ND*	ND*
2-methyl naphthalene	1.967	0.073	96.29	ND*	100
Total	48.208	23.425	51.41	11.293	76.57

*ND = not detected

The mechanism of preozonation effect is identified as the decrease of colloidal charge density of the humic at early stages of oxidation. So preozonation was found to decrease the required alum dose by 13–30% and improved the quality of water after coagulation [20]. Accordingly, the amount of alum used after preozonation in this study was decreased from 30 mg/L alum (as used with chlorine and chlorine dioxide) to 20 mg/alum.

The removal of PAHs using 0.5 mg/L and 2 mg/L ozone doses was studied. As shown in Table 3, the removal % of naphthalene were different from its derivatives (acenaphthylene and 2-methyl naphthalene). Their removal % were 86.6% for naphthalene and 99.7% and 96.8% for acenapthylene and 2-mthyl naphthalene, respectively, using 0.5 mg/L ozone, while they were totally removed using 2 mg/L ozone (Table 5 and Fig. 5).

Ozone showed higher removal for naphthalene and its derivatives than chlorine dioxide and chlorine, and this was attributed to selective ozone attack on aromatic naphthalene derivatives. Also, acenaphthylene had higher removal % than acenaphthelene due to the presence of the double bond in pentene ring, then an electrophilic addition of molecular ozone takes place at the electron rich parts of organic molecules like C–C double bonds [7] which enhances the ability of ring rupture as mentioned in Fig. 5 which shows low molecular weight by-products such as carbon dioxide and water. The intermediates and the final byproducts were identified by GC/MS (Varian 4000).

Ozone is a strong oxidant and has higher selectivity in attacking the aromatic benzene ring. Accordingly, increasing the number of benzene rings and/or the molecular weight does not decrease their removal %. For example, benzo (a) anthracene (4 benzene rings) had higher removal than anthracene (3 benzene rings). Indeno (1,2,3-cd) pyrene (5 aromatic benzene rings and 1 pentane ring) showed more removal than lower molecular weight PAH compounds such as anthracene, fluorancene, phenanthrene, and chrysene. The variation in removal was attributed to the competition between molecules during hydroxyl radical attach via chain radical mechanism [7]. As example, the ozonation of pyrene, four benzene rings, leads to ring rupture and formation of aliphatic by-products (Fig. 6). The intermediates and the final byproducts were identified by GC/MS (Varian 4000).

As mentioned before, some PAHs were not detected in Ismailia Canal raw water during this study such as benzo (k) fluorancene, benzo (a) pyrene, dibenzo (a,h) anthracene, benzo (g,h,i) pyrelene and 2-methyl naphthalene. Some other PAHs were almost totally removed

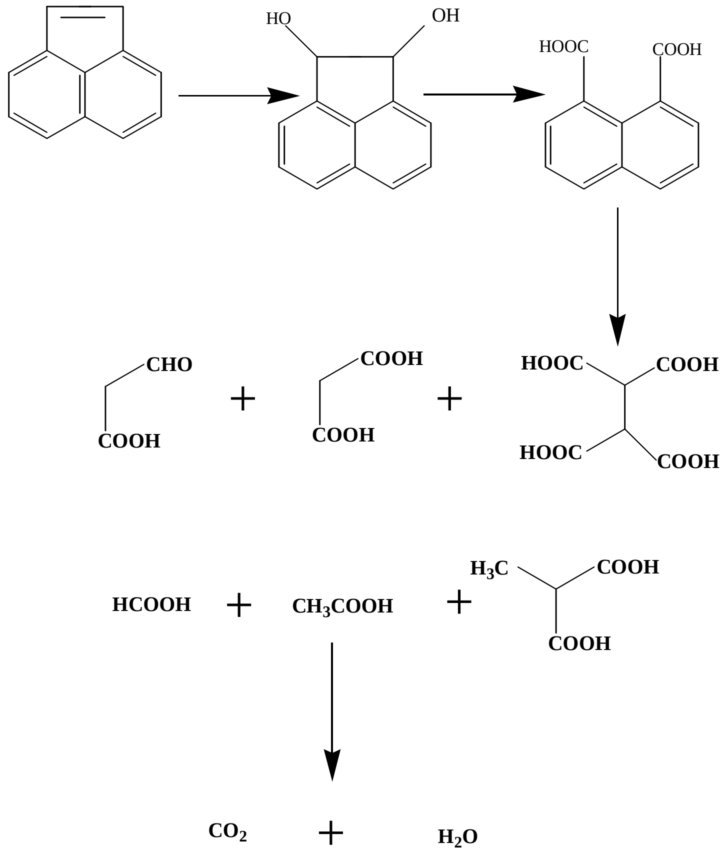

Fig. 5. Oxidation of acenaphthylene by ozone and the by-products formed.

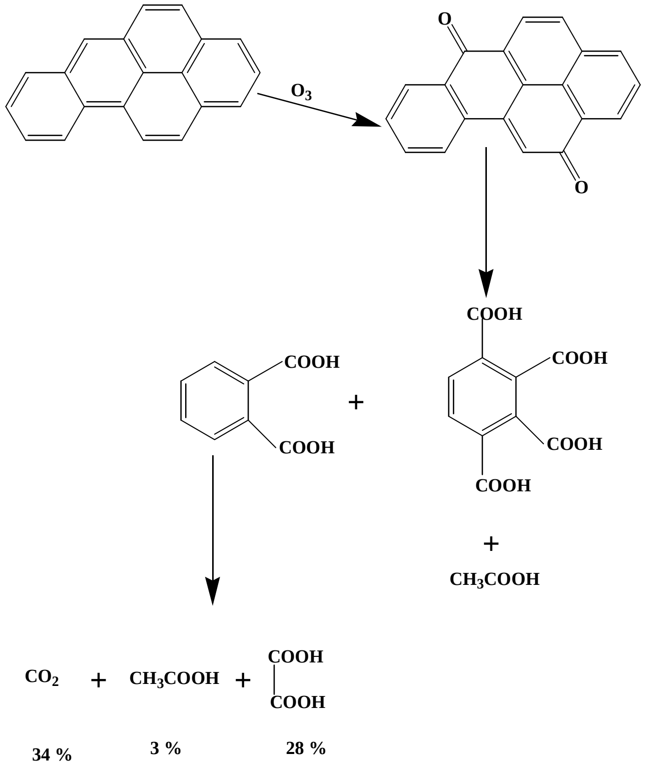

Fig. 6. Oxidation of 3, 4-benzopyrene by ozone and the by-products formed.

using 2 mg/L ozone dose during this study (acenaphthylene, benzo (a) anthracene, 2- methyl naphthalene, fluorancene and naphthalene).

The order of removal for total PAHs with different oxidants was as follows: ozone > chlorine dioxide > chlorine.

Usage of 2 mg/L ozone showed the highest removal, while usage of 2 mg/L chlorine was the lowest. The order of all oxidizing agents using different concentration was as follows: 2 mg/L O_3 > 2 mg/L ClO_2 > 0.5 mg/L O_3 > 4 mg/L Cl_2 > 0.5 mg/L Cl_2 > 2 mg/L Cl_2.

Accordingly, it is better for drinking water treatment plants that their intake located in Ismailia Canal raw water to use 0.5 mg/L ozone in preozonation with 20 mg/L alum for coagulation or 2 mg/L chlorine dioxide in preoxidation step with 30 mg/L alum for coagulation in order to avoid formation of halogenation by-products and their hazardous effect.

4. Conclusion

Ozone had the highest removal among the studied oxidants to oxidize the PAHs from Ismailia Canal raw water which is contaminated with petroleum oil due to the presence of several oil companies in the studied area (8 km from the start of the canal). Using 0.5 mg/L ozone in preozonation step with 20 mg/L alum for coagulation

Table 5
Treatment of Ismailia Canal raw water with ozone

Organic compounds	Raw	0.5 mg/L ozone	% removal	2 mg/L ozone	% removal
Naphthalene	1.838	0.243	86.80	0.086	95.30
Acenaphthylene	0.230	0.001	99.73	ND*	100
Acenaphthelene	0.586	0.163	72.25	0.092	84.32
Fluorene	2.110	0.617	70.75	0.569	73.05
Phenanthrene	2.688	1.012	62.36	0.657	75.55
Anthracene	1.532	0.524	65.76	0.330	78.46
Fluoranthene	6.066	0.805	86.73	0.239	96.06
Benzo (k) fluorancene	ND*	ND*	ND*	ND*	ND*
Pyrene	3.278	0.716	78.17	0.243	92.58
Chrysene	4.831	1.606	66.75	0.557	88.4
Benzo (a) anthracene	0.288	0.006	97.92	0.000	100
Benzo (b) fluoranthracene	9.520	2.424	74.54	1.239	86.99
Benzo (a) pyrene	ND*	ND*	ND*	ND*	ND*
Indeno (1,2,3-cd) pyrene	14.593	3.813	73.87	2.689	81.58
Dibenzo (a,h) anthracene	ND*	ND*	ND*	ND*	ND*
Benzo (ghi) perylene	ND*	ND*	ND*	ND*	ND*
1-methyl naphthalene	ND*	ND*	ND*	ND*	ND*
2-methyl naphthalene	1.967	0.063	96.78	ND*	100
Total	48.208	11.995	75.12	6.614	86.28

*ND = not detected

or 2 mg/L chlorine dioxide in preoxidation step with 30 mg/L alum for coagulation shows so much better removal for PAHs than using chlorine. Pre-ozonation was found to decrease the required alum dose by 33.3% and improved the quality of water after coagulation.

References

[1] M.A. El-Dib and K.A. Rizka, Chlorinated disinfection by products in drinking water at Beni-Sueif, Egypt: A case study. IV International Conference, Water Supply and Water Quality, Poland, September 2000, pp. 92–102.

[2] S.J. Tarek, development of water treatment technologies for the removal of hazardous pollutants. PhD thesis, Cairo University, 2008.

[3] M.A. El-Dib, M.I. Badawy and K.A. Rizka, Alternative pre-oxidation procedures for the control of disinfection by products. IV International Conference, Water Supply and Water Quality, Poland, September, 2000, pp. 615–622.

[4] M.A. El-Dib and K.A. Rizka, THMs formation during chlorination of raw Nile River water, Water Res., 29 (1995) 375–378.

[5] D.A. Reckhow, P.C. Singer and P.L. Malcolm, Chlorination of humic materials: by-product formation and chemical interpretations, Environ. Sci. Technol., 24 (1990) 1655–1664.

[6] A. Nyström, A. Grimvall, C. Krantz-Rülcker, R. Sävenhed and K. Ackerstand, Drinking water off flavour caused by 2,4,6,-trichloroanisole, Water Sci. Technol., 25 (1992) 241–249.

[7] A. Kornmuller and U. Wiesmann, Ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions: mass transfer and reaction kinetics, Water Res., 37 (2003) 1023–1032.

[8] C.E. Corless, G.L. Reynolds, J.D. Graham and R. Perry, Ozonation of pyrine in aqueous solution, Water Res., 24 (1990) 1119–1123.

[9] B.W. Long, R.A. Husley and R.C. Hoehn, Complementary uses of chlorine dioxide and ozone for drinking water treatment, Ozone Sci. Eng., 21 (1999) 465–476.

[10] D. Sales, M.J. Valcárel, L. Pérez and E. Martinez-Ossa, Activated sludge treatment of wine-distillery wastewaters, J. Chem. Technol. Biotechnol., 40 (1987) 85–99.

[11] U. Z´wietlik, S. Rackzyk-Stanislawiak, W. Bilozor, J. Ilecki and L. Nawrocki, Adsorption of natural organic matter oxidized with ClO_2 on granular activated carbon, Water Res., 36 (2002) 2328–2336.

[12] Y. Sun and D.S. Argyropoulas, A comparison of the reactivity and efficiency of ozone, chlorine dioxide, dimethyldioxitane and hydrogen peroxide with residual Kraft lignin, Holzforschung, 50 (1996) 175–182.

[13] V.A. Demin, V.V. Shereshovets and J.B. Monakov, Reactivity and the problems of oxidative destruction of lignin with peroxyreagents, Uspiekhi, 1999, pp. 1029–1050.

[14] J.P. Chen, S.L. Kim and Y.P. Ting, Optimization of membrane physical and chemical cleaning by statistical design approach, J. Membr. Sci., 219 (2003) 27–45.

[15] Standard Methods for the Examination of Water and Wastewater, 20th ed., 2000.

[16] J.G. Smith, S.F. Lee and A. Netzer, Model studies in aqueous chlorination: The chlorination of phenols in dilute aqueous solutions, Water Res., 10 (1976) 985–990.

[17] A.S. El-Din, A. Bermond, N. Rutledge and C. Ducouze, Analysis of the ozonation products of aliphatic acid in water using combined HPLC, Mass Spectrometry Analyst, 109 (1984) 817–821.

[18] S.J. Tarek, Comparative studies on the removal of organic micro-pollutant from drinking water by chlorine dioxide, ozone and activated carbon. MSc thesis, Cairo University, 2001.

[19] J.E. Wajon, D.H. Rosenblatt and E.P. Burrowa, Oxidation of phenol and hydroquinone by chlorine dioxide. Environ. Sci. Technol., 16 (1982) 396–402.

[20] M.R. Farvardin and A.G. Collins, Preozonation as an aid in coagulation of humic substances-optimum preozonation dose, Water Res., 28 (1989) 307–316.