# MONITORING AND TREATMENT OF VOCs IN DRINKING WATER

(COMPARATIVE STUDY)

# Submitted By Ehab Zaki Abdel-Hady Ahmed

B.Sc. of Science (Chemistry), Faculty of Science, Ain Shams University, 1994

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Master Degree

In

**Environmental Sciences** 

Department of Environmental Basic Sciences Institute of Environmental Studies and Research Ain Shams University

### APPROVAL SHEET

### MONITORING AND TREATMENT OF VOCS

### IN DRINKING WATER

(COMPARATIVE STUDY)

### **Submitted By**

### **Ehab Zaki Abdel-Hady Ahmed**

B.Sc. of Science (Chemistry), Faculty of Science, Ain Shams University, 1994

A thesis submitted in Partial Fulfillment

The Requirement for the Master Degree

**Environmental Sciences** 

Department of Environmental Basic Sciences

This thesis Towards a Master Degree in Environmental Sciences Has been approved by:

Name Signature 1-Prof. Dr. Mansoura Ismail Mohamed Prof. of Organic Chemistry, Department of Chemistry Faculty of Women Ain Shams University 2-Dr. Reham Lotfy Abdel Aziz

Expert of Public Health Manager of Environmental Health Egyptian Environmental Affairs Agency

#### 3-Prof. Dr. Nadia Gharib Kandile

Prof. of Applied Organic Chemistry, Department of Chemistry Faculty of Women Ain Shams University

### 4-Prof. Dr. Mahmoud Ahmed Ibrahim Hewehy

Prof. of Public Health, Department of Environmental Basic Sciences Institute of Environmental Studies & Research Ain Shams University

# MONITORING AND TREATMENT OF VOCs IN DRINKING WATER

(COMPARATIVE STUDY)

## Submitted By Ehab Zaki Abdel-Hady Ahmed

B.Sc. of Science (Chemistry), Faculty of Science, Ain Shams University, 1994

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Master Degree

In

**Environmental Science** 

Department of Environmental Basic Science

Under The Supervision of:

### 1-Prof. Dr. Nadia Gharib Kandile

Prof. of Applied Organic Chemistry, Department of Chemistry Faculty of Women Ain Shams University

### 2-Prof. Dr. Mahmoud Ahmed Ibrahim Hewaihy

Prof. of Public Health, Department of Environmental Basic Sciences Institute of Environmental Studies & Research Ain Shams University

### Acknowledgments

I would like to express my sincere appreciation to **Prof. Dr. Nadia** G.Kandile for providing her best efforts in supporting and guiding me through this work, as well as promoting it in many ways.

I would also like to thank **Prof.Dr. Mahmoud A.I.Hewehy** for his supporting advice and suggestions, which enhanced the quality of this work.

I would like to acknowledge the support I received from reference laboratory, Ain Shams University and Institute of environmental studies and research, administratively.

I would like to show my appreciation to my friends and colleagues in reference laboratory for their invaluable help and for debugging both my work and this thesis.

Finally, I would like to express my deep gratitude to my family for their unconditional love, encouragement and support by any possible means, without which this work would not be possible.

> Ehab Zaki 2018

### **ABSTRACT**

VOCs present in drinking water because of industrial and agricultural discharges onto water streams or chlorination step in the treatment process, which form a disinfection by-products (DBPs). These compounds have negative impact on the human health and environment. Disinfection byproducts of Volatile Organic Compounds (DBPs-VOCs) {Chloroform Bromodichloromethane (CHBrCl<sub>2</sub>), (CHCl<sub>3</sub>), Dibromochloromethane (CHBr<sub>2</sub>Cl) and Bromoform (CHBr<sub>3</sub>)} were classified as possible human carcinogens, if they exceeded the permissible limits of Egyptian guidelines (100  $\mu$ g/l) (**Decree 458, 2007**). The identification and quantification of VOCs performed by purge & trap GC/MS instrument, using a reference analytical method (EPA 524.2, 1995). A monthly monitoring comparative study established during 2016 in both input and output of Shubra El-Kheima (Water Treatment Plants WTP) (1 km Far from Nile River on Al-Sharqawia canal at the northern border of capital Cairo) and **South Alamein** WTP (270 km downstream far from the Nile River on Alhamam canal at North Coast of Egypt).

Our study revealed the absence of VOCs in raw water but (DBPs-VOCs) detected in final treated water of both investigated plants. Values of (DBPs-VOCs) obtained from Shubra El-Kheima WTP were comply the Egyptian guidelines, and recorded the highest level in October 2016 (90  $\mu$ g/l), while the values obtained from South Alamein WTP were near or greater than the permissible limits. The highest level was recorded in August 2016 (193  $\mu$ g/l), as well as most values recorded from the boosters output (6 boosters) next to South Alamein WTP were higher than the permissible limits. The values gradually increase as the booster moves away from the

production plant due to increasing the contact time of final treated water with residual chlorine.

As regards the negative effect on health of these (DBPs-VOCs) which are carcinogenic, the study concerned to find an appropriate way for reducing their values in South Alamein WTP to be comply with the Egyptian guidelines using Granular Activated Carbon (GAC). Lowering of (DBPs-VOCs) precursor concentrations has the additional advantage of reducing overall disinfectant demand, thereby reducing the possibility of the formation of all disinfection byproducts.

Finally the study succeeded in estimating the amount of GAC required and its duration time to reduce the total concentration of produced (DBPs-VOCs) from the maximum recorded concentration (178  $\mu$ g/l) in the final treated water of South Alamein WTP to (94  $\mu$ g/l) which is lower enough than the permissible limit (100  $\mu$ g/l). About 581-ton GAC consumed every 17 day where the plant works at maximum production capacity (172000 m³/day).

### Contents

Aims of the work	1
Introduction	3
Problem definition	4
Study Area	4
Overview on Shubra El-Kheima City	4
Overview on Marsa Matrouh governorate	5
Literature Review	7
1- Sources of volatile organic compounds VOCs	7
1.1 VOCs from industrial sources and human dwellings	7
1.2 VOCs from agricultural activities	8
1.3 VOCs produced from disinfection processes	9
2- Disinfection processes	10
2.1 Chlorine Disinfection	11
2.1.1 Mechanism of chlorine action	13
2.1.2 Reaction of Chlorine with natural organic matters (NOMs)	14
2.1.2.1 With aromatic compounds	14
2.1.2.2 With aliphatic compounds	15
2.1.3 Mechanism of chlorination pollutant removal	16
2.2 Chloramine Disinfection	16
2.3 Ozone Disinfection	18
2.4 Disinfection By-products (DBP)	19
2.4.1 Factors Affecting Formation of Disinfection By-Products (DBP)	20

3-	· Natural organic matters (NOMs)	21
	3.1 Fractions of Natural organic matters (NOMs)	21
	3.2 Quantification of Natural organic matters (NOMs)	24
4-	Health effect of Some VOCs	25
	4.1 Toluene	25
	4.2 1,1,1-Trichloroethane	26
	4.3 Chloroform	27
	4.4 Bromoform	27
	4.5 Dibromochloromethane	28
	4.6 Bromodichloromethane	28
	4.7 Benzene	29
5-	Regulation of VOCs in drinking water	29
	5.1 WHO Regulations and Sources of VOCs in drinking water	29
	5.1.1 WHO guidelines for VOCs produced from disinfection processes	30
	5.2 Egyptian ministry of health Regulation of VOCs in drinking water	31
6-	Removal of volatile organic compounds VOCs and (NOMs) from	1
	treated water.	31
	6.1 Air stripping	32
	6.2 Activated Carbon Adsorption	32
	6.2.1 Types of Activated Carbon	37
	6.2.2 Mechanism of activated Carbon pollutant removal	38
	6.3 UV decomposition	38
	6.4 Effective coagulation	38

6.5 Enhanced coagulation	41
Materials and Methods	43
1 Selection of Study area	43
2 Sampling	45
3 Materials	46
4 Methods	47
4.1 Monitoring of VOCs in the selected WTPs.	47
4.2 Monitoring of TOC in the selected WTPs	48
4.3 Monitoring of residual free chlorine	48
4.4 Measuring of pH.	48
4.5 Removal of VOCs from treated water using granular activated carbon Ga	AC49
4.5.1 FIXED-BED Column studies	51
4.5.2 Batch Adsorption Study	52
4.5.3 Isotherm measurements	53
Results and discussion	54
1 General	54
2 Monitoring of VOCs & TOC in Shubra El-Kheima WTP	54
2.1 In Raw water (Intake)	54
22 In Treated water (Product).	56
3 Monitoring of VOCs &TOC in South Alamein WTP and its b	ooster
	59
3.1 In raw water (intake)	59
3.2 In Treated water (Product)	61
3.3 In output of South Alamein booster (1).	64
3.4 In output of Sidi Abdel-Rahman booster (2)	66
3.5 In output of Aldabaa booster (3)	68

3.6 In output of Fuka booster (4)	70
3.7 In output of Ras-Al-Hekma booster (5)	72
3.8 In output of Garawla booster (6)	74
4 Comparative results of VOCs in the studied areas during 20	<b>16.</b> 76
5 Removal of the formed VOCs in the Product water of South	Alamein
WTP	77
5.1 FIXED-BED Column studies on South Alamein WTP	79
5.2 Batch Adsorption Study	89
5.2.1 Effect of GAC Dose on TOC removal	89
5.2.2 Effect of GAC Dose in CHCl <sub>3</sub> removal	91
5.2.3 Effect of GAC Dose in CHBrCl <sub>2</sub> removal	93
5.2.4 Effect of GAC Dose in CHBr <sub>2</sub> Cl removal	95
5.2.5 Effect of GAC Dose in CHBr <sub>3</sub> removal	97
Conclusion and Recommendation	102
Summary	105
References	109
Arabic Summary	
Arabic Abstract	

### **List of Tables**

Table 1: Chemicals from industrial sources and human dwellings8
Table 2: Chemicals from agricultural activities8
Table 3: Disinfection by-products present in disinfected waters based on
International Programme on Chemical Safety (IPCS, 2000)10
Table 4: Methods of analysis, sample preservation, handling and storage45
Table 5: Characteristics of GAC utilized in experimental columns50
Monthly TOC levels in raw water of Shubra El-Kheima WTP during 2016
Table 7: Monthly VOCs levels in raw water of Shubra El-Kheima WTP
during 2016
Table 8: Monthly TOC levels in produced water of Shubra El-Kheima WTP
during 2016
Table 9: Monthly VOCs levels in produced water of Shubra El-Kheima WTP
during 2016
Table 10: Monthly TOC levels in raw water of South Alamein WTP during
2016
Table 11: Monthly VOCs levels in raw water of South Alamein WTP during
2016
Table 12: Monthly TOC levels in produced water of South Alamein WTP
during 2016
Table 13: Monthly VOCs levels in produced water of South Alamein WTP
during 2016
Table 14: Monthly TOC levels in output water of South Alamein booster (1)
during 2016
Table 15: Monthly VOCs levels in output water of South Alamein booster (1)
during 2016

Table 16: Monthly TOC levels in output water of Sidi Abdel-Rahman booster
(2) during 201666
Table 17: Monthly VOCs levels in output water of Sidi Abdel-Rahman
booster (2) during 2016
Table 18: Monthly TOC levels in output water of Aldabaa booster (3) during
2016
Table 19: Monthly VOCs levels in output water of Aldabaa booster (3)
during 2016
Table 20: Monthly TOC levels in output water of Fuka booster (4) during
201670
Table 21: Monthly VOCs levels in output water of Fuka booster (4) during
201670
Table 22: Monthly TOC levels in output water of Ras Al-Hekma booster (5)
during 2016
Table 23: Monthly VOCs levels in output water of Ras Al-Hekma booster (5)
during 2016
Table 24: Monthly TOC levels in output water of Garawla booster (6) during
201674
Table 25: Monthly VOCs levels in output water of Garawla booster (6)
during 201674
Table 26: % removal of analytes from produced water of South Alamein
WTP with different contact time with GAC in glass column during August
201778
Table 27: % removal of analytes from produced water of South Alamein
WTP with different contact time with GAC in glass column during August
201780
Table 28: TOC removal by various amount of GAC, TOC initial
concentration was 4.60- mg/l.

Table 29: CHCl3 removal by various amount of GAC, CHCl3 initial
concentration was 100-µg/l91
Table 30: CHBrCl2 removal by various amount of GAC, CHBrCl2 initial
concentration was 100-µg/l93
Table 31: CHBr2Cl removal by various amount of GAC, CHBr2Cl initial
concentration was 100-µg/l95
Table 32: CHBr3 removal by various amount of GAC, CHBr3 initial
concentration was 100-µg/l97
Table 33: Summary of Parameters obtained from Freundlich and Langmuir
Isotherm models
Table 34: Summary of important figures when a GAC bed removal applied in
South Alamein WTP

### **List of Figures**

Figure 1: Shubra El-Kheima DWTP and its covered areas5
Figure 2: South Alamein DWTP and its boosters & covered areas6
Figure 3: Hypothetical structure of humic acid
Figure 4: Fractionation of DOC and best removal technique24
Figure 5: Breakthrough curve
Figure 6: Shubra El-Kheima DWTP44
Figure 7: South Alamein DWTP44
Figure 8: Sampling processes from Al Hammam canal
Figure 9: Purge & Trap GC/MS-Ion Trap 4000 detector instrument48
Figure 10: Sievers 5310 C Total organic carbon analyzer
Figure 11: Continuous flow Glass column laboratory scale setup52
Figure 12: Monthly VOCs & TOC levels variation in raw water of Shubra El-
Kheima WTP during 2016
Figure 13: Monthly VOCs & TOC levels variation in produced water of
Shubra El-Kheima WTP during 2016
Figure 14: Monthly VOCs & TOC levels variation in raw water of South
Alamein WTP during 201661
Figure 15: Monthly VOCs & TOC levels variation in produced water of
South Alamein WTP during 201663
Figure 16: Monthly VOCs & TOC levels variation in output water of South
Alamein booster (1) during 2016
Figure 17: Monthly VOCs & TOC levels variation in output water of Sidi
Abdel-Rahman booster (2) during 201667
Figure 18: Monthly VOCs & TOC levels variation in output water of
Aldabaa booster (3) during 201669
Figure 19: Monthly VOCs & TOC levels variation in output water of Fuka
booster (4) during 201671

Figure 20: Monthly VOCs & TOC levels variation in output water of Ras Al-
Hekma booster (5) during 201673
Figure 21: Monthly VOCs & TOC levels variation in output water of
Garawla booster (6) during 2016
Figure 22: Comparative results of VOCs levels in the output water of the
studied areas during 2016
Figure 23: % removal variation of Analytes from produced water of South
Alamein WTP with different contact time with GAC in glass column during
August 2017
Figure 24: Variation of effluent concentration Ce of TOC from the produced
water of South Alamein WTP after passing through GAC glass column at
constant contact time (10 min) with volume during August 201781
Figure 25: Variation of effluent concentration Ce of CHCl3 after passing
through GAC glass column at constant contact time 10 min from the
produced water of South Alamein WTP with volume during August 201782
Figure 26: Variation of effluent concentration Ce of CHBrCl2 from the
produced water of South Alamein WTP after passing through GAC glass
column at constant contact time (10 min) with volume during August 2017
83
Figure 27: Variation of effluent concentration Ce of CHBr2Cl from the
produced water of South Alamein WTP after passing through GAC glass
column at constant contact time (10 min) with volume during August 2017
84
Figure 28: Variation of effluent concentration Ce of CHBr3 from the
produced water of South Alamein WTP after passing through GAC glass
column at constant contact time (10 min) with volume during August 2017
85
Figure 29: Variation of effluent concentration Ce of DBPs-VOCs from the