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## RESEARCH ARTICLE

### Fate of natural organic matter and THMs formation for raw and conventionally treated waters of El-Fayoum Governorate, Egypt

\*M.E.M. Hassouna<sup>1\*</sup>, M. J. Badawy<sup>2</sup>, T. A. Gad-Allah<sup>2</sup>, M. H. said<sup>3</sup>

1. Chemistry department, faculty of Science, Beni-Suef University, Beni-Suef, Egypt
2. National research center, Water pollution research department, Dokki, Cairo, Egypt
3. Central laboratories of FADWASC, holding company for water and waste water, Fayoum, Egypt

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##### \*Corresponding Author

M.E.M. Hassouna

#### Abstract

Dissolved organic matter (DOM) from raw and processed waters at a selected conventional water treatment plant was fractionated into hydrophobic, hydrophilic and transphilic fractions by physicochemical fractionation methods to study its characteristics. Contributions to dissolved organic matter (DOM) and formation potential of trihalomethanes (THMs) of the isolated fractions were investigated. The results showed that the hydrophilic fraction contributes to dissolved organic matter weight greater than both the hydrophobic and transphilic fractions; whereas the formation potential of trihalomethanes (THMs) was highly influenced by the hydrophobic fraction. However conventional treatment in New Al Azab drinking water treatment plant showed greater removal performance for the transphilic fraction than the hydrophilic one, while it didn't show any removal performance for the hydrophobic species. Hydrophobic species of dissolved organic matter (humic substances (HS)) were further investigated. Trihalomethanes formation potential of hydrophobic matter showed significant correlations with hydrophobic concentration as well as UV absorbance at 254 nm, 260 nm and 280 nm.

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## 1. INTRODUCTION

Trihalomethanes (THMs) are the most important groups of disinfection by-products (DBPs). The formation of THMs mainly involves treatment plants that process surface water, generally rich in natural organic matter. A recent review [1] dealt with the quantification of NOM and characterized it into four different categories among them humic substances. NOM in raw water reacts with free chlorine to form DBPs consist mainly of humic substances[2]; humic matter typically makes up about 50% of the dissolved organic matter (DOM) in surface water. NOM is derived primarily from plant and/or microbial residues, animal and plant material decaying down [3]. NOM is a complex mixture of various compounds with widely different chemical properties.

Total concentration of THMs and the distribution of their individual species depend on raw water characteristics and operational parameters of treatment process. NOM is partially removed through the conventional drinking water treatment processes such as coagulation/sedimentation and sand filtration. Conventional treatment can remove more NOM with additional water treatment processes to lower the DBP levels before releasing the water to the distribution system. Characterization of natural organic matter fractions have been performed by different methods [4-6]. The need to characterize NOM before attempting to remove it is based on the fact that its aromaticity, functional group distribution, molecular weight and elemental composition have a great influence on how NOM can be effectively removed from water [7]. Literature suggested that not all NOM fractions react with chlorine and contribute to formation of DBPs through water treatment. The relative mass contribution as DOC and distribution of each fraction and compounds in each fraction differ depending upon the type of water. To understand the role of HS

in water chemistry, it is often necessary to fractionate NOM. The composition of HS could be investigated by numerous methods including physicochemical fractionation and spectroscopic measurements. XAD resin method has been applied in many applications for fractionation of NOM [8] Systematic fractionation of HS using the XAD resin is generally considered as the state-of-art method that is used to study HS in physicochemical water treatment processes [9-11]. In the analytical fractionation scheme, XAD-4 and XAD-8 resins are employed to separate NOM into hydrophilic, hydrophobic and transphilic fractions. NOM could thus be quantified according to the relative proportions of these fractions. It is important to understand the behaviors of organic matter in the processed waters at real water treatment plant as well as to characterize HS from water source. Therefore, the main purposes of this study are to compare the characteristics of isolated organic matter from raw and processed waters, and to investigate the relationships between the formation potential of THMs and various characteristics of HS. Knowledge of the interactions of chlorine with HS as well as characteristics of HS is essential to establish optimal treatment strategy for DBPs control. Therefore, the paper attempted to estimate THMs generated by the different properties of the humic matter in waters, to provide an indication of THMFP by considering the spectroscopic properties of HS and understand the characteristics of HS which is considered the main contributors for DBPs formation.

## 2. Material and Methods

### 2.1. Sampling site and strategy

Hassan Wassef stream is located in Fayoum governorate in Egypt; it is the main water source in the district. The physicochemical characteristics of this water stream are: pH 7.55-7.35; dissolved organic carbon (DOC) 2.73-3.66 mg/L; dissolved oxygen (DO) 5.3-8.5 mg/L;  $\text{Ca}^{2+}$  29.8-43.9 mg/L;  $\text{Mg}^{2+}$  8.6-14mg/L;  $\text{Cl}^-$  30-105mg/L;  $\text{SO}_4^{2-}$  33-172 mg/L;  $\text{SiO}_2$  0.8-7.2 mg/L. The New Al Azab water treatment plant is designed to treat 3,000 L/second adopts conventional treatment processes consisting of pre-chlorination, coagulation/sedimentation, sand filtration and chlorination, and uses Hassan Wassef stream as a water source. Samples were collected from Hassan Wassef stream and from the different treatment processes in amber glass bottles. Samples were preserved and kept at 4 °C to the laboratory.

### 2.2. DOM fractionation

The fractionation of DOM of waters was carried out based on the method by Leenheer [5] and Aiken et al.[12]. Resins of DAX-8 and XAD-4 (Supelco Bellefonte, PA, USA) were used and purified by Soxhlet extraction before experiments. DOM fractionation was carried out using small (8 mL) resin volumes packed into a 30 cm × 1.0 cm (24 mL) glass column. DAX-8 and XAD-4 resins were used for all fractionation procedures, in order to separate NOM into hydrophobic (HPO), transphilic (THP) and hydrophilic (HPI) fractions. Waters used in these experiments were first filtered through a 0.45 $\mu$  glass filter to remove particulate matter and acidified to pH 2.0 with orthophosphoric acid. The acidified samples were passed through a small XAD-8 column at a flow rate of approximately 5 mL/min, resulting in removal of the hydrophobic fraction. The effluent was then passed through a small XAD-4 column, removing transphilic material and leaving only hydrophilic matter in the final effluent. After each use, columns were rinsed with a total of 100 mL, 0.1 N NaOH and 100 mL 0.1 N HCl, alternating between acid and base, followed by 200 mL Milli-Q water (flow rate 20 mL/min). Fractionation was repeated 2 times for every sampling round. Fractionated effluent samples from DAX-8 and XAD-4 columns were adjusted at pH 7.0 with sodium hydroxide and buffered with 0.03 mol/L of phosphate buffer prior to be analyzed or used for chlorination experiments.

### 2.3. Analyses

DOC was measured by UV persulfate TOC analyzer (phoenix 8000, Teledyne tekmar). Potassium hydrogen phthalate was used as the standard according to standard method 5310C [13]. For measuring UV absorbance of fractions, solutions were placed in a 1-cm quartz cuvette and scanned with a UV-VIZ spectrophotometer (lambda 25, Perkin Elmer). For measuring THMFP under standard conditions, samples were buffered at pH 7.0 ± 0.2, chlorinated with an excess of free chlorine, and stored at 25 ± 2°C for 7 d to allow the reaction to approach completion. As a minimum, pH is buffered at a defined value and a free chlorine residual of 3 to 5 mg  $\text{Cl}_2$  /L exists at the end of the reaction time. THMs were quantified by liquid/liquid extraction with n- hexane followed by gas chromatography (Agilent, 7890A GC) with  $\mu$ ECD detector and HP5 Capillary Column according to the EPA Method No. 501.2.

### 3. Results and Discussions

#### 3.1. Contribution of DOM fractions

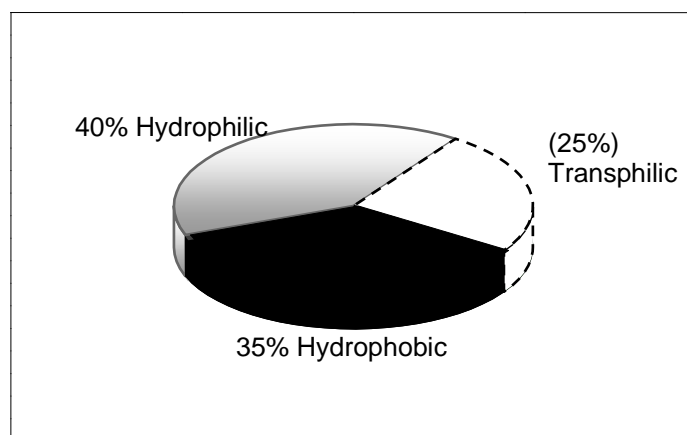
After dissolved organic matter (DOM) in raw water samples was separated into hydrophilic, hydrophobic and transphilic fractions using XAD fractionation method, each fraction was quantified as DOC. Results for the relative contributions of each DOM fraction and their aromaticity content are presented in Table (3-1).

**Table 3-1: DOC, SUVA<sub>254</sub>, and UV<sub>254</sub> values of isolated DOM fractions**

Parameter	Unit	bulk	Hydrophilic	Hydrophobic	Transphilic
DOC	mg/L	3.127	1.271	1.103	0.772
SUVA <sub>254</sub>	l/mg*m	3.453	1.73	3.35	1.036
UV <sub>254</sub>	cm <sup>-1</sup>	0.108	0.0220	0.0390	0.0080

Relative contributions of hydrophilic, hydrophobic and transphilic fractions of DOM in Hassan Wassef waters are illustrated in Figure (3-1). Data revealed that hydrophilic fraction was predominantly, accounting for 40.7%, and hydrophobic species were accounting for 35.3%, while transphilic fraction was the minor with a relative contribution of 24.7%. Differences in distribution of NOM fractions may be related to the various sources of the NOM and their formation environment. High levels of hydrophilic NOM have been observed in water supplies with a large proportion of Autochthonous vs. Allochthonous NOM [14].

UV absorbance at 254 nm is often used to represent the content of aromatic structures in humic samples [15]. The presence of light absorbing structure is thought to be related to the eventual formation of DBPs upon chlorination, the UV absorbance exhibited by these fractions may be an indication that they will eventually make an important contribution to the overall load of THMs in the finished water. Results revealed that the hydrophobic fraction is the most UV<sub>254</sub> absorbing species. UV<sub>254</sub> absorbance of the hydrophilic and hydrophobic fractions were 0.022 cm<sup>-1</sup> and 0.039 cm<sup>-1</sup> respectively, while UV<sub>254</sub> absorbance of the transphilic fraction was 0.008 cm<sup>-1</sup>.



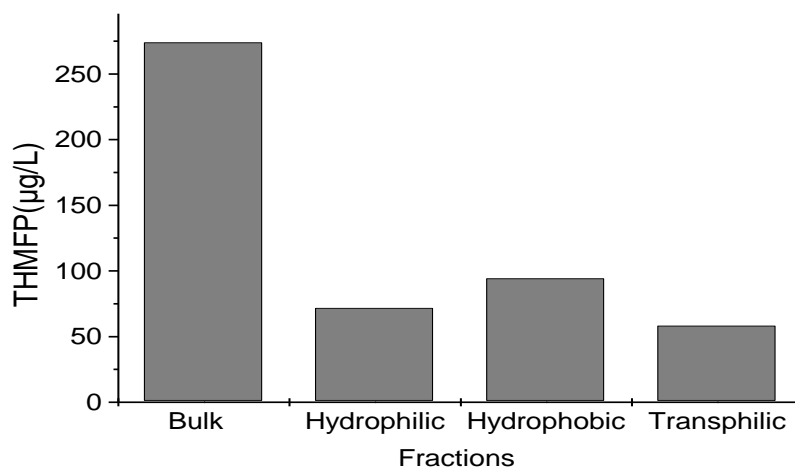
**Figure 3-1: Relative contributions of DOM fractions in raw waters**

#### 3.2. THMs formation potential of DOM fractions

Trihalomethanes formation potential (THMFP) was measured for each of the isolated NOM fractions to estimate the contribution of each fraction to THMs formation values within chlorination. Results illustrate that the formation potential of THMs was mainly influenced by the hydrophobic fraction and it was the main THMs precursors within chlorination (with specific yield of 85.6 µg/mg C), followed by the hydrophilic fraction, while the transphilic fraction yielded low concentrations of THMFP. It was reported [16] that the distribution of chlorinated and brominated DBPs species are strongly related to the bromide concentration of the water. Bromide concentrations of the water solutions were very low (under 40µg/L). In this study, the THMs species detected after chlorination were

only chloroform and bromodichloromethane. Chloroform was the major THMs species during chlorination, while bromodichloromethane was the minor one. Bromodichloromethane accounts for 3–24 % of the total yield of THMs in chlorination. The lower production of brominated THMs than that of chloroform is due to the low bromide concentration in the DOM fractions.

The differences of DBPs yields between the fractions are possibly due to their different characteristics of functional groups and structures [17]. It was shown [18] that the active aromatic moieties have high halogen consumption and DBPs production.  $SUVA_{254}$  was found to be a good surrogate of the aromatic carbon content of natural organic matter [16]. The hydrophobic fraction showed the highest THMFP values combined with the highest  $UV_{254}$  and  $SUV_{254}$  values despite not being the largest DOC weight counterpart. In this study, the results also, showed that aromatic moieties of the DOM fractions play an important role in the formation of chlorinated DBPs. These findings are meeting the widely held assumption that most THMs are formed from the hydrophobic fraction due to the intrinsic chemical characteristics of hydrophobic species.



**Figure 3-2:** Contribution of DOM fractions to THMFP

### 3.3. DOM fractions through treatment processes

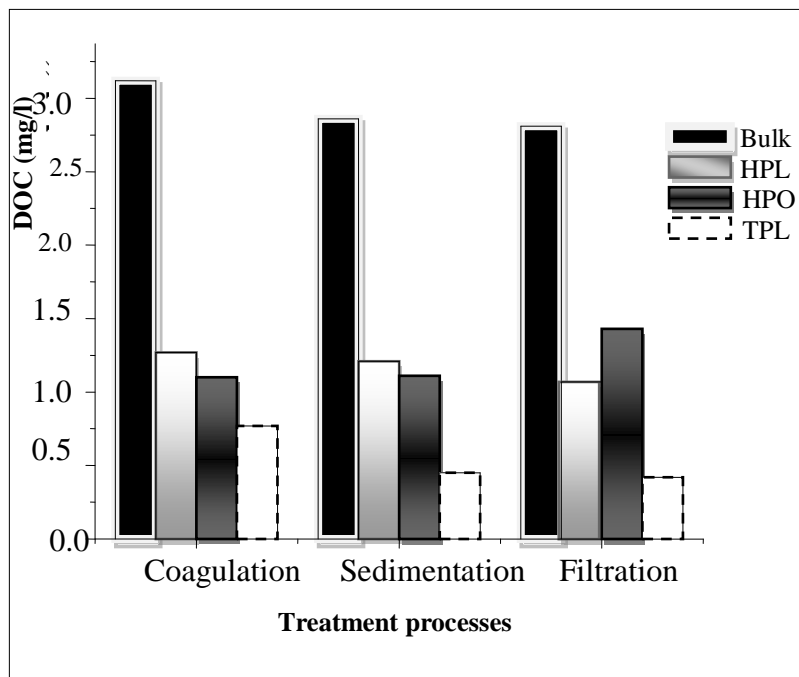
To understand the behavior of natural organic matter in the processed waters at the New Al Azab treatment plant, samples were collected from the coagulation, sedimentation and filtration processes and fractionated. As shown in Table (3-2), hydrophilic fraction weight was the most predominant one in both the coagulation and sedimentation processes. However, the hydrophobic fraction becomes the predominant one at the filtration process. Also, data revealed that the transphilic fraction was the lowest weight counterpart through the treatment processes. Hydrophilic fraction concentration was nearly constant in both the coagulation and sedimentation processes (1.271 mgC/L and 1.219 mgC/L, respectively) and then a decrease to 1.068 mgC/L has been encountered after the sand filtration. It was reported [19] that the hydrophilic fraction of NOM causes irreversible fouling of microfiltration and ultrafiltration membranes.

However, the hydrophobic fraction concentration was nearly constant, i.e., 1.10 mg C/L in the coagulation and 1.118 mg C/L in the sedimentation outlets, then unexpectedly reached 1.428 mg C/L in the filtration process. Hydrophobicity increase may be attributed to chemical transformation [17]. Conventional treatment in the New Al Azab treatment plant showed greater removal performance for the transphilic fraction than the hydrophilic one, while it didn't show any hydrophobic removal performance.

**Table 3-2: Effect of treatment processes on DOM fractions (DOC (mg/L), (SUV<sub>254</sub> (1/mg\*m)), (UV<sub>254</sub>))**

	Coagulation				Sedimentation outlet				Filtration outlet			
	Bulk	HPL	HPO	TPL	bulk	HPL	HPO	TPL	Bulk	HPL	HPO	TPL
DOC	3.127	1.271	1.103	0.772	2.864	1.219	1.118	0.453	2.809	1.068	1.428	0.419
SUV <sub>254</sub>	3.45	2.12	2.99	2.59	3.25	1.56	2.77	2.42	2.67	1.69	2.03	2.15
UV <sub>254</sub>	0.108	0.027	0.033	0.020	0.093	0.019	0.031	0.011	0.075	0.0180	0.029	0.009

UV-VIZ absorbance had been widely used to characterize the properties of organic matter in waters [20]. UV<sub>254</sub> of DOM fractions was measured to investigate the change in aromaticity through treatment processes. A substantial drop was observed in the UV<sub>254</sub> of bulk waters through water treatment processes from 0.108 cm<sup>-1</sup> in the coagulation process to 0.093 cm<sup>-1</sup> in sedimentation, finally reached 0.075 in the filtration outlet. UV<sub>254</sub> absorbance of hydrophobic species decreased slightly through the treatment processes from 0.033 cm<sup>-1</sup> in the coagulation to 0.029 cm<sup>-1</sup> at the filtration outlet. On the other hand hydrophilic species also slightly decreased from 0.027 cm<sup>-1</sup> in the coagulation process to 0.018 at the filtration outlet demonstrating that New Al Azab water treatment plant may have poor performance removal for UV absorbing compounds with hydrophobic and hydrophilic characteristics. However, transphilic compounds encountered aromaticity removal.

**Figure 3-3: DOM fractions through treatment processes**

### 3.4. Influence of hydrophobicity

Results have shown that the hydrophobic fraction is playing an important role in the fate of trihalomethanes formation because most of THMs are formed by large molecular weight hydrophobic compounds and eventually make an important contribution to the overall load of THMs in the finished water. Series of concentrations of hydrophobic species were chlorinated to study the correlation of the most commonly used organic parameters with TTHMFP. Absolute THMFP refers to the reactivity of NOM in the sample while normalized THMFP refers to reactivity per unit of NOM, as shown in Fig (3-4), there is a significant linear correlation with regression coefficient ( $R^2 = 0.84$ ) between absolute TTHMFP and hydrophobic concentrations. Correlation between normalized THMFP

and hydrophobic concentrations had  $R^2 = 0.89$ . These linear relationships implied that the hydrophobic fraction is the most active species for the THMFP.

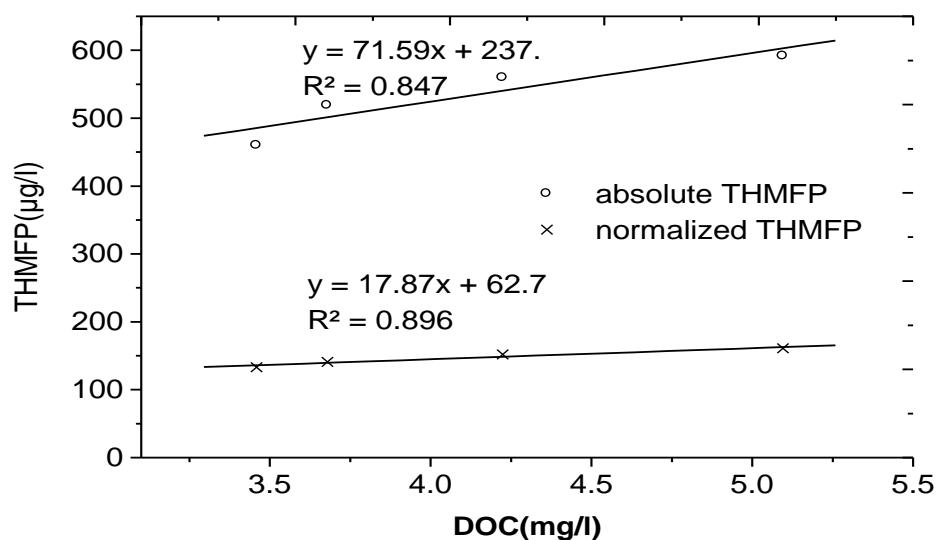


Figure 3-4: Hydrophobic concentrations with THMFP

### 3.5. UV/VIZ spectroscopic analysis of hydrophobic species

UV-VIZ absorbance had been widely used to characterize organic matter in waters [21]. As shown in figure (3-5), humic substances generally show strong absorbance in the UV-VIZ range particularly in the UV region because of the presence of aromatic chromophores and/or other organic compounds [22 & 23]. Specifically, absorbance at 254 nm is often used to represent the content of aromatic structures in humic samples [13].

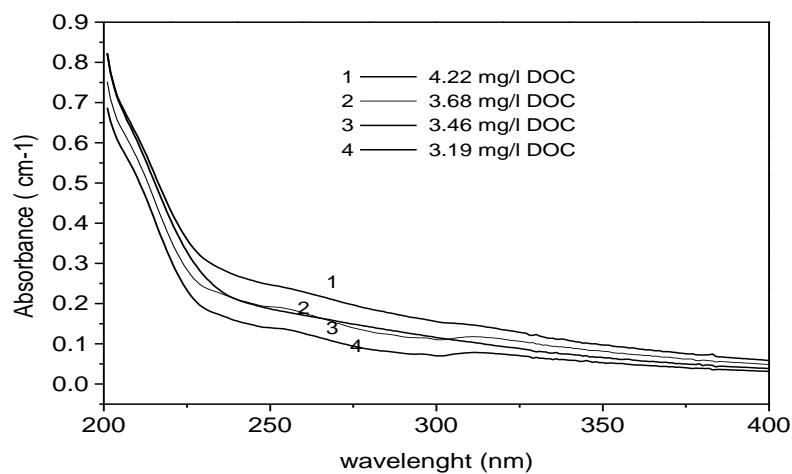
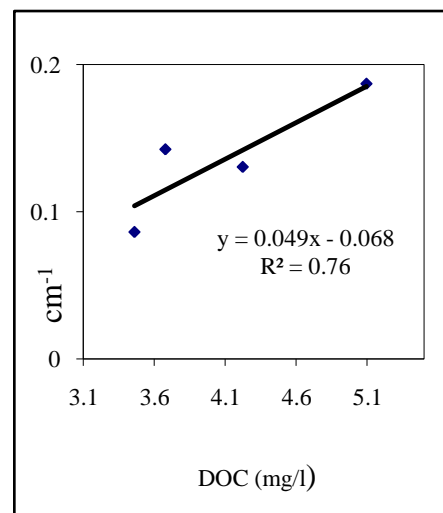
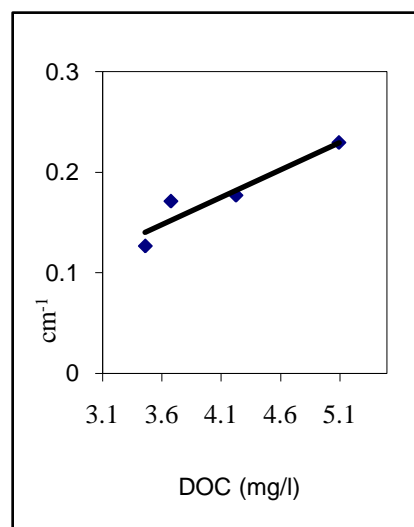
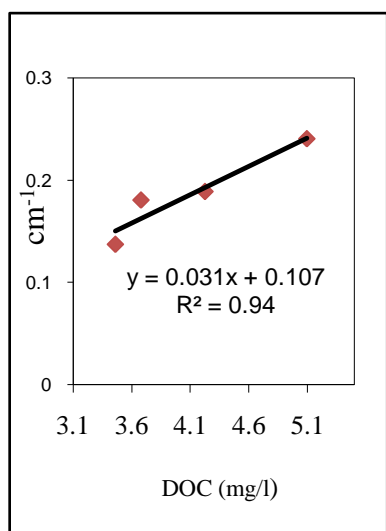


Figure 3-5: UV Scanning of hydrophobic solutions

UV absorbance in the range 254-280 nm reflects the presence of unsaturated double bonds and electron interactions such as those found in aromatic compounds [24].  $SUVA_{280}$  may provide important information for the degree of aromaticity, sources, extent of humification and molecular weight of DOM. Furthermore, UV absorbance at 260 nm is commonly used to determine the relative abundance of aromatic C=C content of NOM because transitions in substituted benzenes or polyphenols occur in this wavelength region [24].



**Figure 3 -6: HPO & UVA<sub>254</sub>**

**Figure 3-7: HPO & UVA<sub>260</sub>**

**Figure 3-8: HPO & UVA<sub>280</sub>**

Figures (3-4, 3-5, 3-6) illustrate correlations between the light absorption at 254, 260 and 280 nm with DOC concentrations of hydrophobic matter in raw water of New Al Azab treatment plant. Results showed linear correlations over a series of DOC concentrations. Correlations at 254 nm and 260 nm showed positive regression coefficients of  $R^2 = 0.94$  and  $R^2 = 0.849$  respectively, while correlation at 280 nm had  $R^2 = 0.76$ .

## Conclusion

In raw water of Fayoum governorate, hydrophilic fraction contributes to dissolved organic matter weight more than both hydrophobic and transphilic fractions; whereas the formation potential of trihalomethanes (THMs) was highly influenced by the hydrophobic fraction. However conventional treatment in New Al Azab treatment plant showed greater removal performance for the transphilic fraction than the hydrophilic one, while it didn't show any hydrophobic removal performance. To understand aromatic characteristics of hydrophobic species (humic substance (HS)) and their influence on THMs formation potentials, hydrophobic species were further investigated. Trihalomethanes formation potential of hydrophobic matter showed significant correlations with hydrophobic fraction weights as DOC as well as UV absorbance at 254 nm and 260 nm. Therefore UV absorbance at these wavelengths may be good indicator for changes in dissolved organic matter characteristics as well as its reactivity with chlorine.

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