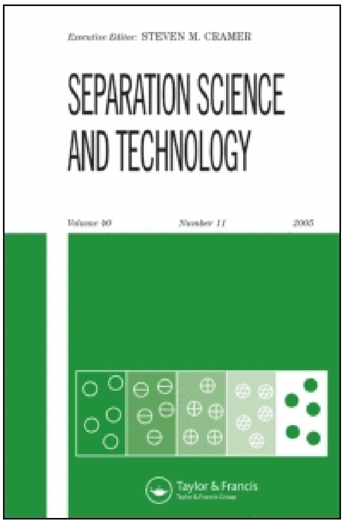

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A Comparative Approach to the Application of a Physico-Chemical and Advanced Oxidation Combined System to Natural Water Samples

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A Comparative Approach to the Application of a Physico-Chemical and Advanced Oxidation Combined System to Natural Water Samples

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Abstract: Natural organic matter removal (NOM) efficiencies of samples from three major drinking water sources (Elmali, Omerli, and Buyukcekmece) of Istanbul were compared using different treatment systems. Enhanced coagulation as a physico-chemical method was applied using ferric chloride and aluminum sulphate as the coagulating agents. Moreover, the application of enhanced coagulation in combination with photocatalytic oxidation using TiO_2 was investigated. The efficiency of NOM removal relevant to each treatment step was assessed through DOC removal, UV_{254} removal, and fluorescence measurements.

Irrespective of the treatment applied as enhanced coagulation, photocatalytic oxidation or their combinations, the highest removal efficiency was determined for Elmali followed by Omerli and Buyukcekmece samples both in terms of DOC and UV_{254}. Enhanced alum coagulation leads to significant variation in DOC removals as 44%, 28% and 26% for Elmali, Omerli, and Buyukcekmece water samples, respectively. Upon application of ferric chloride as the coagulant, the DOC removals achieved were found to be slightly higher as compared to alum. Moreover, the combined treatment incorporating photocatalytic oxidation subsequent to alum coagulation leads to 36%, 37%, and 50% of DOC removal for Omerli, Buyukcekmece, and

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Elmali respectively. The improvement of removal efficiencies in combined treatment systems were scrutinized with an emphasis on induced water properties as supported by the specific fluorescence intensities of the samples.

Keywords: Coagulation, combined treatment, natural organic matter, photocatalysis

INTRODUCTION

Natural organic matter (NOM) represents the heterogeneous mixture of organic colloids and truly dissolved organic molecules present in aquatic systems. It comprises biochemically defined compounds such as proteins and carbohydrates, operationally defined substances such as fulvic and humic acids, and any supramolecular assembly of those molecules and macromolecules. Since NOM is an ill-defined matrix of compounds in dissolved, colloidal or particulate forms, which vary in molecular weight, functionality and hydrophobicity, coagulation can remove NOM by colloid destabilization, precipitation, or co-precipitation (1). The removal of NOM from the solution via coagulation occurs either by (1) precipitation of metal-humic complexes or (2) adsorption of humic substances onto metal hydroxide precipitates (2–6). The mechanism that occurs is dependent on the pH of the system and the applied coagulant dose. Generally, precipitation of metal-humic complexes is the dominant mechanism at lower coagulant doses and lower pH conditions whereas adsorption of humics onto metal hydroxide precipitates is dominant at higher coagulant doses and higher pH conditions (2, 6, 7).

Aqueous Al(III) and Fe(III) species are most frequently used as coagulating agents in water treatment. When added to water, Al(III), and Fe(III) salts dissociate to their respective trivalent ions as, Al^{3+} and Fe^{3+}, and then hydrolyze to form hydroxy complexes such as $Al(H_2O)6^{3+}$ and $Fe(H_2O)_6^{3+}$. Through a sequence of hydrolytic reactions, H_2O molecule in the aqua metal complex are replaced by OH^- ions (reactions 1–5).

$$Fe^{3+} + 2H_2O \Longleftrightarrow Fe(OH)_2^+ + 2H^+ \tag{1}$$

$$Fe(OH)^{2+} + H_2O \Longleftrightarrow Fe(OH)_2^+ + H^+ \tag{2}$$

$$2Fe^{3+} + 2H_2O \Longleftrightarrow Fe_2(OH)_2^{4+} + 2H^+ \tag{3}$$

$$Al^{3+} + H_2O \Longleftrightarrow Al(OH)^{2+} + H^+ \tag{4}$$

$$7Al^{3+} + 17H_2O \Longleftrightarrow Al_7(OH)_{17}^{4+} + 17H^+ \tag{5}$$

Several soluble complexes such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_2^{4+}$ are formed possessing high positive charges and are adsorbed onto the surface of the negative colloids. This leads to a reduction of zeta potential charge to a level where the colloids are destabilized. The metal cation and the complexed NOM remain in solution until either the binding capacity of NOM has been fulfilled, or the solubility of the metal–NOM complex is exceeded. Moreover, at high coagulant doses, the insoluble metal hydroxide can be removed by enmeshment or surface adsorption. The concentration of coagulant has to be high to ensure rapid precipitation of $Al(OH)_3$. Colloidal NOM can act as nuclei for precipitate formation, or can become entrapped during floc aggregation (8).

These mechanisms apply mainly to the removal of colloidal NOM, typically the higher molecular weight humic acids. These acids generally have low charge densities and therefore need low coagulant doses to induce destabilization. However, the more soluble fraction of NOM (fulvic acids) has higher anionic charge density that facilitates their dissolution. Hence, the high coagulant doses required by soluble fulvic acids correspond to an overdosing of humic acid colloids which leads to a restabilization of the colloids. The characteristics and quantities of NOM present in the water bodies determine whether NOM controls the coagulant doses and how much NOM is removed by coagulation. Coagulation has been shown to be most effective in removing NOMs in the intermediate and high molecular weight ranges. Analytical techniques to fractionate organic matter are very complex and expensive, and this makes it impossible to routinely monitor parameters to control coagulation at the drinking water plants on a daily basis. For that reason, the concept of specific ultraviolet absorbance (SUVA) was developed as an indicator of the nature of NOM and the effectiveness of coagulation in removing NOM, dissolved organic carbon (DOC), and DBP (disinfection byproduct) precursors (9, 10).

Enhanced coagulation overuses coagulant to increase DOC removal to improve the quality of drinking water, and thus prevent the formation of DBPs as well as trihalomethanes (THM), without degrading the quality of the water (6, 10–14). Notably, Volk et al. indicated that the enhanced coagulation is useful only for removing large and hydrophobic organic molecules, but not for small or hydrophilic molecules (15). Moreover, USEPA points out enhanced coagulation, joined to granular activated carbon (GAC) adsorption and precipitative softening among the best available technologies (BATs) for THMs control (16).

Although a vast number of research have been conducted on the effect of preoxidation on the coagulation of NOM (17–23) only a limited number of studies exist that investigate the effect of enhanced coagulation on oxidation (24, 25). In the work of Urfer et al., it was reported that enhanced coagulation could substantially improve disinfection capability of a postsedimentation ozonation system (25). Moreover, Paralkar, and Edzwald, studied the effect of ozonation on the coagulation of extracellular organic matter using model compounds and did not report any significant effect of ozone on coagulation (24). On the other hand, there is a limited number of publications that report on the effects of coagulation of NOM prior to photocatalysis

(22, 23) although some studies present comparisons between photocatalytic oxidation and coagulation relavant to NOM removal efficiencies (26). Complementary to previous research, the current investigation explored the use of enhanced coagulation with alum and ferric chloride in conjuction with photocatalytic oxidation. These processes were compared with regard to natural organic matter (NOM) removal evaluated in terms of the removal of DOC and UV_{254}.

MATERIALS AND METHODS

Raw Water Samples

Raw water samples of different origins were collected in March 2005 from three major drinking water reservoirs—Elmali, Omerli, and Buyukcekmece in Istanbul, Turkey. The characteristics of the water reservoirs have been presented elsewhere (21, 27). After collection, the samples were filtered through a 0.45 μm glass fiber filter and stored at 4°C in the dark until use.

Enhanced Coagulation

Enhanced coagulation was applied using reagent grade aluminum sulfate (commonly referred to as alum, $Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) as coagulants. Jar test coagulation experiments were performed at room temperature (20–25°C) using 500 mL samples. Following the incremental addition of either alum or ferric chloride until the pH of the water sample was lowered to the target pH which is specified by USEPA guidelines according to the DOC and alkalinity ranges of the samples, they were mixed for 1 min at 100 rpm, and then flocculated for 30 min at 30 rpm and then settled for 60 min (16).

Photocatalytic Oxidation and Combined Treatment System

A combined treatment system composed of enhanced coagulation and photocatalysis was applied to Elmali, Omerli, and Buyukcekmece water samples. Subsequent to enhanced coagulation using alum and ferric chloride, samples were subjected to photocatalytic oxidation using TiO_2 Degussa P-25 as the photocatalyst ($0.50\,\mathrm{mg\,mL^{-1}}$) in a cylindrical continuosly mixed photoreactor. The details of the photocatalytic oxidation experiments were presented elsewhere (22, 28, 29).

Analytical Measurements

Prior to analysis, all the samples were filtered through 0.45 μm glass fiber filters. Source water parameters as pH, alkalinity, bromide, color, and conductivity were determined according to the procedures given in Standard Methods (30).

The THM formation potential (THMFP) measurements of raw and partially oxidized samples were carried out according to a standard procedure as explained elsewhere (31). The specific THMFP measurements were also assessed through TOC and THM measurements.

Absorbance measurements of the samples at 254 nm (UV_{254}) and 280 nm (UV_{280}) were recorded on a Shimadzu UV160A double beam UV-vis spectrophotometer. DOC contents of the samples were measured on a Shimadzu TOC-V CSH total organic carbon analyzer. Specific UV absorbance ($SUVA_{254}$, $m^{-1}\,mg^{-1}\,L$) was calculated to represent DOC normalized aromatic moieties (UV_{254}). Fluorescence spectra in an emission scan mode ($\lambda_{exc} = 350$ nm) were acquired on a Perkin Elmer LS 55 luminescence spectrometer. Specific fluorescence intensities of raw and treated samples were calculated by normalizing the fluorescence intensities of each treated sample at the maximum intensity wavelength of the corresponding raw water sample (λ_{max} for Omerli: 438 nm, λ_{max} for Elmali: 434 nm, λ_{max} for Buyukcekmece: 434 nm) with respect to their DOC contents.

RESULTS AND DISCUSSION

General Water Characteristics of the Samples

The main quality parameters of the water samples collected from Elmali, Omerli and Buyukcekmece reservoirs were presented in Table 1.

Under almost neutral pH conditions, the alkalinities of water samples expressed quite different values ranging from 61 to 133 $mg\,CaCO_3\,L^{-1}$. The variation associated with the composition of natural water samples in terms of organic matter is attributed to the complex nature of the formation of aquatic NOM which can vary depending on source, location, and vegetation as expressed by UV_{254} and DOC contents. The water characteristics for the Elmali reservoir are already deteriorated both in terms of land and water resources as reflected to its high DOC, UV_{254} and color values compared to the other reservoirs of Istanbul. Based on the classification of the quality of the drinking water reservoirs of Istanbul, Elmali was ranked the most polluted resource with the worst general and trophic class (32). Chlorine reactivities were presented in terms of THMFP as 169, 179 and 178 $\mu g\,L^{-1}$ for Omerli, Elmali, and Buyukcekmece water samples (29). Significantly high Br^- content of Buyukcekmece is associated with the results which were previously assessed by considerably higher brominated THMFPs (22).

Table 1. General water quality parameters

Parameter, unit	Natural water source: Omerli	Elmali	Buyukcekmece
pH	7.40	7.59	7.69
Turbidity, NTU	2.4	5.5	2.8
Conductivity, μS/cm	252	312	536
Color, Pt-Co units	10	33	6
Bromide, μg L^{-1}	60	95	274
Alkalinity, mg $CaCO_3$ L^{-1}	61	71	133
DOC, mg L^{-1}	3.78	5.29	4.39
UV_{254}, m^{-1}	10.7	22.5	9.40
[a]THMFP, μg L^{-1}	169	179	178

[a](29).

Enhanced Coagulation

The water samples were subjected to enhanced coagulation through jar tests using alum and ferric chloride. The coagulant dose requirements were assessed as 50 mg L^{-1}, 80 mg L^{-1}, and 60 mg L^{-1} for Omerli, Elmali, and Buyukcekmece water samples respectively for both of the coagulants to achieve the target pH goals (16). A comparison of the percent removal efficiencies of the samples based on DOC and UV_{254} were presented in Table 2.

From a general point of view, a comparison of the percent removal efficiencies either in terms of DOC or UV_{254} reveals that under the enhanced coagulation conditions UV_{254} removal is more efficient than DOC removal irrespective of water samples as well as coagulants. This is in accordance with the findings of other studies revealing the importance of the reactivities of the UV absorbing centers in coagulation process (6, 33). Enhanced alum coagulation leads to significant variation in DOC removals as 44%, 28%, and 26% for Elmali, Omerli, and Buyukcekmece water samples, respectively. Upon the application of ferric chloride as the coagulant, the DOC removals achieved were found to be slightly higher as compared to alum. On the other hand, no sample specific change was observed in the ordering of the removal percentage of the samples. The percent removals of DOC increase as Buyukcekmece < Omerli < Elmali for both alum and ferric chloride. Although no significant variation in UV_{254} was attained for both alum and ferric chloride coagulants, comparatively higher efficiencies were attained for the removal of UV absorbing centers with respect to DOC. The Omerli water sample has relatively lower UV_{254} absorbance after coagulation that does not change with the coagulant type. As presented in Table 2, no significant difference is observed in UV_{254} values between the samples of Elmali and

Table 2. Removal efficiencies of water samples in terms of DOC, UV_{254} and $SUVA_{254}$ after enhanced coagulation

	%DOC removal		$\%UV_{254}$ removal		$\%SUVA_{254}$ removal	
	EnhCoag Al	EnhCoag Fe	EnhCoag Al	EnhCoag Fe	EnhCoag Al	EnhCoag Fe
Omerli	28	34	65	65	50	48
Elmali	44	48	77	78	59	58
Buyukcekmece	26	29	47	50	28	29

EnhCoag Al: enhanced coagulation with alum, EnhCoag Fe: enhanced coagulation with ferric chloride.

Buyukcekmece after enhanced coagulation either with ferric chloride or alum (<5% difference). On the other hand, for ferric chloride coagulation, approximately 18%, 8%, and 14% higher DOC removal percentages were observed compared to alum coagulation. Similar findings were also reported by Edzwald and Tobiason via the evaluation of the treatment efficiencies in terms of the SUVA parameter (10). Given the DOC and UV_{254} values in Table 1, $SUVA_{254}$ of the water samples could be calculated as 4.04, 2.83, and 2.14 m^{-1} mg^{-1} L for Elmali, Omerli, and Buyukcekmece, respectively. The results of the percent removals of DOC for both alum and ferric chloride coagulation as illustrated in Table 2 are also in accordance with the corresponding $SUVA_{254}$ removal percentages exhibiting relatively higher removal efficiencies for those with a higher proportion of hydrophobic and hydrophilic NOM (higher SUVA). Under neutral pH conditions, reorganization of humic macromolecules to a coiled conformation may take place upon interaction with coagulant species. Hence, the coagulant dosage should then depend on the complex interplay between the rate of collisions of organic colloids/coagulant species and the rate of macromolecules reconformation. Due to the complex nature of the coagulation process in relation to the applied coagulant type (reactions 1–5) the organic matter content of the natural water samples would yield non-coagulated fractions of diverse chemical composition expressing lower DOC contents and UV-vis properties.

Photocatalytic Oxidation and Combined Treatment System

Photocatalytic degradation profiles of water samples were assessed prior to the application of the combined treatment system composed of enhanced coagulation followed by photocatalysis. As previously reported, the photocatalytic oxidation revealed pseudo first order reaction rate constants as 1.58×10^{-2}, 2.01×10^{-2}, and 1.09×10^{-2} min^{-1} for Omerli, Elmali, and Buyukcekmece raw water samples, respectively in terms of UV_{254} (29). Complementary to the degradation kinetics of UV_{254}, removal data of UV_{280} and DOC were also evaluated in terms of first order reaction rate model (Table 3). The use of UV_{280} is also established as a specific parameter in accordance with UV_{254} revealing descriptive information related to the aromatic core of the organic structure (28).

As expected, the rate constants for DOC removal indicate comparatively slower degradation efficiencies compared to both UV_{254} and UV_{280} removals (>40%). Following the irradiation period of 30 minutes, approximately 37%, 57%, and 60% removal of UV_{254} was attained for Buyukcekmece, Omerli, and Elmali water samples, respectively. Moreover, a further irradiation period of 60 minutes resulted in an improvement of removal efficiencies as 55%, 71%, and 76%, for Buyukcekmece, Omerli, and Elmali water samples. Due primarily to the source dependent diverse nature of the organic matter in water samples, degradation rates were not found to be directly related to the

Table 3. Pseudo first order reaction rate parameters of the water samples (29)

	UV_{254}		UV_{280}		DOC	
	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^{-3}$ (min^{-1})	$t_{1/2}$ (min)
Omerli	1.58	44	1.74	40	9.24	75
Elmali	2.01	34	2.11	33	6.60	105
Buyukcekmece	1.09	64	1.16	60	6.45	107

DOC contents following the sequence of Elmali > Omerli > Buyukcekmece. On the other hand, the photocatalytic degradation rate constants expressed noticeable similarities to the rate constants observed for model NOM compounds such as commercially available humic acids as well as IHSS standard humic/fulvic acids (28). Therefore, no significant effect could be attributed to the diverse nature of the water matrix of the studied samples (Table 1).

The effect of precoagulation step on the oxidative behaviour of photocatalytic oxidation could be visualized by the respective first order kinetic parameters (Table 4).

The most significant variation of the photocatalytic degradation kinetic parameters before and after coagulation was observed for Buyukcekmece water sample where 42% and 50% higher rate constants were calculated subsequent to alum and ferric chloride coagulation. Considerably higher photocatalytic degradation rate constants were achieved for UV_{254} and UV_{280} for Omerli and Buyukcekmece water samples in a combined system. The Elmali water sample exhibited rather slower UV_{254} removal rates irrespective of the applied coagulant type, whereas a distinct effect was observed for the alum coagulated sample as expressed by a higher UV_{280} rate constant. The overall UV_{254} removal tendency followed Buyukcekmece ≈ Elmali > Omerli trend for alum coagulated water samples and Buyukcekmece > Omerli > Elmali trend for ferric chloride coagulated water samples. Although a similar trend was also assessed for UV_{280} removal trend for alum coagulated water, ferric chloride coagulated Omerli water sample expressed a greater removal tendency with respect to Buyukcekmece and Elmali water samples. As a result of the diminished concentration of the UV absorbing centers via a coagulation process, the tabulated rate constants would yield lower degradation rates following the same sequence of water samples. A notable exception was assessed for ferric chloride coagulated Buyukcekmece water sample expressing comparatively slower UV_{254} degradation rate (Table 4).

The NOM components of the natural water samples exhibited an initial adsorption step (instantaneous introduction of TiO_2 to the samples without

Table 4. Pseudo first order reaction rate parameters of the water samples after enhanced coagulation

	UV_{254}				UV_{280}			
	EnhCoag Al + PC		EnhCoag Fe + PC		EnhCoag Al + PC		EnhCoag Fe + PC	
	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)	$k \times 10^{-2}$ (min^{-1})	$t_{1/2}$ (min)
Omerli	1.82	38	1.77	39	2.37	29	2.28	30
Elmali	1.89	37	1.16	60	2.46	28	1.62	43
Buyukcekmece	1.91	36	2.19	32	2.66	26	2.19	32

EnhCoag Al + PC: enhanced coagulation with alum and photocatalysis.

EnhCoag Fe + PC: enhanced coagulation with ferric chloride and photocatalysis.

any UV illumination) onto TiO_2 prior to photocatalysis by 23%, 38%, and 50% for Buyukcekmece, Omerli, and Elmali samples, respectively. However, no significant level of adsorption ($\leq$5%) was observed for coagulated water samples except for the ferric chloride coagulated Buyukcekmece sample (20%). Due to the surface oriented nature of photocatalysis, an initial attack of the hydroxyl radicals could only be achieved by the presence of the attached humic moieties through electrostatic attraction onto TiO_2. However, the charge neutralization/complexation mechanism of coagulation could possibly lower the number of the negatively sites of humic molecules that would be present due to the deprotonation of the carboxylic groups under the neutral pH conditions. The surface charge of the TiO_2 could be considered as neutral, since under neutral pH conditions the pH_{zpc} of TiO_2 (6.25) would yield an equal number of positively and negatively charged surface sites (34). Therefore, the expected attractive and repulsive forces between the species would yield a state of probable oxidation reaction resulting in noticeably slower rates.

Considering the respective half life values of the degradation kinetics, photocatalytic degradation removal efficiencies were evaluated for 30 min of the irradiation period for the comparative assessment of the removal efficiencies with respect to the applied methods (Table 5).

Through the non-selective oxidation mechanism of the hydroxyl radicals, the non-coagulated moieties of the organic matter content of the water samples revealed quite similar degradation efficiencies. A combined treatment incorporating photocatalytic oxidation subsequent to alum coagulation leads to 22%, 12%, and 32% increase in DOC removal efficiencies compared to alum coagulation alone for Omerli, Elmali, and Buyukcekmece, respectively. On the other hand, ferric chloride coagulation following photocatalysis does not show a significant difference for Omerli and Elmali (<5%) but for Buyukcekmece an 18% decrease is observed in the combined treatment using alum coagulation.

Moreover, the effect of the combined treatment on the removal efficiencies of UV_{254} values is significantly different compared to the application of enhanced coagulation alone (Table 2 and Table 5). The removal percentages could be ordered as Elmali > Omerli > Buyukcekmece for both enhanced coagulation and combined treatment irrespective of the coagulant type.

Table 5. Removal efficiencies of water samples in terms of DOC and UV_{254} after the application of combined treatment systems

	%DOC		$\%UV_{254}$	
	EnhCoag Al + PC	EnhCoag Fe + PC	EnhCoag Al + PC	EnhCoag Fe + PC
Omerli	36	37	79	80
Elmali	50	48	87	84
Buyukcekmece	37	30	70	67

A further assessment could also be verified by the interpretation of the DOC normalized UV as well as fluorescence spectroscopic properties. $SUVA_{254}$ and specific fluorescence intensity (SFI) values of the treated water samples were presented in Table 6. Specific fluorescence intensities of raw and treated samples were calculated by normalizing the fluorescence intensities of each treated sample at the maximum intensity wavelength of the corresponding raw water sample (λ_{max} for Omerli: 438 nm, λ_{max} for Elmali: 434 nm, λ_{max} for Buyukcekmece: 434 nm) with respect to the corresponding DOC contents of the samples.

The $SUVA_{254}$ values for Omerli, Elmali, and Buyukcekmece are 2.83, 4.04, and 2.14 respectively. After enhanced coagulation no significant difference was observed in the percentage of $SUVA_{254}$ removal based on the use of different coagulants. The lowest removal of $SUVA_{254}$ was observed for Buyukcekmece as 28% and 29% using alum or ferric chloride, respectively. The highest removal for $SUVA_{254}$ was attained for Elmali after a combined treatment utilizing enhanced coagulation with alum prior to photocatalysis (74%).

The SFI values determined from the emission spectra of the studied natural water samples considerably vary according to the origin of the samples. The Elmali water sample which is from a highly colored, polluted water source has the highest SFI compared to Omerli and Buyukcekmece. Although no significant variation was observed in SFI values within each water sample during enhanced coagulation using both alum and ferric chloride, noteworthy differences were attained after a combined treatment. In all cases, the highest removal of SFI was achieved for a combined treatment utilizing alum coagulation prior to photocatalysis. The lowest $SUVA_{254}$ as well as SFI values after each treatment process were obtained for the Omerli water samples. From a general point of view, an overall decrease of both $SUVA_{254}$ and SFI values was observed in parallel with the treatment efficiency. The results are similar to the findings of others where a good linear relation between florescence intensity and DOC removal rate

Table 6. Specific spectroscopic parameters of the water samples with respect to treatment methods

	Omerli		Elmali		Buyukcekmece	
	$SUVA_{254}$	SFI	$SUVA_{254}$	SFI	$SUVA_{254}$	SFI
Raw	2.83	19.14	4.04	33.80	2.14	16.89
EnhCoag Al	1.40	15.41	1.64	35.99	1.54	16.90
EnhCoag Al + PC	0.92	4.56	1.04	7.91	1.01	8.43
EnhCoag Fe	1.47	16.92	1.68	30.0	1.51	16.43
EnhCoag Fe + PC	0.88	5.62	1.24	14.7	1.02	12.64

was reported to predict the DOC residual concentration after enhanced coagulation for raw water samples (35).

CONCLUSIONS

In the present study, NOM removal efficiencies of samples from three major drinking water sources (Elmali, Omerli, and Buyukcekmece) of Istanbul Metropolitan City were compared by the application of enhanced coagulation, photocatalysis, and a combined treatment utilizing photocatalysis subsequent to enhanced coagulation. The efficiency of NOM removal relevant to each treatment step was assessed through DOC removal, UV_{254} removal, and fluorescence measurements.

Differences were attained during each treatment with regard to source related properties of NOM. Irrespective of the treatment applied as enhanced coagulation, photocatalytic oxidation, or a combined treatment systems, the highest removal efficiency in terms of both UV_{254} and DOC was determined for the Elmali water sample followed by the Omerli and Buyukcekmece samples. After enhanced coagulation no significant difference was observed in the percentage of $SUVA_{254}$ removal based on the use of different coagulants. The lowest removal of $SUVA_{254}$ was observed for Buyukcekmece as 28% and 29% using alum or ferric chloride, respectively. The highest removal for $SUVA_{254}$ (74%) was attained for Elmali after a combined treatment incorporating photocatalytic oxidation subsequent to alum coagulation. Moreover, combined treatment leads to 36%, 37%, and 50% of DOC removal for Omerli, Buyukcekmece, and Elmali respectively. On the other hand, ferric chloride coagulation following photocatalysis does not show a significant difference for Omerli and Elmali ($<5\%$) but for Buyukcekmece an 18% decrease is observed in the combined treatment using alum coagulation. The improvement of removal efficiencies in combined treatment systems were scrutinized with an emphasis on induced water properties as supported by the specific fluorescence intensities of the samples.

The efficiency of removal of combined treatment systems could be improved by a further investigation of the solution matrix. Considering that enhanced coagulation generally removes large molecular size components expressing different hdrophobicity/hydrophilicity characteristics, the treatment efficiencies after photocatalysis are also expected to be altered. Hence, depending on the solution matrix, better results leading to application conditions of higher removal efficiencies could also be attained.

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