

ENHANCING PURIFICATION OF SURFACE WATER BY POTASSIUM PERMANGANATE ADDITION

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ABSTRACT

The aim of the present research is studying the effect of potassium permanganate addition on the pre-oxidation and coagulation of the surface water. River Nile and El Rayah El Tawfegy of Benha city, Egypt were the surface water supply used in this research. The results showed that El Rayah El Tawfegy raw water had higher turbidity concentration and humic acids absorbance (8.5 NTU and 0.024, respectively) than that of River Nile (6.5 NTU and 0.018, respectively). The optimum dose of potassium permanganate ranged between 4 and 6 mg/L for coagulation process, while for oxidation of humic acid, at higher dose of potassium permanganate a higher removal can be achieved. At a constant dose of potassium permanganate (6 mg/L), the optimum dose of alum ranged between 40 - 60 mg/L and it was 85 - 105 mg/L for ferric sulfate. Addition of potassium permanganate (6 mg/L) to the raw water of El Rayah El Tawfegy and River Nile without using of any coagulant resulted in a turbidity removal of about 35%. Therefore, potassium permanganate addition led to a significant turbidity removal. At alum dose of 40 mg/L and potassium permanganate dose of 6 mg/L, the turbidity and humic acid removal were 70 and 75%, respectively, for the raw water of El Rayah El Tawfegy and were 58 and 44%, respectively, for the raw water of River Nile. At ferric sulfate dose of 85 mg/L and potassium permanganate dose of 6 mg/L, the turbidity and humic acid removal were 53 and 50%, respectively, for the raw water of El Rayah El Tawfegy and were 20 and 17%, respectively, for the raw water of River Nile. Therefore, the alum had better results than the ferric sulfate. The optimum pH was 6.0 - 8.5, which is similar to that of raw water of El Rayah El Tawfegy and River Nile, i.e. no need for pH adjustment.

Keywords: humic acids; jar test; pre-oxidation; potassium permanganate; surface water purification

INTRODUCTION

Traditionally, chlorine is used for pre-oxidation of water. Recently, it was found that addition of chlorine to raw water leads to the formation of chlorination by-products, like trihalomethane (THM), which has a carcinogenic effect [1, 2, 3]. Therefore, pre-

chlorination is being progressively restricted in most of western countries [4, 5]. Pre-oxidation aims to improve the coagulation process. Pre-oxidation is generally used to destroy the organic coating on the surface of particles or destroying the stabilization effect of algae species on the colloidal particles. It has been previously demonstrated that the organic matters have a very strong relation with the presence of algae and bacteria, like Cholera, Typhoid, Salmonellosis and Shiyellosis. Permanganate pre-oxidation has been used to remove iron and manganese from ground water and to control taste and odor, in particularly of algal origin [6, 7, 8, 9]. It has also been used as a disinfectant. In comparison to the existing special process for treating water with high organic content such as ozonation and activated carbon process etc., permanganate pre-oxidation has the advantages of low cost, easy operation and maintenance.

Observations reported for potassium permanganate (KMnO_4) use at the Crum and Pickering plants of the Philadelphia Suburban Water Company illustrated its effectiveness as a disinfectant. At these locations, taste and odor control was achieved by treatment with KMnO_4 at dose rates between 0.5 and 1.5 mg/L in conjunction with feeds of 30.8 mg/L alum and up to 10 mg/L powdered activated carbon. In addition, when treated with 0.75 mg/L of potassium permanganate, raw water showed a MPN reduction, corresponding to a 95 percent reduction [10]. A plant scale treatment study [11] was conducted at the Kansas City, Missouri, water purification plant. KMnO_4 dosages were applied in accordance with the actual permanganate demand of the water. The monthly averages were as follows: December, 1.0 mg/L, January, 1.1 mg/L, February, 1.3 mg/L, March, 2.7 mg/L. With a few exceptions, the coliform content was reduced to less than detectable levels; fecal streptococci removal ranged from 48 to 96 %. Actinomycetes removal was as high as 96 % and as low as 27%. Betty and Ty [12] studied the removal of monomeric precursors by alum coagulation. They concluded that, the use of KMnO_4 as a pre treatment process preceding alum coagulation, significantly reduced the level of chloroform in the treated water when the raw water contained high portions of monomeric precursors.

Ma et al. [13] had investigated the effective and mechanism of KMnO_4 oxidation for the removal of acrylamide from water. They found that potassium permanganate is a strong oxidant on acrylamide. Small amount of KMnO_4 was needed to reduce acrylamide concentrations to an acceptable level. Some reducing agents in water may influence the oxidation effectiveness of KMnO_4 , hydrogen sulphide has a large influence and its presence at molar ratio in water may greatly reduce the oxidation efficiency. The influence of iron (II) on the oxidation of acrylamide is also very clear, the presence of humic and fulvic acids may reduce slightly the oxidation efficiency of acrylamide. Nitrate and manganese appear to have little impact on the oxidation of acrylamide by potassium permanganate. Petrusevsici et al. [14] studied the capability of different treatment strategies to improve algae removal and to diminish KMnO_4 on algae and particle removal in direct filtration. They showed the effect of permanganate pretreatment followed by coagulation with dual coagulants (ferric sulphate and cationic polymer). They found that, efficient removal of algae and other particulate matter in direct filtration supported by KMnO_4 preoxidation and coagulation with

ferric sulphate and a cationic polymer was suggested to be a consequence of several process mechanisms. Permanganate preoxidation causes coagulation and agglomerate formation before the addition of flocculants/ coagulants. The subsequent application of dual coagulant resulted in further preoxidation through enmeshment in precipitate and adsorption and charge neutralization. Ma et al. [15] studied the ability of permanganate preoxidation to achieve substantial reductions of chloroform formation potential for most of the model THM precursors, i.e. resorcinol, hydroquinone catechol, humic acid and tannic acid. They concluded that permanganate preoxidation can achieve substantial reduction of chloroform formation potential for most of selected THM precursors. Ma et al. [4] studied the effect of permanganate preoxidation in enhancing the coagulation of surface waters which containing a high organic content. They concluded that KMnO_4 preoxidation has a significant beneficial effect. Soluble manganese in the water as found to depend on the water pH. At neutral or moderately acid pH soluble manganese in the filtrate was satisfactorily low, while at lower pH values the residual soluble manganese concentration increased with increasing permanganate dosage. Ma et al. [5] studied the laboratory and full-scale experiment for enhancing the coagulation of stabilized surface waters with high organic content by permanganate preoxidation and the role of manganese dioxide produced in situ enhancing the coagulation and filtration processes. It was indicated that permanganate preoxidation enhanced both the processes of coagulation and filtration of surface water, preliminary comparative simulation tests demonstrated that permanganate preoxidation is much more effective than prechlorination in enhancing the coagulation of surface water with high organic content. The experimental results suggested that manganese dioxide may adsorb bigger particulates, thus increasing the flocs density and improving the removal of organic particulates and possibly the inorganic fine particles. Manganese dioxide was shown to adsorb humic acid and enhance its removal by filtration.

The aim of the present research is studying the effect of potassium permanganate addition on the pre-oxidation and coagulation of the surface water. Alum and ferric sulfate were used as a coagulant. The surface water supply used in this research was the surface water of River Nile and El Rayah El Tawfky in Benha City, Egypt.

MATERIAL AND METHODS

The jar test was used to determine the optimum operating conditions in this research. At the beginning the jar testing apparatus containers are filled with 500 ml of water sample, then the oxidant (KMnO_4) was added followed by coagulant (aluminum sulfate or ferric sulfate) addition to each container at stirring speed 250 rpm for 30 sec. After that, the stirring speed are reduced to 35 rpm and continue mixing for 5 minutes, this slower mixing speed helps to promote floc formation by enhancing particle collisions which lead to larger flocs. These speeds are slow enough to prevent sheering of the flocs due to turbulence caused by stirring to fast. Finally the mixers are stopped and the containers are allowed to settle for 15 minutes. These previous experimental conditions were done as described by Ma et al. [4] for permanganate preoxidation. Then, the characteristics of the water in each container were measured. The pH

adjustment for the water sample was carried out before Jar test by addition either sodium hydroxide or hydrochloric acid for increasing or decreasing pH, respectively. The applying doses of the KMnO_4 were 1, 2, 3, 4, 6, 8 mg/l and were 20, 40, 60, 100 mg/L and 20, 40, 60, 85, 105 mg/l for aluminum sulfate and ferric sulfate, respectively. Table 1 shows the operation conditions of the Jar test experiments. Turbidity, humic acid and residual permanganate were measured for the raw water samples and at the end of the each jar test. Turbidity was measured (by Turbidity meter: Orbeco, Hellige) for water with and without filtration, while humic acid and residual permanganate was measured for filtered water by using spectrophotometer.

Table 1. Operation conditions of the Jar test experiments

Run No.	KMnO_4 (mg/l)	pH	Coagulant	Time of gentel mixing (min.)
Run 1	1 - 8*	8.2	-	5
Run 2	-	8.2	Alum (20 - 100) mg/l or Ferric sulfate (20 - 105) mg/l*	5
Run 3	6	8.2	Alum (20 - 100) mg/l or Ferric sulfate (20 - 105) mg/l*	5
Run 4	6	2 - 12*	Alum = 40 mg/l or Ferric sulfate = 85 mg/l	5
Run 5	6	8.2	Alum = 40 mg/l or Ferric sulfate = 85 mg/l	5 - 20*

* the variable parameter in the run

RESULTS AND DISCUSSION

Characteristics of the sources of water

Table 2 shows the characteristics of the water sources of the study. The results demonstrated that El Rayah El Tawfegy and River Nile had almost the same pH, Total dissolved solids and conductivity, which are in acceptable range. It is cleared from the results that El Rayah El Tawfegy had more organic than that of River Nile, due to higher values of turbidity, TOC and humic acid in the El Rayah El Tawfegy.

Table 2. Water quality characteristics of El Rayah El Tawfegy and River Nile in Benha

Parameter	Unit	El Rayah El Tawfegy	River Nile
pH	-	8.5	8.2
Turbidity	NTU	8.5	6.5
Total Dissolved Solids	mg/L	234	240
Conductivity	$\mu\text{S}/\text{cm}$	332	341
Temperature	$^{\circ}\text{C}$	23.60	24.0
TOC	mg/l	5.77	3.68
Humic acid	Absorpance	0.024	0.018

Pre-oxidation with KMnO_4 without coagulant addition

Figure 1 shows the effect of KMnO_4 on the turbidity and humic acids removal. The result clearly showed that the KMnO_4 was effective for both turbidity and humic acids removal. The optimum dose of KMnO_4 for turbidity removal ranged between 3 – 6 mg/L, while at increasing KMnO_4 dose, the humic acids removal increased. At optimum turbidity removal dose, 37 and 46% of the turbidity and humic acids, respectively, were removed from the raw water of El Rayah El Tawfeky, while 34 and 44% were, respectively, removed from the raw water of the Nile River. The previous results confirm that the KMnO_4 was not only a preoxidant, but also a coagulant. The latter mechanism occurs due to formation manganese dioxide, as proposed by Ma et al. [5]. The results demonstrated that KMnO_4 had almost similar removal of turbidity and humic acids for the raw water of El Rayah El Tawfeky and Nile River at optimum turbidity dose.

Coagulation without preoxidation

Figures 2 and 3 present the effect of alum and ferric sulfate, respectively, addition on turbidity and humic acids removal. The results showed the optimum dose was 40-60 and 85-105 mg/L for alum and ferric sulfate, respectively. At optimum dose of alum, turbidity and humic acids removal were 47% and 88%, respectively, for El Rayah El Tawfeky and were 69% and 72%, respectively, for River Nile. At optimum dose of ferric sulfate, turbidity and humic acids removal were 45% and 88%, respectively for El Rayah El Tawfeky and were 42% and 78%, respectively for River Nile. Therefore, it can be concluded that the alum is more efficient than the ferric sulfate at optimum dose and normal pH of the water (8.2).

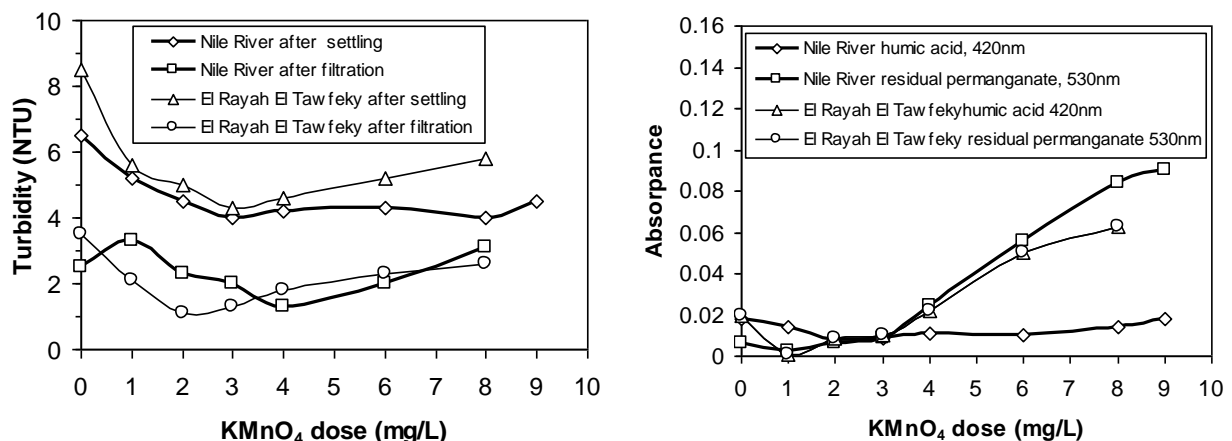


Figure 1. Effect of KMnO_4 addition on the turbidity and humic acids removal. pH = 8.2, gentle mixing time = 5min.

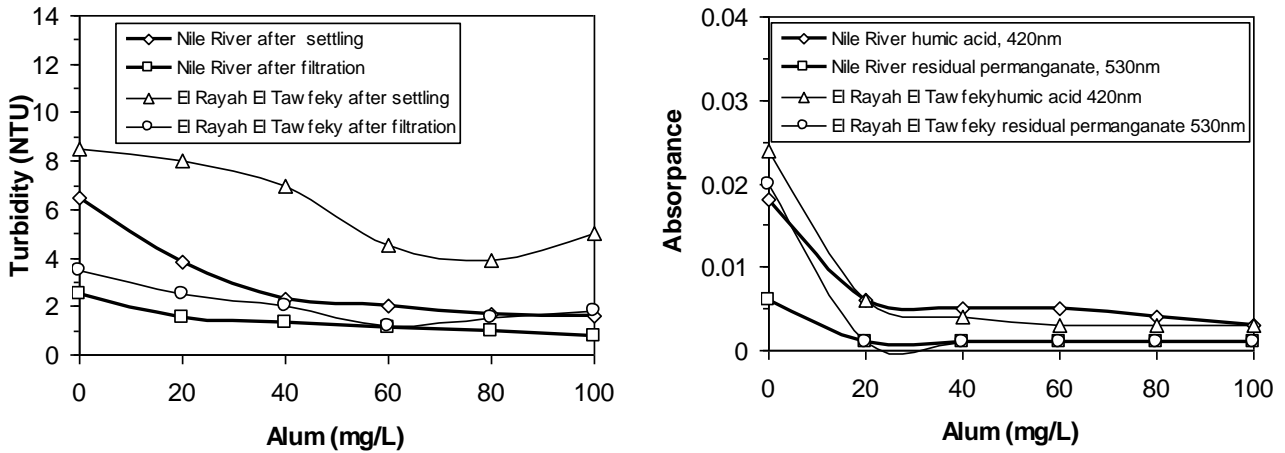


Figure 2. Effect of alum (20-100 mg/L) on the turbidity and humic acids removal. pH = 8.2, gentle mixing time = 5 min.

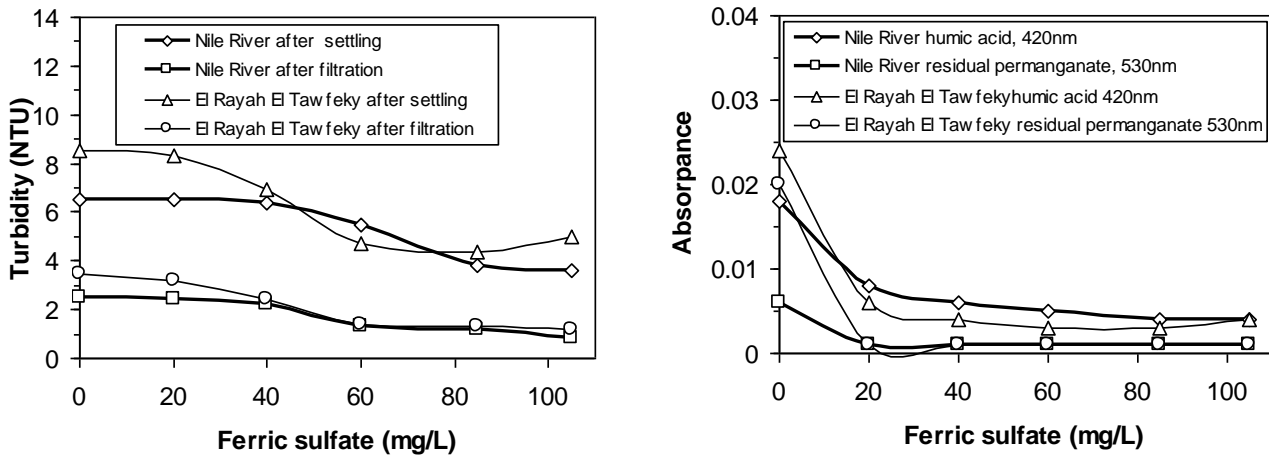


Figure 3. Effect of ferric sulfate (85-100 mg/L) on the turbidity and humic acids removal. pH = 8.2, gentle mixing time = 5 min.

Preoxidation with coagulation

Figure 4 and 5 show the effect of preoxidation with $KMnO_4$ on the coagulation with Alum and ferric sulfate, respectively. The alum or ferric sulfate dose was constant (40 and 85 mg/L, respectively) and was selected based on the results of Jar testes in the previous paragraph. The result showed that the optimum dose of $KMnO_4$ was between 3 - 6 mg/L, which is similar to the results of applying $KMnO_4$ without alum or ferric sulfate. At dose of 6 and 40 mg/L, for respectively $KMnO_4$ and alum, the turbidity and humic acids removal were 70% and 75%, respectively, for El Rayah El Taw feky and were 58% and 44%, respectively, for Nile River. The higher removal of turbidity and humic acids for El Rayah El Taw feky than the Nile River was due to higher concentration of turbidity and humic acids in raw water of El Rayah El Taw feky. At dose of 6 and 85 mg/L, for respectively $KMnO_4$ and ferric sulfate, the turbidity and humic acids removal were 53 and 50 %, respectively, for El Rayah El Taw feky and

were 34% and 28%, respectively, for Nile River. Similarly, it was found that higher removal of turbidity and humic acids for El Rayah El Tawfegy was obtained than the Nile River.

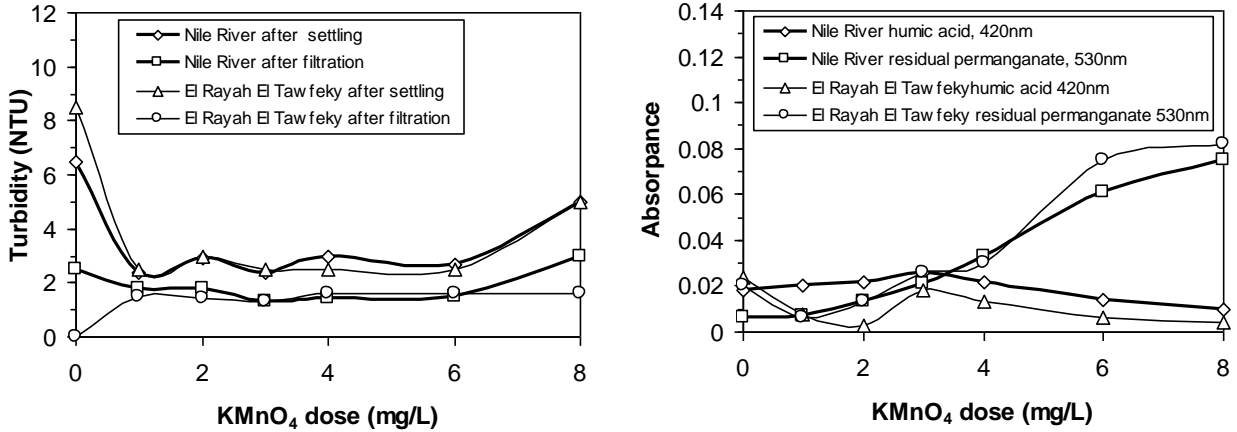


Figure 4. Effect of preoxidant ($KMnO_4$) and coagulant (alum) on the turbidity and humic acids removal. Alum = 40 mg/L, pH = 8.2, gentle mixing time = 5 min.

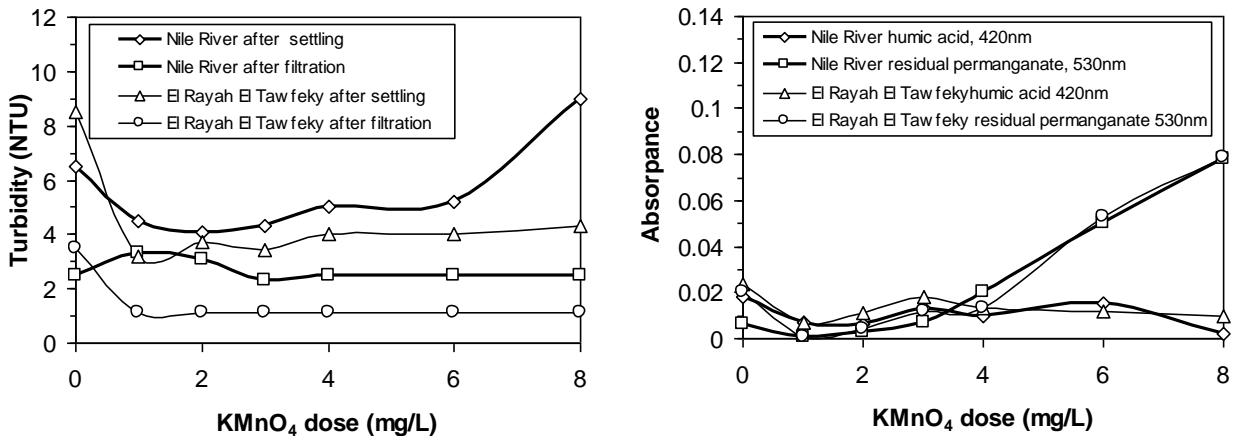


Figure 5. Effect of preoxidant ($KMnO_4$) and coagulant (ferric sulfate) on the turbidity and humic acids removal. Ferric sulfate = 85-100 mg/l, pH = 8.2, gentle mixing time = 5 min.

Effect pH and gentle mixing time on preoxidation with coagulation

The results of the effect of pH on the preoxidation of humic acid by potassium permanganate are presented in Figures 6. These data showed that pH had no influence on humic acid concentration, while for turbidity, it can be concluded that the optimum pH ranged between 6.0-8.5. The results showed that increasing the gentle mixing time slightly increased the turbidity removal and had no effect on humic acids removal (Figures 7 and 8).

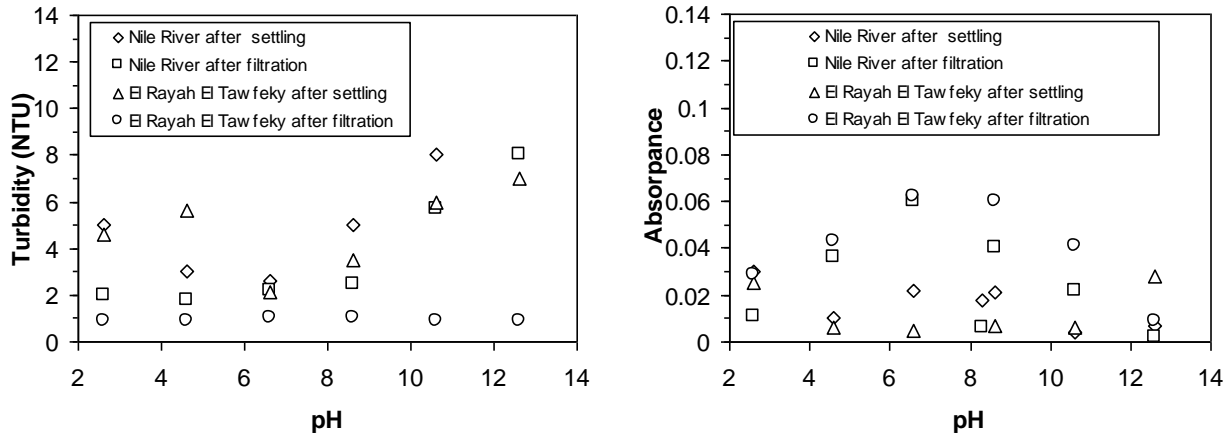


Figure 6. Effect of pH on turbidity and humic acids removal.
 $\text{KMnO}_4 = 6 \text{ mg/L}$, alum = 40 mg/L, gentle mixing time = 5 min.

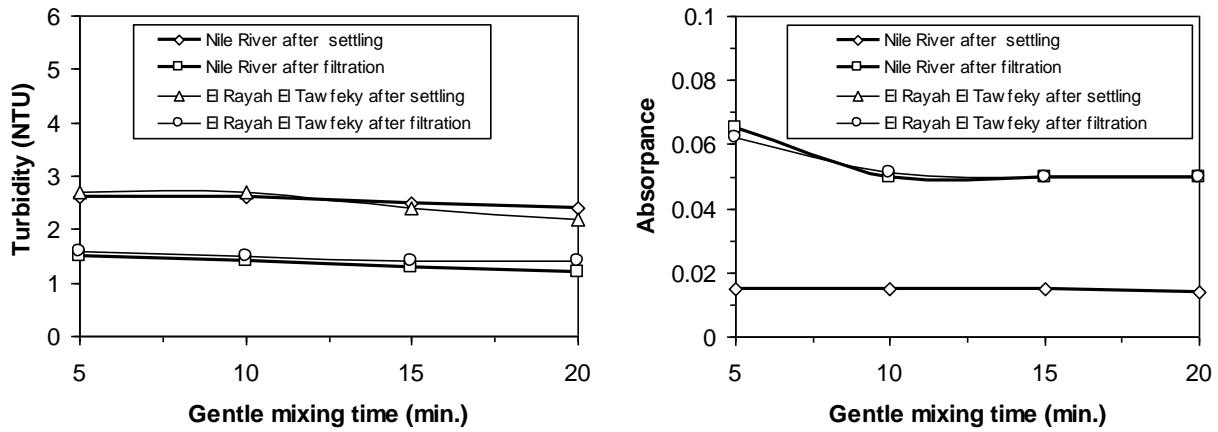


Figure 7. Effect of gentle mixing time on turbidity and humic acids removal.
 $\text{KMnO}_4 = 6 \text{ mg/L}$, alum = 40 mg/L, pH = 8.2.

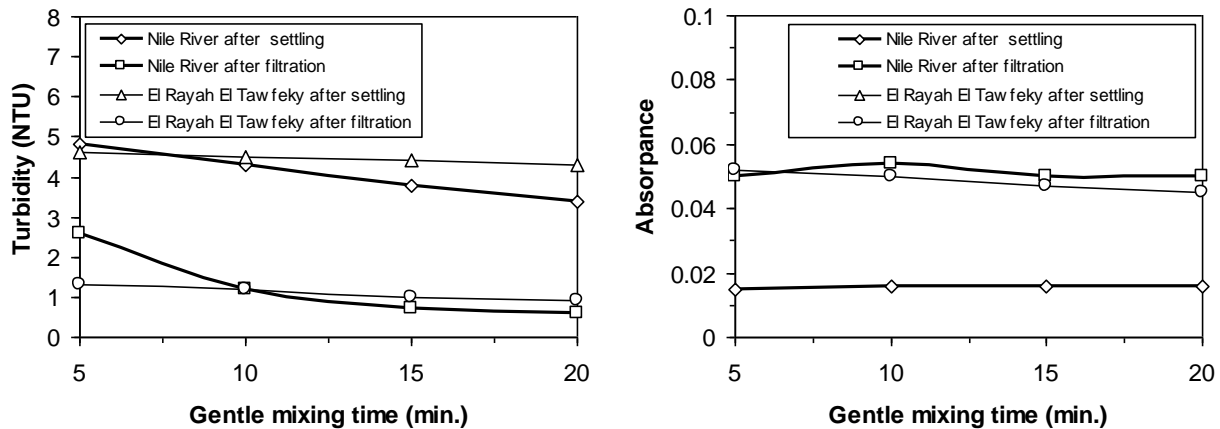


Figure 8. Effect of gentle mixing time on turbidity and humic acids removal.
 $\text{KMnO}_4 = 6 \text{ mg/L}$, ferric sulfate = 85 mg/L, pH = 8.2.

Final Discussion

The experiments carried out on both El Rayah El Tawfegy and River Nile surface water have demonstrated that potassium permanganate preoxidation can have a beneficial effect on the performance of a chemical coagulation of such water. At lower coagulant dosages (aluminum sulfate or ferric sulfate), the effectiveness of permanganate preoxidation on the turbidity removal was obvious. It has been shown that the coagulation of the organic-rich water is particularly enhanced by permanganate preoxidation, as demonstrated by a much greater reduction of residual turbidity. Thus, relatively larger floc sizes were observed when the samples were subjected to permanganate preoxidation. The results showed that the addition of only KMnO_4 had a significant effect on both coagulation and preoxidation, as shown in Tables 3 and 4. At ferric sulfate dose of 85 mg/L and potassium permanganate dose of 6 mg/L, the turbidity and humic acid removal were 53 and 50%, respectively, for the raw water of El Rayah El Tawfegy and were 20 and 17%, respectively, for the raw water of River Nile. Therefore, the alum had better results than the ferric sulfate.

Table 3. Comparison between El Rayah El Tawfegy and River Nile by using Alum

	KMnO_4 (6.0 mg/l) with Alum (40.0 mg/l)		KMnO_4 (6.0mg/l) without Alum	
	Turbidity removal (%)	Humic Acid removal (%)	Turbidity removal (%)	Humic Acid removal (%)
El Rayah El Tawfegy	70	75	37	46
River Nile	58	22	34	44

Table 4. Comparison between El Rayah El Tawfegy and River Nile by using ferric sulfate

	KMnO_4 (6.0 mg/l) with Ferric Sulfate (85.0 mg/l)		KMnO_4 (6.0 mg/l) without Ferric Sulfate	
	Turbidity removal (%)	Humic Acid removal (%)	Turbidity removal (%)	Humic Acid removal (%)
El Rayah El Tawfegy	53	50	37	46
River Nile	20	17	34	44

CONCLUSIONS

1. El Rayah El Tawfegy raw water had higher turbidity concentration and humic acids absorbance (8.5 NTU and 0.024, respectively) than that of River Nile (6.5 NTU and 0.018, respectively).

2. The optimum dose of potassium permanganate ranged between 4 and 6 mg/L for coagulation process, while for oxidation of humic acids, at higher dose of potassium permanganate a higher removal can be achieved.
3. At a constant dose of potassium permanganate (6 mg/L), the optimum dose of alum ranged between 40 - 60 mg/L and it was 85 -105 mg/L for ferric sulfate.
4. Addition of potassium permanganate (6 mg/L) to the raw water of El Rayah El Tawfegy and River Nile without using of any coagulant resulted in a turbidity removal of about 35%. Therefore, potassium permanganate addition led to a significant turbidity removal.
5. At alum dose of 40 mg/L and potassium permanganate dose of 6 mg/L, the turbidity and humic acid removal were 70 and 75%, respectively, for the raw water of El Rayah El Tawfegy and were 58 and 44%, respectively, for the raw water of River Nile.
6. At ferric sulfate dose of 85 mg/L and potassium permanganate dose of 6 mg/L, the turbidity and humic acid removal were 53 and 50%, respectively, for the raw water of El Rayah El Tawfegy and were 20 and 17%, respectively, for the raw water of River Nile. Therefore, the alum had better results than the ferric sulfate.
7. The optimum pH was 6.0 - 8.5, which is similar to that of raw water of El Rayah El Tawfegy and River Nile, i.e. no need for pH adjustment.

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