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The simultaneous removal of turbidity and humic substances from water using the enhanced coagulation process

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ABSTRACT

This study aimed to investigate the efficiency of the enhanced coagulation (EC) process for the simultaneous removal of turbidity and humic substances (HS) from raw water from the Sanandaj Water Treatment Plant (SWTP). This study was conducted on a laboratory scale using a jar test device and ferric chloride ($FeCL_3$) as the coagulant. Accordingly, the effects of pH and coagulant dosage variations on the simultaneous removal efficiency of turbidity and humic substances in the enhanced coagulation process were investigated. Furthermore, certain parameters including the total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance (UV_{254}), and chemical oxygen demand (COD) were determined as the indices of the humic substances and turbidity in the water samples. The results of the raw water analysis showed that the mean values of TOC, DOC, UV_{254}, COD, and turbidity parameters were 4.41 mg/L, 4.11 mg/L, 16.47 1/cm, 15 mg/L, and 4.37 NTU, respectively. Moreover, the results of the present study showed that the average efficiency of the enhanced coagulation process in the removal of TOC, DOC, UV_{254}, COD, and turbidity was 65%, 62%, 70%, 69%, and 93%, respectively. Accordingly, the EC process using $FeCL_3$ coagulant is a suitable, cost-effective, and highly efficient method for the simultaneous removal of turbidity and humic substances from water. Furthermore, this process can be used as an applicable method in SWTP as well as in other similar water treatment plants.

Keywords: Humic substances; Enhanced coagulation; Ferric chloride; Turbidity

Introduction

Coagulation and flocculation are common methods for removal of turbidity and organic compounds from water.[1] Humic substances (HS) are among the most important organic compounds and the main component of the natural organic matter (NOM) in water resources.[2] These substances are complex organic compounds derived from the natural decomposition of plant and animal tissues by microorganisms.[3, 4] Many of the quality problems of drinking water, including color, smell, and taste are attributed to the presence of humic substances in water.[5] These substances can increase the biological regrowth in water distribution networks, membrane erosion, and required chlorine.[6, 7] In addition, the major problem of the presence of humic substances in water is their reaction with disinfectants and creating the carcinogenic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAA).[7, 8]The United States Environmental Protection Agency (USEPA) has determined the maximum allowable concentration of 80 and 60 mg/L for THM and HAA in drinking water, respectively.[8, 9]

So far, the various methods including the adsorption process,[7] ion exchange,[10] the nano-

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photocatalytic processes,[11, 12] the membrane technologies,[13, 14] ultrasonic,[3] electrocoagulation,[15] coagulation, and the recently enhanced coagulation process (EC) have been used for the removal of humic substances from water. [16, 17] However, the EC process has-been considered more due to its desirable features which include the low investment and utilization costs, high efficiency, and higher reliability than the other treatment procedures.[18, 19] Indeed, EC is the optimization of the coagulation process for the simultaneous removal of turbidity and precursor organic matter of THMs in the common water treatment processes, which is performed using coagulants such as aluminum and iron salts as well as the cationic polymers.[20, 21] The USEPA has introduced the EC process as the best available technology (BAT) for the removal of humic substances and meeting the requirements of the first stage of disinfectants/disinfection byproducts law (D/DBP) to reduce the total organic carbon (TOC) and remove the precursors of disinfection byproducts.[9] The EC process can meet the maximum allowable concentration of THMs specified by USEPA.[22] In general, increasing the coagulant dosage and adjusting pH are the two major ways to achieve the EC objectives.[23] The most important mechanisms through which EC removes humic substances include precipitation (formation of iron and aluminum humates and fallouts), the neutralization of colloidal humic substances' charges, and coprecipitation by adsorption on metal hydroxides.[22, 24]

The present research aimed to apply the EC process to the simultaneous removal of turbidity and humic substances from the raw water of SWTP.

Materials and Methods

Chemicals

All the chemicals used in this study were analytical grade and were purchased from Merck. Besides, the coagulant used in this research was $FeCL_3$, provided by the SWTP. This chemical is commonly used as the main coagulant in this treatment plant.

Water resource and sampling

The water sample used in this study was the raw water of the SWTP. The raw water entering this treatment plant was of a surface type, which came from the Vahdat Dam, located 5 km from the city of Sanandaj. To analyze the indices of the humic substances, the samples derived from raw water, as well as from the various stages of the jar test process, were kept in a dark place at 4 ºC until the analysis.

Enhanced coagulation process method

In this study, the average dose of the coagulant used in the conventional coagulation process and the average natural pH of raw water were considered as the base for the study. According to the available information, the mean coagulant used for conventional coagulation was 60 mg/L and the average pH of the raw water was considered to be 8. According to the EPA documents, in the EC process (for the simultaneous removal of turbidity and humic substances), reduced pH and increased coagulant dosage lead to the increased removal of humic substances.[8] Thus, in this study, the EC process was performed on the raw water on a laboratory scale (jar test apparatus) using $FeCL_3$ as the coagulant. So, at first and in order to determine the optimal pH, the coagulant dosage was constant at 60 mg/L and pH was variable (control, 5, 6, 7, 8, and 9). At this stage, pH was adjusted using 1N $FeCL_3$ and 1N soda (NaOH). The optimal pH of coagulation was determined as the maximum pH, in which the maximum removal efficiency of humic substances and turbidity was obtained. At the next stage, after specifying the optimal pH, by keeping pH at a constant value, the concentration of the $FeCL_3$ coagulant was increased, so that the first container was the control container, and 70, 100, 130, 160, and 190 mg/L of the coagulant were added to the containers 2, 3, 4, 5, and 6, respectively. To perform the analysis, the samples were taken from the depth of 2 cm below the water surface in each container, and all the given variables were determined.[25]

Methods of analysis

In this study, in addition to turbidity, the parameters of TOC, DOC, COD, and UV absorption at the wavelength of 254 nm (UV_{254}) Were determined as the indices related to the humic organic matter in the samples.[26] The TOC and DOC samples (after filtering the samples with a 0.45 μm filter) were analyzed using the TOC-meter device (TOC/TN model, Skalar, Netherlands).[8] The COD concentrations were determined by standard spectrophotometric methods as outlined in Standard Methods for the Examination of Water and Wastewater.[27] In this test, the COD reactor (HACH, United States) and the UV/VIS spectrophotometer (model T80, PG Co., England) were used. Furthermore, the UV_{254} value was determined using the spectrophotometer (DR-5000, HACH, United States). The specific UV absorption (SUVA), as a computational parameter, was determined by dividing the absorption of UV_{254}(m^{-1}) by DOC (mg/L).[8] Besides, the turbidity of all the samples was measured by a HANNA turbidity-meter. Also, the JENWAY pH-meter (model 3510) was used to determine pH.

Results and Discussion

Characteristics of raw water

The simultaneous removal of humic substances and turbidity using the coagulation process is affected by various factors such as the concentration and characteristics of humic substances, the level of turbidity, the concentration of inorganic compounds, the characteristics of raw water, the design, as well as the method of operation and maintenance of the water treatment plant.[28, 29] The results obtained from the qualitative analysis of the parameters of the raw water of SWTP are presented in Table 1. As seen in this table, the mean value of most of the measured parameters was in the range of the concentrations found in common surface water. By determining the raw water's characteristics in Table 1, the notable point was the low turbidity of water, the mean value of which was obtained to be 4.37 NTU. The reason for such low turbidity could be probably the desirable quality of the upstream resources as well as the duration of water retention behind the Vahdat Dam. In addition, it is seen in the table that the values of the indices of humic substances were in the range of concentrations usually found in surface water.

Table 1. Mean of raw water qualitative parameters in SWTP

Parameter	Unit	Minimum	Maximum	Mean
Turbidity	NTU	2.39	8.5	4.37
pH	-	7.11	8.24	8
Alkalinity	mg/L Ca-CO_3	181	223	203
TOC	mg/L	2.33	4.41	4.18
DOC	mg/L	2.07	4.11	3.23
UV_{254}	Cm^{-1}	7.21	16.47	13.55
SUVA	L/mg-m	3.5	4.25	4.05
COD	mg/L	4	15	11
Total Iron	mg/L	0	0.25	0.1

Effect of pH

pH is one of the major parameters in the coagulation and flocculation processes, which significantly affects the processes; besides, due to the relationship between pH and alkalinity, pH variations have a considerable effect on the removal of humic substances and turbidity.[30] According to various reports, pH of water resource is one of the major and effective factors in the EC process and should be taken into account in order to achieve the optimum removal of humic substances.[29, 31] Further, due to the relationship between pH and alkalinity and the effect of these parameters on the removal of humic substances, pH variation is particularly important.[30] Figs. 1 and 2 show the results of the effect of pH variations on the removal of humic substances and turbidity. As can be observed, the EC process with $FeCL_3$ as the coagulant at a pH of 6 had the highest efficiency in the removal of humic substances. Besides, it is observed from these figures that the decrease and increase in the pH value affected the removal of turbidity. In Fig.1, by increasing the pH value from 7 to 8, the turbidity removal rate was reduced, while increasing pH to 9 led to a considerable reduction in the turbidity removal rate. Moreover, direct observations of the samples also demonstrated that increasing the pH value from 7 to 9 resulted in the turbidity of the superficial color of the samples, as well as the formation of very fine and scattered clots, which lacked the capability for sedimentation. Results of similar studies indicated that the optimal pH range for iron salts as the coagulant is in the range of 5.4–6 and the removal efficiency of DOC is reported to be nearly 29% to 70%.[24] Accordingly, Yan et al. (2008) reported that the optimal pH range for the removal of DOC and turbidity using $FeCl_3$ coagulant was 4–5.5 and 5.6–8.2, respectively.[8] Also, Ciner et al. (2013) showed that the optimal pH range for enhanced coagulation using the $FeCL_3$ coagulant was 5.5–6.5.[32] The reason for the increased removal of humic substances and turbidity at this pH can be expressed as follows:

First, the pH of the isoelectric point of $FeCL_3$ for the neutralization of colloidal substances is in the range of neutral to slightly acidic pH and second, the dominant mechanisms for the removal of turbidity is adsorption and neutralization. Besides, other characteristics of water, such as high alkalinity and low turbidity are other reasons for such changes.[24] At high levels of water alkalinity, the presence of hydroxyl ions (OH^-) causes a reduction in the hydrolysis of the metal ions and therefore, the conditions are not suitable for the removal of humic substances.[8] Also, at high pHs, enormous numbers of anionic sites are created due to the deprotonation of the carboxylic acid groups.

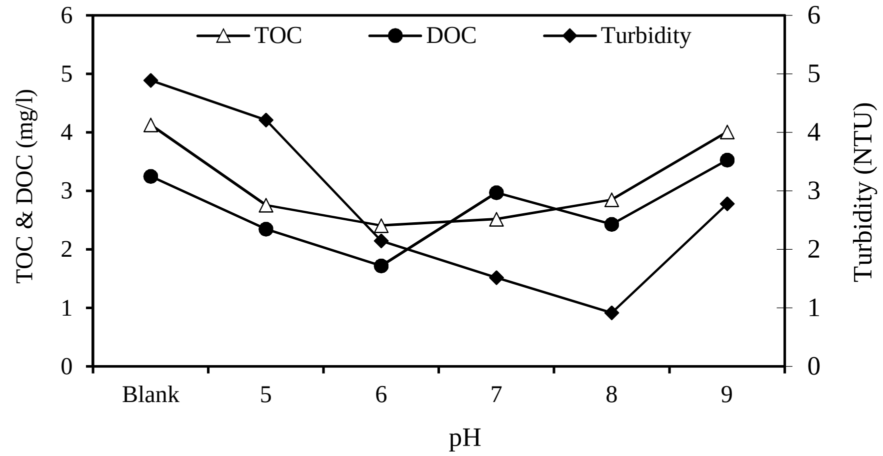

Fig. 1. Effect of pH variations on removal of TOC, DOC, and turbidity in EC process

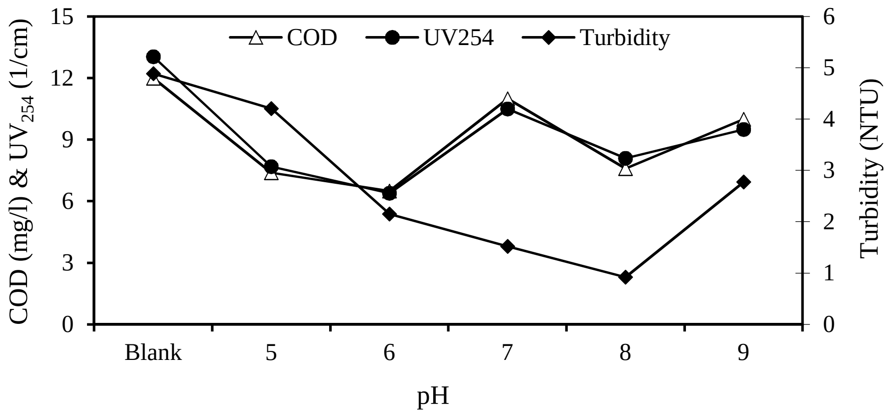

Fig. 2. Effect of pH variations on removal of COD, UV_{254}, and turbidity in EC process

Therefore, the coagulant's capability to neutralize the negative charge of the humic substances is reduced, and the removal of such substances does not occur properly.[33]

Effect of coagulant dosage

One of the most important variables in the EC process for achieving the removal of humic substances and turbidity is the increase of the coagulant dosage. The effect of the $FeCL_3$ coagulant dosage on the removal of humic substances and turbidity is shown in Fig. 3 and 4. According to the results obtained in the present study, an increased dosage of the coagulant up to 130 mg/L led to a reduction in the humic substances and turbidity indices; in fact, it can be said that there was a stoichiometric relationship between the dosage of the coagulant and the concentration of such indices in the treated water sample, which depended on the type of the coagulant as well as the features of the solution including alkalinity and pH. Uyak et al. (2007) showed that the maximum removal of DOC and UV_{254} was obtained at the coagulant ($FeCl_3$) dosage of 100 mg/L.[29] As can be seen in Fig. 3 and 4, the increased coagulant dosage led to reduced values of TOC, DOC, COD, UV_{254}, and turbidity indices, which was mainly caused by the negative charge of the humic substances. The charge density of the functional groups of the humic substances is usually 10–100 times higher than that of the mineral particles.[8] Various coagulants with a positive charge, by creating a complex with the negatively charged functional groups, can create a humic-metal compound that can be easily deposited and removed in the following solid isolation processes.[18] The findings of the present study are consistent with those of the similar studies.[25, 29, 34]

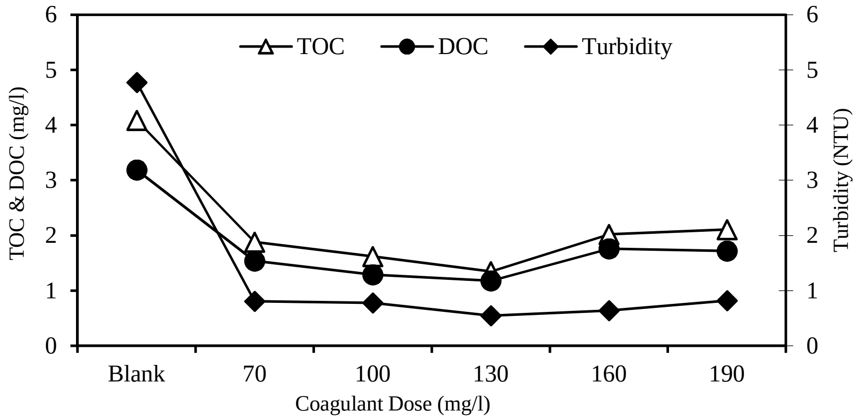

Fig. 3. Effect of $FeCL_3$ coagulant dosage variations on removal of TOC, DOC, and turbidity in EC process

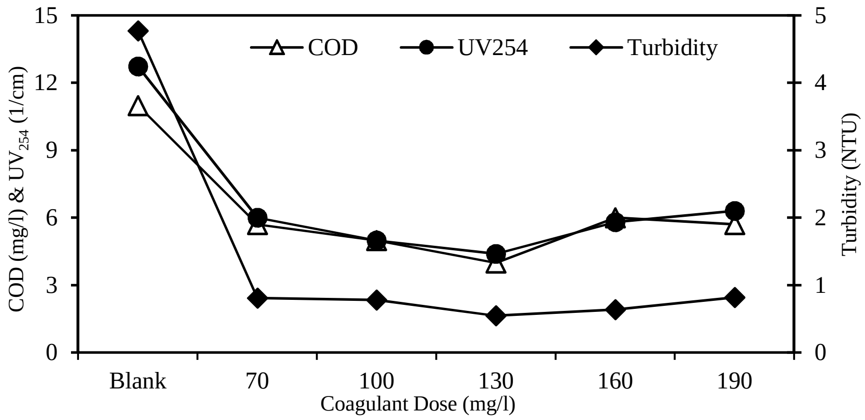

Fig. 4. Effect of $FeCL_3$ coagulant dosage variations on removal of COD, UV_{254}, and turbidity in EC process

Comparing conventional and enhanced coagulation

Fig. 5 demonstrates the efficiency of the conventional and the enhanced coagulation processes using $FeCL_3$ coagulant for the removal of humic substances and turbidity in the raw water samples of the SWTP. The average dosage of $FeCL_3$ for the removal of turbidity in conventional coagulation is 50 mg/L, while the coagulant dosage required to achieve the optimal removal of humic substances is 130 mg/L. As can be seen in this figure, the removal efficiency of the humic substance indices including TOC, DOC, COD, and UV_{254} was 43%, 41%, 50%, and 38%, respectively, in the conventional coagulation process, while the removal efficiency of these indices in the enhanced process was 65%, 62%, 69%, and 70%, respectively. Furthermore, the removal efficiency of turbidity in the conventional and the enhanced coagulation processes was obtained to be 90% and 93%, respectively. Comparing the efficiency of the conventional and the advanced coagulation processes in the simultaneous removal of turbidity and humic substances showed that the removal efficiency of humic substances in the EC process was higher than that of the conventional coagulation process. Besides, the removal efficiency of turbidity in the EC process not only was not reduced but also, was a little more than that in the conventional coagulation. Usually, the most important issue causing worry in relation with advanced coagulation for the removal of humic substances is that the modification of the process for the removal of humic substances results in a significant increase in the required coagulant dosage compared with the required dosage for the removal of turbidity in the conventional coagulation process. In some cases, the conventional coagulation process alone suffices for meeting the requirements of the advanced coagulation. Such results indicate that most of the conventional water treatment plants would be able to meet the requirements of EC by applying a few changes to the conventional coagulation processes.

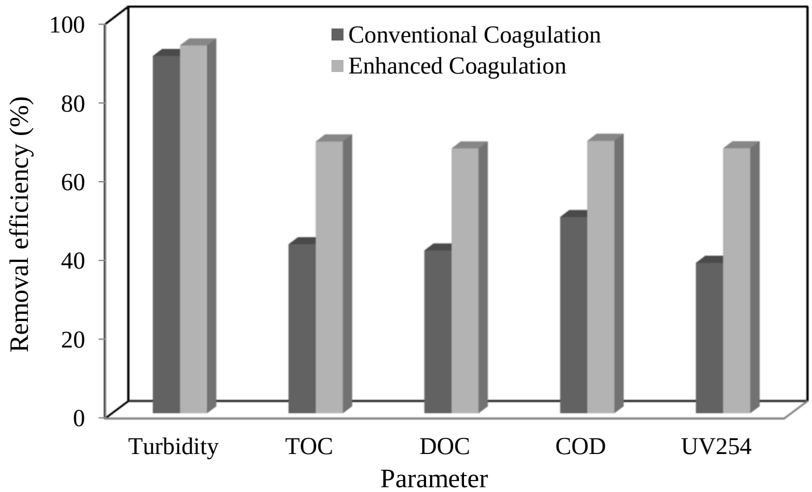

Fig. 5. Comparing $FeCL_3$coagulant's efficiency in removal of humic substances and turbidity between enhanced and conventional coagulation processes

Conclusion

In this study, the simultaneous removal efficiency of turbidity and humic substances from raw water entering the SWTP was investigated using the EC process. The findings indicated that the average efficiency of this process was 69%, 67%, 69%, 67%, and 93% for the removal of TOC, DOC, UV_{254}, COD, and turbidity, respectively. Furthermore, the obtained results demonstrated that the $FeCL_3$

coagulant at pH of 6 had the maximum efficiency in the removal of organic matter and turbidity. Besides, increasing the coagulant dosage to 130 mg/L resulted in the reduction in all the humic substances and turbidity indices. On this basis, it can be concluded that by using the EC process, alongside the efficient removal of the suspended substances and reducing the turbidity to the desirable limit, humic substances can also be reduced to the favorable limit without adding another unit to the conventional water treatment plant.

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