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ORIGINAL ARTICLE

Selecting the optimal coagulant in turbidity removal and organic carbon of surface water Using AHP

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ABSTRACT
Water treatment and healthy potable water supply are the most important environmental priorities and coagulation process is of great important in water treatment plants. Various researches have been done about the best coagulant for turbidity and organic matter removal. The present study is aimed to compare the performance of five coagulants including poly ferric sulfate, Ferric chloride, alum, poly aluminum chloride, and poly aluminum ferrous chloride in turbidity and organic material removal. In the present study, at first by conducting various Jar tests, optimal dose of applied coagulants in turbidity removal, has been obtained in high turbidities (to 300NTU) and low turbidities (10 NTU), then the efficiency of each of the applied coagulants in organic materials removal has been investigated. Based on the importance of applied coagulant in water treatment plants for better operation and achieving high-quality water, the current study applies a Multi-Criteria Decision making support system using analytic hierarchy process (AHP) to help the selection of the best coagulant.
Keywords: *Water treatment, Coagulation and Flocculation, Poly aluminum ferrous chloride, Analytic Hierarchy Process (AHP)*

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INTRODUCTION

Increasing population growth, improvements of living standards, urbanization development, industrial and agricultural developments are among the factors increasing the community's water consumption and waste water production and causing environmental pollution [1].

The water that is contaminated naturally or by human must be treated through the various processes to be drinkable. Common processes of water treatment include: coagulation, flocculation, sedimentation, filtration and disinfection. Coagulation is the process by which non-settled particles called colloids are attached to each other and form larger clumps. In water resources turbidity is caused by chemical, biological or physical factors [2]. The size of colloidal particles in water is between 0.001 to 1 micron. However, the spontaneous sedimentation rate of a particle with a diameter of 0.1 micron is about 3 meters per one million year. Thus, filtration process of water is impossible without the use of substances increasing the rate of sedimentation of colloidal particles [3].

Water from any source has some impurities arising from earth erosion, mineral materials dissolution, gases dissolution and the materials of disintegration of plant or animal organic materials. If these materials exceed definite amount, not only they eliminate the drinkability of water, but also the content of the mentioned materials is not used mostly or it is not used in ordinary consumptions before water treatment operation.

By development of urbanization and advancement of industries and dumping industrial wastewater and sewage into water and the increase of pollution, surface water as the most important resources of water supply, the need to water treatment operation is increased.

Sludge processing problem is one of the major challenges of users in water treatment plants and it can create profound environmental effects (water treatment plants sludge is classified as dangerous wastewater).

One of the major factors of increasing the sludge volume and unsuitable dewatering is the type of applied coagulant and by using suitable coagulants, besides the reduction of chemical materials and sludge volume, its dewatering properties can be improved.

Despite the presence of various primary coagulants and coagulants aids, selecting the type of coagulant by considering the quality of water entering water treatment plant is of great importance.

The common coagulants don't have good performance mostly in low and high turbidities and in this case, the operation authorities are obliged to use coagulant aids. Thus, a coagulant is necessary to be used under critical conditions and considerable pollution of water resources and users can drink high quality water.Vitriol (aluminum sulfate) consumption in murky waters dates back to Babylon and Assyria civilization .Indeed, this substance was used in water treatment in two thousand BC .Based on the investigations around the Ziggurat Temple in Iran ,100 kilometer of the south of Ahvaz, settling ponds that used for water treatment in Karkheh River ,have been discovered. Karkheh River is one of the rivers with very high turbidity in most of the time [4].

In the fifteenth century in the Mediterranean, Vitriol has been widely produced and used. It is doubtable that based on the background of using Vitriol by people around the Mediterranean Sea, vitriol is not used in these pools.

In 1881 in the city of Boston in UK, vitriol was used officially for the first time in water treatment of cities. Afterward, coagulation practically was recognized and recommended as a prerequisite for filtration and sedimentation.

Ferric and Aluminum salts are mostly applied in coagulation and flocculation process. Many factors are effective on efficiency of coagulation and flocculation method as temperature, pH, mixing time, coagulant concentration and flocculate [5].

By half of the twentieth century, Vitriol and ferric salts were used as only coagulants in water treatment and they were the required parameters for the treatment and removal of pathogenic bacteria causing cholera and typhoid. In 60 decade, coagulation technology advanced rapidly way polymeric materials were used in water treatment. Later, deep understanding of coagulants use was achieved and water treatment plants were changed. In 1980, based on the researches conducted, mineral polymers entered the market as coagulants [4].

Some of the polymers are poly aluminum chloride and poly ferric sulfate. Poly aluminum chloride is with chemical formula $AL2(OH)CL_{6-n}$ as yellow powder ,its AL_2O_3 27 -30 %,PH of 1% solution is 5/3 - 5 and in case of hydrolysis in water strong cationic charge is created[6]. The benefits of using poly aluminum chloride are:

-Improved turbidity removal

- Improved color removal

-Increased TOC (Total Organic Carbon) removal

-Simplified operation (eliminating pH regulating materials, secondary polyelectrolyte)

-Lower overall treatment costs [7].

As it was stated, poly ferric sulfate is among the newest materials applied for coagulation in water treatment and waste water purification in some advanced industrial countries.

This material combined with water turns to yellow water solution, which consist of ferric sulfate polymers. Basic part of poly ferric sulfate solution is trivalent iron [8].

Another point that its role in making this changes from coagulation types aspect in technological systems should not be ignored is improvement and review of water quality standards , specially potable water that is done by responsible Health institutions once every few years in different countries at international level by and according to the latest data from the hygienic effects of different constituents and elements ,some quantities as guideline values or maximum permissible limit are recommended. It is obvious, efficiency and performance of different coagulation systems in achieving water to desired level of quality is not the same and application of a appropriate treatment system is mandatory.

In this study poly aluminum ferrous chloride is tested in Iran for the first time for water treatment .it is a chemical polymer that ferric polymer is formed based on poly aluminum chloride. This increases the molecular structure and improves coagulation and sedimentation. This matter can treat raw water with low temperature and high turbidity or low turbidity and low temperature.

The present study by emphasis on the effect of various coagulants to reduce or remove turbidity and organic materials based on the experiments, by AHP approach, the optimal coagulant in water treatment was selected.

MATERIALS AND METHODS

For the experiments, the samples of Tehran city water were applied. The turbidity and organic materials were obtained artificially by adding clay passed through the sieve no.200 and natural organic materials

(the rotten leaves of trees).The experiments were carried out in laboratory scales and by using jar test apparatus with five coagulants including: poly ferric sulfate, ferric chloride, alum poly aluminum chloride and poly aluminum ferrous chloride. The studied variables in turbidity removal included concentration of coagulant, PH(6,7,8,9,10,11,12) and turbidity (NTU 300,150,100,10).
chloridric acid and sodium hydroxide with concentration (0.5, 0.1 Molar) and PH meter were used to adjust the PH. Temperature of laboratory environment was averagely 20℃ and water temperature was averagely 12℃.
After preparing the samples by using 1 L glass breakers containing 900ml of water, jar test was conducted. The samples in jar apparatus underwent rapid mixing with speed of 120rpm(revolution per minute) for 1 min and slow mixing speed of 25rpm for 20 min ,then allow the samples in the beakers to *settle* for *30 minutes*, then the residual turbidity of the samples was measured by turbidity meter and efficiency of each coagulant was determined in turbidity removal and the Figures were plotted. After jar test and achieving the optimum dose and PH of tested coagulant in turbidity removal, in the next experiments, the PH of all breakers was set on optimum PH ,but dose of tested coagulant set in higher ,equal, or lower than the optimum dose of turbidity removal were added to breaker to obtain the removal percentage of organic carbon after coagulation, flocculation and sedimentation process.

Results of experiments

The result of this study on the performance of five coagulant (poly ferric sulfate , Ferric chloride,alum ,poly aluminum chloride and Poly aluminum ferrous chloride) in turbidity and organic materials removal from drinking water are:
Figures 1 to 4 compared the removal efficiency of tested coagulant in optimum dose and PH. As the results in Figures show ,in the input turbidity NTU300(Figure 1) removal efficiency of five coagulants are close together and in all cases turbidity removal efficiency is above 90 percent , but the best turbidity removal efficiency is for poly aluminum ferrous chloride with an efficiency of 98.25 %.
In input turbidity NTU150 (Figure 2),the highest turbidity removal efficiency of tested coagulants is obtained as Poly ferric sulfate (98.66%), poly aluminum ferrous sulfate (96.24%) , Ferric chloride (95.11%),poly aluminum chloride (94.63%) and alum (93.62%), respectively.
In input turbidity 100 NTU (Figure 3) the highest turbidity removal efficiency is for poly ferric sulfate with 98.87%. and the input turbidity NTU10 (Figure 4), as it was expected polymeric coagulant had better removal efficiency than alum and ferric chloride ,while the consumable dose was lower and poly ferric sulfate with 95.27% had the highest removal percent.

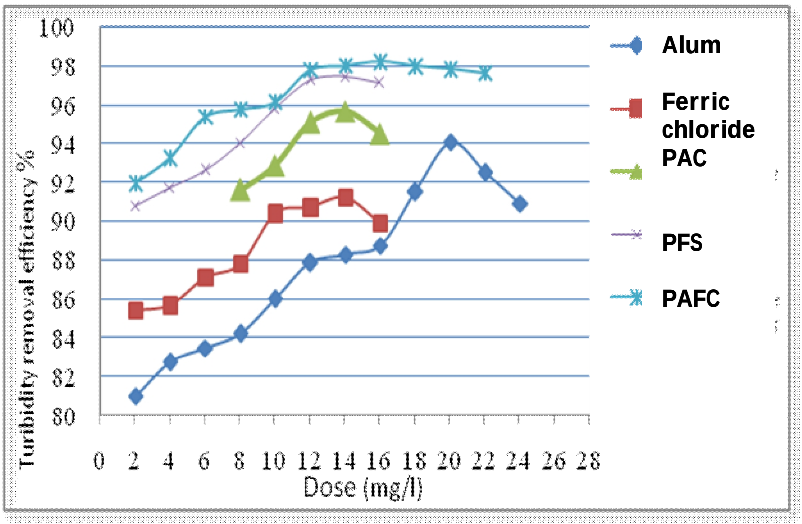

Figure 1.Turbudity removal efficiency of coagulant in turbidity of 300 NUT

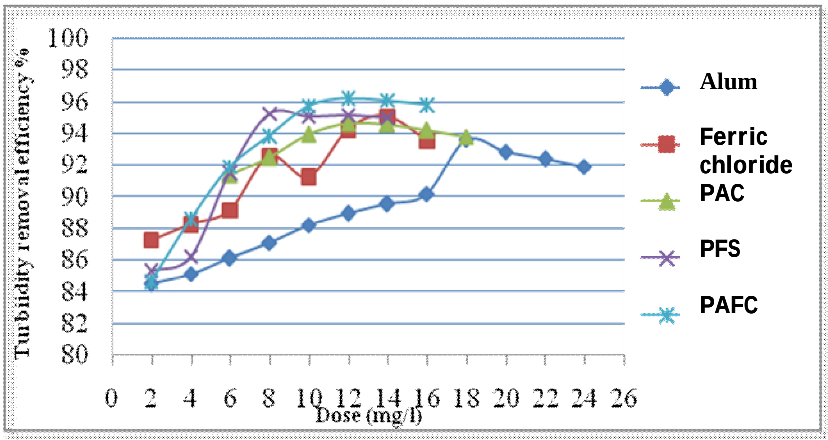

Figure 2.Turbudity removal efficiency of coagulant in turbidity of 150 NUT

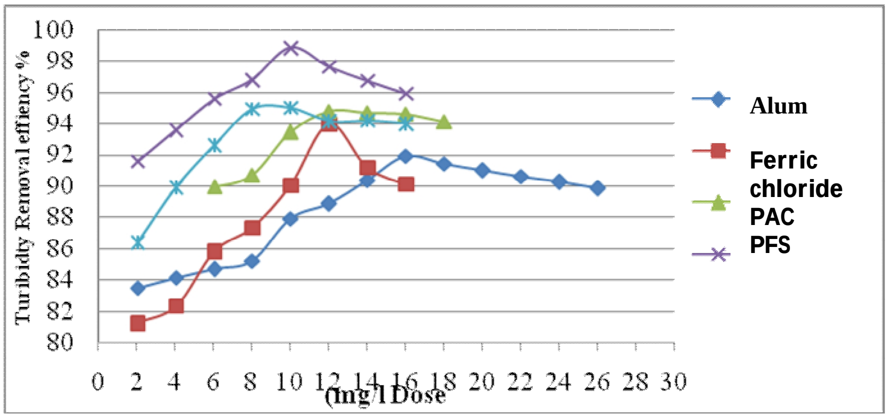

Figure 3.Turbudity removal efficiency of coagulant in turbidity of 100 NUT

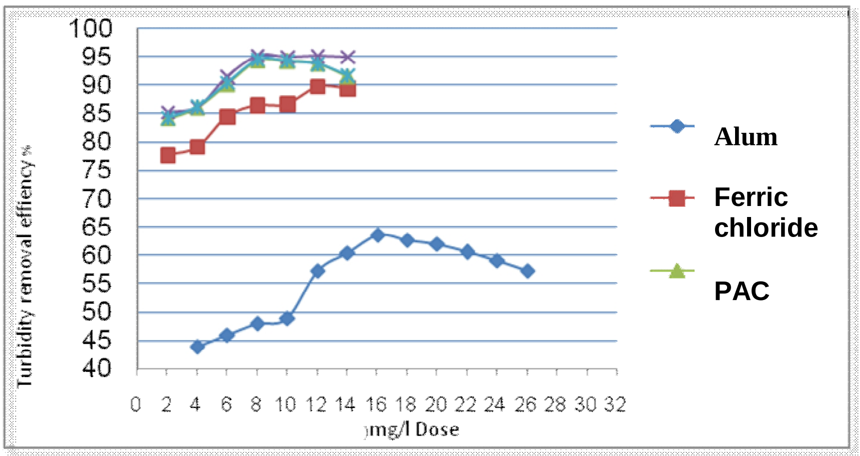

Figure 4.Turbudity removal efficiency of coagulant in turbidity of 10 NUT

In Figure 5 (TOC=10mg/L) and Figure 6 (TOC=20mg/L) , TOC removal efficiency of five tested coagulant is shown. With regard to the results of Figures 5,6, poly ferric sulfate has the highest TOC removal efficiency .

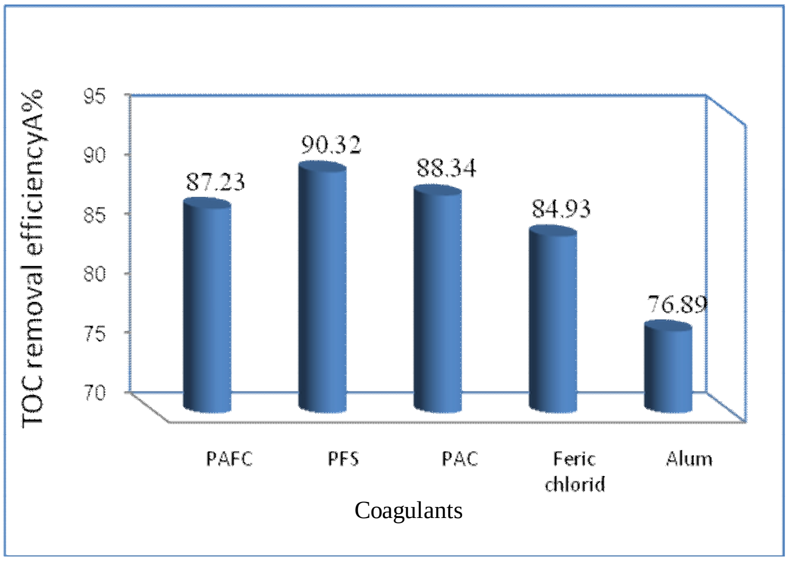

Figure 5.TOC removal efficiency of TOC=10mg/L

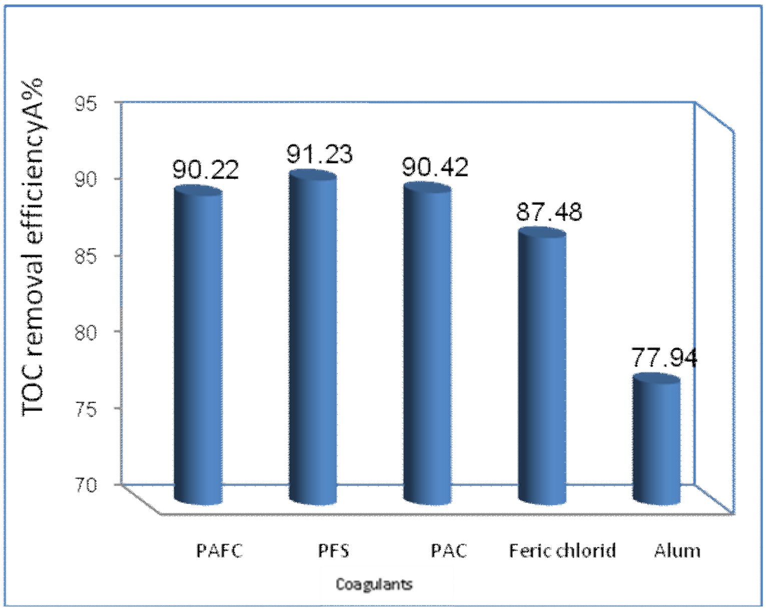

Figure 6.TOC removal efficiency of TOC=20mg/L

The effective factors in selecting coagulant

To select the optimum coagulant for water treatment, at first the effective factors on selection are recognized and then in comparison of these factors with the tested coagulant features, the best coagulant is selected.

It is worth to mention that it is not possible to select and introduce a coagulant as the best matter for coagulation and Flocculation in water treatment in all water treatment plants and for any water. In other words, we can not prescribe for all water (with different features) a coagulant as the best and based on the quality conditions of entrant raw water to water treatment plant, the coagulant is selected.

The elements of decision making process

There are three important components for each selection as : Goal, criteria and alternatives. These three principles are true about the selection of the best coagulant in water treatment. Thus, goal is "selecting the best coagulant in coagulation and Flocculation operation in water treatment", criteria are the effective factors in selecting the best coagulant in water treatment and it is discussed later. Finally alternatives are five tested coagulants being introduced in the previous section.

The effective factors on selection of coagulant in water treatment and its importance

To identify the effective factors on coagulant, some researches including the scientific texts study have been conducted and a survey was done of the users of water and wastewater companies, academic lecturers with activities in this regard and the students doing the research works on coagulants and the effective factors on selection of coagulant were extracted from them.

Also, the comments of some group of experts on water treatment were collected by the questionnaires designed based on AHP methodology.
After these researches, finally 6 factors were identified after combining and summarizing as effective factors and these factors were investigated as five coagulants as decision making criteria.

Table 1- Effective factors on selecting coagulant

Decision making criteria	Effective factors	No.
Poly aluminum ferrous chloride (PAFC)	Dose	1
Poly ferric sulfate (PFS)	Turbidity removal efficiency	2
Ferric chloride	TOC removal efficiency	3
Alum	Easy operation	4
Poly aluminum chloride (PAC)	Economic	5
	Production capability in country	6

Despite the efforts to separate the effective factors, the relationship and overlapping between some of the classified factors is not eliminated completely.
After determining 6 important and effective factors in decision making for coagulant, the next step is making a decision making support system including determination of the importance of each factor in decision making process. As the importance of these factors and sub-factors was not binary (0,1) and each factor dependent upon the special type and features of each project, the importance is 0 to 100 %. Thus, "relative importance" or "relative preferences" of them is decision making criterion.
In this study, to determine these relative importance, Delphi method (experts views) was applied by the aid of designed questionnaires based on pair wise comparison technique. Based on the study population of the water industry experts and by relationship "determining the sample size with the quality data in finite population", the required number of questionnaires were defined and finally 21 questionnaires were completed by the experts. In these questionnaires, the experts were asked to score the relative importance or preference of each factor/ criterion on factor/ another criterion (based on problem purpose) and the relative importance or preference of each management method to another method (based on each criterion/effective factor) based on Table 2.
It is worth to mention that to keep the reliability of the model, some items as at least 5 years of work experience in the water and wastewater companies-related activities, introduction with different types of coagulants and having related education at least in an academic level of water industry are considered as the minimum features of experts.
Finally, the results of summary of completed questionnaires were analyzed to identify the optimum method of coagulant by "hierarchy analysis process".

Table 2- The numerical scales of pairwise comparisons [9]

Preference	**Preference**	**Numerical value**
Extremely important or extremely preferred	Extremely Preferred	9
Important preference or very strong preferred	Very Strongly	7
Important preference with strongly preferred	Strongly Preferred	5
Moderately preferred or moderately important or moderately good	Moderately Preferred	3
Important preference or equally preferred	Equally Preferred	1
Preferences among the mentioned items	--	2,4,6,8

Analytic Hierarchy Process (AHP)

AHP is based on pairwise comparisons and its relative preference structure is based on Table 2. This technique was coined in 80s, by "Thomas **L.** Saaty" and then it was applied for solving multi-criteria decision making problems. As it was said, AHP process applied pairwise comparisons for selection. It means that for decision making and selecting an alternative among some alternatives, they are compared two by two based on the given criteria and the preference of each one to another one about each criterion is obtained and after applying the criteria weight in the results, an alternative with highest score is selected. This technique is based on four principles as reciprocal condition, homogeneity, dependence, and expectations

AHP stages

Generally, for decision making by AHP process, the following steps are taken:

- Determining the goal, criteria and alternatives
- Determining the relationship between hierarchy structure constituents
- The calculation of the weight of each of criteria in relation to the goal and weight of alternatives in relation to the criteria (relative weight)
- The calculation of the final weight of each of the alternatives in relation to goal by the aid of weights chain from the alternative to goal
- Ranking the criteria and alternatives in relation to the goal

It is worth to mention that to compute the relative weights, at first the elements are compared as pairwise and the pairwise comparison matrix (for elements of each level) is formed, then by this matrix, the relative weight is computed. Generally, a pair wise matrix as equation 1 is shown in which aij is preference ith to jth element, by knowing aijs, the weight of Wi elements is obtained.

A=[aij] i,j=1,2,3,...,n Equation 1

An important point here is inconsistency ratio of pairwise comparison matrix. Each pair wise comparison may be consistent or inconsistent. If the matrix is consistent, the calculation of Wis weight is simple and is obtained of normalization of the elements of each column. If the matrix is inconsistent, the weight calculation is not simple and to obtain it, four major methods are used as least square method, logarithmic *least square* method, Eigen vector method and approximate methods. It can be said that the maximum acceptable inconsistency ratio according to "Saaty" is 0.1. The alternatives pair wise comparison with each other and determining the preferences should be done by "a decision maker aware of the alternatives and criteria"[9]:

The structure of the model in AHP

The problem structure in AHP process is called "hierarchy". Hierarchy is a graphic view of actual complex problem as the general goal of problem on top and then criteria, sub-criteria and alternatives, respectively are in the lower ranks. Thus, a hierarchy is at least consisting of three levels (goal, criteria and alternatives). Figure 7 shows a view of hierarchy structure of selecting the optimum coagulant.

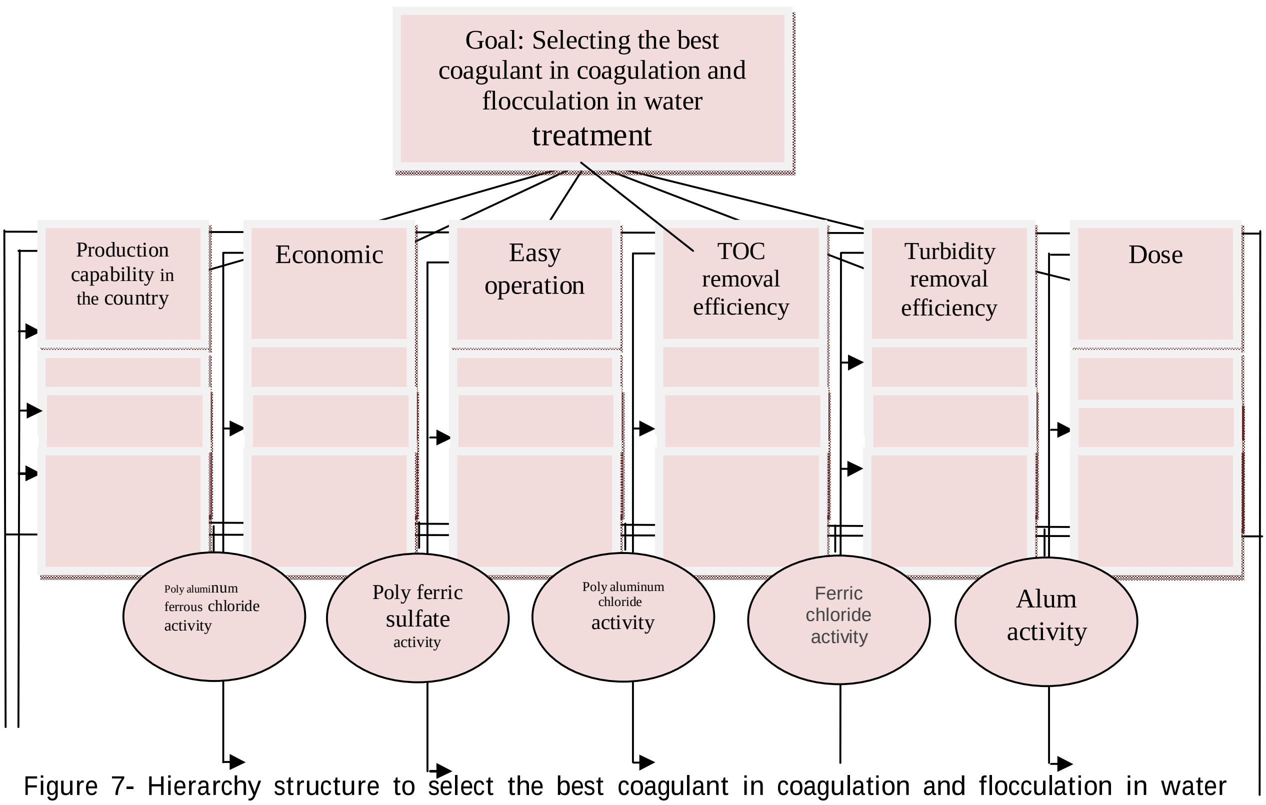

Figure 7- Hierarchy structure to select the best coagulant in coagulation and flocculation in water treatment

EC Software
Various support software is developed for AHP and the most important one is Expert Choice© software that was created by Saaty et al. This software has more capabilities and besides the design of hierarchy, decision making and designing the questions, determining the preferences and priorities, calculation of the final weight, calculation of inconsistency ratio, analysis of decision making sensitivity to the change in problem parameters, various states inference and applied Figures and graphs are other capabilities of this software.
Inference feature provides the determination of the best management method by considering only one of 10 main groups. The sensitivity analysis enables the decision makers to consider the effect of preferences and final selections in case of the change in relative importance of criteria (decision making factors).
The analyses are done by various Figures in EC software
The results of AHP analysis by EC
After the calculation of questionnaires and eliminating the end points (inacceptable answers statistically), the results were summarized and entered EC software as the initial input.
As it was said, this software can analyze by AHP method.
Finally, the initial result, the results of inferences and sensitivity analyses are extracted and estimated as followings.
Final results
The priority of tested coagulants is observed in Figure 8 based on the calculations. The final result to select the best coagulant shows that generally**,** Poly ferric sulfate had highest relative importance.

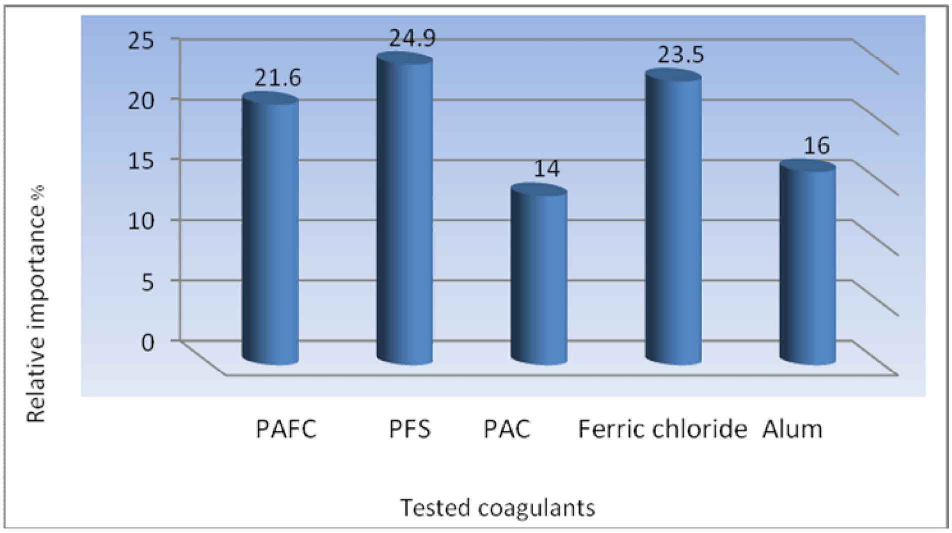

Figure 8- The relative importance of tested coagulants under the interference of all factors
One of the reasons that Poly ferric sulfate is of great importance from the view of respondents is its consumption dose, high turbidity removal and wide Ph range performance.
In the general form of selecting coagulant as is shown in Table 3, the factor "dose" has the highest importance among the effective factors in decision making. Other results are shown in Table 3.

Table 3- Ranking the weight of criteria based on goal

No.	Factors (criteria)	Preference degree
1	Dose	0.480
2	Turbidity removal efficiency	0.338
3	Economic	0.200
4	Production capability in country	0.177
5	TOC removal efficiency	0.136
6	Easy operation	0.100

Inferences
Inference is an analysis in which the importance of effective factors is changed to the initial value and is achieved the maximum, in other words, one factor is alone the decision making factor to select optimum coagulant in water treatment. For example, the change of importance of "TOC removal efficiency" to

achieving maximum 100%, means that only this factor is considered for decision making and as is shown in Table 4, Poly ferric sulfate is the best coagulant in water treatment.

Table 4- The relative weight of effective factors in selection of coagulant in coagulation and flocculation in water treatment in case of considering the factors separately

Effective factors on decision making	Changing the importance of factors	The percentage of relative weight of each coagulant in case of considering only one of the factors				
		PAFC	PFS	$FeCl_3$	Alom	PAC
Dose	Increasing this factor to 100% and residual to 0%	33.2	31.7	11.1	7.6	16.3
Turbidity removal efficiency	Increasing this factor to 100% and residual to 0%	38.7	26.3	11.4	5.8	17.9
Economic	Increasing this factor to 100% and residual to 0%	13.9	25	38	15.2	8
Production capability in country	Increasing this factor to 100% and residual to 0%	21.2	23.3	33.4	15.9	6.3
TOC removal efficiency	Increasing this factor to 100% and residual to 0%	18.3	31	22	9.6	19.1
Easy operation	Increasing this factor to 100% and residual to 0%	10.1	18.3	29.8	29.8	12.1

If each of economic factors and production capability in the country are the only decision making factors. Ferric chloride (FeCl3) is selected as the suitable coagulant and by the increase of the importance of some factors as dose or turbidity removal efficiency, poly aluminum ferrous chloride (PAFC) is selected as the best coagulant.

Sensitivity analysis

EC software analyzed the sensitivities by 5 different graphs as performance analysis, dynamic analysis, moving analysis, 2-D analysis and Break Even analysis. To analyze sensitivity by this software, by changing the factors importance in 0% to 100%, the change in the selected alternative is observed. The increase of relative importance of each factor to level 100% (with zero relative importance of other factors) is the inference feature that is analyzed in the previous section.

In this section, with the aim of investigation the limit points, change (reduction) in relative importance of each of the factors are investigated to level 0% (meaning the lack of interference of the factor in decision making process). It is said that in actual conditions and for each special city, by regulating the importance of factors, the best method for consumption management is selected.

As is shown in Table 5, the elimination of each of consumption doze factors, production capability in the country and easy operation, Poly ferric sulfate is selected as suitable coagulant. Eliminating the turbidity removal efficiency leads to the selection of $FeCl_3$ and in other cases PAFC had the highest score.

Table 5- The relative weight of effective factors in selection of coagulant in coagulation and flocculation in water treatment in case of not considering each of the factors

Effective factors on decision making	Changing the importance of factors	The percentage of relative weight of each coagulant in case of considering only one of the factors				
		PAFC	PFS	$FeCl_3$	Alom	PAC
Dose	Decreasing this factor to 100% and residual to 0%	23.6	25.2	24.8	13.2	13.2
Turbidity removal efficiency	Decreasing this factor to 100% and residual to 0%	16.6	25.2	30.7	16.5	11
Economic	Decreasing this factor to 100% and residual to 0%	26.6	25.7	20.7	12.3	14.7
Production capability in country	Decreasing this factor to 100% and residual to 0%	24.7	26	22.2	12.2	14.8
TOC removal efficiency	Decreasing this factor to 100% and residual to 0%	25	24.7	24.5	13.4	12.4
Easy operation	Decreasing this factor to 100% and residual to 0%	25.6	26.3	23.6	11	13.5

DISCUSSION AND CONCLUSION

The results of various experiments showed that turbidity removal efficiency by various coagulants is mostly affected by initial turbidity and all the tested coagulants in turbidity 300 NTU had good removal efficiency, but the dose of Poly ferric sulfate, poly aluminum chloride and poly aluminum ferrous chloride was much less than ferric chloride and alum.

In turbidity 10NTU ,Poly ferric sulfate, poly aluminum chloride and poly aluminum ferrous chloride had high removal efficiency and the dose of these materials is low. As the raw water entering water treatment plants in the country is more supplied through surface water, using coagulants that under critical conditions and sudden pollutions can have good performance is of great importance. This issue shows the importance of technical and economic feasibility of substituting common coagulants with polymeric coagulants.

It is obvious that each of coagulants had special advantages and disadvantages. Thus, the operator in selection should find the coagulant with highest value for the costs taken. This is fulfilled when the client operator at first identify various coagulants and their features and then determine the conditions of treatment water and the existing capabilities.

The results of various experiments showed that turbidity removal efficiency by various coagulants is mostly affected by initial turbidity and all the tested coagulants in turbidity 300 NTU had good removal efficiency, but the dose of Poly ferric sulfate, poly aluminum chloride and poly aluminum ferrous chloride was much less than ferric chloride and alum.

In turbidity 10 NTU, Poly ferric sulfate, poly aluminum chloride and poly aluminum ferrous chloride had very high removal efficiency and the consumption dose of these materials is very low. As the raw water entering water treatment plants in the country is more supplied through surface water, using coagulants that under critical conditions and sudden pollutions can have good performance is of great importance. This issue shows the importance of technical and economic feasibility of substituting common coagulants with polymeric coagulants.

The present study identified some of the effective factors for decision making and the relative importance of each of them was defined by the comments of water treatment experts. Later, an analytic approach based on AHP methodology was used to select the best coagulant. It was defined that PFS was the best coagulant in coagulation and flocculation in water treatment.

By sensitivity analysis, the importance of each of the factors in decision making and the change of selected methods based on the change in importance of the decision making factors was investigated.

The importance of each of the factors could change ranging 0% to 100% (from the factor without effect to the only effective factor) and in this paper, two limit states of the changes were investigated.

In case of interference, only one of the factors was recognized as the effective factor on decision making and in most cases $FeCl_3$ was recognized as the best coagulant and PAFC was in the next rank.

In case of eliminating the effective factors on decision making, PFS was selected as the best coagulant and PAFC was in the second rank.

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