

The Separation Method for Removing of Colloidal Particles from Raw Water

A. Koohestanian, M. Hosseini and Z. Abbasian

Faculty of Chemical Engineering, Babol Noshirvani University

Abstract: The objective of this study was to develop a treatment system that can effectively reduce the concentration of colloidal particles in raw water that can greatly reduce the cost of treatment and improve the subsequent steps of treatment. Aluminum sulphate (alum) and ferric chloride as a coagulant and anionic polymer as coagulant aid were used in the process that changed the scale of particles from nanoscale to microscale and larger by a physico-chemical process. The influence of PH, temperature, coagulant and coagulant aid dosages on the coagulation process was studied and conditions were optimized corresponding to the best removal of organic matters, viruses, colloids, bacteria, color and decrease in turbidity. 85-98% reduction of turbidity from raw water can be achieved by using the optimum coagulant dosage (8ppm, ferric chloride/10 ppm, alum) in the optimum PH range (9.2, ferric chloride/8.5, alum) in the optimum temperature (20°C, ferric chloride/24°C, alum). Ferric chloride produced better results than alum. Higher dosages did not significantly increase pollutant removal and were not economical. The results provide useful information for raw water treatment.

Key words: Colloidal particles . Clarification . Coagulation . Flocculation . Water treatment

INTRODUCTION

Solids are present in water in three main forms: suspended particles, colloids and dissolved molecules. Suspended particles, such as sand, vegetable matter and silts, range in size from very large particles down to particles with a typical dimension of 10 μm . Colloids are very fine particles, typically ranging from 10 nm to 10 μm . Dissolved molecules are present as individual molecules or as ions. Figure 1 illustrates the size ranges of solids in water.

In general, suspended particles are simply removed by conventional physical treatment like sedimentation and filtration. Dissolved molecules cannot be removed by conventional physical treatment. Thus, the removal of colloids is the main objective and the most difficult aspect in conventional water treatment.

There are two types of colloids: hydrophilic colloids and hydrophobic colloids. Hydrophobic colloids, including clay and non-hydrated metal oxides, are unstable. The colloids are easily destabilized. Hydrophilic colloids like soap are stable. When these colloids are mixed with water, they form colloidal solutions that are not easily destabilized. Most suspended solids smaller than 0.1 mm found in waters

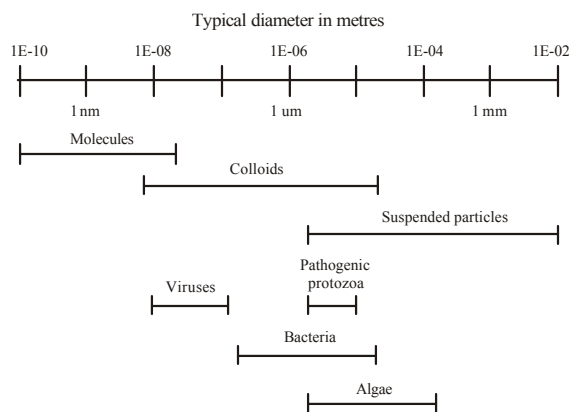


Fig. 1: Size range of particles of concern in water treatment

carry negative electrostatic charges. Since the particles have similar negative electrical charges and electrical forces to keep the individual particles separate, the colloids stay in suspension as small particles.

The magnitude of the zeta potential (Z_p) is usually used to indicate colloidal particle stability. The higher the zeta potential, the greater are the repulsion forces between the colloidal particles and, therefore, the more stable is the colloidal suspension. A high Z_p represents

strong forces of separation (via electrostatic repulsion) and a stable system, i.e. particles tend to suspend. Low Z_p indicates relatively unstable systems, i.e. particles tend to aggregate.

To remove colloids, small particles have to be destabilized first and then they will form larger and heavier flocks which can be removed by conventional physical treatment. This process can be described by clarification mechanisms, that includes: coagulation, flocculation and sedimentation.

The chart below shows the length of time that is required for particles of different sizes to settle through the water. Coagulation is the process of decreasing or neutralizing the negative charge on suspended particles or zeta potential. This allows the van der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form microflock. Rapid, high energy mixing is necessary to ensure the coagulant is fully mixed into the process flow to maximize its effectiveness. The coagulation process occurs very quickly, in a matter of fractions of a second. Flocculation is the process of bringing together the particles to form large agglomerations by physically mixing or through the bridging action of coagulant aids, such as long chain polymer.

Destabilization by bridging occurs when a polymer of a high molecular weight becomes attached at a number of adsorption sites to the surface of negatively charged particles along the polymer chain. The remainder of the polymer may remain extended into the solution and may adsorb on available surface sites of other particulates, thus creating a 'bridge' between the surfaces as shown in Fig. 2.

Flocculation time is commonly 10-30 minutes; however the optimum flocculation time will vary depending on the raw water quality and downstream clarification process. Sedimentation is the process of allowing the flock formed during flocculation to settle out and separate from the clarified water. Typical retention time is 4-6 hours for settling.

Process of clarification (coagulation, flocculation and sedimentation) as shown in Fig. 3.

And flocks are made from complex arrangements of solids particles, hydroxide precipitates and water taken in during their growth. As shown in Fig. 4, they have irregular shapes and rather loose structures thought to be made up of three basic units corresponding to three size scales. In this three-tiered particle structure notation, primary particles are supposed to group into clusters (level 1) containing dry solids and associated

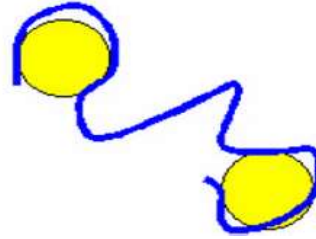


Fig. 2: Bridging flocculation

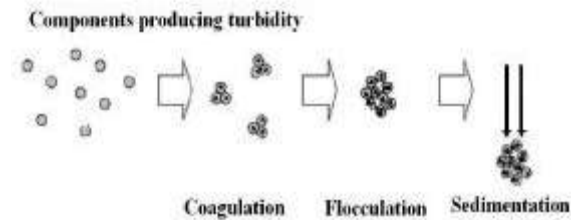


Fig. 3: Coagulation, flocculation and sedimentation process

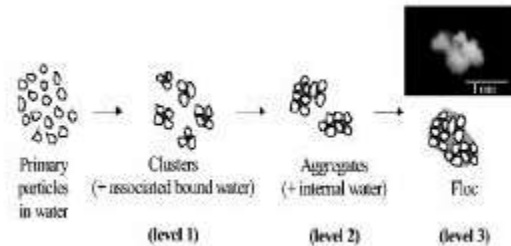
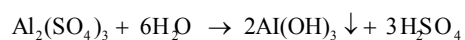
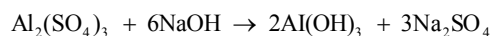
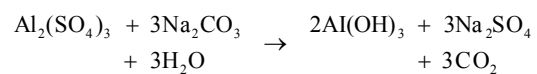
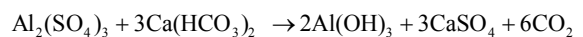


Fig. 4: The three basic units of flock structure

bound water. Aggregates (level 2) are produced by association of these clusters along with internal water, retained between clusters as part of the flock structure. Under low shear rates, aggregates form large-size flocks (level 3) through loose associations.

Coagulation reactions: The coagulation reactions are as follows:



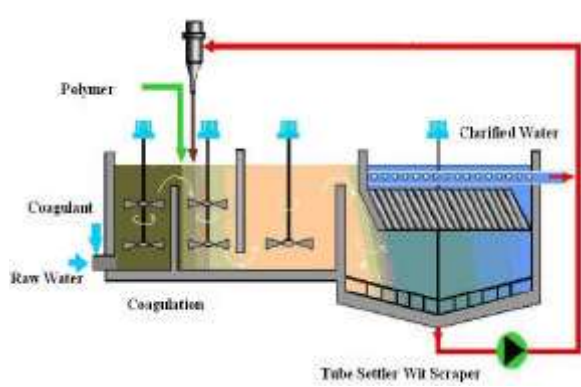


Fig. 5: A simple type of clarifier

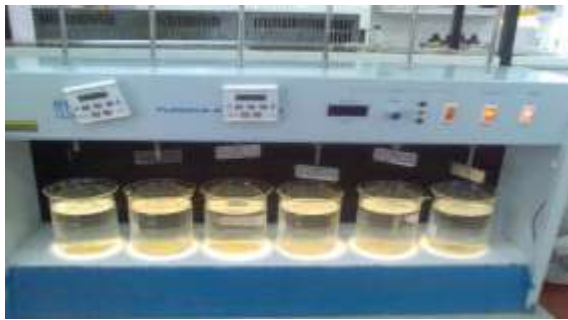
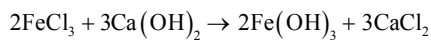
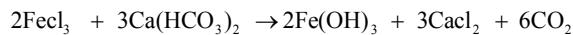


Fig. 6: A standard jar test apparatus



The simplest form of clarification uses a large tank or horizontal basin for sedimentation of flocculated solids, as shown in Fig. 5. The basin may contain separate chambers for rapid mix, slow mix and settling.

MATERIALS AND METHODS

The coagulation-flocculation tests were carried out following the standard practice for coagulation-flocculation testing of raw water to evaluate the chemicals dosages and conditions required to achieve optimum results. Raw water quality characteristics are summarized in Table 2.

Jar tests: The best approach for determining the treat ability of a water source and determining the optimum parameters (more effective coagulant, required dose rates, PH, flocculation times, most effective coagulant aids) is by use of a jar tester.

Table 1: Settling time for particles of various diameters

Diameter of particle	Type of particle	Settling time through 1 m of water
10 mm	Gravel	1 seconds
1 mm	Sand	10 seconds
0.1 mm	Fine sand	2 minutes
10 micron	Protozoa, Algae, Clay	2 hours
1 micron	Bacteria, Algae	8 days
0.1 micron	Viruses, Colloids	2 years
10 nm	Viruses, Colloids	20 years
1 nm	Viruses, Colloids	200 years

Table 2: Raw water quality characteristics

Parameter	Concentration
Turbidity (NTU)	16-43
COD (ppm)	3-39
PH	8-8.3
Conductivity ($\mu\text{s cm}^{-1}$)	1050-1320
Temperature ($^{\circ}\text{C}$)	5-24

It is the quickest and most economical way to obtain good reliable data on the many variables which affect the coagulation and solid removal process. The normal procedure when conducting a jar test is to initially find the best performing coagulant and dose rate and then to determine the optimum PH and temperature for the chosen coagulant and dose rate. Performance is usually judged on turbidity and then on color removal. Jar tests can also be used to compare the usefulness of different coagulant aids.

The coagulation-flocculation process consists of three distinct steps. First, the coagulant is added to the raw water and a rapid and high intensity mixing is initiated. Second, the suspension is slowly stirred to increase contact between coagulating particles and to facilitate the development of large flocks. Third, mixing is terminated and the flock is allowed to settle.

For each jar test, the following procedure was followed. Each jar was filled with 500 ml of sample measured with a graduated cylinder. The coagulant dose destined for each jar was carefully measured into 150 ml beakers and then distilled water was added to yield equal volumes in all the beakers. The stirrer speed was set on 80-100 rpm and test solution added. After 3-4 minutes, the mixing speed was reduced and was set on 30-40 rpm for 10 minutes. After this time period, the

Table 3: Water treatment inorganic coagulants

Chemical name	Formula	Molecular weight	Common color and form
Aluminum sulfate (Alum)	Al ₂ (SO ₄) ₃ .14H ₂ O	594.4	Tan to gray green: powder granules, liquid and lump
Ferric chloride	FeCl ₃	162.2	Anhydrous: green-black powder Heptahydrate: Yellow-brown lump Liquid: dark-brown solution

Table 4: Anionic polymer used as coagulant aid

Type	Chemical name	Formula	Molecular weight
Anionic	Hydrolyzed polyacrylamide	$\left[\begin{array}{c} \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH} \\ \qquad \qquad \\ \text{C} = \text{O} \qquad \text{C} = \text{O} \\ \qquad \qquad \\ \text{NH}_2 \qquad \text{ONa} \end{array} \right]_n$	10 ⁴ -10 ⁷

stirrer was turned off and flock allowed settling for 20 minutes. Samples were then withdrawn from the where located 10 cm below the water level for analysis.

List of coagulants and coagulant aid in Jar Test:

Experimental procedure

Effect of adding coagulants on pH: A known volume of prepared aluminum sulphate or ferric chloride solution was added to the jars with 500 ml of raw water. The coagulant dosages ranged from 0 to 12 ppm as aluminum sulphate or ferric chloride. The jars were stirred for 15 min at 40-60 rpm, after which the PH value of each sample was measured.

Optimization of PH and coagulant dose in the coagulation process: A known volume of prepared aluminum sulphate or ferric chloride solution was added to jars containing 500 ml of raw water at different PH values adjusted with H₂SO₄ and NaOH. The mixing speed was same as that explained in 2.1 section. To optimize the PH of the coagulation process, jar tests were conducted over the PH range of 4.5-11.5 and coagulant dosages of 2-12 ppm. To investigate the optimum coagulant dose, the PH value of the raw water was maintained at an optimum PH as determined above.

Optimization of coagulant and coagulant aid dose in the coagulation process: This tests were performed in the same manner as the before test procedure over coagulant aid dosages of 0.1-0.2 ppm but the PH value of the raw water was maintained at an optimum PH as determined above. The coagulant dosages ranged from 2 to 12 ppm, same as before.

Optimization of temperature for decreasing turbidity: A known volume of prepared aluminum sulphate or ferric chloride solution was added to the jars with 500 ml

of raw water, in this test the PH value of the raw water was maintained at an optimum PH as determined above. The coagulant dosages ranged from 0 to 12 ppm. The jars were stirred for 15 min at 40-60 rpm, after which the temperature of each sample was measured.

RESULTS AND DISCUSSION

Effect of coagulants on PH of the raw water: The solution PH is an important factor in determining the physical and chemical properties of the sample and it can be affected by the coagulants. Figure 7 shows that an increase in the coagulant dose is associated with a decrease in the solution PH. The initial pH of the sample was 8.3. After the addition of alum and ferric chloride at a concentration of 2-12 ppm, the pH decreased. The maximum rate of PH reduction occurs where the concentration of coagulant is in the range of 10-12 ppm, which gives a final PH value of 7.6 (alum) and 7.3 (ferric chloride). Figure 7 shows that effect of ferric chloride on reduction of PH is stronger than alum.

Effect of PH on turbidity of raw water: The effects of PH on decreasing of turbidity from jar tests for coagulation of raw water using alum and ferric chloride are shown in Fig. 8 and 9.

As it was shown, in higher PH there's reduction of turbidity because in higher PH there's a tendency toward sedimentation and fundamentally alkaline basic is a suitable place for sedimentation. Effect of increasing PH value on reduction of turbidity for ferric chloride is stronger than alum and ferric chloride dosage is less than alum dosage in the same PH value. Optimum PH for ferric chloride at a concentration of 8 ppm, is in the range of 9 to 9.2 and for alum at a concentration of 10 ppm is 8.5.

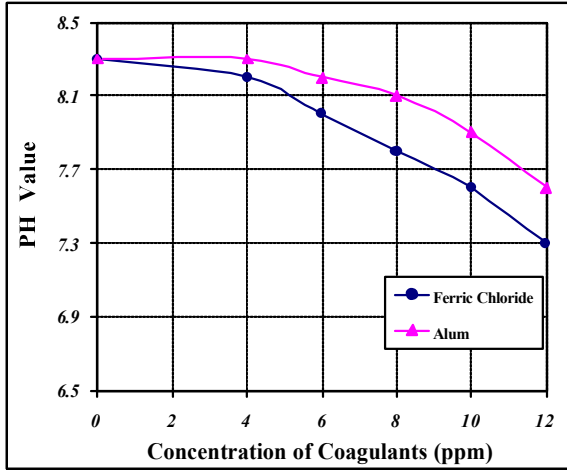


Fig. 7: Effect of coagulant dose on pH of the raw water

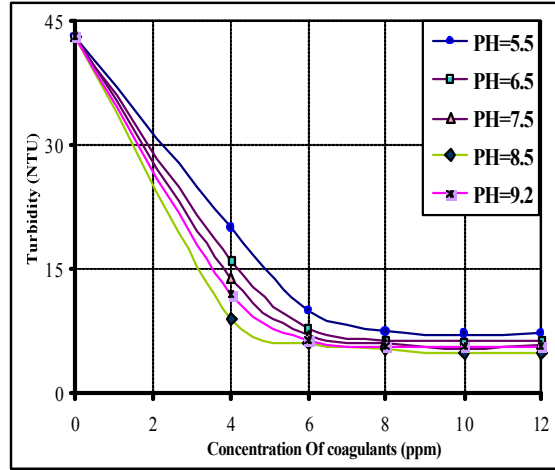


Fig. 9: Effect of pH on turbidity of the raw water-Alum

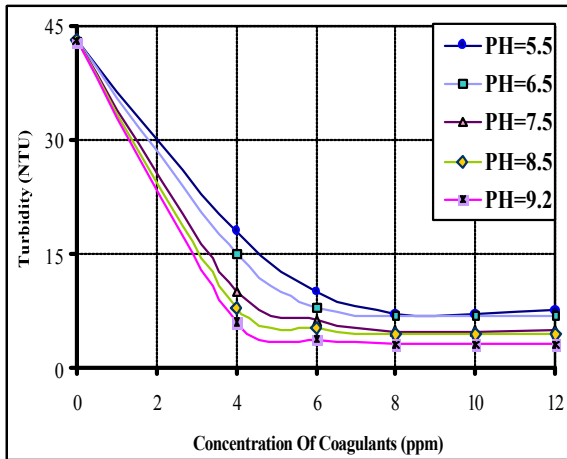


Fig. 8: Effect of pH on turbidity of the raw water-Ferric chloride

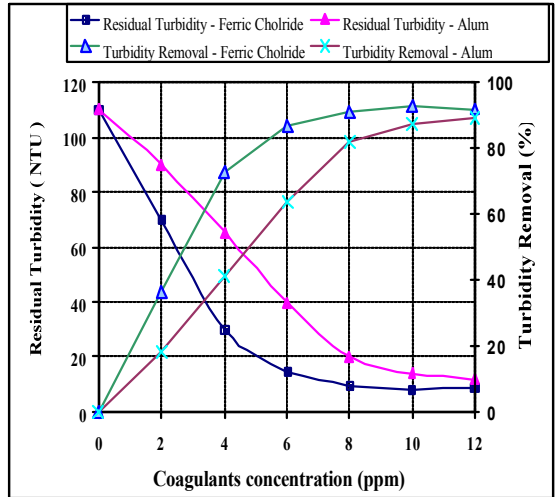


Fig. 10: Residual turbidity of water

It should be noted that in the more primary turbidity or in other words with more suspended particles in water, flocks are formed more quickly and during sedimentation they take other particles inside them; as a result the portion of final turbidity to primary turbidity in this state in comparison to raw water with lower primary turbidity is lower. In figure below you see an example in which primary turbidity is 110 NTU, but at the end through clarification we reach turbidity 8-12 NTU, Fig. 10.

Effect of coagulant aid dosage on turbidity of raw water: Coagulant aid can be used for better coagulation and more decrease in turbidity. So that if low turbidity is required it's possible to make bigger flocks by adding

coagulant aid to make more particles sediment in addition to increase the rate of sedimentation. Here, a polymeric (anionic) coagulant is used. This type of coagulant aid, in addition to neutralize the positive charges in water, causes the formation of flocks more quickly and increases the rate of sedimentation by bridging and connecting the already-formed flocks so that with the network formed during sedimentation they take other tiny particles which couldn't form flocks inside them and make them sediment among with themselves. It should be noted that the coagulant aid dosage in comparison to coagulant dosage is very low and we should determine the optimum dosage for different types of water using the jar test. In figure blow, coagulant aid

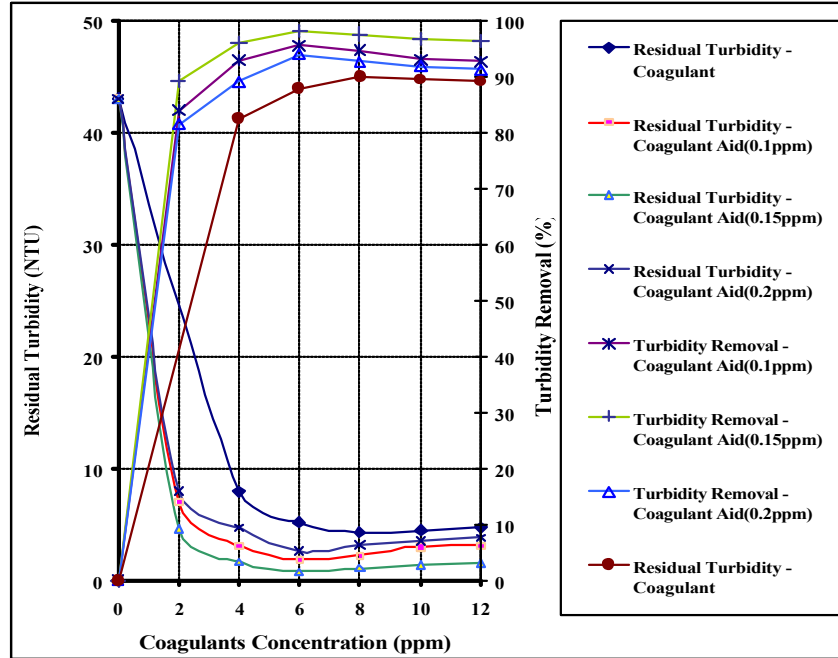


Fig. 11: Effect of coagulant aid (Poly Electrolytes) dose on turbidity-ferric chloride

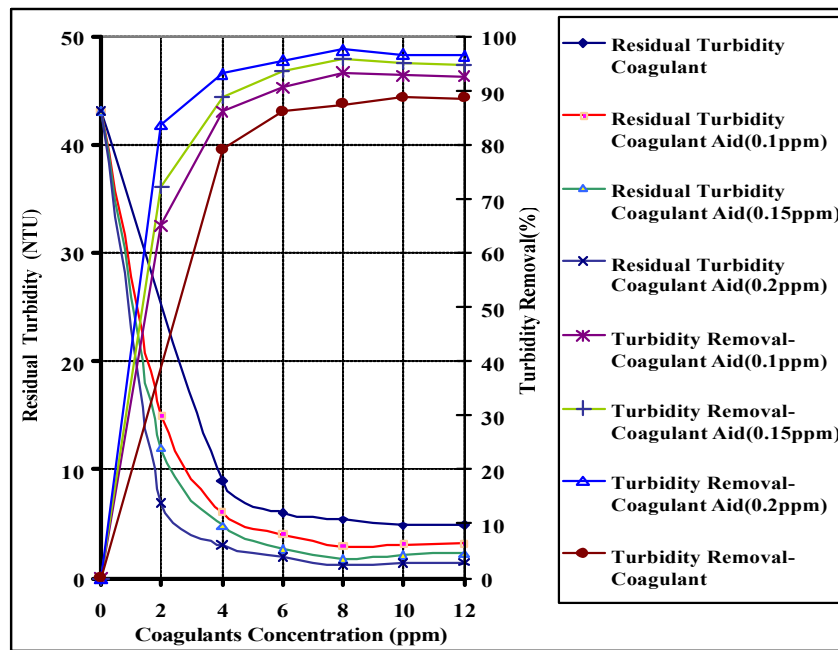


Fig. 12: Effect of coagulant aid (Poly Electrolytes) dose on turbidity-Alum

concentration and the type of polymer which facilitates coagulation process is shown.

As it was illustrated in Fig. 11 and 12, adding coagulant aid was very influential in decreasing turbidity and turbidity wouldn't decrease as much as it

would with coagulant aid, no matter how optimum other conditions are. And also it's significant that the lower dosage of coagulant is perceptible for alum turbidity to 8 ppm and for ferric chloride 6 ppm concentration so that it is in lowest concentration possible, however

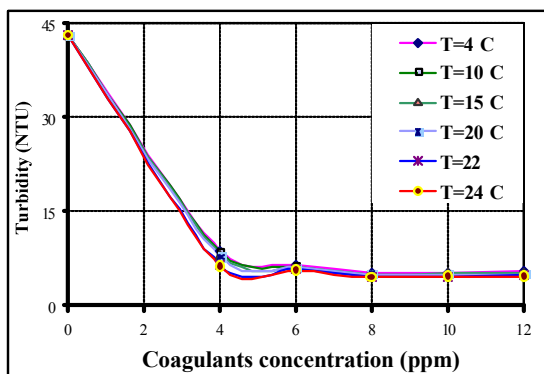


Fig. 13: Effect of temperature on turbidity of raw water- Ferric chloride

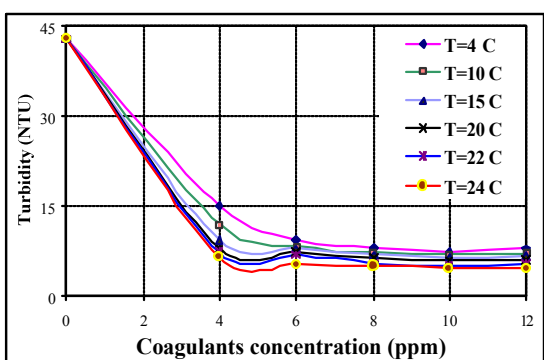


Fig. 14: Effect of temperature on turbidity of raw water- Alum

these measures were higher in this condition without coagulant aid (Fig. 13 and 14) and also the rate of reduction in turbidity is much more than its rate when only coagulant is used. It is understood from the gradient of Fig. 11 and 12 of course the rate of reduction in turbidity with ferric chloride and more coagulant aid in comparison to alum with coagulant aid is the same.

Effect of temperature on turbidity of raw water: The effects of temperature on decreasing the raw water turbidity by using alum and ferric chloride are shown in Fig. 13 and 14. Temperature, like PH, affects clarification of course it should be noted that PH variation influences filtration more. But we should consider this parameter as well for a perfect clarification process. As it's shown in figures below decrease in temperature has negative effect on turbidity and we won't have an optimum transparency while in 20-24 centigrade the conditions for coagulation and flocculation is better provided.

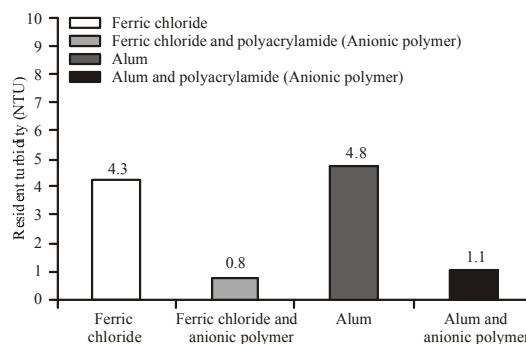


Fig. 15: Comparison of coagulants on the removal of turbidity

Observing Fig. 13 and 14 and comparing alum with ferric chloride it's obvious that temperature effects on alum during filtration are more but susceptibility of ferric chloride is less. In low temperature, ferric chloride is able to decrease turbidity of raw water easier while not only alum doesn't produce optimum decrease in turbidity but also by increasing coagulant dosage in cold water turbidity rate is decreased too much. Gradient of Fig. 13 in lower concentrate (4-6 ppm) is much more than Fig. 14, which shows decrease in turbidity of raw water.

RESULTS

In order to determine the most effective coagulant to separate nano-sized particles in raw water a comparison was made on basis of the percentage of residual turbidity (Fig. 15).

CONCLUSIONS

This investigation has demonstrated that coagulation with aluminum sulphate and ferric chloride is an effective method to clarify raw water by reducing the turbidity and will lead to reduce treatment costs for industries. Pollutant removal efficiency at various pH and coagulant doses was evaluated. Ferric chloride produced better results than aluminum sulphate in decreasing the turbidity.

But poly electrics should be used in order to produce more decrease in turbidity. Polyelectrics with ferric chloride have more effect in omitting turbidity in comparison to alum and also decrease in coagulant dosage when using coagulant aid is perceptible.

The efficiency of the coagulation of raw water is highly dependent on the control of PH and coagulant dose within an optimum range. The results show a

significant reduction of water pollution of about 85-98% for turbidity. Clarification process can be used in waste water treatment and reduces the operational cost too.

REFERENCES

1. Babcock, D.B. and P.C. Singer, 1979. Chlorination and coagulation of humic and fulvic acids. *J. Am. Wat. Works Assoc.*
2. Springer, H., 1994. Treatment of industrial waste of the leather industry. Is it still a major problem? *J. Am. Leather Chem. Ass.*, 89: 153-187.
3. Duan, J., J. Wang, N. Graham and F. Wilson, 2002. Coagulation of humic acid by aluminium sulphate in saline water conditions, *Desalination*, 150: 1-14.
4. Letterman, R.D. and C.T. Driscoll, 1988. Survey of residual aluminium in filtered water. *J. AWWA*, 80: 154-158.
5. Bailey, D.G., M.H. Tunick and M.A. Huzma, Effect of sulfide, chromium and phosphate ions on methane.
6. Arvanitoyannis, I. Eleftheriadis and E. Tsatsaroni, 1989. Influence of pH on adsorption of @e-containing effluents with different bentonites. *Chemosphere*, 18 (9/10): 1707-1711.
7. Song, Z., C.J. William and R.G.J. Edyvean, 2004. Treatment of tannery wastewater by chemical coagulation, *Desalination*, 164: 249-259.
8. Charongpun Musikavong, Suraphong Wattanachira, Taha F. Marhaba, Prasert Pavasant, 2005. Reduction of organic matter and trihalomethane formation potential in reclaimed water from treated industrial estate wastewater by coagulation. *J. Hazardous Materials*, B127: 58-67.
9. Wong, S.S., T.T. Teng, A.L. Ahmad, A. Zuhairi and G. Najafpour, 2006. Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation.
10. Franceschi, M., A. Girou, A.M. Carro-Diaz, M.T. Maurette and E. Puech-Costesb, 2002. Optimisation of the coagulation-flocculation process of raw water by optimal design method.
11. Wilson, F., 1981. Design Calculation wastewater treatment.
12. Water and Wastewater engineering system by Barnes-Gould, 1981.
13. Handbook of degremont, 1979.
14. Water and Wastewater Examination Manual v. Dean Adams 2nd Edn., 1991 by Lewis Publishers, INC.
15. Talaat, H.A., M.H. Sorour^a, N.A. Rahman and H.F. Shaalan, 2002. Pretreatment of Agricultural Drainage Water (ADW) for large-scale desalination; *Desalination*, 152: 299-305.
16. Christelle Turchiuli and Claire Fargues, 2004. Influence of structural properties of alum and ferric flocs on sludge dewaterability. *Chem. Eng. J.*, 103: 123-131.
17. Muhammad H. Al-Malack M., Nabil S. Abuzaid and Aarif H.El-Mubarak, Coagulation OF Polymeric Wastewater Discharged by A Chemical Factory; PII: S0043-1354 (98) 00219-X
18. James, M. Ebeling, Philip L. Sibrell, Sarah R. Ogden and Steven T. Summerfelt, 2003. Evaluation of chemical coagulation-flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. *Aquac. Eng.*, 29: 23_42.
19. Peter Jarvis, Bruce Jefferson and Simon A. Parsons, 2006. Floc structural characteristics using conventional coagulation for a high doc, low alkalinity surface water source; *Water Research*, 40: 2727-2737.