

Review on Chemical treatment of Industrial Waste Water

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ABSTRACT: Industrialization played an important role for scio-economy of the country. Generally, a lot of water is used and lot of wastewater generated from industries due their processes and washing purpose. A large number of chemicals are used for the production of potable water and in the treatment of wastewater effluents. In potable water treatment chemicals such as inorganic salts and polymeric organic coagulants are used for primary coagulation, as coagulant aids and for sludge dewatering; lime and soda ash allowed for pH correction and water stabilization; caustic soda is used for pH adjustment, powdered activated carbon (PAC) can remove taste and odour compounds and micro pollutants such as atrazine, bentonite aid's coagulation, and ammonium hydroxide is used in chloramination. The main object of review is focus on research work done as well as the basic concept behind treatment and application by the researcher on different industry's waste-water treatment. ©JASEM

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Coagulation is an essential process in water and industrial wastewater treatment. In the area of potable water treatment, clarification of water with coagulating agents has been practiced since ancient times, using a variety of substances the most notable among them being crushed seeds. The Egyptians, as early as 2000 BC, used almonds smeared around a vessel to clarify river water. The early Romans were also familiar with alum, though it may not have been for water treatment (Bratby, 2006). Nevertheless, its use of a coagulant by the Romans was mentioned in ca. 77 AD. By 1757, alum was used as a coagulant in water treatment in England, and more formally for the treatment of public water supplies in 1881 (Bratby, 2006). In modern water treatment, coagulation and flocculation are still essential steps in the treatment processes.

Coagulation is one of the most important physicochemical operations used in water, and wastewater treatment can be achieved by chemical and electrical means (Pernitsky and Edzwald, 2006). Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. Coagulation has been defined as the addition of a positively charged ion of metal salt or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation targets the colloid particles of size 10^{-7} to 10^{-14} cm in diameter. The colloid particles exhibit Brownian movement through the water; their surface is negatively charged so they repel one another, and they form a stable dispersed suspension (Bache et al., 1999). If colloid particles or ions of positive electric

charge are added it neutralizes the electric negative charge. Flocculation refers to the successful collision that occurs when destabilized particles are driven toward each other by the hydraulic shear force in the rapid mix and flocculation basin. It agglomerates of a few colloids then quickly bridge together to form microflocs which is turned into visible floc masses (Gregory, 2006), which is shown in Fig.1.

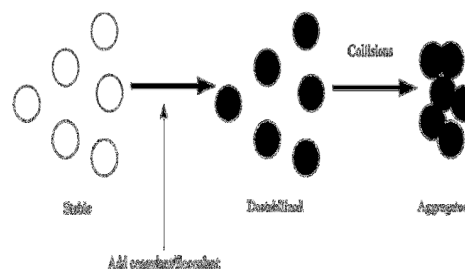


Fig. 1: Mechanism of Coagulation (Gregory, 2006)

The separation of particulate matter from the liquid phase is one of the important steps in most wastewater treatment processes. All waters, especially surface waters, contain both dissolved and suspended particles. Coagulation processes are used to separate the suspended solids portion from the water. The suspended particles vary considerably in source, composition charge, particle size, shape, and density. Correct application of coagulation processes and selection of the coagulants depend upon understanding the interaction between these factors. Coagulant chemicals come in two main types' primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges

of particles into the water which causes the particles to clump together (Schulz and Okun, 1984). Chemically, coagulants are either metallic salts (such as alum) or polymers. Polymers are man-made organic compounds made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged). Chemical coagulation has been in practice for several decades to precipitate the soluble heavy metals present on the waste water, as hydroxides and facilitate their removal by physical separations through the sedimentation process. The process of coagulation separation consists of four steps, which shown in Fig. 2.

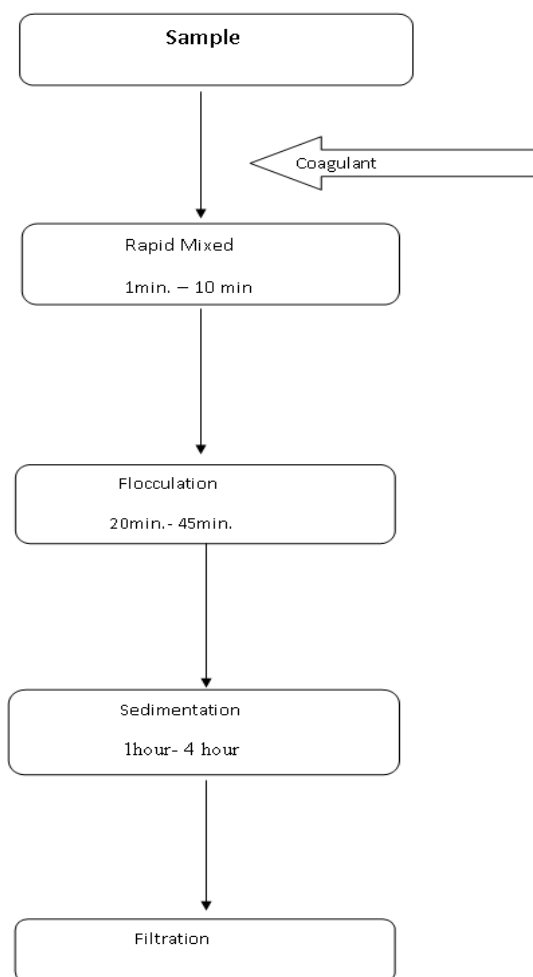


Fig. 2: Steps of coagulation process

The initial step is simple: the chemical is added to wastewater. This is followed by the second step, where the solution is mixed rapidly in order to make certain that the chemicals are evenly and homogeneously distributed throughout the wastewater. In the third step, the solution is mixed again, but this time in a slow fashion, to encourage the formation of insoluble solid precipitates, the

process known as "coagulation." The final step is the removal of the coagulated particles by way of filtration or decantation (Yılmaz et al., 2007).

The inherent disadvantage to this process is the generation of large quantities of chemical sludge and its classification as hazardous waste, necessitating the need for secured land filling of hazardous solid wastes. The process also increased the total dissolved salt content in the treated waste water increasing the desalination costs by a reasonable margin. On the other hand, coagulant aid is an inorganic material, when used along with main coagulant, improves or accelerates the process of coagulation and flocculation by producing quick forming, dense and rapid-settling flocs. Coagulant aids when added increase the density to slow-settling flocs and toughness to the flocs so that they will not break up during the mixing and settling processes (Holt et al., 2002).

Selection of Coagulant: The selection of coagulation is one the most important decision for the waste-water treatment, but the different coagulation works in different quality parameter of water. Several studies have been reported on the examination of coagulation–flocculation for the treatment of industrial waste-water treatment, aiming at performance optimization, i.e. selection of the most appropriate coagulant, determination of experimental conditions, and assessment of pH effect and investigation of flocculants addition Holt et al., (2002). Basically, coagulation is divided among four categories, according to their application and nature.

Aluminum salts (alum) Ferric and ferrous salts
Lime Polymers Cationic Anionic and non-ionic
polymers Natural

Coagulation with aluminium salt: The most common and economical salt of aluminum is alum ($\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) and widely used as a coagulant in the water treatment. The aqueous chemistry of aluminum is complex and upon addition of an aluminum coagulant in water treatment, multiple reaction pathways are possible. The mechanism by which aluminum functions depend on which aluminum species react to remove dissolved or colloidal contaminants. Destabilization involving aluminum monomers is referred to as charge neutralization or coagulation of colloidal particles in the presence of $\text{Al}(\text{OH})_3$ is termed as enmeshment or sweep floc. Dissolved organic can be removed by adsorption on aluminum precipitation (Benschoten, 1990). From the numerous reviews of the fundamental theory and mechanisms of coagulation, various mechanisms for destabilizing contaminants

using chemical coagulants have been identified. These mechanisms include double layer compression, adsorption charge neutralization, sweep coagulation and inter particle bridging. The type of inter actions between the chemical coagulant and contaminants determine the mechanism of coagulation. The predominance mechanisms observed during conventional coagulation with metal coagulants are adsorption charge neutralization and sweep coagulation. For aluminum salts, the mechanism of coagulation is controlled by the hydrolysis speciation (Dennett et al., 1996) shown in Fig.3.

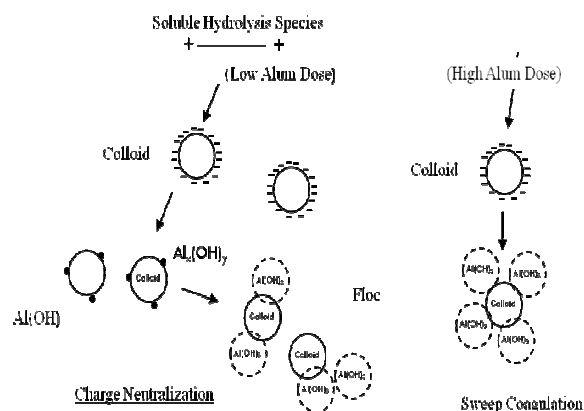


Fig. 3: Reaction Schematics of Coagulation (Dennett et al., 1996)

The positively charged polyhydroxo-complexes such as $[Al_8(OH)_{20}]^{+4}$ in the pH range between 4 and 7, are the effective flocculants. Over saturation and formation of amorphous hydroxide precipitate $[Al(OH)_3](s)$ enmeshes colloidal particles in a “sweep floc”. Many other monomeric and polymeric species have been reported and are shown in Fig.4.

Monomers: $[Al(OH)]^{+2}$, $[Al(OH)_2]^{+}$, $[Al_2(OH)_2]^{+4}$, $[Al(OH)_4]^{-}$ **Polymers:** $[Al_6(OH)_{15}]^{+3}$, $[Al_7(OH)_{17}]^{+4}$, $[Al_8(OH)_{20}]^{+4}$, $[Al_{13}(OH)_{34}]^{+5}$

The coagulation process with alum as the sole coagulant is capable of achieving significant organic removal. The pH of the water during coagulation has profound influences on effectiveness of coagulation for organic removal. Organic removal is much better in slightly acidic condition. The optimum pH for alum coagulation is influenced by the concentration of organic matter in the water. For water of higher organic content, the optimum pH is displaced to be slightly more acidic values (AWWA, 1979). An adequate amount of alkalinity in raw water is required during the flocculation process for two reasons i) the need for a buffer capacity in order to

avoid a steep drop of pH due to alum addition and ii) a sufficient supply of bicarbonate to form metal hydroxide (Kawamura, 1996).

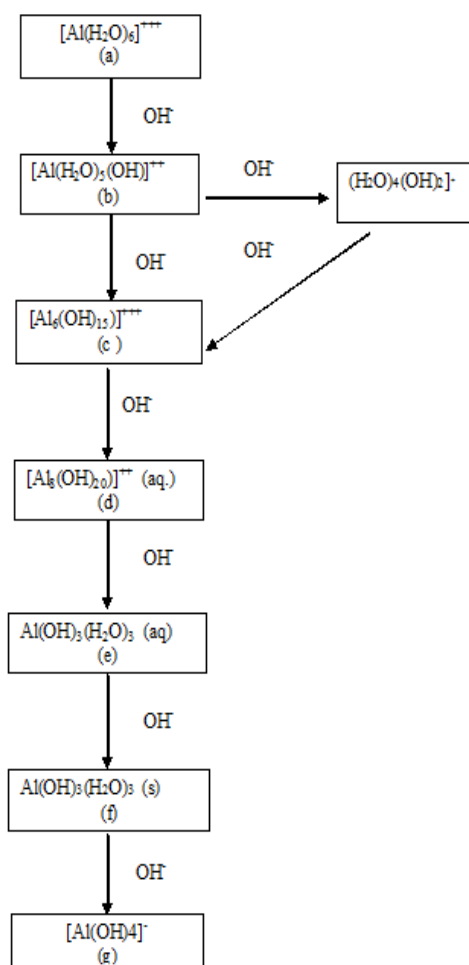


Fig. 4: Stepwise Conversion of the Tri-Positive Aluminum Ion to the Negative Aluminate ion (Stumm and Morgan, 1962)

Thus conventional coagulation practices may provide excellent organic removal if the coagulant dose and pH conditions are adjusted into the optimum range. Organic removal increased with an increasing alum dose and alum doses higher than the normally used for turbidity removal, are needed to obtain the best organic removal. Alum dose and pH were the most important variables. The influence of pH was very great (Semmens and Field, 1980). Several research efforts have been devoted to improve the efficiency to a coagulation flocculation process. After studying the aquatic chemistry and the behavior of simple Al salts, the way for improvement seemed to be there (partial) polymerization. The result from these efforts was the production of a range of pre-polymerized aluminium solutions, referred as Polyaluminium

chlorides (PACl), Polyaluminium sulfates (PAS), or Polyaluminium chloro-sulfates (PACS), with variable degrees of polymerization. These products and especially the first one (PACl) are used extensively worldwide during the last decades, with an ever increasing demand. Their properties were intensively examined and have proven to be more efficient in lower dosages, in wider pH, temperature and colloids concentration ranges, than the conventional simpler ones, leading to cost and operative more effective treatment (Sinha et al., 2004; Crittenden et al., 2005). Polyaluminium chlorides (PACl) are similar to Alum except contain high charge polymeric aluminium species as well as the monomer. An Al_{13} with the formula $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ has been shown to dominate species (Parthasarathy and Buffle, 1985; Bertsch and Thomas, 1986; Bertsch, 1987). Sodium aluminate, $NaAlO_2$, has a variety of industrial uses and has been utilized as a coagulant in drinking water treatment as a supplement to alum and may be encountered in lime-soda softening processes. It has been used in wastewater treatment as a coagulant in the phosphorous removal process. While the other aluminum and iron salts act as acid's consuming alkalinity, sodium aluminate acts as a base. Each mg/l of sodium aluminate contributes nearly 2 mg/l as $CaCO_3$ of alkalinity. Thus, sodium aluminate may be useful in soft, low alkalinity water (Engelhardt, 2010).

Coagulations with iron salt: Iron compounds possess pH coagulation ranges and floc characteristics similar to aluminum sulfate. The cost of iron compounds may often be less than that of alum. However, the iron compounds are generally corrosive and often present difficulties in dissolving, and their use may result in high soluble iron concentration in process effluents. The iron salts most commonly used as coagulants include ferric sulfate, ferric chloride and ferrous sulfate. These compounds often produce good coagulation when conditions are too acidic for best results with alum. Sometimes the particles are best removed under acidic conditions, and iron compounds give better results (Tripathy and De, 2006). Mahesh et al. (2006) was studied many hydrolysis products are cationic and these can interact strongly with negative colloids, giving demineralization and coagulation, under the correct conditions of dosage and pH. Excess dosage can give charge reversal and restabilisation of colloids (Cohen and Hannah, 1971). At around neutral pH, Fe (III) has limited solubility, because of the precipitation of an amorphous hydroxide, which can play a very important role in practical coagulation and flocculation processes. Positively charged precipitate particles may deposit on contaminant particles (heterocoagulation), again giving the possibility of

charge neutralization. A further possibility is that surface precipitation of hydroxide could occur, with similar consequences. More importantly in practice, hydroxide precipitation leads to the possibility of *sweep flocculation*, in which contaminant particles become enmeshed in the growing precipitate and thus are effectively removed (Duan and Gregory, 2003).

Monomeric hydrolysis products: All-metal cations are hydrated, to some extent, in water in terms of a primary hydration shell, where water molecules are in direct contact with the central metal ion, and more loosely held water in a secondary hydration shell. In the cases of Fe^{3+} , it is known that the primary hydration shell consists of six water molecules in octahedral co-ordination (Richens, 1997). Owing to the high charge of the metal ion, water molecules in the primary hydration shell are polarized, which may lead to a loss of one or more protons depending upon the solution pH. Effectively, this means that the water molecules in the hydration shell are progressively replaced by hydroxyl ions, giving a lower positive charge, according to the following equation:



This is an oversimplified scheme, as it is known that dimeric, trimeric and polynuclear hydrolysis products of Fe can form. However, these can often be ignored, especially in dilute solutions, and may not greatly affect the overall metal speciation. The hydrolysis scheme as given above will proceed from left to right as the pH is increased, giving first the doubly and singly-charged cationic species and then the uncharged metal hydroxide, $Me(OH)_3$. Iron hydroxide is of very low solubility, and an amorphous precipitate can form at intermediate pH values. This is of enormous practical significance for the action of these materials as coagulants. With the further increase in pH, the soluble anionic form $Me(OH)_4^-$ becomes dominant (Gregory and Carlson, 2003). Although the most stable solids are crystalline forms of iron hydroxides, such as gibbsite and goethite, these are usually formed very slowly (typically in weeks or months). In the context of coagulation mechanisms, it is more relevant to consider the solubility of the amorphous precipitates that form initially. However, solubility constants for the amorphous forms, $K_{s_{amo}}$ are not known precisely and only estimated values can be quoted. Using this solubility values one can plot, as a function of pH, the concentrations of the various species in equilibrium with the amorphous hydroxide precipitate.

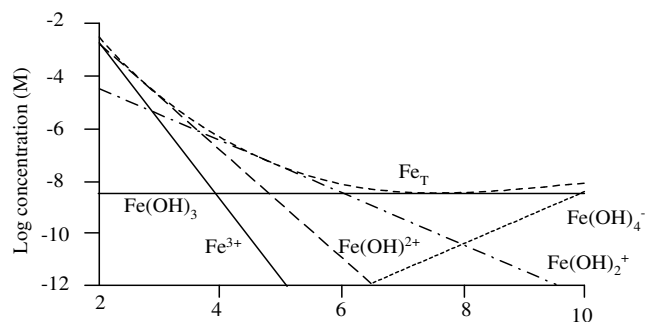


Fig. 5: Concentrations of monomeric hydrolysis products of Fe(III) in equilibrium with the amorphous hydroxides, at zero ionic strength (Duan and Gregory, 2003)

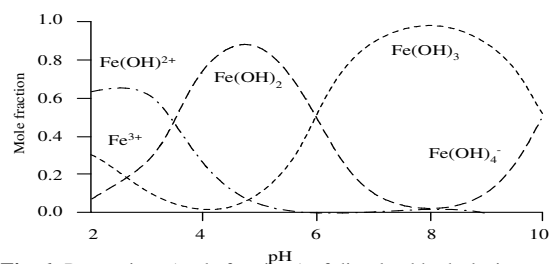


Fig. 6: Proportions (mole fractions) of dissolved hydrolysis products in equilibrium with amorphous hydroxides (Duan and Gregory, 2003)

As shown in Fig. 5 and 6 the total amount of soluble species in equilibrium with the amorphous solid is effectively the solubility of the metal, and it can be seen that in each case, there is a minimum solubility at a certain pH value. For Fe, the minimum solubility is much lower, $< 0.01 \mu\text{M}$. All of the hydrolysed species retain the octahedral co-ordination, and the stepwise deprotonations show the expected spread of pK values (Duan and Gregory, 2003).

Polynuclear species: In addition to the formation of simple monomeric hydrolysis products, there are many possible polynuclear forms that could be considered. It is shown that the Fe dimer $\text{Fe}_2(\text{OH})_2^{4+}$ could become significant in acidic solutions ($\text{pH} < 3$). From the standpoint of coagulation with simple Fe salts, only monomeric hydrolysis products and the amorphous hydroxide precipitate need be considered

Precipitate formation: It precipitated metal hydroxides can be formed in various ways. However, the precise mechanisms and structure of the precipitate have been the subject for much debate and there is a rather extensive and confusing literature about the topic. In the case of iron, there is redox as well as hydrolytic reactions to consider (Deng, 1997) and the subject becomes quite complex. The surface charge characteristics of precipitated metal hydroxides are of great importance in coagulation. The precipitates show an isoelectric point (i.e. p) at

which the apparent (electro-kinetic) surface charge is zero. At pH values below the i.e.p. the precipitate is positively charged and at higher pH values it has a negative charge. For amorphous ferric hydroxides, the i.e.p. is somewhat lower. For ferric salts, pre-hydrolysed forms give precipitates with i.e.p. values shifted upwards by one or more pH units. The varying charge with pH can greatly affect the precipitation process. The presence of highly charged anions, such as sulfate, can have a large effect on hydroxide precipitation. Sulfate can reduce the positive charge of the precipitate in the acidic region, so that large flocs are formed over a wider pH range. This was clearly shown by Hayden and Rubin, (1974) and others. The sulfate effect has been known since the 1930s (Cohen and Hannah, 1971) and is very important in practice since aluminium, and ferric sulfates are commonly used as coagulants and natural waters can contain significant amounts of sulfate.

Coagulation with polymer: Polymers or polyelectrolytes consist of simple monomers that are polymerized into high-molecular-weight substances (Metcalf and Eddy, 1991) with molecular weights varying from 10^4 to 10^6 Daltons. Polymers can vary in molecular weight, the structure (linear versus branched), amount of charge, charge type and composition. The intensity of the charge depends upon the degree of ionization of the functional groups, the degree of copolymerization and/or the amount of substituted groups within the polymer structure. With respect to charge, organic polymers can be cationic (positively charged), anionic (negatively charged) or nonionic (no charge). Polymers in solution generally exhibit low diffusion rates and raised viscosities, thus it is necessary to mechanically disperse the polymer into the water. This is accomplished with short, vigorous mixing (velocity gradients, G values of 1500 sec^{-1} , although smaller values have been reported throughout the literature, 300 to 600 sec^{-1}) to maximize dispersion, but not so vigorous as to degrade the polymer or the flocs as they form (Wakeman and Tarleton, 1999).

Lower coagulant dose requirements, a smaller volume of sludge, a smaller increase in the ionic load of the treated water, reduced level of aluminum in treated water, Cost savings of up to 25–30% (Wakeman and Tarleton, 1999; Nozaic et al., 2001)

Polyelectrolytes act in two distinct ways: charge neutralization and bridging between particles. Because wastewater particles are normally charged negatively, low molecular weight, cationic polyelectrolytes can act as a coagulant that neutralizes or reduces the negative charge of the

particles, similar to the effect of alum or ferric chloride. The mechanism is shown in Fig.7.

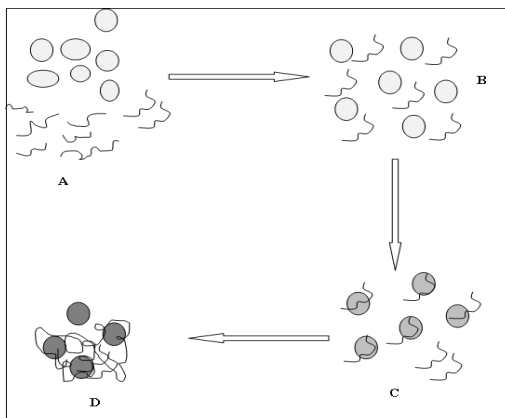


Fig. 7: Mechanism of polymer coagulation (Bolto and Gregory, 2007)

This has the effect of drastically reducing the repulsive force between colloidal particles, which allows the van der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form microflocs (James et al., 2003). The coagulated particles are extremely dense, tend to pack closely, and settle rapidly. If too many polymer is used, however, a charge reversal can occur, and the particles will again become dispersed, but with a positive charge rather than negatively charged (Bolto et al., 1998). Higher molecular weight polymers are generally used to promote bridging flocculation. The long-chain polymers attach at a relatively few site on the particles, leaving long loops and tails who stretch out into the surrounding water. In order for the bridging flocculants to work, the distance between the particles must be small enough for the loops and tails to connect two particles (Bolto, 2005). The polymer molecule thus attaches itself to another particle forming a bridge. Flocculation is usually more effective for the higher the molecular weight of the polymer. If too many polymer is used, however, the entire particle surface can become coated with polymer, such that no sites are available to “bridge” with other particles, the ‘hair-ball effect’. In general, high molecular weight polymers produce relatively large, loosely packed flocs, and more fragile flocs (Wakeman and Tarleton, 1999).

Because the chemistry of wastewater has a significant effect of the performance of a polymer, the selection of a type of polymer for use as a coagulant/flocculation aid generally requires testing with the targeted waste stream, and the final selection is often more of an “art” than a science. Hundreds of

polymers are available from numerous manufactures with a wide variety of physical and chemical properties. And, although the manufacturers can often help in a general way, the end user must often determine from all the various product line, which is best for their particular application and waste stream, i.e. most cost effective (Ebeling et al., 2004).

Cationic Polymer: There are many varieties of cationic polymers available, as has been reviewed in detail (Bolto, 1995). Some natural products or their derivatives, such as chitosan, are also employed in water treatment. Types of cationic polymer are like, Poly (diallyldimethyl ammonium chloride) (Wandrey and Jaeger, 1985), Epichlorohydrin/dimethylamine polymers (Vorchheimer, 1981), Cationic polyacrylamides (PAMs) (Hoover, 1970; Baade et al., 1989). Hydrolysis of the ester groups and consequent loss of cationic charge is CD and pH dependent, with hydrolysis encouraged by more alkaline conditions:

$$\text{Pol} - \text{COOCH}_2\text{CH}_2\text{NMe}_3^+ + \text{OH}^- \rightarrow \text{Pol} - \text{COO}^- + \text{HO} - \text{CH}_2\text{CH}_2\text{NMe}_3^+$$
 (2) It has been observed that some degradation occurs even at pH 6 for polymers having a CD of 24%, with a half-life of 24h at pH 7 and 0.25h at pH 8.5(Aksberg and Wagberg, 1989).

Natural Cationic polymer: There are several naturally-occurring polymers that have inherent cationic properties or the polymer can be modified to yield a cationic polyelectrolyte. The most prominent of these is chitosan, a partially deacetylated chitin which is as a 1:4 random copolymer of N-acetyl-a-D-glucosamine and a-Dglucosamine (Rinaudo, 2006). The commercial product is of medium MW and has a CD that is pH dependent [43]. It can be quite effective at NOM removal (Bolto et al., 1998, 2001; Eikebrokk and Saltnes, 2002), even though it is but slightly charged (17%) at neutral pH levels. Such a weakly basic polymer may be operating via hydrogen bonding through the free amino groups in the polymer and aliphatic and aromatic hydroxyl groups on the NOM. The use of chitosan in water purification applications generally has been extensively reviewed, with references to its use in decolorizing dye house effluents, the treatment of food-processing wastes, metal ion removal and sludge conditioning (Pariser and Lombardi, 1989). The effect of MW and degree of deacetylation on the coagulation and flocculation of bentonite suspensions has been explored (Roussy et al., 2005)

Anionic : The most commonly used anionic polymers contain weakly acidic carboxyl acid groups, so the CD depends on pH. Anionic PAMs high MW carboxylic acid polymers derived from PAM are

extensively employed as flocculating agents on the water and other process industries, where a low CD is the general rule. Copolymers with the anionic structure can be prepared either by copolymerisation of acrylamide and acrylic acid or its salts, or by polymerisation of acrylamide followed by partial hydrolysis (Vorchheimer, 1981). The former approach gives a roughly random copolymer, whereas some clustering of anionic groups can occur when alkaline hydrolysis is employed. The CD can be determined by potentiometric titration of the copolymers or by direct polyelectrolyte titration (Wassmer et al., 1991). Anionic PAMs, or APAMs, containing varying proportions of acrylamide comonomer are in terms of their CD, as mol% and calculated on a theoretical basis in meq/g of polymer.

Natural anionic polymers: Many sulfated polysaccharides are available as natural biopolymers or their derivatives, some examples being heparin, dextran sulphate, mannan sulphate and chondroitin sulphate, but the applications are mainly medical (Voycheck and Tan, 1993). One proposed for use in the water industry is the modified natural polymer lignin sulphonate, made by sulfonating low MW kraft pine lignin (Meister and Li, 1990). Certain of these polymers are equivalent in performance to cationic PAMs for the dewatering of sludge. Tannins have also received attention (Rice et al. 1964)

Factor Affecting The Coagulation: *Coagulant dosage:* The concentration of coagulant required for coagulation is to be proportional with the concentration of an organic matter present in solution, and it was stated that before turbidity can remove the coagulant must be added in sufficient amounts to destabilize the organic matter. Apparently, these substances react with the coagulants before the coagulants can destabilize clay suspensions. Coagulant dosage decreases with decrease pH because more carboxylic groups become prorogated and do not interact with coagulant. There is no reliable formula to determine the effective dosage. However, a jar test is the most reliable method to determine both the effective type of coagulant and their proper dosage (Kawamura, 1996; Bolto and Gregory, 2007). Proper coagulation is essential for good clarification and filtration performance and for the control of pathogens and disinfection by-products. Improper coagulation can cause high residual coagulant residuals in treated water and post-treatment precipitation of particles causing turbidity, deposition and coatings of pipes in the distribution system. Minimizing of solids residuals from coagulation has also become a more important part of utility operations due to increased disposal costs and land filling restrictions (Pernitsky,

and Edzwald, 2006). These issues have put additional pressure on utilities to optimize coagulation to meet the multiple treatment objectives (modified after (Edzwald and Tobiason, 1999)):

To maximize the removal of particles, turbidity and microorganisms/pathogens by downstream solid-liquid separation, To maximize TOC and DBP removals To minimize residual coagulant concentrations, To minimize solid residuals (sludge) production, and To minimize operating costs.

Edzwald (1993) presented a review on coagulation in water treatment, emphasizing the importance of raw water chemistry, pollution concentration and type, and the chemistry of coagulants. NOM rather than particles in water supplies can control coagulant dosage and selection. The removal of pollution with Al coagulants can involve hydrolysis, complexation, precipitation, and adsorption reactions. SUVA can be used to estimate whether the NOM is high or low in hydrophobic acids and to estimate removals of DOC by coagulation. O'Melia et al (1999) stated that adsorption of NOM on oxides depends significantly on complex formation reactions between specific sites on oxide surfaces and functional groups on the NOM. Coagulation requirements can and often are set by the TOC concentration in a water source. Frequently, there is a stoichiometric relationship between the required coagulant dosage and the TOC of the water to be treated. Other important factors include pH and the concentration of divalent cations.

Eikebrokk (1996, 1999, 2001) demonstrated in contact filtration pilot experiments with aluminium, and iron based coagulants that compliance with the total residual coagulant concentration standard of 0.1 mg. Me/L was the determining factor with respect to identifying minimum coagulant dosage requirements when treating low turbidity surface waters with NOM concentrations measured as colour and TOC in the range of 15-50 mg Pt/L and 2-6 mg TOC/L, respectively. Compliance with the turbidity (<0.2 NTU) and colour (<5 mgPt/L) could be obtained with lower coagulant doses. He distinguished between absolute and practical minimum doses; the difference being that for the absolute minimal dose leveled the maximum residual metal concentration of 0.15 mg Me/L can be obtained only within a very narrow pH-window. When using the 25% higher feasible minimum dosage, the pH window for optimum process performance and compliance with the water-quality standards can be obtained within a wider range of pH.

Gregory and Carlson (2003) studied the impact of coagulation pH, zeta potential and floc formation

kinetics on particle removal during settling and filtration. They concluded that higher coagulation pH – and thus higher alum coagulant doses – could be advantageous during periods of rapidly changing water quality conditions, such as high-NOM runoff events. The rate of floc formation measured immediately following coagulant addition could be indicative of overall process performance. Budd et al. (2004) stated that optimization of coagulation is central to the drinking water industry's ability to meet goals for particulate (turbidity) and NOM removal. They stressed the importance of adopting a holistic view of treatment objectives when considering possible changes in the coagulation process, and highlight the necessity of evaluating coagulation as a multiple input process that can be fine-tuned through adjustment of two fundamental parameters – pH and coagulant dose. Changes that might be undertaken include trying a different coagulant dose and pH, using alternative coagulants, and adding coagulants in a different sequence. Their recommendations were based on coagulation evaluations performed at a number of US water treatment facilities over the past 15 years. Pernitsky and Edzwald (2006) presented guidelines for the selection and use of polyaluminium chloride (PACl) and alum coagulants in terms of raw water quality and treatment method. The concentration of NOM was found to be the most important parameter affecting coagulant dose. The superlative dose of coagulant depends on the type of wastewater, pH, coagulant, as well as the criteria chosen to determine the perfect dose (Mehta and Chavan, 2009). Therefore, different dosage rang was tested with varying intial pH levels. The optimum coagulant dose (OCD) in this study is defined as the lowest coagulant dosage at which maximum COD removal efficiency is achieved. The OCDs in the pH range of 7–9 were 3.0 g/L, 3.5 g/L and 4.0 g/L, respectively, but the OCD was only 1.25 g/L at pH 6. On the other hand, less satisfactory COD removal efficiency (69%) is attained at pH 6 compared to those at higher pH levels (>80%). Amud and Amoo (2007) was studied the removal of COD increased with increasing dose of ferric chloride The COD percentage removal increased from 20.3 to 75.8% when the dose of the ferric chloride was increased from 200 to 600 mg/l, respectively. Increasing the dose of the ferric chloride would increase the super saturation of the $\text{Fe}(\text{OH})_3$ which increased the nucleation rate and hence the floc growth rate. As a result, suspension of a greater number of flocs was enhanced, and subsequently; removal of larger amounts of COD was achieved, due to the availability of larger surface area on which adsorption of the organic matter took place. On the contrary, low doses of ferric chloride led into the

formation of larger but fewer flocs as a result of faster growth rate relative to nucleation rate, which resulted in a smaller surface area on which adsorption to organic matter occurred. Changing the alum dose from 500 to 1000 mg/l, at a pH value of 6.9 gave the results. From the result, it indicates that the COD removal efficiency increased from 37.8 to 72% by greatly the alum dose from 500 to 700 mg/l respectively. The predominant removal mechanism at low doses of alum is adsorption and charge neutralization. However, at high doses of coagulant is sweepfloc coagulation by enmeshment in the aluminum hydroxide precipitate (Gregory and Duan, 2001). Further, increase with the alum dose from 700 to 1000 mg/l exerted slight improvement in COD removal, i.e. by a value of 2.6%. Therefore, the optimum dose of alum that enhanced maximum removal of COD was taken as 700 mg/l. A higher dose of alum (3.0 g/l) aided with 1 g/l lime was used for coagulation–precipitation of cosmetic wastewater industry (Aloui et al., 2009). Anionic surfactant, COD and BOD_5 removal was 53.3, 37.3, and 51.2% respectively.

Alkalinity/pH: Alkalinity refers to the acid-neutralizing capacity of water, and is a general indication of water's buffering capacity. Alkalinity and pH are related; higher alkalinity waters have been higher pH. Metal coagulants are acidic, and coagulant addition consumes alkalinity. For low alkalinity waters, coagulant addition may consume all the available alkalinity, depressing the pH to values too low for effective treatment. High alkalinity waters (highly buffered) may require elevated coagulant additions to depress the pH to values favorable for coagulation. Alum and ferric chloride are more acidic than PACls, and therefore, result in greater alkalinity consumption after addition. For PACls, alkalinity consumption is related to basicity. Higher basicity PACls will consume less alkalinity than low or medium basicity ones. The pH at which coagulation occurs is the most important parameter for proper coagulation performance, as it affects the (David and Pernitsky, 2003):

Surface charge of colloids, Charge of NOM functional group, Charge of the dissolved-phase coagulant species, Surface charge of floc particles, Coagulant solubility.

For aluminum-based coagulants, the best coagulation performance is generally seen at pH values that are as close as possible to the pH of minimum solubility of the coagulant. This controls dissolved Al residuals, as well as maximizing the presence of floc particles for adsorption of NOM. If pH is lowered to improve coagulation and organic removal, it is typically

necessary to raise pH in the final effluent from the plant to provide less corrosive finished water. The pH may be adjusted at one or more points for the treatment, including rapid mixing, prefiltration and postfiltration. In case of enhanced coagulation, it is recommended to readjust the pH after the filtration process as compare to prefiltration. This is because some animate matter may be adsorbed onto the floc that may be carry-over from the clarification process, and any prefiltration pH adjustment may then result in "release" of that biological matter, which could pass through the filters and contribute to subsequent DPB formation. One of the greatest practical problems faced in removing soluble NOM from low turbidity waters is inability to produce an acceptable floc (Gregor et al., 1997). Natural turbidity provides a ready source of nucleating sites for floc development, and once present; these flocs act as adsorption sites for soluble NOM. For low turbidity waters, these essential floc nuclear sites can be provided by lime that is used for pH and alkalinity correction, provided the lime is added in sufficient quantity and at the point where it retains some particulate nature. If pH adjustment with lime is not needed, bentonite clay or activated silica can be used as a coagulant aid.

Temperature: Temperature affects the solubility of the metal hydroxide precipitate and the rate of formation of the metal hydrolysis products. Low temperature affect's coagulation and flocculation processes by altering coagulant solubility, increasing water viscosity, and retarding the kinetics of hydrolysis reactions and particle flocculation. Higher coagulant doses, the addition of flocculation or filter aids, longer flocculation times, and lower flotation, sedimentation, and/or filtration rates are often required to produce low turbidity treated water. Sedimentation processes are most affected. In full-scale plants, processes are sometimes operated at subordinate hydraulic loading rates in the winter due to decreased water demands. This tends to compensate for the lesser settling rates (David and Pernitsky, 2003). Cold-water temperatures often cause decreased performance for sedimentation and make proper coagulant selection more important. High-basicity PACl is reported to be less affected by cool temperatures than alum is (Dempsey, 1974 a, b; Edzwald and Bunker, 1994), and the presence of sulphate in a PACl resulted in a better settling floc. As mentioned chilled water decreases the solubility of alum and PACl coagulants, increases water viscosity, and retards the kinetics of hydrolysis reactions and particle flocculation. Thus, higher coagulant dosages and additional flocculation time are required at a low temperature (Frank et al., 2000). Low water temperatures decrease the rates of coagulant dissolution, precipitation, cell enmeshment

and floc formation, especially when alum was used (O'Connor and Brazos, 1990). Warm water often causes an increased level of algae and other organic matter in raw water. Temperature also significantly affects turbidity and particle counts during coagulation (Braul et al., 2001). However, dissolved organic carbon (DOC) and colour removal are not sensitive to temperature (Knocke et al., 1986; Hanson and Cleasby, 1990; Randtke, 1998). The The negative effect of temperature tends to be greatest with dilute suspensions. Direct filtration and DAF processes are much less affected by cold-water temperatures than sedimentation (Pernitsky and Edzwald, 2006).

Mixing: Rapid mixing after coagulation is an important design parameter. The coagulant must be uniformly mixed in the waste water. In case mixing is indigent local under- and overdosing occurs, resulting in woeful performance during the process. The parameter expressing mixing intensity is called the velocity gradient or G-value (s^{-1}). Recommended G-value for rapid mixing is minimally $1500 s^{-1}$. Mixing intensity and time has the significant effect of the mechanisms (e.g. sweep coagulation, sedimentation) involved in the following process of coagulation (Chichuan et al., 2002). Between the hydrolysis of the coagulant in water and the development of large flocs, short-lived water soluble aluminium and iron(III) hydroxide complexes, metal hydroxide sols are formed, which also carry a positive charge (Licsko et al., 1996). These latter two metal hydroxide types (which also exist for a brief period - a few seconds-only) are the ones capable of destabilizing the dispersion and adsorbed NOM on the surfaces. The bond between the suspended solids to be removed and the metal hydroxide sols and water soluble metal hydroxide complexes must be established within this short period. Quick mixing of the coagulant will ensure rapid hydrolysis of the coagulant, contact between the sols and the suspended solids and will retard the development of large flocs which are inactive in destabilizing the dispersion and removing of a pollutant.

When using sodium aluminate in conjunction with aluminium sulphate the two reagents must never be mixed before addition to the water. The sodium aluminate must be added until the water a short time (0.5 to 2 min.) before the alum. Polyelectrolyte solutions are extremely viscous and often only very small doses are required. It is therefore, essential that there is sufficient turbulence at the dosing point to ensure rapid and thorough mixing of the small amount of reagent with the main water flow. Dilute polyelectrolyte solutions are easier to disperse into the flow than concentrated solutions, but a balance must be struck otherwise the volume of

polyelectrolyte solution added will become a significant proportion to the flow (Bourke et al., 2002). When used as coagulant aid's polyelectrolytes should be dosed after the inorganic coagulant. Effective delay time (from one to several minutes) should be allowed following the addition of the inorganic coagulant to allow 'microflocs' to form before dosing the polyelectrolyte. In addition to turbulence at the point of injection, it is also important to allow enough delay time following polyelectrolyte addition to permit mixing and/or reaction before the subsequent solids-liquid separation. Delay times of approximately one minute are generally satisfactory, but the required time will depend on the hydrodynamic conditions obtaining on the plant.

Timing of the addition of conditioning chemicals and coagulants, as well as of coagulant aids, is important and is usually critical for effective clarification performance, satisfactory filter performance, as a consequence, and hence the quality of the final water. Appropriate separation of the dosing points for the distinctive chemicals and provision of appropriate delay times between chemical additions can be of

considerable importance in achieving optimum coagulation. A study by the Water Research Centre of the clarification of five unlike water types by flotation showed that dosing the coagulant chemicals directly into the raw water feed pipe gave improved quality in the flotation treated water, compared to dose them into the flash mixer. The order of chemical addition had little influence on the treated water quality – either equal or slightly better results were obtained dosing the pH adjustment chemical first. At one plant, where the distance from the feed pipe separating the points of addition of chemicals could be varied; the quality of water deteriorated if the separation was less than 2 m.

Application Of Coagulation/Flocculation In Water/Wastewater Treatment: From review, we find that the coagulation method is one of the suitable methods to treat the water/industrials waste water by using different coagulation. But some other factor like dosing, pH and Temperature also affected the processes, which are concluded with the application in water and water treatment in Table 1.

Table 1: Application of different coagulant on industries

S · N o	Industries	Coagulant	Dosing	Optimum Alkalinity/pH	Temperature	Max. Mixing/rpm	Parameter	Remark	Author
1	Sugar Industries	(Al ₂ (SO ₄) ₃ +FeSO ₄) and Aluminium salt Al ₂ (SO ₄)	5mg/l	7.1	nm	nm	COD	75% AND 77% COD REDUCTION	Khan et al., 2003
2	Pulp and paper	Calcium benoite+alum	100mg/l/+ 200mg/l	7	nm	120	color	88% of color reduction found	Dilek et al., 2001
3	Pulp and paper	polyaluminium chloride (PAC) as the chemical coagulant and bagasse fly ash (BFA)	3kg/l PAC, 2kg FOR FLY	PAC=pH3 Fly ash =pH 4	nm	120	Color and COD	COD and colour to 87 % and 95 %, respectively	Srivastava et al., 2005
4	Pulp and paper	Poly-Aluminum-Silicate-Chloride	40mg/l	7	nm	200	Turbity and COD	93.13% and 91.12%	Kadhun et al., 2011
5	Pulp and paper	aluminium chloride, poly aluminium chloride and copper sulphate	PAC=8ml/l AlCl ₃ =5ml/l CuSO ₄ =5ml/l	PAC=pH5 AlCl ₃ =pH4 CuSO ₄ =pH6	18	flash-mixed	COD and color	PAC= COD to 84 % and 92 % AlCl ₃ = 74 % COD and 86 % colour CuSO ₄ = 76 % COD reduction and 78 %	Kumar et al., 2011
6	Textile Industry	PAC	25mg/l	7	nm	100	COD, TDS and turbidity	90.17, 74.09 and 93.47%	Sabur et al., 2012

7	Distillery (cane molasses based DWW, BDE, and the anaerobic lagoon effluent (LE).)	FeCl ₃ , AlCl ₃ and polyferric-hydroxysulfate	40mg/l	6	nm	150	Color, TOC	Polyferric-hydroxysulphate 32, 87, 94 % color reductions and 21 %, 73 %, 73 % TOC (total organic carbon) reductions	Migo et al., 1993
8	Distillery waste water	alum and iron salts	10 g/l	nm	nm	nm	COD and Color	82.5% COD removal and 67.6% reduction in color	Inanc et al., 1999
9	Distillery Industries	FeCl ₃ , AlCl ₃ and PAC	60 mM/l AlCl ₃ , 60 mM/l FeCl ₃ and 30 ml/l of polyaluminium chloride	pH 3 as the optimum for FeCl ₃ and pH 5.5 as the optimum pH for both AlCl ₃ and PAC	20	flash mixed	COD and Color	55, 60 and 72% COD reductions and about 83, 86 and 92% colour reductions	Chaudhari et al., 2007
10	Molasses Waste water	Ferric Chloride	3.5g/l	pH=8	Nm	150	COD and Color	86% of COD and 96% of color	Liang et al., 2009
11	Pharmacy	FeSO ₄ , FeCl ₃ , and alum	FeSO ₄ (500 mg/L), FeCl ₃ , (500 mg/L), and alum (250 mg/L).	pH9	Nm	nm	COD, SS	24-28% and 70%,	Gupta and Gupta, 2006
12	Oil waste water	Zetag 32 + 0.1 g/l Bentonite, Zetag 32+ 5 mg/l ferric sulfate	bentonite dosage of 2 g/l of oily wastewater in the presence of 4 mg/l Zetag32.	pH 8.2	25	nm	COD and SS	COD=99.96%, SS=99.34%	Abdela, 2004
13	Mining waste water	Zetag 32 + 0.1 g/l Bentonite, Zetag 32+ 5 mg/l ferric sulfate	5g/l ferric and 1g/l benonite	7.7	25		COD and SS	COD= 76% SS=99.7%	Abdela, 2004
14	Grease waste water	Aluminum sulfate ferric chloride and ferrous sulfate,	2.0mg/l	pH 9.5	25	250	Total Solid	Aluminium sulphate =90% Ferric chloride=88% Ferrous sulphate=28%	Ghaly et al., 2006
15	Synthetic Wastewater	Ferric Chloride	150mg/l	3	nm	100	dye removal	96.3% dye removal at	Moghaddam et al., 2010
16	Personal care waste water	Ferric chloride (FeCl ₃ ·6H ₂ O), alum (Al ₂ (SO ₄) ₃ ·18H ₂ O) and ferrous sulfate (FeSO ₄ ·6H ₂ O)	800 mg/l ferric chloride, 1000mg/l, 100mg/l	pH=8.23, alum 6.9, 9.1	nm	267	COD	ferric chloride, ferrous sulfate and alum was 75.8±9.7, 77.5±9.6 and 76.7±9.9%, respectively.	El-Gohary et al., 2009
17	Aqueous Solution	aluminium sulfate, turmeric extract	18,367 mg L ⁻¹ , 82 mg L ⁻¹	pH=7	nm	80	Boron	Boron removed 95%	Halim et al., 2012
18	Dye waste water	Polyferric chlorides (PFCs)	30mg/l	nm	nm	100	COD	55% reduction	Yu-li, et al., 2006
19	Leachate	Poly Aluminum Chloride, alum, ferrous sulfate	PACl=2500mg/l Alum=100mg/l FeSO ₄ =1500mg/l	For all coagulant pH=12	20	150	COD	COD removal, 60%, 62.33% and 70.66%, Suspended matter 39.14% , 58.37% and 35.58%, respectively	Samadi et al., 2010
20	Tar contains waste water	Alum+ Lime and Alum+ Lime + Activated carbon.	lime and alum was found to be 0.8 g/L and combination 0.8-0.8g/l	pH=6.5	nm	140	color	lime=92 Alum=91.4 lime+alum=86.21	Mehta and Chavan, , 2009
21	Vegetable tannery waste water	PACl (Poly aluminum chloride)	60mg/l	4	40	150	TSS, COD and color	45, 20 and 80%.	Smita et al., 2012
22	Dairy waste water	ferrous sulfate and alum	200mg/l, 100mg/l	4.5(alum)	Room temp.	120	COD, TDS, Turbidity	75, 99%, 70%	Kokila et al., 2011
23	Intensive Aquaculture Systems	alum/polymer	50mg/l, 5mg/l	7.4	19.4		TSS, Phosphorous ,nitrogen, Total ammonium	99%, 98%, 64, 50, 68, and 87%, 96.4%.	Rishel and Ebeling, 2006

							nitrogen, nitrate-nitrogen, COD		
24	Municipal waste water	alum and ferric chloride)	5mg/l, 7.5mg/l	alum=pH6.5 FeCl ₃ =pH7.2	nm	80	COD, phosphours	50%. 90%	Tassoula et al., 2007
25	Plam oil effluent	Chitosan, alum and PAC	0.5 g/l, 8.0 and 6.0 g/l	pH 4, for alum and PAC 4.5	nm	120	Oil removal	99%	Ahmad et al., 2006
26	Food industry waste water	Ferrous sulphate	450mg/l	Dairy=pH7.69 Meat=pH7.08 Fish=pH 7.34	nm	400	COD	Dairy ind.=77.3 Meat ind.=84.6 Fish ind.=48.8	Konieczny et al., 2005
27	Tannery leather waste water	PACF/Ca(OH) ₂	900mg/l	pH=8.5	15-20	100	COD, TSS	76% COD and 98% TSS	Lofrano et al., 2006
28	Vegetable oil industry waste water	Alum, Ferric chloride	Alum=1.8g/l FeCl ₃ =0.8g/l	pH=6.2 pH=7.05	nm	100	COD, oil grease	92.11% and 92.99% by alum and 96.25, 96.16 by FeCl ₃	Saatci et al., 2001
29	Petroleum waste water	PACl, FeCl ₃	10mg/l	pH=7.5	nm	150	Color, COD	PAC= 885 Color and 72% COD, FeCl ₃ =79 color and 67% COD	Farajnezhad, and Gharbani, 2012
30	Pesticides waste water	FeSO ₄ and Al ₂ SO ₄ with H ₂ O ₂	2mg+20ml	pH=5.5	nm	120	COD	FeSO ₄ =57.77%	[Upadhyay and Mistry, 2012

Conclusion: Coagulation has impactive impression on treatment of water and waste-water treatment, especially for non-settleable solids and colour, from the water being treated. Coagulation used ahead of gravity settling may be expected to yield suspended solids removals of about 90% as compared to about 35% without coagulation. Especially alum is one of the common and cheapest coagulants used to the treatment purpose. Some different polymeric coagulants are also being used for industrial application. However, further research and development activities are required in order to limit the technical, economic, social and environmental impacts. Other alternative coagulants, like lanthanide salts and natural organic coagulants need to be evaluated at the industrial scale and commercialized in order to guarantee a large range of coagulants available in the treatment of all waters and waste water in all conditions.

The ultimate goal of wastewater management is the protection against the environment in a manner commensurate with public health and socio-economic concerns. Based on the nature of wastewater it is decided which type of coagulant will be used before final disposal. Understanding the nature of wastewater is fundamental to design suitable wastewater treatment process, to adopt an suitable procedure, determination of acceptable criteria for the residues, determination of a degree of evaluation required to validate the procedure and decision on the residues to be tested based on toxicity. So it is necessary to ensure the safety, efficacy, quality of the treated wastewater.

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