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COMPARATIVE STUDY BETWEEN FLOCCULATION - COAGULATION PROCESSESIN RAW/WASTEWATER TREATMENT

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Abstract

In this study is present the advantages and disadvantages of the use of different type of coagulants and flocculants for industrial wastewater treatment. This paper details how to survey and select appropriate reagents permit resolve of many problems appear in wastewater treatment. It is designed to be used as a study to learn about the operation of flocculation-coagulation process. The industrial wastewater can be regards as black box where mechanical operational-chemical operation are interconnected. Troubleshooting problems in primary system have direct influence over secondary systems (heavy metal removal, emulsion breaking, sludge thickening, dewatering etc.). To reduce the harmful effects that wastewater can produce, some form of treatment is necessary environmentally friendly, with minimize energy consumption. The relationship between water and energy and necessity for better managing energy consumption continues to have a great attention in raw water and wastewater treatment plants. The use of electricity and different reagents for water and wastewater treatment, impose unitary analysis. Appling unitary practice, function of the kind of wastewater treatment plant, will be possible to adopt the best solution considering all processes that concur to obtain a clean water. The aim of this study was analysis of characteristics of flocculants and coagulants, that can be used in wastewater treatment, for establish the application conditions.

Key words*: coagulation, flocculation, advantaged, requirement.*

INTRODUCTION

The treatment raw and wastewater have a crucial importance in industrial plants and environmental protection (Buema et al., 2013; Harja et al., 2007, 2011 and 2017; Kotova et al., 2017; Rusu et al., 2014, 2017). The first stage in the strategy of chemicals selection for purification and solids-liquid separation is a complete Mechanical-Operational-Chemical (MOC) system investigation to increase understanding of the possible restrictions on chemicals that cannot be used, as well as understanding the mechanical treatment system and equipment i.e. mixing energy, separation equipment (Aziz et al., 2007; Harja and Szep, 2013). Understanding chemicals selection for natural or wastewater purification can appear to be complicated as there are many commercially coagulants and flocculants, and researchers develop new other types (Amuda et al., 2006; Li et al., 2016; Momeni et al., 2018, 2017a and 2017b). Finally, the only way tochoose the best product to fit the application is to test the different chemicals toreach the desired result at the best cost/performance ratio (Ganjidoust et al., 1997). To help narrow down the time and products to test it is best to understand the requirements of the application, properties of various compounds, how they can be used in various applications, and the advantages and disadvantages of its usage. Some of the major differences between coagulants chemical families include: sludge generation, alkalinity consumption and efficiency function of water temperature.

Sustaining reliable treatment performance for natural or wastewater treatment is critical for minimizing impact to other plant operations, the environment, or operating cost. Final water quality can be caused by the mechanical condition of the equipment, variability of operational applies, or the type and content of the contaminants in the source water. Small process fluctuations are normal and expected; however, too much variability can result in treatment failure. The goal is to minimize the variability of results even though the conditions may not be optimum. Examples of sources of variability in natural water treatment are presented in Figure 1.

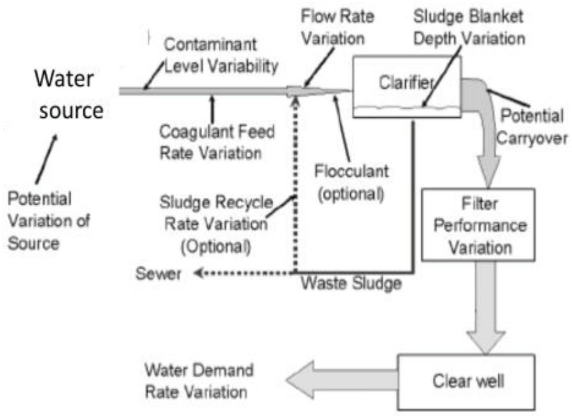

Figure 1. Variability in raw water treatment plants with effect over water quality

Wastewater treatment plants have larger parameter variability, function of type of sources waters and the complexity of the treatment processes. Treatment efficiency wastewater will be different between treatment plants, between unit processes, and for different contaminants (Marzougui et al., 2017), factors that determines removal efficiency.

The inefficient operation can be determined by:

- The suspended solids in large quantities, that increase the solids loading on filters;
- The improvement hardness reduction can determined the lime achieved, ion exchange run length and cooling tower cycles of concentration can increase;
- The aluminium used inpurification is fouling heat exchangers;
- Silica in greater concentrations in the boiler.

While the primary goal of a wastewater treatment plant is production of desired quality water at the lowest cost, the final goal is to help minimize the overall operating cost of the skill (Ebeling et al., 2003; Natarajan et al., 2018). In general this canbe accomplished in several ways:

- Decrease operating costs;
- Increase quality of water output;
- Minimize environmental, health, and safety issues;
- Efficiency improvement of treatment processes;
- Minimize impact of contaminant or process variability.

It is easy to identify the cost of the reagents used to treat wastewater. However, this is only a part of the cost of operation that should be considered. The different plants have different direct reagents costs, but it is possible to produced different quality water, or sludge characteristics, which lead to indirect savings. For an industrial plant, changes in water quality can have major impact on other costs.

Coagulants can be used in many different purification applications and are the following basic chemistry families: Organic; Inorganic; Blends - Inorganic/organic. Basic flocculants include cationic, anionic andnon-ionic charge.

MATERIALS AND METHODS

The wastewater was characterized by different physic-chemical parameters: °C, pH, conductivity, suspended matter, etc. The pH, temperature and electrical conductivity was measured by a Multi-parameter SHOTT ProLab2000 is used for pH, temperature and conductivity measurements, while the turbidity was measured by a HACH 21009 turbidimeter. The solid mater materials were determined by filtering on a filter. The flocculation-coagulation tests were carried out according to the Jar-Test protocol, with VELP FP4/ Analogic. The different type of flocculant and coagulant were used for comparison studies.

RESULTS AND DISCUSSIONS

The coagulation is the process of addition of reagents to destabilization of colloidal particles by charge neutralization to allow the particles to agglomerate and separate from liquid media. Coagulants are thus, smaller molecules with the sole purpose of neutralizing surface charge on the particles dispersed in the water.

The flocculation determines promotes agglomeration and helps the particles to settle down. Into a lot of application these processes are combined.

Inorganic coagulants

Inorganic coagulants used in clarification are mostly based on trivalent metal salts. The high valence neutralizes surface charge on particles allowing them to come together and form larger particles (Benradi et al., 2016; Rana and Suresh, 2017; Tetteh et al., 2017). The most commonly used metal saltsare aluminium and iron based (Table 1).

Table 1. Comparison of various inorganic coagulants

Al	Widely used for colour and turbidity reduction Optimum pH: 5.5-6.5 Requires added alkalinity to produce $Al(OH)_3$ Large volume of difficult to dewater sludge Liquid corrosive
PACl	Higher coagulant charge per weight Consumption of alkalinity is lower Lower volume of sludge produced Savings in dewatering and disposal Higher cost of product than Al Partial Al replacement
Ferric Sulfate Iron	Used for highly turbidity waters Forms denser, faster settling floc Effective over a wider pH range - 4.0-11.0 Remove colour at higher pH levels

Both of these chemicals must react with alkalinity to form insoluble precipitates of $Al(OH)_3$ or $Fe(OH)_3$.

Aluminium based inorganic coagulants include:

- Aluminium sulfate or aluminium $(Al_2SO4)_3$
- Polyaluminium chloride (PACl)
- Sodium aluminate ($NaAlO_2$)
- Polyaluminium silica sulfate/chloride (PASS, PASS-C)
- Aluminum chlorohydrate (ACH)
- Basic aluminium polychloride (PCBA)

Aluminium chemistry is very complex and it can be polymerized to form polyaluminium chloride (PACl). PACl can be formed in a variety of ways, but there are two basic methods of manufacture. One starts with $AlCl_3$ solution and adds a base such as caustic or lime to partially neutralize $AlCl_3$. Total neutralization will form $Al(OH)_3$, but partial neutralization will form polymeric aluminium compounds, or PACl. The second method starts with $Al(OH)_3$ or aluminium trihydrate and adds acid to form a partially neutralized aluminium compound. The methods produce different aluminium species, which will affect the overall coagulation properties. Hence, two products with identical specifications can behave very differently in an application (Jaoudiand Amdouni, 2013).

The introduction of aluminium sulphate into water the hydrolysis reaction takes place, in the 6.5-7.5 pH range (minimum solubility), the aluminium hydroxide $Al(OH)_3$ is formed, able to retain the suspended particles of wastewater. Studies on aluminium sulphate coagulation have shown the existence of several ionic species that are formed upon the dissolution and hydrolysis of aluminium salts. The formation of these hydroxo-metal ion species depends on the pH of the medium. In figure 2 shows the distribution of ionic species depending on pH and precipitation range of $Al(OH)_3$.

Aluminium hydroxide formation starts at pH = 4.5 and at pH > 8.5 the aluminium hydroxide is dissolved to form alumina. $Al(OH)_3$ exhibit amphoteric properties, depending on the pH of the medium. In the case of aluminium salts, the coagulation process is sensitively influenced by pH and temperature. Thus, in periods of low temperatures, the coagulation - flocculation process is difficult, forming small, hard sedimentary flocs (Wang et al., 2017).

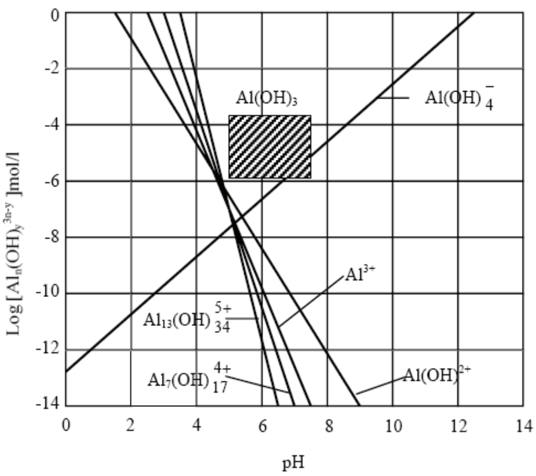

Figure 2. The equilibrium composition of the solution in contact with $Al(OH)_3$ precipitate

Aluminum sulfate added as a coagulation agent also ensures removal of phosphorus from water by precipitation, according to the reaction (An et al., 2017):

$Al_2(SO_4)_3 + 2PO_4^{3-} = 2AlPO_4 + 3SO_4^{2-}$ (1)

Counter ions such as sulphates, phosphates and silicates, can enhance PACl performance in certain waters. Sulphated PACl products generally perform better in cold water where aluminium reacts more slowly with alkalinity to form $Al(OH)_3$. It should be noted that the PACls product chemistry will change once diluted with water, but the process is generally slow. Thus, for testing purposes, a diluted PACl product can be used without excessive activity loss for about 2 to 4 hours. Polyaluminium silicate sulphate (PASS) chemistry reacts with alkalinity faster than PACl and thus, dilution with water quickly destroys coagulation power (Zhang et al., 2017).

Iron based coagulants include: ferric sulphate; ferric chloride and ferrous sulphate.

The iron salts are used for the purification of wastewater, the precipitation range of $Fe(OH)_3$ is more extensive than with $Al(OH)_3$, beginning at pH = 3 (Jiang and Wang, 2009). Figure 3 shows the distribution of ionic species according to pH solution.

Optimal coagulation with ferrous sulphate takes place in the alkaline medium with the addition of lime, in the first stage is ferrous hydroxide, which is unstable and in the presence of O_2 from the water is converted into ferric hydroxide. Mixed with aluminium salts in 1/1 ratio, results large and easy sedimentary flocs.

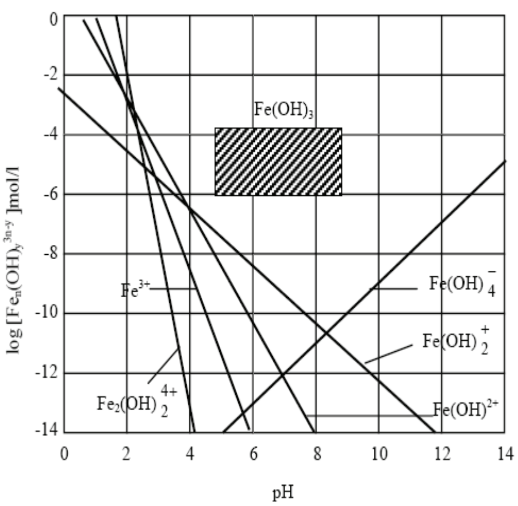

Figure 3. The equilibrium composition of the solution in contact with $Fe(OH)_3$ precipitate

Iron coagulants form a heavy floc and are commonly used for their lower cost. Iron reacts with alkalinity to form $Fe(OH)_3$ providing the coagulation and precipitation action.

Organic coagulants

The most common organic coagulant chemistries are polyDADMAC and epi-DMA (Table 2). These product chemistries have been known for many years and have been used as primary coagulants in a variety of applications. Their use has expanded over the years because of their fast reaction in cold water and their low impact on water pH. The polyDADMAC chemistry is considered resistant to chlorine andcan be used in pre-chlorinated water without loss of performance. In generally, different coagulants if applied correctly will work in chlorinated medium.

Dilution of concentrated chlorine to 1-2 ppm greatly slows the degradation impact on polymer. With proper dilution of chlorine, and thefact that the coagulation rate is much faster than the degradation rate, little impact on performance should be observed.

Table 2. Organic coagulants

Coagulant	Product information
PolyDADMAC	Various molecular weights: very high, medium and lower
Epi-DMA	Cross-linked; Linear
Others	Melamine-formaldehyde

Inorganic/Organic blends

Coagulant blends have several advantages over single coagulants. The blended coagulants have lower cost products (contain less expensive inorganic compounds) and this supplements the more expensive organic materials. The blended coagulants have superior performance compared with singular coagulant, due to of potential synergy between the inorganic and organic components to form a faster settling floc and produce cleaner water. On the other hand the speed of coagulation is improved. The blended coagulants doearnthe cost for blending, but this is compensated by performance enhancement.

The product selection is difficult and random, because there are numerous coagulants. Experience and seat testing becomes very important to product selection. The advantages and disadvantages for various coagulants are presented in Table 3.

Flocculants

Flocculants are organic based polymers supplied in liquid (emulsion, dispersion) and dry form. They are typically very high molecular weight forming high viscosity solutions. Flocculants are generally non-ionic, anionic or cationic charge. The amount of charge and the molecular weight can be different for different products. Is recommended does not blend coagulants and flocculant products together. The reason is one of what products to blend, what ratio and what is the performance advantage? Since the possibilities for such blended products becomes so complex and the flexibility of adjusting coagulant and flocculant dosages at the necessity.

Table 3. Comparison of coagulant families

Type	Advantages	Disadvantages
Inorganic	Low cost per pound Cost effective in certain applications Sweep floc mechanism	Dependent of pH and T; Alters pH; Sludge; Corrosive
Organic	For cold waters; React faster; Less corrosive; Cationic charge; Higher charge; Short chain polymers; Produce less sludge; Resistant to chlorine	Higher cost Easier to over dose
Blends	Reduces total solids Efficiently for purification Not pH adjustment Minimizes settled sludge volume; Easy to feed, easy to handle, easy to store	

A summary of typical properties are presented in Table 4.

Table 4. Flocculant/polymer product offering

Type	Information
Emulsion	Highmolecular weight; Charge range: Low to high 30-42% actives Typically fed at 0.05-0.5% solution to the application point
Dry	Requires activation, 0.25% Dust problems Fedat 0.1-0.25% solution
Dispersion polymers	15-25% actives No oil solvent Salt solution with dispersed polymer

Dosages for the coagulants and flocculants can vary greatly, and depend mostly on solids loading and surface charge demand. Dosages for raw water treatment can be relatively low, where as the dosages for treating wastewater can be very high. Typical ranges are presented in Table 5, and are directly related to the type of solids and solids loading in the system.

In raw water or wastewater purification, feeding too much product results in what is called over- dosing. An over dosage of polymer can cause the solids to take on a net positive charge, and actually re-disperse in the water. When bench testing, one needs to evaluate a variety of dosages ranging from low to high. If the dosage is too high, one may see a phenomenon called a false minimum. This false minimum is the second performance indicator (i.e., turbidity) minimum in the dosage curve (Figure 4).

Table 5. Typical coagulant and flocculants dosages

Type	Raw water	Wastewater
Inorganic coagulants	0.55-20 mg/L	25–5000 mg/L
Organic coagulants	0.1-10 mg/L	10–5000 mg/L
Clays	1.0-20 mg/L	15–4500 mg/L
Flocculants	0.1-1.0 mg/L	2.0–100 mg/L

Over dosing a coagulant can give the impression that the coagulant is being underfed, since the normal turbidity or suspended solids reduction performance is not being achieved. The natural response is to increase the dosage, but this would be an incorrect direction to take. Without performing jar tests or reducing coagulant dosage, it will not be clear if the coagulant is actually being overfed.

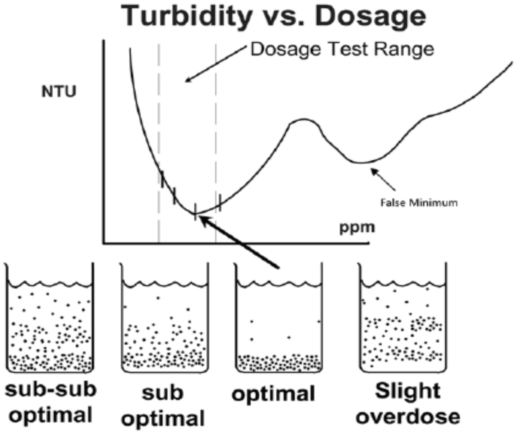

Figure 4. Coagulant dosage curve

The water pH has a main role in choosing treatment plants (Zhan et al., 2013). The impact of pH on performance includes: coagulant demand; sludge production; alkalinity consumption; coagulant solubility. Increasing pH will generally increase coagulant demand and thus dosages will be higher. Establishing the optimum pH should be investigated and pH correction implemented, for significant performance and cost savings (Figure 5). Using coagulants at a higher pH will generate sludge due to an increase in coagulant demand/dosage. Inorganic coagulants can undergo hydrolysis as part of their reaction and this consumes alkalinity, which will lower the pH. Post treatment pH correction may be required, this operation increase the cost of the treatment plant. Residual soluble aluminium from aluminium- based coagulants will increase if the pH is outside the 5.5-6.5 pH range.

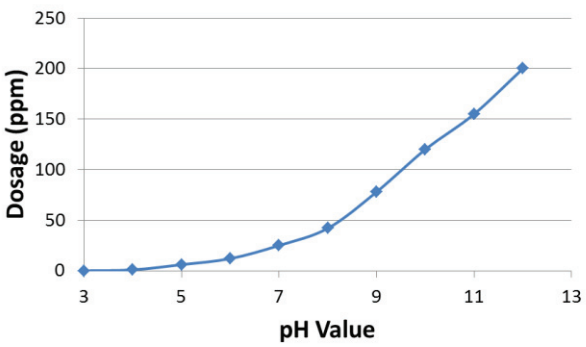

Figure 5. Effect of pH on coagulant demand

An effective flocculant is not a priority known, for each type of water the general flocculant applications are presented in Table 6.

Table 6. Flocculant/polymer applications

Application	Typical Coagulant/Flocculant selection
Raw water clarification aid	Cationic coagulant/anionic flocculant
Primary treatment	Cationic flocculant Cationic coagulant/anionic flocculant
Emulsion breaking	Cationic coagulant/anionic flocculant; High charge cationic flocculant
Metals removal	Cationic coagulant/anionic flocculant
Secondary treatment	Cationic flocculant
Solids Thickening/Dewatering	Cationic coagulant/cationic flocculant

Selecting the appropriate productwill require a little bench testing.

CONCLUSIONS

Maintaining reliable treatment performance for raw water or wastewater treatment is important for minimizing impact to other plant operations, the environment, or operating cost. Wastewater treatment is dynamic processes with variable treatment efficiency, caused by the equipment types, operational practices, contaminants as type and quantities in the inlet water.

The aimof this study was analysis of characteristics of flocculants and coagulants, that can be used in wastewater treatment, for establish the application conditions. Study of the major differences between coagulants and flocculants include, sludge generation, alkalinity consumption and effectiveness in cold water, aspects that was discussed in this paper. The first stage in the strategy of chemicals selection, for purification and solidsseparation is a Mechanical-Operational-Chemical system investigation to understanding the possible restrictions on chemicals that cannot be used. Understanding chemicals selection for natural or wastewater purification can appear to be complicated because there are many commercially coagulants and flocculants. The only way to choose the best product to fit the application is to test the different compounds to reach the desired result at the best cost/performance ratio. To saving the time and energy, it is the recommended to understand the requirements of the application, properties of reagents usable in the various applications, and its advantages and disadvantages.

The water quality is caused by the mechanical condition of the equipment, variability of operational applies, or the type and content of the contaminants in the source water.

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