CHAPTER 3

PRECIPITATION, COAGULATION AND FLOCCULATION

DEFINITION

Suspended matter can be removed by settling, but colloidal or soluble impurities are too small for gravitational settling. The aggregation of these particles into large more regular particles which will settle is necessary for successful separation by sedimentation.

Soluble ions can be precipitated by forming an insoluble salt, e.g. soluble phosphate ions can be precipitated by adding aluminium ions because insoluble aluminium phosphate is formed:

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \qquad (3.1)$$

Colloidal particles often possess an electrical charge, which creates a repelling force and prevents aggregation. Stabilizing ions are adsorbed to an inner fixed layer, which gives its particles its electrical charge, the latter varying with the valence and number of adsorbed ions. Ions of an opposite charge are held near the surface by electrostatic forces. The psi potential is defined as the gradient between the interface of the colloidal particles and the solution, while the zeta potential is defined as the gradient between the slipping plane and the solution. The zeta potential is related to the particle charge and to the thickness of the double layer. It is not possible to measure the psi potential, but the zeta potential can be determined and expressed.

The zeta potential can be used as an expression for the stability. It is possible to measure it on the basis of the following equation:

$$\text{zeta potential} = \frac{4\pi\mu}{X \cdot E} U \qquad (3.2)$$

where

E = the dielectric constant of the medium,

μ = the viscosity of the medium,

X = the thickness of the double layer,

U = the electrophoretic mobility.

The zeta potential is determined by measuring the mobility of the colloidal particles across the electrophoresis cell, viewed through a microscope. Several types of zeta meters are commercially available.

La Mer (1964) distinguishes between two types of particle destabilization: coagulation and flocculation.

According to La Mer, coagulation results from compression of the electric double layer surrounding the colloids, while flocculation refers to a destabilization by adsorption of large organic polymers with a subsequent formation of bridges between particles and polymers. These definitions of the two terms - coagulation and flocculation - are not universally accepted, but they can have a practical significance.

Fig. 3.1 is a schematic presentation of destabilization by flocculation.

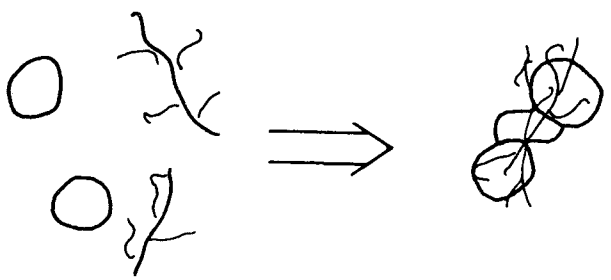


Fig. 3.1. Destabilization by flocculation.

Destabilization by metal ions

Metal ions can be used to destabilize the colloidal particles found in waste water. In particular Al^{3+} and Fe^{3+} are used for this purpose. The coagulation effect is highly dependent on the valency of the metal ions. Table 3.1 shows an identical coagulation effect by different salts for a colloidal solution of As_2S_3.

TABLE 3.1

Coagulation effect, identical

Salt	Mol. concentration
KCl	$50 \cdot 10^{-3}$
$CaCl_2$	$0.65 \cdot 10^{-3}$
$AlCl_3$	$0.095 \cdot 10^{-3}$

To understand the ability of metal ions to destabilize the colloidal particles it is necessary to consider aquatic chemistry as presented by Stumm (1967) and Stumm and Morgan (1970).

Fe^{3+}, Al^{3+}, Ca^{2+} and H^+ do not exist in natural waters. The nomenclature for these cations is chemical shorthand. The actual species present in water are aquo-complexes such as $Fe(H_2O)_6^{3+}$, $Al(H_2O)_6^{3+}$, $Ca(H_2O)_6^{3+}$, $H(H_2O)^+$ and even $H(H_2O)_4^+$.

By adding Fe^{3+} and Al^{3+} salts to water in a concentration less than the solubility of their metal hydroxides, soluble monomeric, dimeric and perhaps even polymeric hydroxo-metal complexes are formed:

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+ \quad (3.3)$$

$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \quad (3.4)$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \quad (3.5)$$

$$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+ \quad (3.6)$$

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+ \quad (3.7)$$

When the quantity added is sufficient to exceed the solubility of the metal hydroxide, formation of colloidal hydroxo-metal polymers or metal hydroxide precipitation (Stumm and Morgan, 1962) takes place. The hydroxo-metal complexes are adsorbed at the interfaces (Matijevic et al., 1961; Stumm and O'Melia, 1968), while aquo-metal ions are not adsorbed. This adsorption neutralizes the electrical charge of the colloidal particles and the colloids are consequently destabilized. The amount of metal ion coagulants necessary to bring about the destabilization depends on the amount of colloids, pH and the presence of other ions in solution; for instance, the coagulation process is highly dependent on the alkalinity (Stumm and O'Melia, 1968). Because of the complex reaction involved, it is necessary to carry out laboratory experiments to establish the optimum pH and coagulant dose for coagulation of any given waste water. The most commonly used procedure is the so-called jar-test, where samples of the waste water are treated at different pH values and with different doses of coagulants. The effluent concentration is measured and the efficiency is plotted against the pH and the coagulant dose as shown in Figs. 3.2 and 3.3. Generally a rapid mixing of each sample for 3 minutes is followed by 12 minutes of slow speed flocculation

after addition of coagulant. Based on the results as shown in the figures, the optimum pH and coagulant dose can be selected.

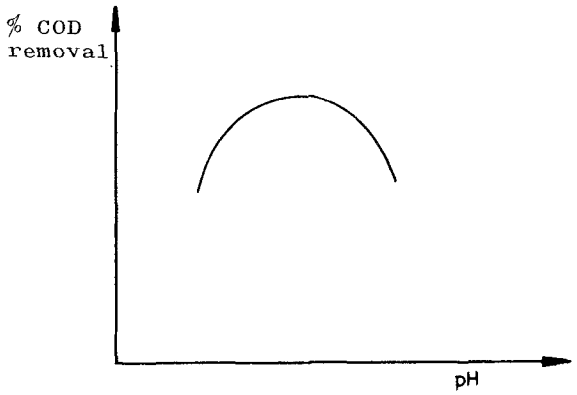


Fig. 3.2. % COD removal plotted to pH by jar-test analysis.

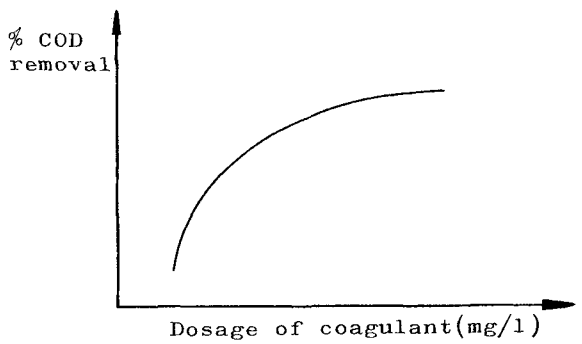


Fig. 3.3. % COD removal plotted to dosage by jar-test analysis.

The application of synthetic organic polymers

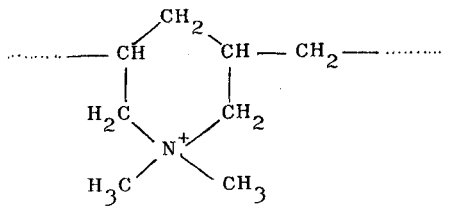
A polymer is a chain of small units called monomers. Many synthetic polymers are used as flocculants. Some polymers contain only one kind of monomer and others two or even three different types of subunit. Polymeric flocculants may be characterized by the number of subunits or their molecular weights. Another characteristic is the linearity of the chains as the polymer may be either linear or branched. Furthermore, the polymer can be either non-ionic or contain ionizable groups.

TABLE 3.2

Synthetic organic polymeric flocculants

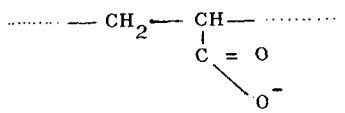
A. Cationic polyelectrolytes

Polydiallyldimethylammonium



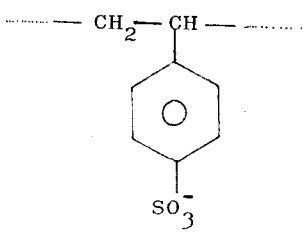
B. Anionic polyelectrolytes

1) Polyacrylic acid



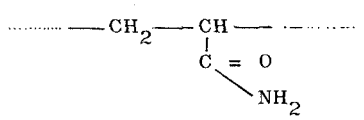
2) Hydrolyzed polyacrylamide: A mixture of subunits B 1 and C 1.

3) Polystyrene sulphonate

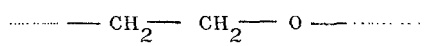


C. Nonionic polymers

1) Polyacrylamide



2) Polyethylene oxide



Depending on the type of ionic groups on the monomeric units, the polymeric flocculant may be termed cationic, anionic or ampholytic.

In Table 3.2 a survey is given of the most commonly used polymeric flocculants. As can be seen, hydrolyzed polyacrylamide is used and it is possible to get polyacrylamide with different degrees of hydrolyzation, which means that the product is partly ionized, partly uncharged.

The concentration of divalent or trivalent cations in the water can exert a great effect on the ability of an anionic polyelectrolyte to aggregate negatively charged colloids (Black et al., 1965; Sommerauer et al., 1968).

Probably the ions compress the diffuse layer surrounding the colloidal particles and thereby reduce the repulsive forces between colloids which prevent the aggregation.

The metal ions can also produce a significant effect in respect to flocculation of negatively charged colloids by cationic polymers. The addition of cationic polyelectrolytes can lead to a charge reversal and subsequent restabilization of negative colloids.

Ortho kinetic flocculation

In many cases agitation is used to accelerate the aggregation of colloidal particles. When particles follow a fluid motion they have different velocities, so that opportunities exist for interparticle contacts. When a contact between particles is caused by fluid motion the process is sometimes called ortho-kinetic flocculation (Overbeek, 1962).

The following equation describes the rate of change in the concentration of particles:

$$\frac{dN}{dt} = \frac{-2\eta \cdot \bar{G} d^3 \cdot N^2}{3} \qquad (3.8)$$

where

η = collision efficiency factor,

$\bar{G}$ = velocity gradient,

N = concentration of particles (number/vol),

d = diameter of particles,

t = time.

$\bar{G}$ can be calculated (Camp et al., 1943) and (Camp, 1955) from

$$\bar{G} = \left(\frac{\bar{P}}{V\mu}\right)^{1/2} \tag{3.9}$$

where

$\bar{P}$ = the power input to the fluid,

V = the volume,

μ = the viscosity of the fluid,

Agitation will not increase the aggregation rate of particles smaller than about 1 μ diameter, whereas particles with a diameter of 1 μ or more will grow as a result of fluid motion. Since 1 μ particles do not settle well, a flocculation tank to allow aggregation must be included in a treatment system which uses sedimentation tanks at a later stage to separate solids from water. Flocculation tanks are designed to provide interparticle contact by orthokinetic flocculation. Design data include selection of velocity gradients, reactor configuration, reactor data and detention time necessary to produce sufficient aggregation. It is difficult to base the design on equations because such parameters as η and $\bar{P}$ are almost impossible to measure, and even the velocity gradient $\bar{G}$ can be difficult to determine. It is therefore necessary to provide information for design based on laboratory and pilot plant experiments. However, the interpretation of such an experiment is only possible using a mathematical description (equation (3.22), see below can be used) of the orthokinetic flocculation.

The design of the flocculation tank can be based on a first order process:

$$R = \frac{\pi d^3}{6} N \tag{3.10}$$

where R = the volume of colloidal particles per unit volume of suspension.

Substitution of equation (3.10) into equation (3.8) gives:

$$\frac{dN}{dt} = -4\frac{\eta}{\pi}\bar{G} \cdot R \cdot N \tag{3.11}$$

- a first order reaction.

Integration of this equation for the boundary conditions $N = N_o$ at $t = 0$ yields:

$$\ln\frac{N}{N_o} = \frac{-4\eta R \cdot \bar{G} \cdot t}{\pi} \tag{3.12}$$

These considerations allow us to apply the equations for a complete mixed flow reactor in combination with an equation for a first order reaction.

A complete mixed flow (CMF) reactor is generally designed on the basis of the following equation - see Fig. 3.4:

$$\frac{VdC_1}{dt} = Q \cdot C_o - QC_1 + V \cdot r(C_1) \tag{3.13}$$

where $r(C_1)$ = the reaction rate.

For steady state condition, provided the reaction is a first order reaction, we have:

$$Q \cdot C_o - QC_1 - k \cdot C_1 \cdot V = 0 \tag{3.14}$$

where k = the reaction coefficient.

Dividing this equation by $Q \cdot C_1$, gives:

$$\frac{C_o}{C_1} - 1 - k \cdot t_m = 0 \tag{3.15}$$

where $t_m = \frac{V}{Q}$, the mean residence time in the complete mixed flow reactor.

The equation can also be written as:

$$\frac{C_1}{C_o} = \frac{1}{1 + k \cdot t_m} \tag{3.16}$$

or

$$t_m = \frac{1}{k}\left(\frac{C_o}{C} - 1\right) \tag{3.17}$$

However, there are advantages in applying a number of reactors in series. Let us consider, m, first order CMF-reactors each with the volume, V. A mass balance identical to the one used for equation (3.16), gives for the second tank:

$$\frac{C_2}{C_1} = \left(\frac{1}{1 + k \cdot t_m}\right) \tag{3.18}$$

where C_2 = the effluent concentration from tank 2.

The effluent concentration from reactor 2 can also be expressed in terms of inflow concentration of the first reactor by multiplying equations (3.16) and (3.18):

$$\frac{C_2}{C_o} = \left(\frac{1}{1 + k \cdot t_m}\right)^2 \tag{3.19}$$

In a similar way, the effluent concentration, C_m, from the last reactor in a series of first order CMF-reactors may be expressed in terms of the concentration of the inflow to the very first reactor:

$$\frac{C_m}{C_o} = \left(\frac{1}{1 + k \cdot t_m}\right)^m \tag{3.20}$$

The total detention time required to achieve a given reaction will therefore be:

$$mt_m = \frac{m}{k}\left(\left(\frac{C_o}{C_m}\right)^{\frac{1}{m}} - 1\right) \tag{3.21}$$

If this consideration is used for the flocculation unit the following equation can be set up:

$$mt_m = \frac{\pi \cdot m}{4\eta \overline{GR}}\left(\left(\frac{N_o}{N_m}\right)^{\frac{1}{m}} - 1\right)) \tag{3.22}$$

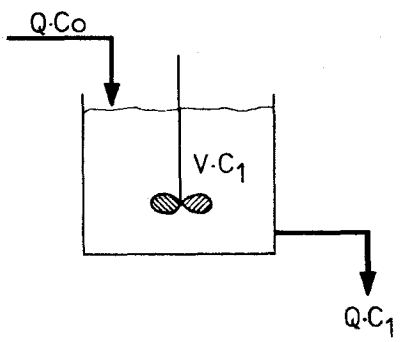


Fig. 3.4. Complete mixed flow reactor. Flowrate Q, volume of tank V, concentration in tank C_1 and the input concentration is C_o.

Example 3.1

Flocculation in a batch system is achieved by stirring at a velocity gradient of 20 sec^{-1} over 30 minutes, by which time the number of particles in suspension is reduced by 99%.

A. Determine $\eta \cdot R$.

B. What detention time is required to produce the same degree of aggregation, if (I) one, (II) three completely mixed continuous flow flocculation tank(s) are used (all tanks have the same volume).

Solution

A. Equation (3.12) is used:

$$\eta R = \frac{\pi}{4\bar{G}T} \ln \frac{N_o}{N} = \frac{3.14 \cdot 2.3 \cdot \log 100}{4 \cdot 30 \cdot 60 \cdot 20}$$

$$\eta R = 10^{-4}$$

B. Equation (3.22) is used:

(I) $$t_m = \frac{\pi}{4 \cdot 10^{-4} \cdot 20} (100 - 1) = 3.89 \cdot 10^4 \text{ sec} = 648 \text{ min.}$$

(II) $$3 \cdot t_m = \frac{\pi}{4 \cdot 10^{-4} \cdot 20} (100^{1/3} - 1)$$

$$t_m = 475 \text{ sec} = 7.9 \text{ min.}$$

Detention time in three tanks: $3 \cdot 7.9 = 23.7$ min.

On the basis of the equation it can be seen that the detention time required for e.g. 99% reduction of the number of colloidal particles is considerably higher than when only 90% reduction is sufficient. Furthermore, it can be seen that there are advantages in using two or more tanks in series. Many flocculation systems used in water treatment consist of three or even more mixed tanks in series.

Industrial waste water treatment by precipitation

Chemical precipitation is widely used to remove phosphate from waste water. The efficiency of the process depends on many variables, but should normally lie between 75 and 95% (Statens Naturvårdsverk, Stockholm, 1963).

Normally, direct precipitation in the treatment of municipal waste water will reduce the $KMnO_4$-number and the BOD_5 by 50-65%, which must be compared with the efficiency (25-40%) obtained by plain settling without the addition of chemicals (Davidsson and Ullmann, 1971).

It is not only phosphate that can be removed by precipitation: many types of industrial waste water can be treated by chemical precipitation with advantage. Table 3.3 gives a survey with references of the use of chemical precipitation for different types of industrial waste water. The process has found wide application, particularly in removing metals from waste water from the metal industry and in reducing the amount of fibre in waste water from the paper industry.

TABLE 3.3

Use of chemical precipitation for treatment of industrial waste water

Type of waste water	Chemical used	Ref.
Metal plating and finishing industry	Lime	Schjødtz-Hansen,1968
Iron industry and Mining	Lime Aluminium sulphate	S.E.Jørgensen,1973
Electrolytical industry	Hydrogen sulphide	S.E.Jørgensen,1973
Coke and tar industry	Lime or sodium hydroxide	S.E.Jørgensen,1973
Cadmium mining	Xanthates	Hasebe & Yamamoto,197(
Manufacturing of glass-and stone wool	Sodium hydroxide	Schjødtz-Hansen & Krogh,1968
Oil refineries	Aluminium sulphate, iron(III) chloride	S.E.Jørgensen,1973
Manufacture of organic chemicals	Aluminium sulphate, iron(III) chloride	S.E.Jørgensen,1973
Photochemicals	Aluminium sulphate	S.E.Jørgensen,1973
Dye industry	Iron(II) salts, aluminium sulphate, lime	S.E.Jørgensen,1973
Fertilizer industry	PO_4^{3-}: Iron(II) salts, aluminium sulphate, lime, NH_4^+: magnesium sulphate + phosphate	S.E.Jørgensen,1973
Plastics industry	Lime	S.E.Jørgensen,1973
Food industry	Ligninsulphonic acid, dodecylbenzensulphonic acid, glucose trisulphate, iron(III) chloride, aluminium sulphate	S.E.Jørgensen,1971
Paper industry	Bentonite, kaolin, starch, polyacrylamide	S.E.Jørgensen,1973
Textile industry	Bentonite, aluminium sulphate	S.E.Jørgensen,1974

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