CHAPTER 6

Removal of Colloidal Solids

The reason that colloidal constituents in industrial waste are so important is obvious. In those constituents, wastes containing only a quarter of total solids in the form of colloids also account for as much as 50% of the total biochemical oxygen demand (BOD). In this chapter, your author examines the characteristics of colloids, their reactions—especially their response to coagulants—and their removal from plant wastes.

Characteristics of Colloids

A colloid may be defined as a particle held in suspension by its extremely small size (1–200 millimicrons), state of hydration, and surface electrical charge. There are two types of colloids: lyophobic and lyophilic. Because of the difference in their characteristics, they react differently to alterations in their environment. Table 6.1 will assist the student in understanding their properties. Colloids are often responsible for a relatively high percentage of the color, turbidity, and BOD of certain industrial wastes. Because it is important to remove colloids from wastewaters before they can get into streams, one must understand their physical and chemical characteristics.

Colloids exhibit "Brownian movement," a bombardment of the particles of the disperse phase by molecules of the dispersion medium. They are essentially "nonsettleable" because of their charge, small size, and low particle weight. They are dialyzable; that is, they can be separated from their crystalloid (low-molecular-weight) counterparts by straining through a semipermeable membrane. The colloids diffuse very slowly compared to soluble ions. Colloidal particles, in general, exhibit very low (if any) osmotic pressure because of their large size relative to the size of soluble ions. They also possess the characteristic of "imbibition" (the taking in of water by gels). In fact, it is by this very process that bacteria spores (often considered colloidal) take up water and germinate. Colloidal gels are very often used as ultrafilters, having pores sufficiently small to retain the dispersed phase of a colloidal system but large enough to allow the dispersion medium and its crystalloid solutes to pass through. For example, Perona et al. (1967) found that the formed membranes may be used to remove up to 90% of the colored material and somewhat less of the chemical oxygen demand (COD) and total dissolved solids of pulp-mill

TABLE 6.1
Types and Characteristics of Colloidal Solids

Characteristic	*Lyophobic (hydrophobic)*	*Lyophylic (hydrophylic)*
Physical state	Suspensoid	Emulsoid
Surface tension	The colloid is very similar to the medium	The colloid is of considerably less surface tension than the medium
Viscosity	The colloid suspension is very similar to the dispersing phase alone	Viscosity of colloid suspension alone is greatly increased
Tyndall effect	Very pronounced (ferric hydroxide is an exception)	Small or entirely absent
Ease of reconstitution	Not easily reconstituted after freezing or drying	Easily reconstituted
Reaction to electrolytes	Coagulated easily by electrolytes	Much less sensitive to the action of electrolytes, so more is required for coagulation
Examples	Metal oxides, sulfides, silver halides, metals, silicon dioxide	Proteins, starches, gums, mucilages, and soaps

sulfite wastes. Colloidal systems show a wide range in viscosity or plasticity. Usually, the lyophobic colloidal suspensions exhibit a viscosity only slightly higher than that of the pure dispersing medium (Figure 6.1), and this concentration increases only very slightly when the concentration of the dispersed material is increased. On the other hand, lyophilic systems may reach very high values of viscosity. With these types of colloids, a parabolic, rather than a linear, relationship exists between viscosity and the concentration of dispersed phase, as shown in Figure 6.1. Woodard and Etzel (1965) have shown that under certain conditions, one may change a lyophilic colloid in an industrial waste to a lyophobic

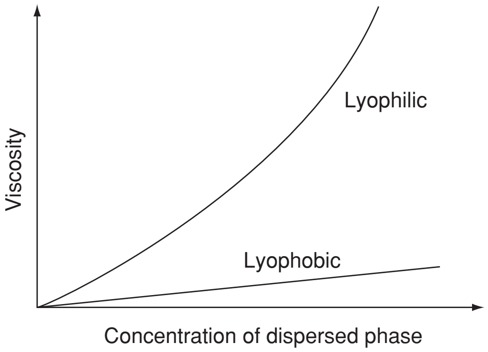


FIGURE 6.1. Effect of colloidal type on viscosity.

one. In this case, lignin was altered by the addition of acetone and sodium hydroxide to render the colloid less stable and to enhance color removal.

Many colloidal systems, especially lyophilic (gel) systems, possess the property of elasticity ("springiness" or resistance). This property enables the gels to resist deformation and thereby recover their original shape and size once they have been deformed. If a concentrated beam of light is passed through a colloidal solution in which the dispersed phase has a different refractive index from that of the dispersion medium, its path is plainly visible as a milky turbidity when viewed perpendicularly. This is known as the *Tyndall effect* (see Table 6.1).

An important property of colloidal particles is that they are generally electrically charged with respect to their surroundings. An electric current passing through a colloidal system causes the positive particles to migrate to the cathode and the negative ones to the anode.

Chemical Coagulation

The removal of oxygen-demanding and turbidity-producing colloidal solids from wastewaters is often called *intermediate treatment,* because colloids are intermediate in size between suspended and dissolved solids. The most common and practical method of removing these solids is by chemical coagulation. This is a process of destabilizing colloids, aggregating them, and binding them for ease of sedimentation. It involves the formation of chemical flocs that absorb, entrap, or otherwise bring together suspended matter, more particularly suspended matter that is so finely divided as to be colloidal.

The chemicals most commonly used are alum, $Al_2(SO_4)_3 \bullet 18H_2O$; copperas, $FeSO_4 \bullet 7H_2O$; ferric sulfate, $Fe_2(SO_4)_3$; ferric chloride, $FeCl_3$; and chlorinated copperas, a mixture of ferric sulfate and chloride. Aluminum sulfate appears to be more effective in coagulating carbonaceous wastes, while iron sulfates are more effective when a considerable quantity of proteins is present in the waste. The use of organic polymers, which can act as either negatively or positively charged ions, has made a significant impact on the efficiency of removal of colloids by chemical coagulation. These polymers, acting as a coagulant aid and applied in conjunction with the coagulant, enhance the formation of flocs and result in improved settling characteristics. Smaller dosages and the elimination of many storage problems are among the major advantages of these polymers. Dey (1965) presents results obtained in various industries where water-soluble polymeric coagulation chemicals are used to achieve improved waste solids settling. Schaffer (1964) found that these polymers were useful in maintaining higher solids concentrations in an anaerobic contact treatment process for meatpacking wastes.

The process of chemical coagulation involves complex equilibria among a number of variables including colloids of dispersed matter, water or another dispersing medium, and coagulating chemicals. Driving forces—such as the electrical phenomenon, surface effects, and viscous shear—cause the interaction of these three variables.

Coagulation by Neutralization of Electrical Charges

This can be accomplished by the following:

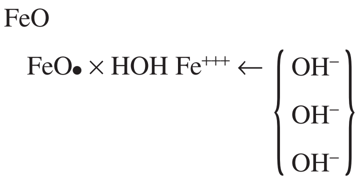
1. Lowering the zeta potential of the colloids (Figure 6.2). “Zeta potential” is the difference in electrical charge existing between the stable colloid and the dispersing medium.
2. Neutralizing the colloidal charge by flooding the medium with an excess of oppositely charged ions, usually hydrous oxide colloids formed by reaction of the coagulant with ions in the water. The coagulant colloids also become destabilized by the reaction with foreign, oppositely charged colloids and produce hydrous oxide, which is a floc-forming material.

From the standpoint of electrical charges, there are two predominant types of colloid in wastewaters:

1. Colloids naturally present, including several proteins, starches, hemicelluloses, polypeptides, and other substances, all possess negative charges (mostly lyophilic in nature).
2. Colloids artificially produced by coagulants, usually the hydroxides of iron and aluminum (mostly lyophobic in nature), are mainly positively charged ions.

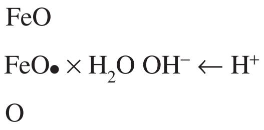
In most scientific circles, it is believed that the charge on colloidal particles is due mainly to the preferential adsorption of ions (H^+ or OH^-) from the dispersing medium. The charge may also be due, in part, to the direct ionization of a portion of its structural groups, such as NH_2^+ and COO^-.

Hydrous aluminum and iron oxides, as well as other metal solids, can acquire both positive and negative charges. Excess Fe^{+++} makes colloids positively charged. The following expression depicts a resultant positively charged colloid:



$$\begin{array}{l} \text{FeO} \\ \quad \text{FeO}\bullet \times \text{HOH Fe}^{+++} \leftarrow \left\{\begin{array}{l}\text{OH}^-\\ \text{OH}^-\\ \text{OH}^-\end{array}\right\} \end{array}$$

Excess OH^- makes colloids negatively charged. The following expression depicts a resultant negatively charged colloid:



$$\begin{array}{l}\text{FeO}\\ \text{FeO}\bullet \times \text{H}_2\text{O OH}^- \leftarrow \text{H}^+ \\ \text{O}\end{array}$$

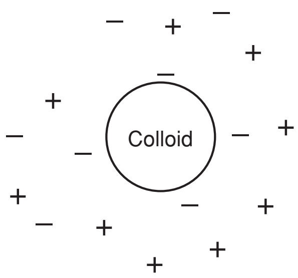


FIGURE 6.2. Stable colloid.

However, a colloid can acquire a charge by means other than adsorption. A protein dissolved in solution can be schematically illustrated as follows:

$$COO^{-}\text{-----------}[\text{protein base molecule}]\text{-----------}NH_2^{+}$$

It may become necessary to add up all the positive NH_2^+ groups and the negative COO^- groups to ascertain the final ionic charge of the solution, because of the inherent charge brought about by direct ionization of the particle. The sol is, thereby, stabilized by inherent ionization of groups within the molecule itself.

Any alteration of the type and number of double-layer ions should reduce the zeta potential to such a point that the colloid will lose its stability. Stability is defined as the ability to resist precipitation and/or coagulation into a relatively large particle. A colloid is most stable when it possesses the greatest electrical charge and smallest size. The coagulating power of ions rises rapidly as the electrical charge increases, as is stated by the Schulze–Hardy Rule. Table 6.2 illustrates the minimum concentration of various chemical coagulants required for anions and cations to complete the reaction. Ratios of concentrations of electrolytes required for valences of 1, 2, or 3 are on the order of 729:11.4:1.

Electrolytes and colloids react readily to changes in the pH of the wastewater. Most negatively charged particles, including the majority of contaminating colloids present in wastewaters, coagulate at an optimum pH value of less than 7.0. Flocculent hydroxide colloids, on the other hand, are insoluble only at pH values above 7.0 and usually more than 9.0. Lime is normally added to raise the pH and to aid in precipitation of colloids.

Alum has a pH range of maximum insolubility between 5 and 7; the ferric ion coagulates only at pH values above 4; and the ferrous ion only above 9.5. Copperas ($FeSO_4 \bullet 7H_2O$) is a useful coagulant only in highly alkaline wastes. Lime, a coagulant in itself, is often added with iron salts to raise the pH to the isoelectric point of the coagulant. At this point, the colloid has its minimum electrical charge and is least stable. Because lime is quite insoluble at pH values of 9 and higher,

TABLE 6.2
Valence and Coagulant Dosage

Electrolyte	*Anion or Cation Valence*	*Minimum Concentration Required, mmol/liter*
	Anion	
KCl	1	103
KBr	1	138
KNO_3	1	138
K_2CrO_3	2	0.325
K_2SO_4	2	0.219
$K_3Fe(Cn)_6$	3	0.096
	Cation	
NaCl	1	51
KNO_3	1	50
K_2SO_4	1	63
$MgSO_4$	2	0.81
$ZnCl_2$	2	0.68
$BaCl_2$	2	0.69
$AlCl_3$	3	0.09

coagulation with lime and copperas together increases the pH range. Aeration of wastewaters before addition of lime enhances coagulation by evolving lime (thus consuming carbon dioxide and supplying oxygen for converting iron to the oxide and hydroxide states).

Because the ferrous ion when oxidized to the ferric ion can also be used as a coagulant at low pH values, oxidation may be carried out by chlorination, as follows:

$$6Fe^{++}\ SO_4 \bullet 7H_2O + 3Cl_2 \leftarrow\rightarrow 6Fe^{+++} + 6SO_4{=} + 6Cl^{-} + 42H_2O$$

Negative ions already present in wastewaters extend the useful range of pH in the acid category and positive ions extend the useful pH range in the basic category. Thus, in soft waters, the negatively charged color colloids coagulate best in the acid pH range, and positively charged iron and aluminum ions are good precipitating chemicals in alkaline waters. Prechlorination of alum-treated wastes sometimes increases color removal. Finely divided clay, activated silica, bentonite, or other coagulant aids are often used for relatively clear waters. The addition of any of these produces an effect similar to that of seeding clouds with silver iodide crystals; they provide nuclei about which the precipitate can gather, agglomerate, and flocculate, with a resultant increase in density and settling rate.

Sometimes the presence of iron and manganese in wastewaters will add to the effect of the cationic coagulants. An increase in the concentration of the coagulant shortens the time of the coagulation reaction considerably. Gentle agitation of the wastewater also enhances coagulation, by increasing the number of collisions and thus causing more rapid floc formation.

Removal of Colloids by Adsorption

A large number of compounds that are not amenable to other types of treatment may be removed from wastes by adsorption. For example, pesticides such as 2, 4-D herbicides and carbamate insecticides may be removed by adsorption onto powdered activated carbon but not onto clay materials such as illite, Kaolinite, and montmorillonite (Schwartz 1967). In addition, colloidal suspensions of DTT, chlorobenzene, and p-chlorobenzenesulfonic acid resulting in DDT production may be removed by using activated carbon (Kul'skii and Shabolina 1967). Cooper and Hager (1966) also suggested activated carbon for advanced waste treatment where reclamation is important. They present three typical activated-carbon treatment systems and a granular-carbon reactivation system (Figure 6.3). The granular carbon used in most reactivation systems in the world is made from bituminous coal. Cooper and Hager (1966) also present a summary of properties for two types of this coal (Table 6.3), and claim that this treatment is especially effective in removing biologically resistant (refractory) compounds.

Examples of industrial wastes that I encountered that contained high amounts of colloids include paint wastes, tomato wastes, textile de-sizing wastes, rag mill pulping wastes, and textile kiering wash waters. Classification of these (and other wastes) is given in the major industrial wastes section following these theory chapters (Chapter 13). More complete discussion of these wastes can be found in Nemerow and Agardy (1998).

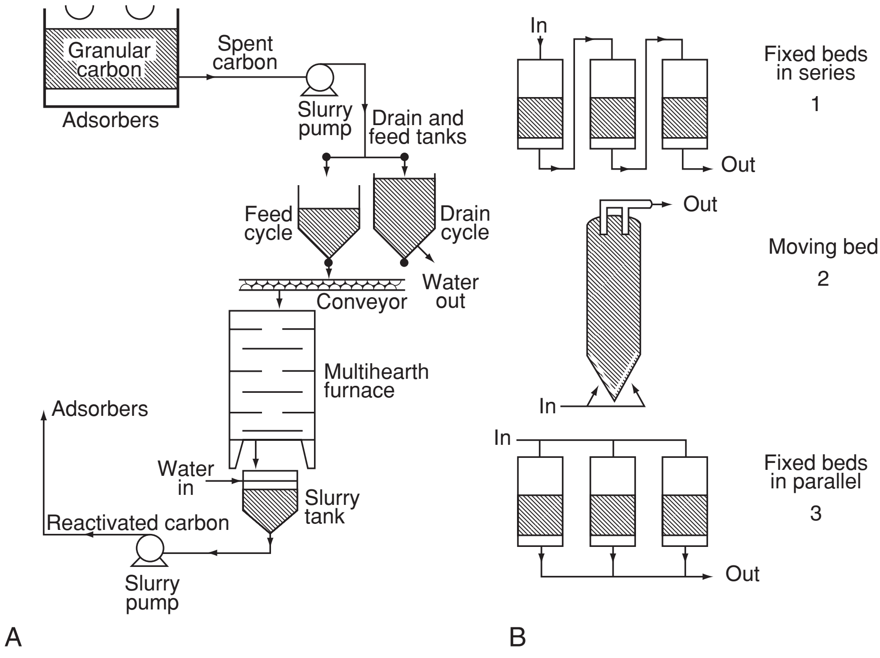


FIGURE 6.3. (**A**) Granula-carbon reactivation cycle. (**B**) Adsorber configuration for granular carbon waste treatment.

TABLE 6.3
Properties of Coal-Derived Granular Carbon for Waste Treatment

Characteristic	*Type SGL*	*Type CAL*
Mesh size, U.S. Sieve Series	8 × 30	12 × 40
Effective size, mm	0.8–0.9	0.50–0.60
Uniformity coefficient	1.9 or less	1.7 or less
Mean particle diameter, mm	1.5	0.9
Real density, g/cm^3	2.1	2.1
Apparent density		
g/cm^3	0.48	0.44
lb/ft^3	30.0	27.5
Particle density wetted with water, g/cm^3	1.4–1.5	1.3–1.4
Total surface area (N_2BET method), m^2/g	950–1, 050	1,000–1, 100
Pore volume, cm^3/g	0.85	0.94

Example of Twentieth-Century Practice of Colloidal Solid Removal

Slapik et al. (1982) reported on the use of foam flotation to remove dissolved material, primarily lead, by adsorption onto colloidal particles followed by removal of the colloid particles and its absorbed material by flotation with a surfactant. They maintain that the values of this method include its simplicity, effectiveness, and moderate costs. That a concentrated and easily handled sludge is obtained is a major advantage over the chemical precipitation method. Hence, the authors have used a novel method—previously described in this chapter—to remove very small and toxic metal particles from wastewaters.

Review Questions

1. What are colloids?
2. Why is it important to remove colloids from wastes?
3. What is the approximate size of colloids?
4. Are colloids all of one type? If of more than one type, what are the differences?
5. What importance should the industrial-waste engineer attribute to changes in density of colloids?
6. In chemical coagulation of colloids, what are the two major economic considerations?
7. What is meant by the “zeta potential” and why is this important to industrial-waste engineers in the chemical coagulation of colloids?
8. For what reasons is lime added to industrial wastes for colloidal solids removal?
9. When would you recommend the use of activated carbon for removing colloidal solids? What is the mechanism involved?

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