Coagulation, Electrocoagulation & Flocculation

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Dear Advice & Counsel,

My company is considering upgrading our wastewater treatment system, which currently treats a wide variety of metals, including some that are complexed, but relatively low in concentration. We periodically have problems with "pinfloc" and wish to pursue a flocculation/coagulation system that is more reliable. I have heard a lot about electrocoagulation as an alternate to the use of chemical additions. What has been your experience with this technology?

Signed,
W. W. Operator

Dear Ms. Operator,

Let's begin with a discussion of coagulation and flocculation:

Coagulation

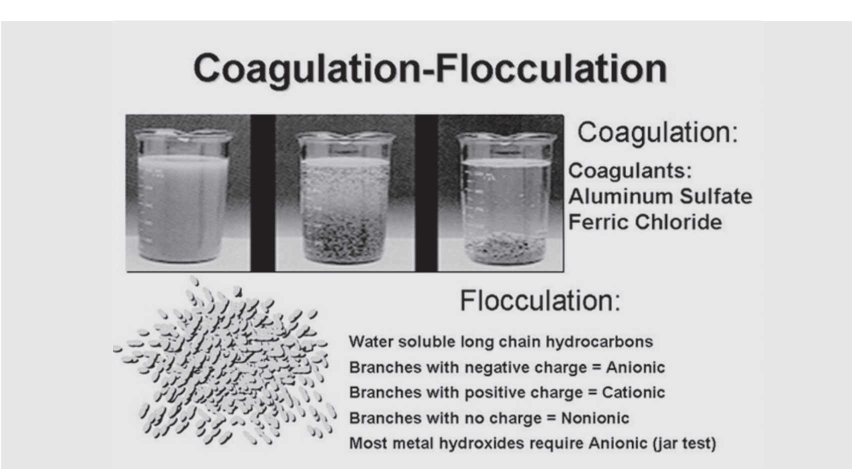
When water-based solutions containing soluble heavy metals are adjusted in pH to a level where the chemistry favors the formation of a metal hydroxide, these metal hydroxides usually form a so-called floc, which can be a voluminous solid particle or a very small particle. In either case, the density of these particles is very close to that of the water matrix. Because metal finishing wastewaters often contain metals such as iron and aluminum that naturally form well settling flocs, coagulation and flocculation of some wastewaters may be very easy.

However, when the waste stream is very dilute, or when the wastewater contains traces of emulsified oils or complexing agents from cleaners or other processing solutions, the flocs produced stay small and tend to repel each other. Such particles have a tendency to float and or take a long time to settle in the clarifier because these small flocculant particles tend to strongly repel each other via electrostatic charges on their surface.

One way to cause these "pinfloc" particles to agglomerate into larger, heavier, denser particles is to add positively charged ionic species to the wastewater to reduce the electrostatic charge on these particles.

The most commonly used coagulants are ferric iron salts such as ferric chloride or sulfate and aluminum salts such as aluminum chloride and aluminum sulfate, which is commonly called "alum." Since iron may be regulated in some locations and aluminum tends to be unregulated, the most common coagulant used in the metal finishing industry is alum. Each of these salts provides the wastewater to be treated with trivalent metal ions, which not only eliminate electrostatic forces, but themselves form large flocculant particles that physically "sweep" the wastewater, as they settle. Ferric iron coagulants can greatly increase the amount of sludge to be handled as a final solids removal step.

Most often such salts as ferrous sulfate, ferric chloride or aluminum sulfate are used in the range of 100 to 300 mg/L as coagulant additions to the waste stream. Coagulants are typically added to the pH adjust system ahead of the flocculation step (assuming one is employed). As the metal hydroxide solids are produced, the anion (sulfate or chloride) becomes free. As a result, the pH of the treated wastewater tends to go down, while the total dissolved solids content goes up. Either the initial pH should be high enough to allow for this depression of the pH, or additional alkali has to be provided.



Flocculation

Flocculation is further agglomeration of insoluble particulates in an aqueous medium, caused by the addition of an organic "flocculant," *a.k.a.*, "polymer" or "polyelectrolyte." These organics are water-soluble long-chain hydrocarbons that have chemical "branches" attached with either a negative (anionic polymer), positive (cationic polymer) or neutral charge (nonionic polymer). The charged flocculant attracts particles with an opposite charge.

Most metal finishing wastewaters form metal hydroxides, which respond well to anionic polymers. However, in some cases, cationic polymers or combinations of either anionic or cationic polymers or non-ionic products have produced better results. Therefore, extensive jar testing is often necessary to determine which polymer is best suited for the variety of wastewater to be treated in any individual case.

Flocculants are added in a special reaction tank equipped with a low speed, low shear agitator (adjustable between 25-100 rpm). The addition rate of polyelectrolyte is typically based upon the manufacturer's recommendation. It is difficult to control properly. Theoretically, the polymer feed rate should be based on the concentration of metal hydroxides produced in the pH adjust system. Since this varies and is nearly impossible to determine, the most common method of adding polymer is by adding a fixed rate, no matter what the concentration of metal hydroxides produced. This often results in floating (when the polymer addition rate is too high) or pinfloc (when the polymer addition rate is too low). A knowledgeable wastewater treatment operator will periodically use jar tests to verify that the addition rate of the polymer is within a workable range.

Factors that affect good flocculation

The higher the metal concentration in the effluent, the larger the floc formation and weight gain by the flocculant particles. This has some practical limitations, however, because very high concentrations of metals create sludge that is difficult to clarify due to the high solids content.

High concentrations of wetting agents, cleaner compounds, silicates and chelates, tend to suspend the flocculant materials and produce milky suspensions that don't clarify well.

Precipitation with calcium hydroxide (lime) in the pH adjust system, either as an alternate to sodium hydroxide or as an additional neutralizing agent along with sodium hydroxide, while creating a larger volume of sludge, will tend to provide a faster settling precipitate.

During neutralization, it is necessary to stir the effluent to provide good mixing and to effect fast chemical reaction between the neutralizing chemicals and the contents of the waste stream. After five minutes, or sometimes less, the flocculant particles will start to appear. Excessive, violent stirring at this point tends to break down the small floc into colloidal material that will be nearly impossible to settle. After neutralization is complete, 5 to 10 minutes should be allowed for flocculation to occur. A typical flocculation chamber has slow agitation to permit the flocculant particles to contact each other and thereby be preconditioned for the next step.

Electrocoagulation

Electrocoagulation (EC) may be an alternative to the use of metal salts as coagulants or polyelectrolytes in some metal precipitation systems. Consider the following advantages and disadvantages:

Advantages:
- Simple to operate
- Solids produced have low water content, are more easily settled or filtered
- Flocs are much larger, contain less bound water and separate from water faster
- Lower TDS, since no chemicals are added
- Effective on colloidal wastewater
- No "chemical" cost, storage or handling

Disadvantages
- Metal anode needs to be replaced regularly
- Cost of electricity needs to be accounted for
- Films produced on the cathode may require frequent cleaning
- May not work well at higher dissolved metal concentrations found in some metal finishing operations
- Gases produced may affect settling in clarifier

EC manufacturers have had success in lowering the concentration of COD, BOD, TOC, TSS, TDS, FOG, MTBEX, heavy metals, organic & inorganic colloids, inks & dyes, chlorinated PCBs, cyanides, suspended particles, chemical and mechanical polishing waste, synthetic detergent effluents and more.

One EC installation (a job shop performing aerospace plating and anodizing) that I have had some experience with, failed to work well on the raw waste, but worked very well reducing the heavy metals in the effluent from the clarifier, after "normal" treatment of the wastewater.

How it works

An electrocoagulation system is made up of an electrolytic cell employing anodes(s) and cathode(s). The electrodes may be made of several metals, including titanium, graphite, platinized titanium and others, but the most common ones are iron (steel) and aluminum. The figure shows a schematic of an EC system using tube-within-a-tube construction. Other designs utilize parallel plates alternating as anodes and cathodes.

When connected to an external DC power source, a number of reactions between the anode and the waste and between the cathode and the waste occur simultaneously:

- ***Flocculation***

The anode corrodes under the potential from the power supply producing dissolved ions that act as coagulants.

- ***De-emulsification***

The oxygen and hydrogen ions produced at the anode and cathode, respectively, react with oil molecules, creating a water insoluble residuals that precipitate from the water. Organic/metallic dye residuals in wastewater from anodizing operations may be broken down into solid residues. The oxidative conditions at the anode may break down traces of cyanide as well.

In a typical EC process, the treated wastewater separates into a floating layer, a sludge and clear water. The three phases are then separated using gravity and or filtration. To avoid flotation in a clarifier, caused by gases generated by the electrodes, de-aeration may be required.

Control of EC systems

Control of the amperage, flow rate and pH of the waste to be coagulated is critical to successful use of this technology, but is typically not difficult to do, once the most effective operating parameters have been identified. Routine inspection and cleaning of the cathodes may be required. Temperature and operating pressure need not be carefully controlled. The EC system works best when the characteristics of the raw wastewater are invariable. *P&SF*