Removal of Chelated Metals

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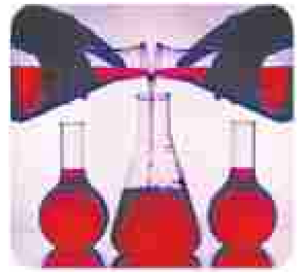
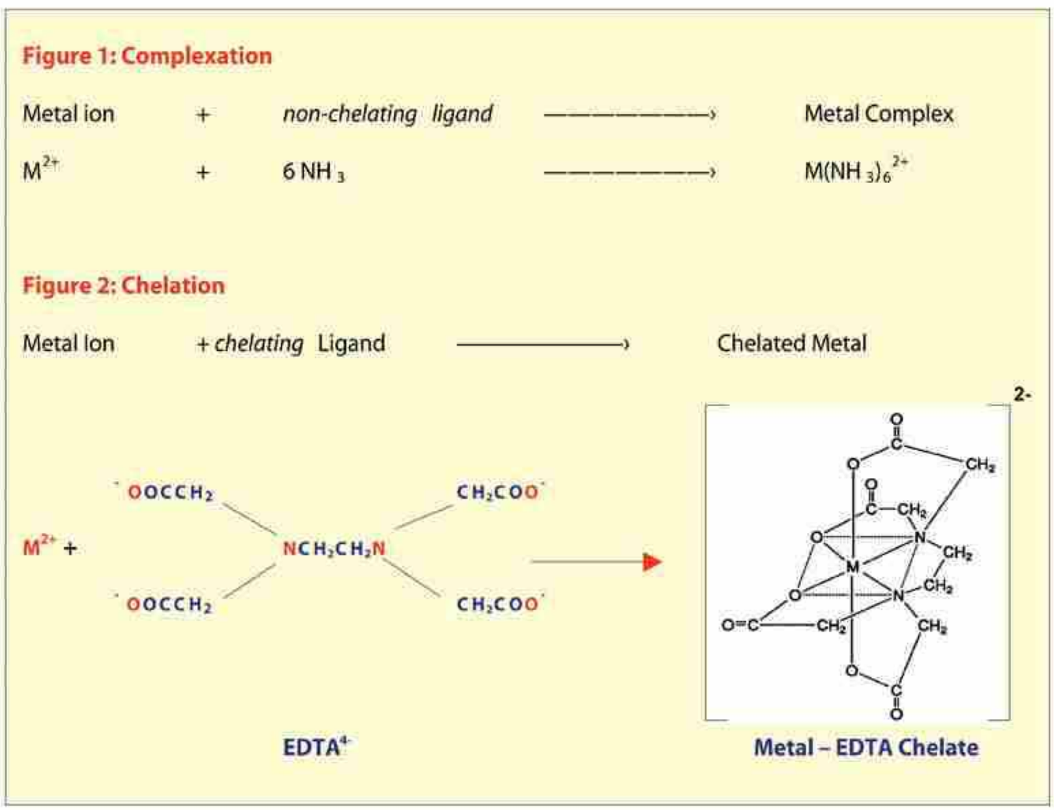


Heavy metals can and do combine with species such as cyanide, hydroxide, ammonia, EDTA, etc. to form metal complexes. These species are called "ligands," from the Latin "ligare," which means "to bind." When a ligand binds to metal through one atom, carbon, oxygen or nitrogen, it is called unidentate. Examples include cyanide, ammonia, etc. and the product is called a metal complex (see Figure 1).



When the ligand binds to metal through more than one atom, it is called multidentate. Examples include ethylenediaminetetraacetic acid (EDTA), gluconic acid, etc. Multidentate ligands are referred to as chelators or chelating agents and a metal-multidentate complex is known as "chelate," from the Greek "chele," which means "crab's claw." Multidentate ligands form ring structures when combined with metals as shown in Figure 2.

Metal chelates are highly soluble, extremely stable and can form over a broad range of pH. They are several orders of magnitude more stable than their non-chelated counterparts. For example, nickel-EDTA chelate, with five chelate rings, is 10^{12} times more stable than the nickel-ammonia complex.

$Ni^{2+} + 6\ NH_3$ ———-> $[Ni(NH_3)_6]^{2+}$ Log K = 8.61

$Ni^{2+} + EDTA^{4-}$ ———-> $[Ni(EDTA)]^{2-}$ Log K = 20.1

Because of their excellent sequestering effects, chelating agents are being used in numerous applications. Consequently, significant amounts of these compounds enter aquatic systems through industrial activities and waste discharges.

Chelated metal-bearing waste streams, treated with conventional hydroxide precipitation alone, most likely do not meet discharge requirements. Industries will have to employ other techniques or add a step to existing treatments. Two techniques are available for removal of chelated metals from wastewater:

1. Removal of the metal-chelate. Ion exchange, reverse osmosis and nanofiltration can effectively remove chelated metals from wastewater. They are costly to operate and generate concentrates (brine) that must be treated.

2. Breaking the metal-chelate species into free metal and free chelating agent. Chemicals such as dithiocarbamate (DTC), hydrosulfite, sulfide, iron salts, etc., singularly or in combination, are often effective in lowering metal concentrations and meeting discharge requirements. However, they are dangerous and generate waste that may still require further treatment to render it suitable for disposal.

Newer batch treatment products have been developed specifically for use with difficult-to-treat chelated waste streams. These products are manufactured with non-hazardous ingredients to make use of the fast kinetics and synergistic effects of several functionalities to simplify the treatment process. They are intended to achieve compliance. The following cases demonstrate these products in treating chelated waste streams.

A view from the top of the reaction tank

Floc quickly forms in the tank

Case I: Electrical contacts manufacturer

A multinational electrical contacts manufacturer on the East Coast was generating a waste stream that contained large amounts of black solids and surfactant/soap with a pH of 9 to 12. The main metallic components in the waste were chelated copper and nickel. The chelator was an amine or EDTA. The conventional batch treatment involved the following steps:

1. Lower pH to about 2 with sulfuric acid
2. Raise pH with lime to about 12
3. Add DTC
4. Add ferric chloride
5. Add flocculent
6. Settle for three to six hours and
7. Filter

This process was laborious and required handling dangerous chemicals. The treatment was pH-sensitive and often failed to meet discharge requirements; failed batches had to be restarted from the beginning.

Utilizing the new treatment, the pH was adjusted to about 8 before the addition of the product. Within 15 minutes, large floc formed, settled and dewatered easily. The entire batch took 45 minutes to 1 hour to complete. All of the other chemicals were eliminated, except for significantly less sulfuric acid. Analysis is shown in Table 1.

Table I

Parameter	Discharge limits, ppm	AQUASIL® Treatment, ppm
Cadmium	0.02	< 0.01
Chromium	0.35	0.02
Copper	1.5	0.69
Lead	0.02	< 0.01
Nickel	1.8	0.35
Silver	0.03	0.01
Zinc	0.30	0.06

Table 2

Parameter	Discharge limits, ppm	AQUASIL Treatment, ppm
Cadmium	0.02	< 0.01
Chromium (total)	0.50	< 0.50
Chromium (VI)	0.20	< 0.05
Nickel	0.50	0.135
Silver	0.05	< 0.01

Case II. Pre-recorded audio & video media

The main metallic components in the waste were nickel and chromium, both present at a concentration of 30 to 70 ppm. The chelating agent was gluconic acid.

The conventional treatment involved chromium reduction at pH of 2 to 3. Then the pH was raised to about 9 with caustic followed by DTC and a flocculent. The batch ordinarily took four to six hours to process, and the treatment frequently failed to meet discharge requirements.

The new treatment took just about 45 minutes and generated a clear effluent with a pH of about 10. This treatment eliminated the caustic, DTC, flocculent, reduced labor and met discharge requirements for all metals. Solids were easily dewatered in a filter press and generated waste passed the TCLP test. Metal analysis of treated water is shown in Table 2.

Challenges ahead

Many challenges still remain in developing more efficient products to deal with extremely difficult-to-treat chelated/complexed wastes. As more effective chelators are introduced into new industrial formulations, treatment of their spent solutions becomes more difficult and expensive. Difficulties encountered in treating electroless waste, where the chelating agents are normally present along with ammonia, aminoborate, alkanolamines, citrate, gluconate, pyrophosphate, hydrazine, borohydride, formaldehye or combinations thereof, are good examples.

Accordingly, the forgoing cases should not be taken to represent a universal strategy to deal with chelated or complexed metals in industrial discharge. Each waste stream has a unique chemistry, each chelating agent has different characteristics and results vary from one case to another. PE

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References

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