THE FATE OF COPPER IN TEXTILE DYEHOUSE WASTEWATER

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Because textile wastewaters are discharged to public water sources, their composition has been a concern of both the public (usually via environmental regulatory agencies) and textile wet processors. For the textile industry, the concern is primarily a matter of meeting pollutant concentration limits that are imposed by regulatory authorities. Increasingly, this includes color limits as well as limits on metals and specific organic compounds.[1] These low limits have increased the need to understand what happens to pollutants in the effluent stream both before and after it enters a wastewater treatment plant. As will be seen, textile effluent compositions can be examined to assess the expected fate (behavior) of their components. Here copper is used as an example, but first it will be useful to give some general information about dyes and copper.

COPPER

Copper is the most troublesome metal for the U.S. textile industry because it is ubiquitous in effluents and its concentration is stringently limited. A 1992 survey of 57 textile finishing facilities reported untreated effluent copper concentrations up to 600,000 μg/L with an overall average of 82,000 μg/L.[2] The U.S. EPA water quality criterion for copper is only 6.5 μg/L.[3] Thus, the allowed total concentration of all forms of copper in treated effluent water may be less than 10 μg/L (10 ppb), depending on the flow rate of the receiving stream.

Copper enters waste streams from dyes, auxiliary chemicals, incoming water, and the mill itself; e.g., plumbing. Copper in dyes may be present as ionic impurities (cupric ion and labile complexes) or as colorant anions in premetallized dyes. Except for some phthalocyanine acid dyes, only direct and reactive dyes contain copperized colorants. All are 1:1 complexes. Most copperized colorants are tridentate azo complexes, a few are formazans (tetradentate), and some are the important phthalocyanine complexes (tetradentate) used for turquoise shades.

The metal content of commercial dyes was examined comprehensively in 1972 by the American Dye Manufacturers Institute who reported the average copper concentrations (Table I).[4] However, these averages are very misleading since it is easily shown from the structure that premetallized colorant anions must contain on the order of 1-10% copper.

In general, textile wastewaters that contain dyes are treated by biological methods to remove biologically degradable compounds. In the United States, this is most often by the activated sludge process (ASP) either on site or at a publicly owned treatment plant (POTW). In any case, the activated sludge process can only remove copper from the wastewater by precipitation and/or by sorption to the biomass either as ionic copper or as the colorant anion itself. The activated sludge process has received much attention because of its low efficiency in removing color due to dyes.[5-10] Thus, it is known that most dye removal from activated sludge systems occurs by sorption on the mixed liquor suspended solids (MLSS) rather than by biodegradation.[5-8,11,12]

Precipitation of ionic copper and its removal with the other suspended solids can be shown to be unlikely on consideration of solubility product constants. However, sorption of ionic copper has been studied and undoubtedly occurs by ion exchange as the divalent cation.[13,14] But, because it is not possible to experimentally distinguish precipitated from sorbed copper in MLSS, any precipitation that does occur is implicitly treated as sorption.

Recently, various treatment approaches have been reviewed from both technical[15,16] and economic perspectives.[9] Efforts have even been made to relate the extent of removal to dye structure.[17] In summary, anionic dyes, in general, exhibit the following behavior in activated sludge systems:

- Stability—the basic structure is not destroyed.
- Removal is primarily by sorption on the biomass (MLSS).
- Direct dyes are removed (sorbed) more effectively than acid or reactive dyes.

However, until recently little attention has been paid to copperized dyes in wastewater treatment systems.

EQUILIBRIA

In the absence of sequestrants, every solution of commercial, copperized colorant can be viewed as an equilibrium involving two metal-containing

TABLE I.

Average Copper Concentration of Selected Dyes[4]

Dye Class	No. of Dyes Analyzed	Average [Cu] (mg/L)
Acid	399	79
Basic	136	33
Direct	285	35
Disperse	153	45
Fiber Reactive	46	71
Vat	59	110

TABLE II.

Sorption of Cu^{+2} and Copperized Reactive and Direct Dyes by MLSS[a]

Sorbate	$K_{(ICP)}$ (L/kg)[b]	% Cu Remaining in Solution
Cu^{+2}	6.1×10^3 ±32%	9
Direct Dyes	8.9×10^3 ±64%	9
Reactive Azo Dyes	6.3×10^2 ±96%	53
Reactive Formazan Dyes	4.0×10^2 ±74%	64
Reactive Phthalocyanine Dyes	3.1×10^3 ±13%	15

[a] From Refs. 19 and 20.

[b] ± Coefficient of variation.

species, the colorant anion, CuL^{-n+2}, the cupric ion, Cu^{+2}, and the colorant ligand, L^{-n}. Thus, all of the cupric ion in the system must come either from salts present in the original dye or from dissociation of the chelate as shown in Eq. 1.

$$CuL^{-n+2} \rightleftharpoons Cu^{+2} + L^{-n} \quad \text{(Eq. 1)}$$

Since copperized dyes contain copper as part of the colorant molecule, it seems likely that these dyes might contain excess cupric ion as an impurity resulting from dye synthesis. Therefore, 19 copperized dyes were analyzed for cupric ion.[18] Except for four phthalocyanine dyes, the results ranged from 0.01-0.7% with an average of 0.15%. The phthalocyanine dyes were all found to have less than 0.01% copper. Based on these data it was concluded that use of dyes having the higher ionic copper concentrations could conceivably contribute ionic copper to untreated waste streams at levels on the order of 100 times the U.S. EPA criterion.[18]

Because sorption is the dominant removal mechanism, it is important to know the strength of sorption (sorption isotherms) for the copperized dyes and cupric ion for two reasons. First, it is desirable to know how efficiently the dye anion is removed by sorption and second, sorption of Cu^{+2} could potentially shift the equilibrium in Eq. 1 to the right.

Consequently, measurements of equilibrium colorant concentration by high performance liquid chromatography (HPLC) were used for calculation of the Nernst isotherm, *K*. This partition coefficient is defined in Eq. 2.

$$K = [\text{dye}]_{\text{in sorbate}} / [\text{dye}]_{\text{in water}} \quad \text{(Eq. 2)}$$

When the equilibrium dye concentrations are in units of mg/kg and mg/L, *K* has units of L/kg and can conveniently be thought of as a concentration factor.

In separate experiments with the same MLSS, Cu^{+2} sorption isotherms were calculated from total copper concentrations determined by ICP-MS. Nineteen reactive and 12 direct dyes were studied with MLSS from four different sources over a period of about two years. Results from these studies (Table II) are based on ICP data because for some dyes HPLC resolution was inadequate although the two methods usually gave comparable data.[19,20]

The data in Table II show that cupric ion and the direct dyes are sorbed much more strongly than the reactive dyes. However, the phthalocyanine reactive dyes are sorbed almost as strongly as the cupric ion. Thus, 85-91% of the copper entering the waste stream as cupric ion, direct dye, or phthalocyanine dye will be removed by sorption on the biosolids. This is demonstrated by the percentage of copper remaining in solution at equilibrium (Table II).

Several other important results not shown in Table II came out of this study. First, the MLSS concentrations and the partition coefficients were remarkably independent of the POTW from which they were obtained; i.e., the presence of textile influent did not matter. This means that the data can probably be extrapolated to other systems. Second, experiments with hydrolyzed reactive dyes revealed partition coefficients similar to the unhydrolyzed compounds. This is important because it is hydrolyzed dye that is most likely to be present in the treatment system. Finally, the results showed that if dissociation (Eq. 1) does occur, the colorant ligand does not accumulate significantly in the aqueous phase.

Copper compound removal by strong sorption prompted consideration of chemical reactions that might convert them to poorly sorbed complexes. The occurrence of such reactions would disadvantageously increase the total dissolved copper concentration. Possible reactants (ligands) must be strong enough complexing agents to compete with the colorant ligand or other ligands for copper. Additionally, the ligands must be resistant to biodegradation to survive the treatment process. This led to consideration of EDTA since it is widely used as a sequestrant, extensively studied, and is resistant to biodegradation.[21]

Experiments with MLSS and either Cu^{+2} or reactive dye showed that when EDTA was added, the sequestrant increased dissolved copper concentrations almost 300%.[22] The equilibrium state of these mixtures can be approximated by a system of simultaneous algebraic equations for the competitive ligand exchange and sorption reactions.

The system of equations can be reduced to a pair of quadratic equations and solved. Then, with values for the equation parameters, it is possible

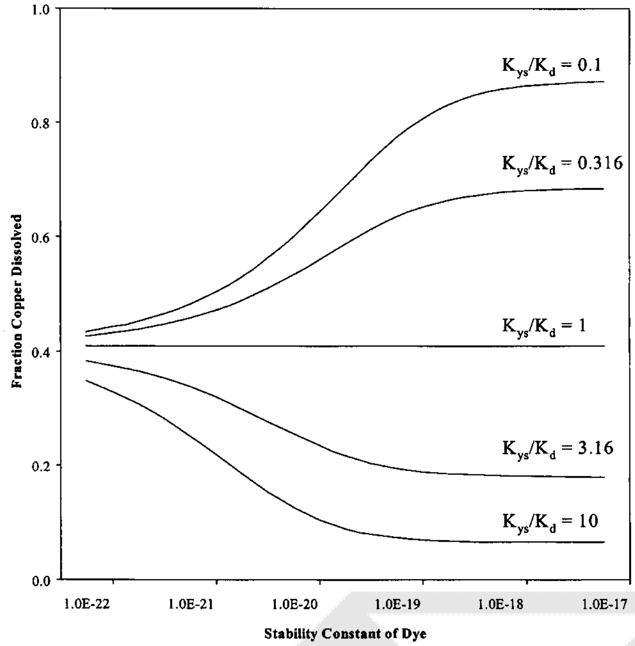

Fig. 1. Fraction of total copper dissolved vs. dye stability constant for different ratios of the sorption coefficients of the EDTA-Cu complex and dye, K_{ys}/K_d[22]

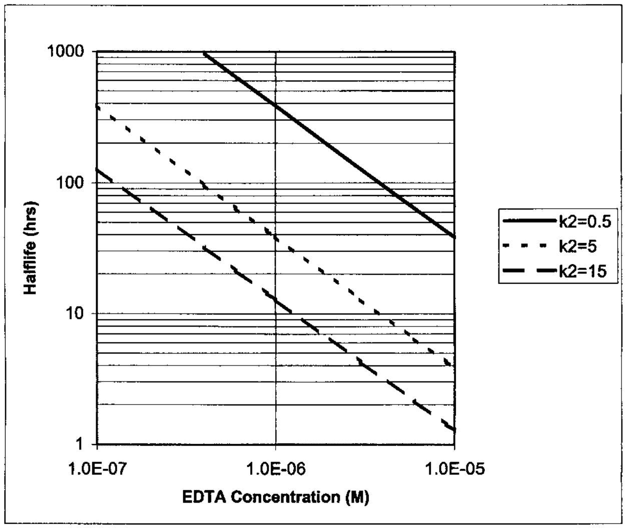

Fig. 2. Halflives of copper complexed azo dyes with different second-order rate constants, *k2*, when [EDTA] >>[Dye].[23]

to estimate the fraction of the total copper that remains dissolved in the system. Unfortunately, there are few values for dye stability constants and no value for the partition coefficient of the resultant EDTA-copper complex. Although the partition coefficient of the EDTA-copper complex is very difficult to measure, it was shown to be less than 100 L/kg. Even with this limitation, it is possible to assess the expected fraction of copper in solution for various ratios of the partition coefficients of the EDTA-copper complex and dye (Fig. 1).[22]

Fig. 1 shows the consequence of EDTA, or other sequestrant, reaction with copper species (including dye) to form copper-sequestrant complexes. If the new complex is less strongly sorbed than the dye (i.e., $K_{ys}/K_d > 1$), then the total dissolved copper concentration will be increased. This approach, of course, only approximates the equilibria in the waste treatment system and does not consider kinetics.

KINETICS

Slow equilibration was believed to explain why experiments with cupric ion or direct dyes gave erratic results depending on the time and order of EDTA or dye addition to MLSS. For example, addition of direct dye or CuSO$_4$ before EDTA addition greatly reduced the release of dissolved copper. This suggests that reaction of EDTA with dye or cupric ion is slow compared to dye or cupric ion sorption rates. This conclusion was consistent with the only kinetic data available at that time. Under this circumstance, sorption of dye or cupric ion can be treated as a rapid pre-equilibrium step that reduces the rate of EDTA reaction in proportion to the fraction of dye that is unabsorbed.

To better assess the role of kinetics, second-order rate constants were measured for EDTA reaction with five reactive azo dyes at pH 6.[23] The rate constants varied from 0.63 to 13 M^{-1}s^{1} or about 0.005-0.1 times the value calculated from the literature for the C.I. Mordant Black 17 complex at pH 7.[24] It is likely that rate constants for most copperized azo colorants are of the same order of magnitude or more since the same reaction center is involved in all cases. Rate constants could not be measured for direct dyes because neither spectrophotometry nor HPLC could adequately distinguish colorant ligand from colorant.

In most cases, the hydraulic residence time in activated sludge systems is on the order of one to two days. If the halflife for dye reaction with EDTA is of this order or less, one could expect significant formation of the unabsorbed EDTA-copper complex.

Based on the rate constants, it is possible to assess the expected extent of reaction in the activated sludge system as shown in Fig. 2. The graph brackets the range of measured rate constants for the reactive dyes, and it can be seen that at EDTA concentrations of 10^{-6} M, or more, halflives of the dyes are less than 300 hours. Under these conditions, five of the six dyes for which there are kinetic data would have halflives of less than 40 hours. This does not even consider reactions that might occur in the mill where concentrations and reaction rates could be much higher before reaching the activated sludge system.

CONCLUSION

Although the approach taken here cannot be considered quantitative, it illustrates the expected trends and highlights some facts that should be useful to the cautious dyer. First, in the absence of sequestrant, sorption by biomass in activated sludge systems should remove most of the dissolved copper except for that contained within reactive azo and formazan colorants. Fortunately, there are only a few copperized formazan dyes. Secondly, overuse of strong, poorly degradable sequestrants will increase the concentration of total dissolved copper (and other transition metals) in treated effluent.

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