

KMED: a two step process to remove color from pulp mill wastewater

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THE ORGANIC COLOR COMPONENT of pulp mill wastewater is made up of by-products that are not readily susceptible to the normal biodegradative processes. These by-products are largely lignin degradation products that form during pulping and bleaching. Methods to remove color from pulp mill wastewaters have varied, and some of these approaches have not been entirely suitable for the aquatic environment. However, the organic color can be removed from pulp mill wastewater by treatment with potassium permanganate and ozone in a process that is not detrimental to the environment.

The potassium permanganate reaction removes the large colloidal color bodies and produces a large floc at high pH and temperature. Ozone is then used to oxidize the smaller colloidal particles to a negligible size. The precipitate from the KMnO_4 reaction can be removed by filtration and can be destroyed by acid treatment. An overall process was designed to encompass all pulp mill wastewaters. This process is called the KMED process, for "kraft mill effluent decolorization" (1).

BACKGROUND

Color in wastewater results from the presence of compounds with electron-dense functional groups that adsorb light in the visible spectrum (2). A portion of the color is colloidal, and a smaller fraction is soluble in water under alkali conditions. Complex ring structures (lignin) and

the sulfates or sulfites attached to them frequently cause color (3).

These visible color components result from the cooking and bleaching of pulp. This processing leads to quinoid structures formed through condensation and oxidation reactions (4). Nonfiltered effluent contains visible color that exists primarily as colloidal particulates of various sizes and molecular weights. A smaller portion of color is soluble, and this soluble color is made up of free, single-ring structures of low molecular weight.

The chromophores and low-molecular-weight phenolics adsorb ultraviolet light. The UV light is adsorbed through compounds with conjugated double-bond configurations. These compounds include not only six-carbon aromatic rings with nitrogen-, sulfur-, and oxygen-containing groups but also heterocyclic compounds containing oxygen, nitrogen, or sulfur (5).

Early methods to remove color from pulp mill wastewaters include limited and massive lime treatment, alum coprecipitation, and precipitation with iron, salts, and lime. More recent methods employ such techniques as chemical oxidation with permanganate, oxygen, ozone, or hydrogen peroxide; adsorption and absorption on activated charcoal; reverse osmosis and electrodialysis; iron flotation or foam separation techniques; and biological treatment (2, 5). Many of the color reduction procedures are chemical procedures, but innovative biological processes are also in development (6).

ABSTRACT

A reaction between caustic bleach water and potassium permanganate was examined for its ability to remove colloidal color. The effectiveness of this reaction was found to depend on concentration and was not affected by pH. Under certain conditions, a large floc formed that was easily removed. The supernatant of the reaction, after being mixed with both acid wastewater and process wastewater, was treated with ozone to further reduce the residual color. The product of the two step process yielded an overall color reduction of more than 97%.

Application:

Pulp mill effluent can be treated with KMnO_4 and then with ozone in a new two stage process to reduce the colloidal color by up to 97%.

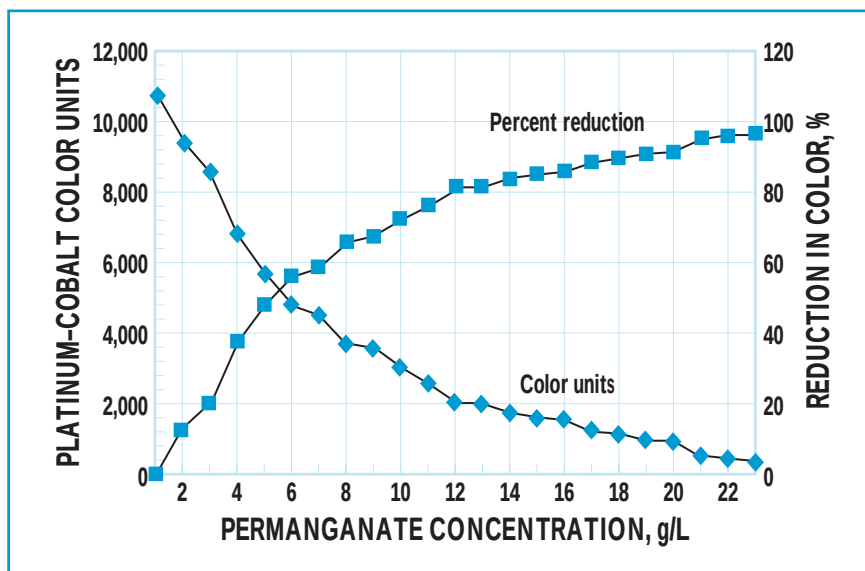
Parthasarathy *et al.* discussed the use of permanganate for removing color, explaining that KMnO_4 is an active decolorization agent which leads to MnO_2 (2). However, MnO_2 is brownish and has to be eliminated from the effluent, causing further complications (2). Potassium permanganate has an extensive history of use in water and wastewater treatment processes. These uses include clarification (7, 8), manganese control (9), disinfection (7), and cannery waste treatment (10). Present-day wastewater treatment processes and pulp and paper industries use potassium permanganate in testing procedures (11, 12), oxidation processes (13, 14), co-polymerization reactions, and environmental treatments such as odor control (15). Ozone, with its strong oxidative capacity, is used to disinfect drinking water, to bleach pulp and textiles, and to clarifying water and wastewater (16).

Few published papers refer to the removal of wastewater color by

Waste-water	pH range	Temp., °C	Color units*	Absorbance at 465 nm
Caustic	10–11	70	8820–12,346	2.5–3.5
Acid	2–3	70	1000–2000	...
Process	6–8	50	1400–2469	0.4–0.7

*Platinum–cobalt color units.

I. Characteristics of effluents resulting from bleaching during softwood processing



1. Removal of colloidal color from E1 at 70°C with increasing concentrations of permanganate.

KMnO₄ (2). One report is that of Hanzawa *et al.*, who recorded the development of a three stage process (coagulation, oxidation, and activated carbon) to treat the spent liquor from the pulping of Japanese oak wood (17). They reported that the residual color of the spent liquor approaches the color of freshwater. Patents that utilize potassium permanganate commonly discuss its use in the pulp bleaching process (18) or disclose alternative chemical methods for removing color from pulp mill effluent (5, 19–22). However, there are few published papers and patents that detail the advantages of combining potassium permanganate and ozone to remove colloidal color from kraft mill effluents.

EXPERIMENTAL PROCEDURES

Sampling and testing apparatus

Samples were collected from the

kraft pulping (23) effluent streams of Leaf River Pulp Operations in New Augusta, MS. The mill's bleaching sequence was D(E+O+P)D(E+P)D. Typical characteristics of the wastewaters are shown in **Table I**.

Experiments were performed during softwood processing because effluent color was highest during these pulping periods. Each small-scale reaction test of less than one liter was conducted either in a 1 L beaker or in 100 mL aliquots in 125 mL Erlenmeyer flasks. Large-scale reaction runs were conducted in 80-L volumes.

Samples were preheated to 70°C (to emulate mill conditions) in a 110 L polypropylene tank with a tank heater fitted with a bulkhead fitting and a gate valve for dispensing. After the target temperature was reached, the water was dispensed

into a second tank, and permanganate was added with slow stirring.

Samples were mixed with a Stirpak laboratory stirrer (Cole-Parmer, Chicago, IL) fitted with a custom-made stirring paddle. The paddle consisted of a 3/8 in. shaft with paddles 1/8 in. thick by 1 in. wide. These paddles were welded 180° from each other on the bottom of the shaft. A second set of paddles was welded 90° offset from the bottom paddles and 10 in. higher on the shaft.

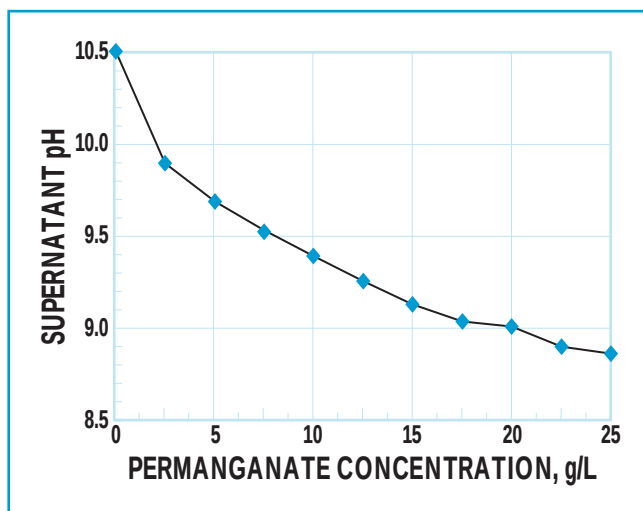
Characterization of the KMnO₄ reaction with E1

Concentration dependence. The precipitation of color from the caustic-stage effluent (E1) was determined over a KMnO₄ range of 0–21 g/L. Each determination was made using a 100 mL volume in an Erlenmeyer flask containing a 1 in. magnetic stirring bar. Samples were stirred at 100 rpm until the flocs began to form.

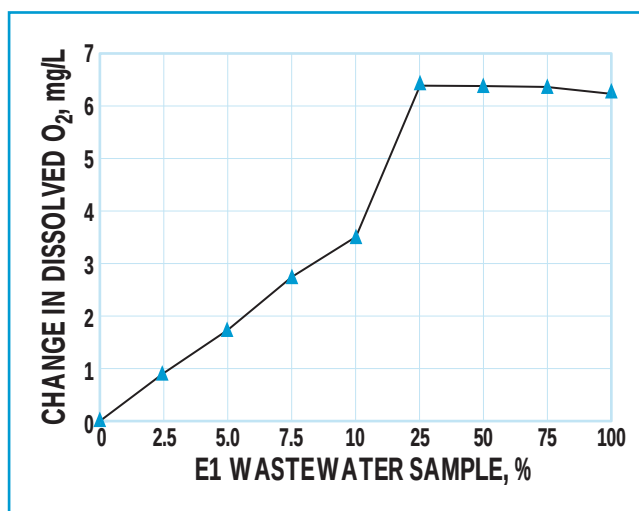
Samples were processed by 0.45 μm filtration or by centrifugation at 5000 rpm for 5 min at room temperature prior to color analysis. We analyzed color in untreated and treated E1 both before and after permanganate treatment by measuring absorbance at a wavelength of 465 nm with a spectrophotometer (Beckmann DU 640) (24). Color units may be derived from the A₄₆₅ values of serial dilutions of a platinum–cobalt color standard (Fisher Scientific, Norcross, GA) by the following formula:

$$\text{Color units} = A_{465} / (2.81 \times 10^{-4})$$

pH. The pH of the caustic effluent was preadjusted from pH 2 through pH 11 in increments of one unit with 2M NaOH and 2M HCl. The A₄₆₅ and pH values were determined with a pH meter before and after the precipitation reaction using KMnO₄ at a concentration of seven grams per liter of E1.



2. Effects of increased concentration of KMnO_4 on the pH of the supernatant.



3. Effect of the reaction on the oxygen concentration of E1. Above 25%, the dissolved oxygen content has been reduced to zero.

Oxygen depletion. Oxygen was monitored (YSI, Yellow Springs, OH) in E1 presaturated with oxygen by aeration with compressed air introduced through a microporous air stone (Aquatic Ecosystems, Apopka, FL). Appropriate control waters were likewise treated. All oxygen depletion experiments were conducted at 26°C.

We set up a series of 300 mL bottles for measurements of biological oxygen demand (BOD). These bottles held 0%, 2.5%, 5%, 7.5%, 10%, 25%, 50%, 75%, and 100% E1 in dilution water (v/v). The dissolved oxygen content of each bottle was measured in milligrams per liter prior to the addition of KMnO_4 at a concentration of 7 g/L. After two hours, the dissolved oxygen was measured again.

Manganese in supernatant. We tested for free manganese in supernatant solutions by using a DR/700 colorimeter (HACH Company, Loveland, CO) according to Method 8149 as described in its accompanying manual.

Colloidal particulate size. The colloidal particles in E1 were serially fractionated using regenerated cellulose ultrafilters (Millipore Corp., Bedford, MA). These filters had molecular weight cutoffs (MWCO) of 1000, 5000, 10,000, and 30,000.

The colloidal color particle size was characterized by serial passage of untreated E1 (500 mL) through a

Whatman #1, a Whatman #42, a 0.45- μm Millipore, a 30,000 MWCO, a 10,000 MWCO, a 5000 MWCO, and finally a 1000 MWCO membrane. Only when the 30,000 MWCO membrane was employed did significant change occur in the filtrate color units.

Kinetics

The temperature for E1 samples in the kinetics experiments was maintained using a double boiler format. A 1 L beaker with 400 mL of water was placed on a heated stirring plate. Inside the beaker, we placed a 100 mL Erlenmeyer flask containing an E1 sample. The sample was allowed to equilibrate to the desired temperature. The system was lighted with two high-intensity lights, one on top and one on the side. The lighting helped us to see the first flocs form.

Constant concentration vs. temperature. For measurements at constant KMnO_4 , we mixed KMnO_4 at a concentration of 7 g/L with preheated E1 samples over a range of temperatures. These temperatures ran from 30°C up to 70°C at intervals of 5°C. Stirring was set at a low speed (100 rpm). The reaction time was determined from the time permanganate was added until the first large floc appeared.

Constant temperature vs. KMnO_4 . For measurements at constant temperature, we carried out the reaction

of E1 and KMnO_4 at 50° and at 70°C. At 50°C, we measured flocculation at KMnO_4 concentrations ranging from 0 g/L to 10 g/L; at 70°C, the range was 0–15 g/L. Supernatants were separated from precipitates, filtered at 0.45 μm , and adjusted for pH with 2M NaOH or 2M HCl. We analyzed the supernatants with a spectrophotometer to measure absorbance at a wavelength of 465 nm.

Collection of supernatant. The supernatant, or treated caustic effluent, was separated from the precipitate by gravity or by the use of a Gore-Tex sock filter (W.L. Gore and Assoc., Elkton, MD). Drained precipitate was dissolved by concentrated acid, or it was dried and maintained as a solid. The supernatant was collected and pumped into another tank for ozone treatment.

Ozone treatment. Ozone treatment of permanganate-treated wastewaters was carried out with an ozone generator. The ozone was generated with extra dry oxygen (Norden Smith, Hattiesburg, MS) or with dried in-house air, and the gas flow was adjusted to optimize ozone production. Treated E1 or refined effluent was subjected to ozonation.

The quantity of ozone introduced was determined on the basis of ozone generator specifications and the nature of the feeder gas. We monitored samples for the buildup of ozone in solution by using the

Initial pH	Absorbance at 465 nm Before	Absorbance at 465 nm After	Final pH	Change in pH
2	0.1592	0.1672	6.28	4.3
3	0.2578	0.2901	7.58	4.6
4	0.3618	0.3317	8.71	4.7
5	0.3510	0.3317	8.87	3.9
6	0.3593	0.3126	8.81	2.8
7	0.3369	0.3175	8.94	1.9
8	0.3379	0.3183	8.94	0.9
9	0.3320	0.3272	9.00	0.0
10	0.3776	0.3228	9.36	-0.6
11	0.3935	0.3456	9.53	-1.5

The pH of E1 was established with 2M NaOH and 2M HCl prior to the reaction with KMnO_4 at 7 g/L.

II. Profile of the pH effects of permanganate oxidation and precipitation of colloidal color from E1

DR/700 colorimeter. The ozone was introduced through a Venturi fitting, and it was recirculated in a batch process.

Refined effluent. "Refined effluent" is our term for a proportional mixture of the various wastewater streams after they have been independently treated in some manner. Refined effluents were prepared from samples designated as treated E1, ozone-treated E1, acid wastewater, acid-soluble precipitate, and process wastewater. Specific volumes of each were mixed in proportion to the volumes of pulp mill wastewaters that composed the final mill effluent.

Refined effluents were characterized by the treatment concentration of KMnO_4 (in g/L) for wastewater, the mix ratio, the amount of O_3 infused, the volume of E1 that was treated, the color value, the pH, both the initial and the final AOX values (adsorbable organic halogens), and the amount of free chlorine in the wastewater.

RESULTS AND DISCUSSION

Methods to remove color from pulp mill effluent commonly utilize chemicals to flocculate colloidal color just prior to discharge, with some treatments being carried out at points upstream in the process lines. Here

we report a method to decolorize an upstream caustic effluent that constitutes about 25% of the total bleach effluent volume and approximately 52% of the total bleach effluent color at Leaf River Pulp Operations.

Color reduction

Potassium permanganate readily precipitates color at the elevated temperature and pH of the E1 line (pH 10–11, 70°C). Under these conditions, the reaction produces a large, settling floc that differs substantially from the fine floc described by Parthasarathy *et al.* (2). There is some variation in the E1 color, which makes it necessary to monitor the changes. The quantity of KMnO_4 has to be adjusted to achieve the desired percentage of color reduction. This E1 caustic effluent consistently has the highest color readings, and it requires the highest quantity of KMnO_4 . The acid and process effluent lines take much less KMnO_4 . In fact, KMnO_4 at a concentration of only 1 g/L removes all color from the process wastewater.

Figure 1 illustrates the reduction in the organic color in E1 wastewater as the KMnO_4 concentration increases from 1 g/L to 21 g/L. Treatment with 7 g/L removed 65.9% of the wastewater color. Doubling the concentration of KMnO_4 to 14 g/L and tripling the strength to 21 g/L

	A ₄₆₅	Color units*	Change, %
Untreated E1	2.8210	10474	...
Whatman #1	2.7800	10321	1
Molecular weight cutoff			
30,000	2.0890	7749	26
10,000	0.8540	3151	70
5000	0.2630	951	91
1000	0.0570	185	98

A Whatman #42 filter and a 0.45- μm Millipore filter were used after the Whatman #1 filter, with no change in absorbance and color units.

*Platinum–cobalt color units.

III. Ultrafiltration of E1 with membranes to classify the particle sizes contributing to visible color

removed 20% and 31% more color, respectively. Above 21 g/L, the color of the water increased as a result of unreacted KMnO_4 . However, the purple color would dissipate with time because the unreacted potassium permanganate would oxidize or react with low-molecular-weight components of the wastewaters. Determinations of the presence of residual Mn^{2+} in treated E1 showed that all of the manganese was consumed during flocculation.

pH effects

As **Fig. 2** indicates, the concentration of KMnO_4 increases from 0 g/L to 25 g/L as the pH of the resulting solution decreases from an initial pH of 10.5 to a final pH of approximately 8.9. When the pH of E1 is adjusted in advance of KMnO_4 treatment, initial pH values of 9 or more produce supernatants with reduced or unchanged pH values, as the results in **Table II** show. Furthermore, initial pH values of 2–8 lead to changes in supernatant pH values of 0.9–4.7. Samples with initial pH values below 4 exhibit a color reduction effect that is probably attributable to acid precipitation.

These data indicate that the reaction between KMnO_4 and the E1 caustic effluent is effective over a wide range of pH. In addition, the reaction drives the pH of the supernatant to an alkaline level of approximately pH 9 as an optimum pH.

Loss of oxygen

The reaction between KMnO_4 and E1 was examined for its effect on the dissolved oxygen concentration (Fig. 3). As the percentage of E1 in the wastewater increased, there was a parallel increase in the number of color bodies available to react with KMnO_4 and a concomitant decrease in the concentration of oxygen in the wastewater. At E1 concentrations of 25% or more, essentially all dissolved oxygen is eliminated from the water.

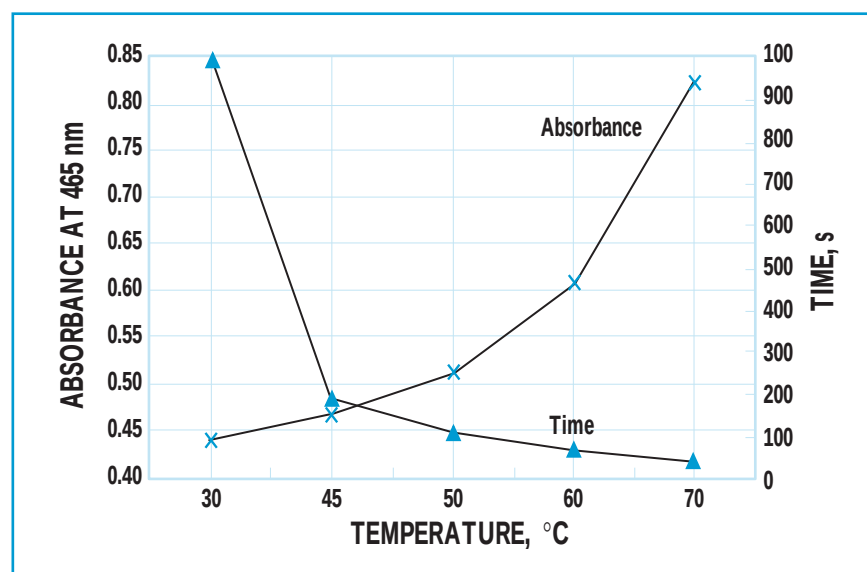
Oxygen may be consumed during the oxidation of double bonds, may become bound in carboxyl or hydroxyl groups on modified compounds, or may become trapped in the floc as it forms. These data indicate that biological treatment should be preceded by aeration or by the mixing of the permanganate-treated wastewaters with the other wastewaters.

Color particle size

Ultrafiltration of E1 demonstrates that color particles vary in molecular weight. In the series, the filters with molecular weight cutoffs of 30,000, 10,000, 5000, and 1000 removed 26%, 70%, 91%, and then 98% of the initial wastewater color, as shown in Table III. In fact, the filtrate after the last filter looked like drinking water. (The residual color after the last filter represents only soluble color.)

These data suggest that a two stage process would be practical. In the first stage, the larger colloidal particles could be removed using permanganate. In the second stage, an oxidant such as ozone could be used to complete the oxidation process.

The data in Fig. 1 and Table III support this concept. A 70% color reduction by the first reaction correlates with the removal of colloids with molecular weights greater than 10,000. In the first stage, the reaction would require between 7 g and 9 g of KMnO_4 per liter of E1. In the sec-



4. Reaction kinetics correlating time and color removal at a constant treatment concentration of 7 g/L of KMnO_4 in E1.

ond stage, the color of the treated E1 would be reduced in proportion to the quantity of ozone used and the length of ozone treatment.

Time and temperature

Figure 4 presents the kinetics of the reaction between KMnO_4 and E1. As the temperature of the reaction was increased, the time of the reaction decreased from approximately 990 s at 30°C to approximately 40 s at 70°C. At the lower temperatures, the reaction is slower but more complete, as evident from the higher absorbance values, which indicate lower residual color. The inverse is true for higher temperatures. The intersection of these curves indicates that the optimum temperature of the reaction would be approximately 46°C and would require approximately 180 s at a concentration of 7 g/L.

Both the caustic effluent and the acid wastewater exit their bleaching towers at approximately 70°C. When they reach the mixing station, the temperatures of these streams have dropped to approximately 50°C.

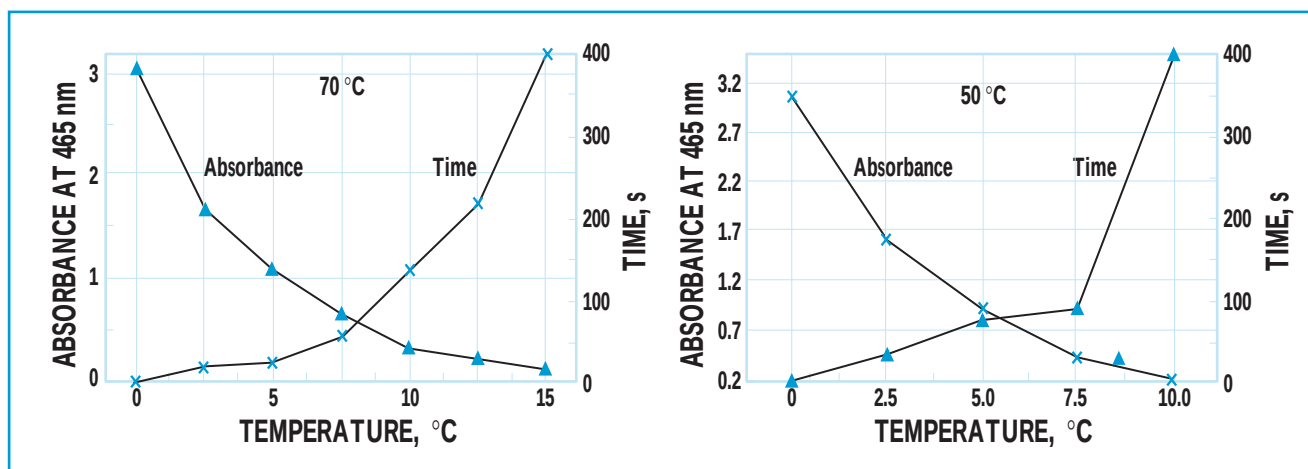
Figure 5 examines the kinetics of two constant temperatures versus increased concentrations of KMnO_4 . At 70°C, the absorbance at 465 nm decreases as the concentration of permanganate increases. The time of the reaction increases as the quantity

of KMnO_4 increases. The amount of KMnO_4 increases because it takes time for the chemical to become soluble and then react with organic colloidal particles. The theoretical optimum at 70°C is 8.1 g/L in 83 s. A similar pattern occurred at 50°C, indicating an optimum concentration of 6.4 g/L in 75 s.

Theoretical considerations

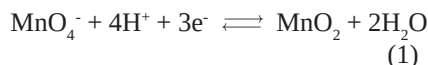
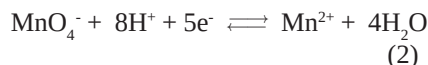
How do we explain the characteristics of the KMnO_4 reaction with E1, such as its kinetics, the oxygen depletion, and pH modifications? To begin with, the caustic effluent is a heterogeneous population of complex reactive ring structures. Furthermore, numerous ionic species in the effluent may bring about the dissociation of KMnO_4 to K^+ and MnO_4^- ions (25). The MnO_4^- ion is the main reactive species in oxidizing the constituents in the water, including the colloidal color component. Presumably, the color components accept oxygen such that the partial negative charge associated with the oxygen allows the particles to flocculate about a manganese oxide center.

Manganese can exist in several valence states (from +2 to +7) and can participate in several coordination complexes depending on the valence state. Therefore, from two to seven negatively charged particles



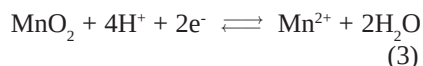
5. Reaction kinetics correlating time and color removal with increasing concentrations of KMnO_4 at constant treatment temperatures of 70°C and 50°C.

can form a complex with the positively charged manganese ion to reach a neutral charge. From the permanganate ion, various oxidation states can be produced, with redox potentials ranging from 0.558 to 1.679. The highest of these states are achieved in the following half reactions at low pH:



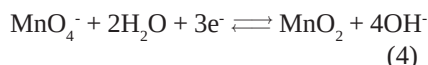
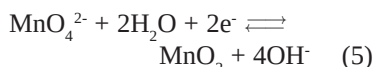
where $E^\circ = 1.679 \text{ V}$ for Eq. 1 and $E^\circ = 1.507 \text{ V}$ for Eq. 2 (in going from the oxidized form to the reduced form of manganese).

In the following half reaction, the redox potential, E° , is 1.224 volts (for the reduction):



At high pH values, the formation

of MnO_2 is established by two half reactions:



where $E^\circ = 0.595 \text{ V}$ for Eq. 4 and $E^\circ = 0.600 \text{ V}$ for Eq. 5 (reduction).

Permanganate permits higher redox potentials than does chlorine dioxide, which is commonly used as an oxidizing agent. The most feasible reaction should occur at low pH, but we have observed that the color removal is substantial at all pH levels when the amount of permanganate remains constant.

Precipitated floc

The precipitate from E1 is a large floc from the reaction with KMnO_4 at 7 g/L, 70°C, and pH 10.5. This floc settles rapidly in approximately a third of the time required for a fine floc to settle when the reaction is performed at room temperature. When a sock filter was used, the floc separated from treated E1 immediately, but the floc also settled readily by gravity.

The volume of thickened floc averaged 0.6% of the total volume treated. The floc contains essentially 100% of the manganese added, as indicated by the absence of free manganese in the supernatant. The

detection range for the low range manganese test was 0.0–0.80 mg/L, and no free manganese was detected by this method.

Thickened floc (0.21% v/v) readily dissolved in concentrated 36M H_2SO_4 , producing a solution we refer to as “acid-solubilized precipitate.” This solution is free of dark precipitate and is colorless to light yellow. When the pH of acid-solubilized precipitate solution was elevated to neutral or alkaline levels, the color of the solution did not increase, indicating that the colloidal color particles had been destroyed.

Ozone treatment

Previous observations in this laboratory had indicated that the colloidal color of the treated wastewater increases as E1 reacts with ozone. We speculate that the increase in color is a result of the fragmentation of large colloidal particles. Presumably, these large particles fragment into particles that fall into the colloidal size range responsible for the reflection of visible light. When the larger colloids are removed by KMnO_4 treatment, however, the ozone treatment does not result in an increase in color.

As the length of ozone treatment increased for the treated E1, the A_{465} value decreased, as Fig. 6 shows. This color reading reached approximately one-half of the original color reading in 137 min of ozone treatment (rep-

KEYWORDS

Color, waste water, decoloration, potassium permanganate, bleaching, ozonization, two stage process, effluents, bibliographies, pulp mills

representing approximately 12 g of O_3 per liter of treated E1).

No ozone accumulation was detected in the treated wastewaters, indicating that all reactive species were used in reducing color. The ozone was introduced by simple fine-pore diffusers. Improved methods of ozone introduction, such as counter-current infusion, would optimize this treatment.

Refined effluents

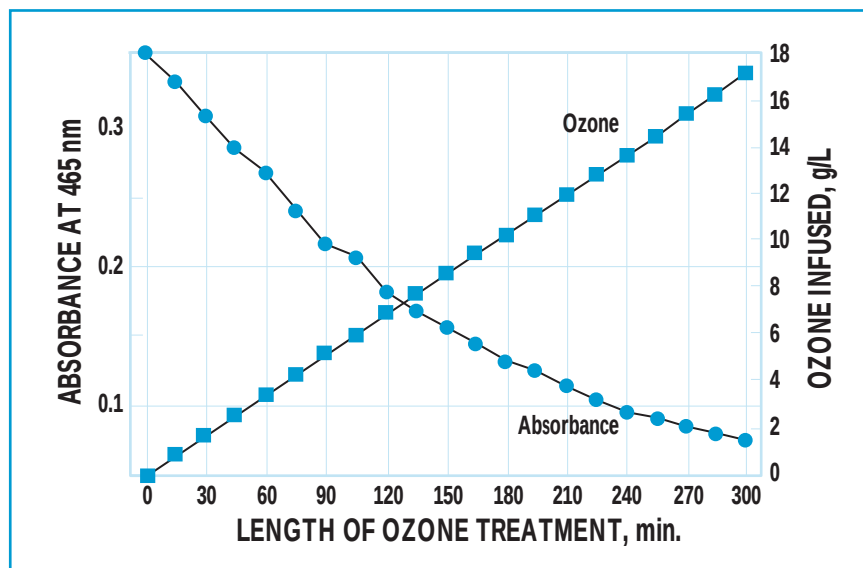
In our early attempts at producing refined effluent, we included a proportional percentage of the acid-solubilized precipitate solution as a fraction of the acid wastewater component. An analysis of these mixtures indicated that the conductivity was high and that the mixtures were toxic during bioassay. Subsequently, we excluded the acid-solubilized precipitate solution from the refined effluent mixtures.

Overall process

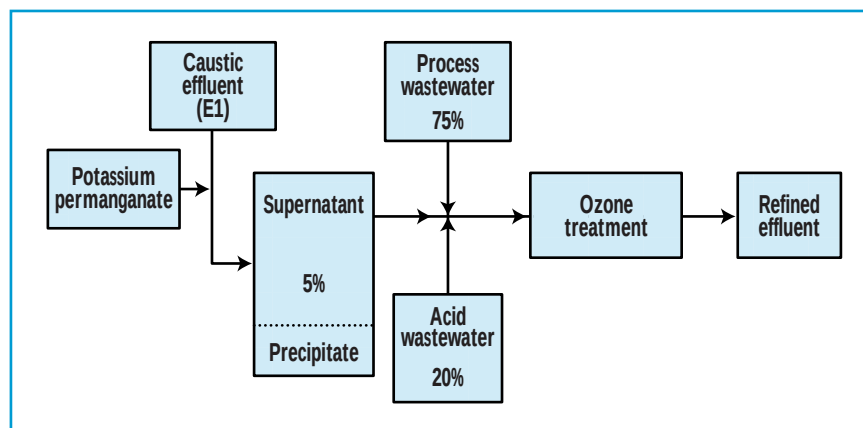
A ratio of 75:20:5 of process wastewater, acid wastewater, and caustic effluent was representative of the final effluent mixture. In our mixtures, we replaced E1 with treated E1. **Table IV** presents the results of three trials using this ratio of wastewaters and a lower level of permanganate (5 g/L). We chose a lower concentration because the large-volume experiments had indicated that the treatment still retained a 70–80% reduction in color with the $KMnO_4$ cut down to 5 g/L.

In all trials, the pH was slightly alkaline (7.2–8.6), the free chlorine ranged from 0 to 0.21 mg/L, and the COD (chemical oxygen demand) and BOD values averaged 1212 and 377, respectively. The color was approximately one tenth of the E1 value, at an average A_{465} of 0.23. Samples were subsequently treated with a microbial consortium.

In brief, the treatment of effluents by the KMED process results in residual compounds that are readily oxidized by biological treatment.



6. After $KMnO_4$ has eliminated the colloidal color from a sample of caustic effluent, ozone treatment removes the remaining soluble color in a few hours.



7. Diagram of the treatment process, with the relative contributions of the individual wastewater streams to the formulation of a refined effluent.

Reductions in BOD of 85–95% were achieved in three days (data not shown). Furthermore, in the permanganate treatment of E1, the concentration of total carbohydrates shifted in favor of a higher percentage of reducing carbohydrates. Additionally, bioremediation experiments indicated that the color removal process is stable unless microbial species that produce large amounts of pigment are present, in which case the increase in color is completely attributable to pigment.

Figure 7 shows the final scheme of the treatment process. Potassium permanganate (5 g/L) is mixed with caustic wastewater, the supernatant

is mixed with the process and acid wastewaters, and the mixture is ozonated to produce the refined effluent. Ozone treatment can be performed on the caustic effluent supernatant, but we moved this treatment in the final scheme to accommodate the removal of color from process wastewater (i.e., about 1/10 the color of E1). The concentrations of $KMnO_4$ and ozone can be adjusted to produce a refined effluent that is colorless and recyclable.

CONCLUSIONS

Organic color can be removed from bleach plant effluents in an effective, two stage process based on potas-

	Trial 1	Trial 2	Trial 3
pH	8.6	7.3	7.2
Free Cl ₂ , g/L	0.04	0	0.21
COD, mg/L	837	1389	1411
BOD, mg/L	242	503	388
Absorbance at 465 nm	0.336	0.218	0.146
Volume of prebiological treated mixture = 228 L of treated E1 prepared using 5 g/L KMnO ₄ .			
Mix ratio of treated E1, acid wastewater, and process wastewater = 5:20:75.			

IV. Characteristics of refined effluents that impact subsequent processing such as bioremediation

sium permanganate and ozone. The permanganate reaction is dependent on concentration and could be configured to eliminate upwards of 97% of the original wastewater color.

The reaction occurred over a wide range of pH and at the elevated temperatures associated with paper mill bleaching effluents. The reaction eliminated oxygen from the wastewater, making aeration necessary later in the process. Process kinetics indicated a correlation between temperature and reaction time. Although the reaction was slower at lower temperatures, it was more efficient and was able to remove more color.

other negatively charged groups that interact with and entrap the manganese in its various valence states.

Some growth experiments were conducted with commercial field corn planted in pots containing various weight percentages of the precipitate mixed with potting soil. Seedlings were watered and measured for growth inhibition caused by the precipitate. No inhibition was noted. In some instances, the soils containing the precipitate supported better growth than did the controls containing no precipitate (data not shown).

The reaction precipitate could be dissolved by concentrated acid, or it could be dried and used as landfill. The precipitate is composed predominantly of organic alcohols, aldehydes, and compounds with

This process has the ability to remove color from the pulp mill upstream wastewaters that do not immediately convert to technology for totally chlorine-free systems. The process can also remove the residual color from upstream wastewaters that are already totally free of chlorine.^{TJ}

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