Removal of Color From Surface Water in Central Florida

1973

Joseph R. Wanielista

University of Central Florida

Find similar works at: https://stars.library.ucf.edu/rtd

University of Central Florida Libraries http://library.ucf.edu

Part of the Engineering Commons, and the Environmental Sciences Commons

STARS Citation


This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
REMOVAL OF COLOR FROM SURFACE WATER IN CENTRAL FLORIDA

BY

JOSEPH R. WANIELISTA
B.S.A.E., The Pennsylvania State University, 1966

RESEARCH REPORT

A Research Report presented in partial fulfillment
of the requirements for the degree
Master of Science in Environmental Systems Management
in the Graduate Studies Program of
Florida Technological University

Orlando, Florida
1973
ABSTRACT

REMOVAL OF COLOR FROM SURFACE WATER IN CENTRAL FLORIDA

by

JOSEPH RICHARD WANELISTA

B.S.A.E., The Pennsylvania State University, 1966

The USPHS limits color in water to 15 color units. However, it is desirable to remove all the color. Color in surface water is mainly due to humic substances and was found in concentrations varying up to 450 color units. Removal of color by coagulation and flocculation has been practiced over the years. The mechanisms involved have not yet been fully understood.

During the course of this investigation, a literature survey, studying the nature of color, mechanisms of color removal, and optimum color removal conditions, has been conducted. Samples have been obtained from surface waters in Central Florida; namely, Big Econ River and Lakes Pickett, Irma, Lee, and Florida. These samples have been examined for color intensity, based on tannic acid, alkalinity and pH. The color intensity varied from 3.25 to 35.5. The alkalinity varied from 2 to 26 ppm, whereas the pH's varied from 5.3 to 6.35.

Aluminum sulfate and ferric sulfate were used to remove the color from the samples. Optimum conditions for color removal of dosages and pH's were made by jar tests. The optimum dosage of Fe₂(SO₄)₃·nH₂O and Al₂(SO₄)₃·18H₂O varied from 33 to 55 mg/l, while the
optimum pH's were found to vary from 6-10. Aluminum sulfate was found to be the better coagulant for removing color.
ACKNOWLEDGEMENTS

I would like to thank the Faculty and Staff for their helpful advise in preparing this report. I would also like to express my sincere gratitude to the members of my committee; Dr. W. McLellan, Dr. E. Goldstein, and especially to my chairman, Dr. Y. Yousef. Special praise is also extended to my typists; Micki Davis, Connie Phillips, and Diane Jawitz.

Finally, an acknowledgement to RETRO and Dr. Block for allowing me to participate in this excellent degree program cannot be overlooked.
TABLE OF CONTENTS

Chapter                                  Page
1. INTRODUCTION                           1
2. OBJECTIVES AND SCOPE                  4
3. LITERATURE REVIEW                     5
   Sources and Nature of Color
   Mechanics of Color Removal
   Common Coagulants
   Experimental Procedures
   Determination of Optimum Coagulation Conditions
   Methods of Measuring Color
4. RESULTS AND DISCUSSION                 23
   Effect of pH
   Effect of Coagulant Dosage
   Effect of Temperature
5. CONCLUSIONS AND RECOMMENDATIONS        34
LIST OF REFERENCES                       36
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1. Water Quality Color Limits for Domestic Use</td>
<td>2</td>
</tr>
<tr>
<td>1-2. Water Quality Color Limits for Industrial Use</td>
<td>3</td>
</tr>
<tr>
<td>3-1. Hydralysis Products of Common Coagulants</td>
<td>14</td>
</tr>
<tr>
<td>3-2. Hypothetical Reactions of Aluminum Sulfate</td>
<td>15</td>
</tr>
<tr>
<td>3-3. Hypothetical Reactions of Ferric Sulfate</td>
<td>16</td>
</tr>
<tr>
<td>3-4. Changes in Residual Turbidity as Related to Time Lag</td>
<td>19</td>
</tr>
<tr>
<td>4-1. Sample Sources</td>
<td>23</td>
</tr>
<tr>
<td>4-2. Coagulant Costs for Removing Color</td>
<td>33</td>
</tr>
<tr>
<td>5-1. Optimum Color Removal Conditions</td>
<td>35</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1.</td>
<td>Proposed Structure of Color Macromolecule</td>
<td>7</td>
</tr>
<tr>
<td>3-2.</td>
<td>Colloidal Particle With Its Accompanying Double Layer and Potentials</td>
<td>11</td>
</tr>
<tr>
<td>3-3.</td>
<td>Jar Test Apparatus</td>
<td>17</td>
</tr>
<tr>
<td>4-1.</td>
<td>Wavelength Search For Minimum Transmission</td>
<td>25</td>
</tr>
<tr>
<td>4-2.</td>
<td>Calibration Curve for Tannic Acid and K₂PtCl₆</td>
<td>26</td>
</tr>
<tr>
<td>4-3.</td>
<td>Effect of Initial pH Values on Color Removal From Surface Water Bodies by Using Aluminum Sulfate</td>
<td>27</td>
</tr>
<tr>
<td>4-4.</td>
<td>Effect of Initial pH Values on Color Removal From Surface Water Bodies by Using Ferric Sulfate</td>
<td>28</td>
</tr>
<tr>
<td>4-5.</td>
<td>Effect of Initial Coagulant Dosage on Color Removal From Surface Water Bodies by Using Aluminum Sulfate</td>
<td>31</td>
</tr>
<tr>
<td>4-6.</td>
<td>Effect of Initial Coagulant Dosage on Color Removal From Surface Water Bodies by Using Ferric Sulfate</td>
<td>32</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

To most people, water that will be used for domestic consumption must be of high aesthetic quality and meet public health standards. Drinking water standards have been set by USPHS to a limit of 15 color units based on a platinum-cobalt scale (1). Because of this, many water treatment facilities are faced with the problems of meeting federal and state regulations that, in essence, comply with human palatable desires, while protecting the health and well-being of individuals and the community.

There are, in many areas of the United States, large bodies of surface water that, but for a high natural color content, could be utilized as a source of public water supply. Although, there is no evidence that the presence of organic color in many waters constitutes a serious hazard to public health, and indeed there are many communities throughout the world that have been drinking a highly colored water for generations with no apparent ill effects, (2) today's public demands a sparkingly clear water.

Table 1-1 shows the range of limits for color and turbidity imposed on drinking water by USPHS. However, in practice, most municipal treatment plants strive to maintain finished waters with color values of 10 or less. Industrial use, on the other hand, requires various degrees of permissible color units. Table 1-2 shows the range of acceptable color units for sundry industries.
### TABLE 1-1 (3)
WATER QUALITY COLOR LIMITS FOR DOMESTIC USE

<table>
<thead>
<tr>
<th>CRITERION</th>
<th>RECOMMENDED UNIT</th>
<th>TOLERANCE UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color, Units</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Turbidity, Units</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

It is obvious, from examining these tables, that a growing demand for clear water will persist. As the demand increases, engineers and chemists must strive to meet the challenge of finding or modifying means of insuring amiable water for the applicable requestor.
<table>
<thead>
<tr>
<th>USE</th>
<th>COLOR UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food Products</td>
<td>10</td>
</tr>
<tr>
<td>Ice Making</td>
<td>5</td>
</tr>
<tr>
<td>Bottled Beverages</td>
<td>5-10</td>
</tr>
<tr>
<td>Pulp and Paper</td>
<td></td>
</tr>
<tr>
<td>Alkaline Pulps</td>
<td>5</td>
</tr>
<tr>
<td>High Grade Paper</td>
<td>5</td>
</tr>
<tr>
<td>Special Papers</td>
<td>5</td>
</tr>
<tr>
<td>Bleached Kraft Papers</td>
<td>25</td>
</tr>
<tr>
<td>Unbleached Kraft Papers</td>
<td>100</td>
</tr>
<tr>
<td>Groundwater Paper</td>
<td>30</td>
</tr>
<tr>
<td>Baking</td>
<td>10</td>
</tr>
<tr>
<td>Textiles</td>
<td></td>
</tr>
<tr>
<td>Cotton</td>
<td>50</td>
</tr>
<tr>
<td>Rayon</td>
<td>5</td>
</tr>
<tr>
<td>General</td>
<td>5-70</td>
</tr>
<tr>
<td>Boiler Feed Water</td>
<td>According to pressure</td>
</tr>
<tr>
<td>Brewing</td>
<td>0-10</td>
</tr>
<tr>
<td>Food Equipment Washing</td>
<td>5-20</td>
</tr>
<tr>
<td>Food Processing</td>
<td>5-10</td>
</tr>
<tr>
<td>Tanning</td>
<td>10-100</td>
</tr>
</tbody>
</table>
2. OBJECTIVES AND SCOPE

Central Florida, with its ubiquitous lakes and streams, is presently experiencing a population boom. Orange County, in particular, has found its population increasing steadily. If Orange County's current means of supplying potable water to the population should become overstressed and/or not sufficient, additional sources, such as surface waters which are heavily loaded with organic color, must be utilized. It is, therefore, conceivable that in the future, the water supply companies in Central Florida will be faced with the problems of removing color from their water sources.

The broad objective of this report is to review the available literature for source, removal techniques, and conditions for organic color. Evaluation of existing methods for color removal as applied to representative lakes and streams in the area were studied. Limited experimentation on color removal from water samples brought from Big Econ River, Lake Irma, Lake Lee, Lake Pickett, and Lake Florida were performed. The efficiency of color removal by reagent grades of Fe$_2$(SO$_4$)$_3$·nH$_2$O and Al$_2$(SO$_4$)$_3$·18H$_2$O under optimum conditions of dosage and pH were evaluated.
Complex physical and chemical mechanisms governing color constituents must be appreciated. Therefore, a literature survey of sources and nature of color, mechanisms of color removal, techniques and procedure utilized in color removal will be presented.

3.1 Sources and Nature of Color

Color in natural water could be of organic or inorganic nature. But since we are only interested in surface waters, the organic nature of color will be investigated. The origin of the color in surface water, for the most part, can be traced back to the decomposition of natural organic matter, such as found in the forests or other vegetation sources, which contribute a multiplicity of organic compounds. According to Christman and Ghassemi, (5) some possible sources of color could arise from:

1. The aqueous extraction of living woody substances,
2. The solution of degradation products in decaying wood,
3. The solution of soil organic matter, or
4. A combination of the above.

It is generally agreed that the primary cause of color in water is the presence of organic substances known as humic (6). The degree, amount or kind of humic substances determines the color of the water.
Because the color of water is organic in nature, carbon, hydrogen, oxygen, nitrogen, and traces of other elements constitute the applicable molecular make-up. The complexity of the make-up unfortunately, makes positive identification nebulous, thus fostering many sundry opinions on what constitutes a color molecule.

Shapiro, (7) utilizing isothermal distillation data, reported an average molecular weight of 456, and that the color molecules contain no phenolic structures, and that they are dibasic polyhydroxy aliphatic acids. Other studies reveal varying molecular weights from less than 800 to as high as 50,000. Black and Christman (8) classifies color solids as aromatic, polyhydroxy methoxy carboxylic acids. Christman, (9) also found in his analysis that the color molecules are similar to those in aqueous extractives of wood and soil organic matter.

In their investigation of the nature of organic color, Christman and Ghassemi (10) have boldly postulated a proposed structure of the color macromolecule (Fig. 3-1). They identified through experimentation seven degradation products of natural color, which according to the authors, provided conclusive evidence for the presence of phenolic nuclei in color macromolecule.

The seven products identified were: vanillin, vanillic acid, syringe acid, protocatechuic acid, resorcinol, catechol and 3,5-dehydroxy benzoic acid.

It is interesting to note that there have been studies conducted to determine whether the humic substances found in water samples vary from place to place. Shapiro, (11) utilizing chromatographic comparison, found similar patterns in water samples taken from
Fig. 3-1.—Proposed Structure of Color Macromolecule (10)
various lake sources across the country. Black and Christman, (12) (13) Packham, (14) in England, and Chalupa (15) in Czechoslovakia, all working independently, found the absorption spectra of water to be remarkably similar:

Because of the complexity of the problem, there was until recently, disagreement on how color particles are found in water. Some authors believed that color exists in water as true solutions, while others maintained that natural color exists as a colloidal dispersion. Fortunately, Black and Christman, (16) utilizing dialysis and membrane filtration techniques, estimated the particle size of organic matter in water to be less than 10 μm. This diameter size clearly indicates that the particles are colloidal in nature.

The question now arises to the charge of the colloidal particle. Humic groups are, for the most part, negative and thus the color particles are more than likely negatively charged with the magnitude of charge depending mostly on the degree of ionization and pH of the water. Stumm and Morgan (17) state, "although the charge on a colloidal particle may be due to preferential adsorption of ions from the surrounding waters, in many instances of importance in water treatment, the charge on a colloidal particle is known to be produced predominantly by direct ionization of one of its constituents".

In summary, the following characteristics can be attributed to color particles in water:

1. Color particles are made up of complex chains of organic molecules.
2. Color particles exhibit colloidal tendencies.
3. Color particles are negatively charged.
3.2 Mechanisms of Color Removal

The principal mechanism of color removal is coagulation and flocculation which are described as the destabilization, aggregation, and binding together of colloids. Coagulation and flocculation are achieved by the addition of chemicals which tend to destabilize the colloidal particle. Coagulation results from particle destabilization by changing the repulsive potential of the double layer (zeta potential neutralization) surrounding the particle. Flocculation, on the other hand, implies a chemical bridging or binding mechanism that enmeshes the particles into groups. Consequently, flocculation will take place after coagulation, and coagulation cannot be achieved without particle destabilization.

To discuss stabilization and destabilization, a knowledge of the forces acting on a colloidal particle must be fully understood. Stability refers to the property of dispersion among the particles while instability or destabilization refers to the property of coalescence among the particles.

The presence of an electrical charge on the surface of the colloidal particle whether from the ionization of complex organic molecules, or some other means, and the encompassing of bound water molecules are largely responsible for the particles stability. Because these particles possess like charges, they repel each other and remain stable in solution. Obviously, this stability is a function of several factors which can be equated to the zeta potential. The Zeta potential is,
\[ \zeta = \frac{4\pi \delta q}{D} \]

where:  
\( \zeta \) = zeta potential - (mv.)  
\( q \) = relative charge on the particle - (mv.)  
\( \delta \) = thickness of the layer around the particle - (cm.)  
\( D \) = dielectric constant of the liquid - (cm.)

As mentioned previously, the colloidal particles possess a negative charge. If the negative charge can be neutralized and decrease the zeta potential, the colloidal system loses some of its stability. This can be achieved by coagulation. Fig. 3-2 shows a colloidal particle with its accompanying double layer and potentials.

Two theories have been proposed to explain the mechanism of coagulation:

1. Chemical Theory
2. Physical Theory

The Chemical Theory assumes that colloidal particles acquire a charge on their surface from the ionization of chemical groups present at its surface and subsequently, coagulation is achieved by the interaction of the said particle with an added coagulant. Stumm and Morgan, (18) in describing the Chemical Theory, states that the primary charge on colloids arise from the ionization of complex ionogenic groups present on the surface of the dispersed particles, and that the destabilization of the colloids is due to the chemical interactions of complex formations and proton transfers. In other words, the charge on the color particle is primarily due to the ionization of its constituent ionogenic chemical groups, such as
Fig. 3-2.—Colloidal Particle With Its Accompanying Double Layer and Potentials (19)
carboxyl, phenolic hydroxyl, and others. Therefore, the strength of the charge depends on the degree of ionization exhibited by the aforementioned ionogenic groups. The mechanism of coagulation occurs when the above said particles are neutralized by the addition of positive ions, considered protons, from the added coagulant.

The Physical Theory, on the other hand, explains coagulation in terms of physical factors such as electrical double layer and counter adsorption of hydralysis products with the ensuing destabilization occurring as a result of the reduction in forces, i.e., the neutralization of the zeta potential. In their discussion on the physical theory, Stumm and Morgan (20) emphasizes the concept of the electrical double layer and the significance of predominantly physical factors, such as counter ion adsorption, reduction of zeta potential, and ion pair formation during the destabilization of colloids.

The coagulants chosen should possess positive zeta potentials and have the ability to precipitate negatively charged particles by neutralization and subsequent coagulation. It has been determined by Schulze (21) and verified by Hardy, (21) that salts having divalent ions of charge opposite to that of the colloidal particle exert coagulant powers far beyond monovalent ions, while salts having trivalent ions of opposite charge are even more effective. Their findings are reflected in the Schulze-Hardy Rule, (21) which states, "the precipitation of a colloid is effected by that ion of an added electrolyte which has a charge opposite in sign to that of the colloidal particles, and the effect of such ion increases markedly with the number of charges it carries. Therefore, the trivalent ions
should be utilized because they are 700 to 1000 times more effective than mono-valent ions and 14 to 20 times more effective than divalent ions (22).

In summary, the preceding section indicates that:

1. Because of the complexity of the colloidal system, either of the previously mentioned theories would be applicable in explaining the coagulation phenomena.

2. The mechanism of coagulation and flocculation must be such as to cause agglomeration of the colloidal particles (de-stabilization) into larger aggregates which can then settle out.

3. In order to bring about the coagulation of a colloidal suspension, it is necessary to offset the various factors which account for its stability. Much of the behavior of colloidal particles is associated with the surface phenomena, i.e.e.

   (a) Extremely large ratio of total surface area to length or width of particle.

   (b) The buildup of the surface charge in the form of a double layer.

   (c) The neutralization of the zeta potential.

3.3 Common Coagulants

   The two most common coagulants used for removing color are forms of aluminum and iron. These coagulants ionize in water and produce a solution that will conduct an electric charge. They produce cations and anions of high valence which react with the alkalinity of the water to form insoluble hydrous oxide precipitates. It has been demonstrated by Stumm and Morgan (23) that it is the hydralysis products which are formed that are the active agents in water coagulation rather than the simple aluminum and ferric ions. Therefore, in water clarification, the addition of an aluminum or
ferric coagulant to the water leads to the formation of a wide range of hydralysis products, the proportions of which vary with pH, water composition and the physical conditions of mixing. Table 3-1 shows some of the hydralysis products of aluminum and ferric coagulants.

**TABLE 3-1 (24)**

**HYDRAULYSIS PRODUCTS OF COMMON COAGULANTS**

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Hydration Products</th>
<th>Aluminum</th>
<th>Ferric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al(OH)$^{2+}$</td>
<td>Fe(OH)$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Al$_2$(OH)$_5$]$^{-}$</td>
<td>[Fe(OH)$_2$]$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al(OH)$_3$</td>
<td>Fe(OH)$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Al(OH)$_4$]$^-$</td>
<td>[Fe$_2$(OH)$_5$]$^{3-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Al(OH)$_2$]$^+$</td>
<td>[Fe(OH)$_4$]$^-$</td>
</tr>
</tbody>
</table>

Aluminum sulfate, Al$_2$(SO$_4$)$_3$·xH$_2$O is a widely used aluminum coagulant. It is used because it is soluble in water and is easily applied. Solutions of aluminum sulfate, or as it is commonly referred to as alum, added to water produces reactions such as:

\[
\text{Al}_2(\text{SO}_4)_3 \cdot \text{xH}_2\text{O} \rightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + \text{xH}_2\text{O}
\]

When the water becomes ionized, hydroxide ions are available, or:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-
\]

and the aluminum ions then react as

\[
2\text{Al}^{3+} + 6\text{OH}^- \rightarrow 2\text{Al(OH)}_3
\]
Combining all the above reactions and consider that the natural alkalinity, in the form of $\text{Ca(HCO}_3\text{)}$ of the water reacts with the coagulant, the reaction becomes:

$$\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O} + 3\text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + x\text{H}_2\text{O} + 6\text{CO}_2$$

However, because the complexity of the natural constituents of the water and the contribution of many factors, it is impossible to accurately predict the reactions.

Table 3-2 shows other hypothetical reactions of aluminum sulfate in the hydralysis form of $\text{Al(OH)}_3$. Other hydralysis products of aluminum also contribute to water coagulation.

**TABLE 3-2 (25)**

**HYPOTHETICAL REACTIONS OF ALUMINUM SULFATE**

- $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 3\text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 6\text{CO}_2 + 14\text{H}_2\text{O}$
- $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 6\text{NaHCO}_3 \rightarrow 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 6\text{CO}_2 + 14\text{H}_2\text{O}$
- $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 3\text{Na}_2\text{CO}_3 \rightarrow 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2 + 14\text{H}_2\text{O}$
- $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 6\text{NaOH} \rightarrow 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 14\text{H}_2\text{O}$
- $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 14\text{H}_2\text{O}$

Ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, is the most commonly used iron coagulant. This solution also breaks down into its hydralysis products. As in the case of alum, ferric sulfate reacts with the natural alkalinity of the water or with added alkaline materials.

Table 3-3 shows some simplified reactions of ferric sulfate in the hydralysis form of $\text{Fe(OH)}_3$. Other hydralysis products of ferric also contribute to water coagulation.
HYPOTHETICAL REACTIONS OF FERRIC SULFATE

\[ \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca}^+(\text{HCO}_3^-)_2 \rightarrow 2\text{Fe(OH)}_3 + 3\text{CaSO}_4 + 6\text{CO}_2 \]

\[ \text{Fe}_2(\text{SO}_4)_3 + 6\text{NaHCO}_3 \rightarrow 2\text{Fe(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 6\text{CO}_2 \]

\[ \text{Fe}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2 \]

\[ \text{Fe}_2(\text{SO}_4)_3 + 6\text{NaOH} \rightarrow 2\text{Fe(OH)}_3 + 3\text{Na}_2\text{SO}_4 \]

\[ \text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{Fe(OH)}_3 + 3\text{CaSO}_4 \]

3.4 Experimental Procedures

3.4.1 Determination of Optimum Coagulation Conditions

Trial determination of coagulant dosage and pH values are made in the laboratory by using a Jar Test Apparatus (Fig. 3-3). The apparatus consists, basically, of a calibrated variable motor (rpm), multiple stirrers, support frame, and applicable beakers.

Tests with combinations of dosages and pH values are required to obtain the optimum or best color removal parameters. The tests also indicate, for the various combinations, the compactness, size, density, sheer strength and compressibility of the flocs. Knowledge of these physical conditions is necessary because the formed flocs are normally removed by gravitational settling and filtration.

Coagulation and flocculation are achieved in the jar test apparatus through rapid mixing followed by gentle stirring.

Rapid mixing, or flash mixing (at 100 rpm), is used to distribute the coagulant throughout the water being treated. This rapid mixing is essential to rapidly and uniformly disperse the coagulant and to promote joining of coagulant metal ions with the
colloidal particles. This mode of mixing, with its associated high turbulent conditions, should be maintained for 30 to 60 seconds, which as previously stated, should be adequate time for the coagulant to hydrolize and join the applicable colloidal particles.

The second step of mixing, gentle stirring, is designed to promote and maintain floc growth or flocculation. This mode of mixing increases the probabilities of particle contact by collision which, in essence, enhances the opportunity of particles to bind and subsequently flocculates. The degree of stirring or agitation must be great enough as to keep the floc particles suspended and in motion, but slow enough as to prohibit the disintegration of newly formed flocs by the prevailing shearing forces.

Because water samples frequently change in physical factors such as pH, alkalinity, and temperature, jar testing is a continuous trial procedure. This procedure is necessary because water varies widely in quality from time to time, and because the coagulation process is so complex.

Determinations of optimum dosage and pH values are made by utilizing the jar test apparatus in a series of exploratory tests. These tests consist of:

1. Approximate optimum pH, i.e., the effects of constant coagulant dosage over a wide range of pH values.
2. Optimum pH, i.e., the effects of constant dosage over a finite range of pH values.
3. Optimum dosage, i.e., the effects of constant optimum pH over a range of coagulant dosages.
The optimum condition for each test is based on the combination of pH and dosage, usually at room temperature (23°C), which produces the best color removal.

Recently, critical research and investigation has been performed on the present operating procedures utilized in jar tests. Bulusu, Kulkarni, Pathak, and Thergaonkar, (27) in India, investigating the effects of time lag on turbidity removal, found that minimum time between coagulant addition and flash mixing proved to be optimum for the formation of flocs as shown in Table 3-4.

**TABLE 3-4 (28)**

<table>
<thead>
<tr>
<th>Time Lag (sec)</th>
<th>Residual Turbidity (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>90</td>
<td>34</td>
</tr>
<tr>
<td>120</td>
<td>36</td>
</tr>
</tbody>
</table>

*Alum Dosage - 40 mg/l, initial turbidity - 150 mg/l

In reference to configuration design, Camp and Conklin (29) determined that various paddle configurations enhance the performance of the jar tests. In his work, Hudson (30) determined, by utilizing Camps and Conklin paddle configurations in conjunction with a controllable coagulant addition device, a series of floc settling velocity curves that can be equated to actual plant data for the purpose of comparing settling basin efficiencies.
In summary, although extensive work has been performed on the design and operation of jar test apparatus, the problem of obtaining applicable data that commensurates with actual plant operations is still elusive. Even though inroads have been made, the problem of not obtaining astute correlation of data seems to stem from the facts that:

1. Water quality varies,
2. Optimum conditions vary with water quality,
3. No concrete jar test operating procedure equated to actual plant operations exists.

3.4.2 Methods of Measuring Color.

Color in water is measured by two different methods:

1. Nessler Tubes
2. Spectrophotometer

Before any measurements can be made, the authenticity of the color must be determined. Color is classified as being either apparent or true. Apparent color indicates not only the color due to colloids in solutions, but also that due to suspended matter. Thus true color of the water can be equated only to the natural color of the water. Apparent color is determined on samples without filtration or centrifugation whereas true color pertains to the residual color left after the filtration or centrifugation.

The Nessler Tube Method relies on visual comparison of the sample with known concentrations of color standard solutions. The color standard solution is made by varying mixtures of Potassium Chloroplatinate, $K_2PtCl_6$, and $CoCl_2$ to encompass color units from 5 to 100 as explained in The Standards Methods for Examination of Water
and Wastewater. This method is used to quantify color intensity of water samples that are yellow-brown in color. When the color is blue or green, the spectrophotometer is used to determine color intensity.

Because of the relatively inexpensive cost in operations, the Nessler Tube Method is used extensively. However, this method does have its disadvantages which can be stated as follows:

1. A visual comparison is required,
2. An accurate set of standard reference solutions is required,
3. It is less precise than spectrophotometric methods.

Therefore, this method should, at most, be used to give only general basic "ballpark" type information on color intensities.

The Spectrophotometer is a measuring device that can make rapid transmittance and absorbance measurements in the near-ultraviolet and visible ranges of the light spectrum.

This instrument is used to obtain quantitative and qualitative analysis of samples when the degree of accuracy requires high resolution.

The degree of accuracy is a function of the choice of wavelength for quantitative analysis of the particular solution. Therefore, a wavelength search must be undertaken. This is important since the sensitivity of analysis and whether or not Beer's Law is followed depends on this choice.

Beer's Law (31) is concerned with light absorption in relation to solution concentration. It states that the intensity of a ray of light decreases exponentially as the concentration of the
absorbing medium increases, or

\[ T = \frac{1}{A} = \frac{I}{I_0} = e^{-kc} = 10^{-kc} \]

where:

- \( T \) = transmittance of light
- \( A \) = absorbance of light
- \( I_0 \) = initial intensity
- \( I \) = measured intensity
- \( k \) = constant for a particular solution
- \( c \) = concentration of a particular solution (ppm)

Thus, if light is absorbed exponentially with concentration over a reasonable and practical range of sample concentrations, the color material is said to conform to Beer's Law. In other words, if the observations of per cent light transmission vs. concentration plot along a straight line on a semilog graph, the material can be considered to obey Beer's Law.

In summary, the above methods indicate two ways of measuring and relating color. When accuracy is required, the Spectrophotometer Method is advantageous. However, if ballpark readings are sufficient, then the Nessler Method should be utilized.
4. RESULTS AND DISCUSSION

A trend showing optimum coagulant and pH conditions used for removing color from surface waters of Central Florida was established by using samples from four lakes and one river. Table 4-1 shows the location and characteristics of water samples evaluated.

**TABLE 4-1**

**SAMPLE SOURCES**

<table>
<thead>
<tr>
<th>Source</th>
<th>pH</th>
<th>Color (ppm)</th>
<th>Alkalinity (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Econ River (located at Union Park - Hwy. 50)</td>
<td>6.35</td>
<td>35.50</td>
<td>26</td>
</tr>
<tr>
<td>Lake Irma</td>
<td>6.25</td>
<td>12.00</td>
<td>10</td>
</tr>
<tr>
<td>Lake Pickett</td>
<td>6.10</td>
<td>6.75</td>
<td>5</td>
</tr>
<tr>
<td>Lake Lee</td>
<td>5.30</td>
<td>3.25</td>
<td>2</td>
</tr>
<tr>
<td>Lake Florida</td>
<td>6.25</td>
<td>23.50</td>
<td>8</td>
</tr>
</tbody>
</table>

The jar tests was used to determine optimum coagulant, coagulant dosage and pH for color removal. A spectrophotometer, Beckman, Model DB-GT was utilized for measurements of color intensity. The percent transmission exhibited by the samples were equated to calibration curves of standard solutions of Tannic Acid and Potassium Chloroplatinate. Since the color in surface water is of humic substances, it would have been preferred to use Humic Acid as the color reference. However, Humic Acids are not readily available. Therefore, Tannic Acid was
chosen as the color reference. Tannic Acid follows similar absorption characteristics to Humic Acid. Theng, Wake, and Posner (32) determined that Humic Acid has the greatest absorption at 250-290 μm. The Tannic Acid exhibited maximum absorption at 266 μm (Fig. 4-1).

The standard Potassium Chloroplatinate color solution was also examined for its maximum absorption. Surprisingly, its maximum absorption was also measured to be approximately 266 μm (Fig. 4-1). Consequently, a calibration curve on semi-log paper showing log percent Transmission vs. Concentrations of Tannic Acid and K₂PtCl₆ was established (Fig. 4-2).

The test results indicate that color removal is effective when optimum conditions are reached. Variations in optimum conditions are dictated by several interrelated factors such as:

1. pH
2. Coagulant Dosage
3. Temperature
4. Chemical Composition of Water
5. Nature of Material in Suspension
6. Mixing Conditions

4.1 Effect of pH

Figures 4-3 and 4-4 show the effect of pH on color removal for the water samples. The graphs clearly indicate that an optimum pH value can be achieved.

The initial pH value of the tested samples were adjusted to read from 4 to 10 by using NaOH or HCl solutions. Optimum color removal occurred in various samples at pH range from 6 to 10, with a majority of the optimum readings occurring between pH 8.25 and 9.75. However,
Fig. 4-1.—Wavelength Search For Minimum Transmission
Fig. 4-2.—Calibration Curve For Tannic Acid and $K_2PtCl_6$
Fig. 4-3.—Effect of Initial pH Values on Color Removal From Surface Water Bodies By Using Aluminum Sulfate
Fig. 4-4.—Effect of Initial pH Values on Color Removal From Surface Water Bodies By Using Ferric Sulfate
the final pH of all the samples tested stayed relatively constant ranging from pH 3.6 to 4.5.

The pH of the water is significant in determining the rate and extent of coagulation. The extent of hydrolysis of both the water and coagulant is predicated on the pH of the water. It is, therefore, understandable that the most important factor in color removal is the optimum pH condition.

A theoretical reaction involving Fe₂(SO₄)₃ and water depicts what is occurring when hydrolyzed in the presence of a high pH:

\[
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} = 2\text{Fe}^{+++} + 3(\text{SO}_4)^{---} + 6\text{H}^+ + 6\text{OH}^-.
\]

The formed hydrolysis products, such as Fe(OH)_3, combine in the sphere of influence of the colloidal particle. This apparent phenomenon causes a reduction in the particle's zeta potential, which previously impeded coagulation from occurring; thus, the following reaction takes place:

\[
\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2 \rightarrow [2\text{Fe(OH)}_3 \cdot (\text{colloidal particle})] + 6\text{H}^+ + 3\text{SO}_4^{--}
\]

Coagulant Coagulation By-products

The above reaction will also take place when Al₂SO₄ is used.

The liberated hydrogen ion is free to either remain in solution or combine with the SO₄ ion. In either case, a reduction of pH will result. The extent of the reduction will depend on the amount of coagulant used and initial pH value.

4.2 Effect of Coagulant Dosage

After establishing the optimum pH, tests were performed to measure the optimum dosage. Various reagent grade dosages of Al₂(SO₄)₃ ⋅ 18H₂O and Fe₂(SO₄)₃ ⋅ nH₂O were used under optimum initial pH. The results of the investigation are shown in Figures 4-5 and 4-6. Initial
dosage, for both coagulants, varied from 20 mg/l to 100 mg/l, whereas the optimum dosages ranged from 33 mg/l to 55 mg/l.

As shown from the graphs, too little or too much coagulant dosage can cause residual color to remain in solution. This is especially true when Ferric Sulfate is utilized as a coagulant. Figure 4-6 shows that deviation from optimum dosage can indeed increase residual color.

Figures 4-5 and 4-6 indicate that for maximum color removal, coagulant dosages of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{nH}_2\text{O}$ range from 33 to 55 mg/l and both coagulants remove approximately the same amount of color. Therefore, selection of a coagulant must become a matter of economics.

Assuming that the maximum dosage required for optimum color removal is 55 mg/l and that the average flow into a treatment plant is 1 MGD, then the amount of chemical coagulant required is 460 lbs/day.

Table 4-2 shows the cost/day of removing the color. The costs are based on the current prices for commercially pure water treatment chemicals. Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is available in granular and liquid form. The granular form contains 17% aluminum as $\text{Al}_2\text{O}_3$ and the liquid form contains about one-half of that. (33) Since the grade of alum is based on percent aluminum, there is no difference between reagent and commercial purity. Ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{nH}_2\text{O}$ contains 20% of $\text{Fe}^{3+}$ or 28.5% FeO$_3$. Commercial grades contain 70-90% $\text{Fe}_2(\text{SO}_4)_3$. (33)
Fig. 4-5. -- Effect of Initial Coagulant Dosage on Color Removal from Surface Water Bodies By Using Aluminum Sulfate
Fig. 4-6.—Effect of Initial Coagulant Dosage on Color Removal From Surface Water Bodies By Using Ferric Sulfate
TABLE 4-2
COAGULANT COSTS FOR REMOVING COLOR

<table>
<thead>
<tr>
<th>Coagulant Commercial Grade</th>
<th>Equivalent Dosage (mg/l)</th>
<th>Cost (34) Dollar/lb</th>
<th>Operating Cost Dollar/Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O})</td>
<td>55</td>
<td>.033</td>
<td>15.18</td>
</tr>
<tr>
<td>(\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O} - 70%\text{ pure})</td>
<td>79</td>
<td>.018</td>
<td>11.70</td>
</tr>
</tbody>
</table>

4.3 Effect of Temperature

To investigate the effect of temperature on coagulation, a test was conducted on a water sample, from Big Econ, cooled to 8°C. The test revealed that flocculation did not occur for the given dosage (50mg/l) of \(\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}\) and pH range (3-9) provided that the temperature of the water during the test remained within 8 to 12°C.

The effect of temperature on coagulation appears to be pronounced. For lower temperatures, the ability of flocculation to occur seems poor or non-existent. It is apparent that as the temperature decreases, the viscosity of the water increases and the mechanism of flocculation becomes inhibited. However, the difficulties that arise from drops in temperature can be overcome by: (35)

1. Conducting the coagulation as near as possible to the optimum pH for that water's temperature.
2. Increasing the coagulant dosage which will increase coalescence probabilities of the particles.
3. Adding coagulation aids such as bentonitic clays or activated silica.
5. CONCLUSIONS AND Recommendations

Results of the investigation indicate that color from surface water was effectively removed by using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ under optimum conditions of dosage and pH. A summary of optimum color removal conditions is found in Table 5-1.

Results of the investigation fosters the following recommendations:

1. Both coagulants are effective in reducing color to satisfy USPHS drinking water standards. However, because ferric sulfate, if not used properly, can add a color residual to the water, it is recommended that aluminum sulfate be used as the coagulant.

2. Because of the wide variations in the optimum conditions, increased investigation on additional sources of Central Florida's surface waters should be undertaken to gain further information on predicting a color removal trend.

3. In dealing with the problems that arise from low water temperatures, Central Florida water supply companies, although not affected, should be aware of the consequences. An indepth study into the effects of temperature on coagulation can nevertheless be beneficial to all parties concerned.

4. The optimum coagulant dosages were determined by using reagent grade chemicals. When conducting the tests for actual plant operation data, commercial grade chemicals should be utilized.
<table>
<thead>
<tr>
<th>Source</th>
<th>Coagulant</th>
<th>Optimum Conditions</th>
<th>Residual Color (ppm)(^a)</th>
<th>% Color Removal(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Econ River</td>
<td>Al(_2)(SO(_4))(_3) \cdot 18H(_2)O</td>
<td>55 mg/l</td>
<td>6.00</td>
<td>9.25</td>
</tr>
<tr>
<td>Lake Irma</td>
<td>Fe(_2)(SO(_4))(_3) \cdot nH(_2)O</td>
<td>55 mg/l</td>
<td>9.75</td>
<td>4.75</td>
</tr>
<tr>
<td>Lake Irma</td>
<td>Al(_2)(SO(_4))(_3) \cdot 18H(_2)O</td>
<td>55 mg/l</td>
<td>9.40</td>
<td>3.75</td>
</tr>
<tr>
<td>Lake Pickett</td>
<td>Fe(_2)(SO(_4))(_3) \cdot nH(_2)O</td>
<td>44 mg/l</td>
<td>9.25</td>
<td>2.25</td>
</tr>
<tr>
<td>Lake Pickett</td>
<td>Al(_2)(SO(_4))(_3) \cdot 18H(_2)O</td>
<td>44 mg/l</td>
<td>8.25</td>
<td>2.00</td>
</tr>
<tr>
<td>Lake Lee</td>
<td>Al(_2)(SO(_4))(_3) \cdot 18H(_2)O</td>
<td>33 mg/l</td>
<td>10.00</td>
<td>0.75</td>
</tr>
<tr>
<td>Lake Florida</td>
<td>Fe(_2)(SO(_4))(_3) \cdot nH(_2)O</td>
<td>55 mg/l</td>
<td>8.25</td>
<td>6.25</td>
</tr>
<tr>
<td>Lake Florida</td>
<td>Al(_2)(SO(_4))(_3) \cdot 18H(_2)O</td>
<td>55 mg/l</td>
<td>9.10</td>
<td>5.25</td>
</tr>
</tbody>
</table>

\(^a\) Reference to tannic acid calibration curve.
LIST OF REFERENCES


   Proceedings of the Society for Water Treatment Examination, 
   13, 1964, p. 316.

   Technology of Water (Czechoslovakia) 1963, p. 57.


   Journal of the American Water Works Association, 59 
   (August, 1962), p. 971. To be cited: "Chemical 
   Aspects of Coagulation".

18. Ibid., p. 972.


   "Chemistry for Sanitary Engineers".


24. Ibid., p. 974.


27. Bulusu, K. R.; Kulkarni, D. N.; Pathak, B. N. and Thergaonkar, 
   V. P. "Significance of Time Lag in the Application of a 
   Coagulant in Jar Test." Environmental Health, 2 (May, 

28. Ibid., p. 236.

29. Camp, T. and Conklin, G. "Towards a Rational Jar Test for 
   Coagulation." Journal of the New England Water Works 
   Association, 84 (September, 1970), p. 325.

30. Hudson, H. E. "Evaluation of Plant Operating and Jar-Test Data." 
   Journal of the American Water Works Association, 65 


35. "Water Quality and Treatment", p. 89.