



Coagulation of organic color with ferric chloride
by C Hunter Nolen, jr

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Environmental Health Engineering
Montana State University
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Abstract:

This study investigates the conditions of pH and ferric chloride dosage required for the removal of organic color from water.

The results of this laboratory study were obtained with the use of a jar testing apparatus. Extensive data were collected and it was found that ferric chloride can be a very effective coagulant for color removal. The data presented in this thesis should provide a useful tool for the operation and design of water treatment facilities when coagulation with ferric chloride is considered.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

This study investigates the conditions of pH and ferric chloride dosage required for the removal of organic color from water.

The results of this laboratory study were obtained with the use of a jar testing apparatus. Extensive data were collected and it was found that ferric chloride can be a very effective coagulant for color removal. The data presented in this thesis should provide a useful tool for the operation and design of water treatment facilities when coagulation with ferric chloride is considered.

INTRODUCTION

Organic color, in natural water supplies, is due primarily to the presence of humic substances, i.e., humic acid, fulvic acid, and humins. Humic substances are undesirable in a potential water supply for a number of reasons including aesthetics, the formation of trihalomethanes and other chlorinated organic substances, utilization of adsorption capacity of activated carbon beds, extension of chlorine demand, and possible transport of organic and inorganic pollutants through water treatment facilities and into the water supply [1].

Coagulation with ferric and aluminum salts is standard treatment for the removal of suspended colloids from water supplies. It has been shown that aluminum sulfate, the most commonly used coagulant for turbidity removal is also effective in color removal [1-6]. The coagulant ferric chloride, in contrast, has been the focus of very few color removal studies. The objective of this research is to determine the effectiveness of ferric chloride in the removal of organic color from water.

This paper deals with the delineation of optimum color removal areas with respect to the operational diagram for ferric chloride coagulation [7]. The independent variables considered are: humic acid (color) concentration, coagulant dosage, and pH. Results for true color removal, apparent color removal, turbidity removal, and electrophoretic mobility are presented.

NATURE OF ORGANIC COLOR

Humic substances are of natural origin, derived from organic material in soil or produced within surface waters and sediments by biological and chemical processes [1]. Schnitzer and Khan [8] characterized them as "amorphous, brown or black hydrophilic, acidic, polydisperse substances of molecular weight ranging from several hundred to tens of thousands." The primary definition of humic substances, however, is operational. They are classified into the three main groups based on their solubilities: (1) humic acid, which is soluble in base, but insoluble in acid; (2) fulvic acid, which is soluble in both base and acid; and (3) humins, which are insoluble in both [9]. Operational definitions are not absolute, however, and humic substances from any single source have a continuous range of solubility, adsorptivity, molecular size, and chemical reactivity [1].

The individual molecules of humic substances are complex as well. The molecules appear to be part aromatic and part aliphatic [10]. There are acidic hydrophilic sites on the molecules which are reactive with cations such as trace metals and the hydrolysis species of aluminum and iron. Also, there are hydrophobic sites which may be responsible for the association between humic substances and certain nonionic, organic compounds [1].

Humic substances contain the following functional groups which affect their stability in water; carboxyl, phenolic, alcoholic, ketonic, quinoniod, and methoxyl. Both the charge density and configuration of the humic macromolecules in solution are affected by pH. Under the pH conditions of most natural waters, humic materials are negatively charged macromolecules (anionic polymers). As the pH is increased, increasing stability results due to dissociation of the functional groups and a resulting increase in the magnitude of the negative charge on the color molecules [3].

THEORY OF COAGULATION

Colloidal particles range in size from about 1 to 100 nanometers and are characterized by large surface area and very slow settling rates [11]. The surface of a colloidal particle tends to acquire an electrostatic charge due to the ionization of surface groups and the adsorption of ions from the aqueous phase. Most colloids in water develop a negative primary charge but a colloidal dispersion does not have a net charge. Charges on the particles are counterbalanced by charges in the solution phase. This need for electroneutrality results in an electrical double layer which consists of the charges on the particle and an equivalent excess of counter ions which accumulate in the water near the surface of the particle. Forces of diffusion and electrostatic attraction spread the charge in the water around each particle in a diffuse layer [12].

The stability of colloids in water is due primarily to their electrostatic characteristics. When two colloidal particles with similar charge approach each other, their diffuse layers interact and produce a repulsive force. The repulsive force is counterbalanced to some degree by an attractive van der Waals force, and the resulting potential of both the repulsive and attractive forces often forms an energy barrier which prevents aggregation [13]. The process of overcoming the energy barrier and allowing aggregation to occur is called coagulation.

O'Melia [12] presents four distinct mechanisms of coagulation. These are: (1) compression of the diffuse layer (DLVO theory); (2) adsorption to produce charge neutralization (adsorption-destabilization); (3) enmeshment in a precipitate (sweep coagulation); and (4) adsorption to permit interparticle bridging. In water treatment, coagulation of colloids

is probably accomplished by adsorption-destabilization, sweep coagulation, or both simultaneously.

In the adsorption-destabilization process, metal cations such as Fe(III) and Al(III) are hydrated in water and are present as aquocomplexes. Hydroxo-metal complexes are formed and are readily adsorbed at interfaces. Because of the adsorption of oppositely charged species, the colloids become destabilized or neutralized, allowing aggregation to occur. Stoichiometry between the colloidal surface area and coagulant dosage exists, and overdosing results in charge reversal, i.e., restabilization [12].

In sweep coagulation, the dosage of the aluminum or iron salt is large enough that a sufficient degree of oversaturation occurs to produce a rapid precipitation of the metal hydroxide. As the precipitate settles, it enmeshes the colloidal particles and sweeps them from the solution.

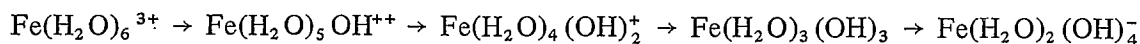
Coagulation of Color

The mechanisms that are responsible for the removal of humic substances when salts of aluminum or ferric iron are used as coagulants are often uncertain but may include direct precipitation of humic substances by dissolved iron species (sometimes described as a ferric or iron humate precipitate), adsorption of humic substances on solid ferric hydroxide $[\text{Fe}(\text{OH})_3 (s)]$, or a combination of the two. In this paper, "precipitation" describes the formation of $\text{Fe}(\text{OH})_3 (s)$ as well as the formation of a solid phase that is composed of previously soluble species of iron and humic acid. "Adsorption" is used to describe the reaction between solid phase ferric hydroxide and the soluble humic acid molecules [1].

AQUEOUS CHEMISTRY OF Fe(III)

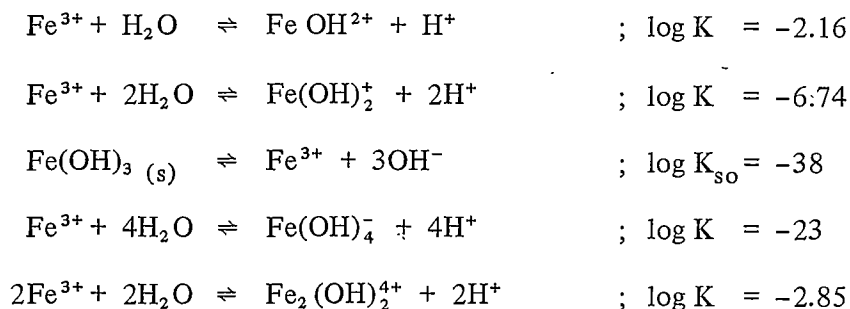
To understand the ability of ferric chloride to destabilize colloidal particles, it is necessary to consider the chemistry of Fe(III). O'Melia [12] stated that all metal cations are hydrated in water and that simple species such as Fe^{3+} do not exist. Rather, Fe(III) is present as part of aquocomplexes such as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Ions or molecules, such as water molecules, which are bonded to a central metal atom are termed ligands.

The addition of an Fe(III) salt to water in concentrations less than the solubility limit of the metal hydroxide leads to the formation of soluble monomeric, dimeric, and small polymeric hydroxo-metal complexes, in addition to the free aquo-metal ion. The hydrolysis of Fe(III) can be described as a stepwise consecutive replacement of H_2O molecules in the hydration shell by OH^- ions. For example:



The OH^- ions are also ligands.

When writing the hydrolysis reactions of a metal ion, it is common to omit the H_2O ligands for brevity. For example, the monomeric hydroxo-metal complex $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ is written as $\text{Fe}(\text{OH})^{2+}$. For Fe^{3+} in pure water, Snoeyink and Jenkins [9] present the following equilibria:



The effect of these hydroxo-complexes on solubility is dramatic and is most conveniently illustrated by using a log concentration diagram or pC-pH diagram (Figure 1). Figure 1 is the most commonly encountered stability diagram when ferric salts are used in coagulation and is developed from purely thermodynamic equilibria. The interior portion of the diagram indicates the area in which precipitation of $\text{Fe}(\text{OH})_3 (s)$ may theoretically occur. Figure 2 is a superposition of the areas of sweep coagulation, adsorption-destabilization, and restabilization, with charge reversed, on the operational diagram. The locations of these zones have been developed in previous work on coagulation of turbidity with ferric chloride [7]. The boundaries and locations of color removal areas are slightly different as will be shown later in this paper.

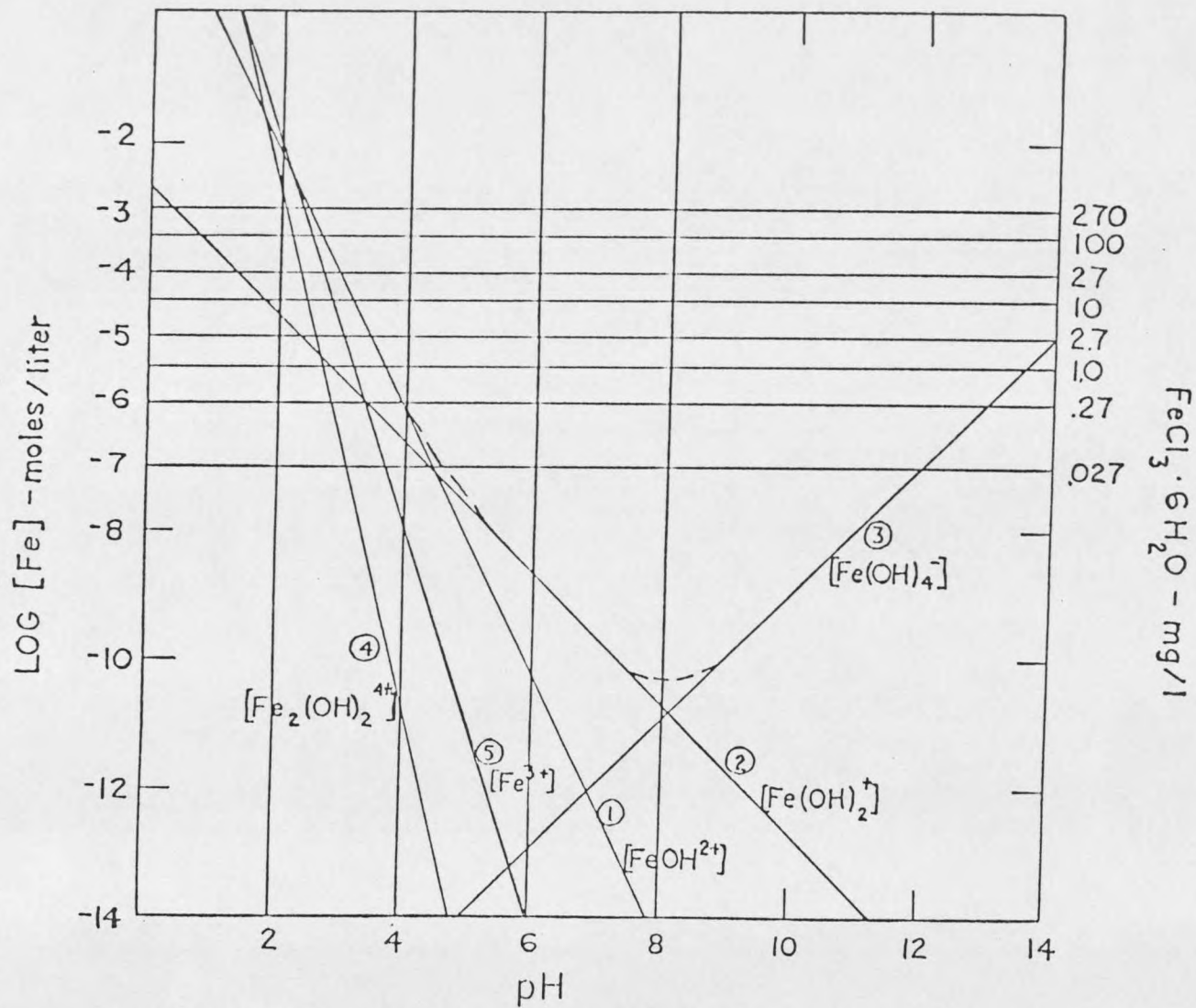


FIGURE I : Fe(III) Log Concentration Diagram

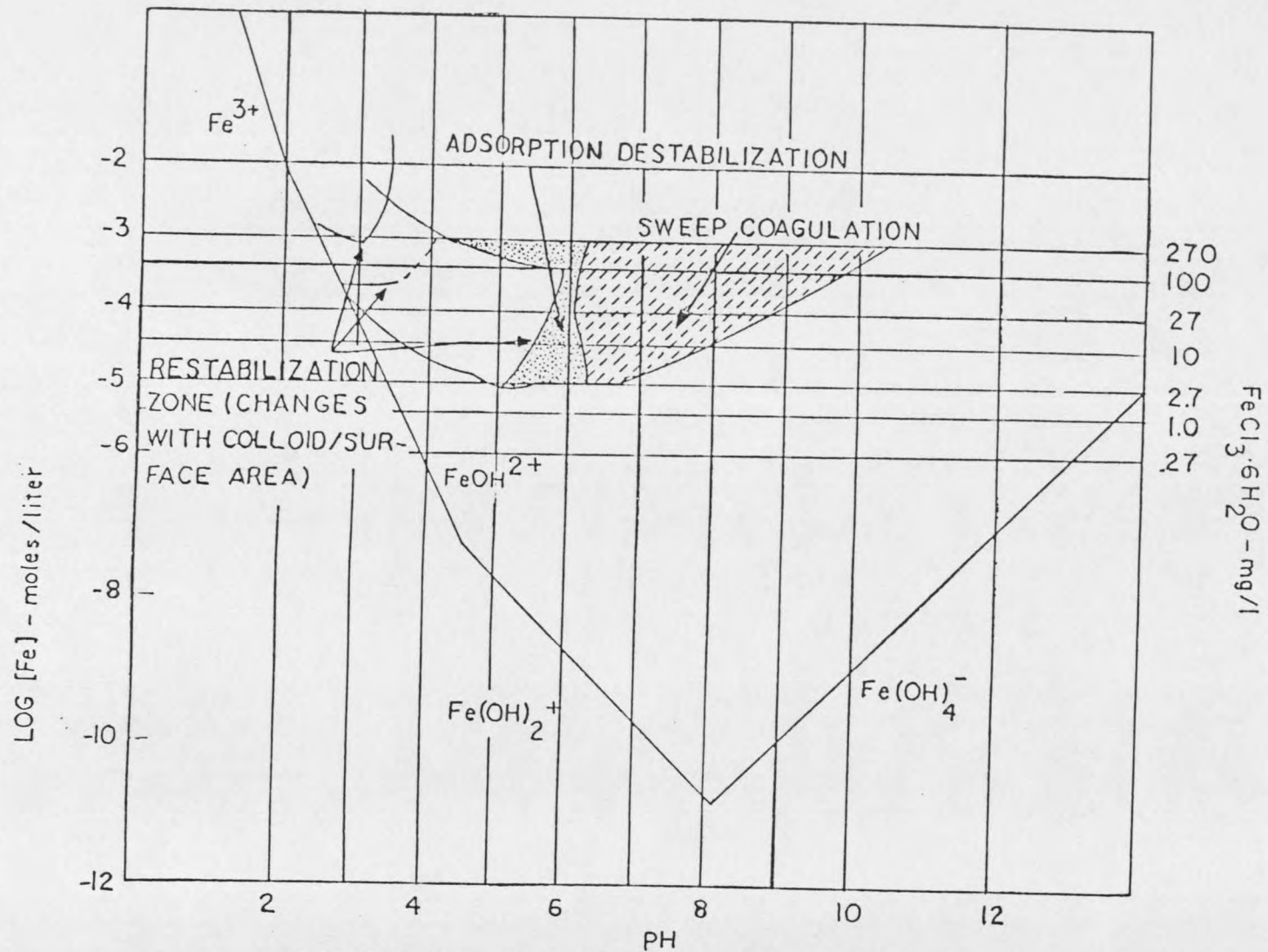


FIGURE 2 : IRON (III) COAGULATION DIAGRAM

MATERIALS AND METHODS

The most critical factors influencing the efficiency of coagulation for color removal are pH, coagulant dosage, and concentration of color [14]. The pH controls both the speciation of the inorganic coagulant and the charge on the organic color molecule.

Synthetic waters were prepared containing the desired concentrations of humic acid, turbidity, and alkalinity. Five solutions of different color concentrations plus turbidity and three varied color solutions without turbidity were used in the color removal tests. Tech Grade humic acid* was used for color, and turbidity, in the range of 27-30 turbidity units (TU), was obtained through the addition of the colloid, Min-U-Sil-30.** Alkalinity was added to the distilled water in the form of NaHCO_3 . Table 1 shows the constituents of the raw water solutions.

Table 1. Color Solutions.

Color Designation	Humic Acid Concentration	True-Color (CU)	Min-U-Sil	NaHCO_3 .2N
Low	4 mg/l	100	1 g/l	5 ml/l
Med. Low	8.2 mg/l	225	1 g/l	5 ml/l
Medium	20 mg/l	500	1 g/l	5 ml/l
Med. High	28.8 mg/l	700	1 g/l	5 ml/l
High	37.5 mg/l	1000	1 g/l	5 ml/l

Standard color solutions without turbidity are similar to those for Low, Medium, and High concentrations, without Min-U-Sil.

Extensive jar testing was conducted so that areas of optimum color removal could be defined. A Phipps-Bird jar testing apparatus with a six unit mixer was used for the tests. Ferric chloride was added during a rapid mix period of one minute at 100 rpm. This was

*Aldrich Chemical Company, Inc., Milwaukee, WI 53233.

**Pennsylvania Glass Sand Corporation, 3 Tenn Center, Pittsburgh, PA 15235.

followed by a slow mix, flocculation stage of 20 minutes at 24 rpm. Sedimentation was then allowed to occur over a 2 hour period.

True color, apparent color, pH, and turbidity values were obtained for all samples. pH values were taken during the slow mix period. True color, apparent color, and turbidity readings were taken after the slow mix and at the end of the 2 hour settling period. Color readings were made with an Hitachi-Perkin Elmer, Coleman 139, Spectrophotometer. The wave length used was 422.2 nm with a slit size of 2.36 mm. Percent transmittance was converted to color units with the use of a standardization curve. Turbidity readings were made with a HACH model 2100 turbidimeter.

In disagreement with the procedure for color measurement presented in Standard Methods [15], the pH of the sample was not adjusted to a common value prior to spectrophotometric analysis. In coagulation experimentation, it is impossible to adjust the pH for color measurement without possibly inducing further coagulation thus interfering with the accuracy of the results.

After turbidity readings and apparent color readings were taken, the samples were centrifuged for 5 minutes at 7500 rpm to remove excess turbidity which could interfere with true color readings. A decrease in color of 90% of the original measurement within the 2 hour settling period was considered to indicate effective color removal. The electrophoretic mobility (EM), which is proportional to the zeta potential or particle charge, was determined with the use of a "Zeta-Meter." Electrophoretic mobility is a measure of the velocity at which particles traverse a measured path in a DC current at a specific voltage.

Because of the variation in initial color concentrations of the different waters tested, removal areas on the operational diagram are defined by percent removal, not the magnitude of the residual color.

For each of the raw waters tested, approximately 50-80 jars were run. This adds up to a total of approximately 500 jars in a series of 83 jar tests. Figure 3 shows the operational

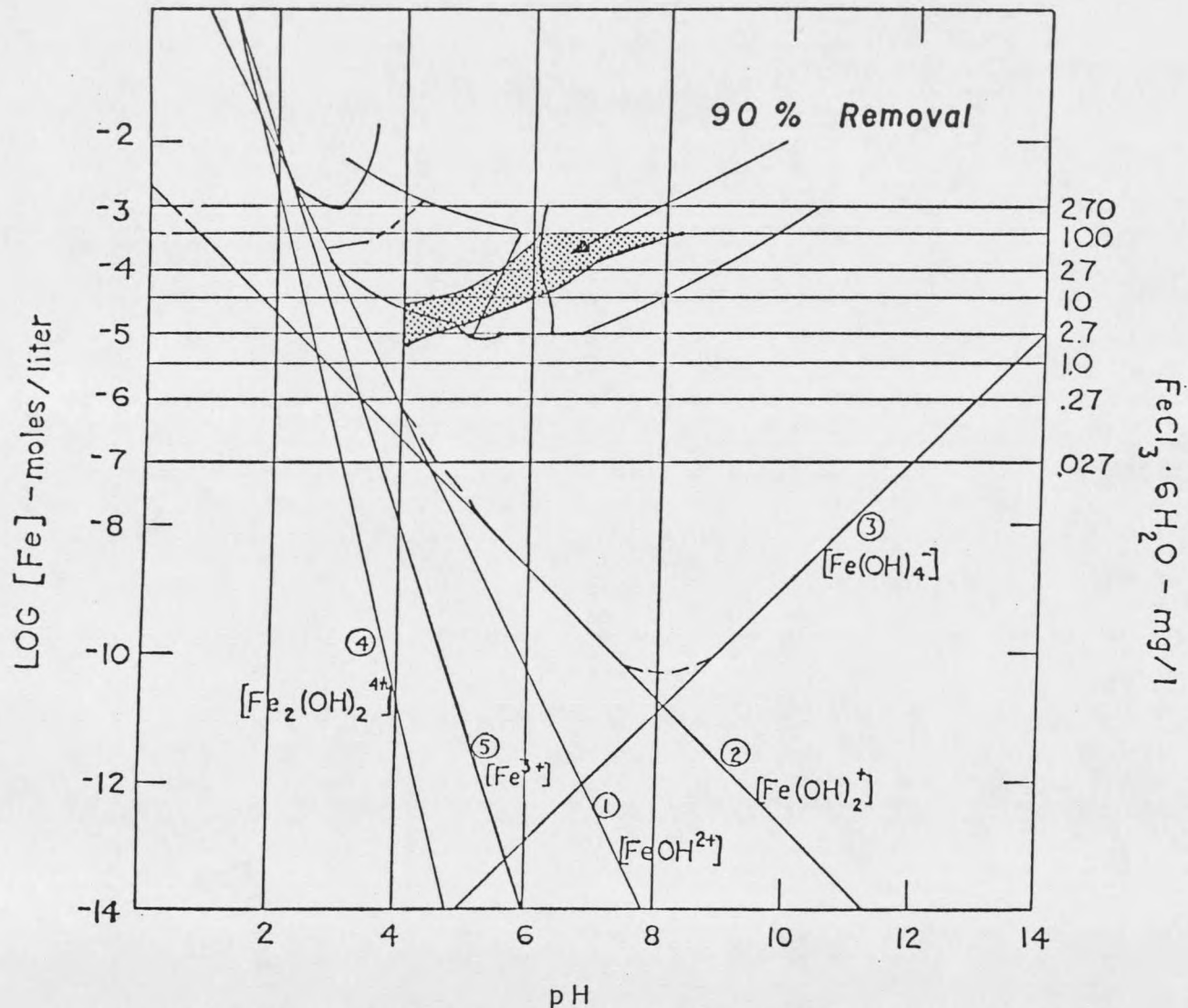


FIGURE 3 : Color Removal Domain – Initial Color = 100 CU, Turbidity = 27-30 TU.

diagram for ferric chloride with the 90% color removal area for a water containing a color concentration of 100 color units (CU) and turbidity in the range of 27-30 TU. Figure 4 is an expanded form of part of the operational diagram. Shown are percent removal values used to delineate the optimum color removal area. This gives an example of the number of points used to define the color removal domains. Similar data were obtained for all of the suspensions tested. Because the boundaries and the extent of the color removal areas can be better seen on the expanded diagram, it will be used in the following presentation of results.

The delineation of color removal areas are restricted to pH values not less than 4 and ferric chloride dosages not greater than 100 mg/l. Data outside of these ranges would be of little use in practice.

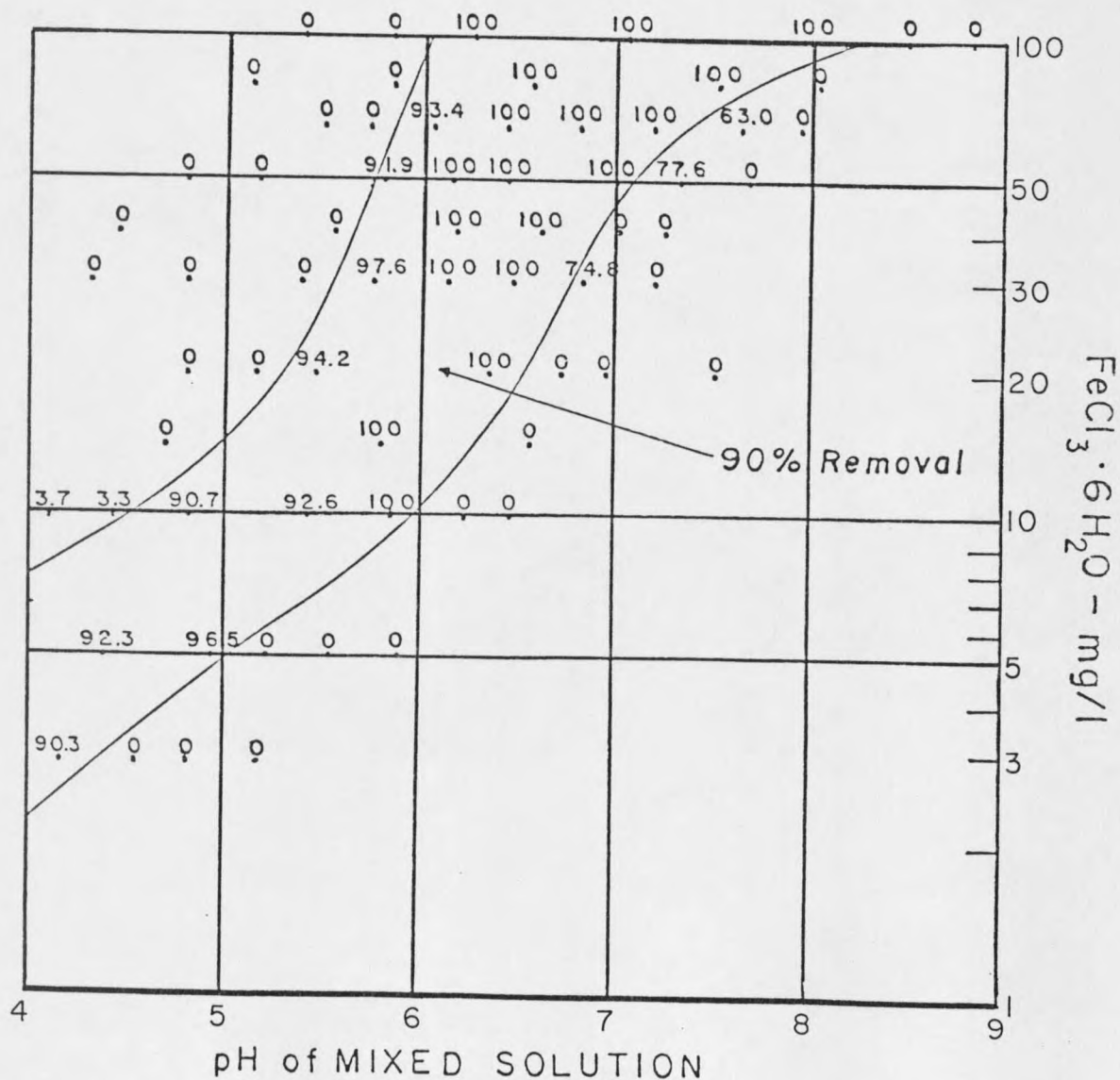


FIGURE 4: Data Points and Corresponding Percent Color Removal Values- Initial Color = 100 CU, Turbidity = 27-30 TU

RESULTS AND DISCUSSION

Color Removal

In this research, ferric chloride was found to be very effective in the removal of color from water. In cases where the dosage of the coagulant was either too low or too high for color removal, however, the color of the water was actually increased as a result of the addition of Fe(III). It is therefore important that correct dosages of ferric chloride be used in order to achieve color removal and to prevent an actual increase in the color of the water.

The area of 90% color removal on the operational diagram varies significantly depending on the initial concentration of color. First, samples which contained color but no turbidity are considered. Three different color concentrations were used, and the optimum removal areas for each were delineated.

Numerous studies [1,2,3] have shown that when alum is used in coagulation, optimum color removal occurs in the range of pH 5 to 6.5. Ferric chloride, on the other hand, can be effective over a wider pH range [16]. Figure 5 shows the color removal domain for a solution containing a color concentration of 100 CU. Ninety percent color removal occurred over a range from pH 4 to pH 8.8. The area of highest color removal occurred in the range of pH 6.1 to 8.8 with ferric chloride dosages greater than approximately 10 mg/l. The dominant removal mechanism here is probably the adsorption of color molecules on ferric hydroxide floc. The presence of an upper boundary for color removal probably results from particle restabilization, i.e., charge reversal. This can be viewed as an excess of positively charged ferric hydroxide interacting with the negatively charged color molecules. The lower boundary for coagulation is probably a function of the magnitude of charge on

