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Research paper

Finding the Reaction Constant Between Humic Acid and Metal Ions by Fluorescence Quenching Effect

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Abstract

Humic acid was used as the removal target for evaluating the coagulation efficiency in this study. When the metal ions mix with humic acid solution, a Fluorescence quenching effect may be observed conditionally. This effect can be described by Stern-Volmer linear equation which can be used for quantifying the quenching constant (K_Q) of the Fluorescence quenching effect. In addition, the result of the quenching constant (K_Q) was used to explain the electron-neutralization capability of the metal ions at different pH. The results indicated that there is no significant Fluorescence quenching effect between the additions of monovalent Na^+ ion, divalent Ca^{2+} and humic acid. Otherwise, when pH of the $FeCl_3$ solution was between 4.5 and 5.5, fluorescence quenching effect obviously occurred. The maximum K_Q value was found to be 305,990 at pH 5. It means that the higher K_Q value is, the better complex reaction between humic acid and aluminum salts will be. Through the K_Q value study, the optimum pH can be quantified when humic acid solution is reacted with ferric ion.

Keywords: *Humic acid, Fluorescence quenching effect, Complex reaction, Titration.*

1. Introduction

Chemical coagulation is often used in water treatment process. The main purpose of the coagulation is to make small particles colliding into each other to become large particles. There are many different types of coagulants due to the various uses. In drinking water treatment, polyaluminum chloride, aluminum sulfate and ferric chloride are commonly used metal salt coagulant. Many studies have proposed that coagulation procedures can be used to remove humic acid [1]. Humic acid contains an aromatic heterocyclic structure. If a humic acid molecule is excited by absorbing a specific radiation, it will eventually release the absorbed energy to the ground state. Normally, the energy is releasing in the form of fluorescence. Therefore, after radiation exciting process, a fluorescence emission phenomenon occurs in the humic acid solution. The fluorescence intensity is linear proportion to the humic acid concentration [2]. Fluorescent technology is often used to measure the concentration of humic acid in natural waters [3-5]. The carboxyl and phenolic functional groups of humic acid contains hydroxyl bonds, which are the main bonding position with the metal ions. If the humic acid and metal ions are bonded to each other, the fluorescence intensity of humic acid will be weakened. This phenomenon is known as the fluorescence quench effect.

The fluorescence quenching effect can involve many kinds of intermolecular interactions, including excitation reaction, energy transfer, charge transfer and static or dynamic collision extinguishment. The interaction between humic substances (Y) and quencher (M) can be described as follows:

$$M + Y = M–Y \quad (1)$$

With the corresponding quenching constant K_Q:

$$K_Q = \frac{[M-Y]}{[M][Y]} \quad (2)$$

The total concentration of the humic acid Y_t can be expressed as a sum of free Y_f and bound to humics Y_b:

$$Y_t = Y_f + Y_b \quad (3)$$

By substituting Eq (2) into Eq (3) we obtain:

$$Y_t = Y_f + Y_f K_Q[M] \quad (4)$$

$$\frac{Yt}{Yf} = 1+K_Q[M] \quad (5)$$

As far as fluorescence intensity ratio of the initial substance and fluorescence in the presence of quencher, F_0/F is proportional to Y_t/Y_f then Eq (5) can be modified to:

$$\frac{F_0}{F} = 1+K_Q[M] \quad (6)$$

However, for practical application the equilibrium concentration of quencher (M) can be replaced by the total concentration M as the concentrations of the M bound to humic. The K_Q is the quenching constant of Stern-Volmer formula [6-7].

The quenching constant value (K_Q) in Stern-Volmer equation can be used as the value of the equilibrium constant in a complex reaction [8-9]. Therefore, in this study, the fluorescence quench effects of complex reactions (i.e., humic acid complexes with aluminum ions) will be quantified, analyzed and discussed under the conditions of various pH and different metal ion salt addition. By using Stern-Volmer linear equation, the value of K_Q will be quantified and

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obtained. The value of K_Q will be used to evaluate the capability of the coagulant to neutralize the electron in the solution. Finally, the optimum coagulant dosage and pH will be found.

2. Experimental Method

2.1Preparing Humic Acid Solution

The method is based on the preparation method of Nakashima [10]. Initially, 200 mg of humic acid (i.e., the product of Sigma-Aldrich) was dissolved in 1 L of 0.1 M sodium hydroxide solution. Then, the solution was stirred at room temperature for 7 days. After the humic acid was completely dissolved, the humic acid solution was neutralized with 0.1 M hydrochloric acid. After quantifying the humic acid concentration with a total organic carbon (TOC) analyzer, the stock solution was diluted to 100 ppm for the further use.

2.2. Metal Chloride Complexes with Humic Acid Experiment

When metal ion is added into the humic acid solution, the reaction conditions are controlled, for example, changing ferric additional amounts and pH values. Hence, the results of the experiments are compared for the discussions. In this study, the humic acid concentration is first diluted to 6 ppm and the diluted solution is used as raw water. For each test, equal amount of raw water (i.e., 1 liter) is tested under a specific reaction condition. The reaction pH is set in the range between 3 and 10 and metal ion concentration is set between 0 and 6×10^{-5} M. To adjust the pH of the test water, 0.1M NaOH or HCl is used. After stirring test water for 10 minutes, samples are taken and analyzed with a fluorescent spectrometer (i.e., HITACHI, F-2000). The excitation wavelength and the emission wavelength (λex) are set to 375 nm and 445 nm to measure the fluorescence intensity.

3. Results and Discussion

No Figure 1 shows the relationship between the fluorescence intensity and the concentrations of the humic acid. According to Figure 1, it is found that the fluorescence intensity (F) is linear proportional to the humic acid concentration (C) when the concentration is below 10 ppm. The humic acid concentration used in this study is 6 ppm, which is less than 10 ppm so that the quantitative relationship is applied.

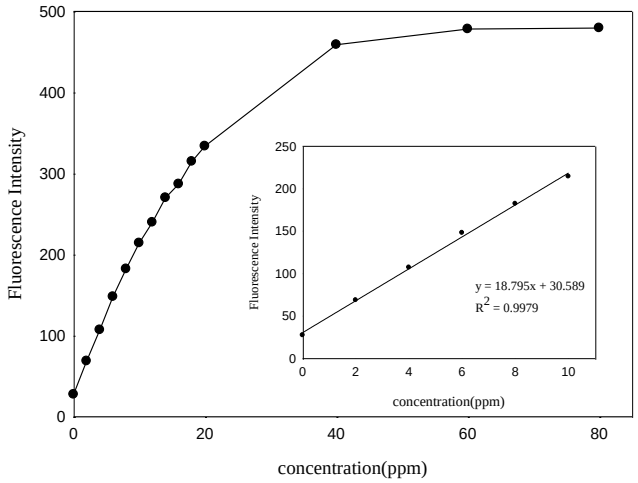

Figure 1: Relationship between fluorescence intensity and humic acid concentrations

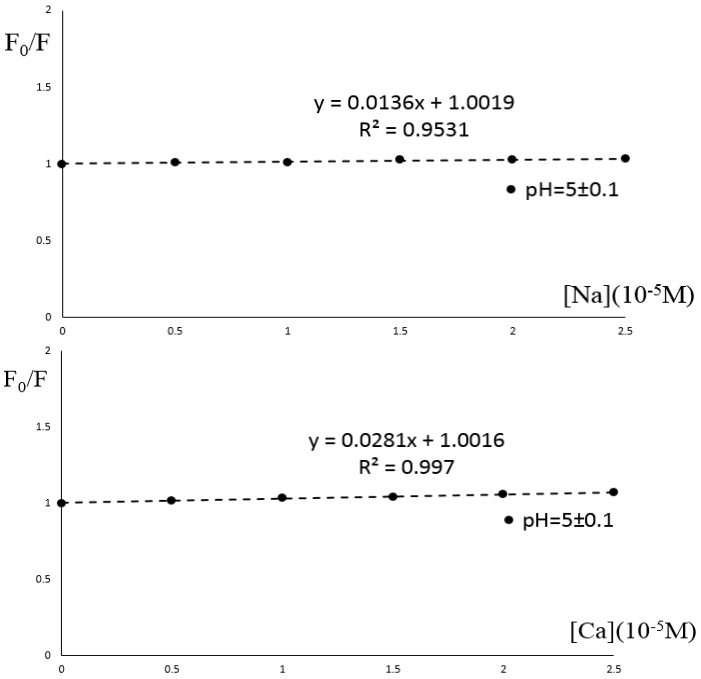

Figure 2: A plot of Fluorescence intensity ratio at various Na^+ and Ca^{2+} concentration.

In Figure 2, shows that the added Na^+ and Ca^{2+} chloride (M=0-5×10^{-3}M) reacts with humic acid under pH=5, whose data followed the Stern–Volmer formula.

$$\frac{F_0}{F} = 1+K_Q[M]$$

The slope of this linear relationship is the extinction reaction constant (K_Q) of the electrical neutralization reaction. According to Equation 1, the fluorescence intensity ratio can be calculated from the fluorescence intensity of the raw water (F_0) divided by that of the Na^+ and Ca^{2+} ions in different concentration (F). It was found that the quenching constant (K_Q) were obtained at 1,361 and 2,805 for Na^+ and Ca^{2+} ions. This observation indicates that the fluorescence quenching effect (or electron-neutralization capability) is not work for Na^+ and Ca^{2+} ions.

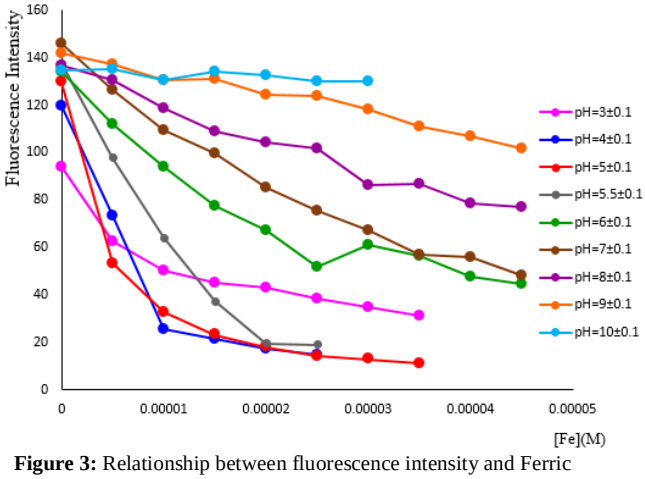

Figure 3: Relationship between fluorescence intensity and Ferric Concentration

According to the data of Figure 3, the fluorescence intensity hardly changes under some pH ranges (e.g.., 3~4 and 9~10). When the solution pH is 3~4, both the Ferric ions added to the solution and the carboxyl groups on humic acid surface are positively charged so that the humic acid can't complex with Ferric ions due to the isotropic charge repulsion reason. Hence, fluorescence intensity was not affected by changing the Ferric chloride concentrations. In contrast, when solution pH is 9~10, both hydroxide ions in the

solution and the carboxyl groups on humic acid surface are negatively charged but the dominate species in the solution is the hydroxide ions. Hence, the ferric ions prefer to react with the hydroxide ions to form a highly hydrolyzed product, such as $Fe(OH)_3$

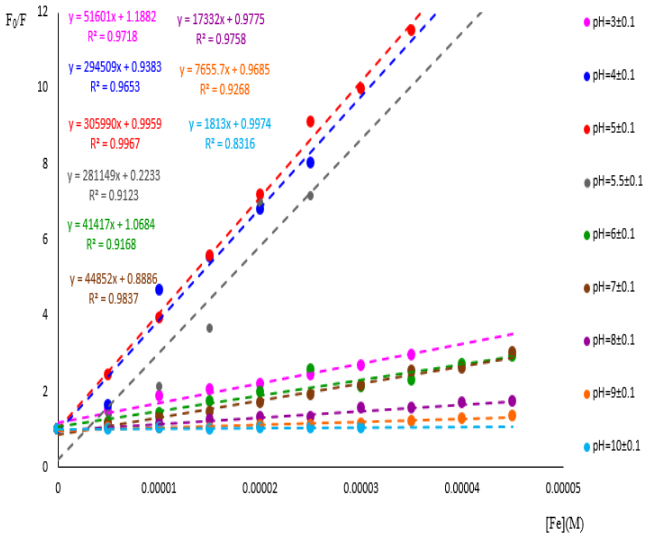

Figure 4: A plot of Fluorescence intensity ratio at various Ferric concentration.

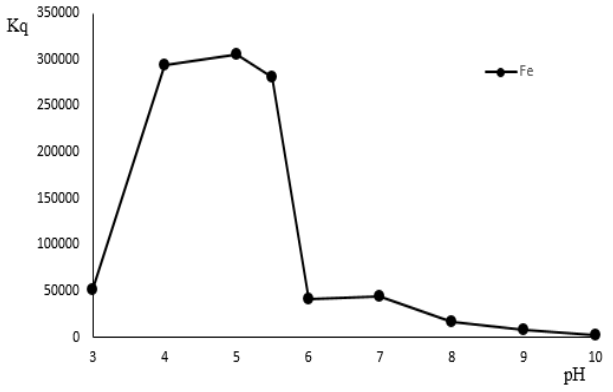

Figure 5: A plot of quenching constants (K_Q) at different pH values.

The data of Figure 3 were taken for calculating the fluorescence intensity ratio at each pH value. Then, the ratio values were plotted against the Ferric concentrations and the slope or extinction reaction constant (K_Q) results was shown in Figure 4. Then, the K_Q values were plotted against pH values and the results were shown in Figure 5. In Figure 5, a maximum value was found at pH 5 and the K_Q value is 305,990.

4. Conclusion

1. When humic acid concentrations of the test water were the same, the waters were tested with adding various amounts of metal ions. The metal ions concentration increased, the fluorescence intensity decreased. This phenomenon is a fluorescence quenching effect. However, when the metal ions concentration was added to a certain concentration, the fluorescence intensity did not further decrease. This phenomenon demonstrated that the complex positions of the functional group on humic acid surface were limited and could not infinitely react with increasing aluminum ions.
2. When no metal ions were added in the humic acid solution, the fluorescence intensity of the solution increased with pH value. When the solution was acidified, the pH was low and the hydrogen ion (i.e., an electron-withdrawing ion) increased. The humic acid functional group was going to bond with hydrogen ions which weakening the fluorescence intensity. Hence, the higher the pH value of humic acid solution is, the stronger the fluorescence intensity will be.
3. After adding various ferric ion concentrations into the humic acid solutions, When solution pH was either 3 or 6~10, the fluorescence intensities at certain pH condition were almost the same. However, when the solution pH was between 4 and 5.5, the fluorescence intensity decreased with the increasing ferric ion concentrations. For example, when the solution pH was between 4 and 5.5, the added Ferric concentration reached 1×10^{-5} M. If the ferric concentration was further increased, the fluorescence intensity was continuously decreasing. This observation indicates that the fluorescence quenching effect is the most obvious effect at pH 4-5.5.
4. Through the Stern–Volmer formula, it was found that the maximum quenching constant (K_Q) was obtained at pH 5. This result demonstrated that the best coagulation capacity to neutralize the electron charge of humic acid was found at such condition.

Acknowledgments

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