Environment Protection Engineering

Vol. 46 2020 No. 2

DOI: 10.37190/epe200202

FUNG HWA CHI[1], WEN PO CHENG[2], RUEY FANG YU[2], ZHAO FENG CHEN[2]

ELECTRICAL NEUTRALIZATION ABILITY OF POLYALUMINUM CHLORIDE (PACl) COAGULANTS WITH DIFFERENT OH^{-}/Al^{3+} RATIOS BY FLUORESCENCE QUENCHING EFFECT

The electrical neutralization ability of polyaluminum chlorides (PACls) with respect to humic acid was investigated by the fluorescence quenching method. The Stern–Volmer constant (K_q) at various pH and coagulation doses was determined for polyaluminum chlorides (PACl-*B*) of various basicities (B, $B = [OH^-]/[Al]$). The experimental results show that under acidic conditions, the order of K_q values of PACl-*B* is PACl-2.5 > PACl-2.3 > PACl-1.5 > $AlCl_3$. In solutions of pH = 7, the order of K_q values is PACl-1.5 > PACl-2.3 > PACl-2.5 > $AlCl_3$. When pH > 7, aluminum ions are rapidly hydrolyzed, thus PACls of various basicities generally do not show capacity for electrical neutralization with humic acid. At pH = 6, all PACls-*B* obtain the maximum K_q values, indicating that humic acid and PACl-*B* coagulation process is less affected by H^+ or OH^- ions, and produces the best electrical neutralization ability. Compared to the past method of using surface potential as a means of determining the ability of neutralization of coagulation, the results of this study show that the K_q value of the quenching effect can reduce the experiment complexity.

1. INTRODUCTION

Polyaluminum chloride (PACl) is broadly used for treating industrial wastewater or purifying drinking water. In PACl, polymeric aluminum or high valence aluminum species (i.e., Al_{13} species, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) can resist the interferences of the background ions in the solution and directly react with particles in the solution to neutralize the electron charge of particles. Traditionally, the aluminum species distribution in PACl coagulant was usually analyzed by a ferron test [1]. Depending on the reaction time between ferron reagent and aluminum species, soluble aluminum species can be

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[1] Department of Environmental Engineering, Kun Shan University, No.195 Kunda Rd., YongKang District, Tainan City 710, Taiwan, R.O.C.

[2] Department of Safety, Health and Environmental Engineering, National United University, Miaoli, Taiwan 360, corresponding author W.P. Cheng, e-mail address: cwp@nuu.edu.tw

operationally defined as monomeric, fast-reacting polymeric, or slow-reacting colloidal species denoted simply as Al_a, Al_b, and Al_c, respectively. The previously discussed Al_{13} was identified as a major Al_b product. The Al-ferron method was not only used for identifying aluminum formats, but it was also the only fast method that was capable of identifying the aluminum format in a water treatment process [2]. Hence, the Al-ferron method gradually became the major method for aluminum species identification in the aluminum hydrolysis solution [3]. Higher percentages of polymeric aluminum species (Al_b) in the PACl can increase the ability of electrical neutralization and enhance the coagulation efficiencies in water treatment processes [4, 5]. Therefore, understanding how the composition of aluminum species affects coagulation has always been a topic of discussion.

Humic acid (HA) is an organic substance and commonly exists in natural water and soil. HA is usually produced from the dead body of animals or plants which are gradually broken down or catabolized by microorganisms. Humic acid accounts for most of the organic matter in natural water and does not have a definite molecular structure. However, many scholars believe that the functional groups of HA such as carboxylic acid and phenolic groups can react with metal ions so that the fate of the metals in the environment is also affected by HA [6]. The existence of HA not only affects the color and smell of water but also produces toxic disinfection by-products, such as organic chlorinated compounds (e.g., trihalomethanes, haloacetic acid). These by-products create a potential threat to human health thus it is important to remove humic acid from drinking water [7]. Many authors proposed that coagulation procedures can be used to remove humic acid [2–4, 6, 7]. Humic acid contains an aromatic heterocyclic structure. If its molecule is excited by absorbing specific radiation, it will eventually release the absorbed energy to the lower electronic energy level. Normally, the energy is released in the form of fluorescence. Therefore, after irradiation, fluorescence occurs in the humic acid solution. The fluorescence intensity is linearly proportionate to the humic acid concentration [8]. Fluorescent technology is often used to measure the concentration of humic acid in natural waters [9–11]. The carboxyl functional groups of humic acid are the main bonding positions with metal ions. According to Jin [12], pK for carboxyl groups is 4–6. Therefore, pH also affects the physicochemical properties of humic acid in water [13], at lower pH (i.e., $5 < pH < 6$), it will make humic acids easier to react with metal ions to become electrically neutral. Kazpard et al. [14] suggested that at low aluminum concentration, hydrolyzed aluminum species bind selectively to carboxylic groups at pH 6. If humic acid molecules and metal ions are bonded to each other, the fluorescence intensity will be reduced. This phenomenon is known as the fluorescence quenching 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:

$$\mathrm{M} + \mathrm{Y} = \mathrm{M{-}Y} \tag{1}$$

with the corresponding equilibrium constant or Stern–Volmer constant K_q

$$K_q = \frac{[\mathrm{M{-}Y}]}{[\mathrm{M}][\mathrm{Y}]} \tag{2}$$

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

$$Y_t = Y_f + Y_b \tag{3}$$

By substituting eq. (2) into eq. (3) we obtain:

$$Y_t = Y_f + Y_f K_q[\mathrm{M}] \tag{4}$$

$$\frac{Y_t}{Y_f}1 + K_q[\mathrm{M}] \tag{5}$$

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, equation (5) can be modified to:

$$\frac{F_0}{F} = 1 + K_q[\mathrm{M}] \tag{6}$$

where F, F_0 are the fluorescence intensities in the presence and without a quencher, [M] is its concentration, and K_q is the Stern–Volmer constant [15, 16].

On the other hand, the complex-formation titration method [17] may be used. The complex reactivity can be evaluated by finding the effective stability constant K'_{MY}. Like the Stern–Volmer formula, when humic acid (Y) reacts with metal ions (M), the complex reaction can be described as equation (1). The equilibrium constant is

$$K_{\mathrm{MY}} = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]}$$

It is known as the primary reaction. However, the reactants M and Y and the reaction product MY may react with other species in the solution. For example, metal ions M may react with $\mathrm{OH^-}$ to form $\mathrm{M(OH)}_n$. This is known as the hydroxyl complex effect, which causes side effects. The side effect's reaction coefficient ($\alpha_{\mathrm{M(OH)}}$) is given by

$$\alpha_{\mathrm{M(OH)}} = \frac{[\mathrm{M}']}{[\mathrm{M}]} = \frac{[\mathrm{M}]+[\mathrm{MOH}]+\ldots+[\mathrm{M(OH)}_n]}{[\mathrm{M}]} \tag{7}$$

where [M′] is the total concentration of metal ions present in various alkali forms. [M] is the initial concentration of metal ions which can react with the humic acid Y.

Y will react with H^+ ions in the solution to form HY, H_2Y, …, H_nY. This is known as the acid effect. It is evaluated by the acid effect coefficient ($\alpha_{\mathrm{Y(H)}}$)

$$\alpha_{\mathrm{Y(H)}} = \frac{[\mathrm{Y}']}{[\mathrm{Y}]} = \frac{[\mathrm{Y}]+[\mathrm{HY}]+[\mathrm{H_2Y}]+\ldots+[\mathrm{H}_n\mathrm{Y}]}{[\mathrm{Y}]} \tag{8}$$

where [Y′] refers to the total concentration of HA present in various acid forms. The [Y] is the initial concentration of HA which can react with the metal ions (M).

MY may react with H^+ and OH^- ions in the solution so that mix complex effects occur but such mixed complexes are mostly unstable and are negligible.

In the complex formation titration experiment, both humic acid Y and metal ions M often exist in many forms in the solution. When the primary reaction reaches equilibrium, humic acid, metal ions, and the reaction products of various forms are also balanced. The balance constant of each component concentration (i.e., expressed as total concentration) is called effective stability constant K'_{MY}. It can be described by

$$K'_{\mathrm{MY}} = \frac{[\mathrm{MY}']}{[\mathrm{M}'][\mathrm{Y}']} \tag{9}$$

In addition, $[\mathrm{M}'] = \alpha_{\mathrm{M}}[\mathrm{M}]$, $[\mathrm{Y}'] = \alpha_{\mathrm{Y}}[\mathrm{Y}]$ and $[\mathrm{MY}'] = \alpha_{\mathrm{MY}}[\mathrm{MY}]$. Mixed complexes (i.e., produced from MY) are rarely formed so that mix complex effects can be disregarded. Hence, K'_{MY} can be expressed as

$$K'_{\mathrm{MY}} = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]} \times \frac{1}{\alpha_{\mathrm{M}}\alpha_{\mathrm{Y}}} = K_{\mathrm{MY}} \frac{1}{\alpha_{\mathrm{M}}\alpha_{\mathrm{Y}}} \tag{10}$$

and in a logarithmic form

$$\log K'_{\mathrm{MY}} = \log K_{\mathrm{MY}} - \log \alpha_{\mathrm{M}} - \log \alpha_{\mathrm{y}} \tag{11}$$

Through manipulating the primary reaction (eq. (1)) and side reaction (eqs. (7)–(11)), the effective stability constant K'_{MY} can reflect the actual formation constant between coagulant and humic acid. Therefore, the value of K'_{MY} can be directly used to evaluate both possibility and completion problems of a complex reaction. This value also represents the electrical neutralization capacity of a coagulant.

Due to the use of the same reaction formula (eq. (1)), the quenching constant K_q in the Stern–Volmer equation can be used as the equilibrium constant K'_{MY} in a complex reaction [18, 19]. Therefore, in this study, the fluorescence quenching 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 type aluminum coagulants. By using the Stern–Volmer linear equation, the value of K_q will be q obtained. It will be used to quantitatively evaluate the capability of polyaluminum chloride (PACl) coagulants with different OH/Al^{3+} values to neutralize humic acid in solutions. Finally, the optimum basicity of PACl-B coagulants will be evaluated.

2. EXPERIMENTAL

Humic acid solutions. 200 mg of humic acid (Sigma-Aldrich) was dissolved in 1 dm^3 of 0.1 mol/dm^3 NaOH solution. Then the solution was stirred at room temperature for 7 days. After the humic acid was completely dissolved, the solution was neutralized with 0.1 mol/dm^3 hydrochloric acid. After determination of the humic acid concentration using a total organic carbon (TOC) analyzer, the stock solution was diluted to 100 mg/dm^3 for further use [20].

Alkali polymerization method. PACl was prepared from $AlCl_3$ solution by slow adding NaOH solution at the speed of 0.2 cm^3/min [21, 22]. Four samples of 50 cm^3 $AlCl_3$ (PACl and three PACl-B) were prepared. Hence, four samples of 50 cm^3 of NaOH solutions differing in concentrations were used to adjust B values to be 1.5, 2.3 and 2.5 and the total aluminum concentrations became 0.1 mol/dm^3. PACl-B solutions, were kept at 30 °C for 3 days for the aging process.

Aluminum chloride complexes with humic acid. Humic acid solutions were first diluted to 6 mg/dm^3. For each test, equal amounts of raw water (i.e., 1 dm^3) as control. pH was set in the range between 3 and 10 and the aluminum concentration between 0 and 6×10^{-5} mol/dm^3. To adjust and control pH of the test water, 0.1 mol/dm^3 NaOH or HCl was used. After stirring the test water for 10 min, the samples were taken and analyzed with a fluorescent spectrometer (i.e., HITACHI, F-2000). The excitation and emission wavelengths and the emission wavelength (λ_{ex}) were set to 375 nm and 445 nm, respectively.

Ferron test. The prepared PACl solution was diluted so that the aluminum concentration was adjusted to the detectable range of the ferron test method (2×10^{-4}–4×10^{-4}

mol/dm^3). Then, 0.75 cm^3 of ferron reagent was added into the mixture of 0.5 cm^3 sample and 1.45 cm^3 de-ionized water. The absorbance was measured by the spectrophotometric method (Thermo, Genesys 10S spectrophotometer) at a wavelength of 366 nm every 30 s for 2 h. It was operationally categorized so that the 1 min absorbance was Al_a and 1 min to 2 h was Al_b, then the concentration of Al_c was obtained from the remainder of Al_T. Table 1 shows the distribution of aluminum species at various B values.

Table 1

pH and aluminum species distribution [%] for PACl at various B

B	pH	Al_T(M)	Al_a	Al_b	Al_c
0	–	0.1	99.48	0.52	0
1.5	3.74		43.93	55.70	0.37
2.3	4.01		17.21	81.56	1.23
2.5	4.99		8.32	75.23	16.45

3. RESULTS AND DISCUSSIONS

The relationship between the fluorescence intensity and the concentrations of humic acid is shown in Fig. 1. It is found that the fluorescence intensity F is linearly proportional to the humic acid concentration C when the concentration is below 10 mg/dm^3. The humic acid concentration used in this study is 6 mg/dm^3, which is less than 10 mg/dm^3 so the quantitative relationship is applied.

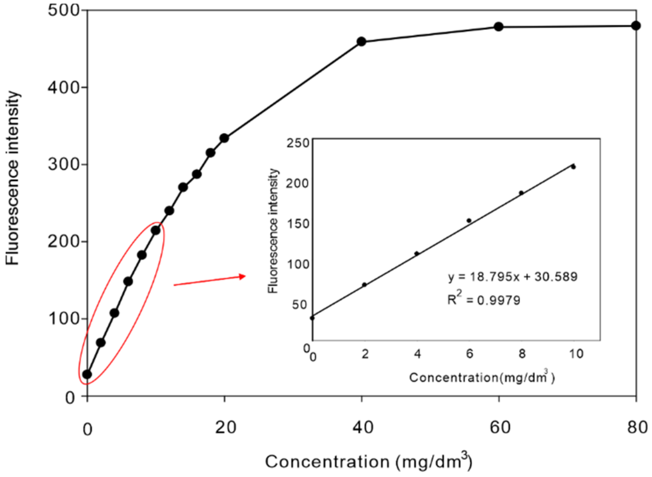

Fig. 1. Dependence of the fluorescence intensity on humic acid concentration

The data of Fig. 2 shows that the added aluminum chloride (up to 6×10^{-5} mol/dm^3) reacts with humic acid under different pH (3–10). First, when no aluminum chloride is added, the fluorescence intensity increases with the increase of pH. The dominant species are hydrogen ions considered as electron-withdrawing ones. Due to this electron-withdrawing effect, carboxyl groups on the humic acid surface prefer to bond with the excess amount of the hydrogen ions. As a result, the fluorescence intensity is reduced. When pH is high, the dominant species are hydroxide ions in an alkaline solution. When humic acid is in an alkaline solution, functional groups on its surface are negatively charged so the fluorescence intensity of humic acid increases with the increase of pH value. It was found that at pH 6, the fluorescence intensity decreased with the increase of the aluminum chloride concentration, which is known as the fluorescence quenching effect. However, when the aluminum concentration increases to a certain level, the fluorescence intensity does not significantly decrease but tends to stabilize because it is affected by the electron-withdrawing effect. The aluminum ion in the solution is considered an electron-withdrawing group. When the functional group on humic acid reacts with the electron-withdrawing group, the fluorescence intensity decreases. However, due to the limited available positions of the functional groups on the humic acid surface, the complex reaction occurring between humic acid and aluminum ions is also limited.

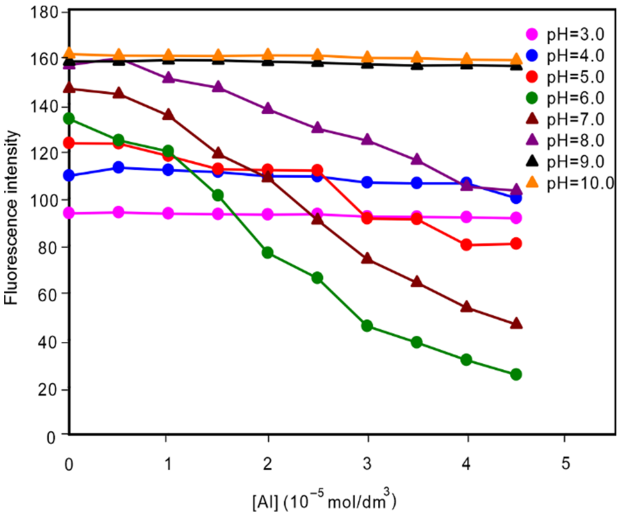

Fig. 2. Fluorescence intensity of humic acid at various $AlCl_3$ concentrations

The fluorescence intensity hardly changes under certain pH ranges (pH 3–4 and 9–10, Fig. 2). At pH 3–4, both aluminum ions and the carboxyl groups on the humic acid surface are positively charged so that they cannot react with each other due to isotropic charge repulsion. Hence, fluorescence intensity was not affected by changing the aluminum chloride concentrations. In contrast, when pH is 9–10, both hydroxide ions in the solution and the carboxyl groups on the humic acid surface are negatively charged but the dominant species in the solution is the hydroxide ions. Hence, aluminum ions prefer to react with the hydroxide ions to form a highly hydrolyzed product, such as $Al(OH)_4^-$. Therefore, only a few aluminum ions react with humic acid so that the increasing dosages of aluminum chloride do not significantly change the fluorescence intensity. Based on the data of Fig. 2, when the pH is 5–8, the fluorescence intensity decreases with increasing aluminum concentration. This observation indicates that the charges of the functional group on the humic acid surface may neutralize the charges of aluminum ions to enhance the fluorescence quenching effect.

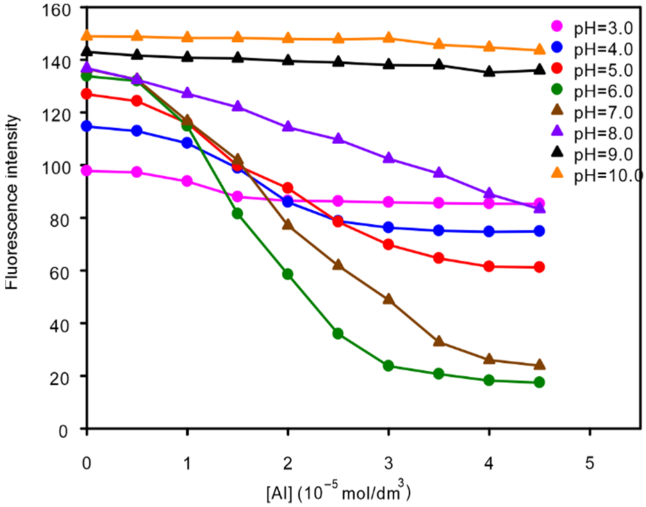

Fig. 3. Fluorescence intensity of humic acid at various PACl-1.5 concentrations

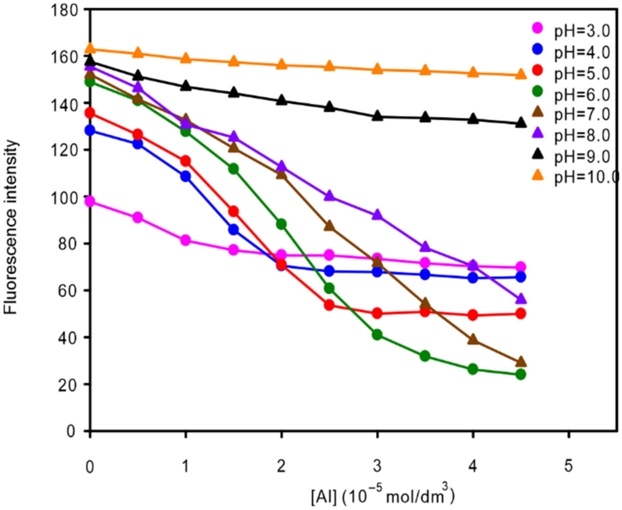

Fig. 4. Fluorescence intensity of humic acid at various PACl-2.3 concentrations

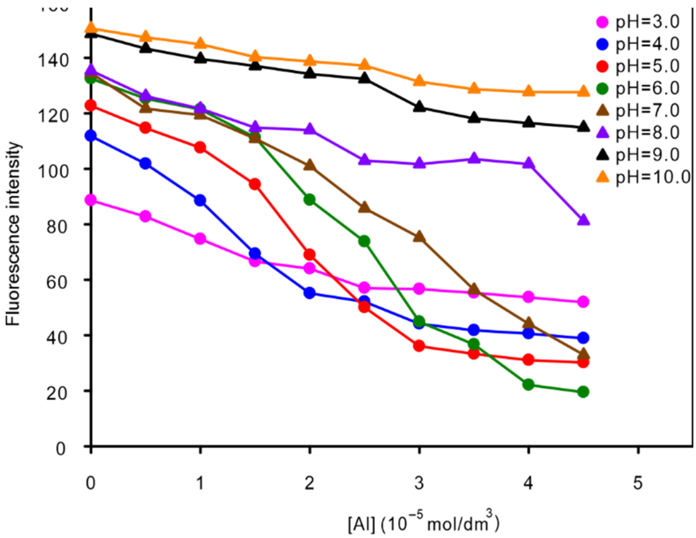

Fig. 5. Fluorescence intensity of humic acid at various PACl-2.5 concentrations

Table 2

Linear equations obtained by applying
the Stern–Volmer formula for $AlCl_3$

pH	Equation	R^2
3	$y = 574.72x + 0.9957$	0.9071
4	$y = 2012.1x + 0.9668$	0.8138
5	$y = 13114x + 0.9172$	0.8867
6	$y = 94132x + 0.3001$	0.8998
7	$y = 48267x + 0.6572$	0.9165
8	$y = 12606x + 0.9207$	0.9495
9	$y = 358.06x + 0.9962$	0.815
10	$y = 320.61x + 0.9999$	0.8412

Table 3

Linear equations obtained by applying
the Stern–Volmer formula for PACl-1.5

pH	Equation	R^2
3	$y = 3499.7x + 1.0212$	0.8169
4	$y = 14456x + 0.9875$	0.9061
5	$y = 28110x + 0.8994$	0.9715
6	$y = 175235x – 0.1418$	0.9339
7	$y = 111050x + 0.1387$	0.8838
8	$y = 14153x + 0.9418$	0.9664
9	$y = 1214.2x + 1.0011$	0.943
10	$y = 593.01x + 0.9854$	0.8526

Table 4

Linear equations obtained by applying
the Stern–Volmer formula for PACl-2.3

pH	Equation	R^2
3	$y = 8286x + 1.0782$	0.8707
4	$y = 24183x + 1.0708$	0.8482
5	$y = 47212x + 0.9349$	0.8957
6	$y = 126524x + 0.0424$	0.9061
7	$y = 84039x + 0.2809$	0.8042
8	$y = 35834x + 0.8041$	0.9087
9	$y = 4393.6x + 1.0224$	0.9585
10	$y = 1550.5x + 1.0073$	0.967

Table 5

Linear equations obtained by applying
the Stern–Volmer formula for PACl-2.5

pH	Equation	R^2
3	$y = 16215x + 1.0406$	0.9548
4	$y = 46539x + 0.9513$	0.9711
5	$y = 81785x + 0.5446$	0.9354
6	$y = 127151x - 0.1628$	0.8084
7	$y = 60031x + 0.5132$	0.8054
8	$y = 11367x + 0.9948$	0.8414
9	$y = 7045.6x + 0.9893$	0.9543
10	$y = 4375.4x + 1.0009$	0.9749

The fluorescence intensity ratio can be calculated using equation (6) from the fluorescence intensity of raw water (F_0) divided by that of fluorescence intensity for water containing aluminum (F). The data of Fig. 2 was gathered from calculating the fluorescence intensity ratio at each pH value. The ratios were then plotted against the aluminum concentrations and the result is shown in Table 2 where data followed the Stern–Volmer formula equation (eq. (6)). The slope of this linear relationship is the Stern–Volmer constant (K_q) of the electrical neutralization reaction. The values of K_q for various B values show the ability of the electrical neutralization of PACl-B in humic acid solution (Figs. 3–5 and Tables 3–5).

The data of K_q obtained from Tables 2–5 was used to discuss the differences of electrical neutralization for various B and pH (Fig. 6). When the humic acid solution is acidic (pH 3–5), the higher the B value of PACl-B, the higher the K_q value is, i.e., it increases in the order: $AlCl_3$ < PACl-1.5 < PACl-2.3 < PACl-2.5. At low pH, the higher the B value, the better the neutralization ability of PACl with humic acid is. When the humic acid solution is acidic, the main functional groups on humic acid have a higher chance of carrying a positive charge; besides, due to the Le Chatelier's principle [23], acidic conditions are not conducive to hydrolysis reactions, therefore the chance of a positive charge of aluminum species is also higher. The higher the *B* value of PACl-*B*, the more complete the degree of prehydrolysis, and the less chance that the aluminum species will have a positive charge. From the distribution of the aluminum species in Table 1, PACl-2.5 contains a large amount of aluminum-type Alc, and it is a polymeric macromolecule with less or no charge; in these conditions, the relative repulsive force of the aluminum species and humic acid is small, and the chance of complexation or electrical neutralization of humic acid and PACl-*B* will increase. However, for *B* = 0 with no prehydrolysis or *B* = 1.5 with less pre-hydrolysis, the positive charges of the aluminum are larger, which generate larger repulsion with humic acid and the less possibility of interaction, resulting in smaller K_q values, and poor ability for electrical neutralization.

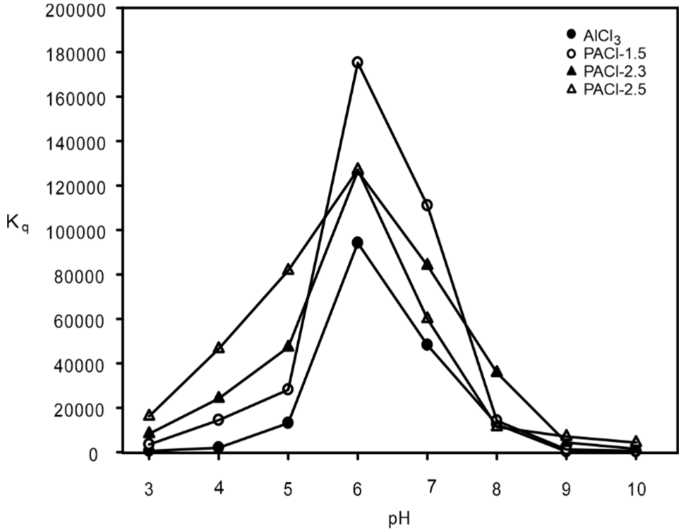

Fig. 6. Dependences of K_q on pH for various PACl-*B*

At higher pH, pH = 7 for example, the K_q value increases in the order: $AlCl_3$ < PACl-2.5 < PACl-2.3 < PACl-1.5. It was thought that when the *B* value was between 2.2 and 2.5, the presence of polyaluminum (Al_b) was the highest, where the polynuclear aluminum species containing a large amount of Al_{13} could be as high as 80%; because of the prehydrolysis during the preparation process and the high electrical charge, there was better electrical neutralization ability. However, the results of this study show that this is not the case, because, in terms of total electrical charge, the total charged number of Al_{13} in PACl is 7+ but the average charged number for each aluminum atom has only (7/13)+; compared with mononuclear Al^{3+}, although Al^{3+} is hydrolyzed faster and the metal ions are harder to control for electrical neutralization. The charge of each aluminum atom is higher than that of Al_{13}, therefore the complexation or electrical neutralization ability of PACl-1.5 is better than that of PACl-2.3. The electrical neutralization ability of $AlCl_3$ is worse than that of PACl at any pH as before. This confirms past literature that states that since PACl is a pre-hydrolyzed aluminum compound, it has a higher chance of resisting hydrolysis and instead electrically neutralize with reactants during the coagulation process [24, 25].

When the humic acid solution is at pH 6, K_q reaches its maximum value (Fig. 6). When the pH of the solution is higher, the aluminum species will react with the OH^- in the solution, therefore [M] will decrease and α_M will increase (eq. (11)); the chance of humic acid functional groups participating in the reaction will be less, therefore [Y] will be larger and α_Y will become smaller. Otherwise, if pH is lower, then the opposite is true. Therefore, K'_{MY} will have a maximum value at a certain pH value. At pH 6 K_q decreases in the order PACl-1.5 > PACl-2.3 > PACl-2.5 > $AlCl_3$. Gao et al. [24] tried to explore the coagulation efficiency by using different B values of PACl and changing the initial pH value of the natural organic solution and discussed the electric potential change of floc formed by coagulation with PACl under different pH conditions. They found that at pH = 6, the maximum potential value was present in all the B values of PACl, and the potential of PACl-1.5 was greater than that of PACl-2.3. Comparatively at pH lower than 6, in the acidic zone, due to the charge density increase at the humic acid surface, the higher the degree of prehydrolysis (the larger the B value), the higher the floc potential is. When the initial pH > 6.0, the potential of the floc of PACl-1.5 is still greater than that of PACl-2.3. The K_q values determined in this study (Fig. 6) are similar to the results by Gao [26]. This shows that determining the K_q value is a feasible way to evaluate the electrical neutralization ability compared with the past method of using the zeta potential [27, 28]. This method can reduce the complexity of the experiment.

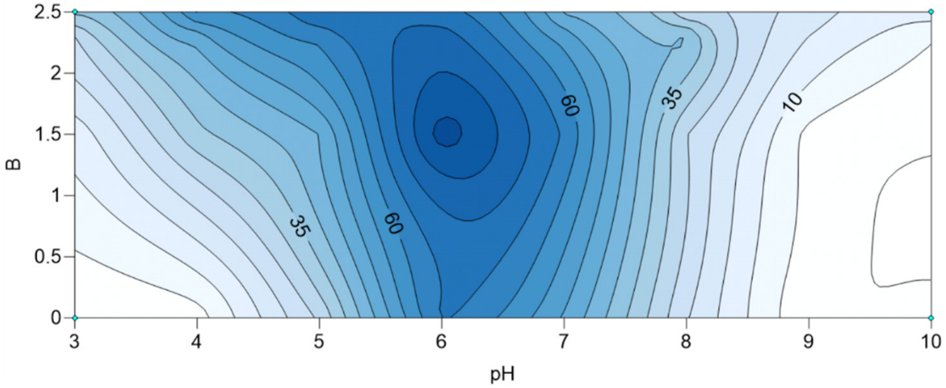

Fig. 7. pH and B dependence of the fluorescence of humic acid quenching rate at a fixed aluminum concentration of 3.0×10^{-5} mol/dm^3

From above, the pre-hydrolyzed PACl has better electrical neutralizing ability than $AlCl_3$ (pH = 6), and the suitable pH range of the humic acid solution is wider. To better understand the electrical neutralizing ability of PACl from different preparation methods, the fluorescence quenching rates $(F_0 - F)/F_0$ (%) of various types of PACls were studied at a fixed aluminum concentration of 3.0×10^{-5} mol/dm^3 (Fig. 7). Observing the fluorescence quenching rate of PACl in humic acid shows that $AlCl_3$ ($B = 0$) has a very narrow suitable pH range. As the B value increases, the suitable pH range also widens. PACl-1.5 has the widest suitable pH range, and at pH 6 the optimal electrical neutralizing ability is obtained. If the B value continues to increase, the pH range will move towards lower values. It is clear from the results that PACl-1.5 has the best electrical neutralization ability, and the electrical neutralizing ability of a high B value will be more significant at low pH.

4. CONCLUSIONS

- The higher the concentration of the humic acid in solution, the higher the fluorescence intensity is. The fluorescence intensity was linearly proportional to the concentration of humic acid below 10 mg/dm^3.
- The fluorescence quenching effect demonstrated that the complex positions of the functional groups on the humic acid surface were limited and they could not infinitely react with increasing aluminum ions.
- When no aluminum was added into the humic acid solution, the fluorescence intensity of the solution increased with pH value. When the solution was acidified, and the pH was low, the humic acid functional groups bond with hydrogen ions which decrease the fluorescence intensity. Hence, the higher the pH value of humic acid solution, the stronger the fluorescence intensity is.
- After adding aluminum ions of various concentrations into the humic acid solutions in the pH range of 3–4 or 9–10, the fluorescence intensities were very close to each other. However, when the solution pH was between 5 and 8, the fluorescence intensity decreased with the increase of aluminum concentrations. This observation indicates that the most obvious fluorescence quenching effect is at pH 6–7. This result demonstrated that the best coagulation capacity to neutralize the electron charge of humic acid is at pH 6, which is consistent with the prediction from the Stern–Volmer formula that the maximum constant (K_q) happened at pH 6.
- In acidic solutions, the K_q value of PACl decreases in the order: PACl-2.5 > PACl-2.3 > PACl-1.5 > $AlCl_3$. The higher the B value, the better the electrical neutralizing ability of PACl, whereas that of traditional aluminum salt coagulant $AlCl_3$ is the worst.
- In basic solutions, contrary to the results obtained from the acidic solutions, the lower the B value of PACl, the better the neutralization ability of PACl is. The K_q value decreases in the order PACl-1.5 > PACl-2.3 > PACl-2.5 > $AlCl_3$.

- At pH 6, all PACls achieve their maximum K_q values; this indicates that the coagulation of humic acid with PACl is not affected by the side reactions of H^+ or OH^- and has the best complex reactions or electrical neutralizing effect.
- The higher the concentration of humic acid solution, the higher the fluorescence intensity is. The fluorescence intensity was linearly proportional to the concentration of humic acid below 10 mg/dm^3.

ACKNOWLEDGMENT

We thank Mr. Chih-Hsiang Chen for the assistance with laboratory work. The authors also acknowledge the financial support of the Ministry of Science and Technology, Taiwan, R.O.C. for this work (106-2221-E-239-002-MY2).

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