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Simultaneous removal of turbidity and humic acid from high turbidity stormwater

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Abstract

This work studied the simultaneous removal of turbidity and humic acid from high turbidity synthetic raw water using polyaluminum chloride (PACl) as the coagulant. The response surface method with the Box–Behnken design of experiments was adopted to investigate the effects of pH, turbidity and alkalinity of suspension, the doses of PACl and the dosed amount of humic acid. The non-dimensional correlations for the residual turbidity and humic acid in the supernatant were obtained by regression analysis. Graphical presentation facilitates data interpretation from designed experiments. The most significant variables to the coagulation and sedimentation process were identified. Simultaneous removal of both turbidity and humic acid from the high turbidity water is reachable at neutral pH, and the PACl dose is selected if the raw water turbidity has not become too high. Extremely high turbidity stormwater may be treated using single-stage PACl coagulation to satisfactorily remove both the turbidity and humic acid from the water. The proposed strategy was applied to successfully treat the extremely high turbidity stormwater, brought by storm Nari on September 16–19, 2001.

Keywords: High turbidity; Polyaluminum chloride (PACl); Humic acid; Drinking water

1. Introduction

In drinking water industries, coagulants, such as polyaluminum chloride (PACl), are used in the raw water to coagulate small particles into settleable flocs. The turbidity of raw water is the target substance to be removed during coagulation–sedimentation treatment. Many factors influence the coagulation performance, including pH and alkalinity of the suspension, turbidity of the raw water, coagulant dose, organic contents and others (Kawamura, 1991; Masschelein, 1992). Humic substances are the main organic compounds affecting the coagulation processes, and their removal has attracted extensive research interest owing to the potential formation of tri-chloromethane (THM) in the disinfection stage (Rebhun and Lurie, 1993).

Narkis and Rebhun (1990) revealed that when both mineral particles and dissolved humic substance exist in the solution, the latter controls the coagulation process. The optimal pH value for humic acid removal ranges from 5 to 6, while that for clay suspensions is 6.5–7.5 (Hall and Packham, 1965; Edwards and Amirtharajah, 1985). Precipitation and adsorption are the two major mechanisms for the removal of organics, using hydrolyzing salts (O'Melia, 1991; Dempsey et al., 1984; Dempsey, 1989). Edzwald proposed a parallel-series reaction pathway for the interactions between alum and the humic substances (Edzwald, 1993). Other authors refined the pathways in their model systems (Dentel, 1988; Hundt and O'Melia, 1988). The presence of humic substances yields bulky flocs, whose settleability is poor hence leading to high supernatant turbidity

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(Tambo and Watanabe, 1979; Rebhun et al., 1984; Rebhun, 1990).

Conventional coagulation and sedimentation processes work very well for raw water of low to medium turbidity. Tropical storms frequently hit Pacific-Rim regions, like Taiwan, and yield heavy rain and produce stormwater of high turbidity. For instance, on 23rd August 2000, the tropical storm Bilis hit Taiwan and caused serious flooding. The raw water for PingTsan Waterworks of Taiwan Water Supply Corporation increased its turbidity up to 1200 NTU for over a week and to several hundred NTU for over a month. The total organic carbon (TOC) of the raw water also increased to more than 10 ppm. Simultaneous removal of turbidity and organic substances from high turbidity water is of practical significance. Pre-sedimentation followed by conventional coagulation and flocculation with a filter aid is commonly proposed for treating high turbidity water (Li and Gregory, 1991; Cotton et al., 1994; Heinzmann, 1994; Zhu et al., 1996; Janssens and Buekens, 1993). Selvapathy and Reddy (1992) and Yu and Somasundaran (1993) demonstrated the superiority of using dual conditioners, hydrolyzing metal salts and polyelectrolyte, rather than a single conditioner to treat high-turbidity water. However, the risk to human health of applying polyelectrolytes and their degradation products in drinking water is still not conclusive. The maintenance and operation of Waterworks would become much easier if the use of a conventional single-stage coagulation process for low turbidity raw water could be successfully applied to high turbidity raw water cases. The removal efficiency of organic substances is also a key issue for tuning process variables.

In this work, we investigated the coagulation and sedimentation treatment of high-turbidity raw water. A large number of experiments are needed to comprehensively investigate the effects of numerous variables on the efficiency of coagulation–sedimentation processes. Herein, we adopted the response surface method using the Box–Behnken design of experiments (Box and Behnken, 1960), to give the correlations for the turbidity and the humic acid level in the coagulated supernatant.

2. Experimental

2.1. Materials and test

Humic acid with a carbon content of 52.6% was purchased from the International Humic Substances Society (IHSS). Other chemicals were from Merck (Taiwan). Raw water samples were prepared by mixing prescribed amounts of UK ball clay powders and stock solution of humic acid with 10^{-2} N $NaClO_4$ solution. The alkalinity was adjusted by adding $NaHCO_3$ salt. The pH was adjusted by using $HClO_4$ and NaOH. The clay powder has a monodispersed distribution with a mean diameter of approximately 4.1 μm. The solid density was determined using a Micromeritics Accupyc 1330 pycnometer as 2,580 kg/m^3. The stock solution of humic acid was prepared by first dissolving the chemicals at pH 12. After filtering with a 0.45 μm membrane, the pH of the filtrate was adjusted back to 7 for further use.

The humic-kaolin suspension was placed into a stirred tank, which was a cylindrical tank whose diameter and height were both 15 cm. The PACl solution (containing 10% w/w Al_2O_3) was gradually injected into the stirred tank at 90 rpm for 1.5 min and subsequently 50 rpm for 8.5 min. The coagulated samples were settled freely for 2 h. Thereafter, the supernatant sample was carefully withdrawn for measurement. The turbidity of the supernatant was measured using a turbidimeter (HACH model 2100 AN). Before coagulation, at pH 7 and 500 ppm clay dose, the turbidities for synthetic raw water was approximately 200 NTU at various humic acid concentrations, presenting high turbidity waters. Moreover, without the addition of clay or PACl, the turbidity of the suspension was generally lower than 0.6 NTU regardless of the concentrations of humic acid or the suspension alkalinity. We hence neglect the role of humic acid in suspension turbidity in the further discussions. The humic acid level in the supernatant, after filtration with a 0.45 μm membrane, was monitored using a UV_{254} absorption test with an UV–Vis Spectrometer (Spectronic Genesys 5). A linear correlation exists between the UV_{254} reading and the humic acid content. The humic acid concentration could be derived from the UV_{254} reading. Before coagulation, the UV_{254} data for synthetic raw water at pH 7 and humic acid dose of 14 ppm and raw water turbidity of 0, 100 and 200 NTU were approximately 0.21, indicating dissolved humic acid concentrations of 4.7 ppm.

Each experiment was duplicated under identical conditions. In most of the cases the reproducibility was within 2%.

2.2. Experimental design

The response surface method using the Box–Behnken design of experiments, gives the correlations for the turbidity and the humic acid concentration of the coagulated supernatant. The response surface method is an empirical modeling method used to evaluate the relationship between a set of controllable experimental factors and observed results. Factors considered in this work include the pH value, the humic acid concentration (ppm), the raw water turbidity (NTU), the PACl dose (ppm) and the alkalinity (ppm as $NaHCO_3$) as the

Table 1
Experimental design

Id no.	pH (X_1)	Humic acid (ppm) (X_2)	Turbidity (NTU) (X_3)	PACl (ppm) (X_4)	$NaHCO_3$ (ppm) (X_5)
1	5(−1)	0(−1)	100(0)	100(0)	100(0)
2	9(1)	0(−1)	100(0)	100(0)	100(0)
3	5(−1)	28(1)	100(0)	100(0)	100(0)
4	9(1)	28(1)	100(0)	100(0)	100(0)
5	7(0)	14(0)	0(−1)	80(−1)	100(0)
6	7(0)	14(0)	200(1)	80(−1)	100(0)
7	7(0)	14(0)	0(−1)	120(1)	100(0)
8	7(0)	14(0)	200(1)	120(1)	100(0)
9	7(0)	0(−1)	100(0)	100(0)	0(−1)
10	7(0)	28(1)	100(0)	100(0)	0(−1)
11	7(0)	0(−1)	100(0)	100(0)	200(1)
12	7(0)	28(1)	100(0)	100(0)	200(1)
13	5(−1)	14(0)	0(−1)	100(0)	100(0)
14	9(1)	14(0)	0(−1)	100(0)	100(0)
15	5(−1)	14(0)	200(1)	100(0)	100(0)
16	9(1)	14(0)	200(1)	100(0)	100(0)
17	7(0)	14(0)	100(0)	80(−1)	0(−1)
18	7(0)	14(0)	100(0)	120(1)	0(−1)
19	7(0)	14(0)	100(0)	80(−1)	200(1)
20	7(0)	14(0)	100(0)	120(1)	200(1)
21	7(0)	0(−1)	0(−1)	100(0)	100(0)
22	7(0)	28(1)	0(−1)	100(0)	100(0)
23	7(0)	0(−1)	200(1)	100(0)	100(0)
24	7(0)	28(1)	200(1)	100(0)	100(0)
25	5(−1)	14(0)	100(0)	80(−1)	100(0)
26	9(1)	14(0)	100(0)	80(−1)	100(0)
27	5(−1)	14(0)	100(0)	120(1)	100(0)
28	9(1)	14(0)	100(0)	120(1)	100(0)
29	7(0)	14(0)	0(−1)	100(0)	0(−1)
30	7(0)	14(0)	200(1)	100(0)	0(−1)
31	7(0)	14(0)	0(−1)	100(0)	200(1)
32	7(0)	14(0)	200(1)	100(0)	200(1)
33	5(−1)	14(0)	100(0)	100(0)	0(−1)
34	9(1)	14(0)	100(0)	100(0)	0(−1)
35	5(−1)	14(0)	100(0)	100(0)	200(1)
36	9(1)	14(0)	100(0)	100(0)	200(1)
37	7(0)	0(−1)	100(0)	80(−1)	100(0)
38	7(0)	28(1)	100(0)	80(−1)	100(0)
39	7(0)	0(−1)	100(0)	100(0)	100(0)
40	7(0)	28(1)	100(0)	100(0)	100(0)
41	7(0)	14(0)	100(0)	100(0)	100(0)
42	7(0)	14(0)	100(0)	100(0)	100(0)
43	7(0)	14(0)	100(0)	100(0)	100(0)
44	7(0)	14(0)	100(0)	100(0)	100(0)
45	7(0)	14(0)	100(0)	100(0)	100(0)
46	7(0)	14(0)	100(0)	100(0)	100(0)

critical variables; they are designated as X_1 to X_5, respectively. All other factors except the PACl dose is considered to be related to the compositions of the raw water.

The low, middle and high levels of each variable were designated as -1, 0 and $+1$, respectively, and are listed in Table 1. The parametric range, which was investigated, covers the high turbidity raw water commonly noted in Taiwan's rivers after the tropical storms. The independent variables X_i and the mathematical relationship of the response Y to these variables can be approximated by a quadratic polynomial equation:

$$Y=b_0+\sum_{i=1}^{5} b_i X_i+\sum_{i=1}^{5}\sum_{j=1}^{i} b_{ji} X_i X_j, \qquad (1)$$

Table 2
Experimental and theoretically predicted values

Id no.	Turbidity (Y_1, NTU)		UV_{254} (Y_2, −)	
	Experiment	Predicted	Experiment	Predicted
1	7.5	7.3	0.20	0.20
2	11.4	11.1	0.06	0.06
3	10.9	10.8	0.03	0.03
4	8.9	8.7	0.36	0.36
5	0.1	0.1	0.19	0.19
6	9.1	9.1	0.11	0.11
7	11.0	10.9	0.05	0.05
8	1.4	1.4	0.21	0.21
9	1.4	1.1	0.09	0.09
10	3.3	3.1	0.14	0.14
11	2.0	2.0	0.10	0.10
12	1.0	1.1	0.18	0.18
13	2.1	2.1	0.06	0.06
14	18.5	18.5	0.22	0.22
15	17.3	17.4	0.16	0.16
16	2.7	2.8	0.19	0.19
17	4.1	3.9	0.08	0.08
18	8.9	8.7	0.19	0.19
19	6.5	6.6	0.24	0.24
20	4.8	4.8	0.09	0.09
21	1.0	0.9	0.06	0.06
22	1.8	1.8	0.14	0.14
23	1.0	1.1	0.11	0.11
24	1.2	1.3	0.16	0.16
25	0.8	0.6	0.13	0.13
26	25.3	25.2	0.25	0.25
27	26.0	25.8	0.14	0.14
28	3.2	3.0	0.21	0.21
29	2.5	2.6	0.09	0.09
30	3.1	3.0	0.13	0.13
31	2.7	2.6	0.12	0.12
32	2.0	1.8	0.16	0.16
33	11.8	12.3	0.10	0.10
34	9.3	9.7	0.21	0.21
35	8.1	8.3	0.14	0.14
36	12.4	12.5	0.23	0.23
37	3.9	4.2	0.12	0.12
38	3.8	3.9	0.19	0.19
39	4.4	4.8	0.11	0.11
40	6.0	6.2	0.16	0.16
41	0.2	0.2	0.10	0.10
42	0.2	0.2	0.10	0.10
43	0.2	0.2	0.10	0.10
44	0.2	0.2	0.10	0.10
45	0.2	0.2	0.10	0.10
46	0.2	0.2	0.10	0.10

where Y=predicted response, b_0=constant, b_i=linear coefficients ($i=1-5$), b_{ii}=quadratic coefficients, and b_{ji}=cross product coefficients ($i \neq j$). Y denotes either the residual turbidity or the UV_{254} absorption data in supernatant. For either of the cases, a total of 41 experiments were needed to estimate the coefficient of the model using multiple linear regression analysis. The above equation was solved using the design expert (Stat-Ease Inc., Statistics made-Easy, Minneapolis, MN version 5.0.7.1999) to estimate the response of the independent variables.

3. Results and discussion

3.1. Experimental results

Table 2 lists the measured turbidity and UV_{254} data under the experimental conditions listed in Table 1. The minimum residual turbidity of supernatant measured with 100 NTU raw water is 0.1 NTU under the condition of pH 7, 14 ppm dosed humic acid, 100 ppm PACl dose and 100 ppm $NaHCO_3$. The minimum UV_{254} absorption datum achievable with 14 ppm dosed humic acid is 0.05, equivalent to 1.13 ppm humic acid (92% reduction), which occurs at pH 7, 120 ppm PACl, 100 ppm $NaHCO_3$ and with no clay addition.

Fig. 1 shows the turbidity vs. humic acid data for the supernatant. No clear correlation between these two variables is noticeable. We tried to fix certain process variables, like pH or PACl dose, for re-plotting Fig. 1. We could not get satisfactory correlation between the turbidity and humic acid data with further constraints.

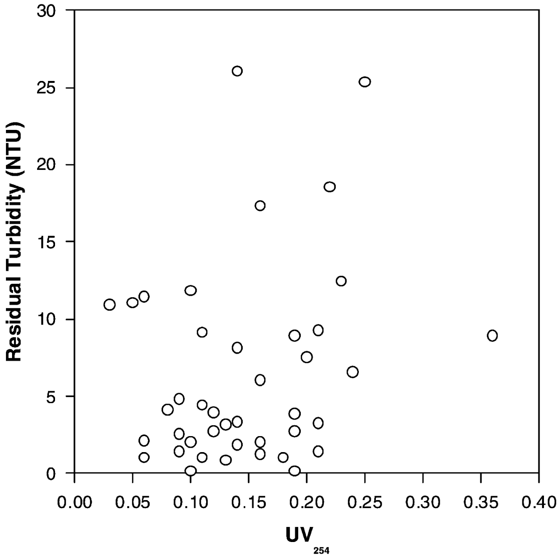

Fig. 1. The residual turbidity vs. residual humic acid data plot.

The removal mechanisms of both substances are hence different.

3.2. Regression model

To obtain the optimal values of independent variables, the regression equation was obtained following the design method. Table 3 lists the fitted coefficients of the regression model, Eq. (1) on the basis of the experimental data, including 5 linear, 5 quadratic and 10 interaction terms and 1 block term. To directly compare the significance of various variables in Eq. (1), the best-fitted second-order polynomials are non-dimensionlized using the reference variables as follows: $X_{10}=7$, $X_{20}=14$ ppm, $X_{30}=100$ NTU, $X_{40}=100$ ppm and $X_{50}=100$ ppm. The non-dimensional equation for residual turbidity in supernatant is as follows:

$$\begin{aligned}\left(\frac{Y_1}{0.15\text{NTU}}\right) ={}& 1+20.0\left(\frac{X_1}{X_{10}}\right)+18.0\left(\frac{X_2}{X_{20}}\right)\\ &+0.16\left(\frac{X_3}{X_{30}}\right)+506\left(\frac{X_4}{X_{40}}\right)\\ &-0.19\left(\frac{X_5}{X_{50}}\right)+2980\left(\frac{X_1}{X_{10}}\right)^2\\ &+153\left(\frac{X_2}{X_{20}}\right)^2+0.375\left(\frac{X_3}{X_{30}}\right)^2\\ &+293\,000\left(\frac{X_4}{X_{40}}\right)^2+0.095\left(\frac{X_5}{X_{50}}\right)^2\\ &-690\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_2}{X_{20}}\right)-90.4\left(\frac{X_1}{X_{10}}\right)\\ &\times\left(\frac{X_3}{X_{30}}\right)-55\,200\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_4}{X_{40}}\right)\\ &+7.90\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_5}{X_{50}}\right)-2.80\left(\frac{X_2}{X_{20}}\right)\\ &\times\left(\frac{X_3}{X_{30}}\right)+2730\left(\frac{X_2}{X_{20}}\right)\left(\frac{X_4}{X_{40}}\right)\\ &-4.80\left(\frac{X_2}{X_{20}}\right)\left(\frac{X_3}{X_{30}}\right)-775\left(\frac{X_3}{X_{30}}\right)\\ &\times\left(\frac{X_4}{X_{40}}\right)-0.0500\left(\frac{X_3}{X_{30}}\right)\\ &\times\left(\frac{X_5}{X_{50}}\right)-110\left(\frac{X_4}{X_{40}}\right)\left(\frac{X_5}{X_{50}}\right).\end{aligned}\tag{2a}$$

While the correlation for humic acid data for supernatant is as follows:

$$\begin{aligned}\left(\frac{Y_2}{2.26\text{ppm}}\right) ={}& 1+3.36\left(\frac{X_1}{X_{10}}\right)+3.20\left(\frac{X_2}{X_{20}}\right)\\ &+0.0450\left(\frac{X_3}{X_{30}}\right)-9.60\left(\frac{X_4}{X_{40}}\right)\\ &-0.0140\left(\frac{X_5}{X_{50}}\right)+25.0\left(\frac{X_1}{X_{10}}\right)^2\\ &+11.0\left(\frac{X_2}{X_{20}}\right)^2+0.0468\left(\frac{X_3}{X_{30}}\right)^2\\ &+330\left(\frac{X_4}{X_{40}}\right)^2+0.00180\left(\frac{X_5}{X_{50}}\right)^2\\ &+8.40\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_2}{X_{20}}\right)-56.0\left(\frac{X_1}{X_{10}}\right)\\ &\times\left(\frac{X_3}{X_{30}}\right)-91.0\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_4}{X_{40}}\right)\\ &-0.0350\left(\frac{X_1}{X_{10}}\right)\left(\frac{X_5}{X_{50}}\right)\\ &+0.188\left(\frac{X_2}{X_{20}}\right)\left(\frac{X_3}{X_{30}}\right)\\ &-50.0\left(\frac{X_2}{X_{20}}\right)\left(\frac{X_4}{X_{40}}\right)\\ &+0.170\left(\frac{X_2}{X_{20}}\right)\left(\frac{X_5}{X_{50}}\right)\\ &+14.8\left(\frac{X_3}{X_{30}}\right)\left(\frac{X_4}{X_{40}}\right)\\ &-0.000250\left(\frac{X_3}{X_{30}}\right)\\ &\times\left(\frac{X_5}{X_{50}}\right)-6.40\left(\frac{X_4}{X_{40}}\right)\left(\frac{X_5}{X_{50}}\right).\end{aligned}\tag{2b}$$

Table 2a and b compares the experimental data with the predicted values from the fitted model equations and the agreement is satisfactory.

3.3. Significant variables

Table 4 lists the analysis of variance (ANOVA) for the response function (Y_i) in the coded level of variables. The results indicate a curvilinear interactive relationship between the response function and the variables, as reflected by the large mean sum of squares and F-values of total quadratic and interactive effects. The model fits the residual turbidity of supernatant at $R^2=0.999$ and F value of 1680 at a significance level of 0.0001. Meanwhile, at the same significance level, the humic acid data could be fit at $R^2=0.999$ and F value$=1950$.

Using Eq. (2a) and Eq. (2b) the 'sensitivity' of the investigated variables to the turbidity and humic acid

Table 3
Regression analysis for the residual turbidity and the organic levels in supernatant and quadratic response surface model fitting (ANOVA)

Source	Turbidity					UV_{254}				
	Sum of squares	Degrees of freedom	Mean square	F value	P value	Sum of squares	Degrees of freedom	Mean square	F value	P value
Model	1800	20	89.8	1680	<0.0001	0.18	20	9.09×10^{3}	1947	<0.0001
Residual	1.34	25	0.053			1.1×10^{4}	25	4.6×10^{6}		<0.0001
Lack of fit	1.34	20	0.067	6.3×10^{7}	<0.0001	1.1×10^{4}	20	5.8×10^{6}	6.3×10^{7}	
Pure error	0.00	5	0.000			0.000	5	0.000		
Correlation total	1440	45				0.18	45			
R^2	R^2	0.999	Adj R^2	0.998		R^2	0.9994	Adj R^2	0.9988	

Table 4
Coefficients of the model

Coefficient	Turbidity (NTU)				UV_{254} (−)			
	Value	Standard error	t for H_0: coeff. = 0	Prob. > /t/value	Value	Standard error	t for H_0: coeff. = 0	Prob. > /t/value
b_0	0.15	0.094			0.10	8.82×10^{4}		
b_1	0.44	0.058	7.63	< 0.0001*	0.048	5.4×10^{4}	89.06	< 0.0001*
b_2	0.27	0.058	4.74	< 0.0001*	0.032	5.4×10^{4}	58.99	< 0.0001*
b_3	−0.10	0.058	−1.81	0.0829	0.018	5.4×10^{4}	33.54	< 0.0001*
b_4	0.76	0.058	13.1	< 0.0001*	−0.0090	5.4×10^{4}	−16.77	< 0.0001*
b_5	−0.29	0.058	−5.09	< 0.0001*	0.014	5.4×10^{4}	26.49	< 0.0001*
b_{11}	9.12	0.078	117	< 0.0001*	0.051	7.3×10^{4}	69.48	< 0.0001*
b_{22}	0.23	0.078	2.92	0.0072*	0.011	7.3×10^{4}	14.58	< 0.0001*
b_{33}	0.90	0.078	11.5	< 0.0001*	0.0075	7.3×10^{4}	10.25	< 0.0001*
b_{44}	4.39	0.078	56.1	< 0.0001*	0.033	7.3×10^{4}	45.22	< 0.0001*
b_{55}	1.43	0.078	18.3	< 0.0001*	0.018	7.3×10^{4}	24.49	< 0.0001*
b_{12}	−1.48	0.12	−12.8	< 0.0001*	0.12	1.08×10^{3}	108.96	< 0.0001*
b_{13}	−7.75	0.12	−67.1	< 0.0001*	−0.032	1.08×10^{3}	−29.84	< 0.0001*
b_{14}	−11.8	0.12	−102	< 0.0001*	−0.013	1.08×10^{3}	−11.57	< 0.0001*
b_{15}	1.70	0.12	14.7	< 0.0001*	−0.005	1.08×10^{3}	−4.63	< 0.0001*
b_{23}	−0.17	0.12	−1.47	0.1538	−0.007	1.08×10^{3}	−6.71	< 0.0001*
b_{24}	0.41	0.12	3.55	0.0016*	−0.005	1.08×10^{3}	−4.63	< 0.0001*
b_{25}	−0.73	0.12	−6.32	< 0.0001*	0.007	1.08×10^{3}	6.48	< 0.0001*
b_{34}	−4.65	0.12	−402	< 0.0001*	0.059	1.08×10^{3}	54.59	< 0.0001*
b_{35}	−0.32	0.12	−2.77	0.0104*	0.001	1.08×10^{3}	0.93	0.3636
b_{45}	−1.65	0.12	−14.3	< 0.0001*	−0.064	1.08×10^{3}	−59.45	< 0.0001*

* Significant factor.

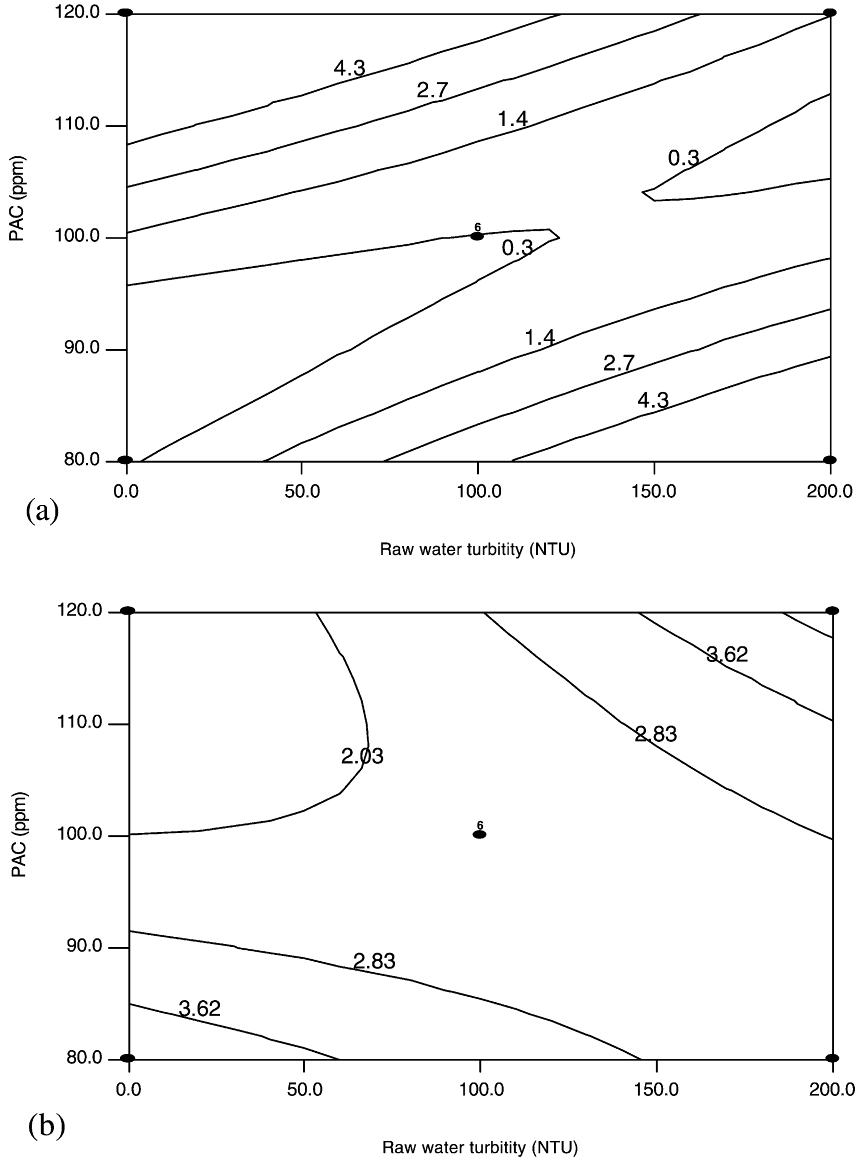

Fig. 2. (a) Contour plot for residual turbidity vs. PACl dose and raw water turbidity. pH 7, 14 ppm humic acid dose, 100 ppm $NaHCO_3$. (b) Contour plot for residual humic acid data vs. PACl dose and raw water turbidity. pH 7, 14 ppm humic acid dose, 100 ppm $NaHCO_3$.

removal efficiencies could be compared. For turbidity removal, the significance of variables follows: X_4 (PACl dose)$\gg X_1$ (pH), X_2 (humic acid)$\gg X_3$ (raw water turbidity), X_5 (alkalinity); while the interactions between X_4 and X_1 or X_2 are the most profound ones. On the other hand, for humics removal, the significance becomes: $X_1 \fallingdotseq X_2 \fallingdotseq X_4 \gg X_3 \gg X_5$; while the most influential interaction pairs remain the (X_1-X_4) and (X_2-X_4) pairs. That is, the PACl dose is the most significant variable to turbidity and humics removal efficiencies. For the latter, the effects of pH value and humic acid concentration are also significant. Under the investigated range neither the turbidity nor the alkalinity of raw water plays an essential role for the coagulation–sedimentation processes.

3.4. Process optimization

Fig. 2a, Fig. 2b, Fig. 3a, Fig. 3b, Fig. 4a and Fig. 4b present the contour plots for residual turbidity and humic

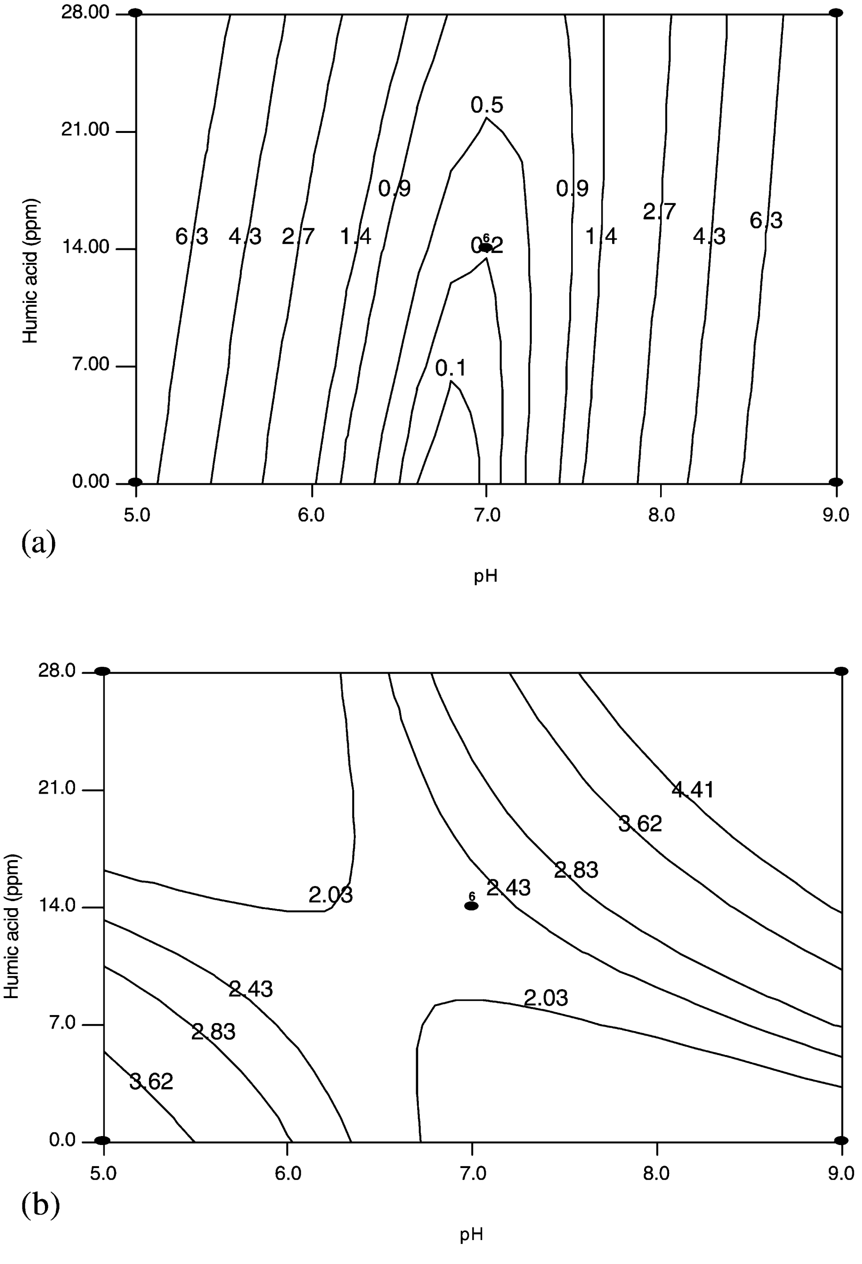

Fig. 3. (a) Contour plot for residual turbidity vs. dosed humic acid and pH value. pH 7, 100 NTU raw water, 100 ppm PACl dose. (b) Contour plot for residual humic acid data vs. dosed humic acid and pH value. pH 7, 100 NTU raw water, 100 ppm PACl dose.

acid data as functions of process variables $X_1 - X_5$. Fig. 2a indicates that an optimal 'window' exists along which the PACl dose required for sufficient turbidity removal increases with raw water turbidity, as commonly noted in practice. Overdosing deteriorates supernatant quality, referring to the 'restabilization' of the suspended particles. For humics removal, as shown in Fig. 2b, at low to medium raw water turbidity, the humic acid data decrease monotonically with increasing PACl dose. The presence of clay particles has a negative impact on humic acid removal, owing to the carryover of the suspended particles with strongly adsorbed humic substance on the clay particle surface, or the competition between clay particles and humics for the dosed PACl.

Fig. 3a and b demonstrated that the optimal pH ranges for turbidity and humics removal from high

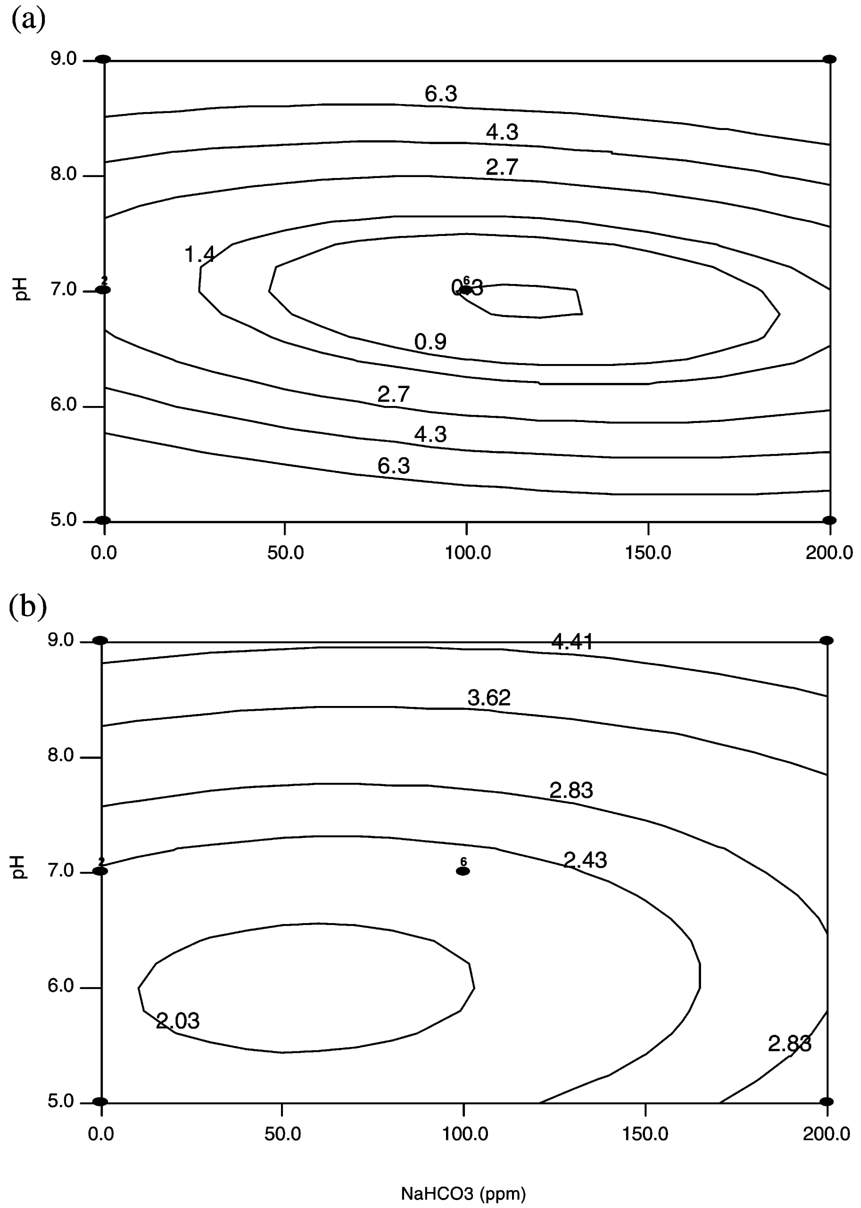

Fig. 4. (a) Contour plot for residual turbidity vs. pH value and $NaHCO_3$ concentration. 14 ppm dosed humic acid, 100 NTU raw water turbidity, 100 ppm PACl dose. (b) Contour plot for residual humic acid data vs. pH value and $NaHCO_3$ concentration. 14 ppm dosed humic acid, 100 NTU raw water turbidity, 100 ppm PACl dose.

turbidity waters are 6.5–7.5 and 5–6, respectively, which correlates with literature results (Hall and Packham, 1965). High humic acid concentration is harmful to turbidity removal at all pH's, but facilitates humics removal around pH 5. At low clay dose, the residual humic acid decreases in a linear manner with the PACl dose over a wide experimental range. (*Note*: The high residual humic acid concentration depicted in Fig. 3b reveals the poor removal efficiency of the released organic matter from clay particles, which is clearly illustrated in Table 2.)

Fig. 4a reveals that the suspension alkalinity is relatively insensitive to the turbidity removal. On the other hand, as shown in Fig. 4b, the humics removal prefers (mildly) high alkalinity.

The Box–Behnken design has been employed in

Table 5
Experimental results for high turbidity raw water after the hit by tropical storm Nari. Raw water turbidity of 1650 NTU, humic acid of 1.34 ppm

Id no.	pH	PACl dose (ppm)	Supernatant turbidity (NTU)	Supernatant humic acid level (ppm)
1	7	80	1.05	0.81
2	7	180	3.52	0.81
3	7	130	0.11	0.90
4	7	130	1.14	0.75
5	5	130	5.18	0.93
6	9	130	2.54	1.02

combination with response surface methodology (RSM) to estimate the minimum residual turbidity and the minimum humic acid level. Under the condition of pH 6.5–7.2, humic acid 0–10 ppm, raw water turbidity 40–45 NTU, PACl dose 90–110 ppm and a wide range of alkalinity, it is estimated that the minimum turbidity of supernatant could be reduced to less than 0.1 NTU. The minimum humic acid level for the supernatant at 0.68 ppm occurs under the condition of pH 5–6, humic acid 21–28 ppm, raw water turbidity 0–20 NTU, PACl dose $>$ 110 ppm and alkalinity $>$ 50 ppm. (*Note*: There is a small range at very low humic acid level that exhibits a low UV_{254} reading. This occurrence is trivial and is neglected in further discussions.) As shown in Fig. 2a, Fig. 2b, Fig. 3a, Fig. 3b, Fig. 4a and Fig. 4b, the variables X_1, X_2 and X_4 do have a strong influence on the turbidity and humics removal efficiencies. Neither the raw water turbidity nor $NaHCO_3$ significantly affect the coagulation–sedimentation efficiency.

3.5. Simultaneous removal of turbidity and humic acid

The ‘optimal’ conditions for removing turbidity or humic acid from high turbidity water are different. Simultaneous removal of both substances in a single unit needs a compromise. In practice the humic acid concentration and the turbidity in raw water are not controllable. The significance of controlling variables includes pH value and PACl dose.

The contours for residual NTU (Fig. 3a) presents an area of minimum value at pH 6.7–7.2. Departing from neutral conditions the supernatant turbidity markedly increases. A neutral pH value is hence selected for facilitating turbidity removal. As addressed above, the contour plot for humic acid data (Fig. 3b) presents a saddle–point characteristic. At pH 6.7–7.2 the residual humic acid supernatant increases with its dose. However, the dependence changes at different humic acid range. At humic acid $<$ 10 ppm, as commonly noted in drinking water treatment practice, all the residual humic acid data approximately ranges from 1.81 to 2.03 ppm, which is close to the background value yielded by the clay particles. Restated, in conjunction with the ‘optimal’ turbidity removal, this pH range presents sufficient humic acid removal as well.

The remaining significant variable is PACl dose. According to Fig. 2a and b the optimal dose for PACl increases linearly with the raw water turbidity. For instance, at raw water turbidity of 100 and 200 NTU, the optimal PACl dose ranges from 92 to 102 ppm and 103 to 113 ppm, respectively. On the other hand, the ‘window’ for optimal PACl dose on humic acid removal is relatively wider. For instance, at raw water turbidity of 100 NTU, 85–120 ppm PACl is required to reach the residual humic acid of 2.0–2.7 ppm (81–93% reduction). Too high or too low PACl dose would yield a marked increase in humic acid in supernatant. The required PACl decreases with increasing raw water turbidity. This trend is inconsistent with that observed for turbidity removal. Hence, the optimal PACl dose for removing humic acid differs from that for turbidity if the raw water turbidity is either higher than 160 NTU or lower than 30 NTU. Only at a medium level of raw water turbidity could coagulation with PACl alone simultaneously remove both turbidity and humic acid from water. For an extremely high turbidity stormwater the chosen dose presents a compromise.

3.6. Field application

On September 16–19, 2001, tropical storm Nari hit Taiwan and brought heavy rain and serious flooding. The turbidity of Da-Han River, Taoyuan, which is the main surface water source for Taoyuan County, Taiwan increased to 1650 NTU and the humic acid concentration was 1.34 ppm. We applied the proposed dosing strategy to treat the high turbidity stormwater in the field. Restated, the most significant variables for treating this high turbidity raw water included the pH value and the PACl dose; a neutral condition is recommended for the former, and comprise should be made for the latter. The alkalinity of suspension is not significant. Hence, we first adjusted the pH value of the raw water to neutral. Then the PACl was dosed at three levels (80, 130 and 180 ppm) while the turbidity and humic acid concentration data for supernatant were monitored and listed in Table 5. Apparently, the best turbidity removal was achieved at a medium PACl dose of 130 ppm. Over- or under-dosing led to an increase in supernatant turbidity. This dose, however, yielded a humic acid concentration of 0.90 ppm (33% reduction), which was greater than those obtained at the other two doses investigated. To remove humic acid to 0.75 ppm (44% reduction) at 180 ppm dose of PACl, however, the turbidity increased to 3.52 NTU, which was unacceptable in practice. Hence, a PACl dose at 80 ppm was recommended to reach acceptable turbidity (1.05 NTU) and humic acid levels (0.81 ppm) of supernatant.

The tests at pH 5 and 9 were also conducted for comparison sake, which were also summarized in Table 5. Apparently the performance is far from satisfactory and is disregarded in practice. The dosing strategy proposed in this work thereby successfully treated the extremely high turbidity stormwater to acceptable levels using single-stage PACl dosing control.

4. Conclusions

Simultaneous removal of turbidity and humic acid from high turbidity raw water was investigated in this work by adopting the response surface method with the Box–Behnken design of experiments. The significant variables considered are the pH, turbidity and alkalinity of raw water, the PACl dose and the humic acid concentration. The turbidity and the residual humic acid level in supernatant do not correspond with each other to a significant level. Their non-dimensional correlations were obtained separately by regression analysis. Graphical presentation was facilitated with each result from designed experiments. The most influential process variable to sufficient turbidity removal is the coagulant dose. For humics removal, besides the PACl dose, both the pH value and the humics concentration are significant variables.

The optimal conditions for removing turbidity and humic acid from a given high turbidity water are different. Simultaneous removal of both substances from water in a single unit needs a compromise. A neutral pH value is selected for facilitating turbidity removal. The supernatant turbidity could reach a sufficiently low value. Meanwhile, most humic acid could be effectively removed at neutral pH using a medium PACl dose, if the raw water turbidity did not exceed 160 NTU. At extremely high turbidity, one cannot use single-stage PACl coagulation to simultaneously remove both the turbidity and the humic acid. The proposed strategy for the single-stage PACl dosing system was successfully applied to coagulate the stormwater brought by storm Nari of turbidity 1650 NTU and humic acid concentration of 1.34 ppm.

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