

Article



Investigation and Optimization of Chitosan Performance in Flocculating Kaolin Suspensions Using a Real-Time Suspending Solid Concentration Measuring Method

Yan Xu^{1,2}, Kemin Gan², Siyi Liang^{1,3}, Haitao Liu¹ and Qunhui Wang^{2,*}

- ¹ MCC Capital Engineering and Research Incorporation Ltd., Beijing 100176, China; xuyan@ceri.com.cn (Y.X.); Liangsy19@mails.tsinghua.edu.cn (S.L.); liuhaitao@ceri.com.cn (H.L.)
- ² Department of Environmental Engineering, School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China; kemin_gan@163.com
- ³ School of Environment, Tsinghua University, Beijing 100084, China
- * Correspondence: wangqh59@sina.com; Tel.: +86-(010)-6233-2778

Abstract: The performance of chitosan in flocculating kaolin suspensions was investigated. A realtime suspended solid (SS) concentration measuring method was applied. The influence of pH was examined from 2.0 to 13.0. The optimal pH value for low-grade (100 mg/L), middle-grade (500 mg/L), and high-grade (1000 mg/L) kaolin suspension samples was 8.0. The optimal dosage of chitosan for the three grades of kaolin suspensions was 5.0 mg/L, regardless of the initial SS concentration. An orthogonal array test was performed to determine the optimal hydraulic conditions. Range analysis and variance analysis showed that all four considered factors significantly influenced the flocculation performance of chitosan in the following order: paddle rotation speed in the mixing period > paddle rotation speed in the flocculating period > mixing period time > flocculating period time. Intermittent agitation tests were also performed, showing that alternating agitation and settling enhanced the flocculation performance of chitosan.

Keywords: chitosan; kaolin suspension; flocculation performance; orthogonal array test; hydraulic conditions; intermittent agitation

1. Introduction

The combined use of inorganic salts and organic polymers is common in municipal water production [1]. In recent years, this traditional treatment method has been disputed due to its potential risks to public health and application difficulties. Aluminum salts (e.g., polyaluminum chloride (PAC) and polyaluminum sulfate), for example, produce Al³⁺ residues, which have been reported to increase the incidence of Alzheimer's disease [2,3] and production of sludge [4]. Ferric salts can stain equipment and are difficult to dissolve. Their solutions are corrosive, and ferric ions may react with organics to form soluble ferrous ions [5]. Polyacrylamide (PAM), a frequently used organic polymeric flocculant, has been found to be able to release neurotoxic acrylamide monomers [6,7]. As a result, natural biopolymers and their derivatives [8–11], as better substitutes for conventional flocculants, have received increasing attention because they are nontoxic, widely available, inexpensive, and effective for removing impurities in water. Chitosan is one such material [12,13]. Chitosan is a deacetylated derivative of chitin, which is the second most abundant natural biopolymer in the world. Chitin is a natural polysaccharide of major importance and can be widely exploited from marine organisms [14] (such as crabs and shrimp), fungi [15], and insects [16]. Chitin turns into chitosan when the deacetylation degree (DD) is over 50% [17], and then becomes soluble in water [18].

Chitosan has been proven to be effective for removing a wide range of contaminants in water [19–23]. Tran et al. [24] used chitosan, as a by-product in the process of producing



Citation: Xu, Y.; Gan, K.; Liang, S.; Liu, H.; Wang, Q. Investigation and Optimization of Chitosan Performance in Flocculating Kaolin Suspensions Using a Real-Time Suspending Solid Concentration Measuring Method. *Water* **2021**, *13*, 513. https://doi.org/10.3390/ w13040513

Academic Editor: Rosa Devesa-Rey

Received: 30 December 2020 Accepted: 11 February 2021 Published: 16 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). chitin from shrimp scraps, to flocculate contaminants in wastewater during the process. Compared with the conventional flocculation applying PAC or PAM, chitosan achieved much better removal efficiency than use of PAC alone and showed comparable efficiency with PAM or the combined use of PAC and PAM. Lee [25] et al. found that chitosan was not suitable for removing dissolved solids when treating palm oil mill effluent. However, chitosan was highly recommended for treating wastewater where the pollutant was mostly composed of suspended solids. Chen [26] et al. investigated flocculation efficiency and the role played by chitosan in the process of coagulating water from the Yellow River reservoir. The results showed that a small quantity of chitosan remarkably increased the removal efficiency and enlarged the floc size. Many factors affect the flocculation efficiency of chitosan. Generally, these factors can be categorized into two types: structural factors (e.g., DD and molecular weight (MW)) and environmental factors [12] (e.g., pH, temperature, ionic strength of the solution, and dose). Optimal application conditions of chitosan should be carefully selected, otherwise the best effectiveness may not be achieved [27]. Kaolin and bentonite suspensions are commonly used as raw water proxies to assess the removal efficiency of suspended inorganic solids [28–32]. There are two indexes commonly used to quantitatively characterize water quality variations before and after flocculation: suspended solid (SS) concentration and turbidity [33,34]. SS concentration is capable of directly reflecting SS quantities, although it is slow and complicated to measure. In contrast, turbidity, a parameter describing the reduction in water clarity due to the presence of suspended matter, has been more widely used as an index in such reports. Compared with the suspended solid concentration, turbidity is much easier to measure. The disadvantage of turbidity is that it cannot directly reflect the SS amount and is easily influenced by objective conditions [35,36]. In addition, conventional SS concentration and turbidity measuring methods merely measure the parameters before and after flocculation. When we want to study the SS concentration variation during the whole process of flocculation, we have to withdraw samples with pipettes at certain flocculating times [32]. This calls for great numbers of trials and a lack of efficiency. Recently, Fujisaki [37] proposed a novel SS concentration measurement method that was able to monitor, in real time, changes in SS quantities. The method was proven to be effective in his study. Subsequently, this method was applied to evaluate the flocculation performance of chitosan in kaolin suspensions [38]. The influence of some environmental factors, including dose and initial SS concentration, was investigated. Continuous variations in SS concentration in the process of flocculation were intuitively shown. However, further investigations with regard to the influence of pH and the optimal selection of hydraulic conditions were not reported. It should be noted that he also conducted investigations on intermittent agitation. The results showed that the flocculation performance was improved during intermittent agitation.

This study aims to investigate the flocculation performance of chitosan in kaolin suspensions with a novel SS concentration measurement method. The influence of environmental factors such as pH, dose, hydraulic conditions, and intermittent agitation, will be evaluated and optimized.

2. Experiment

2.1. Materials

Chitosan properties should be properly selected [32]. As suggested in previous reports, the enhancement of DD and MW leveled off when DD was over 80% or MW was over 1.0×10^5 g/mol. Therefore, we selected a chitosan agent (purchased from Fujifilm Wako Trading Corporation, Guangzhou, China) with DD = 88.5% and MW = 8.44×10^5 g/mol in this study. Kaolin was obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). The ignition loss was 13.2%, and the main constituents were 47.1% SiO₂, 38.1% Al₂O₃, 0.54% Fe₂O₃, 0.12% CaO, 0.14% MgO, 0.37% K₂O, 0.12% Na₂O, 0.15% TiO₂, and 0.11% P₂O₅. Hydrochloric acid (36.0 w/w%, analytical reagent grade) and sodium hydroxide (analytical reagent grade) were also bought from Sinopharm Chemical Reagent Co., Ltd.

(Beijing, China) to prepare the hydrochloric acid solution and NaOH solution. The other chemicals, which were of analytical reagent grade, were purchased from the same company.

The 1 w/w% HCL solution was prepared by adding 27 mL of hydrochloric acid solution to 973 mL of demineralized water. The 0.1 M HCL solution was prepared by diluting 1.73 mL of 36.0 w/w% hydrochloric acid solution in 200 mL demineralized water. The 0.1 M NaOH solution was prepared by dissolving 0.8 g sodium hydroxide into 200 mL demineralized water. All the solutions were stirred with a glass rod for about 10 min to mix evenly.

All the materials were used as received unless otherwise specified.

2.2. Preparation of Kaolin Suspension

Kaolin suspension samples (100 mg/L, 500 mg/L, and 1000 mg/L) were used in this study. The preparation method was as follows. Firstly, 20.0 g of kaolin powder were added to 2.0 L demineralized water (DW) in a jar. Secondly, the mixture of kaolin powder and DW was stirred with a YSJ-500 laboratory disperser (purchased from Shanghai Yile Electromechanical Equipment Co., Ltd., Shanghai, China) at 1000 rpm for 0.5 h. Subsequently, the stirring speed was decreased to 500 rpm, and the stock solution was kept for test use. The kaolin suspension was diluted with DW as necessary to obtain the SS concentrations required for the experiments. All suspensions were prepared immediately before each set of experiments. The initial SS concentrations of the kaolin suspensions included three grades: low-grade (100 mg/L), middle-grade (500 mg/L), and high-grade (1000 mg/L).

2.3. Preparation of Chitosan Flocculant

Chitosan is easier to dissolve in acidic solutions than in neutral water [39]. Therefore, 1 g chitosan was dissolved in 1 w/w% hydrochloric acid solution (1 L), and the solution was continuously stirred with an 85-2 constant-temperature magnetic stirrer (purchased from Changzhou Ronghua Instrument Manufacturing Co., Ltd., Changzhou, China) for 2 h. The solution then stood for 12 h before being used.

2.4. Jar Test

A conventional jar test was used for flocculation experiments. Flocculation was carried out on a six-spindle multiple stirrer unit with 75 mm \times 25 mm rectangular stainless-steel paddles. The six-spindle multiple stirrer, purchased from Wuhan Hengling Technology Co., Ltd. (Wuhan, China), was used herein to obtain precise control of paddle rotation speed, dosing time, and paddle rotation time. In fact, only one paddle was used in each trial. All experiments were carried out at laboratory scale at room temperature (approximately 24 °C). The pH values of the suspensions for all trials were adjusted to the desired values by titration with 0.1 M HCl or NaOH. The flocculation test was divided into three periods: a mixing period, flocculation period, and settling period. In the beginning of the mixing period, the required volume of chitosan solution was dosed to each suspension and mixed at a specified paddle rotation speed (RS₁) for a certain time (T₁). In the flocculation period, the paddle rotation speed decreased to a lower level, i.e., RS₂, for another time T₂. In this study, RS₁, T₁, RS₂, and T₂ were 150 rpm, 5 min, 50 rpm, and 15 min, respectively, if not otherwise specified. However, the default settling period time after flocculation was 30 min.

The performance of the chitosan flocculants was assessed using the percent removal of SS (PR), as depicted in Equation (1).

$$PR(\%) = \frac{c_0 - c}{c_0} \times 100\%$$
(1)

where c_0 is the initial SS concentration and c is the SS concentration at time t.

2.5. Measurement of SS Concentration

Fujisaki [37,38] reported a novel testing method for evaluating SS concentrations in suspension and verified its effectiveness. The system comprised a settling jar, fiber amplifier, digital multimeter, direct current (DC) power supply, computer, and attachment devices. A schematic of the setup of the components is illustrated in Figure 1. The power supply was connected to the fiber amplifier and provided 18 V DC power. The laser transmitter and receiver of the fiber amplifier were fixed at the two sides of the settling cylinder with attachment devices. The laser emitted by the laser transmitter first penetrated the settling jar and decayed because of scattering and adsorption by SS. The decayed laser signal was subsequently received by a laser receiver. The intensity of the laser received was translated into a voltage and shown on a digital multimeter (DMM). The voltage from the laser receiver was negatively correlated with the SS concentration. A high SS concentration results in low transmittance and thus corresponds to a small voltage value. In contrast, a low SS concentration corresponds to a large voltage value. For a certain SS system, e.g., a kaolin suspension, a one-to-one correspondence between SS concentration and voltage can be built. The SS concentration can be confirmed by looking up the one-to-one correspondence. In this study, kaolin suspension concentration was divided into 3 sections, which were 0–100 mg/L, 100–1000 mg/L and 1000–2000 mg/L. Standard kaolin suspensions used for calibrating the one-to-one correspondence of voltage and concentration were prepared for every 20 mg/L for the 0–100 mg/L section and for every 200 mg/L for the latter two sections. Each of the measurement for the standard kaolin suspensions was repeated five times and the mean was used for the subsequent calculations.



Figure 1. Schematic of real-time measuring setup.

3. Results and Discussion

3.1. Calibration Curve

Figure 2 shows the voltages measured for kaolin suspensions with different SS concentrations. A large SS concentration resulted in low water transmittance. As a result, the laser received by the receiver of the fiber amplifier became weak. Then, the voltage translated from the laser signal became small. In contrast, a small SS concentration led to a large voltage. Depending on the results measured above, linear and quadratic fitting were used to depict of the correlation between voltage and SS concentration. As shown in Figure 2, the R² values of linear fitting in Sections 2 and 3 were slightly smaller than those of quadratic fitting. Quadratic fitting performed much better than linear fitting in Section 1. Therefore, quadratic fitting was used to draw calibration curve in this study. The quadratic fitting results are shown in Equation (2), where x is the voltage measured and y is the SS concentration obtained from the calibration curve.

$$y = \begin{cases} 0.026^2 - 0.84x + 4.95 & 3.94V < x \le 5.72V \\ -0.038x^2 + 0.046x + 1.98 & 5.72V < x \le 7.63V \\ 1.032x^2 - 16.51x + 65.96 & 7.63V < x \le 7.79V \end{cases}$$
(2)



Figure 2. Calibration curve drawn with quadratic fitting between voltage and suspended solid concentration. Error bars represents range of observed values.

3.2. Influence of pH on SS Decantation

Chitosan flocculants were added to kaolin suspensions at a dosage of 5 mg/L, which was reported as optimal in a previous study by Li et al. [31]. The test range of pH was from 2.0 to 13.0. As shown in Figure 3, the maximal removal percentage for all three grades occurred at pH = 8.0. At this point, 88.7% of the SS was removed in the low-grade sample, in contrast to 92.1% and 96.3% in the middle-grade and high-grade samples, respectively. The percentage removal deteriorated when either increasing or decreasing the pH of the kaolin suspensions. For example, the percentage removal decreased to 79.4%, 58.7%, and 44.3%, respectively, when the pH decreased to 2.0. Chitosan flocculates contaminants in water by the mechanism of charge neutralization and bridging [28]. The former is determined by the protonation percentage of amino groups on the molecular chain, while the latter relies on the long-chain conformation of chitosan [12]. The protonation percentage of amino groups positively correlates to the acidity of solutions. The more acidic the solution is, the higher the electropositivity that chitosan possesses. The surface charge of kaolin is strongly dependent on pH [40]. Kaolin is constructed of octahedral layers of alumina and tetrahedral layers of silica [41], which alternate in a 1:1 ratio. As depicted in the report by Gupta [40], the silica tetrahedral face of kaolin is negatively charged at pH > 4.0, whereas the alumina octahedral face is positively charged at pH < 6.0 and negatively charged at pH > 8.0. Generally, the overall surface charge of kaolin colloids is weakly negative or even positive

in acidic solutions. The electronegativity reached a peak at pH = 8.0; however, further increases in alkalinity attenuated the charge density. Therefore, the electrostatic attraction between chitosan and kaolin colloids was weak when the pH was low. The electrostatic attraction even changed into repulsion when the acidity was strong enough (i.e., pH < 4.0). Therefore, chitosan appeared to be inefficient for flocculating kaolin suspensions in acidic environments and performed worst at pH = 2.0. The strong electronegativity at pH = 8.0 explained why chitosan performed best. High alkalinity is harmful to the existence of chitosan, as the long chain can be broken into short molecular groups. In chitosan flocculants, fracture of the long chain conformation dramatically deteriorates the bridging effect, which dominates the chitosan flocculation process [28,30,32].



Figure 3. Influence of pH on the percent removal of SS in kaolin suspension samples with different initial concentrations. The error bars represent range of the observed values.

Figure 4 presents the SS concentration variation curve during the flocculation of high-grade kaolin suspensions at differing pH values. The mean deviations of the SS concentration values observed were within 5% of the means. Acidic suspensions required a much shorter time (10 min) to settle as compared to alkaline suspensions (approximately 20 min). An explanation is that the weakening of the bridging effect caused by the breaking of chitosan chains decreased the floc size and thereby reduced the settling speed. The settling time did not decrease substantially owing to the presence of sweeping flocculation [42]. The best flocculation efficiency was achieved at pH = 8.0. In this case, the system settled 20 min after stirring, and the residual SS concentration was lower than 40.0 mg/L; in other cases, the residual concentration was over 100.0 mg/L.



Figure 4. Continuous variation in residual SS concentration of high-grade kaolin suspension samples at different pH values. The mean deviations of the SS concentration values observed were within 5% of the means.

3.3. Optimization of Chitosan Dosage

The "simple charge neutralization" theory [43] suggests that there is an optimal dosage of flocculant in a flocculation system [44]. As depicted in Figure 5, the percentage removal of SS dramatically increased with increasing chitosan dosage until the dosage was over 5.0 mg/L. The pH of the kaolin suspensions was 8.0. The efficiency for middle-grade samples leveled off, while that of low-grade and high-grade samples decreased. When the flocculants were added to the flocculation system at the optimal dosage, the suspended colloids became destabilized and aggregated into large flocs. However, as the flocculant dosage continued to increase and exceeded the optimal dosage, the colloids regained charge and restabilized [45]. Consequently, the SS could not settle in the flocculation system. Therefore, the optimal dosage is very important to optimize flocculant performance and should be carefully determined. Usually, higher turbidity calls for a larger flocculant dosage. However, the optimal dosages for low-grade, middle-grade, and high-grade kaolin suspension samples differed little from one another. One explanation is that the bridging effect plays the most significant role in the flocculation of chitosan. Additionally, chitosan becomes slightly soluble at pH = 8.0 and can physically entrap small colloids from water. This is the so-called sweeping flocculation mechanism.



Figure 5. Variation in the percent removal of SS by different dosages of chitosan. The error bars represent range of the observed values.

3.4. Optimization of Hydraulic Conditions

Hydraulic conditions [46] are also important for enhancing flocculation, as they can influence both the mixing of agents and raw water and the collision frequency of flocs. A high agitation intensity heightens the collision frequency. However, the intensity should still be controlled in a certain range so that the flocs cannot be broken into small pieces again. An L_9 (3⁴) orthogonal array design [47–50] based on jar tests was applied to determine the optimal hydraulic conditions for the chitosan flocculants. High-grade samples were used. As shown in Table 1, the hydraulic factors included paddle rotation speed in the mixing period (RS_1), the first period time (T_1), the paddle rotation speed in the second period (RS_2), and the second period time (T₂). They were labeled as factor A, factor B, factor C and factor D in turn. The percent removal of SS concentration was used as the assessment indicator. The dosage and pH used corresponded to the optimal conditions determined from the previous results, which were 5.0 mg/L and 8.0, respectively. As indicated by the results in Table 2, based on the comparison of different values, $A_2B_2C_3D_3$ was the best combination in our study range. The subscript numbers represent the levels of factor. Further variance analysis results are presented in Table 3. All four factors had a significant impact on the final results. The ranking of the significance of each factor was A > C > D > B. The results indicated that the paddle rotation speed in period 1 should be carefully determined, as the efficiency of chitosan dramatically decreased when the speed was too fast or too slow.

Table 1. Factors and levels in the orthogonal array design.

	Factors					
Levels	Paddle Rotation Speed in the Mixing Period (RS ₁) A (rpm)	Mixing Period Time (T ₁) B (min)	Paddle Rotation Speed in the Flocculation Period (RS ₂) C (rpm)	Flocculation Period Time (T ₂) D (min)		
1	100	3	30	10		
2	150	5	50	15		
3	200	7	70	20		

Test Number	Factors				Percent Removal of SS (%)		
	Α	В	С	D	1	2	Sum
1	1	1	1	1	85.83	85.31	171.14
2	1	2	2	2	86.52	86.14	172.66
3	1	3	3	3	87.56	88.30	175.86
4	2	1	2	3	97.46	97.51	194.97
5	2	2	3	1	98.54	98.66	197.20
6	2	3	1	2	98.22	98.12	196.34
7	3	1	3	2	87.92	87.74	175.66
8	3	2	1	3	88.63	88.54	177.17
9	3	3	2	1	85.43	85.11	170.54
K1j	519.66	541.77	544.65	538.88			1631.54
K2j	588.51	547.03	538.17	544.66			
K3j	523.37	542.74	548.72	548.00			
Range	68.85	5.26	10.55	9.12			

Table 2. The L₉ (3⁴) orthogonal array test and range analysis for hydraulic conditions.

Table 3. Variance analysis and significance assessment.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-Value	<i>p</i> -Value
А	499.85	2	249.93	3967.06	** <0.0001
В	2.61	2	1.31	20.71	** 0.0004
С	9.44	2	4.72	74.92	** <0.0001
D	7.10	2	3.55	56.35	** <0.0001
Error	0.57	9			
Total	519.57	17			

** Significant at 1%.

3.5. Settling Time

Figure 6 shows the SS concentration variation in the settling period. The chitosan dosage was 5.0 mg/L and the pH had been adjusted to 8.0. It took only 15 min for the flocs to settle down in the high-grade sample, while it took 20 min and 25 min in the cases of the middle-grade and low-grade samples, respectively. Although a high SS concentration theoretically requires more charge to neutralize and thus calls for a higher chitosan dose, SS particles can aggregate with neighboring particles by the charge-patching effect [51]. This is because positive and negative charges are unevenly distributed [52] on the surface of kaolin particles and the electrostatic attraction forces among the particles allow them to bind with each other. Additionally, the collision frequency in high-grade samples was much higher than those in the other samples and hence enhanced the sweeping effect. Sweeping played a more significant role in flocculating dense samples than sparse samples.



Figure 6. Percent removal of SS in kaolin suspensions after different settling period times.

3.6. Influence of Intermittent Agitation

The influence of intermittent agitation on the flocculation performance of chitosan was also investigated in this paper. As seen in the previous report by Fujisaki [38], SS removal efficiency got higher and higher in the intermittent agitation. Therefore, the intermittent agitation process was designed to include alternating agitation and settling and to investigate the influence of paddle rotation speed and rotation interval. In this study, the agitation time was equal to settling time. The pH of the kaolin suspension samples was adjusted to 8.0, and the dosage of chitosan was 5 mg/L. The initial SS concentration of the suspension samples was 500 mg/L.

Figure 7 shows the SS concentration variation with different paddle rotation speeds during intermittent agitation. As illustrated, there was no obvious boundary between agitation and settling when the paddle rotation speed was as low as 60 rpm. The SS concentration gradually decreased to 28.0 mg/L in 100 min. Two reasons contributed to the absence of a distinction. First, the SS collision frequency was low in the slowly agitated suspension; hence, the flocs grew slowly, which resulted in slow sedimentation of the flocs. Second, the agitation force was so weak that the settled flocs could not be stirred up, thus enhancing the measured SS concentration. As the paddle rotation speed increased, the growth of flocs became faster in the agitation period, and flocs settled faster in the settling period. Sharp changes in SS concentration emerged at the boundary of the agitation period and settling period. The bottom SS concentration during the settling period increased as the number of iterations increased. This result indicated that repeated agitation and settling significantly enhanced the floc settling speed and final percentage removal of SS. The optimal paddle rotation speed was 100 rpm. When the speed reached as 120 rpm, the floc breakage resulting from paddle rotation became more dominant than the collision effect and thus deteriorated the SS removal effect.



Figure 7. SS concentration variations with different paddle rotation speeds during intermittent agitation.

Figure 8 shows the SS concentration variation with different agitation and settling period times. The optimal paddle rotation speed obtained in the previous paragraph was used. Three times were investigated. The results show that chitosan performed better with longer agitation and settling periods. When the time was 4 min, the residual SS concentration sharply fell to 1.49 mg/L during the settling period. The settling speed increased as the number of iterations increased. In fact, the time had little effect on the final percentage removal of SS if the settling period was long enough.



Figure 8. SS concentration variations with different intervals between agitation during intermittent agitation.

4. Conclusions

The flocculation performance of chitosan in kaolin suspensions was investigated in this study. An experimental setup that was capable of real-time monitoring of SS concentration was used to measure the kaolin concentration variations in the samples. The results showed that chitosan performed best at pH = 8.0 for all three kinds of kaolin suspensions. The optimal dosage of chitosan was 5.0 mg/L, regardless of the initial SS concentration. An

orthogonal array test was carried out to determine the optimal hydraulic conditions. The flocculation process was divided into mixing and flocculating periods. The paddle rotation speed and time of the two periods were used as factors. The range analysis results showed that the paddle rotation speed was the most important factor. Further variance analysis showed that the significance of the four hydraulic factors ranked as follows: paddle rotation speed in the mixing period > paddle rotation speed in the flocculation period > flocculation period time > mixing period time. The SS concentration variation during the settling period was subsequently investigated. The results showed that kaolin suspensions with high SS concentrations required a short time to settle. The sweeping effect was more significant in dense samples than in sparse samples. Iteration of agitation and settling enhanced the flocculation perior was the best. Changing the agitation and settling period times did not significantly affect the performance.

Author Contributions: Conceptualization, Y.X. and S.L.; methodology, Y.X. and Q.W.; validation, K.G. and Y.X.; formal analysis, Y.X.; investigation, K.G; resources, Q.W.; data curation, K.G.; writing—original draft preparation, Y.X.; writing—review and editing, Y.X., S.L. and Q.W.; visualization, K.G.; supervision, H.L. and Q.W.; project administration, Y.X.; funding acquisition, Y.X. All authors have read and agreed to the published version of the manuscript.

Funding: The research presented in this paper was financially supported by postdoctoral program of MCC Capital Engineering and Research Incorporation (KB2018-C-064-404344-0). The funding source had no role in the design and conduct of the study, the analysis and interpretation of data, or in the preparation, review, or approval of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Acknowledgments: The authors would like to thank Kazuhiro Fujisaki, a senior academic at the Kyushu Institute of Technology, Japan, for his help and instruction. The authors also thank the MCC Capital Engineering and Research Incorporation for financial support for postdoctoral research.

Conflicts of Interest: The authors have no conflicts of interest to declare.

References

- 1. Edzwald, J.K. Coagulation in Drinking Water Treatment: Particles, Organics and Coagulants. *Water Sci. Technol.* **1993**, 27, 21–35. [CrossRef]
- Rondeau, V.; Commenges, D. Chapter 3—The epidemiology of aluminium and Alzheimer's disease. In *Aluminium and Alzheimer's Disease*; Exley, C., Ed.; Elsevier: Amsterdam, The Netherlands, 2001; pp. 59–73.
- 3. Campbell, A. The potential role of aluminium in Alzheimer's disease. Nephrol. Dial. Transplant. 2002, 17, 17–20. [CrossRef]
- 4. Renault, F.; Sancey, B.; Badot, P.-M.; Crini, G. Chitosan for coagulation/flocculation processes—An eco-friendly approach. *Eur. Polym. J.* **2009**, *45*, 1337–1348. [CrossRef]
- 5. Pal, P. Industrial Water Treatment Process Technology; Butterworth-Heinemann: Oxford, UK, 2017.
- 6. Bolto, B.; Gregory, J. Organic polyelectrolytes in water treatment. Water Res. 2007, 41, 2301–2324. [CrossRef]
- 7. Bratby, J. Coagulation and Flocculation in Water and Wastewater Treatment; IWA Publishing: London, UK, 2006.
- 8. Guibal, E.; Van Vooren, M.; Dempsey, B.A.; Roussy, J. A Review of the Use of Chitosan for the Removal of Particulate and Dissolved Contaminants. *Sep. Sci. Technol.* **2006**, *41*, 2487–2514. [CrossRef]
- 9. Dao, V.H.; Cameron, N.R.; Saito, K. Synthesis, properties and performance of organic polymers employed in flocculation applications. *Polym. Chem.* **2015**, *7*, 11–25. [CrossRef]
- 10. Zhong, Q.-Q.; Yue, Q.-Y.; Li, Q.; Gao, B.-Y.; Xu, X. Removal of Cu(II) and Cr(VI) from wastewater by an amphoteric sorbent based on cellulose-rich biomass. *Carbohydr. Polym.* **2014**, *111*, 788–796. [CrossRef]
- Krentz, D.-O.; Lohmann, C.; Schwarz, S.; Bratskaya, S.; Liebert, T.; Laube, J.; Heinze, T.; Kulicke, W.-M. Properties and Flocculation Efficiency of Highly Cationized Starch Derivatives. *Starch-Stärke* 2006, *58*, 161–169. [CrossRef]
- 12. Yang, R.; Li, H.; Huang, M.; Yang, H.; Li, A. A review on chitosan-based flocculants and their applications in water treatment. *Water Res.* **2016**, *95*, 59–89. [CrossRef] [PubMed]
- Li, Q.; Dunn, E.; Grandmaison, E.; Goosen, M. Applications and Properties of Chitosan. J. Bioact. Compat. Polym. 1992, 7, 370–397.
 [CrossRef]

- 14. Younes, I.; Rinaudo, M. Chitin and Chitosan Preparation from Marine Sources. Structure, Properties and Applications. *Mar. Drugs* **2015**, *13*, 1133–1174. [CrossRef] [PubMed]
- 15. Kettles, G.J.; Kanyuka, K. Dissecting the Molecular Interactions between Wheat and the Fungal Pathogen Zymoseptoria tritici. *Front. Plant Sci.* **2016**, *7*, 508. [CrossRef]
- 16. Kramer, K.J.; Koga, D. Insect chitin. Insect Biochem. 1986, 16, 851-877. [CrossRef]
- 17. Muzzarelli, R.; Muzzarelli, C. *Chitosan chemistry: Relevance to the biomedical sciences, In Polysaccharides I.*; Heinze, T., Ed.; Springer: Berlin/Heidelberg, Germany, 2005; pp. 151–209.
- 18. Rinaudo, M. Chitin and chitosan: Properties and applications. Prog. Polym. Sci. 2006, 31, 603–632. [CrossRef]
- 19. Roussy, J.; Van Vooren, M.; Guibal, E. Influence of chitosan characteristics on coagulation and flocculation of organic suspensions. *J. Appl. Polym. Sci.* **2005**, *98*, 2070–2079. [CrossRef]
- 20. Roussy, J.; Chastellan, P.; Van Vooren, M.; Guibal, E. Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers. *Water SA* 2007, *31*, 369–376. [CrossRef]
- Roussy, J.; Van Vooren, M.; Guibal, E. Chitosan for the Coagulation and Flocculation of Mineral Colloids. J. Dispers. Sci. Technol. 2005, 25, 663–677. [CrossRef]
- Onsøyen, E.; Skaugrud, O.; Onsosyen, E. Metal recovery using chitosan. J. Chem. Technol. Biotechnol. 2007, 49, 395–404. [CrossRef] [PubMed]
- Zeng, D.; Wu, J.; Kennedy, J.F. Application of a chitosan flocculant to water treatment. *Carbohydr. Polym.* 2008, 71, 135–139. [CrossRef]
- 24. Tran, N.V.N.; Yu, Q.J.; Nguyen, T.P.; Wang, S.-L. Coagulation of Chitin Production Wastewater from Shrimp Scraps with By-Product Chitosan and Chemical Coagulants. *Polymers* **2020**, *12*, 607. [CrossRef]
- 25. Leea, M.D.; Leea, P.S.; Chongb, K.H. Treatment performance of palm oil mill effluent by utilizing Chitosan and ferric chloride coupled with activated carbon and ultrasound bath. *Desalin. Water Treat.* **2020**, *174*, 136–142. [CrossRef]
- 26. Chen, F.; Liu, W.; Pan, Z.; Wang, Y.; Guo, X.; Sun, S.; Jia, R. Characteristics and mechanism of chitosan in flocculation for water coagulation in the Yellow River diversion reservoir. *J. Water Process. Eng.* **2020**, *34*, 101191. [CrossRef]
- 27. Vidal, R.R.L.; Moraes, J.S. Removal of organic pollutants from wastewater using chitosan: A literature review. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 1741–1754. [CrossRef]
- 28. Huang, C.; Chen, S.; Pan, J.R. Optimal condition for modification of chitosan: A biopolymer for coagulation of colloidal particles. *Water Res.* **2000**, *34*, 1057–1062. [CrossRef]
- 29. Chen, L.; Chen, D.; Wu, C. A New Approach for the Flocculation Mechanism of Chitosan. *J. Polym. Environ.* 2003, *11*, 87–92. [CrossRef]
- 30. Roussy, J.; Van Vooren, M.; Dempsey, B.A.; Guibal, E. Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions. *Water Res.* 2005, *39*, 3247–3258. [CrossRef]
- 31. Li, J.; Song, X.; Pan, J.; Zhong, L.; Jiao, S.; Ma, Q. Adsorption and flocculation of bentonite by chitosan with varying degree of deacetylation and molecular weight. *Int. J. Biol. Macromol.* **2013**, *62*, 4–12. [CrossRef]
- 32. Li, J.; Jiao, S.; Zhong, L.; Pan, J.; Ma, Q. Optimizing coagulation and flocculation process for kaolinite suspension with chitosan. *Colloids Surf. A Physicochem. Eng. Asp.* **2013**, 428, 100–110. [CrossRef]
- 33. Likens, G.; Benbow, M.; Burton, T.; van Donk, E.; Downing, J.; Gulati, R. *Encyclopedia of Inland Waters*; Elsevier: Amsterdam, The Netherlands, 2009.
- 34. Altaher, H. The use of chitosan as a coagulant in the pre-treatment of turbid sea water. J. Hazard. Mater. 2012, 233–234, 97–102. [CrossRef] [PubMed]
- 35. Hannouche, A.; Chebbo, G.; Ruban, G.; Tassin, B.; Lemaire, B.J.; Joannis, C. Relationship between turbidity and total suspended solids concentration within a combined sewer system. *Water Sci. Technol.* **2011**, *64*, 2445–2452. [CrossRef] [PubMed]
- 36. Daphne, L.H.X.; Utomo, H.D.; Kenneth, L.Z.H. Correlation between turbidity and total suspended solids in Singapore rivers. *J. Water Sustain.* **2011**, *1*, 313–322.
- 37. Fujisaki, K. Comparison of Flocculation Properties with Use of a New Flocculation Tester. *Mod. Environ. Sci. Eng.* **2016**, *1*, 304–310. [CrossRef]
- Fujisaki, K. Experimental study on flocculation performance of Chitosan-Based Flocculant using a Novel Jar Tester. J. Civ. Eng. Environ. Sci. 2018, 4, 038–043. [CrossRef]
- Qin, C.; Li, H.; Xiao, Q.; Liu, Y.; Zhu, J.; Du, Y. Water-solubility of chitosan and its antimicrobial activity. *Carbohydr. Polym.* 2006, 63, 367–374. [CrossRef]
- 40. Gupta, V.; Miller, J.D. Surface force measurements at the basal planes of ordered kaolinite particles. *J. Colloid Interface Sci.* 2010, 344, 362–371. [CrossRef] [PubMed]
- 41. Varga, G. The structure of kaolinite and metakaolinite. Epitoanyag 2007, 59, 6–9. [CrossRef]
- Yang, Z.; Yang, H.; Jiang, Z.; Cai, T.; Li, H.; Li, H.; Li, A.; Cheng, R. Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide. *J. Hazard. Mater.* 2013, 254–255, 36–45. [CrossRef] [PubMed]
- 43. Duan, J.; Gregory, J. Coagulation by hydrolysing metal salts. Adv. Colloid Interface Sci. 2003, 100, 475–502. [CrossRef]

- 44. Yang, Z.; Shang, Y.; Huang, X.; Chen, Y.; Lu, Y.; Chen, A.; Jiang, Y.; Gu, W.; Qian, X.; Yang, H.; et al. Cationic content effects of biodegradable amphoteric chitosan-based flocculants on the flocculation properties. *J. Environ. Sci.* **2012**, *24*, 1378–1385. [CrossRef]
- 45. Yang, Z.; Shang, Y.; Lu, Y.; Chen, Y.; Huang, X.; Chen, A.; Jiang, Y.; Gu, W.; Qian, X.; Yang, H.; et al. Flocculation properties of biodegradable amphoteric chitosan-based flocculants. *Chem. Eng. J.* **2011**, *172*, 287–295. [CrossRef]
- Sun, J.; Qin, L.; Li, G.; Kang, Y. Effect of hydraulic conditions on flocculation performances and floc characteristics in Chinese herbal extracts by chitosan and chitosan hydrochloride. *Chem. Eng. J.* 2013, 225, 641–649. [CrossRef]
- 47. Wheeler, R.E.; Atkinson, A.C.; Donev, A.N. Optimum Experimental Designs. Technometrics 1993, 35, 450. [CrossRef]
- 48. Weissman, S.A.; Anderson, N.G. Design of Experiments (DoE) and Process Optimization. A Review of Recent Publications. *Org. Process. Res. Dev.* **2015**, *19*, 1605–1633. [CrossRef]
- 49. Aydın, Y.A.; Aksoy, N.D. Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. *Chem. Eng. J.* **2009**, 151, 188–194. [CrossRef]
- 50. Maazinejad, B.; Mohammadnia, O.; Ali, G.A.; Makhlouf, A.S.; Nadagouda, M.N.; Sillanpää, M.; Asiri, A.M.; Agarwal, S.; Gupta, V.K.; Sadegh, H. Taguchi L9 (34) orthogonal array study based on methylene blue removal by single-walled carbon nanotubes-amine: Adsorption optimization using the experimental design method, kinetics, equilibrium and thermodynamics. *J. Mol. Liq.* 2020, 298, 112001. [CrossRef]
- Bratskaya, S.; Avramenko, V.; Schwarz, S.; Philippova, I. Enhanced flocculation of oil-in-water emulsions by hydrophobically modified chitosan derivatives. *Colloids Surf. A Physicochem. Eng. Asp.* 2006, 275, 168–176. [CrossRef]
- 52. Gupta, V. Surface Charge Features of Kaolinite Particles and their Interactions. Ph.D. Thesis, The University of Utah, Salt Lake City, UT, USA, 2011.