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Research and Application of Gangue for the Preparation of Polymerized Aluminum Magnesium Chloride Flocculant

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Abstract: Polymerized aluminum magnesium chloride (PAMC) flocculant was prepared from gangue as a raw material, and the effects of pH, the polymerization time, and the polymerization temperature on the performance of the PAMC were investigated by a one-factor test, based on which, orthogonal experiments (three-factor and two-level) were conducted to optimize the relevant parameters. Meanwhile, FTIR and SEM were used to characterize the polymerized aluminum magnesium chloride, and the sample was applied in printing and dyeing wastewater treatment. The results showed that a pH value of 2.2 and a reaction at 60 °C for 4.5 h were the optimal preparation conditions; the characterization analysis showed that the synthesized product was polymerized aluminum magnesium chloride; the turbidity removal rate of the PAMC for printing and dyeing wastewater was increased by 2.1%, the COD removal rate was increased by 3.1%, the ammonia nitrogen removal rate was increased by 2.1%, and the chromaticity removal rate was increased by 9.2% compared with that of PAC.

Keywords: coal gangue; polymeric aluminum magnesium chloride; turbidity removal; COD removal rate

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1. Introduction

Coal gangue is a solid waste discharged in the process of coal mining and washing. According to incomplete statistics, current accumulation of coal gangue has exceeded 6 billion tons, and it not only occupies a large amount of land and involves spontaneous combustion of gangue and release of heavy metal elements, but also causes a serious impact on the environment around the mining area [1–6]. Strengthening the comprehensive utilization of coal gangue is of great significance in solving the problems of land compaction and environmental pollution caused by the massive accumulation of coal gangue. Coal gangue is rich in SiO_2, Al_2O_3, and Fe_2O_3, making it an ideal material for the production of flocculants [7]. The use of coal gangue in the production of flocculants and its application in water treatment can not only effectively solve the problems caused by the massive accumulation of coal gangue but also reduce the cost of water treatment. Therefore, the use of coal gangue to prepare flocculants has important practical significance and theoretical significance.

Since the appearance of inorganic polymer flocculants in the 20th century, they have been widely developed in many countries due to their advantages of easy production, low price, and good coagulation effects. Among them, aluminum and iron salts are the most common flocculants nowadays, and the cations generated by the hydrolysis of metal salts neutralize the electronegativity of colloids in water, which can be effective in electroneutralization mechanisms [8,9]. However, due to the complexity and diversity of water environments requiring treatment, the demand for more efficient flocculants is increasing. Magnesium salt as a water treatment agent has the advantages of fast floc generation, coarser particles, higher density, faster floc settling speed, and lower sludge water content, and its turbidity removal and decoloration effect are better than those of aluminum salt [10].

Magnesium salts and metal salts are combined to form magnesium salt composite flocculants, which combine both the electrical neutralizing ability of metal salts and the decolorizing ability of magnesium salts, greatly improving the flocculation performance of these flocculants [11,12]. Magnesium salts and other magnesium-containing compounds are not widely used in wastewater treatment as a separate treatment agent, but because magnesium-containing compounds have a good effect on the decolorization of printing and dyeing wastewater, they have been widely applied and studied in the treatment of printing and dyeing wastewater. Ji Ming et al. used magnesium hydroxide to decolorize direct-dyeing wastewater, and the results showed that the decolorization rate could reach more than 98% [13]. Qin Nicco et al. found that the decolorization effects of magnesium salt on reactive dye, acid dye, direct dye, and other water-soluble anionic dye wastewater were better, and this was because dye molecules in the sulfonic acid, carboxyl, -NH_2, -OH, and other anionic groups are easily adsorbed into the point of action of magnesium hydroxide; therefore, through the adsorption effect, the entirety of dye molecules is removed, the decoloration effects are good, and the chemical oxygen demand removal rate is often higher than 70% [14]. Zhao Jiang et al. used magnesium hydroxide to directly decolorize gray printing and dyeing industrial wastewater [15]. Therefore, the addition of magnesium salt to aluminum and iron salt flocculants can improve the decolorization and coagulation effects of the flocculants.

Therefore, this paper used gangue, hydrochloric acid, and MgO as the main raw materials to carry out the polymerization of aluminum magnesium chloride in order to explore the best conditions for the alkaline polymerization and the primary and secondary effects of these factors on the removal rate of turbidity, the best acid leaching conditions for the preparation of the acid leaching solution, and the alkaline polymerization process for orthogonal experiments. In addition, the use of an infrared spectrometer (FTIR) and a scanning electron microscope (SEM) to explore the flocculation mechanism provides a certain theoretical basis for the comprehensive use of gangue as a raw material for wastewater treatment.

2. Experimental Section

2.1. Experimental Materials

The gangue was collected from a mine in Datong, Shanxi Province, and the main chemical components of the gangue, i.e., SiO_2 (silicon molybdenum blue spectrophotometry), Al_2O_3 (fluoride salt substitution EDTA complex titration), Fe_2O_3 (iron reagent spectrophotometry), CaO (EGTA complex titration), and MgO (EGTA complex titration), were analyzed, and the results are shown in Table 1. The simulated water sample was a kaolin suspension (1000 NTU), and the actual water sample (printing and dyeing wastewater) was collected from a printing and dyeing wastewater plant in Jilin Province.

Table 1. Analysis of the content of the main components of the gangue.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
51.0%	25.1%	6.4%	5.4%	1.4%

2.2. Preparation of PAMC

The gangue was put into a solid grinder (Nanjing Dongmai Technology Co., Nanjing, China) and ground to a certain particle diameter (<0.18 mm), put into a muffle furnace (Shaoxing Shangcheng Instrument Manufacturing Co., Shaoxing, China), when the temperature reached 800 °C, held and heated for 2 h, taken out and cooled to room temperature. After that, the activated gangue (20 g) was put into hydrochloric acid (Beijing Chemical

Plant, Beijing, China) solution (20%) for a period of time, and the solid–liquid separation (30 min) to obtain the acid leach solution. Take a certain amount of acid leaching solution add magnesium oxide (Tianjin Komeo Chemical Reagent Co., Tianjin, China) to adjust pH, placed in a water bath (Changzhou Surui Instrument Co., Changzhou, China) at a certain polymerization temperature reaction for a period of time, solid–liquid separation to obtain the liquid polymerized aluminum magnesium chloride, the liquid polymerized aluminum magnesium into the drying box (Shaoxing Shangcheng Instrument Manufacturing Co., Shaoxing, China) drying to obtain the solid polymerized aluminum magnesium chloride.

2.3. Determination of Turbidity

Place an appropriate amount of raw water or flocculant treated water samples in the SGZ-1A Turbidimeter (Hash Corporation of America, CO, USA) to measure turbidity. The turbidity removal rate formula is as follows:

$$\text{Turbidity removal rate} = \frac{T_0 - T_1}{T_0}$$

where T_0—initial turbidity of water samples. T_1—turbidity of treated water samples.

2.4. Methods of Analysis

The main chemical composition of coal gangue is analyzed according to "Coal ash composition analysis method", and the coal ash composition analysis method mainly includes chemical analysis method, physical analysis method and instrumental analysis method. In this paper, the instrumental analysis method, i.e., X-ray fluorescence spectrometry, was used to analyze the gangue samples. The gangue powder was dried, then ground through a 200 mesh sieve and filled with more than 1 mL. It was pressed into a thin block, and the sample size was 32 mm, and the test area was 30 mm in diameter at the center.

The effective metal ion content and salinity of the flocculant were determined according to the methods in the provisions of "Water Treatment Agent Polyaluminum Chloride". The Nicolet 380 Fourier (Thermo Fisher Scientific, Waltham, MA, USA) transform infrared spectrometer was used to analyze the home-made polymerized aluminum chloride-magnesium flocculant by the potassium bromide tableting method. The samples to be tested were placed in an oven at 105 °C for a certain period of time after drying, and then taken out, and then completely ground and mixed with the ratio of potassium bromide: powder sample = 100:1 in an onyx mortar, and then pressed into tablets through the molds after even mixing to produce the test samples. The analytical conditions were as follows: resolution of 2 cm^{-1}, scan times of 20 times, and scan range of 4000–400 cm^{-1}.

The JSM-7500F scanning electron microscope (Shenzhen East Measurement Technology Co., Shenzhen, China) was used to analyze and test the home-made polymerized aluminum chloride-magnesium flocculant, the samples to be tested were placed in the oven at 105 °C for a certain period of time after drying, taken out and ground, and placed in a dry bowl for closed storage, first, the samples that did not contain water were sprayed with gold pretreatment so that the powder samples could have good electrical conductivity, and the conditions of analysis were as follows: the voltage was 5. 0 kV, the current was 10 μA, the working distance was 8.0 mm, and the magnification was 1000 and 2000 times, respectively.

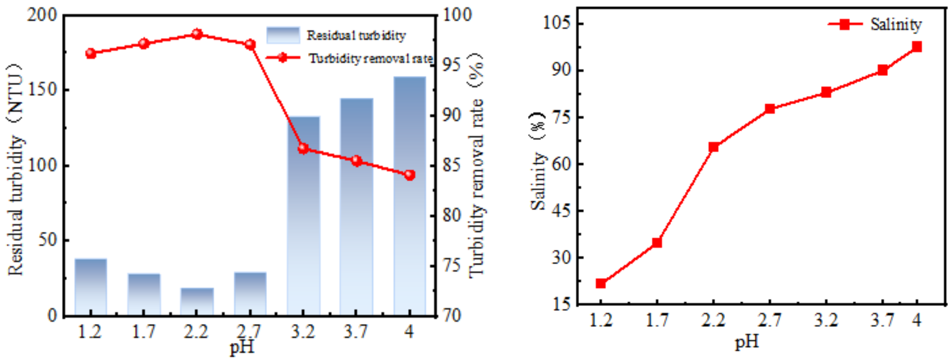
2.5. Coagulation Experimental Methods

Take a certain amount of water samples, add an appropriate amount of flocculant, use an electric mixer for uniform mixing, and after a period of standing time, take the top layer of water for turbidity, Chemical Oxygen Demand (COD), color, and other tests.

3. Results and Discussion

3.1. Determination of Optimal pH for PAMC

Acid leaching experiments were carried out using hydrochloric acid (concentration 20%), the acid leaching solution obtained was highly acidic and the pH was increased by MgO. Therefore, in order to investigate the effect of pH on the product, the pH of the product was changed by the addition of MgO while keeping all other conditions unchanged, the salinity of the product was determined and coagulation experiments were carried out using kaolin suspension (1000 NTU) and the results are shown in Figure 1.



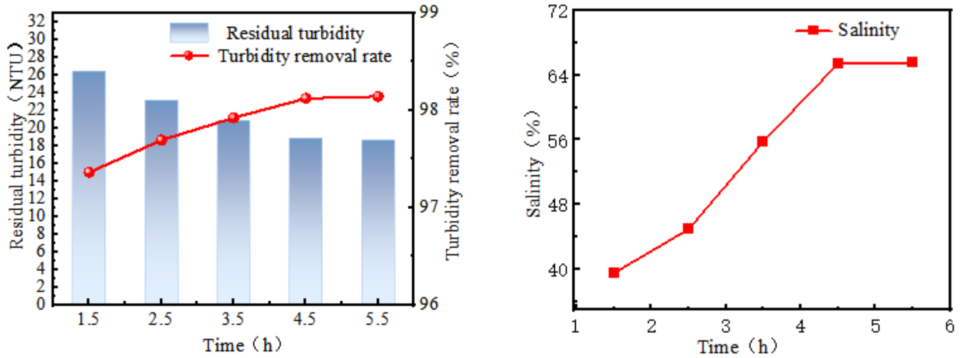
(**a**) (**b**)

Figure 1. (**a**) Influence of pH value on the turbidity removal rate of polymerized aluminum magnesium chloride; (**b**) Effect of pH on the salinity of polymerized aluminum magnesium chloride.

As can be seen from Figure 1a, when the pH is 1.2 to 2.2, the turbidity removal rate increases with the increase in pH, the turbidity removal rate reaches the maximum when the pH is 2.2, and after the pH is greater than 2.2, the turbidity removal rate starts to decrease, and as can be seen from Figure 1b, when the pH increases, the salinity of the product increases, and the salinity of the product increases with the increase in pH. As the pH increases, the degree of polymerization of metal ions (aluminum, magnesium) also gradually increases, and the electric neutralization and electric sweeping network of the product is stronger, and the coagulation effect is better. When the pH is 2.2~4, the salinity of the product still increases with the increase in pH, but the turbidity removal rate is reduced. There are two reasons for this phenomenon: On the one hand, because of high salinity is very easy to make the metal ions (aluminum, magnesium) can not polymerize the formation of hydroxide, reducing the ability of its electrical neutralization, turbidity removal ability to reduce; On the other hand, in the polymerization reaction process will generate a high degree of polymerization of the product particle diameter and flocculation and precipitation performance is strong, for the removal of turbidity of wastewater is more effective, but when salinity However, when the salinity is too high, it is easy to decompose into low polymer with poor flocculation effect, which leads to the decrease in flocculation performance of polymerized aluminum magnesium chloride [15]. And in the experimental process, it was found that when the solution pH is 3.2, if the pH is further increased, the stability of the reactant is low, and it is very easy to produce flocculent precipitates, and these precipitates will also greatly increase the difficulty of solid–liquid separation, thus increasing the cost of its preparation. Therefore, in summary, the optimum pH is 2.2.

3.2. Determination of the Optimal Polymerization Time of PAMC

To investigate the effect of polymerization reaction time on the product, other conditions were kept unchanged, and the alkaline polymerization time was changed to investigate the effect of polymerization time on the salinity of the product and the turbidity removal rate of the kaolin suspension (NTU), and the experimental results are shown in Figure 2. With the extension of the polymerization reaction time, the salinity and turbidity removal rate were improved, and the salinity and coagulation performance of the product remained basically unchanged after 4. The polymerization reaction dominated the time from 1.5 h to 4.5 h, with the increase in salinity and coagulation performance improved, and the equilibrium state between polymerization and depolymerization was basically reached at 4.5 h. After 4.5 h, the polymerization and depolymerization basically reached the equilibrium state. Therefore, the optimum time for the polymerization reaction in this experiment is 4.5 h.

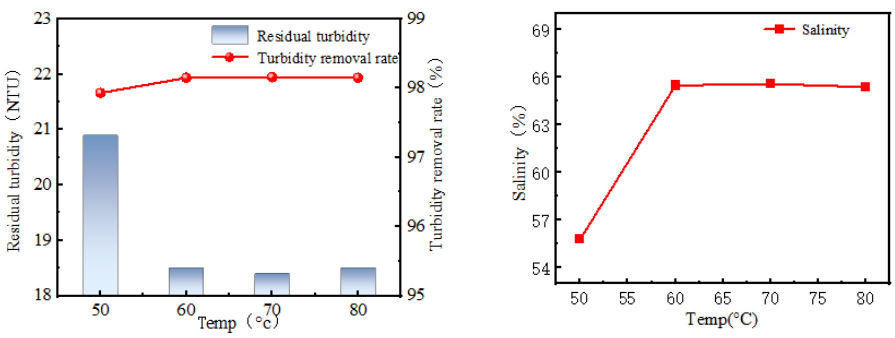


(**a**) (**b**)

Figure 2. (**a**) Effect of polymerization time on the turbidity removal rate; (**b**) Effect of polymerization time on salinity.

3.3. Determination of the Optimum Polymerization Temperature of PAMC

To investigate the effect of the alkaline polymerization temperature on the salinity of the product and the turbidity removal rate of the kaolin suspension (1000 NTU), the other conditions were kept unchanged and the alkaline polymerization temperature was changed, and the experimental results are shown in Figure 3. With the increase in polymerization temperature, the salinity and turbidity removal rate of the product also increased, and it was basically unchanged after 60 °C. The results are shown in Figure 3. When the temperature increases, it can make the product to polymerization direction, the salinity and coagulation performance is improved, when the temperature reaches 60 °C, the polymerization and depolymerization reaction basically reaches the equilibrium. Therefore, 60 °C is the best polymerization temperature for this experiment.



(**a**) (**b**)

Figure 3. (**a**) Effect of polymerization reaction temperature on the turbidity removal rate of polymerized aluminum magnesium chloride; (**b**) Effect of polymerization reaction temperature on the salinity of polymerized aluminum magnesium chloride.

3.4. Orthogonal Tests

In order to investigate the optimal process conditions for the best preparation at the polymerization stage, the orthogonal experimental method was used to conduct a 3-factor, 2-level orthogonal test with three factors: pH, polymerization time, and polymerization temperature. The factor levels are shown in Table 2, and the results are shown in Table 3.

Through the test, the combination of the optimal process was derived as $A_2B_2C_1$, i.e., the acidic leach solution was adjusted to pH 2.2 with MgO, and the reaction was carried out at 60 °C for 4.5 h.

Table 2. Experimental factors and levels.

Math	Factor (A)	Factor (B)	Factor (C)
	pH	Time (h)	Temp (°C)
1	1.7	3.5	60
2	2.2	4.5	70

Table 3. Orthogonal test data table.

Experiment Number	Factor (A)	Factor (A)	Factor (A)	Turbidity Removal Rate (%)
	pH	Time (h)	Temp (°C)	
1	1	1	1	96.96
2	1	2	2	97.11
3	2	1	2	97.66
4	2	2	1	98.13
K_1	$K_1{}^A$ = 97.04	$K_1{}^B$ = 97.31	$K_1{}^C$ = 97.55	
K_2	$K_2{}^A$ = 97.90	$K_2{}^B$ = 97.62	$K_2{}^C$ = 97.39	
R	0.86	0.31	0.16	

3.5. PAMC Characterization Analysis

3.5.1. Component Analysis

Effective metal ion content and salinity are two important factors that affect the coagulation performance of flocculants [16]. Therefore, in this experiment, the metal elements and salinity of the product were analyzed with reference to the detection method in "Water Treatment Agent Polyaluminum Chloride", and the results are shown in Table 4. From Table 4, it can be seen that the salinity of the product is 65.6%, which indicates that there is OH^- in the product, Cl^- in the acidic leaching solution is gradually replaced by OH^-, and the product has a certain degree of polymerization as a polymerization-type flocculant [17].

Table 4. Product composition and salinity.

Constitute	Al_2O_3	MgO	Salinity
Mass fraction (%)	20.1	7.1	65.6

3.5.2. FTIR Analysis

The infrared spectra of the products are shown in Figure 4. The absorption peaks at 3380 cm^{-1} and 1636 cm^{-1} represent the Al-OH coordination bonds generated by aluminum ions and carboxyl groups [18,19]; the absorption peaks around 2300 cm^{-1} are mainly generated by O-Al bonds [20]; the absorption peak at 1090 cm^{-1} is generated by the bending vibration of -OH in Al-OH and Mg-OH; the absorption peak at 618 cm^{-1} is generated by the asymmetric attraction of O in -OH due to the different electronegativities of Al^{3+} and Mg^{2+}; the absorption peaks at wave numbers from 670 cm^{-1} to 1510 cm^{-1}, there are stronger absorption peaks at wave numbers from 670 cm^{-1} to 1510 cm^{-1}, in addition to the coupling effect of the absorption peaks of Al-OH and Mg-OH in the product, there may be the effect of the bending vibration of Al-OH, Mg-OH and Al-OH by the neighboring groups, which leads to a certain degree of deviation of the bending vibration, partly due to the role of low-frequency redshift [21–23]. The infrared spectrogram of the product is basically consistent with the description of related literature; therefore, the product is polymerized aluminum magnesium chloride.

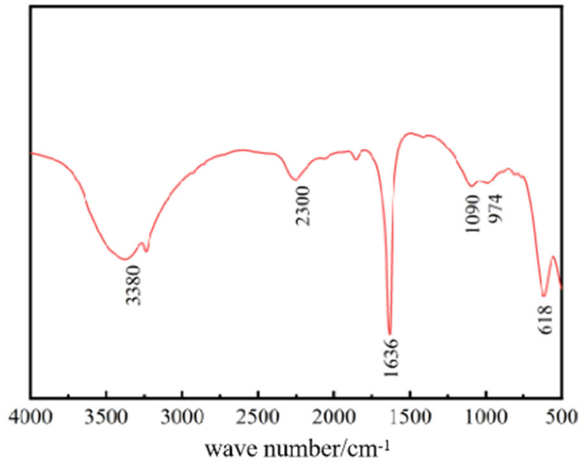


Figure 4. Infrared spectra of polymerized aluminum magnesium chloride.

3.5.3. SEM Analysis

Due to the poor electrical conductivity of the sample, the sample was treated with gold sputtering before the test, and then it was magnified 1000 and 2000 times by scanning electron microscope to observe its morphological characteristics, as shown in Figure 5. The polymeric aluminum-magnesium chloride showed a net-like structure, and this structure can increase its specific surface area, which makes the adsorption bridging and net trapping and sweeping ability improved [24].

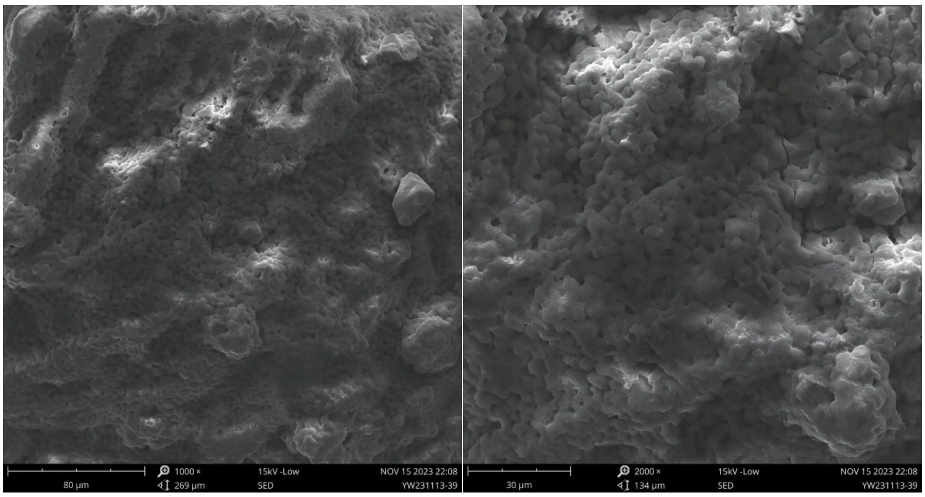


Figure 5. Scanning electron microscopy of polymerized aluminum magnesium chloride.

3.6. Response Surface Analysis

3.6.1. Regression Modeling and Analysis

To investigate the interaction between various factors in the flocculation process of polymerized aluminum magnesium chloride and the degree of influence of each factor on the turbidity removal rate. Based on single-factor experiments, Box-Behnken design (BBD) in Design-Expert 10.0 software was used to conduct response surface experiments with three factors of dosage, settling time, and pH as the influencing parameters and the turbidity removal rate of the simulated water samples (kaolin suspension) as the index. The experimental factors and levels were obtained with three factors and three levels in Table 5, and the experimental design scheme and results are shown in Table 6.

Table 5. Test factors and levels.

Factors	Coding Level		
	−1	**0**	**1**
A Dosage (mg/L)	100	200	300
B Settlement time (min)	5	10	15
C PH Value	7	8	9

Table 6. Experimental design program and results.

Experiment No.	A	B	C	Turbidity Removal Rate (%)
	Dosage (mg/L)	**Settlement Time (min)**	**pH**	
1	0	−1	1	89.97
2	0	0	0	98.57
3	1	1	0	94.47
4	0	0	0	98.35
5	0	1	−1	98.46
6	0	0	0	98.11
7	−1	0	1	97.58
8	−1	1	0	97.45
9	1	0	1	94.22
10	0	−1	−1	90.73
11	−1	0	−1	97.39
12	−1	−1	0	90.06
13	1	0	−1	94.31
14	0	0	0	98.18
15	0	0	0	98.42
16	0	1	1	98.49
17	1	−1	0	86.69

Design-Expert 10.0 was used to analyze the functional relationship between the turbidity removal rate and dosage, settling time, and pH (1), and a response surface regression model was constructed with respect to Y, where Y represents the turbidity removal rate and the independent variables X_1, X_2, and X_3 represent the dosage of polymerized aluminum magnesium chloride, the flocculation and settling time, and the pH of the initial water sample, respectively.

$$Y = 98.33 - 1.71X_1 + 3.82X_2 - 0.079X_3 + 0.32X_1X_2 - 0.070X_1X_3 + 0.20X_2X_3 - 2.24{X_1}^2 - 0.37{X_2}^2 - 0.22{X_3}^2$$

ANOVA and significance test of the data can be obtained, the model's $p < 0.0001$, indicating that the established model has reached a significant level, which can more realistically reflect the influence of various factors on the turbidity removal rate of kao-lin suspension; the p value of the loss of fit term is 0.0523 > 0.05, indicating that the loss of fit term of the model is not significant, and the model error is small. The R_2 of the model = 0.9965, indicating that the actual value of the turbidity removal rate of polymerized aluminum-magnesium chloride and the predicted value of the model have a good degree of fit; Adj-R-squared (Adj-R^2) is 0.9919, indicating that 99.19% of the results of the turbidity removal rate of polymerized aluminum-magnesium chloride on the turbidity removal rate of kaolin suspension can be interpreted and analyzed by this model.

3.6.2. Response and Contour Analysis

The steepness of the slope of the three-dimensional surface of the response surface can reflect the effect on the experimental results, the steeper the three-dimensional surface, the more significant the effect of the interaction between the two factors on the experimental results; At the same time, the contour plots of the response surface can also illustrate the effect of the interaction between the two factors on the experimental results, the contour presented as a circle indicates that the interaction between the two factors is not significant, and if it is presented as an ellipse, it indicates that the interaction between the two factors has a significant effect on the experimental results. If the contour line is round, it indicates that the interaction between the two factors has no significant effect on the experimental results, and if it is oval, it indicates that the interaction between the two factors has a significant effect on the experimental results [25–28].

From Figure 6, it can be seen that the slope of the three-dimensional surface map of the two factors of dosage and settling time is steeper, which can be concluded that the interaction between the two factors of dosage and settling time has a significant effect on the experimental results; at the same time, it can be seen from the contour map, the contour map shows an elliptical shape, which can also be obtained by the same conclusion, that is, the dosage and settling time have a more obvious interaction. Therefore, a comprehensive analysis can be obtained that the interaction between the two factors of dosage and settling time is significant.

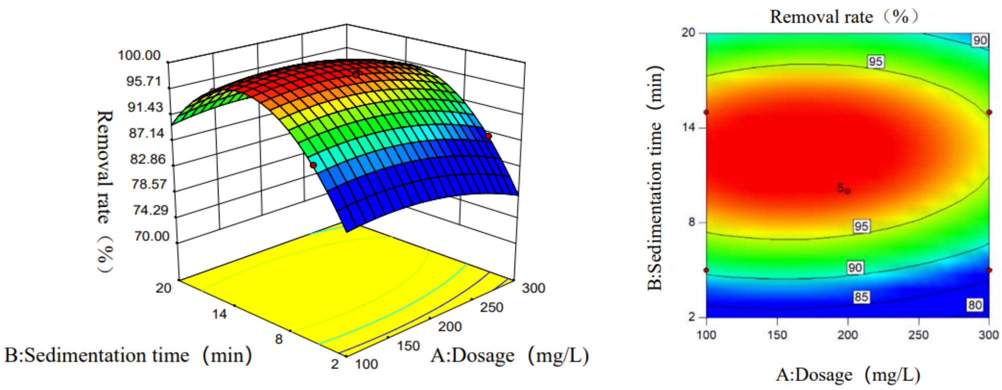


Figure 6. Response surface and contour of turbidity removal rate by dosage and settling time.

Figure 7 shows the three-dimensional surface plot of pH and dosage on the turbidity removal rate, from the figure we can see that the slope of the surface plot is gentle, indicating that the interaction between the two factors is not significant for the turbidity removal rate; and then combined with the pH and dosage on the turbidity removal rate of the contour plot, which is presented in a circular contour plot, and the same conclusions can be obtained. Therefore, it can be concluded that the effect of pH and dosage on the turbidity removal rate is not significant.

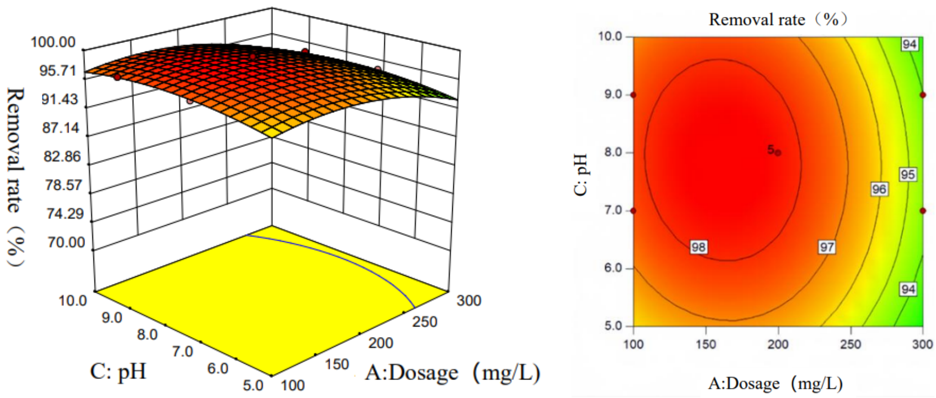


Figure 7. Response surface and contour of pH and dosage on turbidity removal rate.

Figure 8 shows the three-dimensional response surface plot of pH and settling time on the turbidity removal rate, we can see that its slope is very steep, indicating that the interaction between the two factors has a significant effect on the turbidity removal rate; after that, by analyzing the contour plots of pH and settling time on the turbidity removal rate, we can see that the contour plots show an elliptical shape, and we can reach the same conclusion. Therefore, it can be concluded that pH and settling time have a significant effect on the turbidity removal rate.

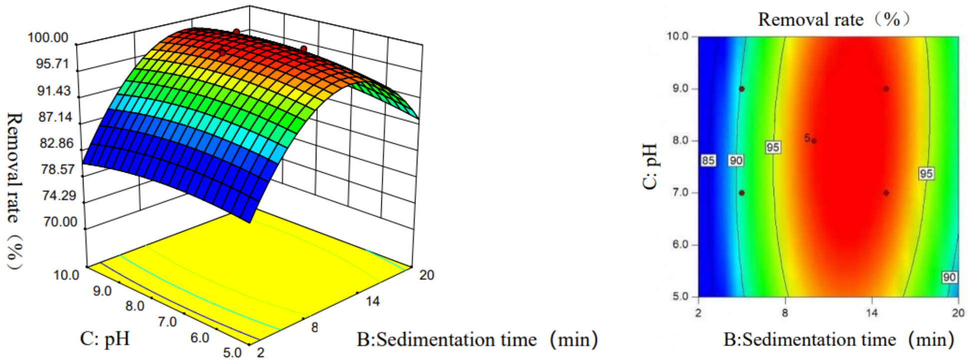


Figure 8. Response surface and contours of pH and settling time on the turbidity removal rate.

3.7. Optimization Prediction and Validation Tests

In order to investigate the accuracy of the model obtained by Design-Expert10.0 software, the optimal flocculation conditions were selected and the relevant parameters were modified in combination with the actual situation, and three sets of flocculation experiments were conducted under the conditions of 200 mg/L, pH 8.5 and a settling time of 15 min to verify the model, and the results of the experiments are shown in Figure 9. The turbidity removal results of the three experiments were 98.51%, 98.60% and 98.46%, respectively, and the average value of the three experiments was 98.52%, and the model predicted that the turbidity removal rate was 98.70%, which was less different from the model prediction. Therefore, the model has a good prediction effect for the turbidity removal rate of kaolin suspension, and the model is reliable.

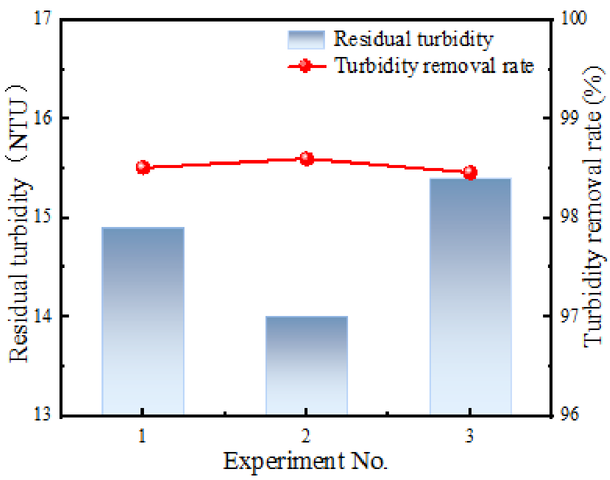


Figure 9. Turbidity removal rate of flocculation experiment with optimal parameters.

3.8. Coagulation Experiment for Printing and Dyeing Plant Wastewater

With the rapid development of the printing and dyeing industry, the water consumption and wastewater discharge of this industry show an increasing trend year by year, and the difficulty of treatment is also increasing [29,30]. The experimental water samples were taken from the wastewater of a printing and dyeing factory in Jilin Province, and the appearance of the raw water showed a deep yellow color, and there was a small amount of impurities floating on the surface of the water. After collecting the water samples, the water samples were immediately analyzed in the water body, and the specific analysis results are shown in Table 7.

Table 7. Indicators related to sewage from printing and dyeing factories.

Watery	Turbidity (NTU)	COD (mg/L)	Ammonia Nitrogen (mg/L)	Chromaticity (Dilution Multiple)	pH
Printing and dyeing sewage	100	1600	20	120×	7.2

3.8.1. Effect of Flocculant Dosage on Turbidity Removal Rate of Printing and Dyeing Wastewater

In order to study the polymerization of aluminum magnesium chloride and polymerization of aluminum chloride two flocculant dosage for the printing and dyeing plant effluent coagulation effect, 200 mL printing and dyeing plant effluent was placed in the 250 mL beaker to go, other conditions were fixed, different flocculants (polymerization of aluminum chloride and polymerization of aluminum magnesium chloride) were added, and the dosages were: 500 mg/L, 600 mg/L, 700 mg/L, and 800 mg/L. After resting for the same amount of time, the upper water body was taken out and the turbidity analysis was carried out using a turbidity analyzer. The experimental results are shown in Figure 10. As the dosage of two flocculants increased, the turbidity removal also increased, reaching a maximum at 700 mg/L, and then decreased with the increase in dosage. This is mainly due to the fact that if the flocculant dosage is too low, the polymerized material generated by hydrolysis is insufficient, so the coagulation effect is poor. On the other hand, if too much flocculant is added, the polymerized material generated by hydrolysis is too much, and the colloidal particles in the water are enveloped, making it impossible for the colloidal particles to coalesce, resulting in poor coagulation. Therefore, the optimum dosage of this experiment is 700 mg/L. At the same time, polymerized aluminum chloride-magnesium is a composite flocculant composed of aluminum and magnesium, which will have a synergistic effect in the treatment of printing and dyeing wastewater, and compared with the single flocculant of polymerized aluminum chloride, which mainly contains the metal element of aluminum, it has a better bilayer pressure and adsorption of electrical neutralization ability, so the turbidity removal effect of polymerized aluminum chloride-magnesium is better than that of polymerized aluminum chloride.

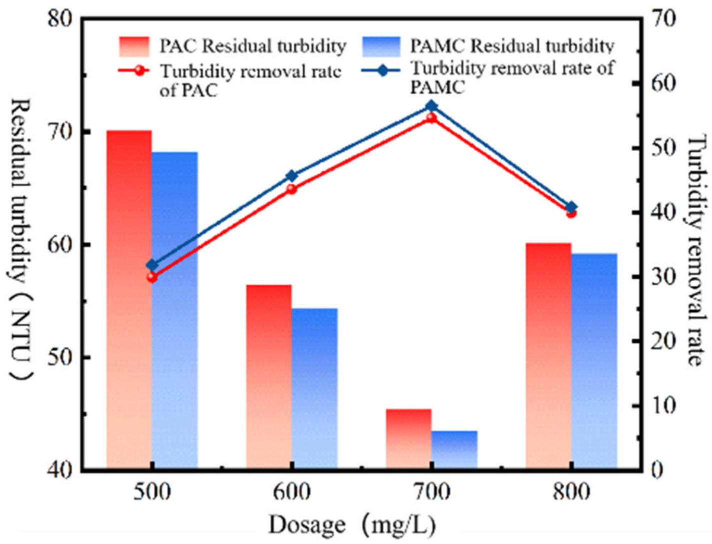


Figure 10. Effect of dosage on coagulation effect.

3.8.2. Effect of Settling Time on Turbidity Removal of Printing and Dyeing Wastewater

To investigate the effect of settling time, on the coagulation effect of printing and dyeing wastewater, in the case of fixing other conditions remain unchanged, change the settling time, the test results are shown in Figure 11. With the increase in the settling time, the turbidity removal rate gradually increased. In the period from 5 min to 15 min, the turbidity removal rate increases faster and remains basically unchanged after 15 min. The main reason for this phenomenon is that when the flocculant is added to the water body, it will produce flocs of different sizes (alu-mina), and in the period from 5 min to 15 min, some larger flocs settle, and the turbidity removal rate increases; after 15 min, the larger flocs basically settle, and only a few small volume flocs are left, so the turbidity removal rate increases more slowly. In conclusion, the best settling time in this test is 15 min, and polymerized aluminum chloride-magnesium has a better coagulation effect at the same settling time. Aluminum chloride-magnesium polymer is a composite flocculant composed of aluminum and magnesium, and the presence of magnesium ions increases the flocculant's bilayer pressure and adsorption electro-neutralization capacity, and its neutralizing ability is enhanced. Therefore, its turbidity removal rate is better than that of polymerized aluminum chloride.

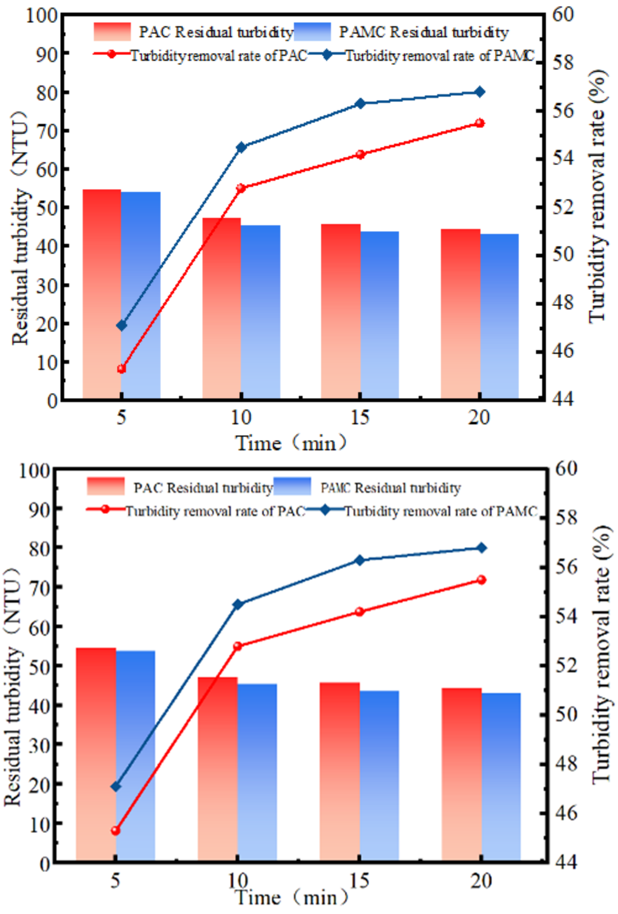


Figure 11. Influence of settling retention time on coagulation effect.

3.8.3. Comparison of Flocculation Effects

In this experiment, the metal elements and salinity of PAMC and PAC were analyzed with reference to the test method in "Water Treatment Agent Polyaluminum Chloride". The experimental results are shown in Table 8. And based on the single experiment, the flocculation experiment of printing and dyeing wastewater was carried out for polymerized aluminum magnesium chloride and polymerized aluminum chloride under the best flocculation conditions, and the experimental results are shown in Table 9.

Table 8. Comparison of PAC and PAMC composition and salinity table.

Samples	Al_2O_3 (%)	MgO (%)	Salinity
PAC	20	-	65
PAMC	20.1	7.1	65.6

Table 9. Comparison of flocculation effect of printing and dyeing wastewater.

Samples	Turbidity Removal Rate (%)	COD Removal Rate (%)	Ammonia Nitrogen Removal Rate (%)	Chromaticity Removal Rate (%)
PAC	54.2	50.0	10.1	45.8
PAMC	56.3	53.1	12.2	55.0

As can be seen from Table 6, homemade flocculant (polymerized aluminum chloride magnesium), in turbidity, COD, color removal effect is better than polymerized aluminum chloride. Polymerization of aluminum magnesium chloride floc generated (alum flower) large and very dense, therefore, has a better turbidity removal effect. COD removal, flocculants to deal with organic substances in the process of adsorption electro-neutralization capacity is mainly due to the polymerization of aluminum magnesium chloride is aluminum, magnesium as the main metal of the composite flocculant, compared with polymerization of aluminum magnesium chloride, such as a single to aluminum as the main metal of the flocculant, in the treatment of dyeing and printing wastewater, aluminum-magnesium and magnesium two metal ions will produce a synergistic effect, so that the adsorption electro-neutralization capacity is enhanced. Therefore, the removal effect of organic matter is better. From the results of this experiment, it can be concluded that the home-made flocculant (polymerized aluminum magnesium chloride) has a better effect on turbidity, organic matter, ammonia nitrogen and chromaticity in the treatment of printing and dyeing wastewater, especially in the removal rate of chromaticity, there is a great improvement, which provides a new way of thinking about the treatment of large chromaticity wastewater. At the same time, the flocculant prepared with gangue as the main treatment raw material has low treatment cost and high economic value, which achieves the purpose of turning waste into treasure and provides a method for pretreatment of printing and dyeing wastewater.

4. Conclusions

(1) The flocculant polymerized aluminum magnesium chloride was prepared with gangue as the main material. Orthogonal experiments were used to determine the best process conditions—pH 2.2, a polymerization time of 4.5 h, a polymerization temperature of 60 °C—when the preparation of the product coagulation performance is best. At that time, the salt content of the product was 65.6%, the MgO content was 7.1%, and the Al_2O_3 content was 20.1%.

(2) Using infrared spectroscopy and scanning electron microscopy to characterize the product, it was determined that the target product, polymerized aluminum magnesium chloride PAMC, was produced. Scanning electron microscopy diagrams showed that PAMC is a polymer with a clustered network structure, which enhances the adsorption and bridging of particles in water, as well as the ability of the network to trap and sweep.

(3) Response surface analysis was performed using Design-Expert 10.0 software. The order of influence of each factor on the turbidity removal rate was dosage > settling time > pH, the interaction between dosage and settling was significant for turbidity removal rate, the interaction between pH and dosage was not significant for turbidity removal rate, and the interaction between pH and settling time was significant for turbidity removal rate.

(4) The results of coagulation experiments on printing and dyeing wastewater with polymerized aluminum-magnesium chloride and polymerized aluminum chloride show that: polymerized aluminum-magnesium chloride is better than polymerized aluminum chloride in terms of turbidity, chromaticity, and COD removal, especially as the paint removal rate has been greatly improved.

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