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Preparation of an inorganic coagulant-polysilicate–magnesium for dyeing wastewater treatment: Effect of acid medium on the characterization and coagulation performance

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ABSTRACT

Polysilicate–magnesium (PSM) was prepared with Mg/Si molar ratios of 1.5 by co-polymerization. It is an inorganic polymer coagulant for dyeing wastewater treatment. Acid medium played an important role in the preparation of PSM. In this study, PSMs were prepared using different acids (H_2SO_4, HCl, HNO_3 and H_3PO_4) as medium, which were denoted as PSM(S), PSM(Cl), PSM(N) and PSM(P) respectively. FTIR, XRD and SEM were used to analyze the structure and morphology of four types of PSM coagulants. The results show that PSM(S) and PSM(N) both have the compact gel network structure, while PSM(Cl) and PSM(P) present layer shape structure and scattered small blocky structure respectively. In the coagulation–flocculation process of dyeing wastewater treatment, PSM(S), PSM(Cl) and PSM(N) exhibit better coagulation performance compared with PSM(P). With an optimal pH of 12 and a settling time of 20 min, the color removal efficiency of the coagulant of PSM(S) can reach above 94% at a relatively lower coagulant dosage of 4 mg/L, whereas PSM(Cl) and PSM(N) brings to about 94% at a higher coagulant dosage of 8 mg/L. However, PSM(P) shows that the highest color removal efficiency reaches only about 63% at a coagulant dosage of 8 mg/L. Therefore, PSM(S) is considered as the best acid modified PSM.

1. Introduction

Large amounts of pure water are used by the textile industry, which generates wastewater containing different types of dyes. Most synthetic dyes in wastewater are difficult to be biodegraded due to their aromatic molecular structures [1]. These effluents cause serious environmental problem mainly in terms of color, chemical oxygen demand (COD), toxicity and salinity. The dyeing wastewater is a serious threat to aquatic ecosystem and public health. Consequently, it is necessary to remove dyes from wastewater before discharging into the environment. Currently, the methods to treat dyeing wastewater generally consist of biological approach [2], oxidation [3,4], adsorption [5,6], and coagulation and flocculation (CF) [7,8]. Despite its effective method to reduce the chemical oxygen demand (COD) in wastewater, the biological approach is unable to fully decolorize the effluents [2,9]. The oxidation, adsorption, and coagulation and flocculation (CF) have their specific advantages in decolorization of dyeing wastewater. Among these methods, the coagulation and flocculation (CF) is widely used due to its simple operation, low capital cost and environmental impact [1,10].

Hence, studies on improving the performance of the coagulation–flocculation process have attracted wide attention [11-15]. Naturally, inorganic polymer coagulants (IPC), such as poly-ferric sulfate (PFS) [16] and polyaluminum chloride (PAC) [17], have been studied. The IPCs can improve the effect of charge neutralization because of their higher cationic charge. Moreover, they have higher molecular weight and so have more effective coagulant performance at comparatively lower dosages. Aluminum and ferric coagulants were used to treat the Congo Red wastewater with the color removal efficiency as high as 99% and the COD removal efficiency as high as 92% at an optimal coagulant dosage of 150–200 mg/L [18]. Apart from aluminum and ferric coagulants, the treatment efficiency of Congo Red was reported using some natural coagulants, where the color removal efficiency was in the range of 74–85% at pH 4 with the initial concentration as low as 60 mg/L [19]. When the initial dye concentration in wastewater was in a very low range of 6.6–48.0 mg/L, the seed cake of *Moringa oleifera* was applied to treat the Congo Red wastewater with the

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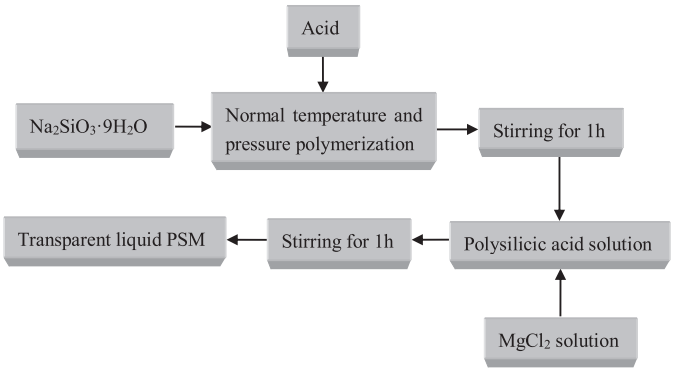

Fig. 1. Schematic drawing of a process for preparing PSM.

color removal as high as 97% at a relatively higher dosage of 520 mg/L [20].

However, aluminum and ferric coagulants still have some disadvantages [21]. They usually produce large quantities of dangerous sludge with residual metal [22]. For example, Al-based coagulants are now disputed regarding their potential adverse effects of Al on public health [11]. Fe-based coagulants can be costly and the excessive iron may cause metallic color and corrosion [23]. Natural coagulants may be used to treat dyeing wastewater with a very low initial dye concentration [22,23]. To solve the adverse effects of aluminum, ferric and natural coagulants on treating dyeing wastewater, magnesium coagulants have received much attention for their attractive features, which is that magnesium ion is non-toxic, the effective color removal and can be removed from the coagulated sludge [7,24]. Although there are many studies on magnesium coagulants in laboratory scale [25-28], there are limited studies on the properties and characterization of polysilicate magnesium (PSM) prepared with different acid. In this paper, a composite coagulant polysilicate–magnesium was prepared by using different acid. First, the structure and surface morphology of PSM were investigated using Fourier transformed infrared (FTIR) spectrophotometer, X-ray diffraction (XRD) and scanning electron microscopy (SEM). According to these references [29-33], the authors had used optimized values/methods to improve the results. Therefore, these parameters in this study, such as the initial value of pH in dyeing wastewater, the coagulant dosage, as well as the settling time on the performance of PSM were also investigated.

2. Materials and methods

2.1. Preparation of coagulant

All acid mediums (H_2SO_4, HCl, H_3PO_4, HNO_3) used for the preparation of PSM were analytical reagent. $MgCl_2 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ used for the preparation of PSM were also analytical reagent. All working solutions were prepared in deionized water.

The preparation of PSM coagulants can be found elsewhere [24]. Fig. 1 showed the process of preparing PSMs. In brief, a predetermined amount of $Na_2SiO_3 \cdot 9H_2O$ was dissolved with deionized water, and then the solution was diluted to the concentration of 0.6 M (as Si). It was dripped slowly into the different acid solution at room temperature. The final pH value of silicic acid solution prepared with different acid was 1.6–2.0. The polysilicic acid (PSA) solution was obtained after mixing with magnetic stirring apparatus for 60 min. Next, a certain amount of diluted $MgCl_2$ solution (1 mol/L) was introduced slowly into the fresh PSA solution under normal stirring at room temperature for 1 h In their paper, Wei et al. [24] found that PSM coagulant with Mg/Si molar ratio of 1.5 achieved the best performance. Therefore, the Mg/Si molar ratio of 1.5 was chosen for this study. PSM coagulants prepared with different acid (H_2SO_4, HCl, H_3PO_4, HNO_3) were denoted as PSM(S), PSM(Cl), PSM (P) and PSM (N) respectively. It should be noted that the dosage of coagulant was calculated as mg Mg/L for PSM coagulants.

2.2. Structure and morphology

In order to obtain dried powder, all liquid PSM coagulants prepared with different acid were dehydrated in oven at 50 °C for several days. The PSM coagulants were analyzed by infra-red (IR) with the Nicolet-380 FTIR Spectrophotometer using conventional potassium bromide (KBr) pellets. The infra-red (IR) spectra of the sample was obtained in the range of 4000–400 cm^{-1}. The crystalline phases in solid coagulants were measured using X-ray diffractometer (MXPAHF, Japan). The morphologies of the four PSM coagulants were examined by SU1510 scanning electron microscope (SEM).

2.3. Jar test procedure

The synthetic dyeing wastewater was prepared by adding designated amounts of dye Congo Red powder in deionized water. The concentration of Congo Red in the dyeing wastewater reached 100 mg/L. The dye was obtained from Shanghai Chemicals, China. The wavelength of maximum absorption and molecular structure are shown in Table 1. And coagulation experiments were carried out in 250 mL beakers. The 250 mL of synthetic dyeing wastewater was placed in a beaker. The solutions were mixed rapidly at 300 rpm for 2 min after adding the coagulant. The slow mixing was applied at 60 rpm for 10 min. The final absorbance of water samples was measured after settling for 20 min. The water samples were collected at 2 cm under the surface of water. The absorbance of water samples was measured using model 722E spectrophotometer.

2.4. Calculation of the color removal efficiency

The absorbance value at λ_{max} varied linearly with the dye concentration. Therefore, the concentration of dye could be clearly analyzed according to the absorbance. The color removal efficiency (η%) was calculated in Eq. (1)

$$\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 is the initial absorbance of the dyeing wastewater, A_t is the absorbance of supernatant at the corresponding settling time (t) after the coagulation run.

3. Results and discussion

3.1. Effects of different acid on the structure and morphology of PSMs

3.1.1. FT-IR spectroscopy

The IR spectra for the PSMs prepared with different acid are shown in Fig. 2. Fig. 2 exhibits that the spectra of three coagulants are somewhat similar but PSM(P). The peak in the range of 3500–3300 cm^{-1} for four PSMs can be attributed to the intermolecular association of the stretching vibration of –OH [34,35]. The medium peak in range of 1650–1630 cm^{-1} can be seen in the four IR spectra for the PSMs. It implies that four coagulants all have the bending vibrations of water. The wave in the range of 1330–1400 cm^{-1} for PSMs except PSM(P) is assigned to the bending vibration of –OH groups. And this indicates that coagulants of PSMs with different acid may contain structural and adsorbed water. The peaks at 1081, 1123, 1067 and 1081 cm^{-1} for PSM(S), PSM(Cl), PSM(P) and PSM(N) are assigned to the Si–O stretching vibration [36]. The

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