Peer-reviewed version available at *Appl. Sci.* **2019**, *9*, 973; doi:10.3390/app9050973

Article

Effects of Mixing Conditions on Floc Properties in Magnesium Hydroxide Continuous Coagulation Process

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Abstract:Magnesium hydroxide continuous coagulation process was used for treating simulated reactive orange wastewater in this study. Effects of mixing conditions and retention time on the coagulation performance and floc properties of magnesium hydroxide were based on the floc size distribution (FSD), zeta potential and floc morphology analysis. Floc formation and growth in different reactors were also discussed.The results showed that increasing rapid mixing speed led to a decrease in the final floc size. Floc formation process was mainly carried out in rapid mixer, rapid mixing speed of 300rpm was chosen according to zeta potential and removal efficiency. Reducing retention time caused relatively small floc size in all reactors. When influent flow is 30 L/h (retention time of 2min in rapid mixer), the average floc size reached 8.06μm in rapid mixer, through breakage and re-growth, the floc size remained stable in flocculation basin. After growth, the final floc size reached to 11.21μm in sedimentation tank. The removal efficiency of reactive orange is 89% in magnesium hydroxide coagulation process.

Keywords:magnesium hydroxide; reactive orange; mixing; coagulation; floc size

1. Introduction

Magnesium hydroxide was used as a potential coagulant for reactive dyes wastewater treatment for many years [1-3]. Typical characteristics of this kind of coagulant include nontoxic, environmentally friendly nature, recoverability and rapid reaction [4]. Magnesium hydroxide precipitate has a positive superficial charge and it can adsorb negative dyes through charge neutralization or precipitate enmeshment [5-6]. Floc size, settling properties are the main parameters influencing reactive dyes removal efficiency in real industrial scale unit operations [7-9]. Photometric dispersion technique and laser technique are useful in monitoring floc physical characteristics [10-11]. As previously found [12-14], magnesium hydroxide nucleation and precipitation processes are very fast, floc size can reach to 15μm. Although floc size is not very large compared with other coagulant, the sedimentation process can meet requirement of pollutant removal.

During magnesium hydroxide coagulation process, mixing conditions influenced the removal efficiency and flocs properties. Rapid mixing brings the reactants together and homogenizes the solution. In rapid stirring process, it will cause nucleation and precipitation

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of magnesium hydroxide. Magnesium hydroxide coagulation process had two stages including fast floc formation and growth of flocs. As for slow mixing, flocs remained stable and re-growth process was not happened apparently in our previously found[13]. Several authors have found that operational conditions influenced the coagulation process and flocs properties especially for mixing conditions[11,15]. Effects of shearing on floc formation and growth are also related to coagulation mechanisms [16-17].

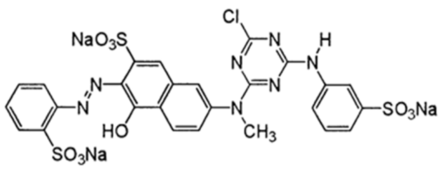
Although there were large amount of data on the characteristics of floc in batch coagulation process, there have been limited studies on the relationship between floc characteristics and mixing conditions using magnesium hydroxide as coagulant in continuous process. The main objectives of this laboratory study were to evaluate the role of rapid mixing speed on coagulation performance, floc properties. Furthermore, the effects of retention time on floc characteristics are also assessed.

2. Materials and methods

2.1. Synthetic test water and coagulant

Reactive orange (K-GN) was purchased from Jinan Xinxing Textile Dyeing Mill, Shandong, China. Reactive dye solutions with pH 12 were prepared with K-GN and deionized water to provide concentration of 0.25 g/L. NaOH solution was used to control the solution pH value (PHS-25 Shanghai Jinke Industrial Co. China). $MgCl_2 \cdot 6H_2O$ (CP. Tianjin Chemical Reagent Co. China) was used to prepare coagulant. Magnesium ion was analyzed with an ICS-1500 (Dionex, USA) ion chromatography system. The concentration of reactive orange in the solution was analyzed by UV-VISIBLE spectrophotometer (UV2550 Shimadzu, Japan). The reactive orange characteristics are shown in Table 1.

Table 1. Reactive orange characteristics.

Name	Molecular Structure	λ_{max} (nm)
Reactive orange (K-GN)		476

2.2. Apparatus and procedures

Continuous experiments were carried out at 20±1 ℃ and in order to obtain a real continuous steady experiment, K-GN removal efficiency remained stable at 2h or longer time. For this process to occur, the 1 L rapid mixer with stirring speed at 250 to 350 rpm. Flocculation basin was divided into three parts (each of 4L) and sedimentation tank (30 L) was designed for the removal of flocs (Figure 1). The slow stirring speed was maintained at 80 rpm in flocculation basin. 0.25g/L Reactive orange and 250mg/L magnesium ion were pumped to rapid mixer, respectively. The total influent flow was chosen at 30L/h and 60L/h, which retention time was 2min and 1min in rapid mixer, respectively. The operational conditions of continuous coagulation process were shown in Table 2.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 30 January 2019 doi:10.20944/preprints201901.0310.v1

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Table 2. Operational conditions of coagulation process

Flux	Rapid mixer		Flocculation basin		Sedimentation tank
	speed	time	speed	time	time
30L/h	250rpm 300rpm 350rpm	2min	80rpm	24min	60min
60 L/h	300rpm	1min	80rpm	12min	30min

2.3. Floc size distribution and properties analysis

During the continuous coagulation process, samples of flocs were taken from rapid mixer, the third flocculation basin and sedimentation tank using a tube with an inner diameter of 5 mm every ten minutes . Floc size distribution (FSD) was measured by Mastersizer 2000 (Malvern, UK) and each sample was measured thirds times and obtained the average results. During the slow mixing period in the third flocculation basin, zeta potential was measured by zetasizer Nano ZS (Malvern, UK). The images of flocs from rapid mixer, the third flocculation basin and sedimentation tank were captured by IX71 digital photomicrography (Olympus, Japan).

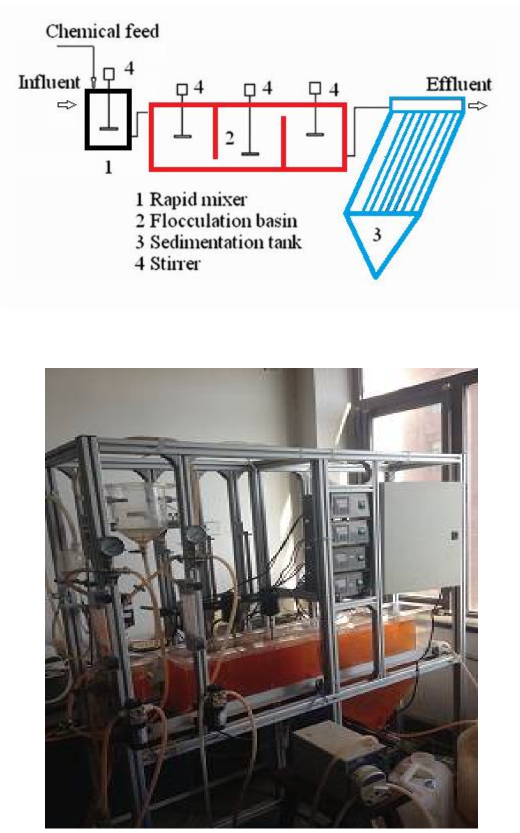

Figure 1. Experimental apparatus for coagulation of magnesium hydroxide.

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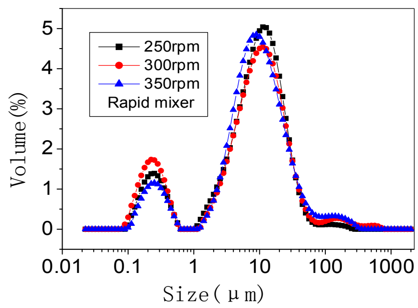
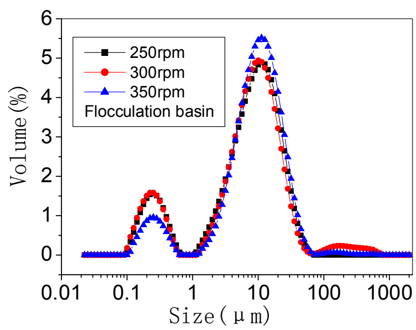
3. Results and Discussion

3.1. Coagulation behaviors under different rapid mixing speed

3.1.1. Floc size distribution in three processes

Continuous experiments were performed under 250mg/L magnesium ion with 30L/h to investigate the effects of rapid mixing conditions on coagulation performance and floc size distribution. According to FSD, average floc size decreased when rapid mixing speed increased in rapid mixer and sedimentation tank. In flocculation basin, floc size tended to stable or slightly broken with the increase of rapid mixing speed to 300rpm. This is consistent with the findings that repulsive forces tend to stabilize the suspension and prevent particle agglomeration [13,18]. As shown in Table 3, the average floc sizes 8.39, 8.06 and 8.04 μm were obtained with rapid mixing speed 250, 300 and 350rpm in rapid mixer, respectively. Small floc had the same trend to aggregate relatively large flocs. Average floc size was 8.06 and 7.89 μm in rapid mixer and flocculation basin when mixing speed was 300rpm. In generally, the flocs will grow in flocculation basin, but it seems that floc size decreases in flocculation process. In fact, during flocculation process, particles larger than 11.25 μm accounted for 4.54% and 4.9% in rapid mixer and flocculation basin, respectively. Particles smaller than 1 μm also decreased in slow mixing period. As can be seen also in Figure 2 (sedimentation tank), particles smaller than 1 μm account for 6.2%, 10.0% and 12.6% with mixing speed 250, 300 and 350 rpm respectively. It was observed that the percentageof smaller particles increased with the increase of mixing speed. This indicates that the high mixing speed will break the flocs, and only part of the flocs will aggregate again after the flocs are broken. The general shape of the curves is broadly similar in different units. The average floc size decreased to a steady state, there is a dynamic balance between floc growth and breakage. When the stirring speed is increased from 250 rpm to 350 rpm, small average floc size can be observed in these three units. Following the breakage and aggregation period, there is only a partial flocs re-growth, showing that the broken flocs can only re-grow to a very limited extent.





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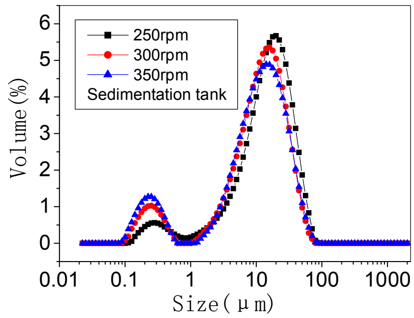

Figure 2. Floc size distribution with different rapid mixing for three stages.

Table 3. Average floc size in different process units.

Rapid mixing (rpm)	**Average floc size (μm)**		
	Rapid mixer	Flocculation basin	Sedimentation tank
250	8.39	7.96	14.41
300	8.06	7.89	11.21
350	8.04	7.95	10.58

3.1.2.Removal Efficiency and Zeta Potential

As shown in Figure 3, the K-GNremoval efficiency after coagulation remained stable about 89% in three different rapid mixing conditions. Although Removal efficiency is not significantly influenced by rapid mixing speed, zeta potential increased with increasing rapid mixing speed. Changes in floc characteristics also lead to changes in zeta potential. Rapid stirring speed may change zeta potential of colloid, because the rapid mixing could change the floc size and their surface properties. Positively magnesium hydroxide acts as charge neutralization species. Similar results were also found in magnesium hydroxide coagulation process for removal of reactive dyes [18,19]. Zeta potential is important in terms of the impact on steady state floc size and the response to increased levels of shear. Under different shear conditions, the break-up flocs may have different physical properties. Floc properties impacted significantly on the overall process efficiency[20]. Electrical charge or colloidal properties of the magnesium hydroxide-reactive orange flocs would be greatly affected. Based on this observation, it can be reasoned that charge-neutralization is one of the mechanisms for destabilization and removal of reactive orange[21]. Normally, slow mixing condition also affects flocs break-up and growth. But in magnesium hydroxide coagulation process, magnesium hydroxide formed and flocs grew fast, then the larger flocs break into relative small particles in slow mixing period. During the process of floc breakage and re-growth there is a limiting floc size to a steady state. As previously found [13], floc growth is not significantly influenced by slow mixing period. In this research, effects of slow mixing conditions on floc properties were not considered. As having been mentioned, large flocs breakage and re-growth will happen simultaneously, there is less opportunity for the break flocs to re-grow.

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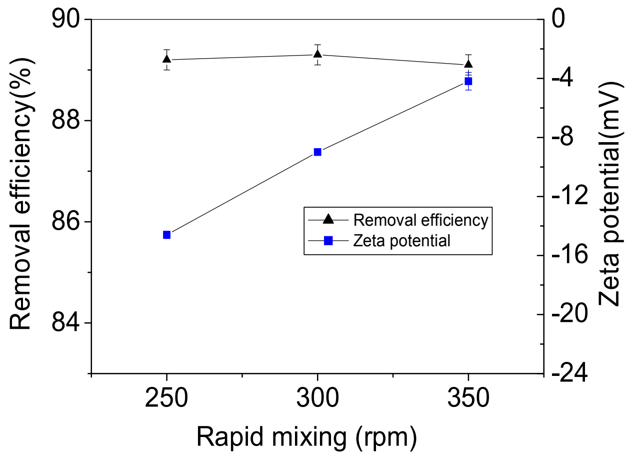

Figure 3. Effects of rapid mixing on removal efficiency and zeta potential.

3.2. Effect of flow on coagulation performance

For continuous coagulation reaction, the flow determines the retention time of reactants in each reactor. The increase of flow indicates the decrease of retention time. In order to investigate the effect of flow on coagulation performance, continuous experiments were performed under magnesium ion 250mg/L, rapid mixing speed 300rpm with 30L/h and 60L/h. The retention time in the rapid mixing tank is 2min and 1min for flow of 30L/h and 60L/h, respectively. As shown in Table 4, the average floc size decreased with increasing influent flow for each operation unit. As for rapid mixer, the average floc size was 8.06 and 7.25 μm for 30L/h and 60L/h, respectively. According to earlier results[14], in the stage of rapid mixing, magnesium hydroxide was formed and particles grew in very short time. A suitable period of rapid mixing was necessary for good coagulation. Reactive orange removal efficiency reached 89% and 83% for 30L/h and 60L/h, respectively. Retention time in each unit for 60L/h is shorter than that of 30L/h, especially in rapid mixer of 1min retention time. It is too short to form magnesium hydroxide-reactive orange flocs.

Table 4. Average size in different process units.

Flow (L/h)	**Average size (μm)**		
	Rapid mixer	Flocculation basin	Sedimentation tank
30	8.06	7.89	11.21
60	7.25	7.52	10.47

Fig. 4 clearly indicates that floc formation and growth in the magnesium hydroxide-reactive orange continuous coagulation system. In rapid mixer and flocculation basin, average floc size remained stable and floc aggregated to relatively large flocs in sedimentation tank. These two figures showed the same trends that magnesium hydroxide coagulation process was similar to the precipitation process. When magnesium ion is added to the alkaline solution, reaction crystallization process will happen rapidly. Magnesium hydroxide coagulation includes magnesium hydroxide nucleation and combination of reactive orange into flocs.

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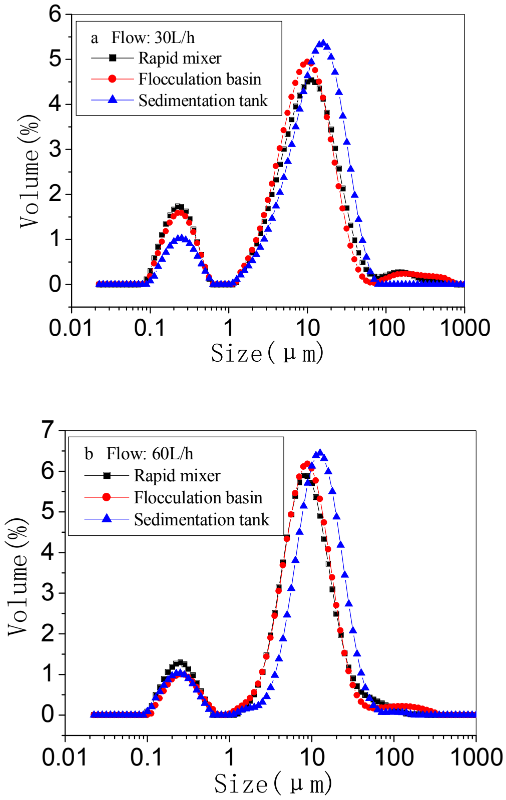

Figure 4. Floc size distribution with different flow for three stages.

3.3. Images analysis

The floc size distribution can tells the percentage of different floc size and the removal efficiency is commonly used to estimate coagulation performance. In order to gain further insight into the floc and sediment properties, image analysis was used to predict floc characteristics by IX71 digital photomicrography. As shown in Fig. 5, clearly indicate that the average size of flocs in different reactor. The floc formation and growth processes were carried out in rapid mixer and there is no more aggregation occurred due to the strong repulsion between positively charged particles of magnesium hydroxide in flocculation basin. In sedimentation tank, flocs aggregated to form relative large particles. This is consistent with the findings of FSD value which are shown in Fig.4. As for Fig.5a and 5d, they were clearly showed that increasing flow caused decreasing the average size in rapid mixer. The average floc size of magnesium hydroxide-reactive orange is 8.06 and 7.25 μm. This is also consistent with the findings of previously study [14].

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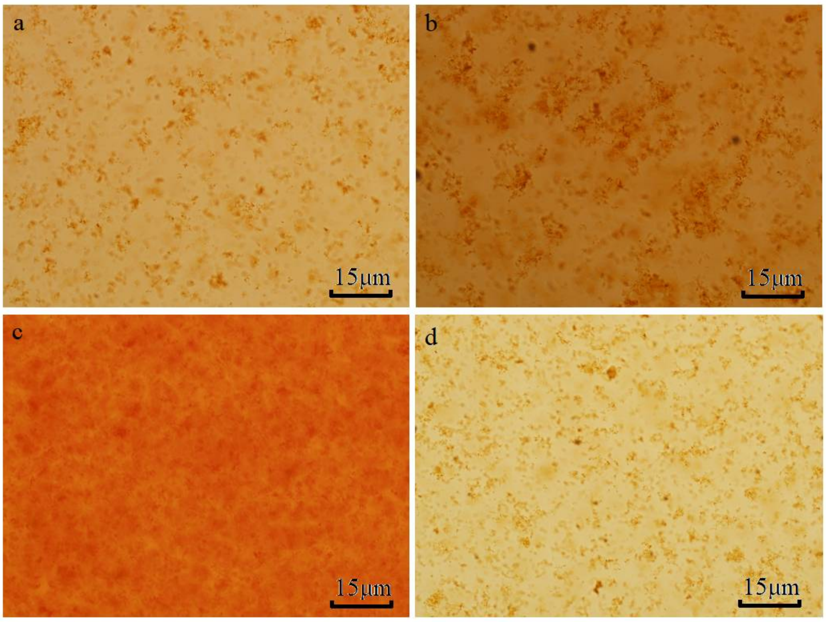

Figure 5. Floc image analysis (a: rapid mixer for 30L/h, b: flocculation basin for 30L/h, c: sedimentation tank for 30L/h, d: rapid mixer for 60L/h).

4. Conclusions

In this research, effects of mixing conditions on magnesium hydroxide continuous coagulation performance and the floc properties were investigated. Rapid mixing speed plays a significant role in floc formation and growth. The function of the rapid mixer is providing a place for the rapid nucleation and precipitation of magnesium hydroxide. In this stage, coagulant and reactive orange formed flocs. In flocculation basin, small flocs will form more dense flocs but average floc size remains stable. After sedimentation process, flocs aggregate to form relatively large flocs. Therefore, appropriate rapid stirring is conducive to the formation of flocculation and the removal of pollutants. Increasing flow will cause short retention time, the average floc size decreases from 11.21 to 10.47μm when flow increases from 30 to 60L/h. The coagulation behavior indicates magnesium hydroxide is an effective coagulant for reactive orange removal with efficiency of 89%.

Acknowledgments: This work is supported by the Technology Research and Development Program of Tianjin, China (No. 16YFXTSF00390).

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