Impact of shock loading with mid-stage pulping wastewater on a magnetic micro-aerobic activated sludge system

Huixia Lan, a,b*, Hao Zhang, a Da Yang, a Shiwen Geng, a Wei Wang, a Shanhong Lan

a) College of Environment and Safe Engineering, Qingdao University of Science & Technology, Qingdao 266042, China; b) State Kay Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China; c) School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China.

*Corresponding author: lanhuixia@163.com

ABSTRACT

The effect of mid-stage pulping wastewater (as shock load) on micro-aerobic magnetic activated sludge system was studied. Micro-aerobic activated sludge systems with and without magnetic particles were shocked with mid-stage wastewater for 16 days. “Recovery” experiments were conducted by using simulated wastewater for 12 days. Upon the addition of mid-stage wastewater, CODCr removal pertaining to the use of magnetic particles reached 71.57% and remained above 80% in the “recovery” experiment. However, the efficiency of the reactor in the absence of magnetic particles was only 37.29%, and reached about 40% in the “recovery” experiment. After the micro-aerobic activated sludge was shocked, the flocculation performance and surface properties of the sludge were analyzed, and the results showed that all indicators of the reactors in the presence of magnetic particles were superior to those of reactors without magnetic particles. After 12 days of “recovery”, the indicators of the sludge pertaining to the reactors containing magnetic particles “recovered” completely.

Keywords: Micro-aerobic magnetic activated sludge; Mid-stage effluent; Pulp and paper; Magnetic particles

1. INTRODUCTION

The mid-stage pulping wastewater contains toxic and non-biochemical ingredients. Pretreatment is required prior to aerobic biodegradation. Sequential anaerobic-aerobic biological process is widely used for the treatment of mid-stage pulping wastewater, but anaerobic and aerobic reactions tend to prolong in two tanks, leading to large space and high cost.

The micro-aerobic activated sludge system involves both anaerobic and aerobic features, which largely mitigates the limitation of sequential anaerobic-aerobic process. However, under conditions of low dissolved oxygen concentration, overgrowth of filamentous bacteria tends to occur, resulting in the reduction of sludge sedimentation. This may also lead to the bulking of activated sludge. Some heavy materials, including polymeric aluminum, ferric iron, and magnetic powder, can be added into the micro-aerobic activated sludge system to solve the aforementioned problems. With the rapid development of magnetobiology, magnetic Fe3O4 is currently widely studied in water treatment field.

Research showed that the addition of Fe3O4 improved the sedimentation performance of activated sludge. Fe3O4 has the properties of biocompatibility, small size, high surface area to volume ratio, and easy separation from solution, offering accessible surface for the free floating bacteria. Fe3O4 is also heavier than activated sludge, which facilitates sludge sedimentation. Studies carried out by Saka et al. showed that the addition of magnetic powder with the dosage of 2000mg/L resulted in an increase of sludge sedimentation rate by 36 times.

Magnetic substances are known to have a noticeable physical effect on sludge sedimentation. Also, the resulting magnetic field has a biological effect on the microorganisms in the sludge. Biodegradation activity of activated sludge can be improved at appropriate magnetic field intensity, thus facilitating wastewater treatment. The effect of magnetic field on formaldehyde-containing wastewater treatment with activated sludge system was studied by Lebkowska et al. The results showed that, when the magnetic field intensity was controlled at 7mT, microorganism growth rate and dehydrogenase activity increased obviously. As a result, formaldehyde removal increased by 30%, and COD removal increased by 26%. Prior studies indicated that, when enzyme was immobilized by magnetic powder, enzyme activity improved, and the immobilized enzyme had better tolerance to toxic substances and variations of pH and temperature.

In this paper, we report a study on the effect of mid-stage pulping wastewater (as shock load) on the performance of micro-aerobic activated sludge systems with and without magnetic particles for sludge modification. The systems were operated with mid-stage wastewater as an extra load for 16 days, and then switched to normal operation for 12 days. The performance of the bioreactors was evaluated in terms of COD removal, flocculation ability, extracellular polymers, polysaccharide and protein ratio, relative hydrophobicity and surface charge density of resulting sludge.
2. EXPERIMENTAL

2.1 Experimental apparatuses

Experimental apparatuses were comprised of aeration tank and a reactor made of organic glass. The inner diameter of aeration tank was 250mm, and the height was 350mm. The inner diameter of the reactor was 60mm, and the height was 700mm. The wastewater was first fed into the aeration tank in which aeration was carried out via a porous air diffuser ball, and then pumped into the reactor from the bottom. A solid-liquid-gas separator was placed on the top of the reactor to prevent the outflow of suspended sludge. Wastewater was recycled into the aeration vessel from the top of the reactor, pumped into the reactor again, and finally discharged through the effluent valve. The dissolved oxygen concentration (DO), the temperature, and pH were controlled at 0.6mg/L, 25°C and 7.2, respectively. The treatment cycle was 24 hours. Two apparatuses were used in the experiments. For one apparatus, magnetic powder was added. In the case of the other apparatus, magnetic powder was not used. Before this study, both of these apparatuses had been operated for 50 days under micro-aerobic condition, feeding with glucose wastewater. COD Cr concentration of the glucose wastewater was 800mg/L. COD Cr removal as regards both reactors reached above 80% before the shock experiments.

2.2 Mid-stage pulping effluent

The mid-stage pulping wastewater was collected from a paper mill in Shandong province, China, and its COD Cr concentration and pH was about 800mg/L and 7.2, respectively after flocculation pretreatment. This wastewater was relevant to screening, cleaning, and bleaching processes of pulping. Lignin-derived components, e.g., phenol compounds, chlorinated phenolic compounds, and polycyclic aromatic hydrocarbons, were contained in the wastewater.

2.3 Magnetic powder

Fe3O4 was used as magnetic powder, and it was magnetized prior to use. The average particle size of magnetic powder was 800nm. Fe3O4 and activated sludge was mixed and then added into the reactor for the culture of micro-aerobic sludge culture. The dosage of Fe3O4 was 2g/L. After 50 days, the micro-aerobic magnetic sludge matured, and the shock experiment was carried out.

2.4 Analytical methods

Dissolved oxygen concentration and pH were determined with a Sension6 analyzer (HACH Company, U.S.). COD Cr concentration was determined with a potable water quality analyzer (DR2007, HACH Company, U.S.). Extracellular polymeric substance (ECPs) was extracted by following the dilute sulfuric acid method.20 mL of sludge sample was added into a centrifuge tube. After centrifugation, the supernatant liquid was discarded. The sludge was washed twice with deionized water and homogenized. 1mL of the homogenized sludge and 9 mL of sulfuric acid solution were added into a 10 mL glass tube with stopper. The volume percentage of sulfuric acid solution was 8%. Then the glass tube with stopper was put in a shaker, and shaking was conducted for 1 hour. Afterwards, the mixture was centrifuged for 5 min. ECPs were extracted into the supernatant liquid. Polysaccharide (PS) was tested by following the anthracene ketone method, in which glucose used as standard substance. 1 mL of the extracted supernatant and 1 mL of 5% phenol-water solution were added into a glass tube, and mixed. 5 mL of 98% concentrated sulfuric acid was added into the tube rapidly. Then the tube was shaken for sufficient mixing. After mixing, the tube was let stand for 10 min, and was then put into the water bath and let stand for another 10 min. The temperature of the water bath was controlled at 25-30°C. PS content was measured by colorimetric determination of mixed liquid at 488nm. Protein (PN) was determined by Folin spectrophotometry, and bovine serum albumin was used as standard substance. 1.0 mL of the extracted supernatant and 5.0 mL of Coomassie brilliant blue reagent were added into a glass tube. The tube was shaken for 5 min at 20-25°C. PN content was measured by colorimetric determination of the mixed liquid at 595nm. Coomassie brilliant blue reagent was prepared by dissolving 100mg of the chemical into 50 mL of 95%(volume percentage) ethyl alcohol, followed by the addition of 100 mL of 85%(volume percentage) phosphoric acid.

Colloid titration was used to determine surface charge (SC). The diluted sludge was prepared by adding 1 mL of sludge sample into 100 mL of deionized water, which was then mixed with 5 mL of polybrene. The mixed solution was titrated with 0.001N of polyvinyl alcohol potassium sulfate (PVSK) using toluidine as indicator. The change of solution color from blue to pink was considered as the endpoint of titration. The consumed volume of PVSK was marked with A. Then the blank test was conducted by changing polybrene to deionized water according to the above step. The consumed volume of PVSK in the blank test was marked with B.

\[ \text{SC(ueq/L)} = \left( \frac{A - BN(1000)}{1} \right) / N \]

where N is the equivalent charge of PVSK.

Relevant hydrophobicity (RH) was determined according to the method described by Chang et al. Two
samples of diluted sludge of 30 mL were collected. One sample was washed with Tris buffered solution. The concentration of the Tris buffered solution was 0.05 mol/L and its pH was 7.1. Then, the sludge was dispersed with 50W ultrasound (2min, 4 °C). The dispersed sludge and 15 mL of hexadecane were transferred to separatory funnel. The separation of the solid phase and liquid phase occurred in the separatory funnel after shaking for 30min. The liquid phase was taken out. The sludge concentration in the separatory funnel was measured, which was designated as MLSSe. The sludge concentration of the other untreated sample was also measured, which was designated as MLSSI.

\[ \text{RH(\%)} = \left(1 - \frac{\text{MLSSe}}{\text{MLSSI}}\right) \times 100\% \quad (2) \]

Flocculating ability (FA) was determined according to the method described by Jorand et al.17 80 mL of sludge sample was added into a beaker. The sludge concentration was 4g/L. Then, the sludge was dispersed with 50W ultrasound for 15s in ice-water bath. 10mL of dispersed sludge was collected and centrifuged for 2 min at 1200r/min. The absorbance of the supernatant liquid was measured at 650nm (A). The remained sludge in the beaker was stirred by magnetic stirrers for 10min at low speed. After keeping stationary for 15min, the absorbance of the supernatant was measured at 650nm (B).

\[ \text{FA(\%)} = (1 - \frac{\text{B}}{\text{A}}) \times 100\% \quad (3) \]

3. RESULTS AND DISCUSSION

3.1 Effect of shock loading with mid-stage wastewater

The effect of shock loading with mid-stage pulping wastewater on CODCr removal is shown in Figure 1. At 0 day in Figure 1, i.e. before shock loading, the feeding wastewater was the simulated glucose-containing water. From 1st day, the shocking experiment was carried out; the feeding wastewater was changed to mid-stage wastewater after the treated effluent of the last cycle was discharged, until the 16th day. From the 17th day, the recovery experiment was conducted, and the feeding wastewater was changed to the synthetic glucose wastewater, until the 28th day. The treatment cycle was 24 hours, i.e. one day.

As shown in Fig.1, the treatment efficiencies of both reactors had no obvious difference before the shock loading. Initial CODCr removals were 84.78% and 81.25%, respectively. When the feeding wastewater was replaced by mid-stage pulping wastewater, the reactor with magnetic powder had a certain buffering capacity; CODCr removal efficiency decreased gradually in the first few days and reached 71.57% on the 16th day. and reached 71.57% on the 16th day.
organics. Therefore, microbial biomass and activity increased simultaneously under the stimulation of magnetic powder. Of both combined actions, COD removal of the reactor with magnetic powder was always higher in comparison with the control reactor, no matter in the shock process or in the recovery process.

### 3.2 Effect of shock loading on physical and chemical properties of sludge

Flocculation performance of the sludge is closely related to the sedimentation performance of the sludge. Changes of sludge flocculation ability under shock loading are shown in Figure 2.

The original FA values of the reactors with and without magnetic powder were 74.54% and 63.21%, respectively. Flocculation ability of both reactors decreased obviously after being shocked by mid-stage pulping effluent. The FA of the reactor with magnetic powder reduced to the lowest value of 39.48% on the 10th day, and then increased to 56.95% on the 28th day under the recovery conditions. The flocculation ability of the reactor without magnetic powder decreased gradually after effluent shock and reached to 29.46% on the 16th day, and then increased slightly to 30.19% in the recovery stage.

Figure 2. Effect of shock loading on flocculation ability (FA)

Flocculation ability was closely related to the amount of extracellular polymers and its composition. In order to reveal the internal factors of flocculation ability changes, the total amount of extracellular polymers and its composition PN/PS were studied under shock loading. The results are shown in Figures 3 and 4.

Under the shock loading, both the total ECPs and PN/PS ratio first decreased and then increased in the case of reactor containing magnetic powder, as shown in Figures 3 and 4. After 12 days of recovery, both ECPs and PN/PS recovered to approximately the initial values. While in the control reactor, both ECPs and PN/PS had shown a significantly downward trend. Even after 12 days of recovery, they were still obviously lower than the initial values. In addition, throughout the shocking periods, the total ECPs and PN/PS values of the reactor containing magnetic powder were significantly higher than that of the control reactor.

Figure 3. Effect of shock loading on the amount of extracellular polymers (ECPs)

Figure 4. Effect of shock loading on the polysaccharide to protein ratio (PN/PS)

Extracellular polymers are the direct cause of flocculation. In addition, according to the studies, when ECPs concentration is in an appropriate range, the composition of ECPs also determines the flocculation performance of sludge. The PN/PS ratio affected the physical and surface characteristics of sludge and sludge flocculation, and had a major impact on sludge physicochemical properties such as SVI, hydrophobicity, and charge characteristics. The increase of polysaccharide and protein concentrations led to increased viscosity of the flocs, but hydrophobicity of the protein was stronger than that of polysaccharide, so the increase of protein concentration made the retention of water in the sludge difficult, resulting easy separation of sludge, the low value of SVI, closely linked between cells. In addition, the bonding capacity of protein with cation was greater than that of polysaccharide. A three-dimensional frame structure was formed by bridging between cation and protein to maintain the integrity and stability of the sludge structure. Not only the total ECPs reduced, but also its composition changed, resulting in decreased ratio of PN/PS under shock loading, which led to the reduction of the sludge flocculation performance. The reduction of the total ECPs and PN/PS ratio was much less significant for the reactor containing magnetic powder in comparison to the control.
This is consistent with the results shown in Figure 2 and Figure 4.

3.3 Effect of shock loading on sludge surface properties

Shock loading resulted in the change of extracellular polymer amount and its composition, leading to the change of the relative hydrophobicity and surface charge. The effect of shock loading on sludge relevant hydrophobicity (RH) and surface charge (SC) is shown in Figures 5 and 6.

![Figure 5. Effect of shock loading on relevant hydrophobicity (RH)](image_url)

![Figure 6. Effect of shock loading on surface charge (SC)](image_url)

As seen in Figures 5 and 6, the change of RH and SC during the shock loading period was in agreement with the change of flocculating ability. Magnetic particles had a significant effect on the surface properties of sludge. The RH of the reactor containing magnetic powder was significantly higher than that of the control reactor, and the surface negative charge of the former was lower than that of the latter.

The mid-stage pulping wastewater contained a lot of colloidal ions which were mainly negatively charged. As a result, the negative charges carried by the sludge increased after being shocked by the mid-stage pulping wastewater, which led to deterioration of the flocculation and sedimentation performance of the sludge.

4. CONCLUSION

The micro-aerobic activated sludge bioreactors with magnetic particles had improved performance in dealing with load shock. Results showed that the CODCr removal of micro-aerobic activated sludge system with magnetic particles first decreased and then increased during the 16-day shock loading period with mid-stage pulping wastewater, and it recovered to the initial value after 12 days. In contrast, the CODCr removal of the control system decreased much more dramatically, and failed to recover after the shock period. Under the shock loading conditions, the physicochemical and surface properties of sludge deteriorated in both cases. However, at the late stage of the shock loading, the sludge characteristics improved in the system with magnetic particles, while sludge bulking occurred in the control system. It was found that the sludge flocculation and settling properties in the reactor with magnetic particles were superior in comparison with the control reactor throughout the whole shock period.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the State Key Laboratory of Pulp and Paper Engineering (201522), Shandong Provincial Natural Science Foundation of China (ZR2017MC032) and the Natural Science Project of Guangdong Education Department (2015KTSCX140).

REFERENCES