Flocculation mechanism by a novel combined 
aluminum–ferrous–starch flocculant (CAFS)
Qintie Lin, Hanping Pan, Haoping Huang, Guoguang Liu and Guangcai Yin

ABSTRACT
A combined flocculant (CAFS) was prepared with Al2(SO4)3·18H2O, FeSO4·7H2O and starch. The flocculation mechanism of reactive brilliant red X-3B was studied. The results showed that CAFS was a cationic polymeric flocculant with high charge density, and its mesh starch chains grafted polyaluminum and polyferrous. At the preliminary stage, the main flocculation mechanism was adsorption and charge neutralization. At a later stage, the high molecular weight and flexible linear chains of CAFS initiated bridge-aggregation and sweep-flocculation. Moreover, the zeta potential and dynamic changes of flocs were closely related to flocculant dosages and the pH. The optimum dosage of CAFS and pH value were 0.990 mg/L and 5.0. Taken together, these results suggested CAFS as a novel flocculant in water treatment, with good results for the studied conditions.

Key words | bridge-aggregation, charge neutralization, flocculation index, starch, sweep-flocculation, zeta potential

INTRODUCTION
Flocculation is one of the most important processes in a water treatment plant. However, most traditional flocculants are micro-toxic and are prone to produce secondary pollution. How to prepare a novel environmentally friendly and efficient flocculant is an urgent task in the water treatment field. Starch has been used in the commercial application of flocculant (Ye et al. 2004) and selective flocculation (Dogu & Arol 2004). It has been related to surface complex and hydrogen bonding between partical surfaces and starch molecules (Balajee et al. 1996), and its main flocculation mechanism is the classical bridging (Weissenborn et al. 1995).

However, its flocculation efficiency is low. Therefore, starch generally is modified. Chemically modified starches, such as starch graft copolymers (Karmakar et al. 2002), cationic starches (Krentz et al. 2006), amphoteric starches (Cansee et al. 2008), composite starches (Zou et al. 2011), have been studied as flocculants. Composite starches, in particular, are attractive reactant candidates, for they are inexpensive and easy to prepare. However, real-time monitoring of modified starch flocculation and precipitation processes has not been considered in detail. A Photometric Dispersion Analyzer (PDA) has been used to monitor the kinetics of floc formation, breakage and re-growth in real-time recently (Yu et al. 2009). Its output, flocculation index (FI), is directly related to the floc size, with high FI values indicating the formation of large flocs (Kim et al. 2008).

Azo dyes are the most common dyes in the textile industry, accounting for over 50% of all commercial dyes (Waring et al. 1990). However, a large amount of azo dyes remains in the effluent and most azo dyes are non-biodegradable (Liakou et al. 1997). Reactive brilliant red (RBR) X-3B is the typical azo dye in textile and printing industry, so it will make sense to choose RBR X-3B as a model compound.

In this study, a combined flocculant (CAFS) was prepared with starch, aluminum sulfate and ferrous sulfate. The floc formation, the break-up and the precipitation properties, in the RBR X-3B suspension system, were characterized by the FI, the zeta potential, shape and other chemical techniques. The objective was to evaluate this new combined flocculant efficiency and to better understand the mechanisms involved in the flocculation process.

doi: 10.2166/wst.2012.110
MATERIALS AND METHODS

Model water

Three hundred milligrams of RBR X-3B (Tianjin Erlun Chemical Science and Technology, China, the molecular structure is shown in Figure 1) was dissolved in 1 L deionized water. Its characteristics were as follows: chemical oxygen demand (COD<sub>Cr</sub>) was 107.4 mg/L, pH was 4.75, and absorbance (λ = 538 nm) was 3.55.

Preparation of CAFS

Modified starch solution was prepared by adding approximately 50 mL of a 0.2 mol/L NaOH to an aqueous slurry containing 4.000 g of maize starch (13.4% moisture content, China) at 50–55°C with continuous low speed stirring (50 rpm) for 1 h. After that, 225 mL of 0.5 mol/L Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O and 70 mL of 0.2 mol/L FeSO<sub>4</sub>·7H<sub>2</sub>O were added, and pH was adjusted to 3.0 using 5 mol/L H<sub>2</sub>SO<sub>4</sub>. The mixture was stirred for 4 h in a water bath at 50–55°C, followed by cooling to room temperature and freeze-drying, as CAFS.

Flocculation experiments

Before the determination of the best dosage of CAFS, for flocculation, the pH of 1 L model water was adjusted to 5.0. Next, different contents of CAFS (0.330, 0.495, 0.660, 0.825, 0.990, 1.155 mg/L) were added to the model water, and mixed at 300 rpm for 3 min and then 40 rpm for 10 min, followed by quiescent settling for 10 min. In addition, at the optimum flocculant dosage, the effects of pH values on the flocculation processes were analyzed by adjusting the solution pH to 3.0, 5.0, 7.0, 9.0, and 11.0, and reacting as above.

After each mixing period, triplicate samples were taken out for the determination of zeta potential respectively; after settling, other triplicate samples were taken for the determination of absorbance and COD<sub>Cr</sub>. Throughout the mixing and flocculation periods, the suspension was monitored online by a PDA to obtain the associated FI. Furthermore, at the optimum pH and dosage, the morphological characteristics of aggregates were observed immediately after different periods.

Flocculation parameters

For dynamic monitoring, the sample was circulated through 3 mm transparent plastic tubing clamped in the PDA (PDA-100, EcoNovel Company Ltd., Korea) by a peristaltic pump, and was illuminated by a narrow light beam (λ = 850 nm). The PDA measured the average transmitted light intensity (dc value) and the rms value of the fluctuating component. The ratio (rms/dc) was called the FI. The FI had been shown to be a sensitive indicator of the aggregation state of a particle suspension (Dean & Kenneth 2003).

Zeta potential was determined using a Nano-2890 Zeta Sizer (Malvern, UK). The COD<sub>Cr</sub> was determined by potassium dichromate using a spectrophotometer analyzer (Hach model DR2800, USA). The morphological characteristics of the aggregates were observed under inverted microscope (BDS200-PH, China) and the color was expressed as the absorbance measured by a spectrophotometer (UV–VIS752, Shanghai Youke Instrument, China), λ = 538 nm. The pH was measured by a pH meter (pHS-3C, Shanghai Precision & Science Instrument, China).

RESULTS AND DISCUSSION

Effects of CAFS dosages on FI

Figure 2 shows the FI with time, when different CAFS dosages were added at pH 5.0. It indicated that the FI value reached the maximum soon after CAFS was added. When the rapid stirring stopped, the FI value decreased quickly to an equilibrium value and to another lower equilibrium value during the settling period. The RBR X-3B suspension system contained some negatively charged colloidal particles such as –SO<sub>3</sub>H, which could attach to the surface of cationic CAFS quickly. These results suggest that during the early mixing stage the main flocculation mechanism was adsorption and charge neutralization: the attachment forces made the FI value reach the maximum quickly. With this type of binding, there still existed repulsion between the chemically bridged particles, resulting in loose and porous flocs.

Figure 1 | Molecular structure of the reactive brilliant red X-3B.
All flocs were subject to breaking up with excessive agitation (300 rpm), thus the FI value decreased quickly. During slow agitation (40 rpm), bridge-aggregation was the principal binding force holding the flocs together. This type of binding was considered much stronger than Van der Waals attractive forces formed during charge neutralization (Jarvis et al. 2005). Meanwhile, floc growth approached a balance between floc formation and floc breakage. At this time, the FI value reached a steady state and the flocs were very dense. During quiescent settling, at first the flocs sedimentation rate was high and then declined, thus the FI value decreased to a lower equilibrium value.

Figure 2 reveals that the flocculation could be markedly affected by CAFS dosages. With the increasing dosages, the FI curve became sharper and the time to achieve a relatively stable value became shorter; furthermore, the FI peak and equilibrium value were increased. However, excessive CAFS dosage resulted in decreased efficiency. At a CAFS dose of 0.990 mg/L, both the FI peak and equilibrium values reached the maximum. The optimum dosage was directly related to the amount of multiparticle adsorption.

The particles might be completely covered by the absorbed polymer layer corresponding to the optimum dosage. Further, the essential requirements for polymer bridging were that there should be sufficient unoccupied particle surface for polymer segments to attach to other particles, and that the polymer bridges should be of such an extent that they spanned the distance over which interparticle repulsion prevailed. With excess polymer, which might involve some steric repulsion (Tripathy & Ranjande 2006), there was no longer enough bare particle surfaces available for attachment of segments, and the particles became destabilized. Thus, overdosing could be a serious mistake as it might create a well-established suspension that was extremely difficult to separate. However, the optimum dosage seems to be difficult to predict because it varies with the ionicity, the molecular weight and other parameters.

Effects of CAFS dosages on zeta potential, color and CODCr.

With the increasing CAFS dosages, the zeta potential changed gradually from negative to neutral, and the change trend at 300 rpm showed good consistency with that at 40 rpm (Figure 3). Figure 3 also depicts the decolorization and CODCr removal rates. These rates increased with increasing CAFS dosages. However, at concentrations higher than 0.990 mg/L, the degree of flocculation decreased, though reversed zeta potential reached the maximum. In the presence of hydrolyzable metal ions such as Al$^{3+}$ and Fe$^{3+}$, or polyelectrolytes of opposite charge, the charge of the particles was neutralized by adsorption. For inorganic flocculants, their flocculation mechanism was pure charge-neutralization, which led zeta potential to be zero at the point of optimum flocculation (Besra et al. 2004). For polymeric flocculants, their high molecular weight and flexible linear chains initiated bridge-aggregation and sweep-
flocculation, which played a much more important part in flocculation than other mechanisms. The main flocculation mechanism depended on molecular weight, charge density and so on. Therefore, the zeta potential at the optimum flocculation was not zero (Nishida et al. 2002).

**Effect of pH on FI**

As shown in Figure 4, the shape of the FI-time curve could be markedly affected by pH change. The FI peak and equilibrium value reached the maximum at pH 5.0, and both decreased with the increase of pH value. When pH value reached 11.0, the FI value was very low (almost zero) during rapid stirring. When the rapid stirring stopped, the FI value increased sharply, and quickly reached an equilibrium value. In strong alkali conditions (pH 11.0), the positive charges of polyaluminum and polyferrous grafting onto modified starch mesh chains were shielded and their charge neutralization capacities were greatly weakened, and bridge-aggregation and sweep-flocculation played an important role at this stage. During subsequent quiescent settling, due to the same charged-surfaces of the floc particles, particles tended to strongly repel each other for their high positive charge, which led to a slow flocculation process.

**Effect of pH value on zeta potential, color and CODCr**

The measured zeta potentials of coated particles (with 0.990 mg/L of CAFS dose) at different pH conditions are presented in Figure 5. These results suggest that zeta potential was closely dependent on the pH value of the suspension. With increasing pH values, zeta potential declined and the change trend during the 300 rpm period, showed good consistency with that during the 40 rpm period. It can be seen that the decolorization and CODCr removal rates were greatly affected by pH value, and they reached a maximum (66.1 and 65.8%, respectively) at pH 5.0.

As indicated above, strong surface charge in the particle could result in significant mutual repulsion. If the charge on these particles was reduced to zero, these
repulsion forces would be eliminated. However, the optimum zeta potential in this experiment was not the 'isoelectric point' or 'point of zero charge', but about $-2.0 \, \text{mV}$. The zeta potential tended to become negative at optimum flocculation because the increasing molecular weight of flocculant preferred bridging to the charge neutralization mechanism (Tripathy & Ranjande 2006). The result also agreed well with flocculation efficiency reaching the maximum when the zeta potential of both the floc and colloid were lowered to a value of approximately $0 \pm 3 \, \text{mV}$ (Hunter 1981). It could be inferred that CAFS had successfully been synthesized to be organic polymer of high molecular weight and charge density by grafting polyaluminum and polyferrous onto modified starch mesh chains.

**Floc figuration**

Under optimal conditions and at different periods, the floc images are presented in Figure 6. The flocs were loose and porous because some negatively charged colloidal particles adsorbed the cationic CAFS quickly, and because of charge neutralization after rapid mixing. During subsequent slow agitation, bridge-aggregation was the principal binding force, which helped colloidal particles and flocs to aggregate, and aggregation gradually formed a cross-linked network structure. During quiescent settling, bridge-aggregation and sweep-flocculation gathered the smaller flocs together to form larger flocs, promoting a very compact and stable floc structure.
**CONCLUSIONS**

In this study, a novel cationic polymeric flocculant with high charge density (CAFS) was developed. CAFS was a combined aluminum–ferrous–starch flocculant with its mesh starch chains grafting polyaluminum and polyferrous. At the preliminary stage, some negatively charged colloidal particles attached quickly to the surface of cationic CAFS, by adsorption-charge neutralization. At the later stage, bridge-aggregation and sweep-flocculation gathered colloidal particles and flocs together to form larger flocs, and the structure of the flocs became very compact and stable. The optimum CAFS dosage for floc formation was 0.990 mg/L and the optimum pH was 5.0. Furthermore, it was found that zeta potentials, decolorization and COD$_c$ removal rates were closely dependent on the dosage and pH. The results have proven that this novel flocculant has potential usage in water treatment and purification systems; however, the detailed mechanisms involved in flocculation and the optimum conditions for a much wider usage need further investigation.

**ACKNOWLEDGEMENTS**

This work was financially supported by the Water Pollution Control and Treatment S&T Major Research Project of the ‘11th Five-Year Plan’ (2009ZX07211-005-03), the National Environmental Protection Public Welfare Science and Technology Research Program of China (201109024), the Cooperation Plan of Industry, Education and Academy Sponsored by the Guangdong Province, Chinese Ministry of Education and Ministry of Science and Technology (2011)B090400255, 2010B090400418).

**REFERENCES**


First received 31 October 2011; accepted in revised form 25 January 2012