FLOCCULATION DYNAMICS OF SYNTHETIC AND ACTIVATED SLUDGE IN WASTEWATER TREATMENT

Nguyen Tan Phong⁽¹⁾, Nidal Hilal⁽²⁾ and John T Novak⁽³⁾
(1)University of Technology, VNU-HCM
(2)The University of Nottingham, University Park, Nottingham
(3)Department of Civil & Environmental Engineering, Virginia Tech, Blacksburg, Virginia (Manuscript Received on November 13th, 2008, Manuscript Revised February27th, 2009)

ABSTRACT: This study has investigated in a comparative fashion the effect of cation, polysaccharide, and Polyelectrolyte on the flocculation dynamics and final properties of both synthetic and activated sludge. The results from experiments indicate that cation, polysaccharide, and Polyelectrolyte could influence sludge floc characteristics as they relate to sludge conditioning. The relationship between polysaccharide and cation concentration was examined at laboratory scale during flocculation with both synthetic and activated sludge; an increase in feed cation concentration led to a decrease in final polysaccharide concentration of the supernatant. The effects of a polyelectrolyte conditioner on sludge conditioning were determined. The results indicated that the cationic Polyelectrolyte had the critical effect on sludge dewatering, and made the improvement of the final properties of sludge. A qualitative link exists between polyelectrolyte conditioner dosage and sludge conditioning for both types of sludge. The two types of sludge also have very similar sludge conditioning. Thus synthetic and activated sludge behave very similarly in terms of their characteristics and sludge conditioning, and synthetic sludge can be used as a surrogate in activated sludge studies.

Keywords: Activated sludge; Synthetic sludge; Calcium ions; Polysaccharide; Polyelectrolyte; Sludge properties.

1. INTRODUCTION

Activated sludge is a heterogeneous mixture of particles, micro-organisms, colloids, organic polymers and cation, whose composition depends on the origin of the sample and the date of sampling [1]. It is a flexible, reliable process, capable of producing a high quality effluent. The main objectives of this process consist in the pollutant degradation by microorganisms, which grow as suspended flocs. Next, the flocs are separated from the effluent in a secondary clarifier. Soluble organic matter is reduced to low levels, and a clear effluent low in suspended solids is produced, due to the flocculant nature of the biomass [2]. The activated process always consists of two liquid stream unit processes-a biological conversion of pollutant in a biological reactor and solids separation, usually in a gravity clarifier.

The flocculation of activated sludge is an active process, and depends on physical, chemical and biological factors. The basis of activated sludge floc formation lies in the ability of micro-organisms to stick to each other and to non-biological particles. Microbial adhesion mechanisms have been studied widely, but are still not understood. It appears that exocellular biopolymers form the bridges between micro-organisms; these biopolymers typically contribute 15 to 20 % by weight of Mixed Liquor Suspended Solid (MLSS) [3]. At the approximately neutral pH values typical of activated sludge, these polymers carry net negative charges. It is thought that divalent cation such as Ca²⁺ and Mg²⁺ interact with negatively charged polymers to form bridges that allow the cells to adhere to each other. Many major

operating problems in the process, such as those which occur in solid-liquid separation, can also be attributed to the properties of the flocs.

1.1. Bioflocculation

Biosolid-liquid separation by gravity settling in a clarifier is one of the most critical operations in the activated sludge process. Bioflocculation of activated sludge determines how the sludge will dewater, flow, and settle, all of which are obvious concerns in the operation of wastewater treatment plants. The identification and eventual control of bioflocculation mechanisms is therefore of major interest [4]. The formation of stable biological flocs is essential for the successful operation of the process. In many cases, the efficiency of the clarifier is the limiting factor in producing a high quality effluent, and it is often regarded as the bottleneck of the process in terms of upgrading or increasing the capacity of the treatment plant. The settling properties of sludge are determined primarily by the conditions prevalent in the aeration basin. The most notably adverse effect of poor or no flocculation is inefficient settling in the clarifier, resulting in a turbid effluent. Poorly flocculated sludge can also have an adverse effect on sludge dewatering.

1.2. Synthetic sludges

The living micro-organism consortium in activated sludge is complicated and unstable. It changes the sludge characteristics continuously, making it practically impossible to carry out controlled experiments during sludge studies. Sanin and Vesilind [5] developed a novel chemical surrogate for activated sludge, which they named *synthetic sludge*, to study sludge dewatering, settling and conditioning characteristics. Synthetic sludge is made up of non-living particles that resemble activated sludge components. The components of synthetic sludge include: polystyrene latex particles of bacterial size, which simulate individual bacteria; alginate simulates extracellular polymeric substances; and calcium ions are used as bridging cation.

The overall objective of this research is thus to investigate how sludge characteristics affect cation; polysaccharide; Polyelectrolyte choice and optimal dosages; the relationship between the cation and polysaccharide content and their important role in floc formation and floc structure, and theirs effect on the final properties of both synthetic sludge and activated sludge. In this fashion, we can establish the validity of using synthetic sludge as a physical and chemical analogue to the real, activated sludge.

2. MATERIALS AND METHODS

2.1. Bacteria simulating particles

The concentrated sulphate polystyrene latex particle was 5% by weight with a 0.5µm mean particle diameter to simulate individual bacteria. The coefficient of variation of particle diameters was usually less than 5%. The procedure of preparing the sulphate latex particles followed the guidelines [6]. About 20% of the surface area of particles is covered with sulphate groups, to give them the necessary stability and negative surface charge. The zeta potential was measured as -14mV. The stock solution was diluted to 0.1%, to match the design particle concentration to that of bacteria in activated sludge.

2.2. Preparation of synthetic sludge

The creation of synthetic sludge follows the procedure established by Sanin and Vesilind [7]. Sulphate polystyrene latex particles were suspended in deionised water. Samples of 500 mL with a pre-selected 0.1% particle concentration and an added alginate concentration of 100

mg/L were rotated horizontally in an incubator at 12 rpm and 25 °C for 12h. Alginate was adsorbed on the particles during the incubation period. When the incubation period was completed, Ca (II) was added to samples in varying concentrations to monitor flocculation dynamics.

Two separate experiments were conducted to investigate the effect of calcium concentration alone and combined calcium together with aluminium ions on the flocculation behaviour of synthetic sludge, respectively. Calcium, iron, and aluminium in the form of CaCl₂ .2H₂O, FeCl₃, and AlCl₃.6H₂O were dissolved in distilled water. The appropriate volume of concentrated salt solution was added to the samples to match the design calcium concentration for each experiment.

2.3. Activated sludge

Four semi-continuous flow and two batch mode six-litre reactors were set up at Environmental Engineering Laboratory, Virginia Tech, USA to study the binding relationship between polysaccharide and cation ions. In addition, a five-litre, continuous-flow, bench-scale reactor was set up at Environmental Engineering Laboratory, The University of Nottingham, UK to study the sludge conditioning and dewatering. The reactors were used to simulate the activated sludge process. The reactor configuration is shown in Fig.1. The reactor consisted of a complete mixing zone and a settling zone, separated by a slanted baffle. An aeration stone provided air and mixing to the system.

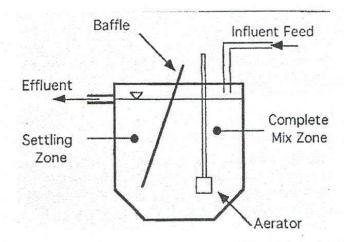


Fig.1. Profile of laboratory scale activated sludge reactor.

The reactors were seeded with mixed liquor from the Blacksburg, Virginia, municipal wastewater treatment plant in USA and from Stoke Bardolph municipal wastewater treatment plant in Nottingham, UK. After collection, the samples were returned to the laboratory (within 1 hour) and stored at 4°C. The influent pH was consistently near 7 for all seed conditions. The hydraulic retention time (HRT) was 0.5 days, and the sludge age was maintained at 10 days.

2.4. Polysaccharide

Alginate (low viscosity, sodium form) from brown algae was supplied by Sigma Chemical Company. Polysaccharide in the supernatant was measured using the method of Dubois [8].

2.5. Fibrous cellulose

Fibrous cellulose was supplied by Sigma Chemical Company to simulate filamentous organisms in activated sludge. Medium fibrous cellulose having a mean size of $50-350\mu m$ is

chosen for the experiments. The concentration of fibrous cellulose add to the samples of synthetic sludge at 0.2 g/L to simulate concentration of filamentous organism exist in activated sludge.

2.6. Conditioning

Cationic polyelectrolyte polydiallyldimethyl ammonium chloride (PDADMAC) was used for the conditioning of thickened sludges from the reactors. Polymer of 1 wt % in stock solution was made to the final design concentration, by diluting the concentrated polymer with distilled water.

2.7. Settling and dewatering properties

Total suspended solids (TSS) were analyzed using method 2540D in Standard Methods (1998). The settling properties of biological suspensions were characterized by the sludge volume index (SVI), as described by method 2710D in Standard Methods (1998). The dewatering characteristics of biological suspensions were determined by capillary suction time (CST), using method 2710G in Standard Methods (1998) [9].

3. RESULTS AND DISCUSSION

3.1. Relationship between cation ions and polysaccharide on the flocculation behaviour of synthetic sludge

Standard synthetic sludges (0.05% latex particles, pH 7.5, 100mg/L alginate) were prepared in 500 mL samples, and the calcium concentration of the samples was varied between 0 and 20 mM Ca(II) with fast (F) feeding for 10 minutes. There was no significant change in the pH of the sample after calcium addition. The results showed that no floc formation occurred without adding calcium ions. The experimental results provide valuable information about the flocculation behaviour of synthetic sludge. The mass of polysaccharide in the supernatant is plotted as a function of the calcium ion concentration in the feed of the laboratory synthetic sludge system without and with low concentrations of iron (1.2 mg/L) and aluminium ions (0.25 mg/L), as shown in Fig. 2 and Fig.3.

The result from experiments by Nguyen et al [10] stated that the rate of the flocculation increases initially with the addition of calcium concentration and then approaches a steady-state rate at the higher concentrations. This suggests that at a higher calcium concentration, saturation of the floc has occurred, and the rate of flocculation is independent of calcium concentration. It was also apparent that for the higher calcium concentrations, the rate of aggregation was faster. The concentration of calcium ions in the solution after flocculation was generally less than the initial feed concentration for each experiment. This indicates that an uptake of calcium ions was occurring during the flocculation process, which confirms that calcium ions are used a medium in the formation of synthetic activated sludge.

Figure 2 shows that, at lower concentrations of calcium added to the samples, the concentration of polysaccharide in the supernatant is higher. On the other hand, when a higher concentration of calcium is added, the concentration of polysaccharide in the supernatant is lower.

This result is in agreement with the work of Higgins and Novak [11]. They found that there was a relationship between exocellular biopolymer concentration and fed cation ions concentration when using laboratory scale activated sludge reactors with bactopeptone as a feed. An increase in the divalent cation ions concentration in the feed to the reactors was associated with a decrease in exocellular biopolymer concentration in the supernatant.

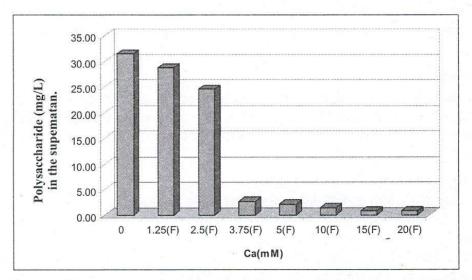


Fig.2. The effect of calcium ions on polysaccharide concentration in the supernatant of synthetic sludge.

The relationship between calcium, aluminium ions and polysaccharide concentration in the supernatant is shown in Fig.3. The conditions for these experiments were similar to the above experiments with calcium ions, except for the addition of a low concentration of aluminium ions to the sample to see whether the trivalent ions could affect the flocculation behaviour. Aluminium was added to the samples with a low concentration of 0.25 mg/L. From Fig.3, it can be seen from comparison with Fig. 2 that, without calcium added to the sample, a small amount of polysaccharide was nevertheless adsorbed by flocculation. This implies that trivalent ions also play an important role in the floc formation. From Fig.2 and Fig.3, it can be seen in each case that the rate of aggregation depends on the cation ions existing in the samples. The combination of both divalent and trivalent ions could increase the rate of aggregation, resulting in the lower concentration of polysaccharide in the supernatant.

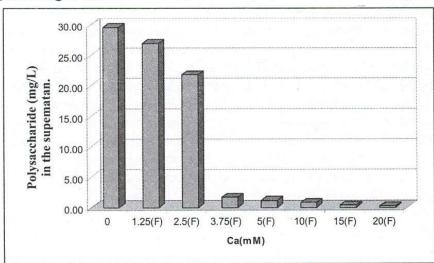


Fig.3. The effect of calcium, iron, and aluminium ions on polysaccharide concentration in the supernatant of synthetic sludge.

3.2. Relationship between cation ion and polysaccharide on the flocculation behaviour of activated sludge

Two separate sets of 6, six-litre reactor experiments were conducted to investigate the effect of cation ions on the flocculation behaviour of activated sludge. Each set experiment consisted of 6 reactors, of which the first 4 reactors were slug (S) for 5 hours to simulate semi-continuous mode and the last 2 reactors were fast (F) feeding for 10 minutes to simulate a batch-mode reactor. Calcium and Aluminium in the form of CaCl₂ .2H₂O and AlCl₃.6H₂O were dissolved in distilled water. The appropriate volume of concentrated salt solution was added to the samples to match the design calcium concentration for each experiment. Laboratory reactors were operated until steady-state conditions were obtained. The feed to the reactor contained bactopeptone plus additional monovalent, divalent and trivalent ions.

In the first set of experiments, the concentration of calcium ions was increased in both slug (S) and fast (F) feeding. The aluminium ions were fed to each reactor with a low concentration of 0.25 mg/L. The conditions applied for the second set of experiments were similar to the first one, except for changes in concentration of aluminium in the feeding regime: the concentration of aluminium was fed at the higher concentration of 0.5 mg/L. The mass of polysaccharide in the supernatant is plotted as a function of calcium ion concentration in the feed of the laboratory activated sludge system with low (0.25 mg/L) and high concentrations of aluminium ions (0.5 mg/L), as shown in Fig. 4 and Fig.5.

The relationship between fed calcium ion concentration and polysaccharide concentration in the supernatant with low fed concentration of aluminium ions is shown in Fig.4. From Fig.4, it can be seen that, at the lower concentration of calcium added to the reactors, the concentration of polysaccharide in the supernatant is higher. On the other hand, a higher concentration of calcium added led to a lower concentration of polysaccharide in the supernatant. One interesting result from these experiments shows that for the same concentration of calcium (0.25 and 2.5 mM) added to the reactor but under a different feeding regime, the polysaccharide concentration in the supernatant was different. The polysaccharide concentration in the supernatant of the activated sludge with semi-continuous (S) feeding was higher when compared to the batch (F) mode with the same concentration of feeding. As seen in Fig.4, it is suggested that the increase in calcium ions results in an increase in bound polysaccharide concentration. The interactions among micro-organism, polysaccharide, and cation ions are thus important for flocculation and depend on the feeding regimes.

This finding could be explained by the work of Higgins and Novak [11]. Their work concluded that when cation ions were present in slow feeding, they could become incorporated within the microbe-biopolymer network into flocs as they form, resulting in a denser floc that is more resistant to shear. In contrast, during fast feeding, the cation ions may not become completely enmeshed in the biopolymer network; binding of cation ions would thus be decreased. This was supported by the lack of change in the floc density during batch tests, while floc density increased over time when cation ions were present in the semi-continuous test. Cation ions would thus have had more chance to bridge with polysaccharide in the supernatant during fast feed, batch mode had a lower concentration when compared to the semi-continuous slow feed mode, with the same concentration of cation ions fed to the reactors in each case.

It has been speculated that Al may have a better flocculating capability for activated sludge. Keiding and Nielsen [12] predicted that when sludge is deficient of Al, many organic compounds would remain unflocculated and washed out of the system. Since the conditions

applied for the second set of experiments involved a higher concentration of aluminium at 0.5 mg/L, this can be clearly seen by comparing Fig.4. with Fig.5.

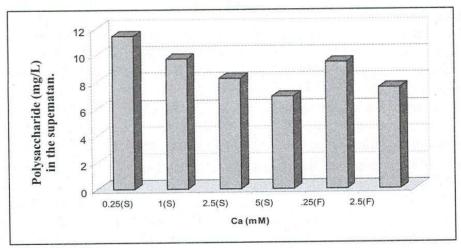


Fig 4. The effect of calcium ions on polysaccharide concentration in the supernatant of activated sludge.

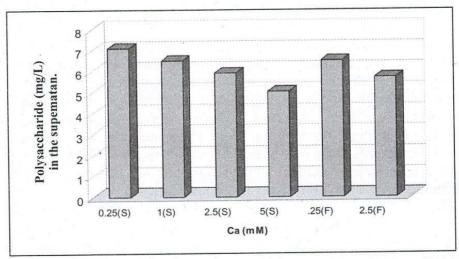


Fig 5. The effect of calcium and aluminium ions on polysaccharide concentration in the supernatant of activated sludge.

The polysaccharide in the supernatant decreased as Al concentration increased in the biomass. Al has a positive effect on the flocculating capability of activated sludge. A similar trend to the previous one was found for the dependence of the flocculation behaviour of activated sludge on the feeding regime. This finding seems to agree with the view of Park et al [13], which indicated that Al was an excellent collector of negatively charged organic matter, because as floc Al increased, biopolymer in solution decreased. Although Al in this form is known to function as an effective coagulant, it is not clear how Al in activated sludge flocs coagulates biopolymer during the flocculation process. Clearly, this area is worthy of further study.

3.3. Settling and dewatering properties

The effect of calcium concentration on the settling and dewatering properties of synthetic and activated sludge are shown in Fig. 6 and Fig. 7. When no Ca(II) ions were added to the synthetic sample, no floc formation occurred; all the particles were dispersed in the liquid

solution. For the activated sludge sample, a non-filamentous bulking occurred. However, the settling improved in both synthetic and activated sludge as the calcium concentration in the feed was increased.

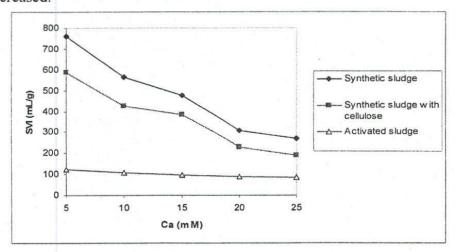


Fig 6. Synthetic activated sludge settling increases with increasing concentration of calcium

As can be seen in Fig.7, the dewatering property measured by CST followed a trend similar to that of the SVI. The CST values indicated a relatively poor dewatering at the lowest calcium concentration, but the dewatering property improved as the calcium concentration increased. Most of the improvement in SVI and CST occurred after the first incremental addition of Ca(II) ion, with a modest improvement beyond this level.

This result is in agreement with the work of Higgins and Novak [11]. They demonstrated that the cation content in a wastewater could have a major impact on the settling and dewatering characteristics of an activated sludge. In our work, there is a similarity in behaviour between the settling and dewatering characteristics of both synthetic and activated sludge when calcium is added. However, the settling and dewatering of activated sludge is improved more than that of synthetic sludge after calcium concentration addition.

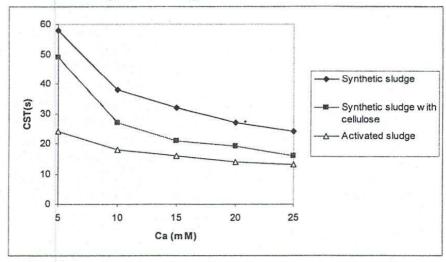


Fig 7. Sludge dewatering of synthetic activated sludge

This phenomenon can be explained by the existence of filamentous organisms in activated sludge. Filamentous organisms also cause an improvement in the compaction and settling of synthetic sludge. The types of compaction and settling effects depend on the causative

filamentous organism involved [14]. In addition, it should be noted that there are interactions between cation and biopolymers in activated sludge. An ion-bridging model has been proposed to explain the effect of cation on biological sludge properties [15]. This model proposes that divalent cation act as a bridge between negatively charged sites on exocellular biopolymer (gel). Therefore, improvements in settling and dewatering due to increased particle sizes should correlate to an increase in the bound exocellular polymer content involved in the aggregation process.

3.4. Sludge Conditioning

A conditioning was performed using thickened sludge samples with 1g/L of total suspended solid (TSS), in both synthetic and activated sludge. The sludge conditioning as a function of cationic Polyelectrolyte addition is shown in Fig.8. The CST of the samples with added calcium decreased over time, but the samples with polymer added showed a better improvement of sludge conditioning, as indicated in Fig. 8.

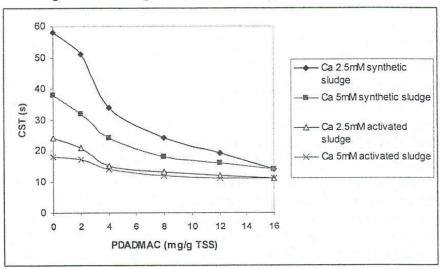


Fig 8. Effect of PDADMAC polymer on sludge conditioning of synthetic and activated sludge

The result from Nguyen et al.'s work [10] also showed that the addition of calcium improves the sludge conditioning of both synthetic and activated sludge. However, the sludge conditioning of activated sludge showed a greater improvement than that of synthetic sludge. Although the solid content was similar in both types of sludges, the variability associated with the sludge, such as viscosity and the surplus polyelectrolyte present in the sludge, could affect the CST values. The polyelectrolyte will increase the liquor viscosity and so increase the rate of absorption by the filter paper. Nevertheless, the Ca (II) ion strongly enhances the conditioning of industrial wastewater sludge, especially biological sludge. The good conditioning when calcium ion is added to the system could possibly result from the interaction of polysaccharide from the biological sludge with calcium ion [16].

4. CONCLUSIONS

The strong relationship between cation and polysaccharides for both synthetic and activated sludge has been explored through the measurement of the concentration of polysaccharide in the supernatant with the changes of cation concentration fed to the reactor. The presence of cation decreases the polysaccharide concentration in the supernatant. An

increase in cation concentration was also associated with an increase in the bound biopolymer concentration.

The cation and polysaccharides play an important role in the flocculation of both synthetic and activated sludge. Calcium ions contribute to the floc formation by constructing calcium ion bridges between polysaccharides or biopolymer gel adsorbed on individual particles/bacteria; aluminium ions also seem to assist in floc binding and the flocculation of other organic material. The cation contribute significantly to the binding of the sludge flocs in both synthetic and activated sludge; this binding appears stronger for a 'slowly fed' sludge.

The effects of calcium and cationic polyelectrolyte on the resulting final properties of sludge, such as sludge conditioning, have also been measured and characterized for both synthetic and activated sludge. The calcium ion content in wastewater can have a major impact on the settling and dewatering characteristics of both synthetic and activated sludge.

The stable and physically/chemically well-defined nature of synthetic sludge makes it very useful as a non-complex analogue for the physical and chemical (i.e. non-biological) properties of activated sludge.

ĐÔNG TỤ SINH HỌC BÙN NHÂN TẠO VÀ HOẠT TÍNH TRONG XỬ LÝ NƯỚC THẢI

Nguyễn Tấn Phong⁽¹⁾, Nidal Hilal⁽²⁾ và John T Novak⁽³⁾
(1)Trường Đại học Bách khoa, ĐHQG-HCM
(2)Đại học Nottingham, University Park, Nottingham
(3)Khoa Kỹ thuật Môi trường, Virginia Tech, Blacksburg, Virginia

TÓM TẮT: Nghiên cứu này tập trung vào việc so sánh ảnh hưởng của các cation, protein, và chất keo tụ đến quá trình động học lên đặc tính của bùn nhân tạo và hoạt tính. Kết quả từ quá trình thí nghiệm cho thấy cation, protein, và chất keo tụ có ảnh hưởng lớn đến quá trình đông tụ và ổn định bùn. Mối quan hệ giữa chất keo tụ và nồng độ cation đã được thực hiện trong phòng thí nghiệm trong quá trình đông tụ trên cả hai loại bùn nhân tạo và hoạt tính; khi nồng độ các cation tăng trong quá trình đông tụ thì kết quả là nồng độ protein trong nước thải sau khi xử lý giảm. Ảnh hưởng của chất keo tụ đến quá trình ổn định bùn cũng được xác định. Kết quả cho thấy chất keo tụ cation ảnh hưởng rất lớn đến quá trình cô đặc bùn, và cải thiện một cách đáng kể đặc tính của bùn. Cả hai loại bùn có đặc tính tương tự nhau sau khi ổn định. Bởi vì đặc tính tương tự của bùn nhân tạo và hoạt tính, vì vậy có thể sử dụng bùn nhân tạo để nghiên cứu các đặc tính của bùn hoạt tính.

Từ khóa: Bùn họat tính; Bùn nhân tạo; Calcium ions; Polysaccharide; Polyelectrolyte; Đặc tính bùn

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