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Effect of biofiltration on particle characteristics and flocculation behavior

Hueysong You,[1] Chihpin Huang,[1]* Hsinghsuong Cheng[2] and Jill Ruhsing Pan[1]

[1]Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
[2]Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan

Abstract: Biodegradable dissolved organic material and ammonia present problems for conventional water treatment processes and may contribute to biological instability in the treated water. One solution may be to use a biological process upstream of the regular water treatment process. Biofiltration may be cost-effective in removing ammonia and the precursors of trihalomethanes but the characteristics of the biotreated effluent may affect to the subsequent coagulation process. A continuous flow biological filter packed with reticulated polyurethane foam markedly altered the particle size distribution and the charge density of the mixed liquor, shifting the granulometric distribution toward larger sizes. The mean and median diameter of the particles increased from 9.7 and 5.9 μm to 97.6 and 37.1 μm, respectively. The average charge density of the biofilter effluent (7.6 meq dm^{-3}) was much lower than that of the raw water (12.7 meq dm^{-3}). The optimum coagulant dosage for the subsequent coagulation was reduced substantially from 10 mg dm^{-3} to 1 mg dm^{-3} as Al due to the lowered charge density of the mixed liquor and the enhanced cation bridging of the extracellular polymers on the bioparticle surface.

Keywords: biofiltration; bioflocculation; cation bridging; coagulation; zeta potential

INTRODUCTION

In many Asian countries water sources have become increasingly contaminated by human and livestock wastes. The most serious contaminants are biodegradable organic materials (BOM) and ammonia, which not only handicap the conventional treatment process but also cause biological instability in the treated water. Prechlorination has been a common practice to remove ammonia. Unfortunately, prechlorination results in the generation of carcinogenic trihalomethanes (THMs) in the treated water. One alternative is to employ a biological process prior to the conventional water treatment processes.[1] It has been identified that the active microbes in the biological treatment for drinking water are oligotrophs[2] due to the low concentration of organic compounds in the water. When exposed to substrate limitation, the oligotrophic microorganisms exist mainly in filamentous aggregates. These aggregates have a strong potential to biosorb and bioflocculate,[3] a process known as biofiltration and by which much of the BOM can be removed from water, reducing the potential of microbial regrowth and the formation of disinfection-by-products (DBPs). The performance of coagulation is directly related to the properties of the particles in the water, eg particle size distribution and surface charge. Since in practice the biofiltration unit is placed before the coagulation unit, the characteristics of the bio-treatment effluent play an important role in the subsequent coagulation process. Zhang *et al*[4] indicate that the efficiency of coagulation may be enhanced significantly by adding a bio-pretreatment process due to the fact that oligotrophic microorganisms can bioflocculate/biosorb fine particles. However, most studies of bio-pretreatment of the water supply have mainly focused on investigating the removal efficiencies of ammonia and the precursors of THMs[5–10]: very few examined the effect of biofiltration on the subsequent coagulation.

The objective of this study was to investigate the effect of biofiltration on the subsequent coagulation. By monitoring the physical and chemical characteristics of the effluent particles, the mechanism of coagulation/flocculation could be better understood and the subsequent coagulation process could be optimized.

EXPERIMENTAL

Bench-scale packed-bed biofilter

The continuous flow biological filter used in this study is shown in Fig 1. The reactor was made of an acrylic column (10 cm id × 100 cm) with a working volume of 5.9 dm^3, of which 70% was packed with reticulated

* Correspondence to: Chihpin Huang, Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
E-mail: cphuang@mail.nctu.edu.tw
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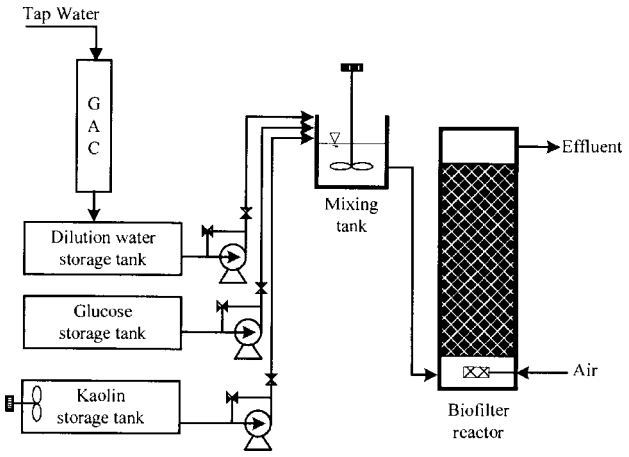

Figure 1. Schematic set-up of the biofiltration apparatus.

Table 1. Operational parameters for the biofilter

Parameter	Value
Reactor length (cm)	100
Reactor id (cm)	10
PU foam porosity (%)	97
Packed ratio (%)	70
Working volume porosity (%)	98
Influent	
NPDOC (mg dm^{-3})	2–3
Turbidity (NTU)	50–55
pH	7.5–7.8
Effluent	
NPDOC (mg dm^{-3})	0.2–0.5
Turbidity (NTU)	23–40
pH	7.5–7.8

polyurethane (PU) foam. The foam, having a void fraction of 97% and an apparent density of about 28 kg m^{-3}, functioned as a macroporous carrier for immobilizing the bacteria.

The glucose solution and the kaolin suspension provided the carbon and turbidity sources for the biofilter. The dilution water was prepared by passing the tap water through a GAC column to remove the chlorine and the organic matter. Stock glucose solution, kaolin suspension and the dilution water were pumped from individual storage tanks into the mixing tank, and the mixture then flowed into the bottom of the biofilter by gravity. The flows of glucose, concentrated kaolin suspension and dilution water were controlled by peristaltic pumps at constant rates of 5 cm^3 min^{-1}, 3 cm^3 min^{-1} and 190 cm^3 min^{-1}, respectively, which amounted to a total flow rate of approximately 200 cm^3 min^{-1}, attaining an empty bed contact time (EBCT) of 30 min. The turbidity of the synthetic raw water was maintained in the range of 50–55 NTU (naphelometric turbidity unit), and the non-purgeable dissolved organic carbon (NPDOC) concentration was in the range of 2–3 mg dm^{-3}. Air was supplied from the bottom of the biofilter. The storage tank of the stock glucose solution was refrigerated at 4 °C to inhibit microbial activity. The specification of the biofilter is given in Table 1.

Flocculation test

Coagulation, flocculation, and sedimentation experiments were conducted at laboratory scale, using a standard jar-test apparatus. The mixing was conducted in a square acrylic vessel (L × W × H, 11.5 cm × 11.5 cm × 21 cm) which is often referred to as a gator jar. The mixing was provided by a 76 mm × 76 mm flat rectangular blade centrally located in the vessel. The blade was driven by a thin spindle via a motor of adjustable speed from 10 to 300 rpm (Phipps & Bird, Inc, PB-700 Jar tester, Richmond, Virginia). The mixing was provided with 1 min rapid-mixing and 20 min slow-mixing at rotational speed of 200 rpm ($g = 350\,s^{-1}$) and 30 rpm ($g = 25\,s^{-1}$) respectively, followed by 30 mins settling. Aluminum sulfate was used as coagulant for all tests. The aluminum sulfate (alum; $Al_2(SO_4)_3{\cdot}18H_2O$; Merck) was reagent grade, and was prepared to give 123.3 g alum dm^{-3} (10 g Al dm^{-3}) as stock solution. Experiments were conducted at room temperature, while their pH values were maintained around 7.5 by using a strong base (0.1 mol dm^{-3} NaOH) and a strong acid (0.05 mol dm^{-3} H_2SO_4). A sampling tap located 10 cm below the surface of the water allowed the sampling of the settled water for analyses.

Particle sizing

Particle size distribution (PSD) was determined with a laser diffraction particle size analyzer (Beckman Coulter, Inc, LS 230, Miami, Florida, USA), in which a laser light (at 750 nm) was used to detect particles from 0.04 to 2000 μm by light diffraction.

Zeta potential measurement

Zeta potentials of the kaolin and the effluent particles of biofiltration were measured with a zeta meter (Zeta-Meter, Inc, System 3.0, Staunton, Virginia, USA). The concentration of the background electrolyte ($NaClO_4$) was kept at 10^{-2} mol dm^{-3}. The pH values of the colloidal suspensions were adjusted to the required values from 2 to 10 with 0.05 mol dm^{-3} H_2SO_4 and 0.1 mol dm^{-3} NaOH. The readings from 20 particles were averaged and taken as the zeta potential.

Surface charge of particles

The surface charge of the particles was measured using the colloid titration technique described by Morgan *et al*.[11] Colloid titration is based on the theory that positively- and negatively-charged colloidal particles combine stoichiometrically with each other and the end point of the titration can be detected with a suitable indicator. Polybrene (hexadimethrine bromide, Aldrich Chem Co, USA) and polyvinyl sulfate kalium (PVSK, Wako Pure Chemicals Ind, Japan) were used as the standard cationic and anionic colloids, respectively, as suggested by Dentel *et al*.[12] To titrate

negatively-charged colloidal particles, a positively-charged polymer (0.0025 meq dm^{-3} polybrene) was added. The excess polybrene was back-titrated with a negatively-charged polymer (0.0025 meq dm^{-3} PVSK) using Toluidine Blue O (TBO, Sigma Chem Co, USA) as the indicator. The end point of the titration was when the electrical neutrality was reached, as indicated by the change of color from blue to pink. An equal volume of polybrene in distilled water was used as the blank.

RESULTS AND DISCUSSION

Synthetic raw water, containing 2–3 mg dm^{-3} NPDOC and turbidity from 50 to 55 NTU, was fed into the biological filter reactor of 30 min EBCT. During the two-month operation period, the NPDOC of the effluent remained at 0.2–0.5 mg dm^{-3} with the turbidity in the range 23–40 NTU. We termed the particles in the synthetic raw water kaolin particles and the particles in the biofilter effluent, bioparticles.

Effect of bioflocculation on subsequent coagulation/flocculation

The jar tests were performed on kaolin particles and bioparticles to determine the effect of biofiltration on the subsequent coagulation/flocculation. The biofilter effluent and the raw synthetic water were coagulated with various dosages of aluminum sulfate and the turbidity of the supernatant at 30 mins settling time were determined and taken as residual turbidity (Fig 2). The optimal coagulant dosage was determined by the criteria described by Hess *et al*[13] as that beyond which the turbidity would not reduce any further. For instance, the optimal dosage is what corresponds to $\Delta TU/\Delta Al^{3+} = -0.2$ NTU/(mg dm^{-3} Al^{3+}), in which Δ TU is the incremental reduction in turbidity with the increase in coagulant dose. To optimize the turbidity removal for kaolin particles, 10 mg dm^{-3} as Al was required. The lowest turbidity of the biofilter effluent water, on the other hand, occurred when 1 mg dm^{-3} as Al was used, as shown in Fig 2. The significant reduction in alum dosage suggested that packed-bed biofiltration was effective in aiding the subsequent coagulation process. Similar results have been reported in the study of biofiltration for drinking water treatment.[5] The following experiments were then conducted to further investigate this phenomenon.

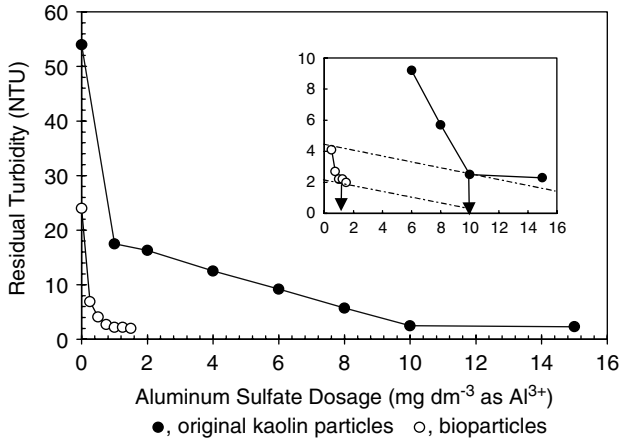

Figure 2. Turbidity of the supernatant from two kinds of water samples as function of alum dosages at pH 7.6 ± 0.2. The inset shows the details around optimal dosage.

Alteration in particle size distribution

Particle size distribution can be reported in terms of particle diameter, surface area or volume.[14] Allen[15] has indicated that in order to compare particle size distribution, it is essential to normalize the frequency distribution so that the area under this curve is 100%. Bouwer[16] has developed a theoretical framework to determine the impact of particle size on the efficiency of the biofilm treatment process. He has concluded that the removal of particles larger than 10 μm is controlled by sedimentation and filtration, and the removal of submicron particles is controlled primarily by diffusion. Based on this, the size range most difficult to remove in the biofilm process is between 1 and 10 μm. Therefore, it is essential to examine the effect of biofiltration on the PSD.

The PSDs of the synthetic raw water and the biofiltered effluent with or without 30 mins settling were monitored and are given in Fig 3. The average mean and median particle diameters of the synthetic raw water and biofilter effluent water during the three-month operational period (Sept–Nov, 2000) are listed in Table 2. Biofiltration changed the PSDs dramatically. The packed-bed biofilter shifted the granulometric distribution toward larger sizes. The mean and median diameter of the particles shifted from 9.7 ± 1.7 μm ($n = 4$) and 5.9 ± 0.3 μm ($n = 4$) to 97.6 ± 59.0 μm ($n = 8$) and 37.1 ± 31.0 μm ($n = 8$), respectively. It implied that larger bioparticles, including bioflocculated solids and detached biofilm,

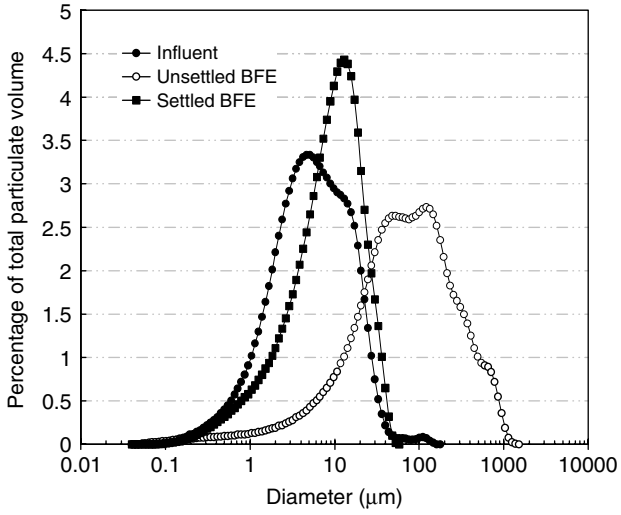

Figure 3. Particle size distribution (in volume) of water samples before and after biofiltration (BFE: biofilter effluent).

Table 2. Mean and median particle diameters of water before and after biofiltration (results are expressed as the average ± standard deviation)

Nature of suspension	Mean diameter (μm)	Median diameter (μm)
Influent	9.7 ± 1.7 ($n = 4$)	5.9 ± 0.3 ($n = 4$)
BFE[a] before settling	97.6 ± 59.0 ($n = 8$)	37.1 ± 31.0 ($n = 8$)
BFE[a] after settling	20.6 ± 14.3 ($n = 8$)	9.5 ± 0.9 ($n = 8$)

[a] BFE: biofilter effluent.

formed from glucose and small kaolin particles of the influent through chemical changes in the biofilter. With settling, the PSD completely changed. A marked reduction in large particles was observed after 30 mins settling, as seen in Fig 3. In fact, most particles larger than 200 μm disappeared. The mean and median particle diameters were also respectively reduced to 20.6 and 9.5 μm, indicating that the remaining particles after 30 min settling were mostly in the colloidal and supracolloidal size ranges, which can be removed successfully by coagulation.

Settling characteristics of particles

The residual turbidities as a function of settling time of raw water and biofilter effluent were determined to detail the settling characteristics of the particles. The residual turbidity decreased gradually with the increasing settling time, as shown in Fig 4. The residual turbidity of the synthetic raw water was significantly higher than the biofilter effluent water at all settling times. At 30 min, the biofilter treatment was able decrease the residual turbidity of the original water by five times, suggesting that a significant portion of kaolin particles can be destabilized and flocculated through biofiltration.

Surface property of bioparticles

pH value and ionic strength of the suspension had the greatest influence on the surface charge of the particles in suspension. The zeta potentials of the

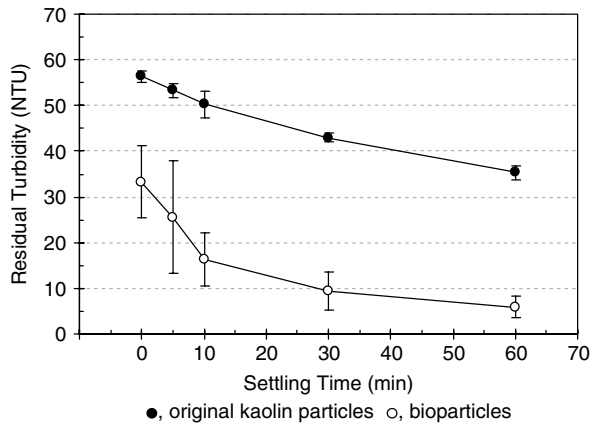

Figure 4. Turbidities of the supernatants of two water samples as a function of settling time ($n = 5$). Results are expressed as the average ± standard deviation.

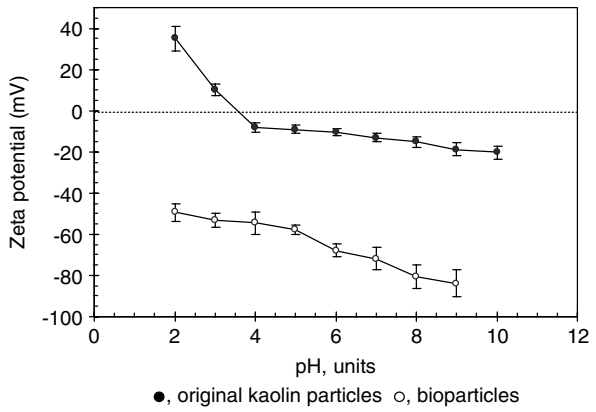

Figure 5. Zeta potential of kaolin and bioparticles as a function of pH at 0.01 mol dm^{-3} $NaClO_4$. The pH was adjusted by 0.05 mol dm^{-3} H_2SO_4 and 0.1 mol dm^{-3} NaOH. Results are expressed as the average ± standard deviation ($n = 20$).

kaolin particles and bioparticles as a function of pH at ionic strength of 0.01 mol dm^{-3} $NaClO_4$ are presented in Fig 5. The zero potential, which is referred as the isoelectric point or zero point of charge (ZPC) of the kaolin particles, was reached at around pH 3.5. The zeta potential of the bioparticles was significantly more negative than that of the original kaolin particles, meaning that the surface of the bioparticles carries more negative charge.

Pavoni *et al*[17] have indicated that microbial flocculation is generally attributed to extracellular biopolymers (ECPs) bridging of bacterial cells. They reported that the ECPs contain functional surface groups, primarily anionic and nonionic in most neutral pH ranges, and that charge neutralization alone cannot explain bacterial flocculation. Particle aggregation involves hydrogen, ionic, dipolar, and hydrophobic interactions, and covalent bonding.[18] Levy *et al*[19] have used a biopolymer produced from *Anabaenopsis circularis* strain PCC 6720 as an anionic flocculant for bentonite flocculation. From adsorption isotherms and zeta potential measurements they have concluded that the mechanism of the flocculation is bridging. Misra *et al*[20] also mentioned that the predominant mechanism for selective flocculation of fine coal particles with the bacterium *Mycobacterium phlei* was hydrophobic interaction. Therefore, the aggregation of microbial cells with inorganic particles is driven by an interaction between ECPs and inorganic particles, which bring a negative or no charge. Biological flocculation results from the interaction of high-molecular-weight extracellular polymers. These polymers bond, either electrostatically or physically, and subsequently link the bacterial cells and particles into a three-dimensional matrix. Therefore, charge neutralization is not a prerequisite for bioflocculation, and the aggregation of colloid particles in bioflocculation does not require reduction in surface potential and charge neutralization.

Charge density

Charge neutralization plays an important role when metal coagulants are used in the coagulation/flocculation process.[21] Although the previous

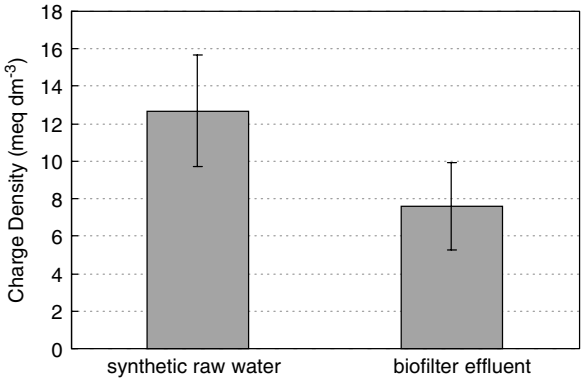

Figure 6. Charge densities of particles in synthetic raw water and biofilter effluent ($n = 6$). Results are expressed as the average ± standard deviation.

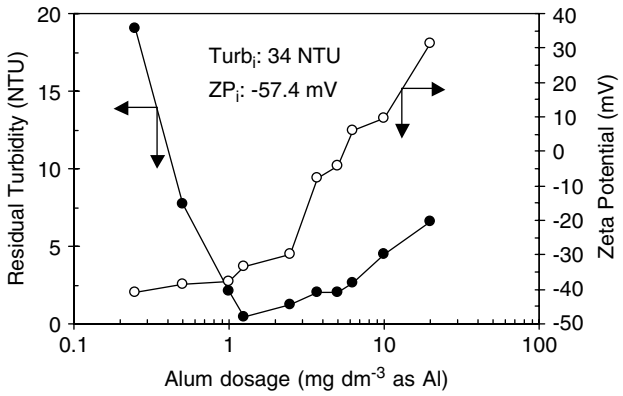

Figure 7. Residual turbidity and zeta potential as functions of alum dosages for biofilter effluent.

section has shown that the zeta potential of the bioparticles was significantly more negative than that of the original kaolin particles, it is the charge density of the mixed liquor that determines the amount of coagulant required for efficient turbidity removal. Colloid titration was performed to determine the charge densities of the synthetic raw water and the biofilter effluent. The result is shown in Fig 6. As expected, both samples carried a net negative charge. However, the average charge density of the biofilter effluent ($7.6 \pm 2.4\,\text{meq dm}^{-3}$, $n = 6$) was substantially lower than that of the raw water ($12.7 \pm 3.1\,\text{meq dm}^{-3}$, $n = 6$). The charge density of the mixed liquor is the product of the surface charge and the number of particles. Since the packed-bed biofilter shifted the PSD of the particles toward the range of larger size, fewer particles were left in the system after biofiltration, resulting in a significant reduction in charge density and in coagulant demand.

Flocculation behavior of bioparticles

To examine the flocculation behavior of bioparticles, jar tests were adopted with alum dosages ranging from 0.25 to $20\,\text{mg dm}^{-3}$($10^{-5.03}$ to $10^{-3.13}\,\text{mol dm}^{-3}$) as Al. Zeta potential (ZP) and turbidity of the particles of the original biofilter effluent were $-57.4\,\text{mV}$ and 34 NTU, respectively. The initial pH of the biofilter effluent was 7.5 and the final pH values after coagulation ranged from 7.4 to 5.8. The ZP and the residual turbidity for each coagulant dosage were measured and are presented in Fig 7, in which the residual turbidity reached a minimum value of 0.5 NTU at $2.0\,\text{mg dm}^{-3}$. Amirtharajah and Mills[21] have concluded that the predominant coagulation mechanism of alum was the combination of adsorption and charge neutralization. Optimal coagulation, as indicated by the lowest residual turbidity, should occur at the ZPC. The previous study in our laboratory by Kan *et al*[22] used the kaolin particles for coagulation, the result also indicated by the lowest residual turbidity, should occur at the ZPC. The zero ZP of the bioparticle was found at around $6.5\,\text{mg dm}^{-3}$, as shown in Fig 7, which did not correspond to the optimum dosage. It indicated that the coagulation mechanism of the bioparticles predominated over charge neutralization.

Interactions among microorganisms, extracellular biopolymers, and cations are all important for the flocculation in activated sludge systems.[23,24] Since bacteria surfaces carry negatively-charged adsorption sites, it has been suggested that cations act as bridges between ECPs.[24] Numerous studies have addressed that divalent cations improved the bioflocculation by acting as a bridge between the negatively charged sites of the biopolymer, a phenomenon known as the cation bridging model.[25,26] The cation bridging model can explain the flocculation behavior of the bioparticles in this study. The surface of the bioparticle contained ECPs, as proved by Frølund *et al*.[27] When aluminum salts are dissolved in water, the metal ion Al^{3+} hydrates, coordinating six water molecules to form an aquometal ion, $Al(H_2O)_6{}^{3+}$.[21] The aquometal ion can then react and form several hydrolysis species. The aluminum precipitate with low cationic charge is generated in the neutral pH zone, while the highly charged soluble cationic aluminum hydroxides are generated in the weakly acidic pH zone.

This theory is illustrated in Fig 8. The addition of alum in coagulation generates the hydrolysis products of multivalent cations which are capable of neutralizing the surface negative charge of the bioparticles due to the adsorption on the ECPs. At optimum dosage, although many negative adsorption sites are neutralized by the positive hydrolysis ions, the bioparticles remain negatively charged. During flocculation, the adsorbed cationic hydrolysis products, already adsorbed on bioparticles, bridge the negatively charged bioparticles to form large aggregates, which can be removed by settling. At insufficient coagulant dosing, although the aluminum cations on the bioparticles can still bridge negative particles, the charge is not strong enough to gather all bioparticles. As a result, more bioparticles remain in the supernatant, which is shown by the increased residual turbidity. At over-dosing, the negative adsorption sites on the surface of the bioparticle are mostly occupied by the multivalent Al cations.

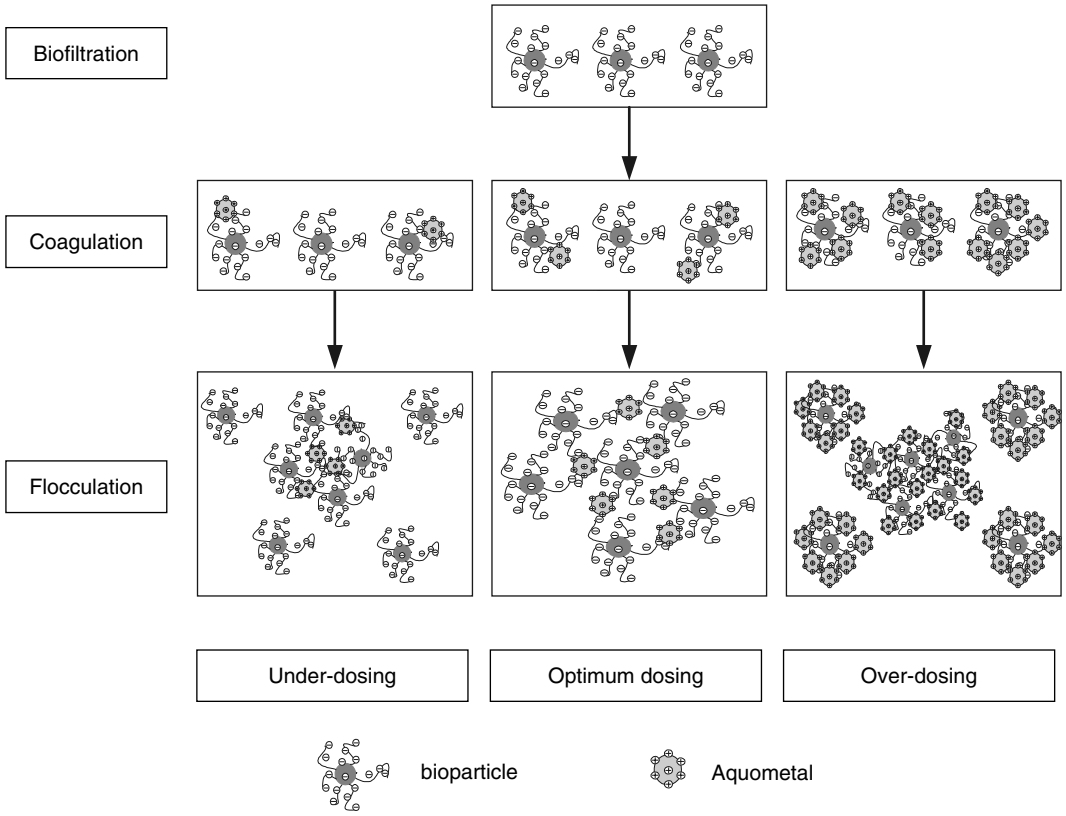

Figure 8. Hypothesized aggregation by cation bridging model for different dosages of alum.

Therefore, no cation bridging occurs, which leaves most bioparticles small and hard to settle as evidenced by the high residual turbidity.

CONCLUSION

Filtration of a continuous flow biological filter packed with reticulated polyurethane foam, glucose and kaolin was conducted to evaluate the effect of biofiltration on the subsequent coagulation process. The following conclusions were drawn from the experiments:

1. Packed-bed biological filter can effectively eliminate the turbidity of the water stream.
2. Biofiltration significantly shifted the granulometric distribution toward larger sizes. The mean and median diameter of the particles in the raw water and the biofilter effluent was increased from 9.7 and 5.9 μm to 97.6 and 37.1 μm, respectively.
3. Biofiltration caused significant change in the zeta potential of particles. The average charge density of the biofilter effluent (7.6 meq dm^{-3}) was much lower than that of the raw water (12.7 meq dm^{-3}).
4. Biofiltration significantly reduced the coagulant demand for the subsequent coagulation process, by lowering the charge density of the mixed liquor as well as through the mechanism of cation bridging. The optimum coagulant dosages of the raw water and the biofilter effluent were 10 and 1 mg dm^{-3} as Al, respectively

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