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Effect of activated carbon on fouling of activated sludge filtration

Herbert H.P. Fang*, Xinlong Shi, Tong Zhang

Environmental Biotechnology Laboratory, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong
Tel. +852 28592660; Fax +852 25595337; email: hrechef@hkucc.hku.hk

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Abstract

The effect of adding activated carbon on the fouling of activated sludge filtration was investigated using a complete-mix cell with a flat-sheet cellulosic membrane at a constant pressure gradient of 70 kN/m^2. Four sludge samples were tested in parallel: a sludge without additive served as control, plus three sludge samples dosed with individual additives, including inert diatomaceous earth, activated carbon pre-sorbed with 112 mg-C/g of EPS (extracellular polymeric substance), and virgin activated carbon. Results showed that the EPS of activated sludge was a major contributor of membrane fouling. Additives may reduce the filtration resistance of the film deposited on the membrane surface, depending upon their EPS-sorbing capacity. As compared with the control, virgin activated carbon reduced the film filtration resistance by 22%, from $6.4 \pm 0.5 \times 10^{12}$ m^{-1} to $5.0 \pm 0.1 \times 10^{12}$ m^{-1}, whereas the reduction was only 14% by the activated carbon pre-sorbed with EPS and negligible by the inert diatomaceous earth. Of the three main constituents of EPS, polysaccharide and humic substance were of significance to the fouling; protein had little effect.

Keywords: Activated carbon; Activated sludge; EPS; Filtration; Fouling; Membrane

1. Introduction

The membrane biological reactor (MBR) process for wastewater treatment has attracted much interest recently [1]. In this process, pollut-ants are degraded by the activated sludge and the clean effluent is obtained by permeating through a membrane under pressure. Compared with the traditional activated sludge process, the MBR process not only allows wastewater to be treated at higher sludge concentrations and loading rates, but also reduces the sludge yield and improves the effluent quality. However, the application of MBR process has been hampered by the problem of membrane fouling [2]. During filtration of MBR mixed liquor, a film is formed on the membrane surface, resulting in a gradual decline of

*Corresponding author.

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permeation flux [3], increase of operational cost and shortening of membrane life [4]. This film is a gel matrix of extracellular polymeric substances (EPS) in which microbial cells of activated sludge and their metabolites are embedded [5,6].

The EPS of activated sludge is mainly composed of polysaccharide, protein and humic substance [7,8], resulting from cell lysis/secretion and shedding of cell surface material. Recent studies found that membrane filtration resistance increased with the EPS concentration in either the mixed liquor [3,9] or the biofilm [10].

According to Darcy's law, the permeation flux through the membrane, J (m/s), is expressed by:

$$J = \frac{\Delta P}{\mu R} \quad (1)$$

where ΔP is the pressure gradient (kN/m^2), μ — the viscosity of the permeate (Ns/m^2), and R — the filtration resistance (m^{-1}). The filtration resistance in a MBR system mainly results from the film deposited on the membrane surface. Recent studies suggested that dosing powdered activated carbon (AC) may improve filtration flux of both aerobic [11] and anaerobic MBR systems [12]. Similar phenomenon was also observed in a batch process in spite of the increase of suspended solids and the reducing of floc size [13]. The positive effect of AC could be due to its formation of a permeable layer [11], or its scouring of colloidal deposits on the membrane surface [12], or the increase permeability and the reduction of compressibility [13].

However, the roles of EPS in filtration of activated sludge as well as the interaction between EPS and AC still remain unclear. One may hypothesize that the reduction of filtration resistance from the dosing of AC is due to its sorption of EPS. This study was thus conducted to validate such a hypothesis. Filtration resistances were compared for membranes fouled by four activated sludge samples: one without any additive serving as control, plus three dosed with individual additives, including inert diatomaceous earth (DE), activated carbon pre-sorbed with EPS (AC_S), and virgin activated carbon (AC_V).

2. Materials and methods

2.1. Activated sludge, EPS constituents and activated carbon

Activated sludge sampled from a local municipal wastewater treatment plant was used in this study. The mixed liquor contained 4,760 mg/l of suspended solids and 3,800 mg/l of volatile suspended solids. The AC (Darco G-60, Aldrich) used in this study was of high purity with 600 m^2/g of surface area and a size of 100–325 mesh.

EPS in the activated sludge was heat extracted [14] as follows: 200 ml of activated sludge was first centrifuged at 2,000 g for 30 min to remove the dissolved organic matters; the pellet was then re-suspended with 200 ml of saline aqueous solution (0.9% NaCl), heated at 100°C for 1 h, followed by centrifugation at 2,000 g for 20 min. All EPS data in this study were expressed as mg/l of organic carbon measured by a total organic carbon analyzer (TOC-5000A, Shimadzu). The supernatant contained 260 mg-C/l of heat-extracted EPS, including 94.6±0.4 mg/l of polysaccharide, 161.1 ± 1.9 mg/l of protein and 156.9 ± 3.0 mg/l of humic substance as measured by the established procedures [7]. The supernatant was used (a) to characterize the AC sorption capacity of heat-extracted EPS, (b) to prepare the AC_S for filtration, and (c) to conduct a preliminary parallel filtration test.

2.2. EPS sorption

For the adsorption isotherm study, eight solutions containing 100–900 mg-C/l of heat-extracted EPS were individually mixed with 1670 mg/l of AC at 25°C for 200 min, the duration of which had been proven to be sufficient to reach equilibrium from a series of preliminary tests. The amount of EPS sorbed by AC in each solution at

equilibrium was the difference between the EPS concentrations before and after the filtration.

2.3. Filtration

One set of fouling experiment was conducted to compare the permeation flux and filtration resistance of the EPS-containing supernatant and the aqueous saline solution re-suspended with the sludge pellet after EPS extraction.

Another set of fouling experiment was conducted to compare the filtration resistance of four activated sludge samples: one without any additive serving as control, plus three dosed respectively with 2,000 mg/l of AC_V, AC_S, and DE. The AC_S was prepared as follows: 400 mg of AC was mixed with 200 ml of EPS-containing supernatant for 15 min, centrifuged at 2,000 g for 20 min, followed by decanting the supernatant. The EPS contents were measured before the filtration and afterwards to determine the amount of EPS sorbed by the AC. After repeating the process three times, each gram of AC_S had sorbed 112 mg-C of EPS.

All continuous fouling experiments were conducted in a complete-mix filtration cell (Model 8200, Amicon) using a flat-sheet cellulosic membrane (GSWP 09000, Millipore) which has a pore size of 0.22 μm, thickness of 150 μm and porosity of 75%. The trans-membrane pressure (ΔP) was kept at 70 kN/m^2. The filtration cell was first filled with 200 ml of activated sludge sample, and the mixed liquor volume was kept unchanged for all experiments. This was done by continuously replacing the lost filtrate volume with de-ionized water from a pressurized vessel. The mixed liquor was mixed with a stirring rod, which was suspended 3 mm above the membrane surface to prevent excess buildup of film deposits. The permeate flux was continuously monitored from the weight of the collected filtrate using an electronic balance connected to a data logger.

3. Results and discussion

3.1. Contribution of EPS to filtration resistance

Fig. 1a compares the permeation fluxes of the EPS-containing supernatant and the saline

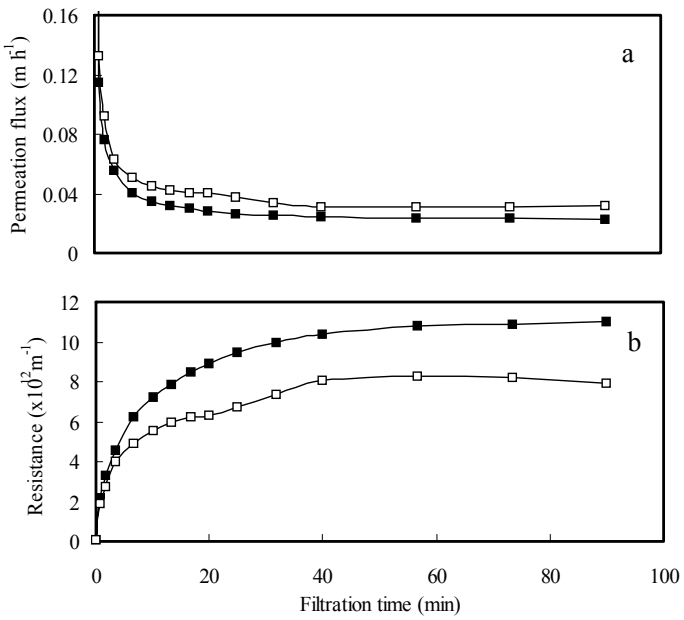

Fig. 1. Continuous filtration of EPS-containing supernatant (•) and sludge solution after EPS extraction (•): (a) permeation flux, and (b) filtration resistance.

solution re-suspended with the sludge pellet after EPS extraction. It illustrates that both fluxes reduced rapidly in the first 10 min and gradually leveled off to 0.056 m/h for the EPS-containing supernatant, which was 12% lower than the 0.063 m/h for the sludge solution after EPS extraction. Fig. 1b shows the corresponding plots for the filtration resistance. It illustrates that, under steady state condition, the EPS-containing supernatant had a filtration resistance of 11.0 $\times 10^{12}\,m^{-1}$, which is 34% higher than the 8.2 $\times 10^{12}\,m^{-1}$ sludge solution after EPS extraction. Assuming the total film resistance was the sum of those of heat-extracted EPS and the sludge solution after EPS extraction, this preliminary experiment shows that the heat-extracted EPS attributed to about 57% of the total fouling resistance. This confirms that EPS of activated sludge is the predominant factor of film resistance, as suggested by previous studies [3,15,16].

Comparing the individual constituents of the heat-extracted EPS solution and those of the filtrate shows that the membrane retained 42% of polysaccharide in the heat-extracted EPS solution, 10% of humic substance and only 1% of protein. This suggests that polysaccharide and humic substance in EPS could affect the filtration resistance, whereas protein was unlikely to have any effect since 99% of protein was in the filtrate. This concurs with the finding of Chu [17] that polysaccharide of EPS is prone to penetrate into membrane pores and to cause membrane fouling. On the other hand, Lee et al. [18] reported that both polysaccharide and protein of EPS affected the filtration resistance of activated sludge.

3.2. Adsorption of EPS by activated carbon

The sorption capacity of a sorbent is dependent on the concentration of the sorbed species at equilibrium. Two most common adsorption isotherms used to correlate these two properties are:

Langmuir isotherm

$$Q_e = Q_m b \frac{C_e}{1 + bC_e} \tag{2}$$

Freundlich isotherm

$$Q_e = kC_e^{1/n} \tag{3}$$

where C_e (mg/l) is the equilibrium concentration of the sorbed species and Q_e (mg/g) is the sorption capacity. Both isotherms have two parameters specific to sorbent and sorbed species. Of the four parameters, only Q_m (mg/g) of the Langmuir isotherm has a physical meaning, i.e. maximum sorption capacity; the other three are empirical parameters.

Although AC can sorb EPS in the activated sludge, its sorption capacity could not be determined because of the difficulty of separating AC from the mixture. However, the AC sorption capacity for the heat-extracted EPS could be determined. Fig. 2 illustrates that both isotherms fit

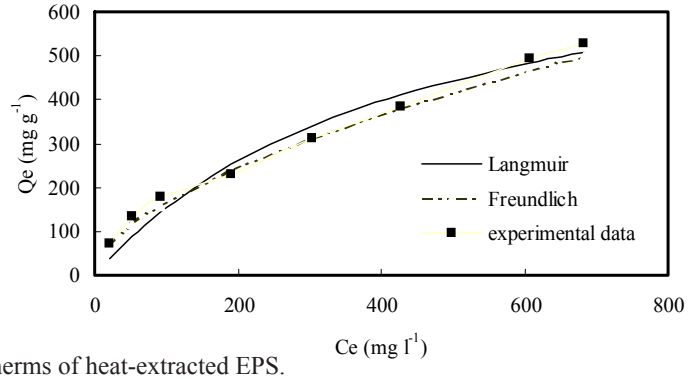

Fig. 2. Adsorption isotherms of heat-extracted EPS.

well with the sorption data of heat-extracted EPS by AC. The best-fitted Freundlich parameters were 12.2 and 0.57 for k and $1/n$, respectively (with a R^2 of 0.99), and the best-fitted Langmuir parameters were 833 mg/g and 0.002 for Q_m and b, respectively (R^2 of 0.97). Judging from the Q_m value, each gram of AC had the maximum capacity to sorb 833 mg-C of EPS. Comparison of the EPS constituents before the sorption and afterwards shows that AC sorbed 46% of polysaccharide in the heat-extracted EPS, plus 28% of protein and 92% of humic substance.

3.3. Effect of activated carbon on filtration resistance

Fig. 3a illustrates the changes of film resistance over the test period of 90 min of four activated sludge samples: the control, plus three dosed individually with 2,000 mg/l of AC_V, AC_S and DE. Each gram of AC_S had pre-sorbed 112 mg-C of EPS. In each case, the resistance increased initially due to the steady buildup of a film on the membrane surface. The resistance gradually leveled off because the mixing action of the stirring rod, which was suspended 3 mm above the membrane surface, limited the further buildup of deposits. Under steady state condition, the control sludge had a filtration resistance of $6.4\pm0.5\times10^{12}$ m^{-1}, which was comparable to the $6.2\pm0.1\times10^{12}$ m^{-1} for the sludge sample dosed with DE. However, the other two sludge samples dosed with AC_V and AC_S had substantially lower filtration resistances.

Fig. 3b compares the differences of resistance reduction between the three sludge samples and the control. It illustrates that differences became constant after about 250 ml of filtrate had been collected. The sludge dosed with AC_V reduced the filtration resistance from the control by 22%, from $6.4\pm0.5\times10^{12}$ m^{-1} to $5.0\pm0.1\times10^{12}$ m^{-1}. The substantial reduction was due to the strong EPS sorption capacity of AC_V. The sludge dosed with

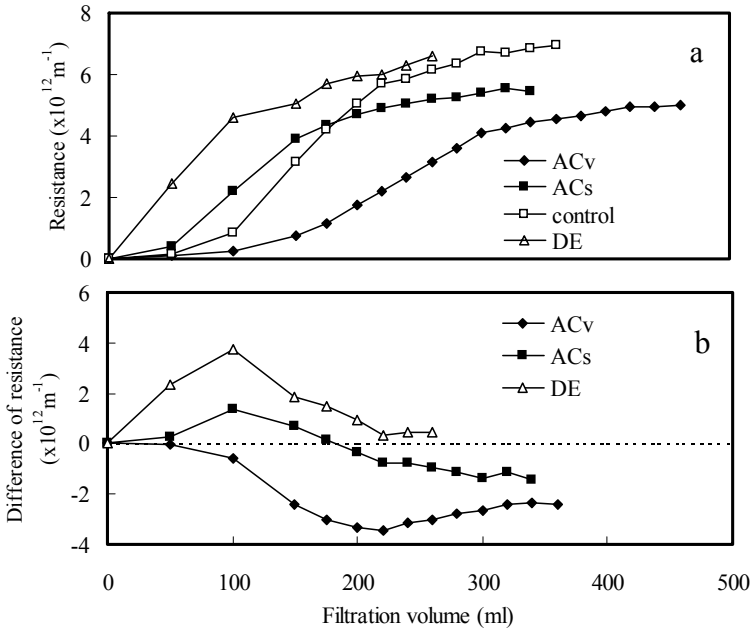

Fig. 3. (a) Filtration resistances of control sludge and those dosed with additives, and (b) differences of filtration resistance between sludges dosed with additives and the control.

AC_S reduced the filtration resistance from the control by 14%, to $5.5\pm0.1\times10^{12}$ m^{-1}. The lesser reduction was because the AC_S had pre-sorbed with 112 mg-C/g of heated-extracted EPS and was thus unable to sorb as much EPS from the activated sludge. On the other hand, the sludge dosed with DE had comparable filtration resistance as the control. These results indicate that: (a) reduction of filtration resistance of activated sludge increased with the additive's sorption of EPS, and (b) an inert additive, like DE, did not affect the filtration resistance of activated sludge.

Fig. 3b also illustrates that sludge dosed with AC_S and DE initially had higher filtration resistances than the control. This could be due to the higher settling velocity of these additives. The settling velocity of activated sludge without additive was 4.3±04 m/h, substantially lower than 14.4±1.3, 12.2±0.9, and 14.4±3.2 m/h, respectively, for those dosed with AC_V, AC_S, and DE. At the initial stage of the filtration, sludge dosed with DE had a high tendency to form a film on the membrane surface, and thus higher filtration resistance, than the control due to DE's higher settling velocity. Such effect was less pronounced for the sludge dosed with AC_S and not noticeable for the sludge dosed with AC_V because it was compensated by the EPS sorption.

4. Conclusions

The following conclusions can be drawn from this study:

(a) EPS in activated sludge caused fouling of membrane, and thus adversely affected filtration resistance;
(b) Of the three main constituents of EPS, polysaccharide and humic substance affected fouling of membrane; protein had little effect.
(c) An additive may reduce the film resistance, depending upon its capacity of sorbing EPS. Dosing virgin activated carbon reduced the filtration resistance of activated sludge by 22%, from $6.4\pm0.5\times10^{12}$ m^{-1} to $5.0\pm0.1\times10^{12}$ m^{-1}, whereas the reductions were only 14% by dosing activated carbon pre-sorbed with EPS and negligible by dosing the inert diatomaceous earth.

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