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Membrane filtration-based recovery of extracellular polymer substances from excess sludge and analysis of their heavy metal ion adsorption properties

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HIGHLIGHTS

- Ca^{2+} reduces membrane fouling of extracellular polymer substance (EPS) solutions.
- Decreased colloid/polymer concentration and increased size reduce membrane fouling.
- Ultrafiltration (> 90% EPS recovery efficiency) is superior to microfiltration.
- Addition of Ca^{2+} has no effect on adsorption of heavy metal ions by EPS.
- EPSs recovered by membrane filtration with added Ca^{2+} can adsorb heavy metal ions.

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ABSTRACT

Excess sludge production by wastewater treatment plants (WWTPs) represents a serious environmental problem that necessitates the development of effective sludge treatment/disposal methods. Excess sludge contains valuable materials such as extracellular polymer substances (EPSs), and their recovery is of great practical importance. However, conventional recovery methods afford EPS solutions with moisture contents of ~100% and the dehydration of these solutions via direct drying methods is considerably energy consuming. Here, we investigate the separation of EPSs extracted from excess sludge by microfiltration (0.5 µm) and ultrafiltration (10 kDa), revealing that Ca^{2+} addition reduces the extent of membrane fouling during EPS isolation since the interactions between Ca^{2+} and EPS carboxylate groups increase the size and reduce the concentration of colloids/polymers in EPS suspensions. Additionally, we establish an ultrafiltration-based EPS separation protocol, demonstrating that it allows highly efficient EPS recovery (> 90%) irrespective of the Ca^{2+} concentration, and show that EPSs extracted from excess sludge samples derived from two different WWTPs exhibit similar filtration resistances at Ca^{2+} concentrations of 0–4 mM. Finally, we demonstrate that the EPSs recovered from excess sludge can be used as adsorbents for the removal of diverse heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}) from wastewater, exhibiting performances that are on par with those of commercial adsorbents and are unaffected by the employed extraction procedure. Based on the obtained results, Ca^{2+} addition is confirmed to be a viable method for reducing filtration resistance during the membrane recovery of EPSs, since this ion does not affect the adsorption capacity for heavy metal ions.

Abbreviations: AO, anaerobic or anoxic/oxic process; A^2O, anaerobic/anoxic/oxic process; CAST, conventional activated sludge treatment; CER, cation exchange resin; DI, deionized; EPS, extracellular polymer substance; EPS-Ca, product of EPS–Ca^{2+} interaction; EPS-Fe, product of EPS–Fe^{3+} interaction; HEPES, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; FTIR, Fourier transform infrared; ICP, inductively coupled plasma; M_w, molecular weight; MWCO, molecular weight cut off; M1, CER extraction method; M2, formaldehyde – NaOH extraction method; M3, high-temperature sodium carbonate extraction method; SBR, sequencing batch reactor; TOC, total organic carbon; TS, total solids; VS, volatile solids; WWTP, wastewater treatment plant; W1, excess sludge from Beijing Gaobeidian WWTP; W2, excess sludge from Beijing Dongba WWTP

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Nomenclature

C	mass concentration of EPS in initial suspension before filtration [g/L]
$C_{0Ca^{2+}}$	molar concentration of calcium ions in initial suspension [mmol/L]
C_{0i}	molar concentration of heavy metal ions in initial suspension [mmol/L]
C_a	mass concentration of adsorbent in initial suspension [mg/L]
$C_{Ca^{2+}}$	molar concentration of calcium ions in filtrate [mmol/L]
C_e	mass concentration of metal ions in solution at equilibrium [mg/L]
C_f	mass concentration of solute in the filtrate without free ions [g/L]
d_m	size of membrane pores [μm]
K	Langmuir adsorption equilibrium constant in Eq. (3)
K_v	Ruth filtration coefficient defined by Eq. (1) [L/mg] [m^2/s]
p	applied filtration pressure [kPa]
q_e	amount of heavy metal ions adsorbed on composite adsorbent at equilibrium [mg/g]
Q_{max}	amount of heavy metal ions adsorbed to form a monolayer coverage [mg/g]
R	EPS recovery rate [mmol/L]
t	settling time
v	cumulative filtrate volume collected per unit effective filtration area [min] [cm]
θ	filtration time [s]

Subscripts

m	Membrane

1. Introduction

The treatment and disposal of large amounts of excess sludge produced by wastewater treatment plants (WWTPs) represents a significant problem, and necessitates the replacement of the traditional regulatory-driven approach by that based on resource recovery [1–3]. According to the Water Pollution Prevention and Control Action Plan (10-Point Water Plan) released in April 2015, the excess sludge generated by WWTPs must be disposed of in a sustainable and harmless manner, and substandard excess sludge should not be used as an agricultural supplement [4]. Since excess sludge contains extracellular polymeric substances (EPSs) that account for 10–40% of its dry weight [5–8], their extraction reduces the weight of excess sludge (in compliance with the 10-Point Water Plan) and improves its dewatering performance [9–11].

EPSs contain mainly substances secreted by microbial cells and produced by cell autolysis or felled out from the cell surface, e.g., polysaccharides, proteins, nucleic acids, phospholipids, and humus, with polysaccharides and proteins being the major constituents [12–16]. Moreover, EPSs recovered using conventional wastewater treatments such as the sequencing batch reactor (SBR), anaerobic or anoxic/oxic (AO), and anaerobic/anoxic/oxic (A^{2}O) processes have a wide range of potential applications [1,2,17]. Fig. 1 shows the compositions and potential applications of EPSs found in activated sludge flocs (biofilms), illustrating that EPSs and their neighboring cells are involved in metal cation-aided bridging to form a cross-linked network, which strengthens the structural integrity of biofilms or biogranules [18]. The recovered EPSs can be used as bioflocculants [19–24], soil conditioners [25], and adsorbents for heavy metal ions such as Pb^{2+}, Cu^{2+}, and Cd^{2+} [26–34]. In particular, the aerobic granular sludge process produces alginate-like exopolysaccharides, which account for up to 20 dry wt% of aerobic granule sludge [25] and are widely used in the food industry, textile printing, and paper and pharmaceuticals production [35].

The high adsorption capacity of recovered EPSs makes them promising adsorbents for heavy metal ions [30–32,34]. However, EPS extraction procedures can influence their metal binding properties significantly [26,36,37] by affecting the functional groups (e.g., carboxyl (–COOH) and hydroxyl (–OH) groups) that are primarily involved in

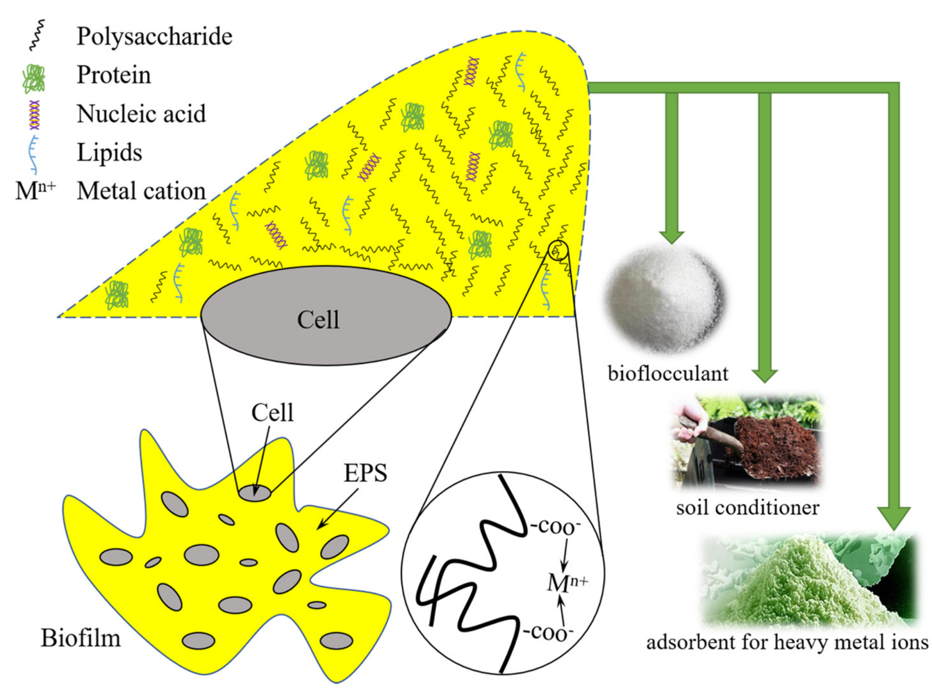

Fig. 1. Compositions and potential applications of extracellular polymer substances (EPSs) in activated sludge flocs (biofilms).