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Combined use of surfactant-induced coagulation of poly(allylamine hydrochloride) with peroxidase-mediated degradation for the rapid removal of estrogens and phenolic compounds from water

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ABSTRACT

Sodium dodecyl sulfate (SDS)-induced coagulation of poly(allylamine hydrochloride) [PAH] was studied for the rapid removal of estrogens and phenolic compounds from water. When electrically equivalent amount (62 mg L^{-1}) of SDS was added into the aqueous solution of 20 mg L^{-1} PAH with vigorous mixing, PAH was quantitatively (>99%) recovered from water as condensed aggregates of PAH–SDS complexes. According to the fluorescence spectrum of a molecular probe, the complexes provided hydrophobic regions suitable for incorporating hydrophobic organic pollutants. However, rather polar estrone, β-estradiol, estriol, and ethynylestradiol were insufficiently removed. Combined use of horseradish peroxidase (HRP) and hydrogen peroxide significantly increased the collection yields of these estrogens, because of their HRP-induced oxidation of and spontaneous binding to PAH. With the HRP activity of 100 U L^{-1} and the hydrogen peroxide concentration of 10 mg L^{-1}, nearly complete (>98%) removal of four estrogens was achieved within 10 min at 30 °C in the pH region from 6 to 7.5. The method was also useful for the rapid removal of different phenolic compounds and selected pharmaceuticals. The applicability to wastewater treatment was successfully demonstrated by using secondary effluents.

1. Introduction

Occurrence and fate of estrogens in environment waters have gained much scientific and public concern [1,2]. The major source of estrogens is the effluents from municipal wastewater treatment plants due to their incomplete removal by current sewage treatment processes such as activated sludge methods [3–8]. Since estrogens can influence endocrine or other physiological systems even at very low concentration (μg or ng L^{-1}-levels) [9,10], they have to be eliminated from wastewaters. Advanced methods such as activated carbon adsorption, chlorination, ozonation, ultra-violet irradiation, and membrane separation have extensively been studied [11–13]. The extent of removal is largely dependent (from <10 to ca. 100%) on the methods or wastewater treatment plants. The significant dependence in removal efficiency is also shown even in the same wastewater treatment facilities. In general, long term treatment or large-scale plants seems to be required for increasing the yields in the degradation or adsorption of estrogens. However, this significantly boosts the cost of wastewater treatment. A rapid but simple method may be necessary to reduce the environmental risk of estrogens in wastewaters.

Recently, we have developed a novel separation method for the rapid removal of phenol from water by using chitosan- or polyallylamine-conjugated thermoresponsive polymers [14–16]. In the presence of appropriate phenol oxidation enzymes, phenol was converted to the oxidized form and spontaneously bound to the amino moieties of the thermoresponsive polymers. The polymers were water-soluble at room temperature, while became water-insoluble by heating the solution above the lower critical solution temperature (LCST, 34–36 °C). With vigorously mixing the solutions, formed deposits were coagulated to a very small aggregate which could be readily collected from the surfaces of water. Phenol were rapidly collected to the polymer deposits and nearly completely removed from water. When horseradish peroxidase (HRP) was employed, the method could be applied to the removal of different phenolic compounds including estrogens [16]. However, heating of large amounts of wastewater for the polymer deposition would boost the cost of wastewater treatment.

An attractive alternative may be the flocculation of surfactant-polyelectrolyte complexes. In the aqueous solutions, oppositely charged surfactant and polyelectrolyte electrostatically interact with each other and can form nanosized assemblies or films

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[17–26]. Their structures [17,19], solution properties [18,20–23], and behaviors at air–water interfaces [23–26] have extensively been studied. On the other hand, only limited applications have been reported for the collection or removal of organic pollutants from water [27–30]. Furthermore, such flocculation systems have never been combined with other methods such as enzyme-mediated remediation techniques.

In the present study, surfactant-induced coagulation of poly(allylamine hydrochloride) [PAH] was studied for the rapid removal of estrogens and phenolic compounds from water. Sodium dodecyl sulfate (SDS) was employed as an anionic surfactant, because of the extensive use in several surfactant-mediated separation methodologies such as admicellar sorption method [31–38], adsorbed micellar flocculation [39–41], and micellar-enhanced ultrafiltration [42–44], as well as its high biodegradability in environment [45–47]. The properties of the coagulation system and the limitation in the removal of hydrophobic organic pollutants were studied. Moreover, HRP-mediated remediation technique was combined with the coagulation system for achieving highly efficient removal of estrogens from water. The factors influencing the extent of the collection were investigated in detail. Effect of HRP on the removal of different phenolic compounds and selected pharmaceuticals was also studied. The practical applicability as an advanced wastewater treatment method was examined by using secondary effluents from municipal wastewater treatment plants.

2. Materials and methods

2.1. Materials

PAH (40.3 wt% solution, $M_n = 1.5 \times 10^5$) was supplied by Nittobo Medical (Tokyo, Japan) and used without further purification. SDS (for biochemistry, Wako Pure Chemical, Osaka, Japan) and sodium oleate (Tokyo Chemical, Tokyo, Japan) was used as 50 g L^{-1} aqueous solutions. Their factors were determined by a toluidine blue titration method [28]. Horseradish peroxidase (HRP, EC 1.11.1.7, Oriental Yeast, Tokyo, Japan) was dissolved in 1 mM sodium phosphate solution (pH 7) and measured the activity spectrophotometrically at 25 ± 0.1 °C using phenol and 4-aminoantipyrine. Estrogens, phenolic compounds, and pharmaceuticals were purchased from the following suppliers: Sigma–Aldrich (St. Louis, MO, USA), estrone, β-estradiol, estriol, and ethynylestradiol; Wako Pure Chemical, *o*-, *m*-, and *p*-methoxyphenol; Tokyo Chemical, bisphenol A, 3-methyl-4-isopropylphenol (biosol), diclofenac, mefenamic acid, triclocarban, and triclosan. A molecular probe, *N*-phenyl-1-naphthylamine (PN, Molecular Probes®, Invirogen, Carlsbad, CA, USA) was used as 1 mM ethanol solution. Other chemicals employed were of analytical grade. Water was purified with a Milli-Q Integral Water Purification System possessing UV radiation components (Merck, Milford, MA, USA).

2.2. Coagulation and characterization of PAH–SDS complex

Prescribed amounts of SDS solution were added to 50 mL of 10–100 mg L^{-1} PAH solution. Immediately, the resulting solution was vigorously (240 rpm) mixed with a rotary shaker for 10 s to induce the coagulation of PAH–SDS complexes. The formed aggregates were collected and freeze-dried for the FT-IR analysis using a Jasco 4200 FT/IR spectrometer (Hachioji, Japan). An Olympus BX-51 polarized optical microscope (Tokyo, Japan) and a Rigaku FR-E/RAXIS-II X-ray scattering system (Akishima, Japan) were employed for observing the microscopic structure of aggregates. For XRD analysis, the aggregates (wet form) were enclosed in a Kapton® polyimide film (DuPont, Wilmington, Delaware, USA) to prevent dryness. PAH remaining the bulk aqueous solution was determined by an *o*-phthalaldehyde spectrophotometric assay [48], while SDS was monitored by a methylene blue extraction method [49]. A fluorescence spectrum of PN was measured by using a PerkinElmer LS-50B luminescence spectrometer (Waltham, MA, USA) with a 1 cm quartz cell. In the fluorescence measurement, solutions were carefully mixed to prevent the coagulation.

2.3. Collection of estrogens or phenolic compounds

To 50 mL of aqueous solution containing 0.1 mg L^{-1} of estrogens or phenolic compounds were added 20 μL of 5.0% (w/v) PAH solution, 50 μL of 100 U mL^{-1} HRP, and 50 μL of 1.0% (w/v) H_2O_2. Solution pH and temperature were typically 7 and 30 °C. However, the effects of pH in the region from 5 to 9 and temperature in the range from 10 to 30 °C were also investigated. After gently (60 rpm) mixing the solution for 10 min, 62 μL of SDS solution was added with vigorously (240 rpm) mixing for 10 s in order to induce the complete coagulation of PAH–SDS complex. After removing the formed aggregates, a 100-μL aliquot of the solution was introduced into a Jasco 2000 Plus HPLC system with an Inertsil® ODS-3 column (length 150 mm, inner diameter 3.0 mm, particle size 5.0 μm, GL Sciences, Tokyo, Japan) for the separation and determination of estrogens or phenolic compounds. Detection wavelengths were 280 nm for estrogens or phenolic compounds and 230 nm for other pharmaceuticals. For studying the applicability to wastewater treatment, wastewater samples were prepared by adding 0.1 mg L^{-1} respective of estrogens and phenolic compounds into the secondary effluents sampled at outfalls of municipal wastewater treatment plants. The effluents were precedently passed through an Omnipore™ membrane filter (hydrophilic PTFE, pore size: 1.0 μm, Merck) to remove particulate materials.

Note that most experiments were conducted with initial concentration of 0.1 mg L^{-1}, which is higher than concentrations typically found in domestic wastewaters or secondary effluents. This concentration was selected since the primary focus of the present study was to establish clear and informative trends with eliminating analytical difficulties and minimizing experimental errors that are inevitable when working at environmentally relevant concentrations.

3. Results and discussion

3.1. Coagulation and characterization of PAH–SDS complex

Effect of the amount of SDS on the recoveries of 10, 15, or 20 mg L^{-1} of PAH was shown in Fig. 1A–C, where the dependence of charge ratio of SDS to PAH (Q_{SDS}/Q_{PAH}) was also indicated. In all cases, the recovery became the maximum when electrically equivalent amount of SDS was added. However, 10 mg L^{-1} of PAH was not completely collected because of the insufficient coagulation. The use of at least 15 mg L^{-1} of PAH was necessary for the nearly complete (>99.8%) collection. In this study, 20 mg L^{-1} of PAH and 62 mg L^{-1} of SDS were typically employed for ensuring the complete and reproducible collection. A popular anionic surfactant, sodium oleate, was also used for the comparison. PAH was nearly completely (>98%) collected by using 65 mg L^{-1} of sodium oleate. The amounts of surfactant required for the complete coagulation of different amounts of PAH are represented in Fig. 1D and these conditions are used in the following study.

Fig. 2 shows the pH dependence on the recovery of PAH–SDS and PAH–sodium oleate complexes. PAH was almost quantitatively (>99.6%) collected as a condensed aggregate in the pH range of 2–8 and the recovery was independent of the temperature (at 10 and 30 °C). The decrease in PAH recovery above pH 8.5 is ascribable to the decrease in the positive charge of PAH due to the