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Short communication

Enhanced solubilization of phenanthrene in Triton X-100 solutions by the addition of small amounts of chitosan

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ABSTRACT

The performances of aqueous mixtures of the model nonionic surfactant Triton X-100 (TX100) and chitosan (CS) for the solubilization of the hydrophobic organic compound phenanthrene (PHE) were evaluated by varying mixture compositions. The addition of minute amounts of CS into TX100 solutions above the critical micelle concentration significantly increased PHE solubility. The PHE solubility was maximized at certain optimal concentrations of CS increasing in proportion to the TX100 concentrations, which were 2, 10, and 20 mg/L CS for 5, 10, and 20 g/L TX100, respectively. At each optimal concentration of CS, PHE solubility was increased by 46%, 39%, and 43% for the 5, 10, and 20 g/L TX100 solutions, respectively. The enhanced solubilization of PHE by the addition of CS to TX100 solutions may be attributable to multiple factors, such as an increase of micellar size and hydrophobicity as well as to the formation of variously configured micelle-polymer aggregates.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread environmental pollutants, and PAHs pose severe and significant threats to human health due to their mutagenic and carcinogenic nature [1]. The major sources of PAHs in the environment are by-products of the incomplete combustion of carbonaceous materials, old gas manufacturing plants, etc. PAHs have low solubilities in water due to their hydrophobicity, and moreover, these are strongly sorbed onto soils and sediments, resulting in long-lasting environmental effects [1].

Soil washing using surfactant solutions is a potentially promising technology for the remediation of PAH-contaminated soil [2,3]. Soil washing using a surfactant mainly promotes mass transfer of PAHs from soil into aqueous solutions by the partitioning of PAHs into the hydrophobic cores of surfactant micelles [3]. In general, nonionic surfactants are used for washing PAH-contaminated soils because of their low cost, low toxicity, and low sorption onto the soil [3]. To reduce the material cost of the surfactants used soil-washing processes, various technologies such as ultrafiltration, pervaporation, precipitation, foam fractionation, solvent extraction, photochemical treatment, and selective adsorption by activated carbon have recently been investigated for recovering surfactants [2,4]. In another approach, nonionic and anionic surfactant mixtures have been used to enhance PAH solubility [5]. However, the solubility was not much enhanced in spite of the use of anionic surfactant in great amounts, and the anionic surfactant itself might be another source of contamination.

Chitosan (CS) is a natural linear biopolymer obtained by the alkaline deacetylation of chitin, which is the second most abundant biopolymer next to cellulose [6]. Numerous reports on the applications of CS in environmental field applications, such as the adsorption of dye or metals from aqueous environments [7,8], have been reported in the literature. CS is also attractive in multiple field applications due to its biocompatibility, biodegradability, and nontoxicity [6,9]. In this study, the effect of CS addition on the apparent solubility of solid phenanthrene (PHE) in Triton X-100 (TX100) solutions was investigated. The solubilization experiments were performed with various combinations of TX100 and CS concentrations. The interaction of CS and TX100 in the aqueous mixture was studied by spectroscopic and size-distribution techniques.

2. Materials and methods

2.1. Materials

CS (>85% deacetylation), PHE (purity >98%), and TX100 were purchased from Sigma Chemical Co., USA. CS obtained from crab shells consists of medium high molecular weight materials and molecular weight range reported for CS is 190–375 kDa [10]. PHE ($C_{14}H_{10}$) is a three-ring PAH with a molecular weight of 178 g/mol. TX100 [octylphenolpoly(ethylene glycol ether)$_{9.5}$] is a nonionic surfactant with a molecular weight of 625 g/mol. The crit-

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ical micelle concentration (CMC) of TX100 in aqueous solution is 0.11 g/L.

2.2. PHE solubility experiments

The PHE solubility experiments using aqueous mixtures of CS and TX100 (CS-TX100) were performed with various concentrations of CS (0–50 mg/L) at fixed concentrations of TX100 (0, 0.05, 5, 10, and 20 g/L) with excess PHE powder (500 or 1000 mg/L PHE). The desired concentration of CS was achieved in aqueous mixtures of CS and TX100 from the stock solution of CS (5 g/L) in 1% (v/v) acetic acid solution. CS is not soluble in water but the presence of amine groups (>85% deacetylation) is making it soluble in dilute aqueous acidic solutions because of protonation of amine groups. At a pH of 6–7, CS is polycationic and at a pH of 4–5 and below, it is completely protonated, which gives rise to higher aqueous solubility in this pH range. The solid PHE powder was added to 10 mL of aqueous CS-TX100 mixture of the desired composition in a 20 mL glass vial fitted with a Teflon-lined screw cap. After solubilization for three days at 30 °C in a thermostatic shaker at 200 rpm, the soluble PHE concentration in the CS-TX100 aqueous mixture was determined after centrifuging the solution at 10,000 rpm for 10 min.

2.3. Analyses

PHE concentration in the solution was determined using high-performance liquid chromatography (Dionex, USA) with a UV detector at 250 nm. The analytical column contained Acclaim® 120, C18 5 μm 120 Å (4.6 mm × 150 mm) and the mobile phase was 85% (v/v) acetonitrile and 15% (v/v) deionized water at a flow rate of 1.5 mL/min.

The absorbance change of a CS solution (5, 10, 20, and 50 mg/L) with stepwise addition of TX100 solution was investigated using a spectroscopic method at 540 nm (DR5000, HACH, USA). Small volumes (50 μL) of aqueous TX100 solution (10 g/L) were added stepwise to 20 mL of CS solution of the desired concentration. After each addition, the aqueous CS-TX100 mixture was held with continuous shaking (200 rpm) for 5 min to measure the absorbance change associated with subsequent TX100 additions.

The size distribution of aqueous CS-TX100 mixtures was analyzed using a Nano-ZS (Malvern, UK) over two composition ranges: various TX100 concentrations (0–5 g/L) at a fixed concentration of CS (10 mg/L) and various concentrations of CS (0–20 mg/L) at a fixed concentration of TX100 (5 g/L).

3. Results and discussion

3.1. PHE solubility in aqueous mixtures of CS and TX100

The solubilization of PHE was examined in CS-TX100 solutions with various concentrations of CS and a fixed concentration of TX100 in Fig. 1. No increase of PHE solubility (0.01–0.06 mg/L) was observed with the addition of CS (0–20 mg/L) to solutions without TX100, indicating that CS molecules themselves did not have any noticeable effects on PHE solubilization. It is worth noting that acetic acid, which is normally added to dissolve CS properly in aqueous solution, also had negligible effects on PHE solubility in separate experiments without CS (data not shown). CS addition to the solution with a TX100 concentration (0.05 g/L) below the CMC also showed very low PHE solubility (0.01–0.09 mg/L), indicating that the complex formation of CS and single molecules of TX100 had negligible effects on PHE solubility. However, in all cases with a TX100 concentration above CMC (5, 10, and 20 g/L), CS addition to the solution, even in minute amounts, significantly enhanced the solubilization of PHE. For example, with 5 g/L of TX100, PHE solubility was increased from 155 (0 mg/L CS) to 226 mg/L (at 2 mg/L CS). The maximum percentage increases were 46%, 39%, and 43% for 5, 10, and 20 g/L TX100 solutions, respectively. The PHE solubility gradually increased in proportion to the CS addition up to a certain optimal concentration of CS and thereafter slightly declined with further increases in CS concentration. This trend suggests that enhancement of PHE solubilization by CS and micelle interactions depends on the CS amount with respect to the concentration of TX100 in the solution. The optimal concentrations of CS, showing maximum PHE solubility, were 2, 10, and 20 mg/L for the 5, 10, and 20 g/L TX100, respectively. The optimal concentration of CS with respect to TX100 was therefore 0.04–0.1%, which was almost constant with the variation of TX100 concentration. The presence of such a constant optimal ratio of CS to TX100 implies that optimal structures between CS and TX100 are formed at this ratio that maximizes PHE solubilization. Thus, the higher solubility of PHE in CS-TX100 solutions than in TX100 solutions suggested that interactions of CS and micelles may have increased the hydrophobicity of micelles by interactions between hydrophilic moieties of both molecules and modified the size and shape of the aggregates.

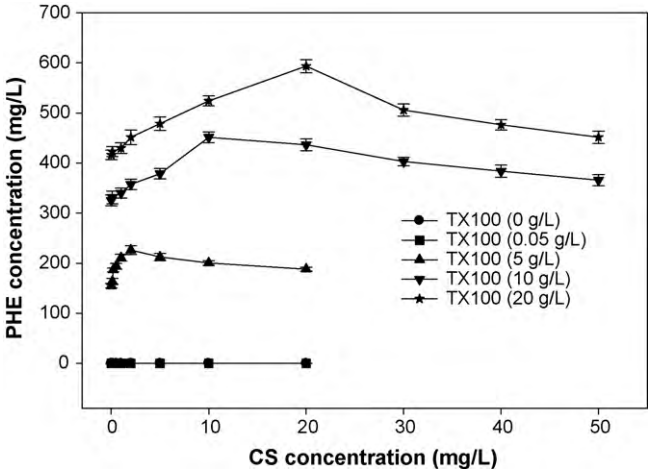

Fig. 1. CS variation in aqueous CS-TX100 mixtures for PHE solubilization.

3.2. Formation of CS-TX100 aggregates

Fig. 2 presents the absorbance changes of CS solutions (5, 10, 20, and 50 mg/L) with stepwise additions of 50 μL TX100 (10 g/L).

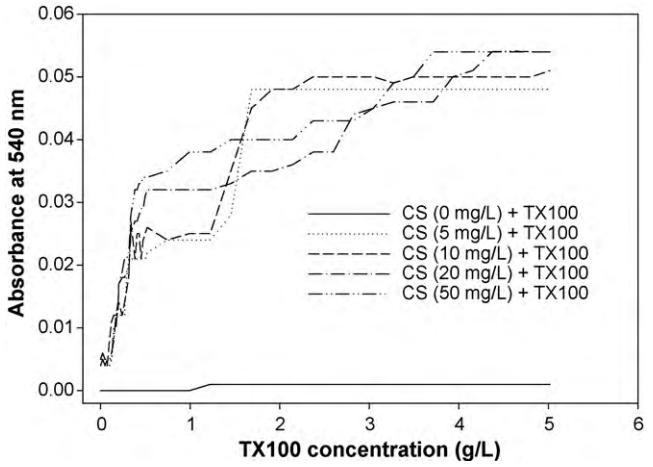

Fig. 2. Absorbance change of a CS solutions with progressive addition of TX100.

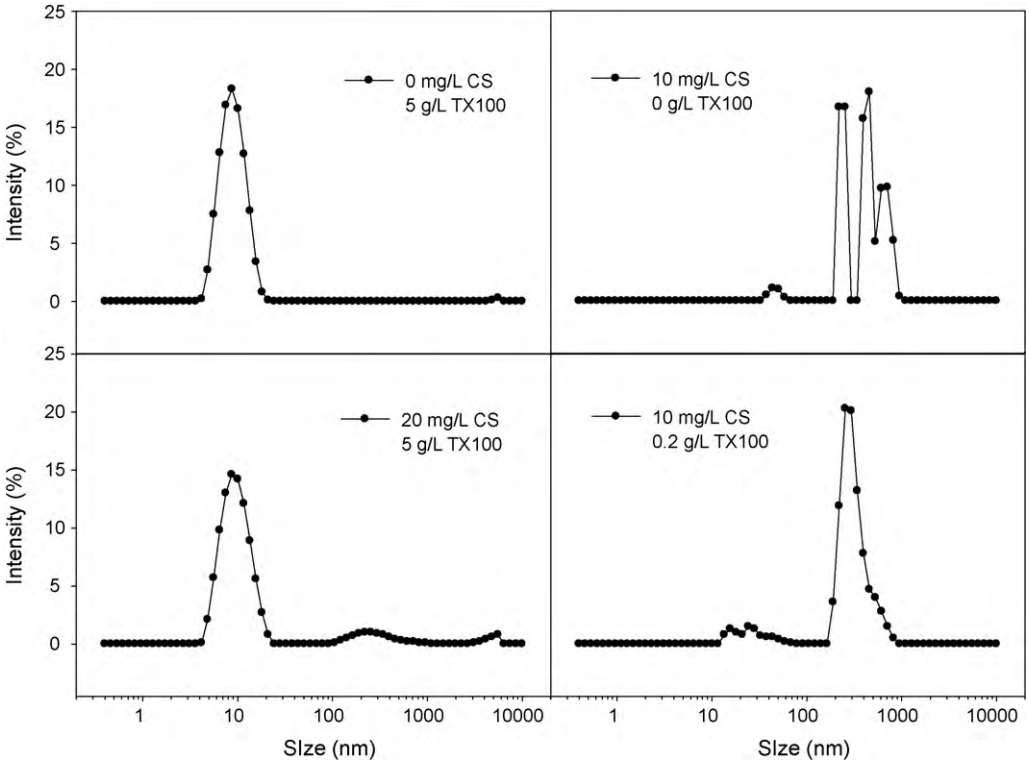

Fig. 3. Size distribution of aqueous CS-TX100 mixtures with various combinations of each concentration.

The CS solutions gave an absorbance of 0.004 at 540 nm before the addition of TX100, and a solution of TX100 alone (10 g/L) showed an absorbance of 0.001. With subsequent addition of TX100 to a 5 mg/L CS solution, absorbance increased gradually, and, moreover, a steady increase in absorbance was found only after attaining CMC (0.11 g/L) in the mixture. This indicates that the putative monomer–CS complex does not form noticeable aggregates, which coincides with the above PHE solubility data. The sharp increase of absorbance was observed over two different regimes: (1) for primary aggregate formation from 0.1–0.3 g/L TX100 and (2) for secondary aggregate formation from 1.3–1.7 g/L. The first increase might be due to the formation of a TX100 micellar complex on a linear CS polymer backbone, while the second increase might be due to the formation of large aggregates by folding of the CS backbone. The secondary aggregates might possess variously shaped micelles with different sizes present in CS fiber networks. The CS-TX100 mixtures showed absorbance maxima (0.048) at 1.7 g/L TX100 concentration in the mixture. With further increases in TX100 concentration up to 5 g/L, no change in absorbance value was found, indicating that only aqueous soluble complexes were formed by CS and TX100 interactions [9]. The stepwise addition of TX100 to 10, 20, and 50 mg/L CS solutions showed a similar trend of absorbance changes. However, in the presence of high CS concentrations (20 and 50 mg/L CS solution), the two-step increase was not observed; rather, steady increases in absorbance values were observed.

3.3. Size-distribution analysis of CS-TX100 aqueous mixtures

Fig. 3 shows the size distribution of aqueous CS-TX100 mixtures with various combinations of each concentration. The TX100 solution at a concentration of 5 g/L in the absence of CS exhibited a distinct peak, with a diameter of 9.192 nm and a width of 2.736 nm, which nearly coincides with the known size of a single TX100 micelle [11]. CS solution (10 mg/L) in the absence of TX100 exhibited three sharp peaks having diameters of 237.6, 442.9, and 673.0 nm and widths of 17.40, 44.99, and 99.80 nm, respectively. This indicates that CS molecules were present in multiple forms with various sizes.

The aqueous mixture with 10 mg/L CS and 0.2 g/L TX100 gave three peaks with diameters of 16.93, 32.20, and 326.6 nm and widths of 2.651, 10.39, and 115.4 nm, respectively. The peak with a 326.6 nm diameter was assigned to CS, and the peak intensity was much higher than the intensities of the other two peaks. The disappearance of large aggregates (673 nm) implies that TX100 separated them into smaller aggregates or that long CS fibers were folded into smaller ones. The peaks with diameters of 16.93 and 32.20 nm were assigned to the complexes of TX100 micelles with small CS molecules because a free TX100 micelle in aqueous solution is approximately 9 nm in diameter. Although TX100 was added above its CMC value (0.11 g/L), the absence of a pure micelle peak implies that TX100 molecules were bound to CS molecules. The increase in the TX100 concentration to 0.5 g/L (well above its CMC) increased the intensity of the peaks for the micellar forms of TX100 in solution (data not shown). The highest-intensity peak for micellar forms of TX100 in solution was observed in the case of the CS (20 mg/L)-TX100 (5 g/L) solution, with a 9.947 nm diameter, and the size of normal TX100 micelle was 9.192 nm as shown in size-distribution results of 5 g/L TX100 solution, indicating that larger micelles were formed by insertion of CS molecules between TX100 micelles. This increase of micelle size might be one possible reason for the increase in PHE solubility. The faint and broad peak with a diameter of 302.3 nm and a width of 171.5 nm indicated the formation of variously shaped complexes of CS and micelles in the mixture. While there were fewer of these large aggregates, their effect on PHE solubilization must be great.

To understand the geometric relationship between CS and TX100 micelles, some simple calculations were performed. The CS molecules are known to be in the form of relaxed two-fold helical fibers, of which one glucosamine unit is 0.51 nm in length and has a mass of 161 g/mol [12]. CS used in this study is a commercial product from crab shells and it consists of medium and high

molecular weight materials. The molecular weight of a CS fiber is considered 300 kDa here because the molecular weight of this CS product are reported in the range of 190–375 kDa [10], and the length and diameter of a CS fiber were calculated as approximately 950 and 1.0 nm, respectively. In contrast, a TX100 micelle is in the form of an oblate spheroid, which has an aggregation number of approximately 140 and a molecular weight of 90,000 [11]. Because the size of a micelle (9.2 nm) is larger than the diameter of a CS fiber (1.0 nm), one to four micelles might surround the CS fiber in a cross-sectional view. Assuming that a single CS fiber is in an elongated form and 950 nm in length, it could make aggregates with a maximum of 400 TX100 micelles. It is noteworthy that the acetylated portion of CS molecules has been reported to have hydrophobic interactions and to be able to self-aggregate, and these points would likely readily interact with TX100 micelles [13]. Single CS fibers may have been present in multiple folded (2–4 times) form considering the measured size peaks (237.6, 442.9 and 673.0 nm). It is also possible that several CS fibers aggregated without a large change in apparent size. In the case that CS fibers were present as a bundle of several fibers (e.g., five) [12], the actual length of a CS fiber should be smaller and large aggregates consisting of many CS fibers should be formed matching the measured size. In these various possible aggregates, the CS fibers may provide ample space for insertion of the micelles into the three-dimensional fiber networks. The aggregates of CS fibers and TX100 micelles may distort the shapes of TX100 micelles and produce various types of micelles. Among these, micelle–micelle agglomerations and enlarged interior spaces, loose micelles with low aggregation numbers, or hemimicelles bound to CS may have contributed to the increase in PHE solubilization [14]. The structures of CS-TX100 aggregates may be diverse and should be studied in more detail.

PHE solubility increases were clearly observed on the addition of very small amounts of CS into the TX100 solutions in the solubilization experiments. The absorbance experiments demonstrated that some aggregates between CS and TX100 were probably formed and had different shapes depending on the concentrations of each component. The size-distribution experiments demonstrated the change of micelle size and the possible formation of various types of aggregates. However, it is not yet clear what shapes these aggregates form and how they contribute to increasing the solubilization of hydrophobic organic compounds. From a practical viewpoint, the addition of such tiny amounts of CS into a surfactant solution (approximately only 0.1% of the surfactant) would be easy to apply in a real-world system, providing a cost-effective reduction of surfactant usage and an ecologically friendly process in using biodegradable compounds, so that this could be readily applied to various processes such as soil washing, enhanced oil recovery, and organic extractions.

4. Conclusions

The effect of CS addition on the apparent solubility of PHE in TX100 solutions was investigated with various combinations of TX100 and CS concentrations. The addition of a tiny amount of CS (approximately 0.1% of the TX100) into TX100 solutions above its CMC significantly increased PHE solubility. On the addition of the optimal CS concentration, PHE solubility in TX100 solutions was increased up to 46%. Thus, the addition of CS into a nonionic surfactant solution may by a simple and effective alternative for the preparation of a washing solution to remove organic compounds from solid waste.

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