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Effect of chitosan addition on phenanthrene solubilization in anionic or cationic surfactant solutions

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ABSTRACT

The solubility of solid phenanthrene (PHE) powder in aqueous solutions of surfactant and chitosan (CS) was evaluated by varying the composition of aqueous mixtures. Cetyltrimethyl ammoniumbromide (CTAB) and sodium dodecyl sulfate (SDS) were used as model cationic and anionic surfactants, respectively. CS at a particular concentration in the mixture especially above the CMC value of the anionic surfactant exhibited somewhat higher PHE solubility values than surfactant itself. CS (20 mg/l)-SDS (20 g/l) solution showed higher PHE solubility (422.05 mg/l) than that of 20 g/l SDS (377.92 mg/g). However, CS-CTAB did not show any additional enhancing effect on PHE solubilization, and CS (5 mg/l)-CTAB (10 g/l) solution showed almost similar PHE solubility (867.23 mg/l) of 10 g/l CTAB (865.25 mg/g). The maximum increase in absorbance value of a 20 ml CS solution (5, 20 and 100 mg/l) at 540 nm with stepwise addition of SDS (10 g/l) was found at a SDS concentration much less than its CMC value (2.33 g/l) in the mixture, indicating strong complex formation between CS and SDS because of oppositely charged molecules in the experimental conditions.

Keywords: Phenanthrene; Surfactant; Chitosan; Critical micelle concentration; Soil washing; Solubilization

1. Introduction

One of the most common types of soil, atmosphere and groundwater contamination arises from polycyclic aromatic hydrocarbons (PAHs) [1]. PAHs are released into the environment as a result of incomplete combustion of fossil fuels, old gas manufacturing plants or from spills of hydrocarbon fuels [2,3]. PAHs, which consist of two or more fused benzene rings, often have allergenic, mutagenic and carcinogenic effects [4]. PAHs contaminated sites pose remediation difficulties because of its hydrophobic nature and moreover, PAHs act as long-term contaminant sources by continuously dissolving into the ground water at low concentrations or strongly sorbing to soil and sediments [5]. Enhancement of aqueous solubility of PAHs is the most important step of remediation for PAHs contaminated sites.

Various remediation processes such as soil washing or soil flushing are often performed using surfactants [6,7]. Surfactants are amphiphilic molecules that contain a hydrophilic head and a hydrophobic tail. Surfactants are classified as ionic (cationic or anionic) and non-ionic with varying chemical structures according to their hydrophilic head group [6]. Surfactants increase the aqueous solubility of PAHs by partitioning the compounds into the hydrophobic cores of surfactant micelles and soil washing process involving surfactants is one of the most important methods for the treatment of PAHs contaminated sites [8,9]. Normally, non-ionic surfactants are used for remediation of PAHs

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contaminated soil because of their low cost, low toxicity, and low sorption onto the soil [10].

Chitosan (CS) is a biopolymer of glucosamine and it is obtained by the alkaline deacetylation of chitin, which is the second most abundant biopolymer next to cellulose [11,12]. CS molecules are widely used for food, pharmaceutical and biomedical, environmental applications like adsorption of organic contaminants, metal ions, coagulation of soil and bentonite particles [13–17]. CS becomes extremely attractive for various applications because of its environmental friendliness, biodegradability and nontoxicity [18]. It was reported in the earlier publication that PHE solubility in aqueous solution containing nonionic surfactants was enhanced by addition of small amount of CS [19]. In this study, the effect of small amount of CS on the apparent solubility of solid PHE in surfactant solutions was investigated using cationic surfactant, cetyltrimethyl ammoniumbromide (CTAB), and anionic surfactant, sodium dodecyl sulfate (SDS).

2. Materials and methods

2.1. Materials

CS (>85% deacetylation), PHE (purity >98%) and two different types of surfactants, including CTAB (cationic surfactant) and SDS (anionic surfactant), were purchased from Sigma Chemical Co., USA. All other analytical grade chemicals were purchased from Sigma Chemical Co., USA. PHE ($C_{14}H_{10}$) is a three-ring PAH with a molecular weight of 178 g/mol. The chemical properties of the surfactants used in this study are listed in Table 1.

2.2. PHE solubilization experiments

The PHE solubility experiments in aqueous mixtures of CS and CTAB were performed using various concentrations of CTAB (0–10 g/l) at a fixed concentration of CS (0, 5 and 20 mg/l), and various concentrations of CS (0–20 mg/l) at a fixed concentration of CTAB (0, 0.2, 2 and 5 g/l) adding solid PHE at a initial concentration of 1000 mg/l. The PHE solubility in aqueous solution of CS and SDS solutions was tested using various SDS concentrations (0–20 g/l) at a fixed concentration of CS (0, 5 and 20 mg/l) and various CS concentrations (0–50 mg/l) in the mixture with a fixed concentration of SDS (0, 0.5, 5, 10 and 20 g/l). The solid PHE powder was added to 10 ml CS-surfactant aqueous mixture of desired composition in a 20 ml glass vial fitted with a Teflon-lined screw cap. The solubilization experiments were carried out for 3 d at 30°C in a thermostated shaker at 200 rpm, and after solubilization, the soluble PHE concentration in the aqueous mixture was determined using high-performance liquid chromatography (HPLC, Dionex, USA) with a UV detector at 250 nm after centrifuging the solution at 10000 rpm. The analytical column contained Acclaim® 120, C18 5 µm 120 Å (4.6 × 150 mm) and the mobile phase was 85% (v/v) acetonitrile and 15% (v/v) deionized water with a flow rate of 1.5 ml/min.

2.3. Absorbance change measurements

Absorbance change of CS solutions (5, 20 and 100 mg/l) with stepwise addition of CTAB solution (20 g/l) was investigated by spectroscopic method at 540 nm (DR5000, HACH, USA). Absorbance change of 20 ml CS solutions (5, 20 and 100 mg/l) was also measured with stepwise addition of SDS from a 10 g/l SDS solution. After each addition, the aqueous mixture was kept under shaking condition (200 rpm) for 5 min in order to measure the absorbance change associated with subsequent CTAB or SDS additions. Thus, absorbance change of CS-CTAB and CS-SDS aqueous mixture was measured with respect to subsequent change in CTAB and SDS concentration of solution, respectively.

3. Results and discussion

3.1. PHE solubility in aqueous mixtures of CS and CTAB

Fig. 1 shows PHE solubilization from solid PHE powder (1000 mg/l) in 10 ml CS-CTAB aqueous solutions as a function of CTAB concentration (0–10 g/l) at a fixed concentration of CS. The solubility of PHE was found to be increased linearly with increase in CTAB concentration in CS-CTAB mixture above its critical micelle concentration (CMC, 0.34 g/l). The results of the linear increment of solubility of PHE with CTAB concentration are consistent with solubilization data provided by other researchers [6,20]. The range of PHE

Table 1
Chemical properties of different surfactants

Surfactant	Type	Chemical formula	Molecular weight (g/mol)	Critical micelle concentration (g/l)
CTAB	Cationic	$C_{19}H_{42}BrN$	365	0.336
SDS	Anionic	$NaC_{12}H_{25}SO_4$	288	2.33

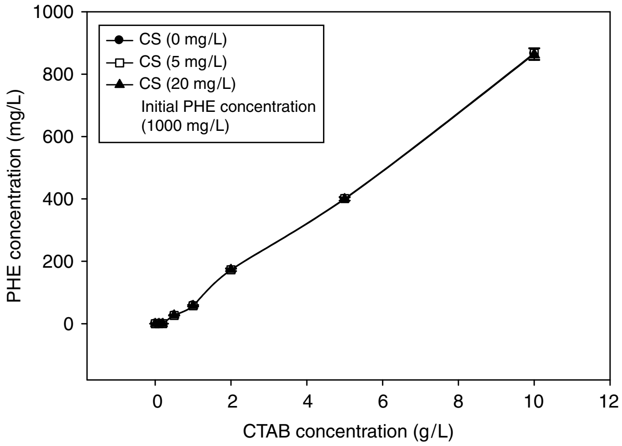

Fig. 1. CTAB variation in CS-CTAB aqueous mixtures for PHE solubilization.

solubility data obtained by CTAB (0–10 g/l) was 0.013 to 865 mg/l. In presence of 5 and 20 mg/l CS in 10 ml CTAB solution of desired concentration range, the range of solubility data was 0.034–867 mg/l and 0.037–864 mg/l, respectively, indicating that increase in CS amount in CS-CTAB aqueous mixtures did not enhance the solubilization of PHE by CTAB.

As shown in Fig. 2, the solubilization of PHE by CS-CTAB solutions did not vary significantly with CS concentration at a fixed concentration of CTAB. The solubility of PHE in CS-CTAB (5 g/l CTAB) from 1000 mg/l solid PHE changed from 397–402 mg/l with CS concentration (0–20 mg/l) variation in the mixture. The CS concentration variation (0–20 mg/l) in the solution without CTAB or with CTAB concentration (0.2 g/l) below CMC showed very low solubility (from 1000 mg/l solid PHE) in the range of 0.01–0.04 mg/l and 0.23–0.25 mg/l, respectively. The CS concentration variation in CS-CTAB (2 g/l CTAB) did not increase solubility significantly (171–175 mg/l). This trend suggests that solubilization of PHE solely depends on micellar concentration of CTAB and there are no possible positive interactions between CS and CTAB micelles.

3.2. PHE solubility in aqueous mixtures of CS and SDS

As shown in Fig. 3, PHE solubilization in 10 ml CS-SDS aqueous solutions from PHE powder (1000 mg/l) increased with increase in SDS concentration from 0 to 20 g/l at a fixed concentration of CS (5 and 20 mg/l) as well as without CS (0 mg/l). The solubility of PHE was higher above critical micelle concentration of SDS (CMC, 2.33 g/l). The range of PHE solubility data obtained by only SDS solution (0–20 g/l) was 0.01 to 378 mg/l. With addition of 5 and 20 mg/l CS in 10 ml SDS solution of same concentration range, the solubility was found to be increased from 0.034 to 396 mg/l and 0.035–422 mg/l, respectively, indicating that the solubilization of PHE by SDS was found to be enhanced at higher CS amount in CS-SDS solutions especially above CMC. The enhancement of PHE solubility by CS-SDS solutions could be possibly due to the interactions of CS and micelles. The electrostatic interaction between cationic CS and anionic SDS played a vital role for the binding of SDS molecules by CS, and this could play an important role in the PHE solubilization process by CS-SDS solutions [21]. The hydrophobic interactions between the alkyl chain of SDS molecule and the possible hydrophobic portion of CS in the solutions could also play another vital role in PHE solubilization by CS-SDS solutions [22]. SDS molecules start to bind cooperatively at critical aggregation concentration (CAC) with coiled structure of CS at

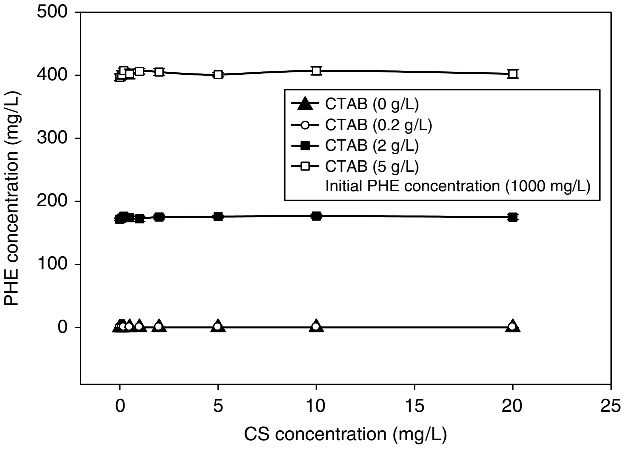

Fig. 2. CS variation in CS-CTAB aqueous mixtures for PHE solubilization.

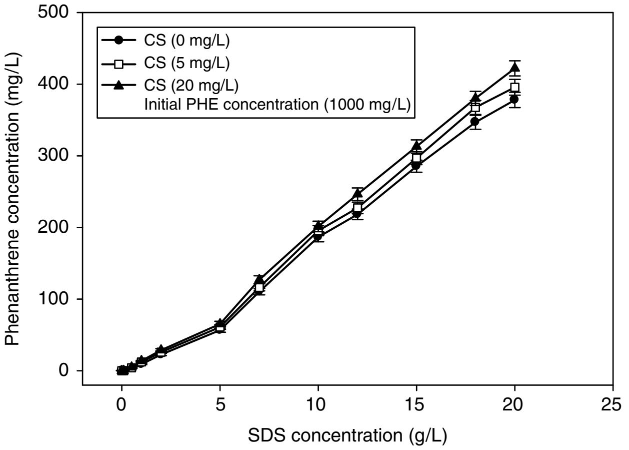

Fig. 3. SDS variation in CS-SDS aqueous mixtures for PHE solubilization.

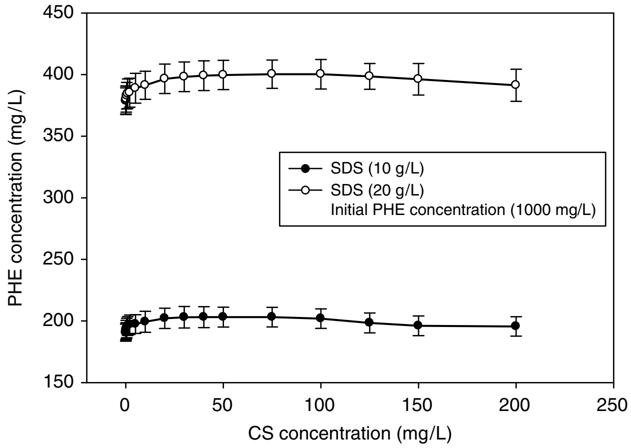

Fig. 4. CS variation in CS-SDS aqueous mixtures for PHE solubilization.

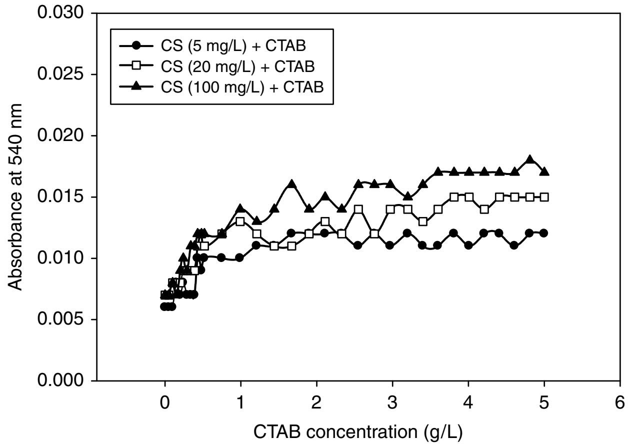

Fig. 5. Absorbance change of CS solution while progressive addition of CTAB.

different positive sites of the polymer. With increase in SDS concentration in the CS solution, the number of SDS molecules bound to CS coil increases and that leads to the shrinking of CS coil [23].

Fig. 4 shows that the variation of solubilization of PHE by CS-SDS solutions with CS concentration variation at a fixed concentration of SDS indicated that CS showed positive effect on solubilization at high concentration of SDS. The solubility of PHE in CS-SDS (20 g/l SDS) using PHE powder (1000 mg/l) increased from 379 to 397 mg/l with increase in CS concentration from 0–20 mg/l. The CS concentration variation (0–20 mg/l) in the solution without SDS (0 g/l) or with SDS concentration (0.5 g/l) below CMC exhibited no positive effect on solubilization. It started to increase solubilization when SDS concentration was increased above its CMC level. The increase in CS concentration from 20 mg/l to 50 mg/l in CS-SDS solution with fixed concentration of SDS (10, 20 g/l SDS) could not significantly enhance solubility of PHE. This result clearly indicated the positive effect of CS on solubilization by CS-SDS solution depends on the CS dosage and it achieves its maximum effect at an optimum dosage of CS.

3.3. Absorbance change of a CS solution while progressive addition of CTAB

Fig. 5 represents the absorbance change of 20 ml CS solutions (5, 20 and 100 mg/l) with stepwise addition of CTAB from a stock solution (20 g/l). CS solution before addition of CTAB gave an absorbance of 0.004 at 540 nm and 20 g/l CTAB solution showed an absorbance of 0.002. The absorbance change at 540 nm by the stepwise addition of CTAB solution (20 g/l) in 5 mg/l CS solution indicated that absorbance was found to be increased only after attaining CMC (0.336 g/l) in the mixture. The increase in absorbance value after attaining CMC could be due to some soluble complexes formed by interaction of CS and micelles in the mixture. The soluble complexes between CTAB and CS molecules above CMC in the aqueous solution could be probably formed by H-bonding interactions between hydrophilic head portion of CTAB molecules in the micelles with amine (-NH_2) and hydroxyl (-OH) groups of CS molecules in solution [24]. The stepwise addition of CTAB in 20 and 100 mg/l CS solution showed similar trend of absorbance change at 540 nm. However, in presence of high CS concentration, the absorbance maxima was higher than that of in lower concentration, indicating that more soluble complex between CTAB and CS are formed at high CS concentration.

3.4. Absorbance change of a CS solution while progressive addition of SDS

Fig. 6a represents the absorbance change of CS solutions (5, 20 and 100 mg/l) with stepwise addition of SDS from a stock solution of SDS (10 g/l). In the experimental pH conditions (pH 6), CS and SDS molecules are oppositely charged. The measurement of absorbance at 540 nm of 10 g/l SDS solution showed an absorbance of 0.002. The measurement of absorbance change of 20 ml CS solution (5 mg/l) with subsequent SDS addition indicated that absorbance reached maxima (0.031) at SDS concentration of 0.27 g/l and moreover, the maximum increase in absorbance was found at a SDS concentration much lower than its CMC (2.33 g/l) in the aqueous solution [25]. The measurement of absorbance change of 20 ml CS solution of CS concentration of 20 and 100 mg/l with subsequent SDS addition exhibited

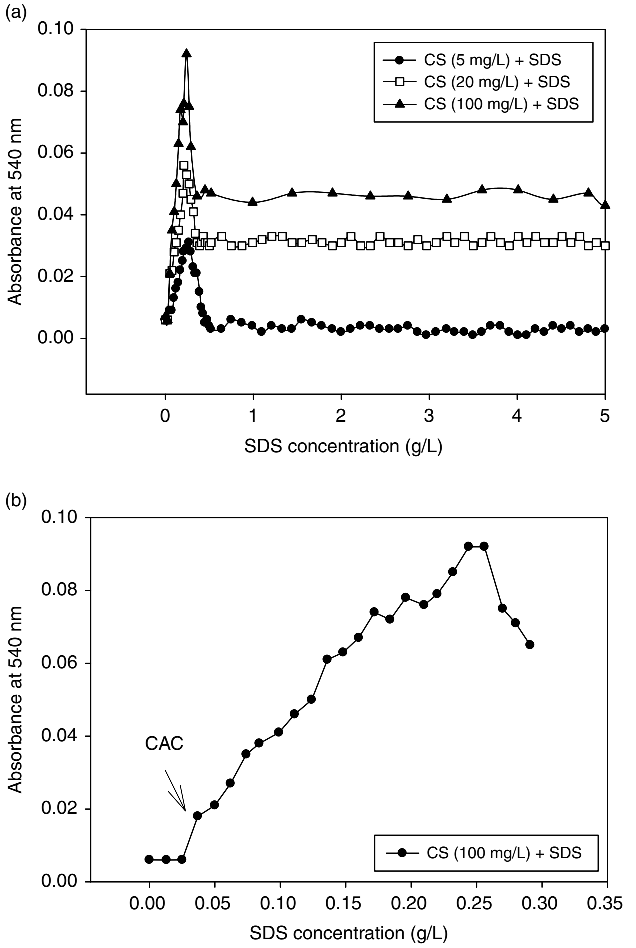

Fig. 6. Absorbance change of CS solution while progressive addition of SDS.

absorbance maxima of 0.056 and 0.092 at SDS concentration of 0.21 and 0.24 g/l, respectively. In fact, complexation between SDS and CS molecules in the solutions gave rise to increased absorbance value and this phenomenon suggested that the soluble complexes were formed in the reaction mixture [25]. Further increase in SDS concentration after 0.27, 0.21 and 0.24 g/l in CS-SDS solutions with 5, 20 and 100 mg/l CS concentrations, respectively, gave rise to sudden drop in absorbance value. It was found that increase in SDS concentration in 5 mg/l CS solution from 0.27 to 0.45 g/l changed the absorbance value from 0.031 to 0.005 and this was close to absorbance value of the CS solution without SDS addition at beginning (0.006). The similar trend in absorbance value was found with other two CS concentrations (20 and 100 mg/l). This phenomenon suggested that increase in SDS concentration beyond a certain level in CS solution caused a transition from water soluble complexes of CS and SDS to water insoluble complexes and certain drop of absorbance value was due to insoluble complex formation.

The association between SDS and CS molecules in aqueous solutions is highly co-operative and starts at a defined concentration known as the critical aggregation concentration (CAC). It was already reported that CAC of CS and SDS in aqueous solution is well below the CMC concentration (2.33 g/l). As shown in Fig. 6b, the increase in absorbance of 20 ml of 100 mg/l CS solution with successive SDS solution addition was first observed at SDS concentration of 0.037 g/l in the mixture. This concentration of SDS indicated the CAC for this particular solution of CS and SDS. After attaining CAC, the absorbance was found to be changed almost linearly with SDS addition up to 0.24 g/l (0.092) and this phenomenon indicated soluble complex formation between CS and SDS molecules. Further increase in SDS concentration beyond 0.24 g/l in SDS solution caused drop in absorbance value and this indicated the transition of soluble complex to insoluble complexes of SDS and CS in the solutions.

4. Conclusions

The solubility of PHE in aqueous mixtures of CS and surfactants was studied using cationic (CTAB) and anionic (SDS) surfactants. The results indicated that apparent solubility of solid PHE powder in aqueous solutions of CS and surfactant was not lower than only surfactant solutions, and the solubility of PHE in CS-surfactant was varied with type of surfactant. CS-SDS solutions exhibited higher PHE solubilization than SDS at the same concentration of surfactant itself, especially above CMC, whereas, CS-CTAB did not produce any significant increase over CTAB solution. The absorbance value reached maximum in CS solution with progressive addition of SDS (10 g/l) much below its CMC value indicating strong complex formation between CS and SDS.

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