

# Adsorptive Partitioning of an Organic Compound onto Polyelectrolyte-Immobilized Micelles on Porous Glass and Sand

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Halting the spread of organic contaminants in subsurface aquifers is a critical environmental problem. We describe a novel “permeable reactive barrier” that results when organophile-solubilizing properties are conferred on siliceous materials by treating them with a cationic polymer and oppositely charged mixed surfactant micelles. Controlled pore glass, quartz sand, and sea sand were treated with poly-(diallyldimethylammonium chloride) and with mixed micelles of Triton X-100 and sodium dodecyl sulfate, either sequentially or simultaneously, following different treatment procedures. A model organophilic compound, Orange OT, was adsorbed and retained under aqueous agitation on the siliceous treated surfaces but not on untreated surfaces or those treated with micelle only. The aspect of the treatment procedure producing the most significant effect on Orange OT solubilization was the ionic strength. The retention of Orange OT in a layer of polyelectrolyte–micelle-treated sand under flow, within a column of untreated sand, demonstrates the possibility of using similar processes as a permeable reactive barrier to trap organic pollutants.

## Introduction

Contamination of the environment by organic compounds is a ubiquitous and costly environmental concern requiring nearly \$10<sup>9</sup>/yr in the United States alone. This pollution typically arises from on-site loss of organic solvents during manufacturing or by leakage from underground storage tanks. Release in the subsurface can result in a “plume” of dissolved and pure phase organic compounds that travels with groundwater flow within an aquifer (1). This contaminated subsurface water can travel hundreds of meters in a year, can be accidentally extracted in well water, and can eventually surface in rivers. Thus, this “invisible” contamination has significant environmental ramifications.

The approaches developed to address this problem are generally poorly effective, are costly, and require decades of active remediation (1). For example, pump-and-treat methods entail pumping out pollutant-containing water from the

earth’s subsurface, removing the contaminants, and then returning the water to its original subsurface location. However, because it is very difficult to track the location of pollutants, this method may require continual monitoring and pumping over a very long period of time (e.g., 20 or more yr) and is therefore excessively cumbersome and expensive. Other strategies, such as soil removal and bioremediation, also are generally poorly effective, are expensive, and require decades of active remediation.

Accordingly, it is desirable to develop a technique that would trap organic compounds, retain them for long periods, and have the reversibility required to allow extraction of the trapped organics at a later date. Recently, technologies for in situ treatment of groundwater contaminants called “permeable reactive barriers” (PRB) are becoming increasingly popular (2–7). A permeable reactive barrier is a passive in situ treatment zone of reactive material that degrades or immobilizes contaminants as groundwater flows through it and may be installed as permanent, semi-permanent, or replaceable units across the flow path of a contaminant plume (8).

Our previous studies on polyelectrolyte–micelle complexes indicated that polyelectrolyte–micelle complexes may be applied as permeable reactive barriers in order to trap organic pollutants. Sudbeck et al. (9) showed that polyelectrolyte–micelle complexes and polyelectrolyte–micelle coacervates have almost the same solubilization efficiency for an apolar organic dye as do free micelles. Consistent with this, Cryo-TEM results on polyelectrolyte–micelle complexes (10) indicated that micelles seem to be intact in complexes and coacervate. Wang et al. (11) showed that complexes and coacervates between negatively charged colloids and positively charged polymers can form with either negative or positive net charge and that complexation can be reversed by ionic strength; in view of the latter, it is not surprising that Wang and Dubin (12) found that adsorbed polycations may be used to immobilize proteins of net negative charge on a negative substrate such as glass. Similar effects may underlie observations of sorption/desorption of organic pollutants on soil or alumina surfaces in the presence of cationic polyelectrolytes and anionic surfactants (13–15).

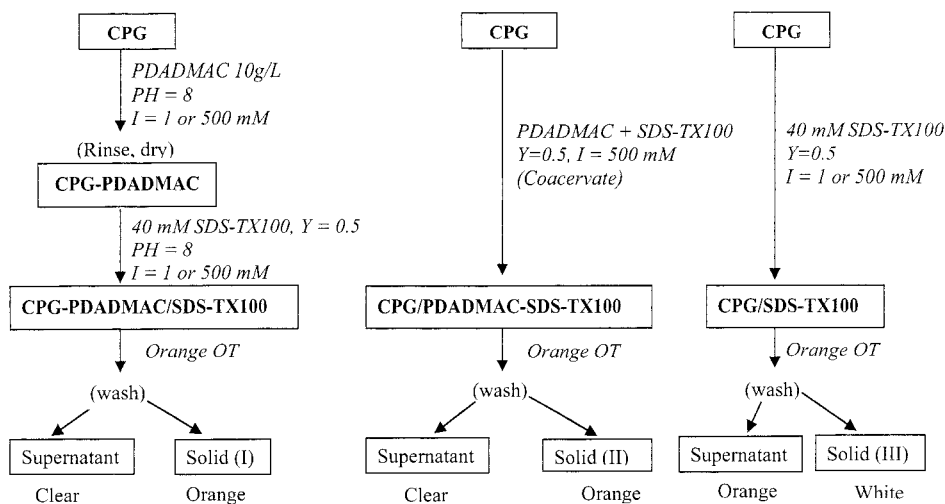
The implication of the reports described above is that complex formation with polycations could more than compensate the negative charge of anionic micelles and that the resultant net-positive complex could adsorb on negative surfaces. However, when polycations are combined with anionic micelles, the result is usually irreversible formation of an intractable precipitate. On the other hand, the use of mixed nonionic–anionic micelles makes it possible to adjust both the charge and the solubility properties of these complexes (11), i.e., to ensure their net positive charge and ability to adsorb to negative substrates. Consequently, polycations could anchor anionic micelles to siliceous surfaces and—based on the preceding observations—might do so without impairing solubilization. Thus, adsorbed polyelectrolyte–micelle complexes could be used to trap organic pollutants. Since complexes readily disperse at high ionic strength, adjustment of salinity might in principle be used to release the apolar solubilizates. The purpose of the present work is a preliminary exploration of this technology (16) with a model system in which silica sand treated with a polyelectrolyte–micelle complex serves as an example of a permeable reactive barrier, and the hydrophobic dye Orange OT is employed as a convenient marker that mimics the behavior of an organic pollutant (17).

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SCHEME 1. Preparation and Evaluation of Polycation-Micelle-Treated CPG



Experimental Section

Polydiallyldimethylammonium chloride (PDADMAC) was a commercial sample (Merquat 100) from Calgon (Pittsburgh, PA). Triton X-100 (TX100) was purchased from Aldrich, sodium dodecyl sulfate (SDS, purity > 99%) was from Fluka, and NaCl was from Fisher. Orange OT [1-(*o*-tolylazo)-2-naphthol; C.I. 12100] was from Aldrich. All were used without further purification. Controlled pore glass (CPG, from Schott Gerate, Batch 91193/00) of 30–60- $\mu$ m grain size with pores of 48.4 nm diameter was washed at room temperature for 1–2 h in a 1% SDS, pH 9, NaOH solution as advised by the manufacturer. CPG was then rinsed with DI water until no foaming was observed and dried in an oven at 50 °C overnight. Quartz sand (99% quartz, 1% dark minerals) and washed sea sand (Fisher) were used without further treatment.

Results and Discussion

CPG was treated with polycation PDADMAC and negatively charged TX100–SDS mixed micelles according to the procedures summarized in Scheme 1. For procedure I, samples of 0.3 g of CPG were first gently agitated with 2 mL of 10 g/L PDADMAC at pH 8 and ionic strengths (*I*) of 500 or 1 mM for about 24 h. The samples were then centrifuged, rinsed with DI water, and oven-dried at 50 °C overnight. The CPG–PDADMAC samples were then agitated with 4 mL of 40 mM TX100–SDS mixed micelles at SDS mole fraction = 0.5 and *I* = 500 or 1 mM for 30 min at the same pH. (The SDS mole fraction is defined as  $Y = \frac{[SDS]}{[SDS] + [TX100]}$ , which is proportional to the average mixed-micelle surface charge density.) For procedure II, CPG was treated with PDADMAC (2 mL of 10 g/L) together with TX100–SDS (4 mL of 40 mM, *Y* = 0.5) at *I* = 500 mM for 24 h. In this case, the macromolecular aqueous solution exhibits coacervation (*11*), which is a liquid–liquid phase separation: the more dense phase (coacervate), dispersed in the continuous phase as microscopic droplets, is relatively concentrated in macromolecules and is in equilibrium with the dilute macromolecular liquid phase (*18*). In procedure III, CPG samples were treated with 4 mL of 40 mM TX100–SDS at *I* = 500 or 1 mM for 24 h without any PDADMAC. The treated CPG from procedures I–III are named CPG–PDADMAC/SDS–TX100, CPG/PDADMAC–SDS–TX100, and CPG/SDS–TX100, respectively. These treated CPGs were agitated with 3 mL of Orange OT solution in ethanol (about 0.2 g/L) for 30 min and equilibrated for 2 days. The samples were then washed with DI water for 30 min.

The solids resulting from these various treatments displayed different colors, corresponding to differences in uptake

TABLE 1. Preparation and Evaluation of Polycation-Micelle-Treated Sand

procedure	I	II	III	IV	V
ionic strength (mM) of PDADMAC treatment <sup>a</sup>	500	1			500 <sup>c</sup>
ionic strength (mM) of TX100–SDS treatment <sup>b</sup>	500	1	500	1	
dye uptake, ranking <sup>d</sup>	B	A <sup>e</sup>	C <sup>f</sup>	C <sup>f</sup>	B

<sup>a</sup> 3 g quartz or sea sand was agitated with 3.5 mL of 10 g/L PDADMAC for 24 h at ionic strength shown. <sup>b</sup> After being rinsed with DI water and dried overnight at 50 °C, sand was agitated with 4 mL of 40 mM TX100–SDS (*Y* = 0.5) for 1 h at ionic strength shown. <sup>c</sup> For procedure V, sand was treated with 10 g/L PDADMAC and 40 mM TX100–SDS at *I* = 500 mM and *Y* = 0.5 in one step. <sup>d</sup> Treated sand was agitated with 3 mL of concentrated Orange OT in ethanol for 30 min and equilibrated for 12 h. Samples were washed with 10 mL of DI water for 30 min and centrifuged prior to comparison of colors. <sup>e</sup> Comparison of this value with those for procedures I and V are constrained by limitations of visual observations on sand that possesses a (pale) tan color prior to dye absorption. <sup>f</sup> For III and IV, no changes in sand color were observed.

of the oil-soluble dye. Procedure I using CPG–PDADMAC/SDS–TX100 (I) at high ionic strength (500 mM) yielded the most dye retention, somewhat higher than at low ionic strength (1 mM). Procedure II with CPG/PDADMAC–SDS–TX100 (II) produced a little less dye retention than procedure I (500 mM), while procedure III with CPG/SDS–TX100 (III) gave no dye retention regardless of ionic strength. The results indicated the similarity of PDADMAC and TX100–SDS two-step treatment with a single-step treatment and also showed that the polycation is necessary to anchor micelles to CPG.

On the basis of the above studies, polycation–micelle-treated quartz and sea sands were prepared and evaluated using the same conditions as for CPG, as indicated in Table 1. Visual observations of treated sands allowed for qualitative assessment of dye absorption on polycation–micelle-treated sands. As seen from Table 1, sand treated with surfactant only, like untreated sand, absorbs no dye (appearance unchanged after addition of Orange OT). Dye is absorbed from sand treated with both polycation and surfactant; when those two components were dissolved in 0.5 M NaCl, the amount of dye absorbed was almost the same regardless of whether polymer and surfactant are added sequentially or simultaneously. There appeared to be some increase in dye uptake when polymer and surfactants were applied from lower ionic strength solutions, but that comparison (procedure II vs procedure I) is a subjective one based on color changes on sand (which itself is not colorless before treatment).

**TABLE 2. Effects of Ionic Strength in PDADMAC and Micelle Adsorption Steps on Uptake of Organic Dye onto Treated CPG**

procedure	I	II <sup>a</sup>	III	IV <sup>b</sup>	V <sup>b</sup>
step 1 (PDADMAC adsorption)	500	500	1	—	—
ionic strength (mM) <sup>c</sup>					
step 2 (TX100–SDS adsorption)	500	500	1	500	1
ionic strength (mM) <sup>d</sup>					
dye uptake (mg × 10 <sup>2</sup> ) <sup>e</sup>	2.37	2.35	1.76	0.00	0.00

<sup>a</sup> Identical to I, except steps 1 and 2 are replaced with a single-step application. <sup>b</sup> No PDADMAC applied. <sup>c</sup> 0.3 g of CPG was agitated with 5 mL of 10 g/L PDADMAC for 24 h at ionic strength shown. <sup>d</sup> CPG/PDADMAC from step 1 was rinsed and dried overnight at 50 °C and then agitated with 4 mL of 40 mM 1:1 TX100–SDS. <sup>e</sup> CPG/PDADMAC–SDS–TX100 from step 2 was treated with 0.6 mL of 0.048 g/L ethanolic Orange OT; depletion of dye was determined by UV (488.5 nm).

To make evaluations of the effect of ionic strength less subjective and more quantitative, we repeated these measurements with colorless CPG porous glass and determined dye uptake by UV spectrophotometry. The results are summarized in Table 2. Although sand is more relevant to environmental substrates than glass, the absence of color on CPG makes it a more convenient substrate to study the dependence of ultimate solubilizing power on the ionic strength during the PDADMAC- and micelle-adsorption steps. CPG treated with mixed micelles only at both high and low ionic strength (procedures IV and V) cannot absorb Orange OT. The adsorption amount of Orange OT for two-step treatment is only a little higher than one-step treatment. For two-step treatment, the adsorption amount of Orange OT appeared to depend on ionic strength: larger for high ionic strength (500 mM) than for low ionic strength (1 mM). Multiple effects may contribute to this observation. While the strength of complex formation between polyelectrolyte and micelles increases with a decrease in ionic strength (11), the adsorbed amount of highly charged polyelectrolytes such as PDADMAC normally increases with an increase in ionic strength (19). Furthermore, the configuration of polymers adsorbed at high ionic strength is less “flat” and therefore more conducive to micelle binding. It appears likely that the latter two effects are dominant, so that micelle adsorption is enhanced when the ionic strength in the two adsorption steps is larger, and this leads to better solubilization of Orange OT for CPG treated at higher salt concentration.

To demonstrate the practical consequences of these findings, 12 g of medium-sized quartz sand treated with PDADMAC (15 mL of 10 g/L) and TX100–SDS (15 mL of 40 mM,  $Y = 0.5$ ) by procedure II, as shown in Table 1, was sandwiched between two layers of untreated sand in a 50-mL buret. About 20 mL of ca. 1 g/L Orange OT dye solution in ethanol was poured into the buret. After the column was rinsed with 200 mL of DI water, the dark orange color seen only in the middle layer of treated sand (Figure 1) indicates that the treated quartz sand can remove and effectively retain the organic dye. It is interesting to note that calciferous sea sand (Clearwater Beach) treated in the same manner would not retain dye. This result is almost certainly attributable to the absence of negative surface charge on calciferous sand, which precludes polycation adsorption (20).

To demonstrate the general principle of surfactant immobilization in this work, we used an oil-soluble dye in sufficient concentrations so as to provide visible proof of the desired effect. This requires concentrations of dye in large excess as compared to those of typical pollutants and also necessitates the use of an organophile-carrying solvent, namely, ethanol, whose effect on solubilization efficiency is unknown. Preliminary experiments in which Orange OT was introduced in a surfactant-solubilized state confirm uptake by treated silica (21). More applications-related studies are



**FIGURE 1. Trapping of an organic solution (Orange OT dye) onto polycation-micelle-treated sand.**

underway using chlorinated hydrocarbons with concentrations below 100 ppm not requiring co-solvency.

Complex formation in solution is reversible with respect to added salt or nonionic surfactant (11). Manipulation of the phase state of the complex through the salinity might be advantageous with respect to two problems. First, it is possible that pollutants could be released from adsorbed complexes upon increase in ionic strength, which would lead to the ability to recover organophiles without much dilution. The second challenge concerns the emplacement of polyelectrolyte–micelle complexes at desired locations in the field, which is problematic because complexes with excess negative charge may be too mobile while complexes with excess positive charge may not transport as needed. One possible solution could arise by manipulation of the phase state through ionic strength. Thus, a soluble mixture of polycation and mixed micelle may be transported at a higher salinity but upon reduction of salinity will form an insoluble complex.

Such delicate manipulations of the phase state of complexes both before and after adsorption will require optimization of selection of polymers and surfactants beyond the scope of this initial report.

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