CHAPTER IV
RESULTS AND DISCUSSION

4.1 Chemically bonded ODS and HFD on silica surface

Silica Hi-Sil® 233 was treated with octadecyltrichlorosilane (ODS) and (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethyl-chlorosilane (HFD) as a monolayer. The IR absorption changes and the increment of carbon percentage ensure that the ODS and HFD were reacted with the silanol group on the silica surface. The changes in the IR absorption for bonded ODS and bonded HFD are shown in Figure 4.1 and Appendix A. Only absorption at 1000-1100 cm^{-1} (Si-O) and 3300-3600 cm^{-1}(Si-OH) were found in pure silica. For ODS treated silica, the spectra of C-H functional groups at 2850-2970 cm^{-1} were also found because of the bonded ODS molecule. For HFD treated silica, the spectra of C-H and C-F functional groups were found due to the bonded HFD molecule. These spectra qualitatively indicate that the ODS and HFD groups were fixed on the silica surface.

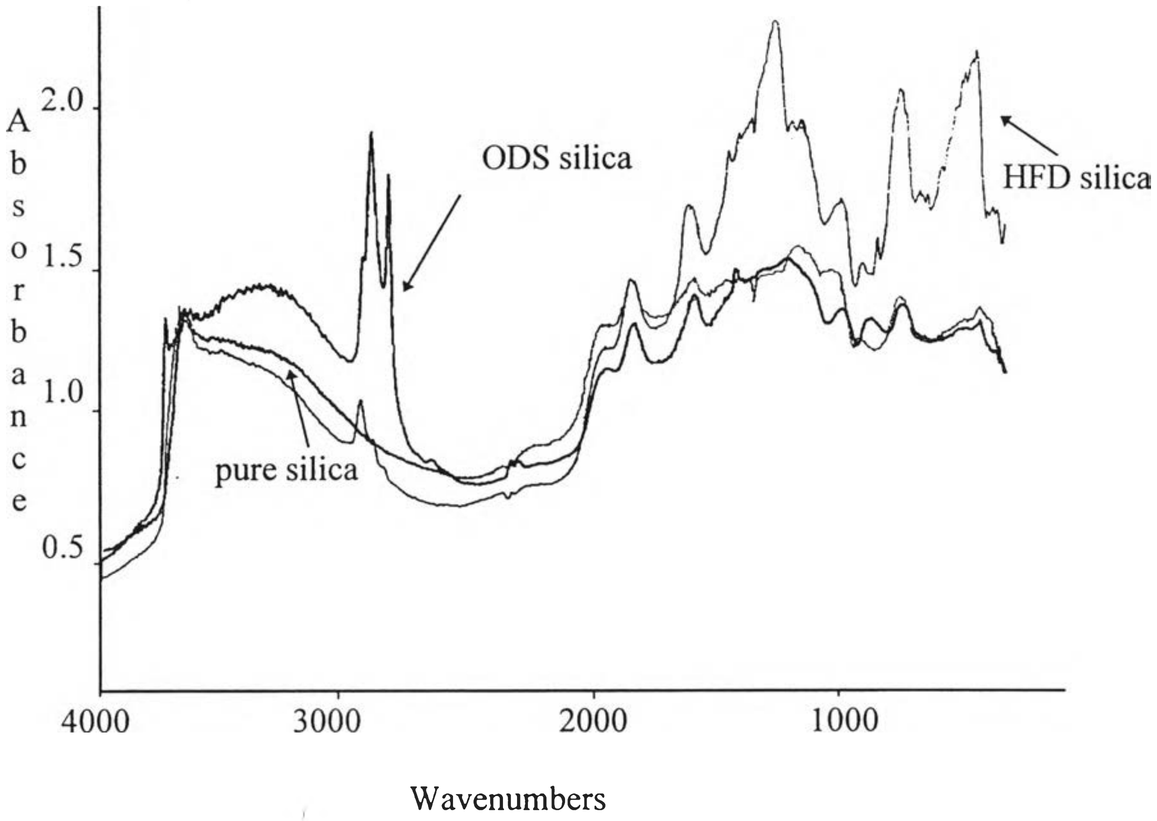

Figure 4.1 Changes of IR spectra of silica by treatment with ODS and HFD.

The elemental analysis results are listed in Tables 4.1 and 4.2. The carbon percentage due to the ODS and HFD group increase with increasing amount of ODS and HFD reagent. The adsorbed molecules are also shown in these tables.

Table 4.1 Increase of carbon percentage with increasing amount of ODS

Silica	%wt carbon	%wt from ODS	Adsorbed molecule (μmoles/g)
Untreated	0.22	0.00	0.00
ODS silica/0.3*	2.44	2.22	95.23
ODS silica/0.5	3.21	2.99	129.60
ODS silica/0.7	4.11	3.89	170.67
ODS silica/1.0	5.59	5.37	240.45
ODS silica/2.0	7.29	7.07	324.23
ODS silica/3.0	8.34	8.12	378.04
ODS silica/4.0	8.65	8.43	394.24
ODS silica/5.0	9.25	9.03	426.01

*ODS silica/0.3 indicates the silica reacted with ODS of 0.3 ml.

Table 4.2 Increase of carbon percentage with increasing amount of HFD

Silica	%wt carbon	%wt from ODS	Adsorbed molecule (μmoles/g)
Untreated	0.22	0.00	0.00
HFD silica/0.3**	0.56	0.34	23.90
HFD silica/0.5	2.04	1.82	134.99
HFD silica/0.7	2.97	2.75	211.32
HFD silica/1.0	3.14	3.14	244.99
HFD silica/2.0	3.56	3.34	262.66

**HFD silica/0.3 indicates the silica reacted with HFD of 0.3 g.

The bonded ODS and bonded HFD adsorption isotherms on silica Hi-Sil® 233 are shown in Figure 4.2. There are no clear regions when compared with that of surfactant admicelles, the isotherms show a high slope at the first region and remain constant at a high concentration region. Since the plateau region indicates the maximum adsorption of bonded monolayer on silica surface, the maximum adsorption of ODS and HFD on silica was found to be approximately 426 and 262 μmoles/g, respectively. That the maximum HFD is less may be due to the shorter chainlength.

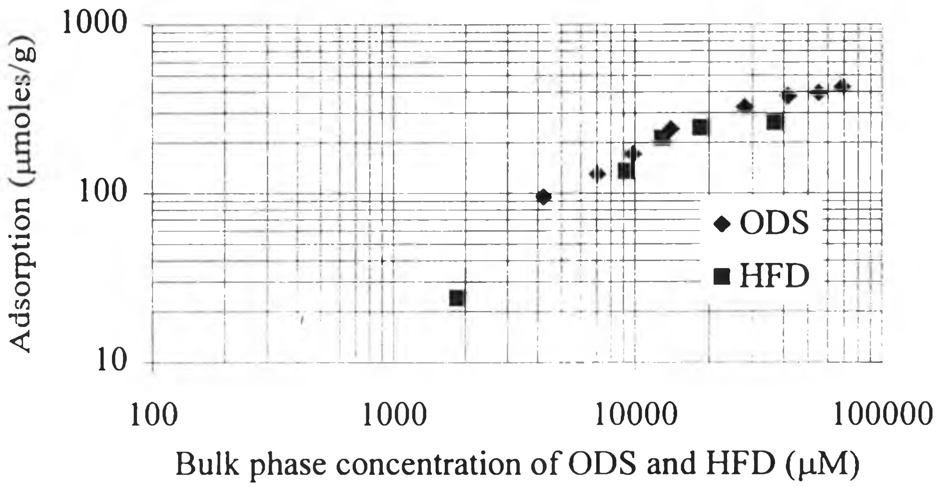

Figure 4.2 The amount of bonded ODS and HFD on silica surface.

4.2 Adsolubilization studies

The plot between the amount of adsolubilized phenol and adsorption of ODS and HFD is presented in Figure 4.3. Both of which show the same trend. In the first region, the higher adsorbed species, the higher adsolubilized phenol. But at the higher surface coverage, the amount of adsolubilized phenol decreases. These results may be explained by the two-site adsolubilization model of alcohol (Lee et al., 1990). There are 2 sites at which alcohols are adsolubilized in surfactant admicelle. One of the alcohol sites is the same as in micelles, at the region between the headgroups of the surfactants. The other is a site not present in micelles, the hydrophobic perimeter arising from patchwise adsorption of the "disk-shaped" admicelle. Both bonded ODS and HFD are hydrophobic monolayers. Their properties look like the hydrophobic perimeter so at low surface coverage, the higher surface coverage, the higher hydrophobic perimeter, result in the higher adsolubilized phenol. On the other hand, at the high surface coverage, the higher surface coverage, the less hydrophobic perimeter, lead to the less adsolubilized phenol.

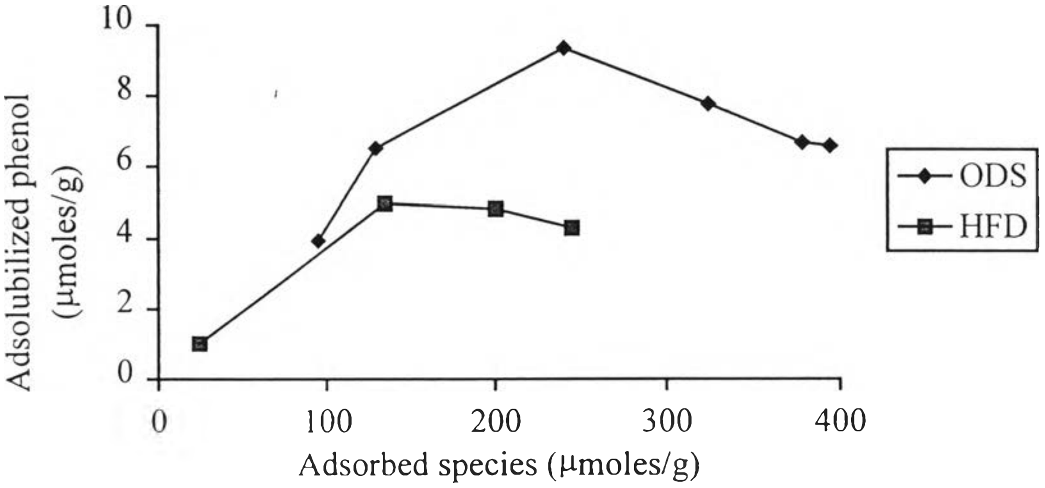

Figure 4.3 Effect of adsorbed ODS and HFD on adsolubilized phenol.

For TCE adsolubilization, since TCE is a hydrophobic molecule, it tends to adsolubilize inside the hydrophobic monolayer. As can be seen in Figure 4.4, the amount of adsolubilized TCE increases over the entire range of coverages of bonded molecules.

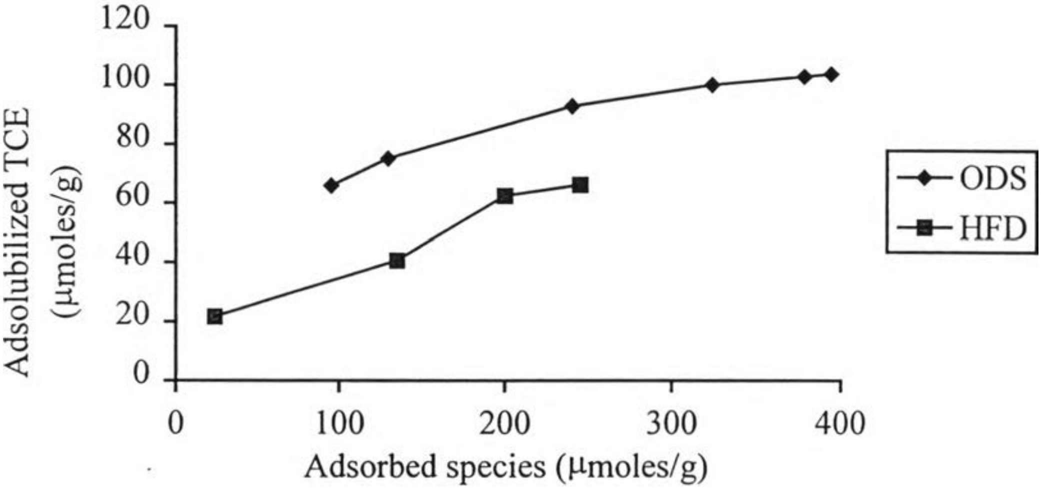

Figure 4.4 Effect of adsorbed ODS and HFD on adsolubilized TCE.

For adsolubilization studies, adsolubilization is quantified using the partition coefficient, P_a, and the adsolubilization constant, K_S. The partition coefficient is defined 'as the ratio of solute concentration in the admicelles (defined as moles of adsolubilized solute per unit total volume) to that in the aqueous phase:

$$P_a = [C^*]/[C] \qquad (4.1)$$

where $[C^*]$ is concentration of solute in the admicelles;

$[C]$ is concentration of solute in the in aqueous phase.

K_S can be written as:

$$K_S = [C^*]/\{[S][C]\} = P_a/[S] \qquad (4.2)$$

where $[S]$ is the adsorbed molecule concentration.

The partition coefficients (P_a) of phenol in bonded ODS and HFD are plotted in Figure 4.5. The data and calculations are shown in Appendix B. For both bonded ODS and HFD, the P_a increases in the first portion of coverages. After that it tends to decrease. For TCE adsolubilization, the P_a increases over the entire range of coverages as shown in Figure 4.6.

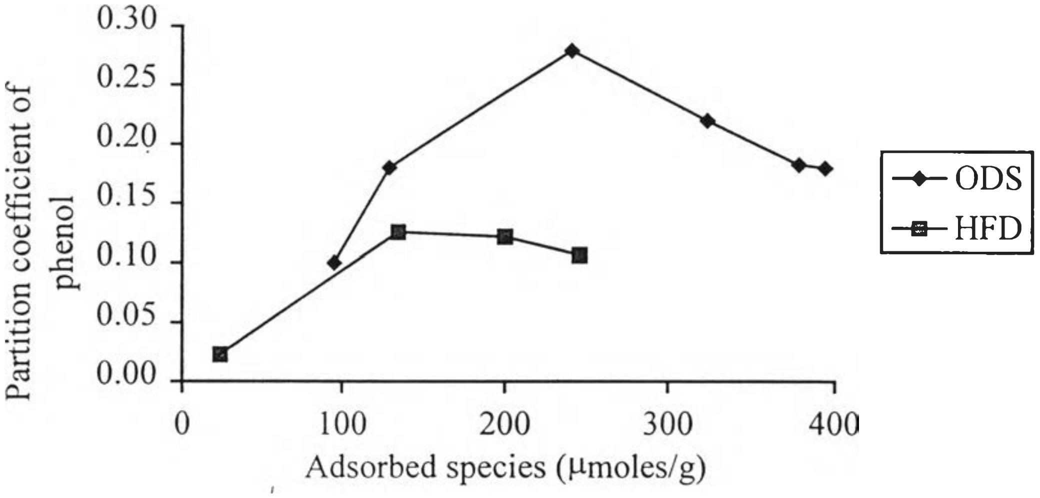

Figure 4.5 Effect of adsorbed ODS and HFD on partition coefficient of phenol.

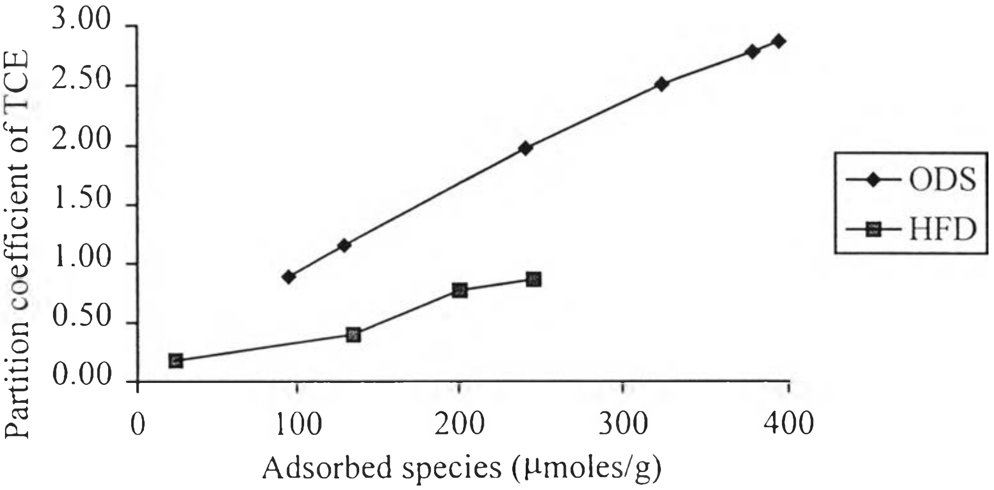

Figure 4.6 Effect of adsorbed ODS and HFD on partition coefficient of TCE.

Figures 4.7 and 4.8 show the variation with surface coverage of the adsolubilization constant for phenol and TCE. The K_S of phenol in bonded ODS increases at the first portion of increasing surface coverage then decreases. For bonded HFD, the K_S decreases over the entire range of coverages.

The K_S of TCE in bonded ODS slightly decreases over the entire range of coverages of the bonded molecule. For bonded HFD, the K_S rapidly decreases at the first range and then becomes approximately constant.

The higher adsolubilization by bonded ODS than bonded HFD is probably due to the longer chainlength of the ODS molecule. The greater adsolubilization of TCE than phenol is because of the high solubility of the polar phenol in water.

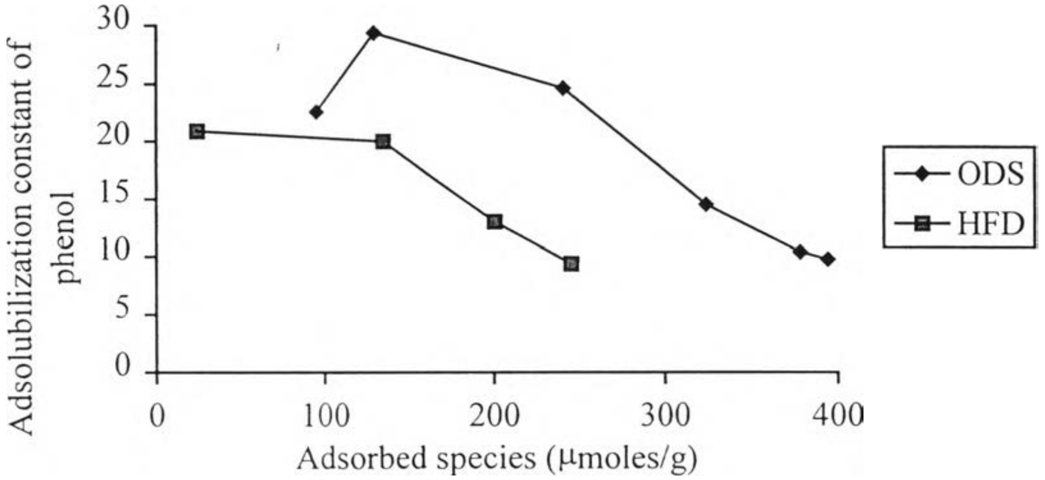

Figure 4.7 Effect of adsorbed ODS and HFD on adsolubilization of phenol.

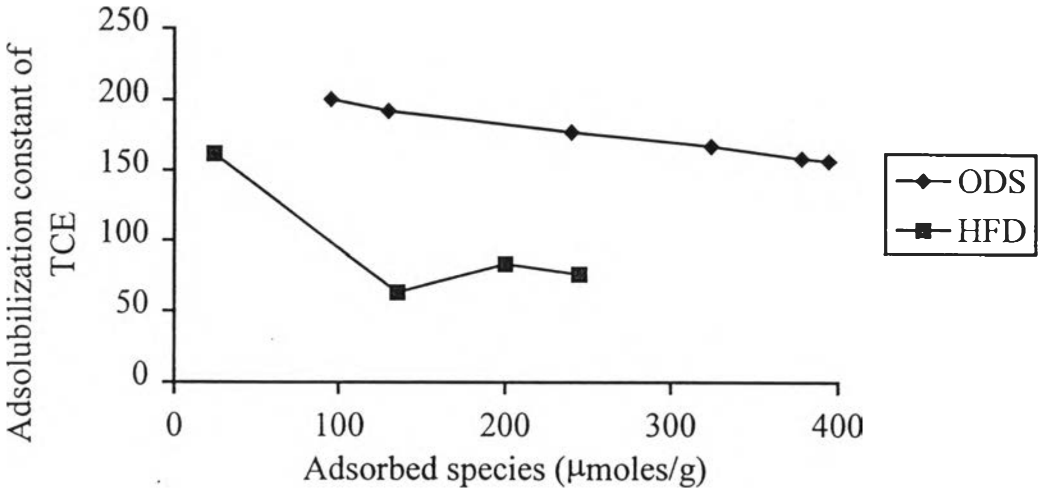

Figure 4.8 Effect of adsorbed ODS and HFD on adsolubilization of TCE.

4.3 Stability studies

The stability of bonded ODS and bonded HFD on silica surface were studied under various conditions of agitation, pH, temperature, and ozonation. The stability is defined as the ratio of the carbon percentage after a stability test to the carbon percentage before a stability test (C/Co).

Figures 4.9 to 4.12 show the effects on bonded molecule stability of varying agitation speed and agitation time, temperature, and pH, respectively. The results indicate that the stabilities of both bonded ODS and HFD are high under agitation speed up to 450 rpm, agitation time up to 2 hr, temperature up to 70°C, and the whole range of pH values.

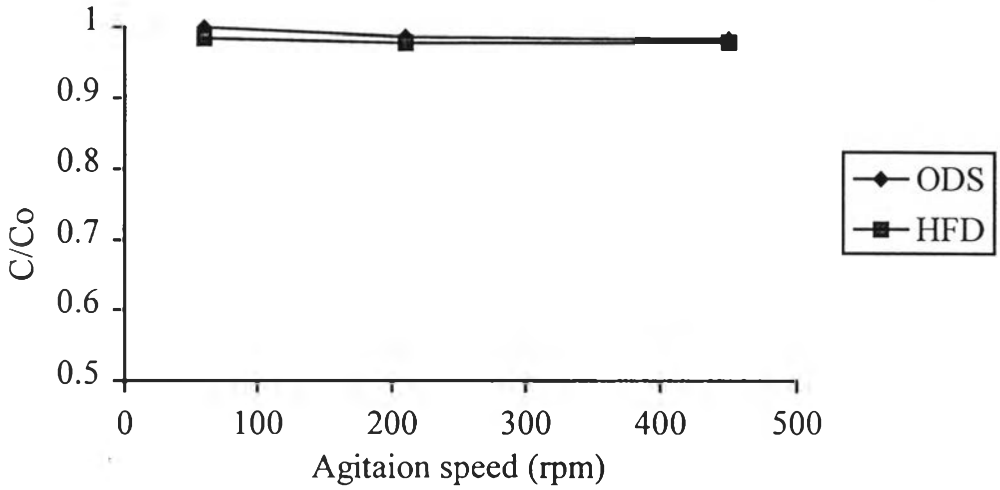

Figure 4.9 Effect of agitation speed on stability of bonded ODS and bonded HFD (30 min, pH7, 25°C).

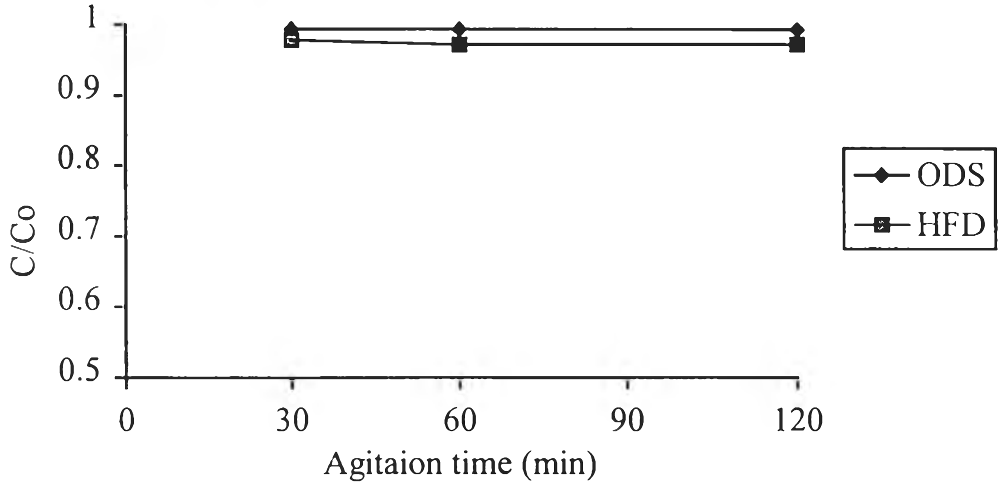

Figure 4.10 Effect of agitation time on stability of bonded ODS and bonded HFD (210 rpm, pH7, 25°C).

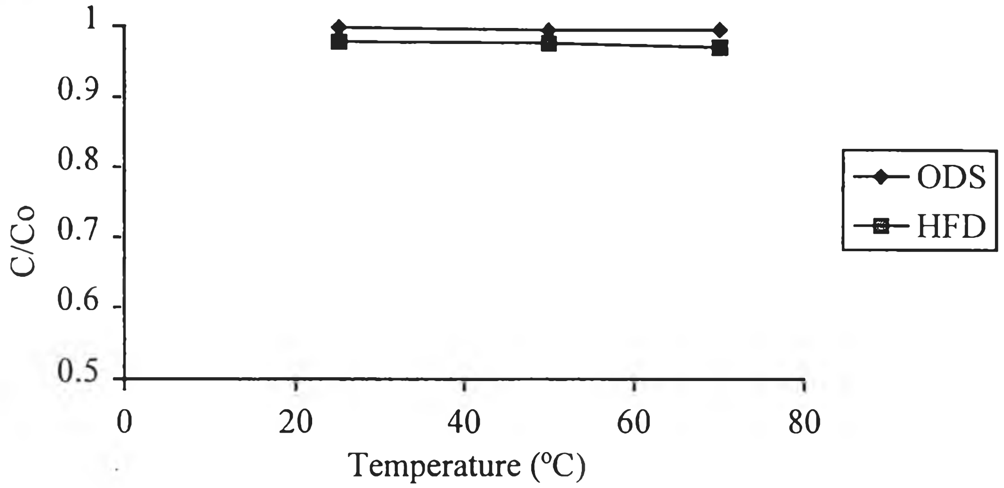

Figure 4.11 Effect of temperature on stability of bonded ODS and bonded HFD (210 rpm, 30 min, pH7).

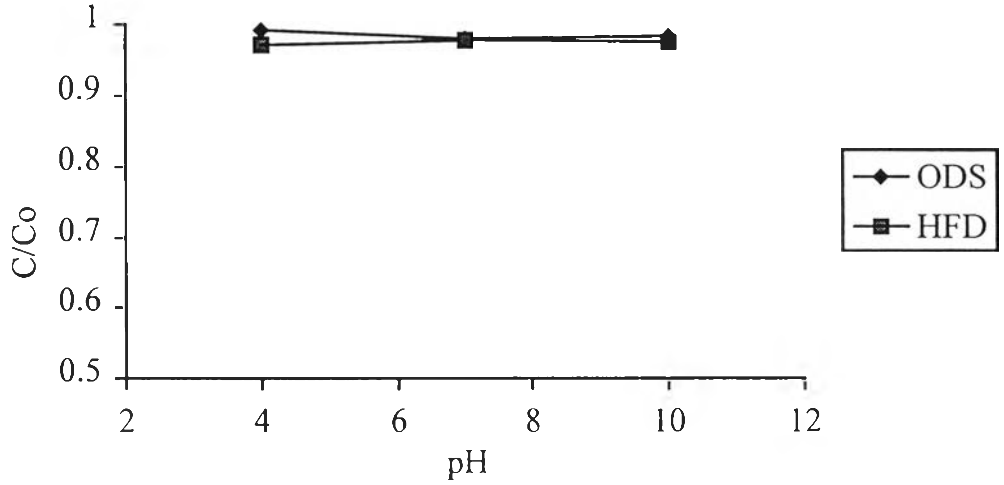

Figure 4.12 Effect of pH on stability of bonded ODS and bonded HFD (210 rpm, 30 min, 25°C).

The stabilities of bonded ODS and bonded HFD under ozone conditions are presented in Figures 4.13 - 4.16. Figures 4.13 and 4.14 show the relationship between stability (C/Co) and oxidation time at various ozone concentrations for bonded ODS and bonded HFD, respectively. It is indicated that the loss of bonded molecules increases with time. At a given oxidation time, the stability of the monolayers decreases with increasing ozone concentration.

Figures 4.15 and 4.16 show the effect of pH on the ozone oxidation for bonded ODS and bonded HFD. It has been shown that ozone oxidation occurs by different mechanisms depending on the pH value. Below the critical pH value of 7, ozone acts as an electrophilic oxidant, but at high pH the hydroxyl radical serves as the main oxidant. As shown in Figure 4.15, the oxidation of bonded ODS increases with increasing pH. But Figure 4.16 shows that the pH hardly affects the oxidation of bonded HFD. Overall, the stability under ozone conditions of bonded HFD is much higher than that of bonded ODS. Thus, for bonded HFD, the pH and ozone concentration can be varied to benefit the desired oxidation reaction without significantly modifying the rate of HFD oxidation or its loss from the silica surface. All of the raw data are presented in Appendex B.

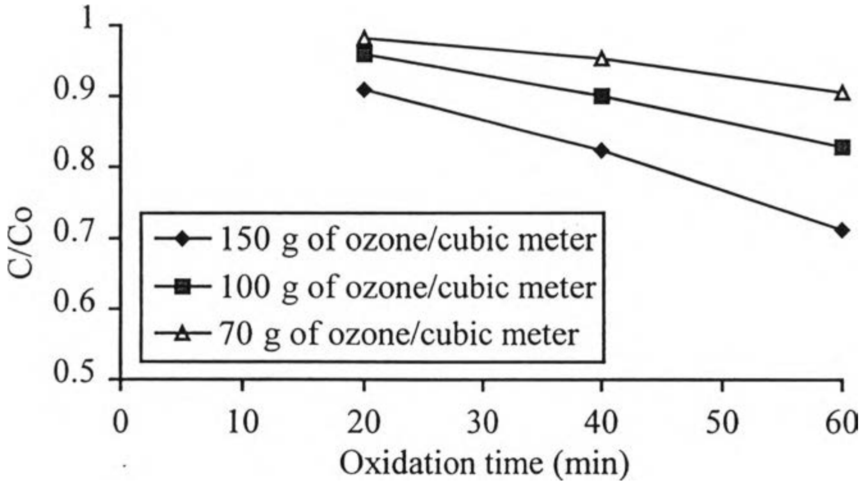

Figure 4.13 Stability of bonded ODS at various ozone concentrations (pH7, 25°C).

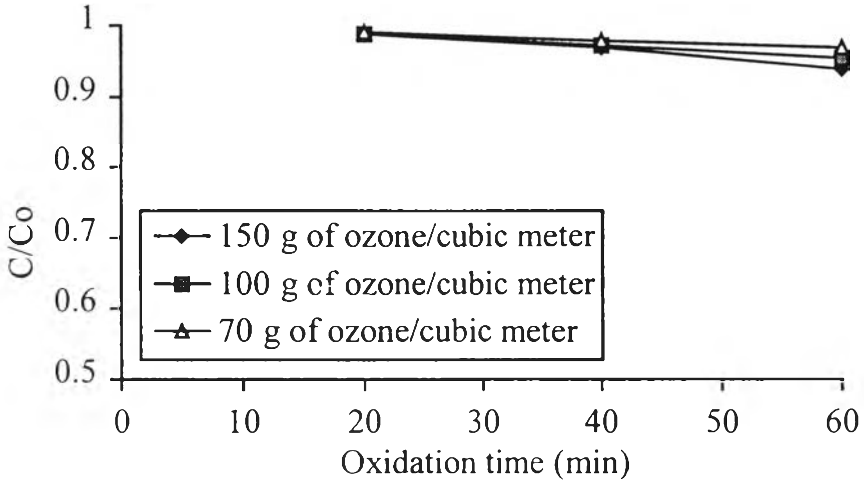

Figure 4.14 Stability of bonded HFD at various ozone concentrations (pH7, 25°C).

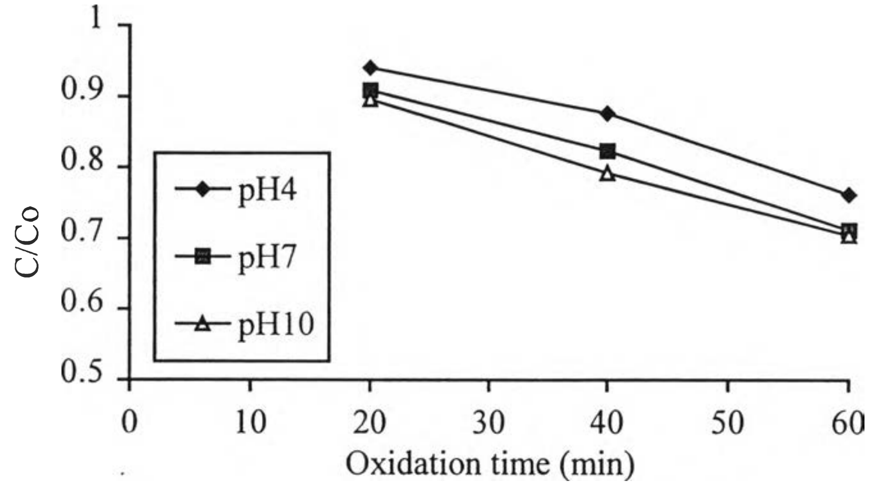

Figure 4.15 Stability of bonded ODS under ozone condition at various pH values (ozone concentration of 150 g/m^3, 25°C).

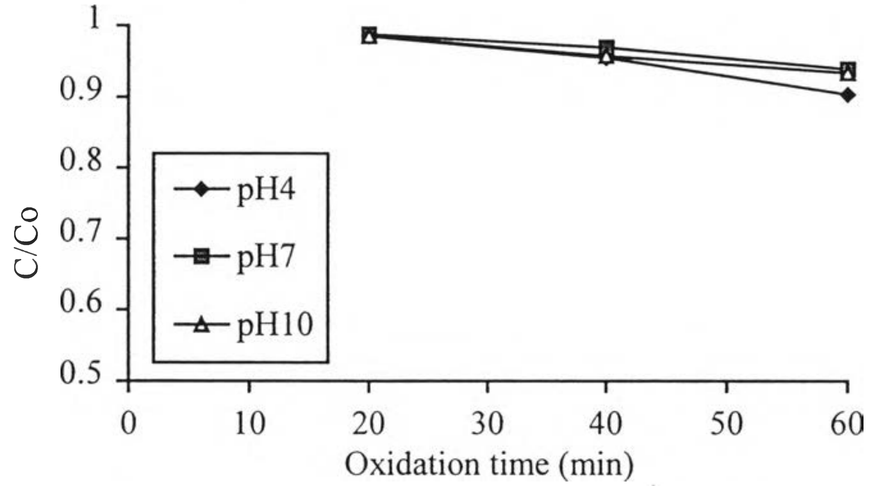

Figure 4.16 Stability of bonded HFD under ozone condition at various pH values (ozone concentration of 150 g/m^3, 25°C).