

CHAPTER VII

SURFACTANT-ENHANCED REGENERATION OF POLYMERIC RESIN IN A VAPOR-PHASE APPLICATION

7.1 ABSTRACT

Surfactant-enhanced carbon regeneration (SECR) was employed to regenerate a polymeric resin saturated with trichloroethylene (TCE), using an aqueous solution of the anionic surfactant sodium dodecyl sulfate (SDS). More than 95% of the sorbed TCE was removed in the desorption operation with a 0.1 M SDS solution at a superficial flow rate of 1 cm/min. The desorption rate of TCE from pores of the resin is limited by the concentration of SDS in the regenerant and its flow rate. From the breakthrough curve of the subsequent adsorption cycle without a flushing step following the desorption, only 40% of the effective adsorption capacity of the virgin resin is observed for the regenerated resin. With a water flushing step following the surfactant regeneration step, the effective adsorption capacity is significantly improved to about 60% of that of the virgin resin. Thermal gravimetric analysis indicates that the reduction in the effective adsorption capacity of regenerated resin resulted from the residual SDS remaining in the pores of the resin. The regeneration step is equilibrium limited whereas the water flushing step is rate limited under the studied conditions. Despite, the loss of subsequent cycle adsorption capacity, SECR may still be economical as an *in-situ*, low temperature regeneration method.

7.2 INTRODUCTION

Although adsorption on activated carbon for removal of organic compounds from aqueous solution and gaseous stream is one of the most frequently applied techniques [1, 2], an important disadvantage is the difficulty and expense of regeneration [3-5]. Polymeric adsorbents have been widely investigated to remove organic compounds from aqueous solution and gaseous stream and have been

extensively used in many applications [6-21]. Moreover, they can be regenerated by acid, base, organic solvent, hot gas or steam at moderate temperatures, ultrasound and bio-regeneration [14-21]. In this work, surfactant-enhanced carbon regeneration (SECR) was applied to regenerate a polymeric resin.

The resin is a rigid, nonionic, cross linked macroreticular copolymer of styrene and divinyl benzene, with high surface area and an aromatic nature of its surface [20]. It possesses excellent physical, chemical and thermal stability and it is also stable over a wide pH range in aqueous solution. Its characteristic pore size distribution makes this resin an excellent adsorbent for organic substances of relatively low molecular weight. A primary reason for its use here is that it is expected to have a more homogeneous distribution of energies of adsorption site than activated carbon, the presence of high energy sites having been hypothesized to account for the difficult-to-desorb heel of adsorbed surfactant following application of SECR to activated carbon [22,25]

Surfactant-enhanced carbon regeneration (SECR) is an *in-situ* regeneration technique in which a surfactant solution at surfactant concentrations well above the critical micelle concentration (CMC) is passed through the spent resin. The sorbate desorbs and solubilizes into micelles which increase total sorbate solubility into the aqueous solution. Following this sorbate desorption step, residual adsorbed surfactant can be flushed from the resin using water. The bed can then be dried with warm air. This technique is well described in detail elsewhere [22].

The objective of this work was to investigate the regeneration of resin saturated with trichloroethylene (TCE) using the SECR technique and measure adsorption capacities of regenerated resin in a fixed-bed adsorber in comparison to virgin resin.

7.3 MATERIALS AND EXPERIMENTAL SECTION

Materials

A polymeric resin XAD-4 supplied by Rohm and Haas Company (Philadelphia, USA), was used in the adsorption experiment. The reported BET surface area and apparent density of resin are $750 \text{ m}^2/\text{g}$ and 1.01 g/cm^3 , respectively. The average pore size of the resin is reported as 5.1 nm [16-18]. The resin was pretreated by extracting with methanol for removal of the residual monomer remaining trapped within the pore structure after polymerization. The resin was then rinsed with deionized water 3 times to eliminate residual methanol and water soluble matter, then dried in an oven at 60°C for 24 h and was kept in a desiccator. Analytical grade 99% purity trichloroethylene (TCE) from Lab-Scan Analytical Sciences (Dublin, Ireland) was chosen as the model gas-phase adsorbate. The surfactant used as the regenerant was an anionic surfactant, chemical grade 95% purity sodium dodecyl sulfate (SDS) supplied by APS Ajax Finechem (Auburn, NSW, Australia). Water for regenerant preparation and flushing was deionized water.

Methods

The adsorption and the regeneration experiments were performed in a 2.5 cm ID glass jacketed column packed with the XAD-4 resin. Dynamic adsorption isotherms of TCE were obtained by using 13.2 g of the resin (corresponding to the bed height of 7.2 cm). The calculated surface area of the sorbent is equivalent to that of 9 g of granular activated carbon (GAC) used in our previous work [22]. The height of the bed was fixed by an adjustable plunger to minimize the void volume in the bed. The breakthrough curve effluent concentration of TCE from an air stream on the resin at 30°C was measured and adsorption capacity calculated from it. The temperature of the column was maintained at 30°C by circulating water from the temperature controlled water bath to the jacket of the column. A continuous feed concentration of TCE in the simulated TCE contaminated air was generated by

continuous bubbling an air stream into a temperature controlled saturator before mixing this TCE-saturated air stream with the main air stream in a mixing chamber at a pre-calculated ratio. A simplified flow scheme of the experimental setup is shown in Fig. 7.1.

Before each dynamic adsorption experiment, the fresh resin was dried with warm air. A simulated contaminated air stream containing 1,030 ppmv TCE was then fed to the bed of resin at a flow rate of 450 mL/min. The TCE concentration in the inlet air stream and in the effluent air stream from the column of resin were analyzed using a gas chromatograph (Perkin Elmer Model AutoSystem XL) equipped with a Carbowax column and a thermal conductivity detector (TCD).

The entire regeneration cycle started with desorption of TCE, removal of the excess surfactant by a washing or water flush step, and drying the bed of resin. The desorption of sorbed TCE from the TCE-saturated resin was performed by pumping the surfactant solution through the adsorption column as shown in Fig. 7.1. The temperature of the bed of resin was kept at 30°C. A solution of SDS at the desired concentration (0.1-0.2 M) was fed upward into the TCE-saturated resin column at the desired flow rate (5-15 mL/min). The fractions of effluent solution were periodically collected and analyzed by a Perkin Elmer gas chromatograph with a Headspace Sampler equipped with a Carbowax column and a flame ionization detector (FID). Deionized water at ambient temperature (30°C) was fed upward at a desired flow rate (5-15 mL/min) to flush out excess surfactant. The fractions of effluent water were collected and analyzed by a Shimadzu total organic carbon analyzer. After the flushing step (or after the desorption step), the bed of resin was drained and dried with heated air stream (50°C) until the moisture in the effluent air was less than 2% relative humidity.

In order to confirm whether residual SDS remained on the surface of regenerated resin, thermal gravimetric analysis (TGA, TG 50 Metler) with a heating rate of 5°C/min was used.

7.4 RESULTS AND DISCUSSION

Breakthrough curve for TCE from air

The adsorption experiment in the packed bed column containing 13.2 g of fresh resin reached the saturation (effluent TCE concentration reaches inlet TCE concentration) at around 400 min (equivalent to 15,000 pore volumes) as shown in Fig. 7.2a. A pore volume is the void space in the column containing resin and was measured to be 12 mL. The criterion indicating a breakthrough point is at C/C_0 (outlet concentration/inlet concentration) of 0.01 as defined in the previous work [22]. The calculated amount of TCE adsorbed in the packed column is equal to 1.02 g of TCE or 0.59 mmole TCE/g of the resin as shown in Fig 7.2b. This adsorbed value is lower than that of GAC with the same surface area, which is 3.87 g of TCE [22].

Desorption of TCE

Organic solutes like TCE solubilize into the hydrophobic micellar interior [23]. Total solubility of TCE in the aqueous solution increases with increasing surfactant concentration above the CMC (CMC = 0.08 M for SDS [24]). An aqueous solution of 0.1 M SDS (approximately 12xCMC) at a flow rate of 5 mL/min or a superficial linear flow rate of 1 cm/min was used for the desorption. The TCE concentration in the regenerant solution and the fraction of TCE desorbed is shown as a function of volume of regenerant solution used in Figs. 7.3 and 7.4, respectively. The sorbed TCE is rapidly desorbed with the first 200 pore volumes. The desorption of TCE rapidly decreases until around 500 pore volume and gradually decreases for the rest of the desorption step as shown in Fig 7.4. From Fig 7.4, approximately 80% of TCE easily desorbs while the other 20% desorbs with difficulty. It is hypothesized that 80% of TCE adsorbs in the macropore of the resin and 20 % in the mesopore. This would indicate that the resin is a macroreticular adsorbent compared to the gas-phase application GAC, which is a microreticular adsorbent where only 20% of TCE

adsorbs in the mesopore and the rest in the micropore and submicropore [22]. However, for both cases, more than 95% of TCE can be desorbed from the bed. In this work, the total regenerant volume used around 1,300 pore volumes as shown in Fig 7.4.

Effect of water flushing

After the desorption of TCE into the surfactant solution, the bed of resin was flushed with water at 30°C with a flow rate of 5 mL/min. This process was conducted until the SDS concentration in the effluent water was below the detectable limit (4 ppm) to ensure that all desorbable SDS were removed. The breakthrough curve for TCE from air using the regenerated resin with the flushing step shows a higher adsorptive capacity than the regenerated resin without the flushing by a factor of two as shown in Fig. 7.2a. The improvement of its adsorptive capacity could be due to the removal of SDS adsorbed on the surface of resin by the flushing, thus, providing more adsorption sites for TCE. This phenomenon is consistent with what have been reported elsewhere [22, 25]. The residual surfactant on the surface of resin is responsible for the reduced adsorption capacity of the regenerated resin and the greater the amount of residual SDS, the worse the effect. This is the same behavior observed for the SECR of liquid-phase and vapor phase applications with GAC [22, 25].

Effect of regenerant flow rate

Experiments using TCE-saturated resin were carried out with 0.1 M SDS at the flow rates of 5, 10, and 15 mL/min corresponding to the superficial velocities of 1, 2, 3 cm/min, respectively, to desorb TCE from the carbon surface. The concentration profiles of TCE in the regenerant solution are shown in Fig. 7.5. The profiles of TCE show the same trend; initially, the concentration of TCE in the effluent solution increases with an increase in the SDS solution volume passing through the bed and reaches a maximum before gradually decreasing towards zero.

From Fig. 7.5, the maximum TCE concentrations in the effluent from different regenerant flow rates are obtained at different times. This is different from the gas phase application GAC where the maximum TCE elutes out at the same time [22]. However, the fractions of TCE desorbed are almost the same with the increase in the total moles of SDS in the regenerant solution passing through the bed of resin at several flow rates as seen in Fig. 7.6. In other words, at 0.1 M SDS, the rate of TCE removal does depend on the flow rate of the SDS solution. With a higher flow rate of the regenerant solution, there are more moles of SDS passing through the bed, so the rate of TCE removal is higher. In other words, the rate of TCE removal depends only on the total number of mole of SDS in the regenerant solution passing through the bed at the flow rates studied. It can be concluded that the TCE removal is controlled by the equilibrium solubilization of TCE into the micellar solution at the flow rates studied. This result is consistent with the regeneration of the liquid phase application with GAC [18], which is a macro reticular adsorbent, whereas with the gas phase application with GAC, which is a micro reticular adsorbent, the TCE removal is controlled by mass transfer [22].

Effect of surfactant concentration in regenerant

Three sets of experiments using TCE-saturated resin were conducted with 0.074, 0.1 and 0.2 M SDS at a flow rate of 5 mL/min to desorb TCE from the resin surface. The removal of TCE as a function of regenerant pore volume is shown in Fig. 7.7. At the same pore volume of the regenerant, the removal of TCE with 0.2 M SDS is higher than that with 0.1 M and 0.074 M respectively. This phenomenon is consistent with the liquid-phase application with GAC [25] but different from the gas-phase application [22] where the removal of TCE does not depend on the surfactant concentration in the regenerant solution. It may be because, with the resin, TCE is adsorbed in the macropores, which is more easily desorbed than that in the mesopores and micropore as in the case of the gas phase application with GAC. However, the fraction of TCE desorbed was almost the same with the increase in the number of SDS mole in the regenerant solution passing through the resin bed at

several concentrations of SDS in the regenerant as seen in Fig. 7.8. This indicates that the rate of the TCE removal does depend on the concentration of SDS in the regenerant solution. Therefore, the TCE removal rate is equilibrium controlled, consistent with the regenerant flow rate effects and with previous studies of liquid phase application with GAC [25]. In addition, even at the SDS concentration of 0.074 M, where surfactant concentration is lower than the CMC (0.08 M), and all surfactants is present as individual monomer, TCE can also be desorbed. It is concluded that the mechanism of TCE desorption is proceeded by the adsorption of SDS monomer. The higher the concentration of the regenerant, the greater the TCE removal, and almost quantitative TCE removal is possible when concentration of regenerant of 2 M was used as seen in Fig. 7.7 and Fig. 7.8.

Effect of water flow rate during flush step

Three sets of TCE desorbed resin beds were flushed with deionized water to remove residual SDS. The flow rates of flushing water were 5, 10, and 15 mL/min (corresponding to the superficial velocities of 1, 2, 3 cm/min, respectively) and results are shown in Fig. 7.9. There is no effect of the flow rate in the fractional removal of SDS. This implies that the removal of SDS is rate limited under these conditions, which is in agreement with previous work for GAC [22, 25]. In this work and previous work [25], it was observed that the SDS removal by the water flushing for the macroporous adsorbent and liquid-phase application with GAC [25] is higher than with gas-phase application with GAC [22]. Although it shows difficulty in removal of SDS during the flush with these conditions, but it seems likely that quantitative removal of SDS could be attained if enough flush at enough flush solution volume is used. This is in contrast in previous work [25] where there appear to be a heel of nearly irreversibly adsorbed surfactant on GAC (which is almost impossible to remove by water flushing. This tends to support the view that the resin has a more homogeneous distribution of energies of adsorption sites (more even distribution of heat of adsorption between SDS and surface adsorption sites. The GAC appears to have extremely energetic adsorption sites corresponding to the 20%

irreversibly adsorbed SDS (even with 2,000 pore volumes of flush solution) whereas, removal of the SDS during the flush with resin is easier than for GAC. So, a reduction of loss of adsorption capacity with resin is possible compare to GAC. This was a central hypothesis in this study. Still, large volumes of flush water are needed to remove a very high fraction of SDS. As already discussed, the residual surfactant after the flush reduces subsequent cycle adsorption capacities to approximately the same extent as for GAC, even though this heel of nearly irreversibly adsorbed surfactant is not present with the resin because it is still difficult to attain high SDS removal levels with the resin. So, advantages of using resin vs. GAC in the SECR process are not as great as anticipated even though a more homogeneous distribution of energy levels of adsorption sites was observed.

The thermograms of thermal gravimetric analysis (TGA) (Fig. 7.10) shows the rate of weight loss of the regenerated resin due to the decomposition of adsorbed SDS upon heating. The thermograms indicate that SDS remains on the resin, whether or not the resin undergoes the flushing step. The amount of SDS remaining on the regenerated resin at 3,000 regenerant pore volumes without the flushing step is greater than that the regenerated resin at the same pore volumes of regenerant with 160 pore volumes of flush solution. So, the flushing step can reduce the residual surfactant heel, but not eliminate it even with 160 pore volumes of flush water used.

7.5 CONCLUSIONS

In this work, the regeneration of TCE saturated resin in packed-bed adsorbers by using SDS was studied in order to investigate the parameters affecting the regeneration. The results showed that more than 95% of TCE can be removed by using a 0.1 M SDS concentration in the regenerant. The water flushing step improved the adsorption capacity of the regenerated resin compared with the regenerated resin without the water flushing (60% and 40%, respectively). The adsorption capacity of the regenerated resin was reduced to about 60% of its original capacity, which is similar to previous work using cationic surfactants and liquid phase application GAC. TCE desorption by this method is equilibrium limited. In addition, the

mechanism of TCE desorption is preceded by adsorption of SDS monomer. The irreversibly adsorbed surfactant left as a heel following regeneration is difficult to desorb, but not as difficult as with activated carbon instead of resin.

7.6 ACKNOWLEDGEMENTS

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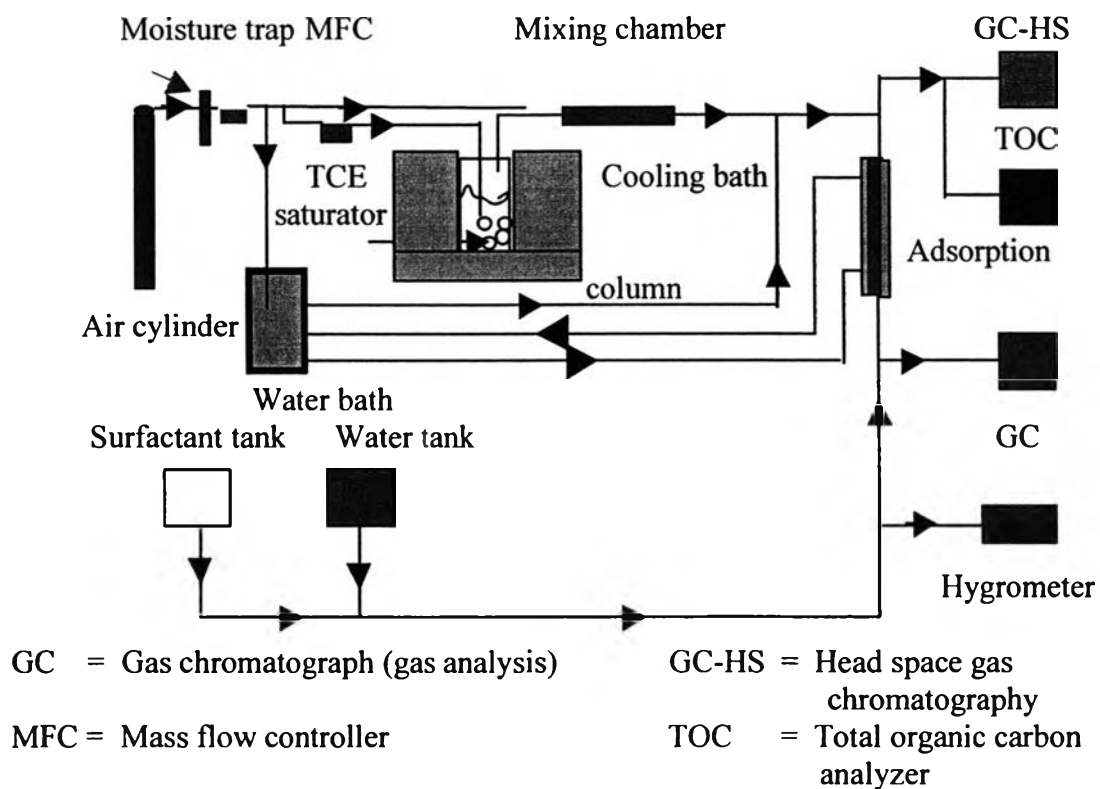


Figure 7.1 Schematic diagram of the experimental apparatus.

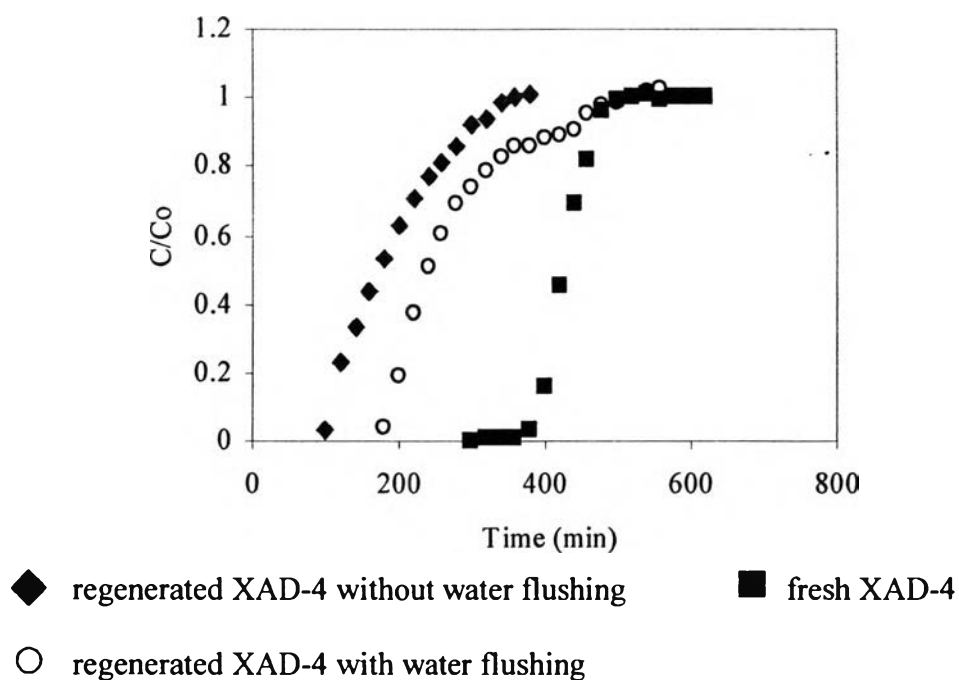
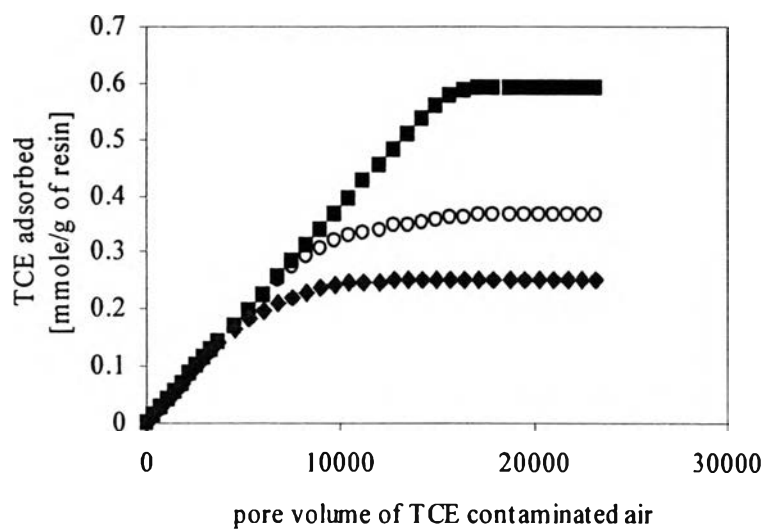


Figure 7.2 a Breakthrough curves for TCE in air with fresh and regenerated resin. (C = Effluent TCE concentration, C_0 = Inlet TCE concentration).



- ◆ regenerated XAD-4 without water flushing ■ fresh XAD-4
 ○ regenerated XAD-4 with water flushing

Figure 7.2 b Adsorption isotherms of TCE on resin

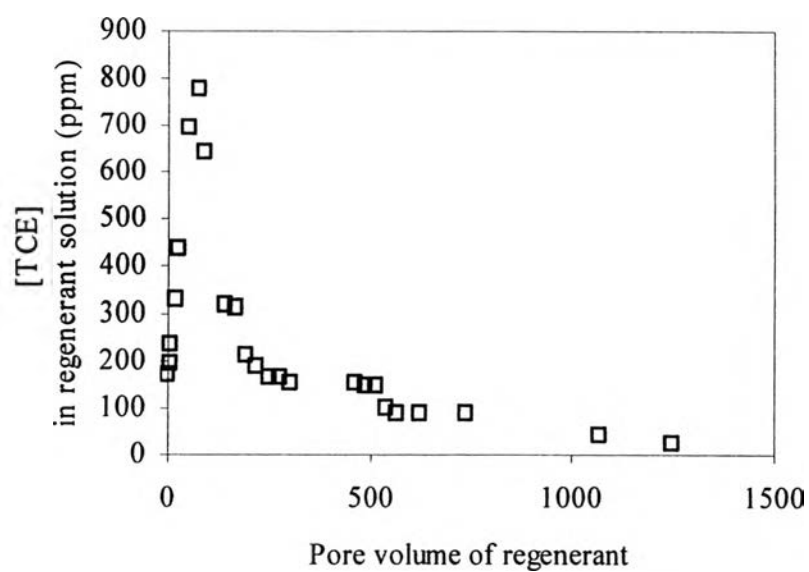


Figure 7.3 TCE concentration in effluent regenerant solution with [SDS] of 0.1 M and flow rate of 5 mL/min.

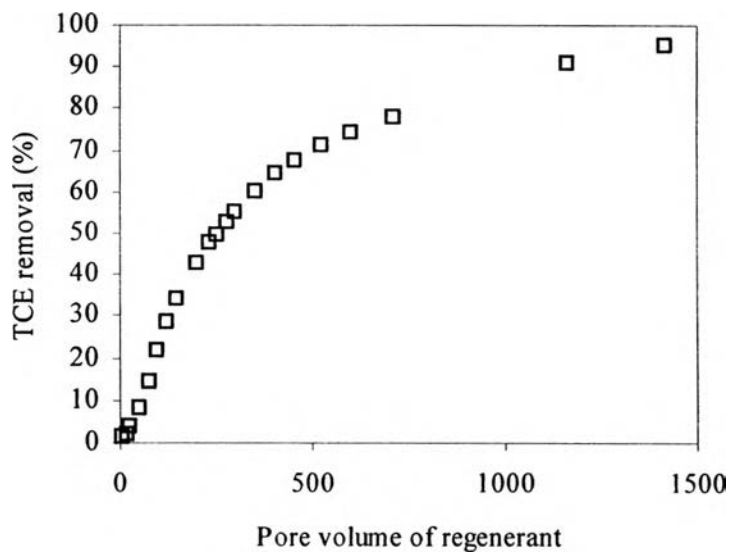
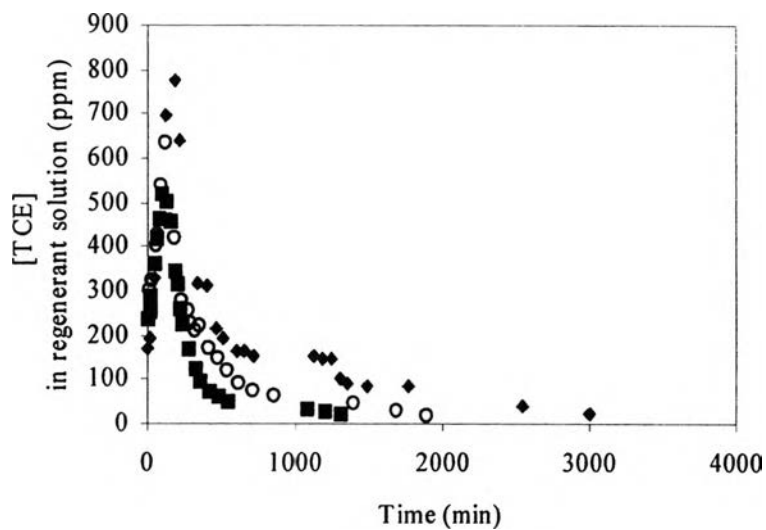
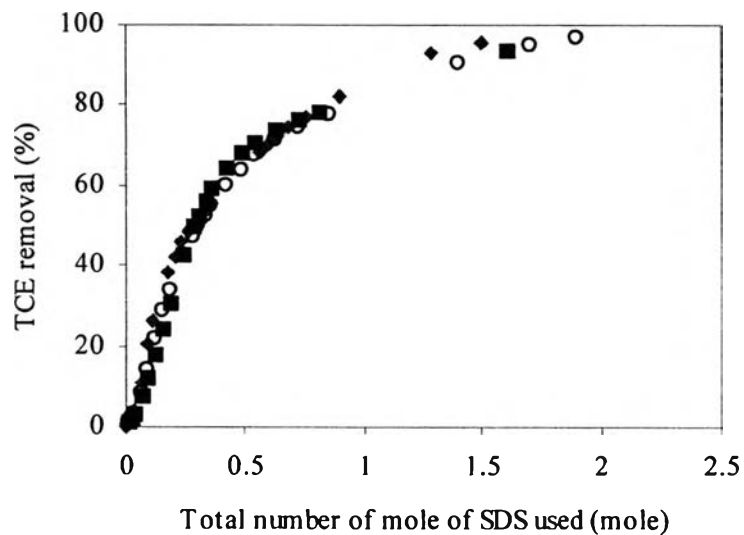


Figure 7.4 Fractional TCE removal during regeneration with [SDS] of 0.1 M and a flow rate of 5 mL/min.



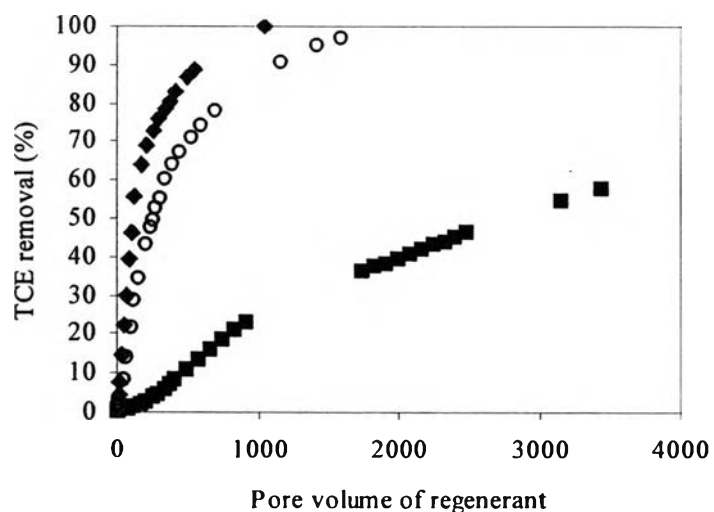
◆ 5 mL/min ○ 10 mL/min ■ 15 mL/min

Figure 7.5 TCE concentration in effluent regenerant solution with [SDS] of 0.1 M at several flow rates.



◆ 5 mL/min ○ 10 mL/min ■ 15 mL/min

Figure 7.6 Fractional TCE removal during regeneration with [SDS] of 0.1 M at several flow rates.



■ 0.0074 M ○ 0.1 M ◆ 0.2 M

Figure 7.7 Fractional TCE removal during regeneration with [SDS] of 0.074, 0.1 and 0.2 M at a flow rate of 5 mL/min.

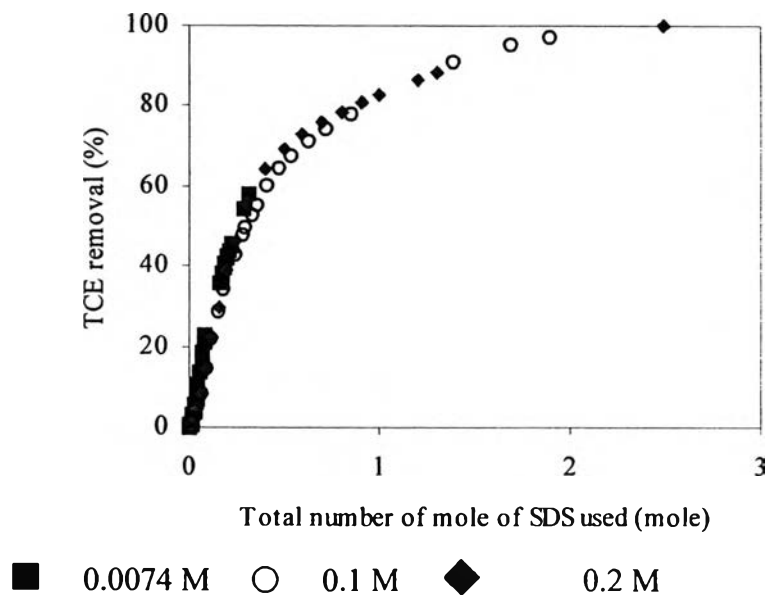


Figure 7.8 Fractional TCE removal during regeneration with [SDS] of 0.074, 0.1 and 0.2 M at a flow rate of 5 mL/min.

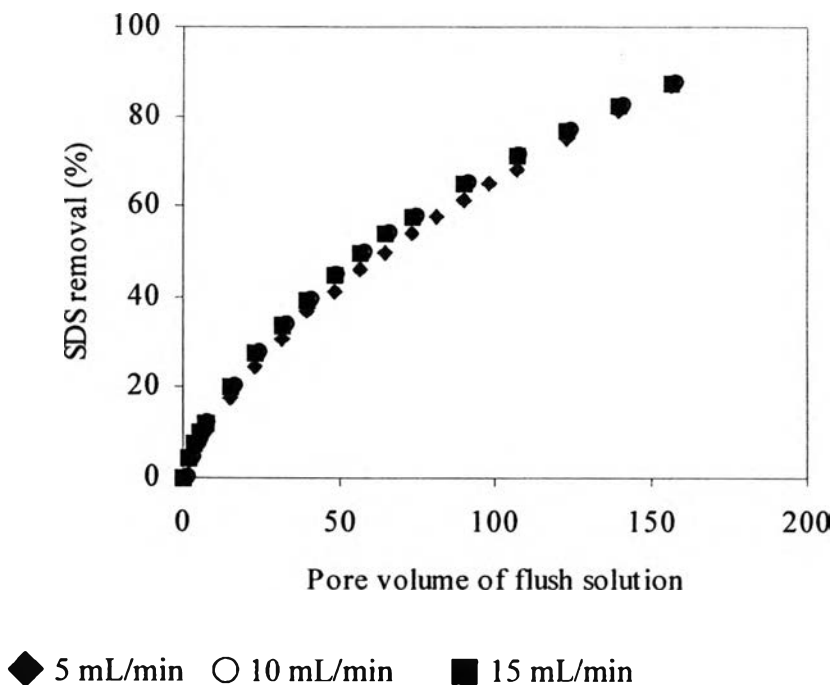
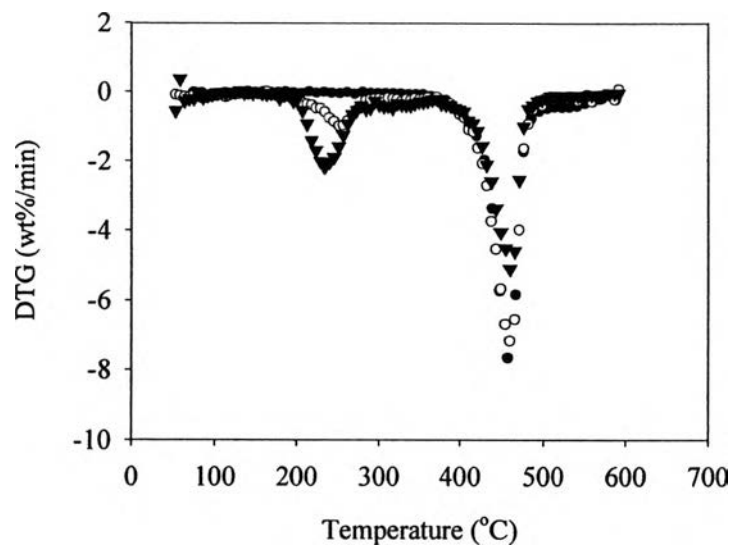


Figure 7.9 Fractional SDS removal during flush with water at several flow rates.



● Fresh XAD-4 ○ Regenerated XAD-4 with flushing

▼ Regenerated XAD-4 without flushing

Figure 7.10 Thermograms from thermal gravimetric analysis of resin (at heating rate of 5 °C/min).