



CHAPTER V

SURFACTANT-ENHANCED REGENERATION OF GRANULAR ACTIVATED CARBON USED IN REMOVAL OF A VOLATILE ORGANIC COMPOUND

5.1 ABSTRACT

Surfactant-enhanced carbon regeneration (SECR) was applied to gas-phase application granular activated carbon (GAC) saturated with a volatile organic compound (VOC), trichloroethylene (TCE), in packed bed adsorbers. An anionic surfactant, sodium dodecyl sulfate, (SDS) was used for this purpose. In this system, more than 95% removal of TCE was achieved. However, after the regeneration, only about 5% in its original capacity was recovered when surfactant solution was used alone. It is speculated that the drastic decrease of its capacity is due to the residual surfactant remaining on GAC. With subsequent rinsing the regenerated carbon with water at ambient temperature, its capacity was greatly improved. The experimental results also revealed that the temperature of the rinsing water has a significant influence on the capacity of the regenerated carbon. Concurrently, the adsorption-desorption isotherms of SDS on GAC were generated in order to gain more information about the mechanistic governing the desorption of the surfactant

5.2 INTRODUCTION

Granular activated carbon (GAC) has been extensively used as an efficient adsorbent to remove organic compounds from water and gas streams by means of adsorption. The spent GAC must either be replaced or be regenerated to restore its adsorptive capability. The predominant industrial practice of using the activated carbon only once and disposal or thermal regeneration is costly. Therefore, other alternatives have been searched to decrease the regeneration cost such as, chemical regeneration, solvent regeneration, supercritical extraction, biological, and ultrasound regeneration (1-11).

Regeneration of spent GAC for gas phase applications using surfactant or surfactant-enhanced carbon regeneration (SECR) is one of the promising alternatives because of its capability in lowering interfacial tension and increasing the solubility of organic compounds by solubilization. The SECR method consists of 3 main steps: passing a surfactant solution through the activated carbon bed, rinsing of excess surfactant by water, and drying the bed with warm air. The process strategy is shown in Fig. 5.1.

Previous studies for both liquid-phase and vapor-phase applications on the carbon regeneration have indicated that organic adsorbates can be desorbed out by the SECR, however, the effective adsorption capacity of the regenerated carbon in subsequent cycles was reduced (12-14). Leng and Pinto (3) investigated the regeneration mechanism of activated carbon, which adsorbed 4 kinds of organic compounds using SDS and CTAB surfactants. Bhummasobhana (14) used SECR to regenerate phenol-adsorbed carbon. In gas-phase applications, Roberts *et al.* (13) used the SECR to regenerate carbon containing either toluene or amyl acetate. However, detailed breakthrough curves were not produced. These initial research works have shown promising results in applying the SECR to GAC for vapor-phase applications. The objective of this work was to investigate important parameters affecting GAC regeneration by SECR and restoration of the adsorption capacity of the regenerated GAC.

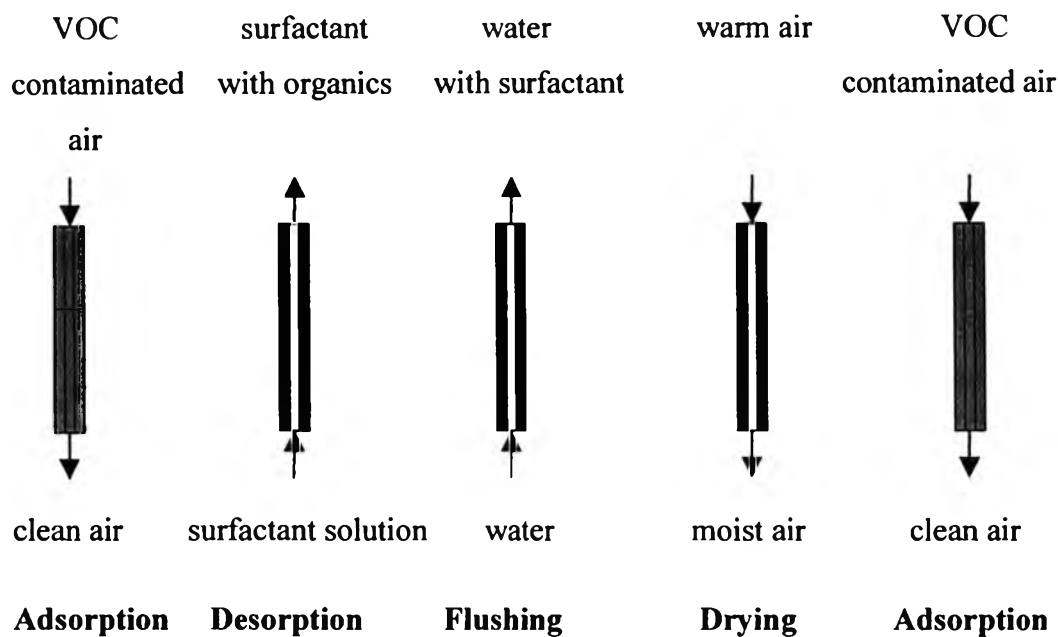


Figure 5.1 Process strategy for surfactant-enhanced carbon regeneration.

5.3 EXPERIMENTAL SECTION

Materials

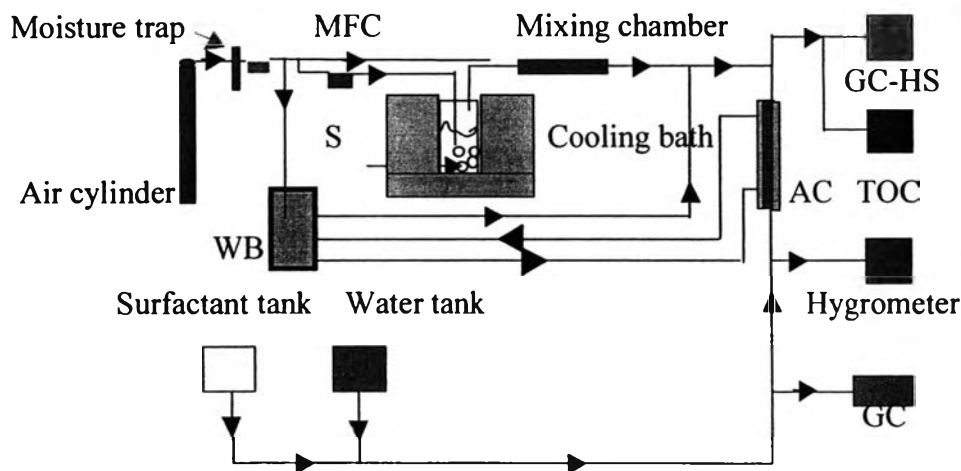
A BPL 4x10 GAC supplied by Calgon Carbon Corporation (Pittsburgh, USA) was used as an adsorbent. The reported BET surface area and appearance density of GAC are 1,100-1,200 m²/g and 0.5 g/cm³, respectively. The carbon was pretreated by boiling in deionized water for 1 h, followed by rinsing with deionized water 3 times then drying in an oven at 110°C for 24 h. The treated carbon was stored in a dessicator. An analytical grade trichloroethylene (TCE) from Lab-Scan Analytical Sciences (Dublin, Ireland) was chosen as the model adsorbate. SDS (chemical grade) used as the regenerant was supplied by APS Ajax Finechem (Auburn, NSW, Australia). Surfactant solution was prepared with deionized water.

Methods

A dynamic adsorption of TCE on fresh GAC was firstly performed until reaching the saturation to obtain a breakthrough curve. The TCE-saturated GAC was then regenerated with surfactant solution. The regeneration consisted of 3 main steps: 1) passing the surfactant solution through the GAC bed, 2) flushing the excess surfactant off with water, and 3) drying the bed with warm air. After the regeneration step, the dynamic adsorption of TCE on the regenerated GAC was carried out in a similar manner to obtain a subsequent breakthrough curve. From these two curves, the adsorption capacity of the fresh and regenerated GAC were calculated and compared. A simplified flow scheme of the experimental setup is shown in Fig. 5.2.

Dynamic Adsorption

The dynamic adsorption of TCE from air stream on GAC at 30°C was performed by packing the desired amount of GAC (2.7-9 g) in a solvent-resistant jacketed column (2.5 cm in diameter) at a corresponding bed height (1-3.6 cm). The height of the bed was fixed by adjustable plunger to minimize the void volume in the bed. The temperature of column was kept constant at 30°C by circulating water from the temperature controlled water bath to the jacket of the column.



- AC = Adsorption column GC = Gas chromatograph
 GC-HS = Gas chromatography head space MFC = Mass flow controller
 TOC = Total organic carbon S = TCE saturator
 WB = Water bath

Figure 5.2 Schematic diagram of the experimental set up.

Prior to the adsorption experiment, the fresh GAC bed was dried by flowing dry air until the moisture content in effluent stream was less than 2% to ensure that the bed is completely dried. The moisture in the outlet air was measured by a digital hygrometer. A simulated contaminated air stream containing 5,000 ppmv TCE was then fed to the GAC bed at the flowrate of 450 mL/min. A mass balance was performed to determine the total amount of TCE adsorbed on GAC. The simulated TCE-contaminated air stream was generated by mixing air main stream and TCE saturated air stream in 500 mL mixing chamber before downward feeding to the adsorption column. The TCE-saturated air stream was generated by flowing a fraction of air stream at predetermined flowrate through a saturator filled with liquid TCE and immersed in temperature controlled cooling bath at 20°C. The TCE-saturated air stream was flowed into a mixing chamber where it was mixed with the air main stream. The flowrate of these two streams was controlled by a mass flow controller (MFC) in order to obtain desired TCE concentration in the influent stream of the adsorber. The concentration of TCE in the influent air stream (C_0) and the

concentration of TCE in the effluent air stream (C) from the GAC column were analyzed by using a gas chromatography (Perkin Elmer Model AutoSystem XL) equipped with a 10 port-valves auto sampler, and a data acquisition unit. The GC column used in GC was Carbowax. The detector used was a thermal conductivity detector (TCD) at 250°C. In order to ensure that the TCE-saturated air stream was saturated with TCE, a set of 2 saturators connected in series was used. It was found that there was no difference in TCE concentration in simulated TCE-contaminated air stream.

Regeneration

Desorption of sorbed TCE: The first step in regeneration is the desorption of sorbed TCE from TCE-saturated GAC using surfactant solution. This was performed by introducing the surfactant solution into the adsorption column as shown in Fig. 5.2. The temperature of GAC bed was kept at 30°C as mentioned above. A solution of sodium dodecyl sulfate at desired concentration (0.1-0.2 M.) was fed upward into the TCE-saturated GAC column at desired flowrate (5-15 mL/min). The fractions of effluent solution were periodically collected and analyzed by the gas chromatograph of Perkin Elmer model AutoSystem GC equipped with Headspace Sampler model HS of Perkin Elmer, and data acquisition.

Water flushing: The TCE-desorbed GAC was drained and switched to water flush line as shown in Fig. 5.2. The GAC bed was kept constant at any desired temperature (30-50°C) as previously described. Deionized water at desired temperature (30 and 70°C) was fed upward at a desired flow rate (5-15 mL/min). The fractions of effluent water were collected and analyzed by total organic carbon analyzer of Shimadzu Model 5000A.

Drying: After the GAC bed water flushing (or after desorption step) was drained and subjected to drying. The GAC bed was heated up to 50°C as mentioned above. Preheated air at 50°C was then fed to the adsorption column until the moisture in the

effluent air was less than 2%. The preheated air was obtained by flowing air through coil submerging in the 50°C water bath.

5.4 ADSORPTION/DESORPTION EXPERIMENTS

In order to gain more understanding on the mechanistic governing the desorption of SDS, the adsorption-desorption isotherms were generated at 30, 50 and 70°C. In this part, 99% SDS from Sigma Chemical Co. was used. A series of SDS solution at various concentrations ranging from 100 to 50,000 micromolar was prepared using deionized water. About 0.1 g pretreated GAC was placed in a 25 mL screw-cap vials and 10 mL SDS solution was added to the vials. The vials were covered with parafilm and capped and placed in shaking bath at desired temperature (30-70°C). The vials were shaken at speed of 100 rpm for 96 h. After equilibrium, the carbon and SDS solution were separated by centrifugation at 3,500 rpm for 5 min. The SDS containing in the solution was analyzed both before and after adsorption. After taking a certain volume of clear solution from the centrifuged mixture, the mixture was diluted with the factor of 5. The capped vials were placed in shaking bath and procedure previously described was conducted for desorption experiment.

5.5 RESULTS AND DISCUSSION

Effect of bed height

The aim of this part was to determine the minimum bed height, which provides a full length of breakthrough curves of both fresh and regenerated GAC. This will not only minimize the time of experiment but all chemicals used. The height of the GAC bed was varied from 1.3, 1.7, 2.4, and 3.6 cm or about 2.8, 4, 6, and 9 g of GAC, respectively. The flowrate of regenerant solution was 5 mL/min. From the experiments, the all breakthrough curves of the fresh GAC were complete. But for regenerated GAC without water flushing, only the breakthrough curve of

regenerated GAC at the height of 3.6 cm showed a full length. Therefore, those breakthrough curves of the bed height of 3.6 cm can be compared. Hence, activated carbon at bed height of 3.6 cm was used as the base length for further investigation: the effect of rinsing, regenerant flow rate, regenerant concentration, flow rate of flushing water and temperature of flushing water. Furthermore, for both fresh and regenerated activated carbon, it can be obviously seen that the higher of the bed height the higher TCE adsorbed on GAC. The corresponded breakthrough curves showed reduction in the adsorption capacity of activated carbon for all cases. For all cases, the desorption of TCE were higher than 95% as illustrated by the case of the bed height of 3.6 cm (9 g of C) shown in Fig. 5.3. The corresponding breakthrough curves of each bed height were shown in Fig. 5.4.

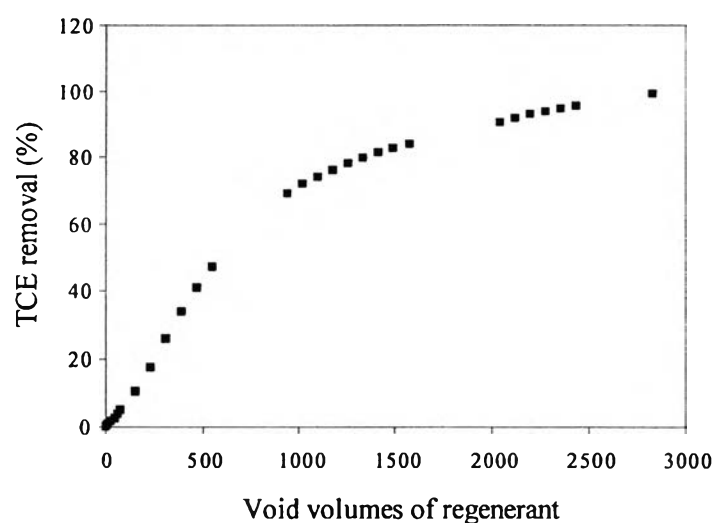
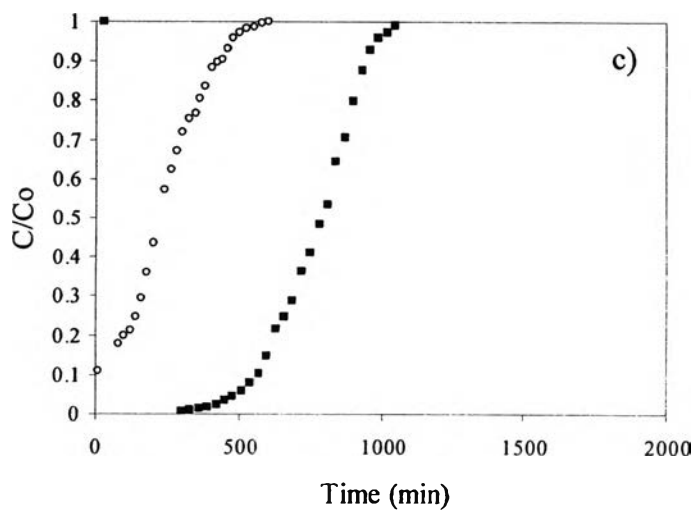
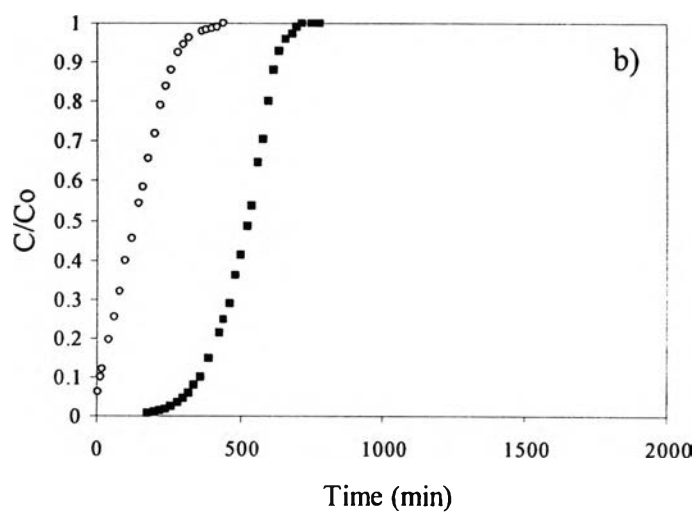
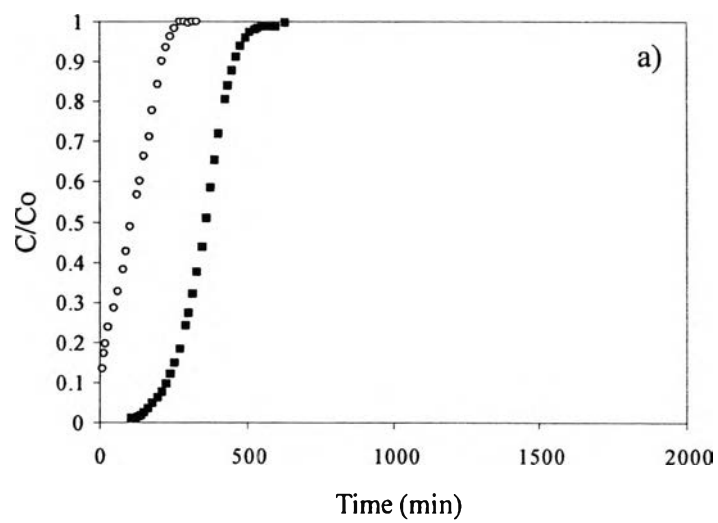
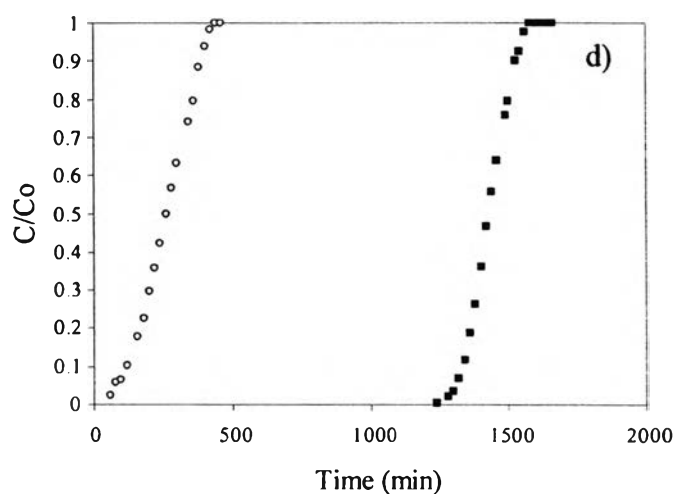


Figure 5.3 TCE removal by using 0.1 M SDS regenerant and regenerant flowrate of 5 mL/min and 30°C.





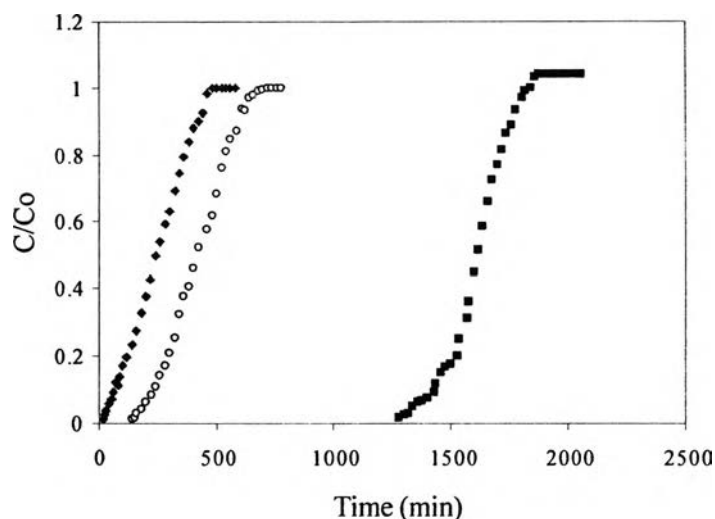
■ fresh activated carbon ○ regenerated activated carbon

Figure 5.4 Breakthrough curves of fresh and regenerated activated carbons at 30°C and different bed heights. (a) 1.3 cm (b) 1.7 cm (c) 2.4 cm (d) 3.6 cm.

Effect of water flushing

After desorption of TCE, the activated carbon bed was flushed with water at 30°C with a flowrate of 5 mL/min. This process was conducted until the difference in the SDS concentration in effluent water was less than 0.1% to ensure that SDS was removed as much as possible. The breakthrough curve of the regenerated activated carbon with water flushing showed a higher adsorptive capacity than the regenerated activated carbon without water flushing by the factor of 2, as shown in Fig. 5.5. The improvement of its adsorptive capacity could be due to the removal of SDS adsorbed on the GAC surface by water flushing, thus, providing more adsorption site on GAC for TCE to adsorb. However, the adsorption capacity of the regenerated carbon with water flushing was relatively low (about 15% of its original capacity). It was postulated that this might be due to the strong adsorption of SDS on the GAC, concurrently the adsorption-desorption isotherm of SDS on/from GAC surface at 30°C was conducted in order to prove the hypothesis. In addition, the adsorption-

desorption isotherms at higher temperature, 50 and 70°C, were studied to assess conditions at which residual SDS can be efficiently removed.



- fresh activated carbon
- regenerated activated carbon with water flushing
- ◆ regenerated activated carbon without water flushing

Figure 5.5 Breakthrough curves of regenerated activated carbon with and without water flushing at 30°C and a water flowrate of 5 mL/min as compared to fresh activated carbon.

Effect of regenerant flowrate

Three sets of experiments using TCE saturated activated carbon were carried out with 0.1 M SDS at flowrates of 5, 10, and 15 mL/min (corresponding to superficial velocities of 1, 2, 3 cm/min, respectively) to desorb TCE from the carbon surface. The concentration profiles of TCE in SDS solution are shown in Fig. 5.6. All concentration profiles of TCE showed the same trend that, initially, concentration of TCE in effluent solution increased with the increase of SDS solution passing through

the bed and reached maximum before gradually decreased and finally almost constant. This indicates that at the beginning, TCE was easily desorbed from the carbon to the bulk solution of SDS and gradually become more difficult to desorb. Considering Fig. 5.6, one can see that the maximum TCE concentration of TCE was obtained at the same time. Moreover, the amounts of TCE desorbed were almost the same with the increase of the time of desorption as seen in Fig. 5.7. This indicates that at 0.1 M SDS concentration, the rate of TCE removal does not depend on flow rate of SDS solution but depends on the time contacting with SDS solution. It can be concluded that the rate of the TCE removal is controlled by the internal mass transfer of TCE from micropore to bulk solution.

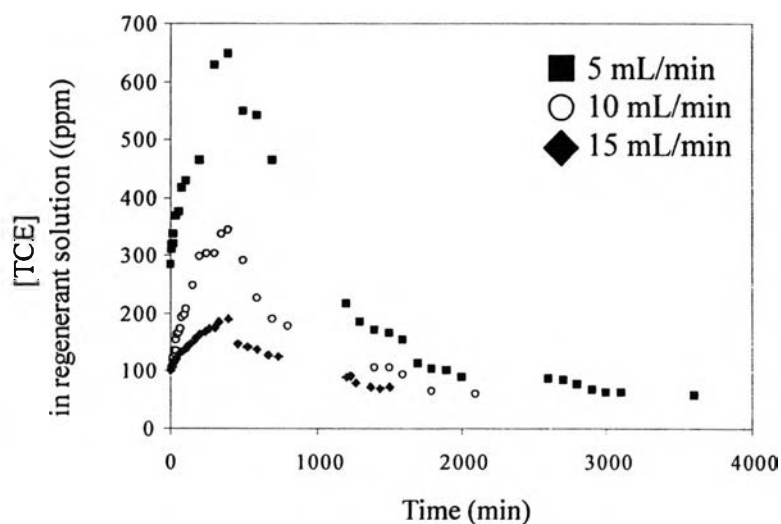


Figure 5.6 TCE concentration in regenerant solution as a function of regenerant flowrate

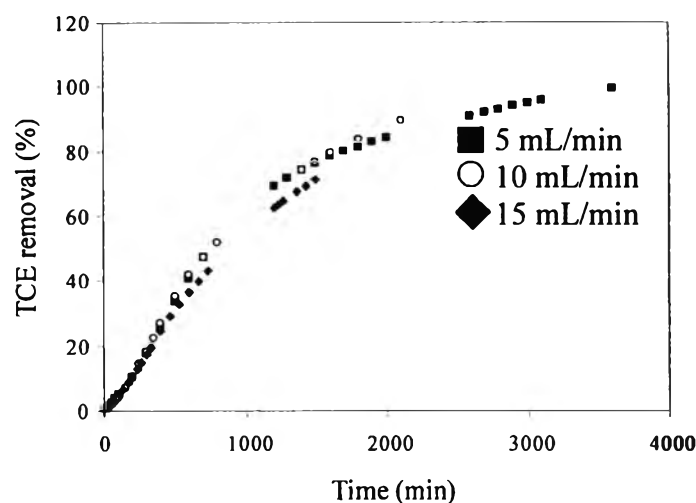


Figure 5.7 TCE removal at different regenerant flowrates and 30°C.

Effect of regenerant concentration

Two sets of experiments using TCE saturated GAC were conducted with 0.1 M and 0.2 M SDS at a flowrate of 5 mL/min to desorb TCE from the carbon surface. The concentration profiles of TCE in SDS solution are shown in Fig. 5.8. At the beginning, TCE concentration in regenerant solution with 0.2 M SDS was higher than that with the 0.1 M. This might be caused by TCE, which adsorbed in mesopores. The adsorbed TCE in the macropores is more easily desorbed than that in the micropore. However, in general, the amount of TCE desorbed was almost the same as the increase of the void volume (or time of desorption) as seen in Fig. 5.9. This indicates that the rate of TCE removal does not depend on concentration of SDS in the regenerant solution and implies that the TCE removal rate is controlled by the internal mass transfer of TCE from micropore to bulk solution.

Effect of water flowrate

Three sets of TCE desorbed GAC beds were flushed with deionized water to remove excess SDS in the bed void and the SDS adsorbed on carbon surface. The flowrates of flushing water were 5, 10, and 15 mL/min (corresponding to superficial

velocities of 1, 2, 3 cm/min, respectively). The results showed that there was no difference in the removal of SDS as shown in Fig. 5.10. This implies that the removal of SDS does not depend on flow rate of flushing water.

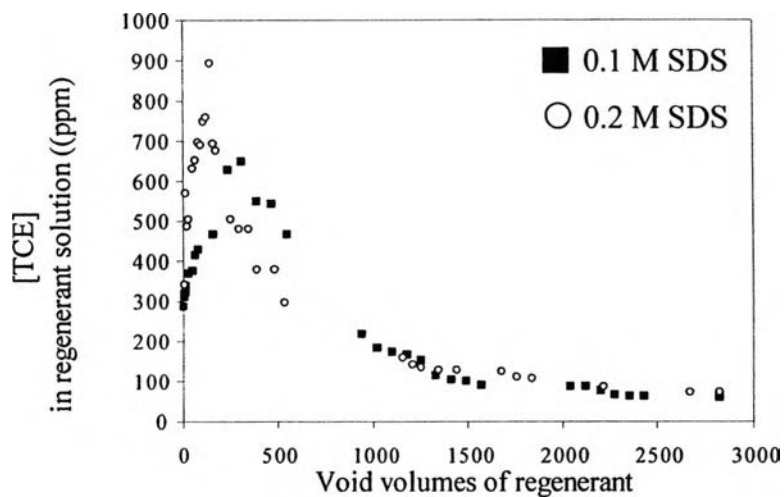


Figure 5.8 TCE concentration in regenerant solution as a function of regenerant concentration at 30°C.

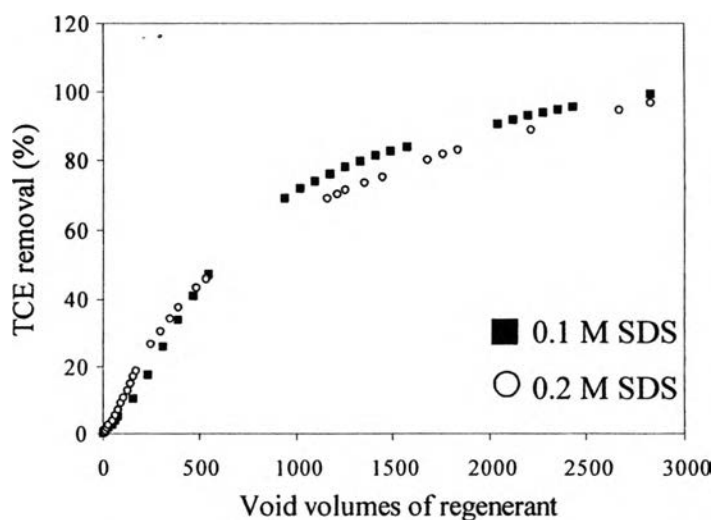


Figure 5.9 TCE concentration in regenerant solution as a function of regenerant concentration at 30°C.

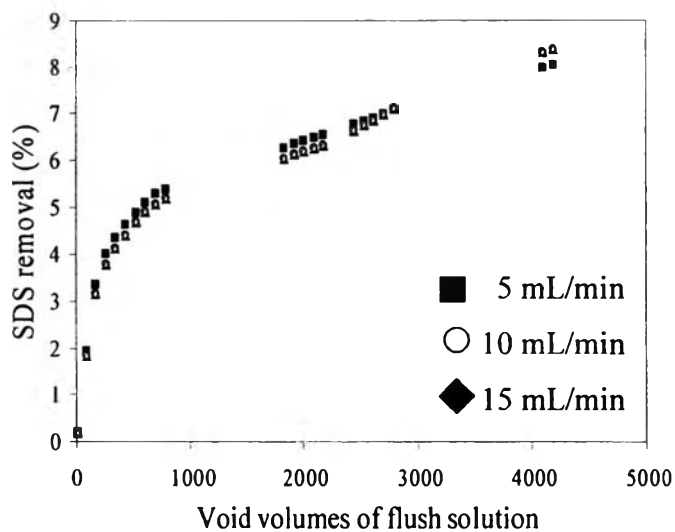


Figure 5.10 SDS removal at different flushing water flowrates at 30°C.

Effect of flushing water temperature

Two sets of TCE desorbed GAC beds were flushed with deionized water at 30°C and 50°C at a flow rate of 5 mL/min. The results shown in Fig. 5.11 indicate that the SDS removal was increased about 2 times when flushing water temperature was increased from 30°C to 50°C. This is consistent with the results obtained from the adsorption-desorption isotherms at 30°C and 50°C (shown in the next section).

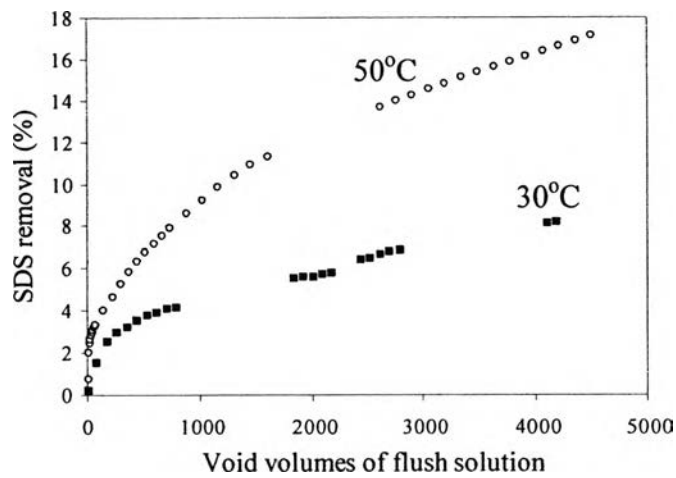


Figure 5.11 SDS removal at different flushing water temperature.

Adsorption-desorption isotherms

The adsorption-desorption isotherms of SDS on/from GAC surface at temperatures of 30, 50, and 70°C were studied to verify the difficulty of SDS removal at 30°C. The isotherms are shown in Fig. 5.12. As expected, there was hysteresis observed in the adsorption-desorption isotherm at 30°C. This means that the desorption of SDS at 30°C is very difficult and more efficient SDS removal can be achieved with higher temperature.

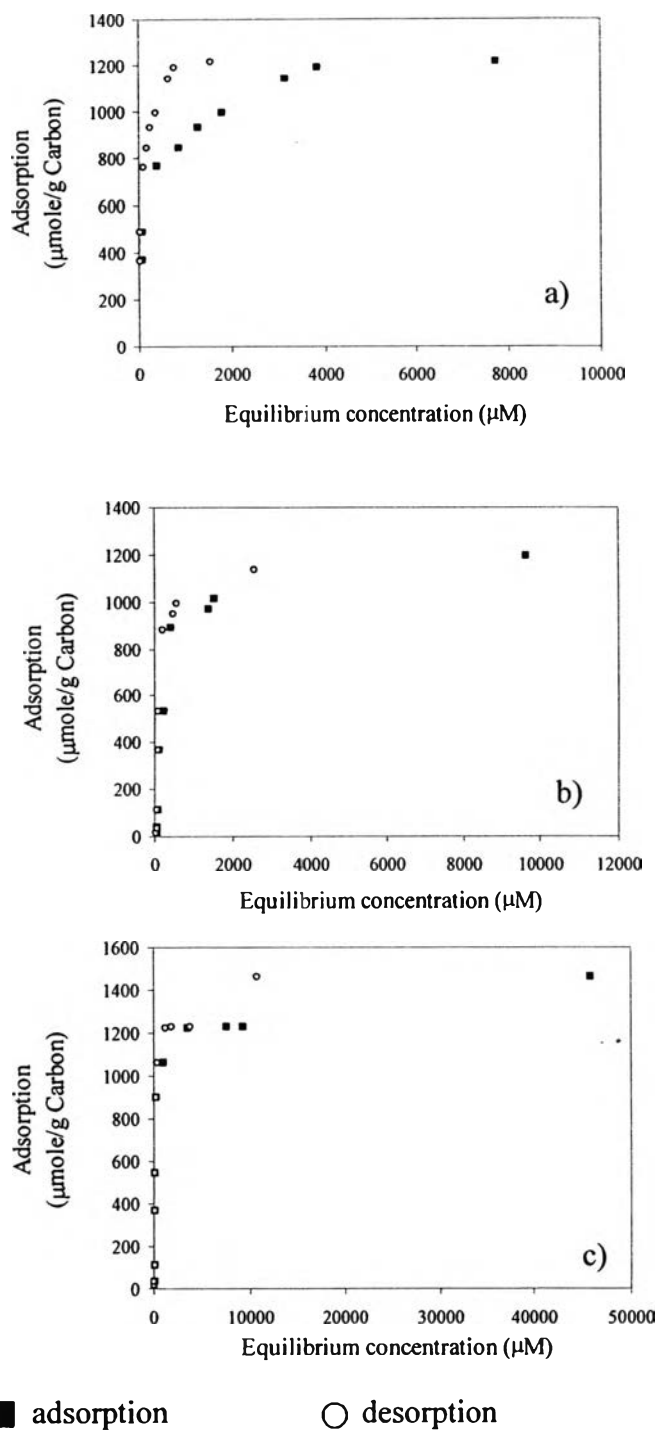


Figure 5.12 Adsorption-desorption isotherms of SDS on/from activated carbon (a) 30°C (b) 50°C (c) 70°C.

5.6 CONCLUSIONS

In this work, the regeneration of TCE saturated GAC 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 carbon by the factor of 2 compared with the regenerated carbon without the water flushing (12-13% and 5-6%, respectively). The adsorption capacity of the regenerated carbon was reduced to about 13% of its original capacity, which is similar to previous work using cationic surfactants and liquid phase application. TCE desorption by this method is internal mass transfer limited as the regenerant flow rate and SDS concentration in regenerant do not significantly affect the removal rate. The irreversibly adsorbed surfactant left as a heel following regeneration is very difficult to desorb. However, when flushing temperature increased from 30°C to 50°C the SDS removal increased twice comparing with SDS removal at flushing water temperature of 30°C. The adsorption-desorption isotherms indicate that residual SDS is difficult to remove by water at 30°C but the removal can be improved with flushing water at higher temperature.

NOMENCLATURE

- C Concentration of solute in effluent stream
- C₀ Concentration of solute in influent stream

5.7 ACKNOWLEDGEMENTS

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