



CHAPTER IV

***IN SITU* REGENERATION OF TRICHLOROETHYLENE ADSORBED GRANULAR ACTIVATED CARBON USING SODIUM DODECYL SULFATE**

4.1 ABSTRACT

An effective treatment of industrial gas streams containing volatile organic compounds (VOCs) is adsorption with granular activated carbon (GAC) as an adsorbent. After the exhaustion of adsorption capacity of GAC, it must be replaced or it must be regenerated. Current technology for carbon regeneration involves a thermal process, which is very costly due to a highly intense energy used and considerable loss of carbon. Therefore, there is of great interest to develop an economical regeneration process. In this work, the preliminary study on the regeneration of spent GAC in a packed bed adsorber using surfactant was conducted with the attempt to reduce the disposal of the spent carbon and extend its operating life time. The regeneration consisted of desorption of trichloroethylene (TCE) adsorbed on GAC with an anionic surfactant, sodium dodecyl sulfate (SDS), water flushing, and air-drying. The results showed that more than 95% of TCE adsorbed on GAC was removed by using 0.1 M SDS solution. It was also found that the water flushing had significant effect on the adsorption capacity of regenerated GAC. With water flushing at ambient temperature, the adsorption capacity of the regenerated carbon was approximately 2 times of that without water flushing. However, for both cases, the adsorption capacity of GAC after regeneration was drastically decreased. This is possibly due to residual surfactant remaining on the carbon after regeneration.

4.2 INTRODUCTION

Volatile organic compounds (VOCs) are among the most common air contaminants emitted by the chemical process industries (CPI) due to their widespread use as solvents, cleaners, and degreasers. Accordingly, VOCs emission

control is a major portion of the CPI's environmental activities [1]. This VOCs-contained gas streams have long been efficiently treated by means of adsorption process with activated carbon [2]. In process services, the activated carbon gradually adsorbs organic compounds from the streams. Eventually, its adsorption capacity is consumed as reaching the breakthrough concentration (the maximum acceptable concentration of the VOCs in effluent gas stream). At this point, the spent activated carbon must either be replaced with fresh carbon or be regenerated to restore its adsorptive capability. The predominant industrial practice use of the activated carbon is only once and disposal or thermal regeneration [3-4]. Use of activated carbon only once is not only inefficient use of carbon but generates excessive waste to the environment. Even though, current regeneration methods of spent activated carbon: thermal regenerations are available but these regeneration methods are energy intensive. In some cases, the activated carbon is deteriorated [5] resulting in requirement of makeup activated carbon and the additional cost is required for unloading the activated carbon from the adsorber and transporting it to the regeneration site. Therefore, there is a considerable impetus to develop an economical regeneration process. Alternative regeneration methods have been searched with attempt to decrease the regeneration cost and to develop for practical use in industry. These methods are hot water regeneration [6], chemical regeneration [7], solvent regeneration [3], supercritical extraction [8, 9], electrochemical regeneration [10], and microwave regeneration [11]. However, these methods have not been settled for industrial use.

Regeneration of GAC by using surfactant as a regenerant is a promising alternative method. Since surfactant possesses two predominant properties: (1) It can lower interfacial tension by adsorption at the interface of two surface. (2) It can solubilize organic compounds in to its micelles (aggregates of surfactant molecules) by preferential solubilization into the core or the palisade layer of micelles. Its lowering interfacial tension property enhances surfactant monomers to reach in to the micropore of the activated carbon by diffusion to replace organic compounds adsorbed on the activated carbon surface by adsorption of surfactant monomer. This phenomenon causes desorption of the organic compounds from the activated carbon

surface. The desorbed organic compounds are migrated out from the activated carbon pore into the bulk solution by the stream of surfactant solution. Then the organic compounds solubilize in to the core or parlisade layer (a region between the core and the outer layer of micelle) of the micelles of surfactant. So the solubility of the organic compound in bulk solution is higher than in water. The significant and potential advantages of this regeneration method are: (1) It can be performed *in situ*. (2) Elimination of the loss of carbon resulting from thermal regeneration. (3) Recovery of valuable adsorbate is possible. (4) The surfactant can be reused by elimination of organic compounds from surfactant solution. The regeneration process consists of 3 main steps: (1) Desorption of adsorbate by passing the surfactant solution through the activated carbon bed. (2) Flushing of the excess surfactant off with water. (3) Drying of the bed with warm air. The process strategy is shown in Figure 4.1.

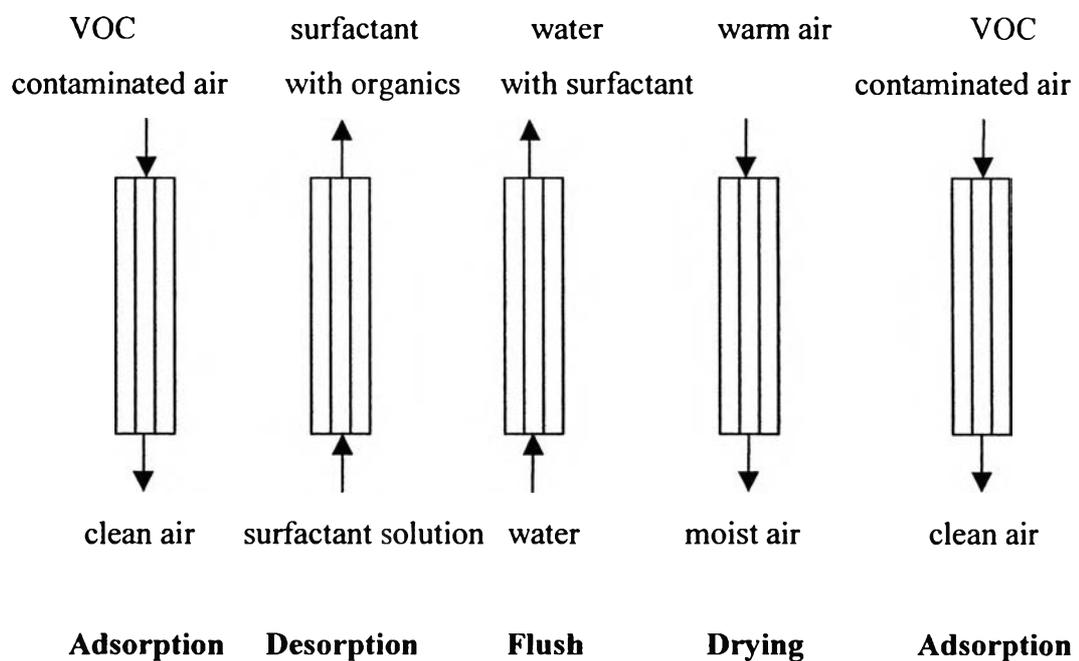


Figure 4.1 Process strategy for surfactant-enhanced carbon regeneration.

Previous studies on surfactant enhanced carbon regeneration (SECR) [12, 13] have demonstrated that the method can provide good removal of the adsorbate. In liquid phase, Blakeburn and Scamehorn [12] found that the first approximately 80% of *tert*-butylphenol can be removed using a regenerant stream containing a cationic surfactant with a reasonable volume of regenerant. The majority of surfactant can be removed by water flush, but large volumes of water are needed for reaching complete removal of surfactant from the carbon. The effective adsorption capacity of the carbon upon subsequent cycles was found to be reduced by this method. However, details of breakthrough curves were not obtained. Bhummasobhana *et al* [14] found that 50% of phenol can be removed using 0.1 M sodium dodecyl sulfate at 500 pore volume of regenerant and nearly 90% of phenol can be removed at 2,000 pore volumes. The breakthrough curves for the adsorption of phenol on fresh and regenerated activated carbon were also obtained.

In vapor phase application, Roberts *et al* [13] studied the application of SECR to regenerate carbon containing either toluene or amyl acetate. However, the details of the breakthrough curves were not generated.

The focus of this study is a preliminary investigation of regeneration of gas phase application GAC. The simulated volatile organic compound used as a contaminant in air stream was trichloroethylene (TCE) and sodium doecyl sulfate, an anionic surfactant was used as a regenerant.

4.3 MATERIALS AND METHODS

Materials

A BPL 4x10 granular activated carbon 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. The carbon was pretreated by boiling in deionized water for 1 h, followed by rinsing with deionized water 3 times then drying in oven at 110°C for 24 h. The treated carbon was stored in a dessicator. An analytical grade trichloroethylene (TCE) was chosen

as the model adsorbate. It was purchased from Lab-Scan Analytical Sciences (Dublin, Ireland). The relevant properties of TCE are shown in Table 4.1. Air zero grade was purchased from Thai Industrial Gas (Rayong, Thailand). Sodium dodecyl sulfate (chemical grade) used as the regenerant was supplied by APS Ajax Finechem (Auburn, NSW, Australia). Surfactant solution was prepared with demineralized water. Some relevant properties of SDS are shown in Table 4.2.

Table 4.1 Some relevant properties of trichloroethylene

Property	Value
Molecular weight	131.39
Solubility in water, at 25 °C (mg/L)	1,100
Boiling point (°C)	87.2

Table 4.2 Some relevant properties of sodium dodecyl sulfate

Property	Value
Molecular weight	288.38
Critical micelle concentration, at 25 °C (mM)	8.2
Aggregate no. in water (molecules)	80 [14.1]

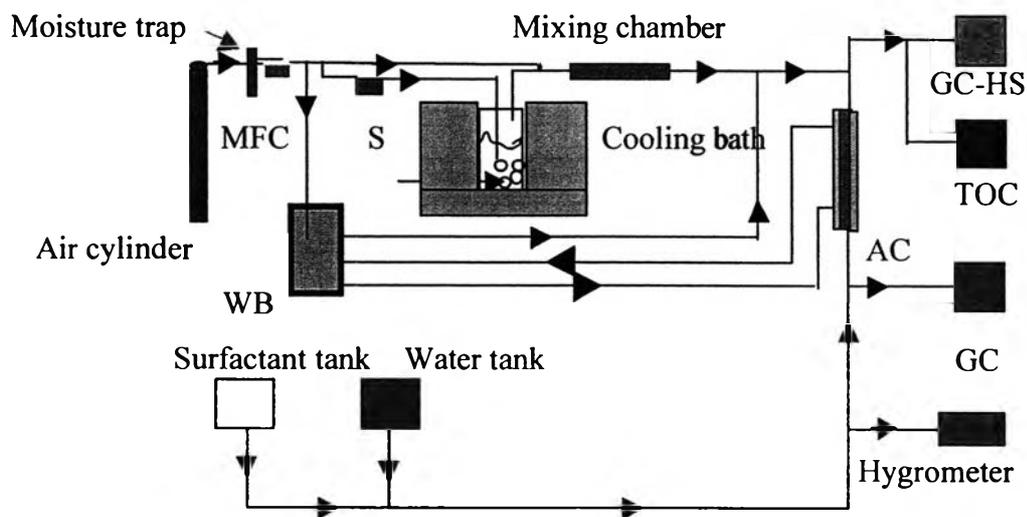
Methods

A dynamic adsorption of TCE on fresh GAC was firstly performed until reaching the saturation to obtain breakthrough curve. The TCE-saturated GAC was then regenerated with surfactant solution. The regeneration consisted of 3 main steps: (1) pass the surfactant solution through the activated carbon bed, (2) flush the excess surfactant off with water, and (3) dry the bed with warm air. After regeneration step, the dynamic adsorption of TCE on regenerated GAC was carried out in a similar manner to obtain another breakthrough curve. From these two curves, the adsorption

capacity of the fresh and the regenerated GAC could be calculated and compared. A simplified flow scheme of experimental setup is shown in Figure 4.2.

Dynamic Adsorption Experiments

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 solvent-resistant jacketed column (2.5 cm in diameter) at corresponding bed height (1-3.6 cm). The height of the bed was fixed with 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 water jacket of the column. This provided isothermal condition throughout the adsorption study. 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 determined by a digital hygrometer. A simulated contaminated air stream containing 5,000 ppm TCE was then fed to the GAC bed at a flowrate of 450 ml/min. A mass balance was performed to determine the total amount of TCE adsorbed on GAC.



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 4.2 Schematic diagram of experimental apparatus.

The simulated TCE-contaminated air stream was generated by mixing air main stream and TCE saturated air stream in a 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 a predetermined flow rate 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 flows of these two streams were controlled by a mass flow controller (MFC) in order to obtain desired TCE concentration in the influent stream. 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 of Perkin Elmer Model AutoSystem XL equipped with a 10 port valves auto sampler, and data acquisition unit. The GC column used 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 Experiments

Desorption of sorbed TCE: The first step in regeneration was the desorption of sorbed TCE from TCE-saturated GAC using surfactant solution. This was performed by introducing the surfactant solution into the column as shown in Figure 4.2. The GAC bed was still kept at 30°C as mentioned above. A solution of sodium dodecyl sulfate at desired concentration was fed upward into the TCE-saturated GAC column at a flow rate of 5 mL/min. The fractions of effluent solution were periodically collected and analysed by the gas chromatograph.

Water flushing: The TCE-desorbed GAC was drained and switched to water flush line as shown in Figure 4.2. The GAC bed was kept constant 30°C as indicated above. Deionized water was fed upward at a flow rate of 5 mL/min. The fractions of effluent water were collected and analyzed for surfactant concentration by using a total organic carbon analyzer of Shimadzu Model 5000A. For investigation of effect of washing, the washing step was skipped.

Drying : The GAC bed after water flush was drained and subjected to drying. The GAC bed was heated up to 50°C by circulating water from the water bath to the water jacket of the column. Preheated air was then fed to column by flowing air through coil submerging in the 50°C water bath until the moisture in effluent air was less than 2%.

4.4 RESULTS AND DISCUSSION

Adsorption of TCE in GAC packed column

The first attempt in this part of the study was to find appropriate bed height for the dynamic adsorption of TCE on fresh and regenerated carbon. The height of

the packing was varied from 1-3.6 cm by using different amount of carbon in the column and the adsorption experiments were carried out to obtain the breakthrough curves of the fresh carbon and regenerated carbon without water flush. Figures 4.3a-4.3d show the breakthrough curves obtained from the adsorption of TCE on fresh carbon and regenerated carbon in the column packed with GAC at 2.79, 4, 6, and 9 g, respectively. The results clearly demonstrate that the height of carbon less than 3.6 cm was not enough to obtain complete breakthrough curve as seen in Figure 4.3a-4.3c. From Figure 4.3d, the GAC with bed height of 3.6 cm (corresponding to GAC weight of 9 g) was the appropriate bed height, which the complete breakthrough curve of TCE was achieved. This bed height was used for all experiments. The pore volume, the corresponding volume of gas containing in an adsorber bed, is 0.76 mL/g carbon.

For the fresh activated carbon, saturation occurred at around 1,500 min (98,000 pore volumes). The calculated equilibrium amount of TCE adsorbed was equal to 3.87 g or 3.27 mmole TCE/g of carbon which agrees reasonably well with the value calculated from the reported value in the literature [17].

Desorption of TCE

When the column was flushed with 0.1 M SDS (approximately 12 CMC) at a flow rate of 5 mL/min, the adsorbed TCE was rapidly desorbed at the first 300 pore volumes. Then the desorption of TCE rapidly decreases until around 1,400 pore volumes and gradually decreases for the rest of the passing pore volumes, as shown in Figure 4.4. From calculation, approximately 25% of TCE was easily desorbed at the first 300 pore volumes, another 55% was moderately desorbed until around 1,400 pore volumes, and the rest was relatively hard to be desorbed as can be seen in Figure 4.5. The result can be related to the pore size distribution of the carbon which has been reported previously [18]. This indicates that 25% of TCE was adsorbed on outer surface and mesopore of carbon, 55% was adsorbed in major micropore, and the last 20% was adsorbed in branched micropore (or submicropore) of the carbon.

However, more than 95% removal of TCE was achieved within around 2,600 pore volumes as shown in Figure 4.5.

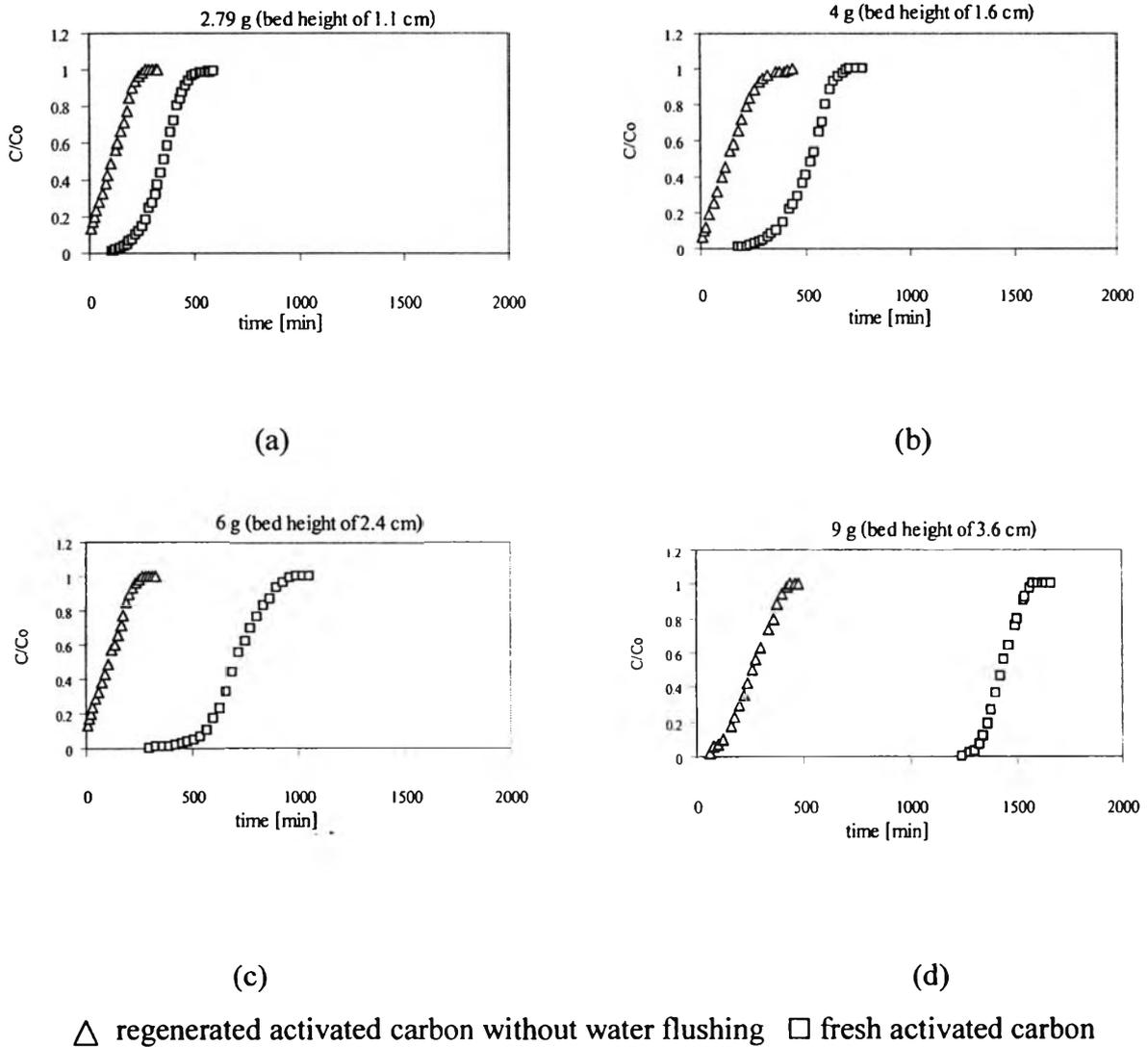


Figure 4.3 Breakthrough curves of fresh and non-flushed regenerated GAC at several bed heights.

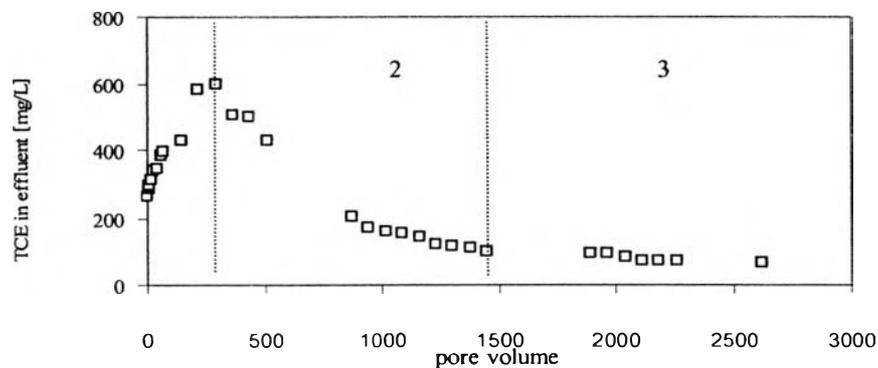


Figure 4.4 Concentration of TCE in the SDS solution.

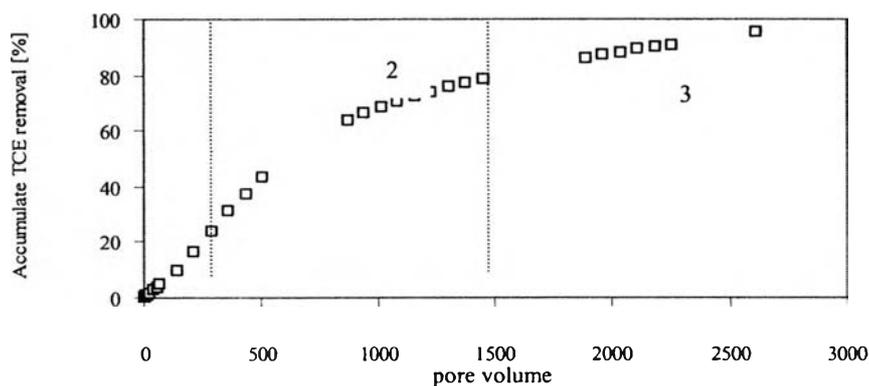


Figure 4.5 Total TCE removal from GAC by SDS.

Water flush

During the flushing step, the SDS concentration in effluent at the first portion is the highest then rapidly decreases and relatively constant, as shown in Figure 4.6. From the results, it is likely that all majority of SDS in the pore of the bed was flushed out by the replacement of water into the pore. Then the adsorbed SDS on the surface of the carbon was removed by diffusion due to the gradient of concentration of SDS on the surface and in the bulk solution, at which no SDS was presented in the bulk solution. The removal of SDS is shown in Figure 4.7.

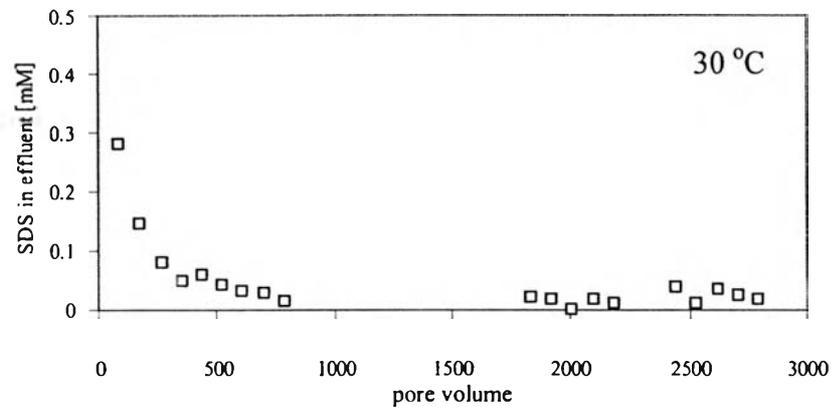


Figure 4.6 SDS concentration in flushing water.

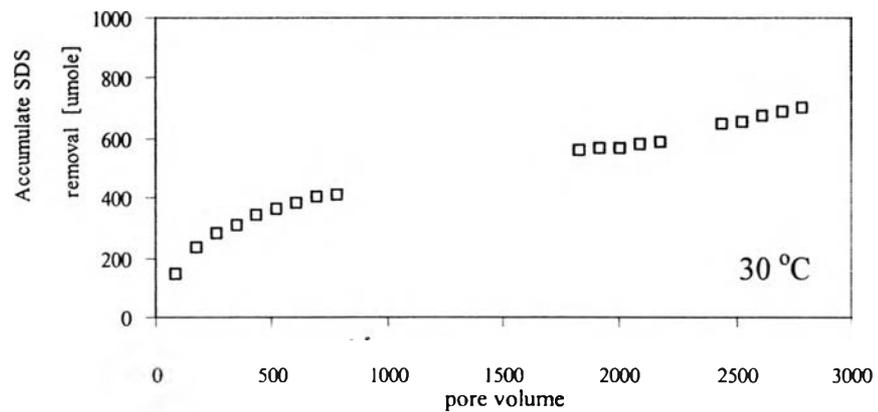
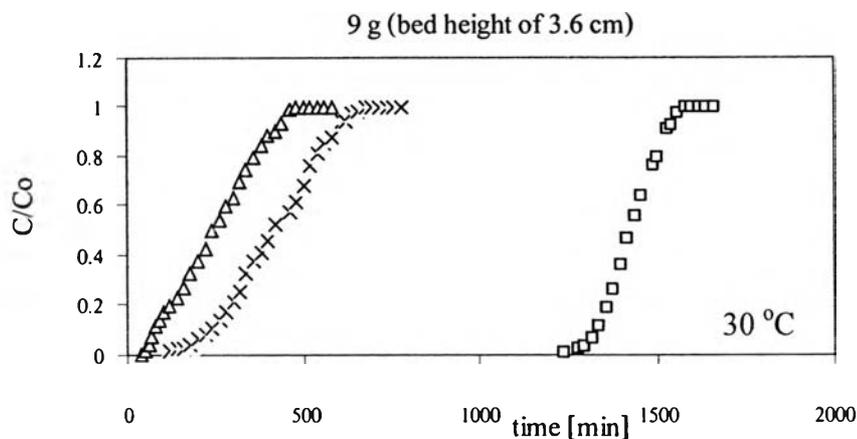


Figure 4.7 SDS removal from GAC.

From breakthrough curves shown in Figure 4.8, the regenerated GAC with or without flushing drastically decreases significantly in adsorption capacities compared to the fresh GAC. However, the adsorption capacity of flushed regenerated GAC was higher than non-flushed GAC. If the acceptable concentration of TCE was set to 100 ppm, 5% of the capacity of the fresh carbon could be recovered after regeneration without flush and 10% for the regeneration with flush. It is indicated that the adsorption capacity of regenerated GAC with flush is higher than the regenerated GAC without flush by the factor of 2.



\triangle regenerated activated carbon without water flushing \times regenerated activated carbon with water flushing
 \square fresh activated carbon

Figure 4.8 Breakthrough curves of the regenerated GAC with and without water flushing as compared to that of fresh activated carbon.

4.5 CONCLUSIONS

This work has shown that GAC used in vapor phase application for TCE adsorption can effectively be regenerated *in situ* by washing with surfactant solution in a continuous operation. Most of TCE adsorbed (more than 95%) on GAC in a packed bed adsorber was desorbed by using an ionic surfactant, sodium dodecyl sulfate (SDS), at approximately 2,500-3,000 pore volume. However, when the regenerated GAC was reused in subsequent TCE adsorption cycle, the dramatic decrease in the adsorption capacity was observed. It is speculated that this is mainly due to the residual surfactant remains adsorbed on the GAC the surfactant regeneration step. Further experiment has been carried out to demonstrate that the residual surfactant on GAC could be removed by flush the column with hot water in order to improve the adsorption capacity in subsequent adsorption.

4.6 REFERENCES

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