Recovery of Bis(2-chloroisopropyl) Ether and 1,2-Dichloropropane from the Waste Water from Propylene Oxide Production

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Received 12 December 1995

Adsorption of chloroorganic compounds bis(2-chloroisopropyl) ether and 1,2-dichloropropane from the waste water on active carbon A and synthetic adsorbents (Amberlite XAD-4, Amberosorbe XE-348) was examined. Amberlite XAD-4 shows the highest adsorptivity (10 g cm^{-3}) and dynamic adsorption (15 g dm^{-3}). Desorption by hot acetone allowed bed regeneration and concentrated (10—14 mass %) solution of bis(2-chloroisopropyl) ether and 1,2-dichloropropane was obtained.

During propylene oxide production by the chlorohydrins method 40—50 t of the waste water per 1 t propylene oxide is formed. It contains about 2.5 t of calcium or sodium chloride and chloroorganic compounds. For every 1 t of propylene oxide 115 kg of 1,2-dichloroethane, 70 kg of bis(2-chloroisopropyl) ether, 59 kg of propylene glycol, and inessential from the material balance point of view amounts of propionic aldehyde, chloroacetone, 1,3-dichloropropane, 1,2,3-trichloropropane, and propylene chlorohydrins are formed. Most of the organic compounds are recovered at propylene oxide distillation. For every 1 t of propylene oxide 13 kg 1,2-dichloropropane, 9 kg bis(2-chloroisopropyl) ether and 45 kg propylene glycol are carried out with the waste water. In modernized plants of propylene oxide production calcium hydroxide is replaced by sodium hydroxide or catholyte from diaphragm electrolysis [1]. The waste water from the saponification, after removing of the organic compounds, concentration or rock-salt saturation is returned to the electrolysis. Organic compounds can be removed by the biological method, adsorption method or by both these methods. It is known from the literature [2] that good results of propylene glycol adsorption from the concentrated solution of the brine are obtained on the synthetic adsorbent Amberosorbe XE-348. Other chloroorganic compounds such as epichlorohydrin and dichloropropanols are recovered from the waste water by adsorption on active carbon A [3, 4]. In this work results of the selection of adsorbents for recovery of chloroorganic compounds bis(2-chloroisopropyl) ether and 1,2-dichloropropane from the waste water from propylene oxide production and methods of regeneration of adsorbents are presented.

EXPERIMENTAL

Waste water composition, w/mass %: bis(2-chloroisopropyl) ether 0.13, 1,2-dichloropropane 0.01, propylene glycol 0.015, sodium chloride 0.35, was used for the adsorption.

Following adsorbents were used: active carbon A from the Destructive Wood Distillation Works in Hajnówka, Poland, Amberosorbe XE-348 and Amberlite XAD-4 from Rohm and Haas, GmbH, Deutschland. The most important properties of adsorbents are shown in Table 1.

Methods of the Adsorption

The adsorption was carried out in a glass tube of 15 mm i.d., packed with 15 cm^3 of adsorbent. The height of the adsorbent layer was 8—9 cm according to its bulk density. The waste water was introduced by peristaltic pump with the rate 100 cm^3 h^{-1} from the bottom of the adsorber. Adsorption was conducted until relative concentration of the sum of chloroorganic compounds (bis(2-chloroisopropyl) ether and 1,2-dichloropropane) was $w/w_o \approx 1$ (w – instantaneous chloroorganic compounds mass fraction in effluent, behind the adsorber, w_o – initial chloroorganic compounds mass fraction in brine, before the adsorber). Adsorption was conducted at temperatures between 20—25 °C.

Methods of the Desorption

Desorptions were performed by hot acetone (40 °C), vapour acetone (57 °C) or water vapour (220 °C) and the desorption medium was introduced in an inverse

Table 1. Characteristics of Adsorbents

Adsorbent	Bulk density	Specific surface	Pore capacity	Average pore diameter
	g dm^{-3}	m^2 g^{-1}	cm^3 g^{-1}	nm
Carbon A	500	740	0.28	1.5
Amberlite XAD-4	350	750	0.98	5
Amberosorbe XE-348	660	500	0.50	40 % $\leq$ 4, 60 % $\in$ ⟨4; 30⟩

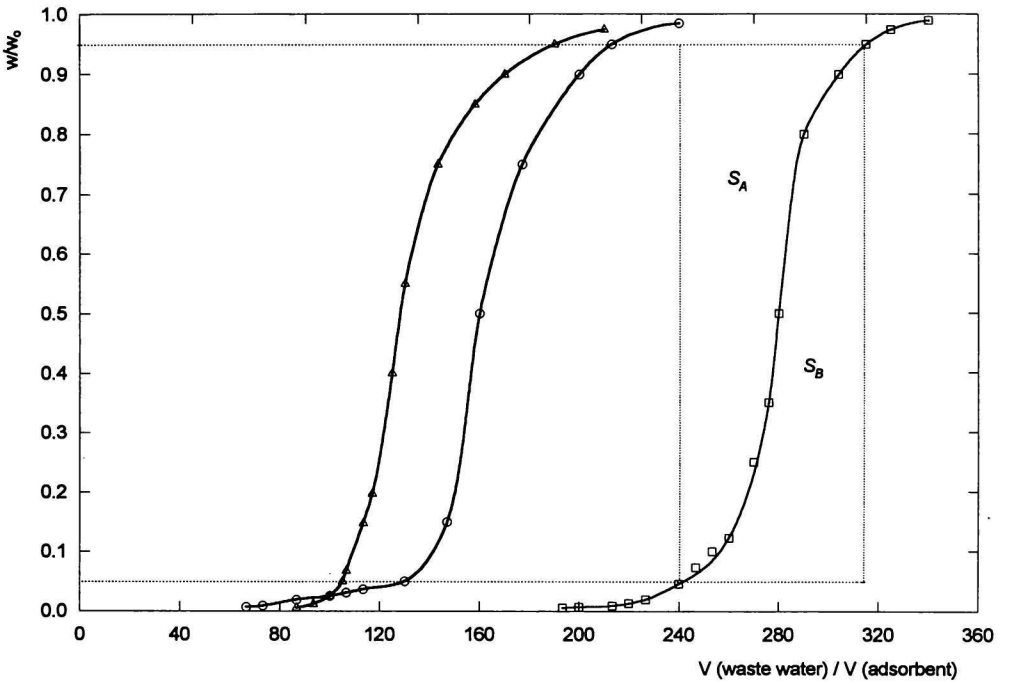

Fig. 1. The course of adsorption of the sum of chloroorganic compounds (bis(2-chloroisopropyl) ether and 1,2-dichloropropane) on various adsorbents. ○ Active carbon, △ Amberosorbe XE-348, □ Amberlite XAD-4.

direction to the adsorption. Displacement flow rate was 80 cm^3 h^{-1}.

Analytical Method

Organic compounds concentrations in brine before and after adsorption, in acetone or aqueous solutions, were determined by gas chromatography. The analyses were carried out using a Chrom 5 type chromatograph with a flame ionization detector. A 2 m × 3 mm stainless steel column, packed with Chromosorb P AW (80/100 mesh), coated with 10 mass % silicone oil OV 225 was used. The temperature of the column was linearly programmed in the range 120—140 °C, the temperature gradient was 2 °C min^{-1}. The injection and detection temperatures were 210 °C.

RESULTS AND DISCUSSION

Adsorption

The course of adsorption of the above-mentioned compounds on active carbon A, Amberlite XAD-4, and Amberosorbe XE-348 is shown in Fig. 1. It results in the highest adsorptivity for Amberlite XAD-4. Fig. 2 shows the course of adsorption of the individual organic compounds on this adsorbent. Adsorptivities of bis(2-chloroisopropyl) ether and 1,2-dichloropropane are similarly high. Propylene glycol was not all adsorbed and it was in effluent at the level $w_1/w_{o1} = 1$ at the volume ratio of the waste water to the volume adsorbent $Z = 1$ (w_{o1} – initial propylene glycol mass fraction in brine before the adsorber, w_1 – instantaneous propylene glycol mass fraction in effluent behind the adsorber).

Setting-up results of the adsorption of all the chloroorganic compounds on the mentioned adsorbents are shown in Table 2 (adsorptivity). These values were obtained in the second and the next adsorption-desorption cycles. Fresh adsorbent shows by 10—12 % higher adsorptivity. From the course of the adsorption curve of all the chloroorganic compounds the following values were calculated:

Z_b – the amount of the brine flowing through the

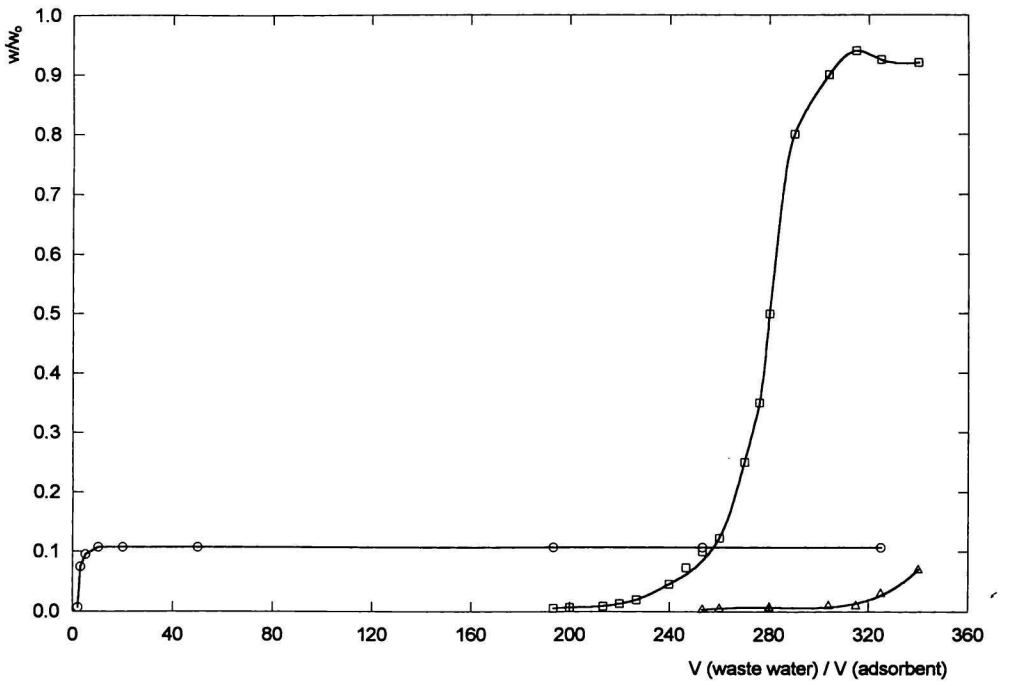

Fig. 2. The course of adsorption of individual compounds from the waste water on Amberlite XAD-4. □ Bis(2-chloroisopropyl) ether, ○ propylene glycol, △ 1,2-dichloropropane.

Table 2. Results of Organic Compounds Adsorption from the Waste Water

	Adsorbent		
	Carbon A	Amberosorbe XE-348	Amberlite XAD-4
Adsorptivity, a/(g dm^{-3})	145	152	336
Dynamic adsorption, a_d/(g dm^{-3})	160	130	300
Desorption degree/%	95	95	87
The amount of the brine flowing till the moment of bed breakthrough, Z_b	130	105	240
The amount of the brine flowing till the saturation of the bed, Z_s	213	190	315
Length of active adsorbent layer, L_o/cm	3.9	4.5	2.2

bed until the breakthrough time of the bed, *i.e.* the amount of effluent obtained at the moment after which the mass fraction of chloroorganic compounds behind the adsorber is a higher limiting value $w_b = 0.05w_o$,

Z_s – the amount of the brine flowing through the bed until the saturation time of the bed, *i.e.* the amount of effluent obtained to the moment after which the mass fraction of chloroorganic compounds behind the adsorber is $w_s = 0.95w_o$,

a_d – the dynamic adsorption, *i.e.* the total amount of adsorbed chloroorganic compounds until the breakthrough time of the bed.

Dynamic adsorption was calculated from the formula [5]

$$a_d = (w_o - w_{min}) \cdot Z_b$$

w_{min} is the minimum mass fraction of the sum of chloroorganic compounds in effluent, determining the obtained degree of the brine purification. The sufficient degree of purification was assumed to be 95 %. Thus $w_{min} = 0.05w_o$, Z_b is the value taken from Fig. 1. Additionally the length of the effective working layer of adsorbent L_o was determined applying a modified *Michaels* formula [6]

$$L_o = L\frac{Z_s - Z_b}{Z_s - (1-\varphi)(Z_s - Z_b)}$$

where L is the total length of adsorbent layer, φ the coefficient of symmetry of adsorption curves

$$\varphi = \frac{S_A}{S_A + S_B}$$

S_A is the area above the adsorption curve till the moment of bed saturation (between $w/w_o = 0.05$—0.95, Fig. 1), S_B is the area below the adsorption

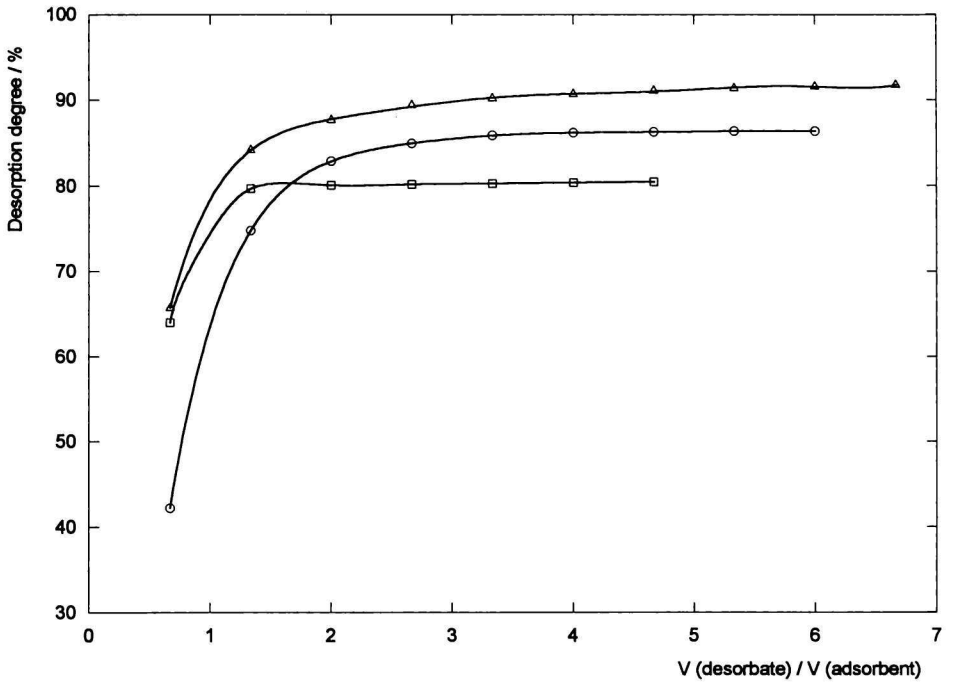

Fig. 3. The course of changed desorption degree of the sum of chloroorganic compounds as a function of the desorbate volume to bed volume ratio. ○ Active carbon, △ Amberosorbe XE-348, □ Amberlite XAD-4.

curve, till the moment of bed saturation (between $w/w_o = 0.05$—0.95, Fig. 1). Values Z_b, Z_s, a_d, and L_o are presented in Table 2.

Desorption

The best desorption results were obtained by the use of hot acetone (40 °C). Desorption degrees of the mentioned chloroorganic compounds are unlike, depending on the kind of adsorbent and are as follows: 80 mass % on Amberlite XAD-4, 85 mass % on active carbon A, 90 mass % on Amberosorbe XE-348. Amount of acetone necessary in this process is 1.5—2 bed volume multiple in the case of Amberlite XAD-4 and 3.5—4 in the case of the remaining adsorbents. The course of the change of the desorption degree of the sum of chloroorganic compounds by hot acetone from these adsorbents as a function of the ratio of desorbate volume to the bed volume is shown in Fig. 3. Amount of acetone necessary to obtain constant desorption degree is the same in the case of hot acetone and acetone vapour. The course of changes of concentrations of chloroorganic compounds at the desorption by hot acetone as a function of the ratio of desorbate volume to the bed volume is shown in Fig. 4. It results that at the beginning of desorption when the volume ratio of desorbate to bed is < 1, the chloroorganic compounds concentration is high. By the use of acetone in the amount of 1.5 bed volume multiple the concentration of ether in acetone is about 1 mass %.

Steam desorption at the temperature 220 °C also gives unsatisfactory results. Desorption degrees were

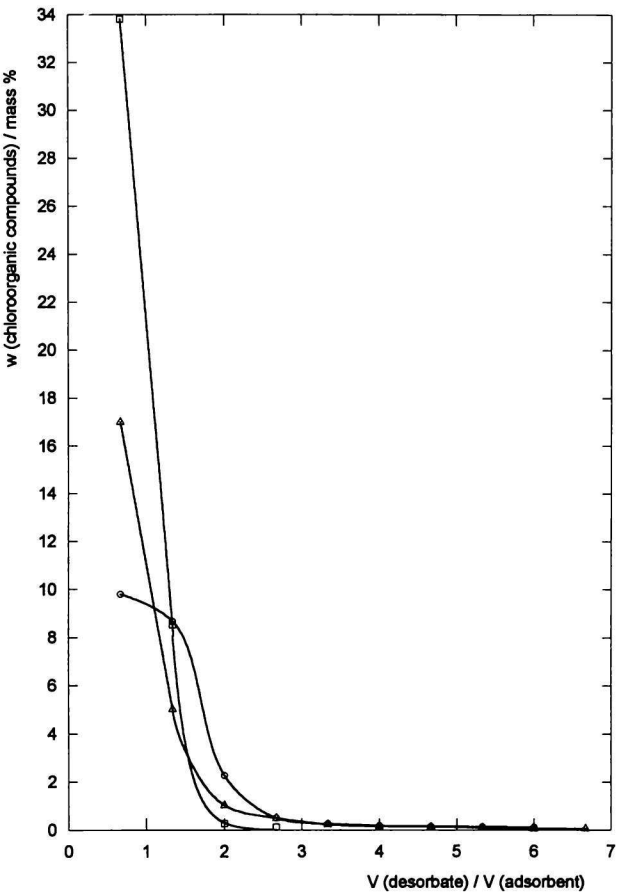

Fig. 4. The course of changed mass fractions of the sum of chloroorganic compounds as a function of the desorbate volume to bed volume ratio. ○ Active carbon, △ Amberosorbe XE-348, □ Amberlite XAD-4.

at the 25—50 mass % level, at the volume ratio of desorbate to bed 7—9.

CONCLUSION

Amberlite XAD-4 is the best adsorbent for the recovery of chloroorganic compounds (bis(2-chloroisopropyl) ether and 1,2-dichloropropane) from the waste water from propylene oxide production. The adsorptivity of all of the aforementioned compounds on this adsorbent is 350 g dm^{-3}. The propylene glycol was not practically adsorbed. It was adsorbed on Amberosorbe XE-348 [2]. Good results of desorption of chloroorganic compounds were obtained by the use of hot acetone (40 °C) in the amount 1.5—2 bed volume multiple. Desorption degree was 80 mass %. By the use of Amberlite XAD-4 for removal of chloroorganic compounds and Amberosorbe XE-348 for propylene glycol [2] any of the organic compounds could be removed from the waste water.

REFERENCES

1. Schulze, J. and Weiser, M., *Chem. Ind. 37,* 175 (1985).
2. Milchert, E., Goc, W., Lewandowski, G., and Myszkowski, J., *Polish J. Appl. Chem. 39,* 395 (1995).
3. Milchert, E., Goc, W., and Myszkowski, J., *J. Chem. Technol. Biotechnol. 56,* 109 (1993).
4. Milchert, E., Myszkowski, J., and Goc, W., *Chem. Stos. 31,* 275 (1987).
5. Hudzik, K., Jędrzejak, A., Paderewski, M., and Szpilski, W., *Przem. Chem. 65,* 366 (1986).
6. Michaels, A. S., *Ind. Eng. Chem. 44,* 1922 (1952).