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NOTE

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Abstract

The separation characteristics of cellulose acetate/reverse osmosis (RO) membranes toward trace levels of lindane in water were investigated. A large fraction of this pesticide readily traversed the membrane; another portion, although tenaciously sorbed in or on the membrane, was slowly released into the product water. The implications of these observations on RO systems for municipal, domestic, and hospital use are discussed.

INTRODUCTION

Reverse osmosis (RO) separation techniques have gained considerable stature in recent years (*1*). The current approach involves the use of polymer membranes with controlled porosity and well-defined chemical and physical adsorption properties in order to achieve separation. Commercial applications include selective removal of ions and organics by small experimental water treatment plants and by laboratories producing high quality water for electronics and medical uses. At present, an RO primary process module for mobile hospital wastewater re-use is under development by the United States Army (*2*), and miniaturized RO systems are now finding their way into domestic water purifiers.

Systems using asymmetric cellulose acetate membranes have reached a high level of performance and dominate the RO field. Such systems function well and adequately discriminate against a wide range of inorganic and organic solutes (*1*, *3*, *4*). However, certain organic compounds are not rejected by such membranes; some interact with the membrane and can permeate selectively. Others are sorbed onto the polymer or else are concentrated at the surface of the membrane and eventually traverse the barrier (*1*, *3–9*). These substances include phenols, some organophosphorus compounds, halogenated pesticides, and other potentially deleterious substances which may reappear in the product water. Some of these compounds can be formed by oxidative water treatment or by chlorination disinfection processes.

The behavior of the membrane system toward each organic solute must be assessed empirically. However, knowledge of the separation pattern of RO membrane systems is essential, in particular for potable and clinical water. Little information is available as to the separation efficiency of cellulose acetate membranes with respect to hydrophobic pesticides. Therefore, the characteristics of asymmetric cellulose acetate membranes were studied using dilute aqueous solutions of lindane (γ-HCH), a widely used pesticide often found in water at trace levels (*4*).

EXPERIMENTAL

Aqueous solutions (6.8–7.0 mg/L) of γ-HCH were prepared using purified water stripped of all organochlorine contaminants according to a technique developed in this laboratory (*10*). Custom-made, radial flow, all-stainless steel RO cells (*11*) and conventional cellulose acetate membranes (*12*) were used. Membranes were subjected to a 10% aqueous ethanol wash at 3450 kPa followed by a pure water wash at 6900 kPa for 7 to 8 hr. Aqueous feed solutions containing 3500 mg/L of sodium chloride were used to characterize the membranes according to previously described techniques (*12*).

Equilibration of aqueous solutions (300 mL) of γ-HCH in the feed reservoir and RO cell system was achieved by circulating the solutions at 23 ± 2°C and at a flow rate of 1.5 mL/min which corresponded to a system pressure of 6200 to 6900 kPa. An aliquot (25 mL) of the feed solution was analyzed at the onset of each run. Flow of the feed solution was adjusted to obtain a recycled feed-to-product volume ratio of 4:1. For each run, 225 mL of feed solution was allowed to permeate through the membrane. Aliquots (25 mL) of feed and permeate were sampled for analysis at the end of the run. The determination of γ-HCH was carried out according to the method of Malaiyandi (*13*).

Attempts were made to strip γ-HCH from the cellulose acetate membrane *in situ* since considerable amounts of the γ-HCH were unaccounted for and were assumed to be retained by the membrane. The membrane was washed with water, and 10 and 20% aqueous ethanol solutions. After each wash sequence (see Table 2), 50 mL portions of permeate were collected for determining extracted γ-HCH content. The analysis of γ-HCH in binary water–ethanol mixtures is impractical using the analytical method (*13*), and therefore only one set of analysis was carried out. At the end of wash Runs #1 and 2, the membrane was removed and ethyl ether extraction of the membrane, according to the method of Kurtz (*8*), gave a recovery of 58 μg out of the total unretrieved γ-HCH (≈ 1400 μg; see Table 2, Runs #1 and 2). More of this pesticide was found in the hexane extract of the dimethylacetamide solution of the same membrane, but could not be quantified due to incomplete extraction by hexane of γ-HCH from the polar phase and due to the interference of dimethylacetamide during GC-EC analysis.

RESULTS AND DISCUSSIONS

Three series of RO separations were carried out using two CA-316 cellulose acetate films from the same membrane casting run. An average distribution of 36 and 24 ± 1.0% of the initial quantity of γ-HCH was found, respectively, in recycled feed and permeate (product) solutions. Thus only 60% of the total γ-HCH was accounted for by mass balance. The remaining 40% of γ-HCH was unaccounted for and was assumed to be adsorbed by the membrane. Therefore, attempts were made to strip membranes of bound γ-HCH without removing them from the RO cell. The amounts of retained γ-HCH leached in the water wash from the first membrane are shown in Table 1. Paradoxically, at a high flow rate (9.9

TABLE 1

Concentration of γ-HCH Found in Wash Water Permeate Using Membrane #1 *in situ*[a]

Volume of water permeated (L)	Flow rate (mL/min)	γ-HCH found (μg)
1.05	9.9	1.9
0.55	9.9	1.5
1.05	5.0	43.9
1.05	5.0	36.6
Σ3.70		Σ83.9

[a] Total γ-HCH used in RO experiment: 1771 μg. γ-HCH unaccounted for: 830 μg. % leached ≈ 10.

mL/min), the efficiency of leaching appeared to be lower than at 5.0 mL/min. Furthermore, only about 10% of the unaccounted pesticide could be recovered from a membrane of 12.6 cm^2 effective area with 3.7 L of wash water. An impractically large amount of time and water would be required to leach all the γ-HCH sorbed on or into the membrane.

The use of water–ethanol mixtures was investigated for expediting the removal of γ-HCH from another membrane. Aqueous solutions containing 10 and 20% ethanol were alternated with water wash and γ-HCH was determined in the washings. Table 2 summarizes these results. It

TABLE 2

Extraction Effeciency of Wash Process on Retained γ-HCH (Membrane #2 *in situ*)

Water/ethanol composition (%)	Permeate volume (L)	γ-HCH found (μg/L)[a]	γ-HCH found in wash permeate (%)
Run #1 (Unaccounted γ-HCH = 772 μg); Flow Rate = 2.0 mL/min			
100/0	2.00	5.1	1.3
90/10	0.10	7.5	0.1
100/0	0.05	14.8	0.1
90/10	0.25	N.D.	
100/0	0.10	N.D.	
"	0.05	2.0	0.0
90/10	0.25	N.D.	
100/0	0.20	N.D.	
"	0.05	1.6	0.0
90/10	0.25	N.D.	
100/0	0.70	N.D.	
"	0.05	1.6	0.0
"	0.50	1.0	0.1
90/10	0.50	N.D.	
100/0	1.00	N.D.	
"	0.05	1.2	0.0
80/20	0.50	N.D.	
100/0	0.95	N.D.	
"	0.05	1.3	0.0
Run #2 (Unaccounted γ-HCH = 639 μg)			
90/10	2.00	N.D.	
100/0	2.00	N.D.	
"	0.05	1.7	0.0
90/10	2.00	N.D.	
100/0	2.00	N.D.	
"	0.05	1.6	0.0

[a] N.D.: not determined.

can be seen that, when large amounts of the contaminant are present on the membrane, as in Run #1, the first wash with water removed 5.1 μg of the retained γ-HCH/L of the permeated wash. When 10% aqueous ethanol is used, the desorption rate has been enhanced (7.5 and 14.8 μg of γ-HCH/L of wash). However, it is apparent that, on further stripping of the membrane, the leaching efficiency drops to about 1.6 to 1.00 μg/L of wash. Even 20% aqueous ethanol failed to appreciably improve the leaching efficiency. Assuming that each wash sequence with ethanol and water leaches 7.5 and 14.8 μg of γ-HCH/L, respectively, then the total (pooled) volume of wash solution permeated would contain about 73 μg of the unaccounted γ-HCH (~9.3%).

In Run #2 (Membrane #2), the amount of γ-HCH retained may have been slightly diminished because of subtle changes in separation characteristics of the membrane after the 20% aqueous ethanol wash. However, washing sequentially with equal volumes of 10% aqueous ethanol and water showed, respectively, 1.7 and 1.6 μg of the pesticide per liter of permeated water wash. Perhaps less polar solvents could ultimately deplete the sorbed γ-HCH. Most of these solvent systems, however, have deleterious effects on the separation properties of many RO membranes.

Using coarse-porosity cellulose acetate membrane ultrafilters, Kurtz (*7*, *8*) showed that, although almost quantitative recovery of pesticides with aromatic nuclei was possible with solvent stripping techniques (diethyl ether), γ-HCH permeated through the membranes nearly unimpeded. However, Chian and co-workers (*5*), using commercial cellulose acetate membranes, claimed that 68% γ-HCH was sorbed on the membrane and only 0.5% of this contaminant traversed through at a driving pressure of about 4100 kPa. In the present study, it has been observed that, using 6200 to 6900 kPa, about 24% of the pesticide permeated through the membrane and 36% remained in the feed (by-pass). Destructive analysis of the membrane for γ-HCH has indicated that the major portion of the pesticide was tenaciously adsorbed and resisted quantitative removal using *in situ* stripping techniques.

CONCLUSION

It appears that γ-HCH and probably other related hydrophobic pesticides are poorly separated by contemporary cellulose acetate membrane RO systems and can appear in the product water. In addition, once exposed to such contaminants, RO membranes of the cellulose acetate type can remain contaminated and slowly release the pollutant to the product water long after the contaminated feed source has been removed. Such an event in clinical or potable water treatment plants using RO units would, in effect, vitiate the quality of the product water for a prolonged period. This form of membrane impairment, which is not usually tested for during routine maintenance of RO plants, should be guarded against.

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