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Adsorption of Polychlorinated Biphenyls from Aqueous Solutions and Sewage

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■ The adsorption of PCB's from synthetic aqueous solutions and raw sewage has been studied on a variety of adsorbents, including activated carbons, polymeric resins, polyvinyl chloride, and polyurethane foams. The carbons, foams, and XAD-2 strongly adsorbed the PCB's from aqueous solutions but were much less effective in raw sewage. The PVC, however, was very effective in raw sewage. A small-scale treatment unit was designed to demonstrate the feasibility of removing PCB's from sewage by this method.

Polychlorinated biphenyls, PCBs (tradename "Aroclor" in North America), are ubiquitous persistent pollutants of the environment with adverse ecological and toxicological effects (1). Since first being introduced in 1929, they have had widespread application in the electrical, paint, paper, and plastics industries (2) and have seen extensive use as hydraulic fluids and pesticide additives. It has been estimated that the total world production during the past 45 years has exceeded one million tons, of which about 400 000 tons have been released to the environment (3). Concerned for environmental quality, the Monsanto Co., the only North American producer of PCBs, restricted sales in 1971 to closed-system applications such as electrical capacitors and transformers; however, it is not known how many PCB-containing items are imported. Even with these restrictions, significant quantities of PCBs are still released into the environment.

For reasons that are not fully understood, raw municipal sewage often contains appreciable amounts of PCBs. For example, raw sewage entering the Hamilton Sewage Treatment plant contains on the order of 10 ppb PCB (mainly Aroclor 1254 and 1260 (4)). Considering Hamilton's flow rate of 230×10^6 L/day (62 mgd), this influent concentration corresponds to approximately one metric ton entering the plant annually. Concentrations of PCBs in sewage from other cities in southern Ontario, while not as high as that from Hamilton, are nevertheless still significant.

The physical chemical properties of PCBs, i.e., low vapor pressure, low aqueous solubility, and chemical inertness to water, acid, alkali, and heat make them extremely persistent environmental contaminants. There are 210 possible combinations of chlorine substitutions on the biphenyl nucleus but only about half that number are sterically possible. The number of PCBs occurring in the environment is of the order of 30–40 (1). The main contributors are the various isomers of pentachlorobiphenyl (Aroclor 1254), hexachlorobiphenyl (Aroclor 1260) and, to a lesser extent, trichlorobiphenyl (Aroclor 1242). However, some lower chlorinated isomers are present as a result of limited degradation. Degradation usually proceeds via successive dechlorination prior to breaking of the stable aromatic biphenyl structure (5).

The low solubility and hydrophobic nature of the chlorinated biphenyls make them relatively easy to adsorb from aqueous solution (6–8). The purpose of this work was to study the feasibility of extracting PCBs from raw sewage by adsorption onto various media. However, because of the varying nature of raw sewage, the adsorption was first studied using synthetic aqueous solutions of Aroclor 1254 and 1242 and then this was followed by measurements on raw sewage collected from the Hamilton Sewage Treatment plant.

Experimental

The two stock solutions of Aroclor 1242 and 1254 were prepared by vigorously mixing an excess of each Aroclor (Monsanto Co.) with water for 8 h, allowing the solutions to stand overnight and carefully decanting off the true aqueous phase. The water used was double distilled, the second distillation being from an all-glass system. The concentration of these solutions determined by gas chromatography was 45 ± 10 ppb, which is consistent with the published solubility for Aroclor 1254 of 56 ppb (6).

All solvents used were glass distilled pesticide grade (Caledon Laboratories Inc.). The activated carbons employed were lignite based Hydrodarco 400 (Atlas Chemical Industries) and anthracite-based Filtrasorb 400 (Calgon Corp.). These were pretreated by heating to 300 °C for 12 h, cooling, and twice extracting each 500 g with 2 L of benzene. The extracted carbon was then filtered and air dried. The polyurethane foams used were DSPC plugs (Canlab Supplies Ltd.) and Foams 1115 and 2328 (B. F. Goodrich Ltd.). The first two digits relate to the density, i.e., 1.1 and 2.3 lb/ft³ and the second two to the hardness. The foams were shredded and successively washed with *n*-hexane (several times), acetone, and distilled water. They were then air dried. The pretreatment was developed to remove trace organic contaminants from the surface of the foams. The macroreticular polystyrene resins Amberlite XAD-2 and XAD-4 (Rohm and Haas Co.) were pretreated by successively washing each 500 g of resin with 1-L batches of water, methanol, and water. The cleaned resins were stored in sealed glass containers under methanol to prevent them from drying out. Polyvinyl chloride chips (Monsanto Co.) were washed several times with *n*-hexane and air dried.

To determine the adsorption characteristics, 100-ml aliquots of stock Aroclor solutions were stirred vigorously with 8–10 weighed amounts of adsorbent for 30 min. The quantities of adsorbent were chosen to cover the range from 1 mg to approximately 1 g. After contacting, the adsorbent was removed by filtration through a prefilter pad (Millipore Ltd.). Five milliliters of *n*-hexane were then vigorously stirred with the filtrate for 45 min and the organic extract was withdrawn. These extracts were analyzed with a gas chromatograph (Varian series) equipped with an electron-capture detector (NiP). The gas column (1.8 m × 1.5 mm I.d.) was packed with 4% OV-101 and 6% OV-210 on Chromosorb W HP 80/100 mesh. Nitrogen was used as a carrier gas at 50 ml/min. The injection port, column, and detector temperatures were 250, 200, and 300 °C respectively. The amount of PCB adsorbed per unit weight of adsorbent was then calculated and plotted as a function of the equilibrium concentration of PCB remaining in solution.

Wastewater was collected from the Hamilton Sewage Treatment plant at the raw sewage inlet pipe. Sampling

was carried out using all-glass containers to ensure against adsorption onto container walls. The samples were stored at a constant temperature of 3 °C and in all cases were treated and/or extracted within 24 h of collection. The concentration of PCBs in the raw sewage ranged from 1–25 ppb but was usually between 5 and 13 ppb. In the evaluation of PCB adsorption from sewage, the procedure described previously for pure Aroclor solutions was followed except that 100-ml samples of raw sewage were stirred vigorously with the weighed adsorbent for 1 h and the adsorbent was separated by filtration through a 60-mesh, stainless steel screen. After washing, the screen did not retain any raw sewage and, with the exception of activated carbon, 100% separation of adsorbent was achieved. The samples were then twice extracted with 50 ml of *n*-hexane in 500-ml separator funnels. The aqueous portion was discarded and the organic phase, after being dried through 15 g of Na_2SO_4, was reduced to about 3 ml, using a rotary evaporator. The sample was purified by liquid–solid chromatography on a florisil support column using petroleum ether to elute the PCB fraction and then the eluate was evaporated to 3 ml (9). Prior to injection of the sample into the gas chromatograph, it was shaken with 0.2 ml mercury to remove residual sulfur compounds.

The PCBs in the samples were identified by comparison with chromatograms of standard Aroclors (Figure 1). Concentrations were determined from the peak height ratios of peaks A, B, C, and D for Aroclor 1254 and peaks of E, F, and G for Aroclor 1260. The minimum amount of PCB that could be detected with confidence by the GC was 22 p/g in a 10-μl injection. When we allowed for the increase in concentrations during extraction from the aqueous phase, the limit of detection in the aqueous samples was estimated as *0.5 ppb with an accuracy of ±0.1 ppb.*

Results and Discussion

Adsorption data for Aroclor 1254 and 1242 on activated lignite carbon, anthracite carbon, two polyurethane foams, Amberlite XAD-2 and XAD-4 and PVC are shown in log-log form in Figure 2. The weight of PCB adsorbed per unit weight of adsorbent is expressed as a function of the equilibrium concentration of PCB remaining in solution. The error bars have not been drawn on Figure 2 as they distract from the clarity of the data: In the worst cases, the diameter of the error circles corresponds to about two-and-one-half times the diameter of the marked points. These are insufficient to linearize the isotherms. The sets of data do not follow any of the common isotherm expressions- e.g., Langmuir, Freundlich, BET, and so forth, and consequently a theoretical interpretation of the results has not been attempted. It is evident that the two carbons and XAD-2 have the greatest adsorption capacities but a residual concentration of less than 3 ppb could not be obtained with lignite carbon. Both polyurethane foams appear to be good adsorbers with relatively high adsorption capacities and low residual levels. DiSPo polyurethane foam plugs were also evaluated but these had identical adsorption properties to the Goodrich foam 1115. The lower efficiency of XAD-4 is surprising in view of the similarity between XAD-2 and XAD-4— they differ only in pore diameter: 90 Å for XAD-2 and 50 Å for XAD-4. The lower efficiency of PVC can be explained by the lower surface area of this adsorbent. The surface area per unit weight is reported as 500–2000 $m^2\ g^{-1}$ for carbon; 750 $m^2\ g^{-1}$ for XAD-4 and 330 $m^2\ g^{-1}$ for XAD-2[10] but only 2×10^{-3} $m^2\ g^{-1}$ for PCV chips, there being no macroreticular structure in PVC. This gives an area ratio XAD-2/PVC of about 10^5.

There are two complicating conditions associated with adsorbing PCBs from raw sewage rather than synthetic aqueous solution: Sewage contains other hydrophobic organic matter that competes for the active sites on the adsorbent and much of the PCB has already adsorbed onto the suspended solids by the time the sewage reaches the treatment plant. The second condition can easily be demonstrated by filtering raw sewage and monitoring the change in PCB concentration. With typical raw sewage containing 10 ppb PCB, vacuum filtration through a Millipore prefilter pad resulted in the removal of about 75%. It is therefore necessary to find an adsorbent that is not only relatively specific to PCBs, but that also has sufficient af-

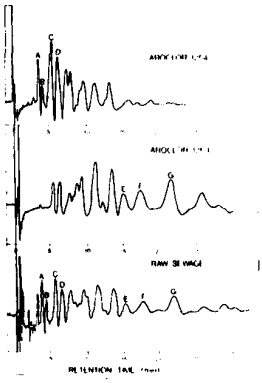

Figure 1. Gas chromatograms of Aroclor 1254, Aroclor 1260, and raw sewage

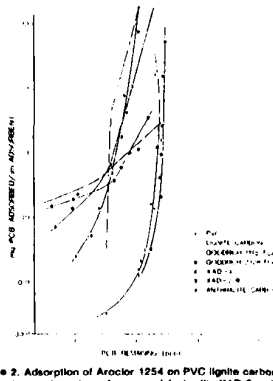

Figure 2. Adsorption of Aroclor 1254 on PVC lignite carbon, anthracite carbon, polyurethane foams, and Amberlite XAD-2 and XAD-4 Asterisk indicates adsorption of Aroclor 1242 rather than 1254

Table 1. Adsorption of PCBs from Raw Sewage

Adsorbent	% PCB adsorbed[a]
Lignite carbon	46 ± 3
Polyurethane foam	36 ± 3
Amberlite XAD-2	23 ± 2
Amberlite XAD-4	80 ± 3
PVC	73 ± 4

[a] Includes both Aroclors 1254 and 1260. Data are averaged over several determinations to minimize the variations in raw sewage.

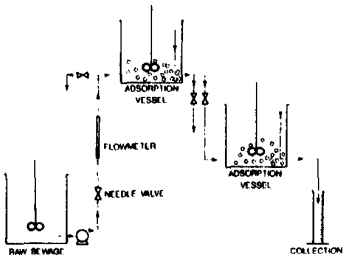

Figure 3. Apparatus used for tank adsorption experiments

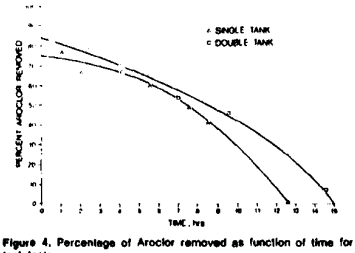

Figure 4. Percentage of Aroclor removed as function of time for tank tests

finity for the PCBs such that the PCB-suspended solid equilibrium is reversed.

Table I shows the percentage of PCB (including both Aroclor 1254 and 1260) adsorbed from raw sewage by five different media. With the exception of the PVC, approximately 1 g of each media was stirred with 200 ml of raw sewage for 45 min; approximately 10 g of PVC were used because of the lower surface area. To minimize the inconsistency of raw sewage, the data have been averaged over several determinations on different days and with different samples of sewage. The data indicate that PVC and XAD-4 are more effective than carbon or polyurethane foams in terms of percentage of PCB removed from raw sewage. This is somewhat surprising since the graphs for PCB adsorption for pure Aroclor solutions (Figure 2) would predict the opposite to be true. The likely reasons for this apparent anomaly are: The active sites on carbon are preferentially occupied by hydrophobic species in sewage other than PCBs and suspended solids adhere to the surface of carbon and foam acting as a barrier to further adsorption.

The above results indicate that PVC is superior to the other media for removing PCBs from sewage. To demonstrate the feasibility of a sewage treatment method based on PVC adsorption, a small-scale flow-through unit was designed, capable of treating about 3 l. of sewage per hour. The unit is shown in Figure 3. Each tank had a capacity of approximately 4.5 l. and was equipped with a paddle and baffle to ensure thorough agitation of the chips. Seven hundred grams of washed PVC were placed in each tank. The flow through the entire system was governed by the feed rate and this could be maintained at 50–60 ml/min (3 l./h) by adjustment of the needle valve on the inlet line. Effluent samples from both tanks were collected for analysis every 30 min.

The 50–60 ml/min flow rate was calculated on the basis of a 1-h retention time in each tank. Earlier batch equilibrium experiments with PVC and sewage had indicated that the adsorption equilibrium was established within the first 15 min of contact if sufficient agitation was employed. An arbitrary factor of four was then selected as a margin in the transfer from batch to flow through conditions.

Data from the flow through system are shown in graphical form in Figure 4. The efficiency of the single tank unit dropped from 75 to 47% during the first 8 h of operation while that of the twin tanks dropped from 94 to 53% over the same period. Although the second tank resulted in a 4–9% better removal of the PCBs, the extra cost involved with the two-stage process would probably not be justified in a large-scale application. Regeneration of the spent PVC was easily accomplished by successively flushing the chips with *n*-hexane, acetone, and water. The acetone and water rinses were to remove all traces of hexane from the surface of the PVC. The PVC was then ready for reuse.

In conclusion, PVC is very effective for adsorbing PCBs from raw sewage. A small-scale unit has been used to demonstrate the feasibility of the method but more engineering design research is required to optimize the technique. A system incorporating continual addition of fresh chips and removal of spent adsorbent would probably yield more uniform results than those illustrated in Figure 4. Further research into the regeneration of spent PVC and degradation of the recovered PCBs is currently under way in this laboratory. The PVC adsorption process should be equally as effective for treating concentrated industrial effluents as municipal sewage. Where a point source of PCB-containing effluent can be located, there would be obvious economic advantages to locating it prior to discharge into the sewer system.

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