

## CHITOSAN AS A TOOL FOR THE PURIFICATION OF WATERS

based on works by

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### INTRODUCTION

It is well known that surface waters are polluted not only by inorganic chemicals such as heavy metals, but also by organic compounds. Owing to the high sorption capacities of chitosan this polymer can be utilized as a tool for the epuration of wastewaters on polluted stream waters. Some typical examples of the application of chitosan to this kind of environmental problems are given here. They include the prevention of water pollution by highly toxic chlorinated aromatic compounds, metal ions, and dyes which are amply used in the textile industry. The recovery of proteins from wastewaters is an example of pollution control utilized in other industries, including shrimp processing, as well.

### ADSORPTION OF POLYCHLORINATED BIPHENYLS (PCB) ON CHITOSAN AND APPLICATION TO DECONTAMINATION OF POLLUTED STREAM WATERS (J. P. Thomé and Y. Van Daele)

In spite of the widespread contamination of aquatic environment by PCB (1), it is surprising that the ability of chitosan to eliminate these xenobiotics from natural waters has not been researched. However, standard methods for water purification used in water softening plants remain largely ineffective to remove PCB (2).

The present study deals with adsorption capabilities of chitosan towards PCB's and especially the most chlorinated ones which are the most frequently detected in aquatic ecosystems. Chitosan, manufactured from shrimp shells (*Crangon crangon*) according to the procedure described by Asano et al. (3), has been used in laboratory experiments to filter low and highly polluted water by PCB (4). The impact of such a treatment on the aquatic environment was tested by following PCB accumulation in young specimens of the sensitive teleost *Barbus barbus* kept in PCB contaminated water filtered or not through chitosan.

#### PCB adsorption capabilities

Adsorption capabilities of chitosan and other adsorbing agents (C 18, activated charcoal, sand and chitin) was tested using the following procedure:

100 ml distilled water spiked with 0.5 ppb PCB (Aroclor 1260) were filtered through cartridges packed with the material tested (100 to 200 mg). PCB remaining in water after filtration was extracted and analyzed by GLC as previously described (5).

According to Table I, sorption abilities of chitosan were more efficient than those of other tested organic substances. Indeed, up to 84% of the PCB present in water was adsorbed by 100 mg of chitosan. Chitin, the structure of which is close to that of chitosan, also had relatively good adsorption properties towards PCB but the reproducibility was poor. Furthermore, the efficiency of chitin was not significantly different from that of activated charcoal and sand ( $P < 0.01$ ).

The concentration of PCB on chitosan was higher than that measured on the other adsorbing materials. C<sub>18</sub> could be used as an efficient PCB adsorbing medium, but its high cost makes it unsuitable for application on an industrial scale.

#### Decontamination of PCB polluted stream water and impact on a test fish species

The ability of chitosan to remove PCB from contaminated stream water was tested using a dynamic flow through a system composed of two 50 liter glass tanks. At the beginning of the experiment, tanks were filled with natural pond water free of PCB. Polluted water (0.5 ppb Aroclor 1260) filtered or not through chromatographic columns packed with 1 to 10 g chitosan enriched, at a constant rate (36 l/day), each of experimental tanks. Chitosan was replaced every day. Thirty barbels (one year old, mean weight:  $1.365 \pm 0.55$  g), originating from experimental fish farms, were placed in each of the experimental tanks. Analyses of PCB concentrations in water and in whole fish were carried out as a function of time as previously described (5).

The evolution of PCB concentration in water (Bob), without filtration on chitosan, was quite similar to the theoretical curve (Bth) quoted in Figure 1 ( $\chi^2$  test:  $P < 0.01$ ).

The amount of PCB in fish linearly increased during 120 h of progressive contamination, reaching a maximum mean value (1.6 ppm) after 120 h and then slowly resuming a lower level.

Table I. Efficiency of various materials to remove PCB from distilled water (100 ml) spiked with 0.5 ppb PCB

adsorbing material		mean percentage of adsorption $\pm$ S.D.	Concentration of PCB on adsorbent $\pm$ S.D. (ng/g)
chitosan	(100 mg)	$83.3 \pm 7.5$	$416 \pm 35$
chitin	(100 mg)	$66.1 \pm 33$	$330 \pm 153$
activated charcoal	(200 mg)	$66.6 \pm 1.2$	$166.4 \pm 3$
sand	(200 mg)	$59.2 \pm 3.6$	$148 \pm 9$
C <sub>18</sub>	(150 mg)	$97 \pm 4.1$	$323 \pm 14$

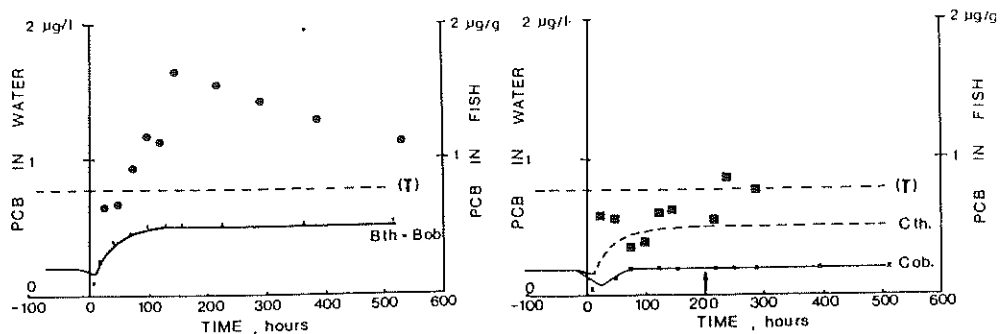


Figure 1 : Evolution of the PCB concentrations in water and in fish (●) in experimental tank receiving contaminated water without filtration on chitosan. Level of contamination of control fish (---T).

Figure 2 : Evolution of PCB concentrations in water (Cob.) and in fish (■) after filtration through chitosan of PCB polluted stream water. Level of contamination of control fish (---T).

The results quoted in Figure 2 were obtained after the filtration of the PCB contaminated stream water on chitosan. The concentrations of PCB in filtered water reached only 0.2 ppb instead of 0.5 ppb and remained unchanged during the 250 h of the experiment. One gram chitosan is thus sufficient to eliminate more than 60 % of PCB from 0.5 ppb polluted stream water (36 liters). Efficiency of such columns allowed the maintenance of contamination in fish at a non toxic level (<1 ppm) (6). Fish contamination in such a water was quite similar to that of controls. Experience has proved that larger amounts of chitosan (10 g) did not result in further purification. As a consequence, while the efficiency of chitosan was not sufficient to completely eliminate PCB from water, it however appeared to be quite sufficient to protect the animals against any further intoxication.

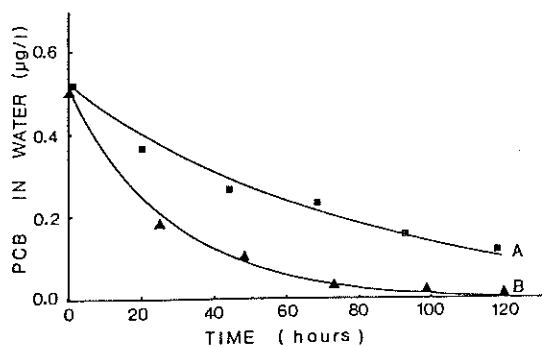


Figure 3 : Evolution of PCB concentrations in water containing 0.5 ppb Arcolor 1260 during filtration in a closed loop system through activated charcoal (1.5 kg)(A curve) and through activated charcoal (1.5 kg) + chitosan (75g)(B curve).

### Elimination of PCB from contaminated water in steady state

The procedure of filtration is suitable to protect "clean" natural water from contamination by PCB polluted effluents. However its efficiency could be very poor to eliminate PCB from water already contaminated by these toxics. With this in mind, we filtered 50 liters of PCB contaminated water (0.5 ppb) in a closed loop system using a chitosan filter (75 g) provided with an activated charcoal filter (1.5 kg). Water circulation was achieved by a pump at a rate of 180 l/h.

Complete removal of PCB from water was rapidly obtained, after less than 120 hours (B curve in Fig. 3). With an activated charcoal filter, without chitosan, concentrations decreased only to 0.2 ppb after the same time (A curve). Activated charcoal would work as an adsorbent of a fraction of PCB present in water but principally as a filter towards particles in suspension able to saturate adsorption sites of chitosan.

The highly efficient purification of PCB contaminated water using a chitosan filter could find favourable application to environment preservation. Chitosan appears to be much more efficient than activated charcoal and chitin for a nearly identical cost. Its powerful adsorption capabilities towards most of the persistent toxics found in aquatic environment make chitosan one of the most suitable polymers to be used for elimination of non biodegradable toxics.

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### ADSORPTION OF DYESTUFFS ON CHITOSAN

(B. Venkatrao, A. Baradarajan and C. A. Sastry)

Effluents from dyehouses, when discharged into any watercourse, at once become obvious on account of the high tinctorial value of many dyes currently used for dyeing a variety of natural and synthetic fibres. Removal of colour from dye waste waters by adsorption has been studied extensively in the recent years. A wide variety of adsorbents have been employed (1-7). More recently, chitin has been used in the removal of colour from direct and acid dyes (8, 9). However, there has only been a limited mention of the adsorption characteristics of chitosan on dyes (10).