Bioregeneration of granular activated carbon: an investigation by radiochemical compounds and microbreakdown

P le Cloirec[1]*, G Martin[1], T Bernard[2].
[1]*Laboratoire Chimie des Nuisances et Genie de l'Environnement, ENSCR, Avenue du General Leclerc, 35000, Rennes, France.*
[2]*UER Sciences de la Vie et de l'Environnement, Universite de Rennes I, 35000, Rennes, France.*

Abstract

The use of a labelled adsorbable biodegradable substance (phenol) in association with a microbreakdown of the media is proposed to study adsorption, diffusion and bioregeneration profiles on an activated carbon grain. The bioregeneration is shown by comparing labelled phenol profiles inside the media before and after biological treatment. The presence of bacteria enables the pores to be cleaned. The depth of bioregeneration is found to be 0,35 mm after a contact time of 100 h between bacteria and activated carbon with adsorbed phenol.

Introduction

Activated carbon beds, used in water and waste-water treatment are colonized to different degrees by bacteria. This phenomenon has been described by numerous workers using various techniques, including scanning electron microscopy (Weber *et al.*, 1978; Gaid *et al.*, 1979; Lafrance *et al.*, 1983), enumeration of bacteria (Werner, 1983) and ATP measurements (Gaid, 1981; Lemarchand, 1981). However, if the presence of bacteria is obvious there are still questions about the interactions between solute and/or substrate, porous media and bacteria (Bancroft *et al.*, 1983; Maloney *et al.*, 1984). This subject has given rise to a great deal of discussion and several previous workers have shown interesting properties of biological activated carbon filters regarding the removal of organic or inorganic compounds. The mechanisms of adsorption/biodegradation seem to be very complex. Gaid (1981), Gaid *et al.* (1982) and Martin *et al.* (1982) proposed a two-phase mechanism involving complementary adsorption and biodegradation-bioregeneration. Peel and Benedek (1983) preferred slow adsorption rather than biodegradation as an explantion for the removal of inert organic compounds. Li and Digiano, (1983) reported enhanced biodegradation on activated carbon in waste-water treatment of biologically degradable compounds as compared to coal and sand. Chudyk and Snoeyink (1984) showed that bioregeneration of activated carbon occurred in bench-scale columns when carbon was presaturated with phenol. All researchers emphasize the major role of porosity and/or bacteria.

Weber *et al.* (1970) and Sontheimer *et al.* (1978) noted that bacterial activity on activated carbon increases the service life of filters. The mechanism proposed for this extension of service life was bioregeneration, which permits a better filter efficiency. Chudyk (1981) calculated amounts of bioregeneration using a mass balance measured from changes in adsorptive capacity. Recently Speitel (1985a) and Speitel and Digiano (1985b) quantified bioregeneration at low substrate concentration using radiochemical techniques. Bacteria used both biodegradable substrate in solution and biodegradable adsorbable substrate in the pore spaces.

The objective of this study is to improve the present knowledge of the mechanisms by which adsorbable compounds are removed on granular activated carbon (GAC). Normally, in such a case, research workers study the variations of solute concentration in the aqueous phase. The authors, however, propose the use of a labelled adsorbable biodegradable compound (phenol) in association with a microbreakdown of the media (Le Cloirec, 1985a; Le Cloirec and Martin, 1985b) to study adsorption, diffusion and bioregeneration profiles on a grain of colonized and uncolonized activated carbon.

Material and methods

Media

Picactif NC60 activated carbon was used for this study, because it is widely used in water and waste-water treatment (Schulhof, 1979). Its characteristics are summarized in Table I (Societe PICA).

The organic model

Two kinds of phenol were used, i.e. labelled (5mCi/mM) (CEA, France) and unlabelled (Merck). The solutions were prepared in deionized distilled water. The solubility of this compound is very high. Various workers have demonstrated that phenol is strongly adsorbed and readily biodegraded on activated carbon and this was confirmed by Le Cloirec *et al.* (1982).

TABLE I
CHARACTERISTICS OF ACTIVATED CARBON USED (SOCIETE PICA, LEVALLOIS, FRANCE)

Parameters	
Raw material	coconut
Specific area ($m^2\ g^{-1}$)	1 200
Packed specific gravity	0,52
Grain size (mm)	2 to 5
Porosity	mesoporous
Pore size distribution (Å)	10^{-2} to 10^{-5}

*To whom all correspondence should be addressed.
Received 28 January 1986.

Embedding of grain

A synthetic resin (Epoxy type) was used to embed grains of activated carbon. Only one face of a parallelopedic grain was left exposed (Figure 1) and a single axis (x) will be available for adsorption (Louboutin, 1981) and biodegradation.

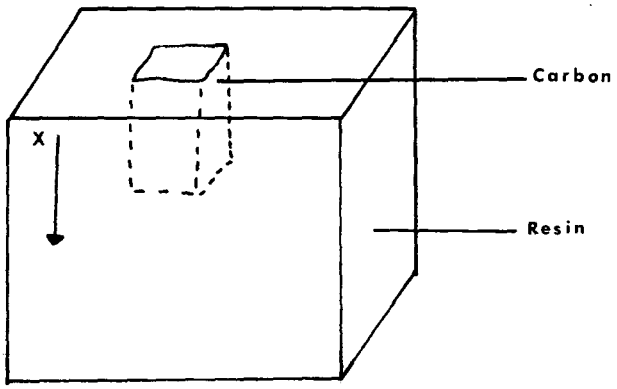

Figure 1
Preparation of sample activated carbon in resin. Dimensions: 10 mm × 10 mm × 10 mm.

Thick sectioning

Mechanical sectioning with a steel knife (microtome) was used to obtain slices of 15 μm thickness. Louboutin (1981) used this method to slice polymers and silicon. For activated carbon grains, this method of sectioning was difficult. The operation required a great deal of care in order to position the blade in the zero position (error in the x direction about ± 10 μm) and cut the embedded grain. However, as the carbon was embedded in the resin, the section was easily collected.

Scintillation counting

Each activated carbon section was placed in a small screw cap vial and 7,5 ml of Bray's scintillation mixture (Bray, 1960) was added. The radioactivity measurement was made with a liquid scintillation counter (Packard Tri-carb model 3385 instrument) with external standardization using the ^{226}Ra source of this instrument. The counting time was 10 min. The results (disintegrations per minute) were converted into mass of phenol.

Procedure for adsorption and bioregeneration

Three carbon samples were embedded in resin and each block was placed in contact with a solution of phenol for 15 h. The solute was a mixture of unlabelled phenol (250 mg/ℓ) and labelled phenol (4 μCi, i.e., about 6,0 μg radioactive phenol). The solution and carbon grain were stirred continuously. Because of the long contact time (15 h) between the high concentration of phenol solution and the block of carbon, it is reasonable to assume that equilibrium is reached inside the grain and between solution phenol phase and adsorbed phenol. This equilibrium corresponded to a plateau in the kinetic curve of phenol adsorption (Le Cloirec, 1985a). The blocks were then washed with distilled water.

One of these blocks was cut with the steel knife (microtome) and the amount of radiation was measured for each activated carbon slice. The second block was placed in contact with the bacteria for 100 h. The bacteria were obtained by washing a biological aerated activated carbon filter that had previously been fed with a synthetic solution containing phenol, ammonium chloride and potassium phosphate. The washing solution of bacteria was concentrated by thickening, and the sludge obtained was washed with distilled water to remove residual phenol. Five milliliters of this sludge (8 g dry volatile matter per liter) were used. At this concentration the labelled phenol is not bacteriostatic and bacteria remove labelled or unlabelled phenol unselectively (Gaid *et al.* 1982). After this biological treatment the block was washed to remove bacteria on the carbon surface and on the resin. The block was then cut and radioactivity of each slice was counted. Radioactivity of the bacteria in solution was also measured. The third block was used to examine possible self-desorption. This bock was placed in contact with 50 ml of distilled water for about 100 h. The radioactivity of the solution was measured every day.

Results and discussion

The results obtained are shown in Figure 2.

The profile of the block without biological treatment was a control. The procedure, for this control, was similar to the other block except for microbial regeneration. Because of the reasons given above (i.e. long contact time, high concentration of phenol in the solution), it is assumed that equilibrium is reached inside this grain. Therefore, the concentration profile of adsorbate should not change very much with the time. Only self-diffusion of phenol could occur and the phenomenon would be relatively slow. The profile of the block has been used to study the mechanisms of mass transport within the adsorbent grain. A model is described in detail by Le Cloirec *et al.*, 1986 and by Le Cloirec (1985a).

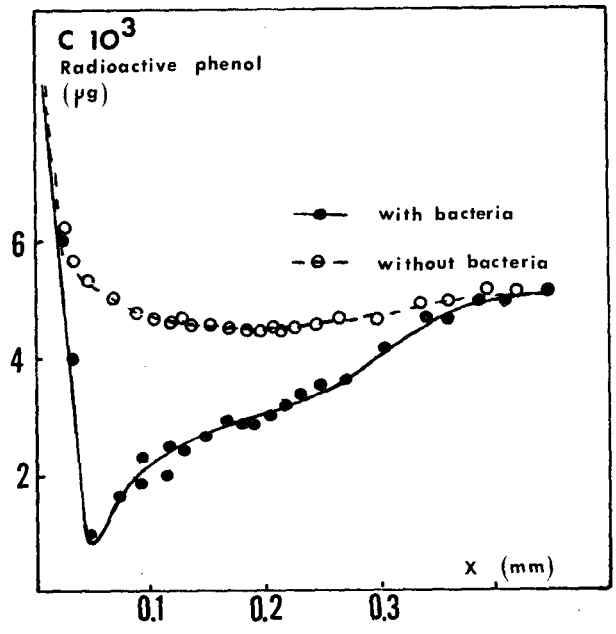

Figure 2
Profile of diffusion of radioactive phenol before and after contact with bacteria.

When carbon which has adsorbed both unlabelled and labelled phenol is brought into contact with bacteria, it is possible to demonstrate how the inner structure of the carbon is regenerated. The comparison between the two curves in Figure 2 shows an important difference in the quantity of phenol in the pore space of the carbon with and without biological treatment. However, for the grain treated with bacteria, a large concentration of activity on the surface of the carbon ($x < 15\ \mu m$) may be due to a small amount of bacteria that has digested labelled phenol; hence they would contain radioactive carbon. These bacteria would not have been entirely removed by rinsing with distilled water. In such a case, a zone where the radioactivity suddenly falls would be found ($x > 0{,}05$ mm). For $0{,}05 < x < 0{,}5$ mm, the quantity of labelled phenol is always less than the quantity found without biological treatment. In these two zones the phenol has been eliminated by the bacteria on the media either directly (if the size of bacteria allows them to enter into the pores), or in the mesopores or micropores.

In the presence of bacteria, the desorption to the exterior of the particle can be motivated by a concentration gradient created by the biological degradation of phenol in the outer layer of the macropores or in the interface between solid and liquid phase microorganisms (Maloney *et al.*, 1984; Schultz and Keinath, 1984). The phenol self-desorption without bacteria cannot explain the difference between the two curves in Figure 2. Indeed, the radioactivity measured in the solution in contact with the third block each day was always negative, showing no self-desorption under these conditions.

The quantity of adsorbed labelled phenol removed by bacteria was about $42 \times 10^{-3}\ \mu g$, i.e. 10,5 mg of total phenol if it is assumed that the labelled and unlabelled compounds were adsorbed to the same extent in the pores. The original quantity adsorbed was about 35 mg, i.e. the percentage of desorption is 30%. Using powdered activated carbon treatment, Schultz and Keinath (1984) found that all phenol initially present was eventually removed from the surface of adsorbent. However, the values found by the authors are very close to the results found by Speitel (1985a) and Speitel and Digiano (1985b), despite the different conditions used by those authors (low phenol concentration and dynamic experimental procedures).

The measurement of the radioactivity revealed that roughly 80% of the labelled phenol desorbed was found in the bacteria. The total balance could not be established because of possible losses (for example, the release of CO_2 owing to metabolism). Schultz and Keinath (1984), using radiochemical compounds, have found that approximately 20% of the radioactivity in metabolic end products was converted to CO_2 by a powdered activated carbon treatment sludge. The authors' results confirm the previous work concerning bioregeneration and interactions between bacteria and substrate adsorbed, as studied by Le Cloirec (1985a) and Gaid *et al.* (1982). These results would explain and emphasize the Neukrug *et al.* (1984) conclusions on the biodegradability and slow adsorption kinetics which appear to play a key role when the adsorptive surface is nearly saturated.

Conclusion

This technique of using radioactive compounds and micro-breakdown to study bioregeneration can successfully be applied to confirm the bioregeneration of activated carbon by studying the inner pores of this material. Based on the profiles obtained on activated carbon after adsorption of labelled and unlabelled phenol, the following conclusions can be drawn:

- the presence of bacteria enables the pores to be cleaned.
- the depth of bioregeneration is found to be 0,35 mm.
- the bioregeneration percentage is about 30% of the original adsorbed phenol after a bacteria – carbon contact time of 100 h.

This method is currently being applied to the study of mechanisms of bioregeneration in activated carbon columns. This method represents an interesting approach to the study of the mechanisms that are operative during adsorption, desorption and bioregeneration of activated carbon or other adsorbents. This technique provides a means to quantitatively track the presence, transformation and movement of adsorbate.

Acknowledgements

The authors thank James N. Jensen, University of North Carolina at Chapel Hill, USA, and Dr. David A. Reckhow, University of Massachusetts, Amherst, MA, USA, for their assistance in the preparation of this manuscript.

References

BANCROFT, K., MALONEY, S.W., MCELHANEY, J., SUFFET I.H. and PIPES W.O. (1983) Assessment of bacterial growth and total organic carbon removal on granular activated carbon contactors. *Appl. Environ. Microbiol.* **46** (3) 683-688.

BRAY, G.A. (1960) A simple efficient liquid scintillator for counting aqueous solution in liquid scintillator counter. *Anal. Biochem.* **1** 279-285.

CHUDYK, W. (1981) The removal of low levels of phenol by activated carbon in the presence of biological activity. Ph.D. Thesis, University of Illinois, Urbana Champaign.

CHUDYK, W. and SNOEYINK, V.L. (1984) Bioregeneration of activated carbon saturated with phenol. *Environ. Sci. Technol.* **18** (1) 1-5.

GAID, K., MARTIN, G. and CAVELIER, C. (1979) Observation au microscope electronique des populations bacteriennes sur charbon actif. *J. Fr. Hydrology* **10** 125-132.

GAID, K. (1981) Mode d'elimination de polluants sur filtres. Thesis, Doctorat es Sciences Physiques, University of Rennes, France, B, 344, 200.

GAID, K., LE CLOIREC, P., MARTIN, G. and BERNARD, T. (1982) Evolution physicochimique et biologique d'un substrat marque apres son adsorption sur charbon actif. *Environ. Technol. Letters* **3** 329-336.

LAFRANCE, P., MAZET, M. and VILLESOT, D. (1983) Bacterial growth on granular activated carbon. *Water Res.* **17** (10) 1467-1470.

LE CLOIREC, P., GAID, K., MARTIN, G. and SIBONY, J. (1982) Role de la porosite du charbon actif lors du lavage des filtres biologiques. *Environ. Technol. Letters* **3** 257-262.

LE CLOIREC, P. (1985a) Etudes des interactions solute charbon actif: modelisation des reacteurs biotiques et abiotiques. Thesis, Doctorat es Sciences Physiques, University of Rennes, France, B, 423, 235.

LE CLOIREC, P. and MARTIN, G. (1985b) Une autre methode d'etude des milieux poreux utilises en traitement d'eau. *Environ. Technol. Letters* **6** 175-180.

LE CLOIREC, P., MARTIN, G. and BERNARD, T. (1986) A new approach for the investigation of the mechanisms of micropollutant removal on activated carbon. Submitted to *Environ. Sci. Technol.*

LEMARCHAND, D. (1981) Elimination de matieres organiques sur filtre a charbon actif. Thesis, Doctorat d'ingenieur, University of Rennes, France.

LI, A.Y. and DIGIANO, F.A. (1983) Availability of sorbed substrate for microbial degradation on granular activated carbon. *J. Wat. Pollut. Control Fed.* **55** 392-399.

LOUBOUTIN, J.P. (1981) Etudes de polymeres dopes. Thesis, Doctorat de 3eme Cycle, University of Rennes, France.

MALONEY, S.W., BANCROFT, K., PIPES, W.O. and SUFFET, I.H.

(1984) Bacterial TOC removal on sand and GAC. *J. Environ. Eng.* **110** (3) 519-533.

MARTIN, G., LE ROUX, A.Y. and SCHULHOF, P. (1982) A mathematical model of biological purification in activated carbon biofilters. *Wat. Sci. Tech.* **14** 599-618.

NEUKRUG, H.M., SMITH, M.G., MALONEY, S.W. and SUFFET, I.H. (1984) Biological activated carbon – At what cost? *J. Am. Wat. Wks. Ass.* **4** 158-167.

PEEL, R.G. and BENEDEK, A. (1983) Biodegradation and adsorption within activated carbon adsorbers. *J. Wat. Pollut. Control Fed.* **55** 1168-1182.

SCHULHOF, P. (1979) An evolutionary approach to activated carbon treatment. *J. Am. Wat. Wks. Ass.* **71** 648-659.

SCHULTZ, J.R. and KEINATH, T.M. (1984) Powdered activated carbon treatment process mechanisms. *J. Wat. Poll. Control. Fed.* **56** (2) 143-151.

SOCIETE PICA, Anonymous. Caracteristiques de charbons actifs. Levallois Perret, France.

SONTHEIMER, H., HEILKER, E., JEKEL, M.R., NOLTE, H. and VOLLMER, F.H. (1978) The Mulheim process. *J. Am. Wat. Wks. Ass.* **70** (7) 393-396.

SPEITEL, G.E. (1985a) Bioregeneration of granular activated carbon: Quantification at low substrate concentrations by radiochemical techniques. Ph.D. Thesis, University of North Carolina at Chapel Hill.

SPEITEL, G.E. and DIGIANO, F.A. (1985b) Bioregeneration at micropollutant concentration in GAC column. Congres Am. Chem. Soc., New York, NY, June.

WEBER, W.J., HOPKINS, C.B. and BLOOM, R. (1970) Physicochemical treatment of wastewater. *J. Wat. Pollut. Control Fed.* **42** 83-99.

WEBER, W.J., PIRBAZARI, M. and MELSON, G.L. (1978) Biological growth on activated carbon: an investigation by scanning electron microscopy. *Environ. Sci. and Technol.* **12** 817-819.

WERNER, P., (1983) Microbiologie du charbon actif lors de traitement d'eau potable. *Eau Ind. Nuisances* **72** 65-69.