



## Biological activated carbon treatment of industrial wastewater in stirred tank reactors

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### Abstract

The industrial effluent under investigation was the simulated aqueous discharge from a carpet printing plant in Northern Ireland, comprising of a ternary solution of acid dyes. This effluent was investigated using the biological activated carbon (BAC) process for colour removal in an aerobic stirred tank reactor configuration. The following systems were experimentally investigated: bacteria immobilised on granular activated carbon (GAC); bacteria immobilised on sand particles; GAC (with no biological activity) and free bacterial cells. The bacterium used in this study was *Pseudomonas putida* (NCIMB 9776) and the activated carbon was Filtrasorb 400. Ternary dye concentrations were determined by spectrophotometry. Results indicated that BAC system outperformed the combination conventional GAC and biological water treatment processes. For biodegradable anthraquinone dyes, this enhanced colour removal was due to higher dye utilisation rates caused by the increase in substrate concentration at the granule surface found in BAC systems. For non-biodegradable azo dyes, increased biosorption was found in BAC systems compared to conventional immobilised systems. © 1999 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

Rice and Robson first suggested the term biological activated carbon (BAC) for “a water or wastewater treatment system in which aerobic microbial activity is deliberately promoted in a granular activated carbon (GAC) system” [1].

#### 1.1. Advantages of BAC systems

The BAC process described by Weber et al. provides simultaneous adsorption of non-biodegradable matter and oxidation of biodegradable contaminants in a single reactor [2]. The BAC system therefore offers advantages, due to the fact that the capital cost for single reactor systems is lower than that for individual processes and to the fact that less frequent regeneration of the carbon will result in lower energy requirements and operating costs [3].

The principle advantage of BAC systems is increased effluent throughput until breakthrough resulting in less frequent regeneration time. This phenomenon has been observed by most authors investigating BAC systems using a wide variety of contaminants [4]. Bouwer and McCarty [5] and Speitel et al. [6] have reported that at low inlet concentrations BAC columns showed capacities larger than their equilibrium capacities. Weber et al. reported an apparent increase in adsorption capacity with the removal of total organic carbon (TOC) by a combination of GAC and biofilm, provided by activated sludge [2]. Ying and Weber reported the extended removal of degradable compounds such as sucrose and *p*-toluene sulphonate [3].

The regeneration of activated carbon by bacterial biofilms has been reported by several authors, with most of the work concentrated on finding the mechanism of this bioregeneration. Andrews and Tein have reported the bioregeneration of GAC using valeric acid, which is biodegradable, and notably reversibly adsorbed [7]. Li and DiGiano have also reported this bioregeneration phenomenon using benzoic acid, *o*-cresol and phenol [8]. These authors also state that reversible adsorption is essential for bioregeneration to occur. The

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aerobic bioregeneration of phenol was also reported by Chudyk and Snoenyink with GAC pre-saturated with phenol in columns containing a high dissolved oxygen level [9]. DiGiano and Speitel used low concentrations of radio labelled phenol to observe the mechanism of bioregeneration with results showing  $^{14}\text{CO}_2$  in the effluent stream indicating that pre-adsorbed compounds had been desorbed and subsequently biodegraded in the biofilm [10,11]. This radio labelling technique was also used by Speitel et al. to observe the mechanism of bioregeneration of 2,4 substituted phenols, again at low concentration [6].

The first theory on bioregeneration of GAC was proposed by Perrotti and Rodman where they suggested that, although the size of the bacteria makes them too large to colonise the micropores of the carbon, enzymes produced by the bacteria could easily diffuse into the micropores and react with the adsorbed substrate [12]. The weak adsorbability of the reaction products subsequently formed would result in eventual substrate desorption into the biofilm, where it would be further degraded. Xiaojian et al. suggested that this hypothesis was incorrect due to the fact that these extracellular enzymes have molecular diameters of 3–4 nm, which would make diffusion into the micropore structure of the carbon difficult [13]. These authors suggested that the BAC process is a simple combination of biodegradation and activated carbon adsorption. Furthermore, Li and DiGiano have suggested that these extracellular enzymes would be adsorbed before they could act [8]. Olmstead and Weber postulated that bioregeneration is due to the simple desorption of the adsorbed species which could then be degraded by the biofilm [4]. This desorption could occur due to a decreased adsorbate liquid phase concentration near the exterior particle boundary, it follows that bioregeneration could only occur in compounds that are both biodegradable and readily adsorbable.

Ehrhardt and Rehm reported the phenol degradation by *Candida sp.* and *Pseudomonas sp.* in both free cell and immobilised cell systems using GAC [14]. While the free cells did not tolerate phenol concentrations above  $1.5 \text{ g l}^{-1}$ , immobilised cells survived phenol concentrations up to  $15 \text{ g l}^{-1}$  where they degraded about 90% of the adsorbed phenol. The authors suggested that the activated carbon acted as a “depot”, with the adsorbed phenol diffusing out of the carbon and being metabolised in the biofilm. Bettmann et al. postulated that an increase in phenol degradation rate with these immobilised cells was due to a decrease in toxic substances in the cell environment [15].

### 1.2. Disadvantages of BAC

Although, the reports above show obvious advantages of BAC columns over conventional GAC systems, in laboratory and pilot plant tests, it has to be noted that few specifically designed BAC system have been employed for industrial wastewater treatment. This may be due to physical disadvantages such as increased pressure drop due

to clogging by microbial growth [16]. This problem may be alleviated however, by frequent backwashing and air scouring to remove excess biomass [3]. The advantage in BAC systems of shielding bacteria from toxic effects could also serve as a disadvantage if pathogenic bacteria attached to the carbon were shielded from disinfection [17]. The American Water Works Association Committee has also expressed concern that potential pathogens may escape from BAC systems into potable water supplies [18].

Most of the work into the advantages of BAC has used target compounds, which are readily biodegradable, and of low molecular weight, such as organic acids or phenols which are also readily adsorbable. In this work the acid dye species are relatively difficult to biodegrade and have large molecular weights, which also make them relatively difficult to adsorb. Lowry and Burkhead reported that adsorption was actually impeded due to biological activity in GAC beds although this may have been due to retardation of the mass transfer of oxygen through the biofilm [19]. If the biofilm becomes too thick the adsorbate species find difficulty in diffusing through the biofilm with a subsequent reduction in adsorption rate. This phenomenon was reported by Schultz and Keinath in PAC systems and it is conceivable that the same effect could happen in biological GAC systems [20].

Ying and Weber have noted that in BAC columns where micro-organisms were grown on sucrose and glucose, that the column performance using non-biodegradable compounds such as *p*-toluene sulphonate was extremely poor, with breakthrough occurring almost immediately [3]. These experiments indicated that the service life of GAC systems was reduced for some components even though the total TOC breakthrough life was increased. Olmstead and Weber have also noted a decrease in adsorption capacities and of surface diffusion rates on GAC due to biological activity [4].

### 1.3. Dye biodegradation

In recent years, the degradation of dyes has received considerable attention albeit in carefully controlled laboratory experiments [21,22]. Some typical studies on dyes degradation are now described. Jiang and Bishop have reported that an azo dye, Acid Orange 8, can be aerobically degraded using a rotating drum biofilm reactor [23]. Harmer and Bishop, using the same reactor configuration have reported the removal of azo dye, Acid Orange 7, with the detection of the intermediate 1-amino 2-naphthol as a by product of aerobic metabolism [24]. Seshadri et al. have described a two stage, anaerobic fluidised bed/aerobic activated sludge, process for the removal of azo dyes [25]. In this system the azo bond was reduced in the anaerobic unit with the resulting amines being aerobically degraded via hydroxylation and ring cleavage. Ganesh et al. reported the aerobic degradation of Navy 106 using activated sludge with an increased biomass resulting in increased decolourisation in batch reactors [26].

## 2. Experimental materials and methods

### 2.1. Filtrasorb 400 (GAC F400)

GAC F400 is one of the most widely used grades of activated carbon in the water treatment industry. GAC F400 is produced by the gas activation of bituminous coal in a two step process: carbonisation and activation. This process produces an activated carbon with a substantial specific surface (1050–1200 m<sup>2</sup>/g) and good mechanical hardness.

### 2.2. Adsorbate dyes

Acid dyes in general are sodium salts of organic acids with the anion being the active coloured component, most in fact are sulphuric acid salts with a few containing carboxyl groups. Tectilon Blue 4R-01 (TB4R) is an acid anthraquinone dye and although the manufacturers Ciba-Geigy have yet to release its structure, previous Tectilon Blue R dyes have a structure similar to (Fig. 1). This class of dye was first produced by Agfa in 1913 with variations now widely used by many firms. It can be used in dyeing and printing wool, silk and in this case nylon. TB4R is supplied in 50% liquid solution containing 40% 6-caprolactam and is miscible in water giving a pH of 6.0–7.5. TB4R gives a royal blue colour in aqueous solution and has the Colour Index classification C.I. Acid Blue 277:1 [27].

Tectilon Red 2B (TR2B) is an acid monoazo dye. The importance of azo dye is shown by the fact that they account for over 60% of the total number of dye structures known to be manufactured. As with Tectilon Blue the manufacturer Ciba-Geigy has yet to release its exact chemical structure, but Tectilon Red B dyes have a structure similar to Fig. 2. This class of dye can also be used for dyeing wool and silk as well as nylon and is manufactured by converting naphthalene to chromotropic acid. TR2B is also supplied in liquid solution and is miscible in water with a pH of 6.0–7.0. TR2B

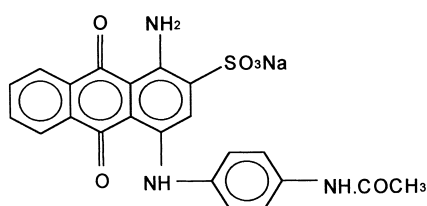


Fig. 1. Chemical structure of Tectilon Blue (Acid Blue 277:1).

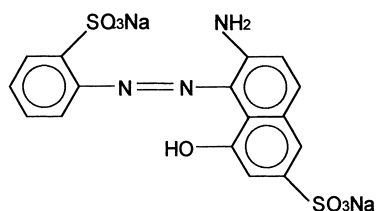


Fig. 2. Chemical structure of Tectilon Red (Acid Red 361).

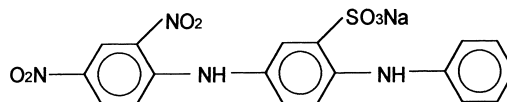


Fig. 3. Chemical structure of Tectilon Orange (Acid Orange 156).

produces a dull blood red shade in aqueous solution and has the Colour Index classification C.I. Acid Red 361 [27].

Tectilon Orange 3G (TO3G) is an acid di-azo dye belonging to one of the earliest classes of synthetic dye discovered. Again the manufacturers Ciba-Geigy have yet to release its exact structure, although its make up is probably similar to previous Tectilon Orange dyes (Fig. 3). This class of dye was discovered by Schmidlin in 1911 and is now produced by a variety of firms. TO3G is supplied in 33% liquid solution containing 2% of 2-(2-butoxyethyl)-ethanol and is miscible in water giving a neutral pH. TO3G produces a dull rusty orange shade in aqueous solution and has the Colour Index classification C.I. Acid Orange 156 [27].

The acid dyestuffs contained in the textile effluent consist of aromatic structures containing functional groups linked to each other by azo chromophore bonds. As the colour of the dye is produced by selective absorption of visible light by these structures, a break down of the aromatic ring and the azo bond may well cause decolouration of the dye.

### 2.3. Bacteria

Much of the research carried out so far on BAC has concerned the use of bacterial consortia such as activated sludge. In this work a specific bacterium, *P. putida* (National Collection of Industrial and Marine Bacteria, UK (NICMB) 9776) was chosen to utilise the aromatic structures. The bacterium was selected because it is in the main, harmless, i.e., NCIMB Group 1, metabolises under aerobic conditions, at 25°C and neutral pH which makes it suitable for use with the treatment of the dyehouse effluent.

### 2.4. Aerated stirred tank reactor studies

In almost all wastewater applications activated carbon is used in continuous processes, with GAC used in fixed and fluidised BAC systems and powdered activated carbon used in powdered activated carbon treatment (PACT) or similar continuous systems. However analysis of batch processes can provide useful design data from which continuous processes can be developed. In this work four batch systems were studied using the aerated stirred tank configuration.

1. Bacteria immobilised on GAC F400,
2. Bacteria immobilised on sand particles,
3. GAC F400 (with no biological activity),
4. Free bacterial cells.

Each of these systems was made in contact with 3 l of an autoclaved “simulated dyehouse effluent”. This contained a ternary dye of concentration 100 mg l<sup>-1</sup> (3 dyes ×

33.3 mg l<sup>-1</sup>) and 5% nutrient broth (CM1). The nutrient broth was used to simulate the substantial amount of thickener, contained in dyehouse effluent, which can act as a nutrient source for biological systems. The ternary solution simulated the composition and concentration of the washings from the carpet printing plant. The reactors were of a standard configuration and were fabricated from 150 mm Perspex giving a total reactor volume of 3.5 l. The reactors were baffled using four Perspex baffles with mixing provided by a impellers powered by a Heidolph variable speed motor.

### 2.5. Process conditions

As the biological system in question has an optimum operating temperature of 25°C each of the reactors was heated in a Grant type water bath which was thermostatically controlled. The systems operated at a pH of 7. An aeration technique using two 6-flat blade impellers was developed. The lower blade, which extended half way down the reactor, provided complete mixing of the particles. The second impeller was positioned at approximately 10 mm beneath the liquid surface, which entrained air bubbles into the dye solution therefore maintaining desired dissolved oxygen levels (5 mg l<sup>-1</sup>). The impeller speed was maintained at 250 rpm.

The four experimental systems were operated simultaneously in four STR reactors. This ensured that the initial microbe concentration was identical for the three bacterial systems. For immobilised cell systems the bacterium culture in nutrient broth (20 ml CM1) was contacted with 5 g of GAC/sand for 24 h before addition to the reaction vessel. The free cell system involved the straight addition of the culture while the “sterile” GAC system involved the addition of 5 g of GAC to the reactor. The “sterile” GAC was autoclaved prior to contacting to minimise bacterial growth. Samples were taken from the reactor by syringe and filtered through a 0.2 µ filter to remove cells from the dye solution. The dye concentration was then measured by spectrophotometry using a matrix calibration method for the calculation of the individual dye concentrations.

## 3. Experimental results and discussion

Results from these STR experiments are illustrated as concentration decay curves over an 8 h period with Figs. 4–6 showing the effect of the four STR systems for the dyes with the *P. putida* strain. In general the results indicate that although colour was removed in all four cases, the cells immobilised on sand give a slightly better performance than the free cells. This result was attributed to a higher biomass growth rates within the reactor found using immobilised cells, which would result in higher rates of biosorption and dye utilisation. After an initial period, the GAC with immobilised cells reduced colour more effec-

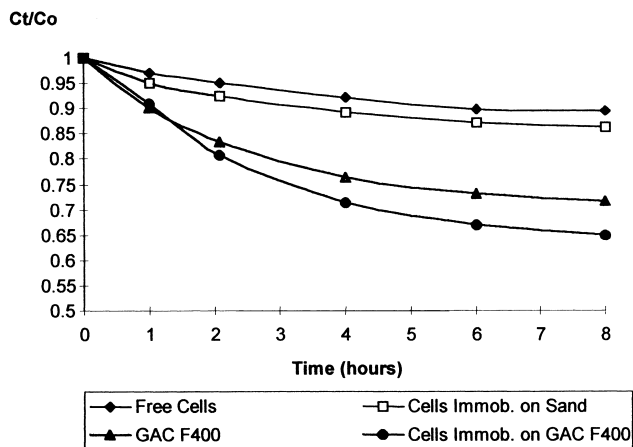


Fig. 4. STR concentration decay curve for TB4R (with *P. putida*,  $T = 25^{\circ}\text{C}$ , rpm = 250, volume = 3 l, 5 g of particles 1000–1400 µm).

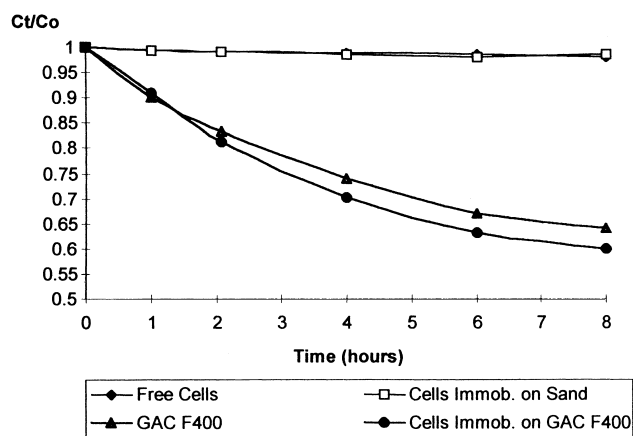


Fig. 5. STR concentration decay curve for TR2B (with *P. putida*,  $T = 25^{\circ}\text{C}$ , rpm = 250, volume = 3 l, 5 g of particles 1000–1400 µm).

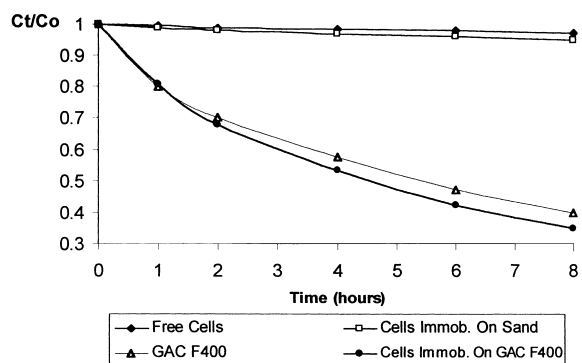


Fig. 6. STR concentration decay curve for TO3G (with *P. putida*,  $T = 25^{\circ}\text{C}$ , rpm = 250, volume = 3 l, 5 g of particles 1000–1400 µm).

tively than the sterile carbon. The slightly lower reaction rate by BAC in the initial stages of the experiments (1–2 h) was probably due to nutrient broth residues blocking the crevices and large macropores of the carbon. The subsequent increase over conventional GAC was a result of the combination of activated carbon adsorption plus biological

Table 1  
Rate constants for *P. putida*<sup>a</sup>

System	$V_0$ (TB4R) (mg h <sup>-1</sup> )	$V_0$ (TR2B) (mg h <sup>-1</sup> )	$V_0$ (TO3G) (mg h <sup>-1</sup> )
(i) Free cells	0.918	0.240	0.558
(ii) Cells immobilised on sand	1.633	0.394	0.625
(iii) GAC F400	5.281	5.400	10.442
(iv) Cells immobilised on GAC	8.297	6.090	12.580
(ii) + (iii)	6.914	5.794	12.067
Improvement with BAC	20%	5%	4%
Langmuir capacity on GAC	163 mg g <sup>-1</sup>	175 mg g <sup>-1</sup>	238 mg g <sup>-1</sup>

<sup>a</sup> The average reaction rate constants were calculated over the first 6 h of each experiment.

degradation and biosorption of the dye. The high agitation rates wound in these STR systems reduced the effect of excess biomass growth on the GAC particles which has been found to reduce adsorption in some fixed bed systems [4].

In the TB4R/*P. putida* system the rate of colour removal in the free cells system is substantial. It is also noted that the combination of colour reduction by the free cells and the sterile carbon is less than the colour reduction in the BAC system (Fig. 4). This indicates that as TB4R is relatively difficult to adsorb (Langmuir isotherm data, Table 1) and relatively easy to biodegrade [28]. The combination of GAC adsorption and biological degradation proves more successful in colour reduction than the individual processes by 20%. This is attributed to the higher concentration of dye at the surface of the carbon relative to the bulk concentration which increases the biological utilisation and biosorption rate. It must be noted however that adsorption processes are still much faster, approximately sixfold, than biological processes and therefore account for much more of TB4R removal.

In the TR2B case where the dye is relatively resistant to biodegradation, the action of free cells and indeed cells immobilised on sand, reduces the dye concentration little (Fig. 5). The small reduction in dye concentration was probably due to biosorption of the dyes unto the biomass. However the rate of dye decolourisation by the BAC system again outperformed the combination of the two separate processes by 5% (see Table 1) emphasising the advantages of BAC systems, even for azo compounds which are resistant to biodegradation. This may be caused by increased growth rate of the cells immobilised on GAC compared to sand resulting in a higher rate of biosorption due to the macropore structure of the carbon providing excellent sites for bacterial colonisation. In this case it must be noted however that free cell biosorption was 35 times slower than the adsorption process. Results from the TO3G/*P. putida* system (Table 1, Fig. 6) show much the same trends as for TR2B systems, in that BAC outperforms the combined effects of GAC and the free cell system by 4%. From these results it can be seen that the *P. putida* strain effectively utilises and decolourised the anthraquinone dye (TB4R). The azo and di-azo dyes (TR2B and TO3G) were not utilised by this strain as it caused decolourisation by breakage of aromatic and not azo bonds. However, biosorption of

these azo dyes, and the anthraquinone dye, did occur using this strain.

Literature on the biological batch adsorption of dyestuffs is scarce, however Rodman and Shunney did produce a detailed report into the effect of activated carbon/activated sludge systems in which cell immobilisation on activated carbon/activated sludge dramatically improved colour removal in batch systems [29]. The results presented in Table 2 show that BAC is an effective form of colour removal for acid dyes with bacterial cells benefiting from the addition of activated carbon in all systems. A direct comparison with the studies of Rodman and Shunney would be difficult as the STR reactors had different carbon concentrations and bacterial species, however, the previous study also reported the same basic characteristics in that cells immobilised on sand performed better than free cells and that BAC outperformed conventional GAC systems.

#### 4. Conclusions

It can be concluded from this work that BAC systems show an increase in dye removal rate from industrial wastewater compared to conventional wastewater treatment albeit in batch STR systems. Assuming that the GAC adsorption capacity for the dyes remains unchanged, the BAC process would result in an increase in capacity and reduction in regeneration costs compared to conventional systems. Furthermore it has been shown that BAC processes remove more dye from solution than the combination of individual conventional GAC and biological processes. This increase is due to enhanced biological activity, found by using GAC as the immobilisation medium, resulting increased utilisation

Table 2  
Colour removal comparison

Dye/system % colour removal (24 h)	Rodman and Shunney [29]		This study	
	Free cells	BAC	Free cells	BAC
Acid Black 26A	80	95	–	–
Acid Blue (TB4R)	–	–	30	90
Acid Red (TR2B)	–	–	5	80
Acid Orange (TO3G)	–	–	5	97

and biosorption on the dyes. For readily biodegradable compounds such as TB4R the increase in removal rates can be attributed to higher utilisation rates caused by an increase in dye concentration at the particle surface and the possible adsorption of inhibiting intermediate compounds from the biological reaction. For azo dye compounds resistant to biodegradation, such as TR2B with the biological dye removal due to solely biosorption, the increased dye removal can be attributed to enhanced cell growth on the macropores of GAC.

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## References

- [1] R.G. Rice, C.M. Robson, *Biological Activated Carbon: Enhanced Aerobic Biological Activity in GAC Systems*, Ann Arbor Science, Ann Arbor, MI, 1982.
- [2] W.J. Weber, M. Pirbazari, G.L. Melson, *Biological growth on activated carbon: an investigation by scanning electron microscopy*, *Env. Sci. Tech.* 127 (1978) 817–819.
- [3] W. Ying, W.J. Weber, *Bio-physicochemical adsorption model systems wastewater treatment*, *J. WPCF* 5111 (1979) 2661–2677.
- [4] K.P. Olmstead, W.J. Weber, *Interactions between microorganisms and activated carbon in water and waste treatment operations*, *Chem. Eng. Commun.* 108 (1991) 113–125.
- [5] E.J. Bouwer, P.L. McCarthy, *Removal of trace chlorinated organic compounds by activated carbon and fixed film bacteria*, *Env. Sci. Tech.* 1612 (1982) 836–843.
- [6] G.E. Speitel, C.-J. Lu, M. Turakhia, X.-J. Zhu, *Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns*, *Env. Sci. Technol.* 231 (1989) 68–75.
- [7] G.F. Andrews, C. Tein, *An analysis of bacterial growth in fluidized bed adsorption column*, *J. AIChE* 282 (1982) 182–190.
- [8] A.Y.L. Li, F.A. DiGiano, *Availability of sorbed substrate for microbial degradation on granular activated carbon*, *J. WPCF* 554 (1983) 392–399.
- [9] W.A. Chudyk, V.L. Snoeyink, *Bioregeneration of activated carbon saturated with phenol*, *Env. Sci. Technol.* 181 (1984) 1–5.
- [10] F.A. DiGiano, G.E. Speitel, *Influence of Adsorption Biofilm Development*, *Proc. ASCE Env. Eng. Div. Speciality Conf.*, 1984, pp. 382–393.
- [11] G.E. Speitel, F.A. DiGiano, *The bioregeneration of GAC used to treat micropollutants*, *J. AWWA* (1) (1987).
- [12] A.E. Perrotti, C.A. Rodman, *Factors involved with the biological regeneration of activated carbon*, *AIChE Symp. Ser.* 70144 (1974) 317–325.
- [13] Z. Xiaojian, W. Zhansheng, G. Xiasheng, *Simple combination of biodegradation and carbon adsorption — The mechanism of the biological activated carbon process*, *Wat. Res.* 252 (1991) 165–172.
- [14] H.M. Ehrhart, H.J. Rehm, *Phenol degradation by microorganisms adsorbed on activated carbon*, *Appl. Micro. Biotechnol.* 21 (1985) 32–36.
- [15] H.M. Bettmann, H.M. Ehrhardt, H.J. Rehm, *Degradation of phenol by immobilized microorganisms*, *Third European Congress on Biotechnology*, vol. 3, Munich, Germany, 1984, pp. 27–33.
- [16] W.G. Characklis, *Fouling biofilm development*, *Biotech. Bioeng.* 23 (1981) 1923–1960.
- [17] M.W. LeChevalier, T.S. Hassenaver, A.K. Champer, G.A. McFetzters, *Disinfection of bacteria attached to granular activated carbon*, *Appl. Env. Micro.* 485 (1984) 918–923.
- [18] AWWA Research and Technical Practice Committee, *An assessment of microbial activity on GAC*, *J. AWWA*, August (1981) pp. 447–453.
- [19] J.D. Lowry, C.E. Burkhead, *The role of adsorption in biologically extended carbon columns*, *J. WPCF* 522 (1980) 389–399.
- [20] J.R. Schultz, T.M. Keinath, *Powdered activated carbon treatment process mechanisms*, *J. WPCF* 562 (1984) 143–151.
- [21] U. Meyer, *Biodegradation of synthetic organic colorant*, *FEMS Symp.* 12 (1981) 371–383.
- [22] J.T. Spadaro, V. Renganathan, *Peroxidase-catalyzed oxidation of azo dyes: mechanism of disperse yellow 3 degradation*, *Arch. Biochem. Biophys.* 1221 (1994) 301–307.
- [23] H. Jiang, P.L. Bishop, *Aerobic biodegradation of azo dyes in biofilms*, *Wat. Sci. Technol.* 2910-11 (1994) 525–530.
- [24] C. Harmer, P. Bishop, *Transformation of azo dye AO-7 by wastewater biofilms*, *Wat. Sci. Technol.* 263-4 (1992) 627–636.
- [25] S. Seshadri, P.L. Bishop, A. Mourad Agha, *Anaerobic/aerobic treatment of selected azo dyes in wastewater*, *Waste Management* 142 (1994) 127–137.
- [26] R. Ganesh, G.D. Boardman, D. Michelsen, *Fate of azo dyes in sludges*, *Wat. Res.* 286 (1994) 1367–1376.
- [27] *Colour Index*, vol. 1, 3rd ed., S.D.C., 1984, A. Ass. Tex. Chem. Colour.
- [28] G.M. Walker, *Industrial wastewater treatment using biological activated carbon*, Ph.D. Thesis, The Queen's University of Belfast, 1995.
- [29] C.A. Rodman, E.L. Shunney, *A new concept for the biological treatment of textile finishing wastes*, *Chem. Eng. Prog. Symp. Ser.* 67107 (1970) 451–457.