

Effluent Treatment by Simultaneous Bio-degradation and Adsorption Technique:

S. D. V. Sagar, D. P. Singh, P. Mondal, C.B. Majumdar and B. Mohanty

Department of Chemical Engineering, IIT, Roorkee, Uttaranchal

In the present paper the application of microbes for the treatment of pulp and paper mill effluent has been briefly reviewed. The paper also discusses the result obtained from experiments on degradation of phenolic compounds (phenol, cresol and chlorophenol) by specific species of bacteria, both in bulk and immobilized phases in a reactor. The microbial decomposition of pheno, o-cresol and chlorophenol has been studied separately. The efficiency of degradation in each case has been found to improve due to the immobilization, where as, pH has been found to increase with the degree of degradation within a small range. Specific uptakes and break through points have been compared for the above three different compounds for a given adsorbents.

INTRODUCTION

The manufacture of paper generates significant quantities of waste water, as high as 60m³/tonne of paper produced [1]. The raw wastewater from pulp and paper mills using kraft process can be potentially very polluting. As per the report [2] the COD of agro based mill is 1000 - 2000 mg/l, where as, recently it has been reported that this value may be as high as 11000mg/l [1]. The organic pollutants, responsible for COD, in paper mill wastewater are mainly lignin, organic acids phenols and chlorinated phenols etc. As per MINAS [3], the total organic chloride present per tonne of paper mill wastewater should be less than 2 kg.

The main water treatment process used at pulp and paper mill plants is primary clarification, in some cases, it is then followed by secondary treatment, generally of biological nature. In the secondary treatment, easily biodegradable compounds are mostly degraded but bio resistant organics like phenols, chlorophenols lignin are less degraded by the conventional bio processes [1], and hence, considerable amount of COD is retained after secondary treatment. But as per the statutory standards,

given in Table 1, the BOD of the discharged effluent should be less than equal to 30mg/l and COD 350 mg/l.

Activated sludge process is the conventional secondary treatment process. It is not so efficient and the removal of BOD and COD are 22 - 60% and 47 - 62% respectively (1,4). The treatment water also contain colour due to coloured toilet tissue or lignin [5]. High performance trickling filters using plastic media may also be used successfully as pre treatment stage prior to an activated sludge plant [6].

Tertiary processes for further treatment, or colour removal are rare at present, but may become more common in the future if legislation becomes more stringent. The main tertiary process which has been employed to date, at a few sites in the industry, are membrane processes, specially ultra filtration. Ozonation has been reported by same researchers(7-9,4) as tertiary treatment process. However, contradictory results on its efficiency have been presented in these report.

These tertiary processes are costly and chemicals used in these processes also reduce the water quality. The

Table 1. Environmental standards for paper mills (3)

| Parameter | Concentration |
|-----------------------------------|---------------|
| pH | 7.5 - 8.5 |
| Suspended solid (mg/l) | 50 |
| BOD (mg/l) | 30 |
| COD (mg/l) | 350 |
| Total organic chloride (kg/tonne) | 2 |

microbes used in secondary treatment processes like *Haliscomenobacter hydrosis*, *Thiothrix I and II*, *Nostocoida limicola*, *Beggiatoa*, *Eikelboom* Type 021N [1], don't have more resistant power to the toxic phenolic and lignin compounds, and their removal efficiencies are not so high. Conventional bio treatment processes are also less effective in removing color. In this backdrop search for more cost effective processes appears to be promising for the decomposition of phenolic compounds and removal of color of the paper mill effluent. Recently, it has been reported that the immobilization technique improves the efficiency of microbial activity as in this technique both the bioconversion of the toxic pollutant and adsorption of the newly formed species are performed simultaneously [10-12].

It was recently that identified [13] the bacterial stains like *Pseudomonas Varioti*, *Pseudomonas*, *Phoma* Sp., *PCP2* etc., present in paper and pulp mill waste water. He has reported that out of these bacteria, *Pseudomonas* Sp. of strains have more colour removal efficiency, ranging from 67% to 82%.

Similarly, two resin-acid-degrading bacteria, *Pseudomonas abietaniphila* BKME-9 and *Zoogloea resiniphila* DhA-35, have also been reported [14].

In the present study *Pseudomonas putida* MTCC 1194 strain, which has more resisting power towards phenolic compounds and highly efficient in lower range of phenolic concentrations, has been used.

MATERIALS AND METHODS

Chemicals

Activated carbon used as the adsorbent was supplied

by M/s s.d.fine-chem. Ltd, Mumbai, India. It was sieved to get 2-4 mm particles. All other chemicals used were got from M/S d.Fine-chem. Ltd, Mumbai.

Source of organism

Pseudomonas putida (MTCC 1194) species, which degrades phenolic compounds obtained from Institute of Microbial Technology, Chandigarh, India.

Batch kinetic studies

Solution of known concentration of phenol, o-cresol and 4-chlorophenol were treated with known weight of adsorbent, i.e. activated carbon, at initial concentration of 200 mg/l, pH at 7.0 and particle size of 2-4 mm at 28° C. The above three compounds were treated with and without microorganism on activated carbon separately. Each experiment with microorganism was carried out in conical flask containing minimal medium and inoculated with *Pseudomonas putida* (MTCC 1194) and was kept at 180 rpm in a shaker. For every 30 min the amount of pollutant degraded was calculated by taking aliquot samples.

Column Studies

Studies on both BAC and GAC column reactor were done separately for all the three compounds phenol, o-cresol, 4-chlorophenol with initial concentration of 200 mg/l.

The reactor specifications and operating conditions are stated below :

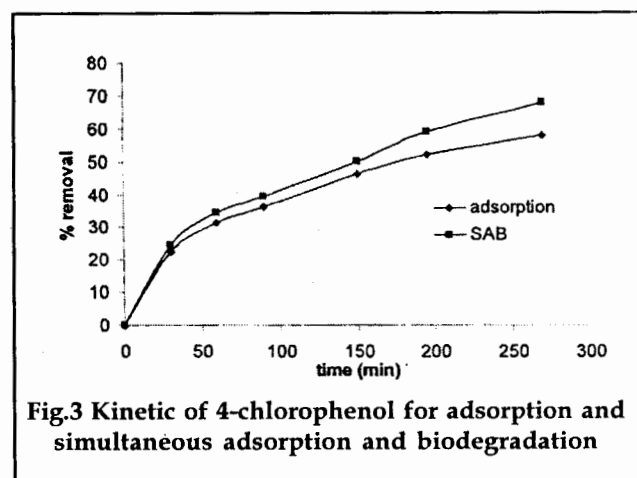
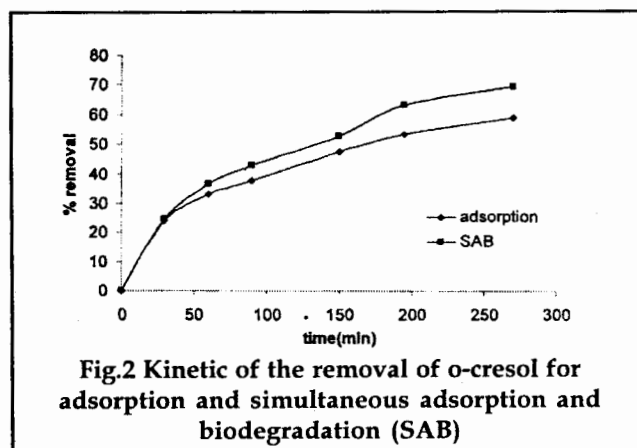
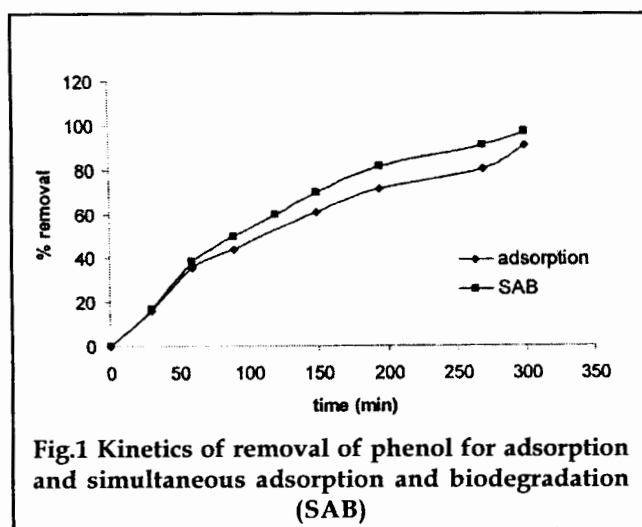
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| Column length | : 62.4 cm |
| Size of the particles used | : 2-4 mm |
| Amount of granular activated carbon loaded | : 60 g |

Internal diameter of the column : 1.1 cm
 Volumetric flow rate : 10 ml/min
 EBCT of the column : 4.9 min

Biologically active column was prepared by adding the inoculum into the down flow column reactor at the flow rate of 10 ml/min, keeping the inoculum in the reactor for 6h followed by recirculation of inoculum for 12h. After the formation of Bio Layer or granular active few carbon (GAC), solution bearing one of the compounds was passed at the flow rate through the down flow column reactor. The samples collected from the bottom of the column reactor were further analyzed find out the concentration of the compounds by using. U V spectrophotometer.

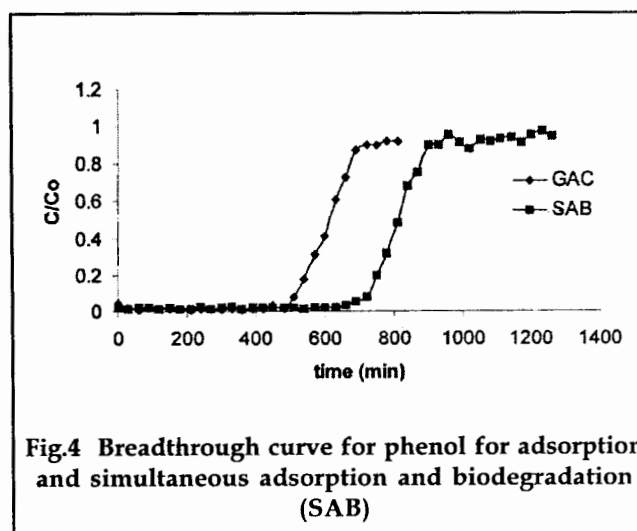
RESULTS AND DISCUSSION

The adsorption isotherm is of fundamental importance in the design of adsorption system. Knowledge of the adsorption capacity of an adsorbent material such as *Pseudomonas putida* immobilized activated carbon, enables the engineer to develop treatment systems for particular adsorbate/adsorbent system. Unlike in adsorption, there is a continuous diffusion of adsorbate into the solid surface and back diffusion of solute into the liquid in simultaneous adsorption biodegradation process (SAB). At equilibrium, the solute remaining in solution are in dynamic equilibrium with that in the surface of the bio film. and there is a defined distribution of solute between the liquid and solid phases, which are generally represented by a series of isotherm.



The present experiment is explained nicely by Freundlich isotherm. Percentage removal of these three compounds with time, for adsorption and simultaneous adsorption - biodegradation (SAB), in batch study, have been separately shown in Fig.1 to 3.

Column studies were done to find out the break



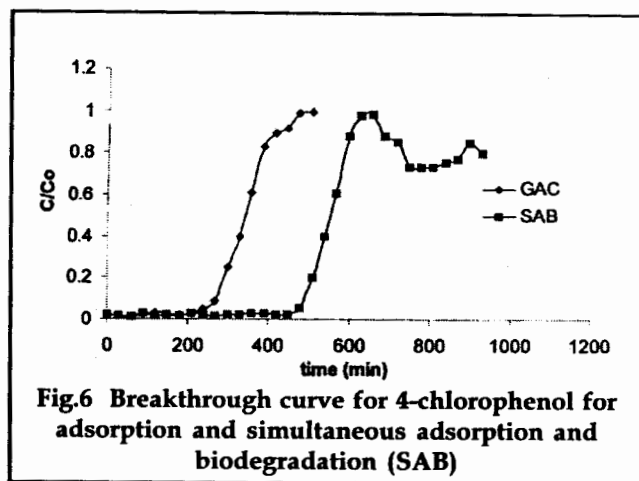
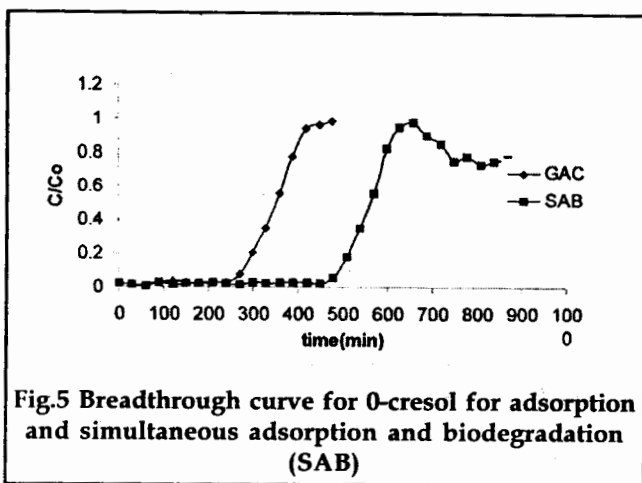


Table 2. Specific uptakes for batch process for GAC as well as for SAB

| | GAC | | | | SAB | | | |
|----------------|-------|-------|------------|-------|-------|-------|------------|-------|
| | Batch | | Continuous | | Batch | | Continuous | |
| | a | b | a | b | a | b | a | b |
| phenol | 18.2 | 91.08 | 19.43 | 69.43 | 14.36 | 97.18 | 27.42 | 70.29 |
| o-cresol | 11.83 | 59.19 | 11.93 | 70.22 | 13.94 | 69.74 | 20.9 | 71.69 |
| 4-chlorophenol | 13.62 | 68.14 | 14.47 | 69.89 | 14.62 | 58.14 | 18.62 | 70.56 |

a : Specific uptake (mg/g)

b: Percentage Removal

thorough curves for phenol, o-cresol and 4-chlorophenol. The reactor efficiency and specific uptakes have been found to determine the feasibility of the column reactor and to compare column reactor with batch reactor. Table 2. contains the data for various processes during batch and continuous studies. In Table 3, the breakthrough points for continuous studies in GAC and SAB column reactors have been shown. Breakthrough curves have been shown in Fig. 4 to 6.

Fig 7. shows the increase of the pH of the culture (6.9 - 7.9) with increases of degradation of phenol.

From Figs. 1 to 3 and Table 2, it is clear that maximum degradation of phenol is obtained in batch reactor, but for other compounds, maximum degradation is obtained in column reactor. Specific uptake is more in column reactor for all the three compounds. The

apparently lower reactor efficiency for phenol, in column reactor, is compensated by its very high specific uptake, just the double in comparison to batch reactor. This high specific uptake makes column reactor feasible for phenol. In both batch and continuous study, SAB has higher removal rate and specific uptake than GAC, it indicates is greater than that of adsorption. In the initial stages both the processes have same percentage removals, it is because of the dominance of adsorption

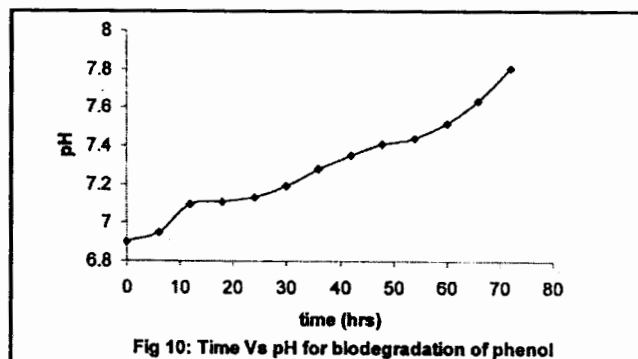


Fig.7 Time Vs pH for biodegradation of phenol

Table 3. Breakthrough points of Phenol, o-cresol and 4-chlorophenol on GAC and SAB.

| | Breakthrough point | |
|----------------|--------------------|-----|
| | GAC | SAB |
| Phenol | 510 | 720 |
| o-cresol | 270 | 480 |
| 4-chlorophenol | 240 | 480 |

over biodegradation, but as time progresses the percentage removals for SAB increases. It can be attributed to the partial saturation of activated carbon pores with solute. Biodegradation dominates when adsorption equilibrium is reached, a reverse gradient is developed in the bulk solution and the total solute, adsorbed on to pores, comes out and is biodegraded.

From Fig. 4 to 6 and Table 3, it is evident that break through point for phenol is maximum for both GAC and SAB column, which is followed by o-cresol and 4-chlorophenol. For o-cresol and 4-chlorophenol the breakthrough points are same, 480, in case of SBA but different, 270 and 240 respectively, in case of GAC. But in all the cases SAB shows more breakthrough points than GAC. From these observation it is clear that simultaneous adsorption-biodegradation is more efficient than the adsorption or biodegradation processes separately for removing phenolic compounds from wastewater.

CONCLUSION

Simultaneous adsorption - biodegradation improves removal efficiency for the removal of phenol, o-cresol and 4-chlorophenol, compared to either adsorption alone or biodegradation alone. Specific uptakes in continuous column reactor for treating phenol, O-cresol and 4-chlorophenol, is higher than the batch process due to the immobilization of microbes on the surface of GAC bed. But for continuous bioactive column reactor specific uptake is almost same for all the three cases.

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