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## DEMINERALIZATION OF PHENOL DERIVATIVES USING SEQUENTIAL ADSORPTION AND BIOLOGICAL DEGRADATION PROCESS

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### ABSTRACT

The present investigation was undertaken to assess the degradation of phenol derivatives by sequential adsorption and biological process. Phenols and their derivatives are recognized toxic compounds and known for their carcinogenic and other toxic properties even in trace quantity. Biological treatment is considered more environmentally friendly and cost-effective in comparison with physicochemical treatment. However, the process is less effective for high concentration pollutants. Activated carbons, prepared from *Jatropha* having micropore size under 125 microns, have been used to carry out the adsorption of Phenol and Chlorophenol in aqueous solution. Observations revealed that the rate of phenol biodegradation was increased because of pretreatment, i.e., adsorption, temperature and glucose concentration. The optimal conditions for Phenol and CP removal were found to be temperature 35<sup>o</sup>C (58-65% removal) and two gpl glucose levels (70-78% removal). The importance of the study is the pretreatment of recalcitrant chemicals with adsorption followed by biodegradation and thus provided with an alternative bioremediation approach.

**Keywords:** Biodegradation, Phenolic Toxicity, Recalcitrance, Integrated Adsorption, Sequential Treatment

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### INTRODUCTION

The unchecked and unconstrained industrialization had resulted in severe pollution of water bodies bringing all kinds of extraneous elements in the environment. Various technologies have been explored, and newer technologies are being tested to remove these contaminants.<sup>1-3</sup> Recently microbial degradation is gaining ground and has the potential to be an inexpensive and sustainable technology.<sup>4</sup> Microbial degradation uses the multitude of microbes present in nature and perform biodegradation. Adsorption is another novel and potential technology gaining widespread attention among scientists working in the field of wastewater treatment. It involves adsorption of organics by solid adsorbents. It is economical, environment friendly, does not generate by-products and works at normal operating conditions and so on.

Water contaminated with phenol is one of the significant environmental concerns. Known to be carcinogenic and mutagenic, phenol could cause great havoc in animals and human beings.<sup>5</sup> Phenol is a priority pollutant with toxic properties, and hence there have to be all-out efforts to remove phenol from wastewaters.<sup>6,7</sup> Several reports in the literature have voluminous data on phenol toxicity and its hazardous nature. It is reported that contact with phenol can cause breathing problems, muscle problems, respiratory problems and so on. Chronic exposure can also lead to various other complications.<sup>8-10</sup> Phenol typically arises from pulp and paper mills, refineries, mine wastewater, and from multiple pesticides industries. There

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are several different sources such as textile industries, solvent plants, etc.<sup>11-15</sup> Unsurprisingly, phenol wastewater treatment is of paramount importance to reduce our overall pollution impact on the society.<sup>16</sup> Both the adsorption and biodegradation of phenol are widely reported in the literature. However, there is fewer study coupling with the two processes. The integrated treatment process comprising adsorption and biological oxidation have a higher potential to mineralize the phenolic wastewater compared to the individual application of these processes.<sup>17</sup> The significance of the combined treatment lies in the fact that Physico-chemical methods are notably better in degrading toxic chemicals like phenol since it can break aromatic linkage, which is a considerable hindrance in biodegradation. Besides, the intermediates generated from such a pretreatment process may also work as critical substrates augmenting the biodegradation of the parent compounds<sup>18</sup>. This work targets the sequential adsorption and biological degradation of phenols present in the wastewater.

## EXPERIMENTAL

### Cultures Used

The mixed cultures were collected from the laboratory of microbiology, PRIST Deemed University, Thanjavur. The composition of the medium with 1% glucose as the sole carbon source is tabulated below (Table-1). Before experimentation, culture acclimatizing has been done with the chemicals for two to four weeks before experimentation. The cultures were maintained at 4°C in nutrient broth and were subcultured every 10 days.

Table-1: Glucose Medium (1%) Composition

S. No.	Component	(g/L)
1	Glucose	10.00
2	Yeast extract	0.340
3	NH <sub>4</sub> Cl	0.840
4	KH <sub>2</sub> PO <sub>4</sub>	0.134
5	K <sub>2</sub> HPO <sub>4</sub>	0.234
6	MgCl <sub>2</sub> .6H <sub>2</sub> O	0.084

### Adsorbents Preparation

Jatropha Deoiled Cake (JDC) used as adsorbents which were prepared using the same method detailed in another article by the same author.<sup>19</sup>

### Preparation of Stock Solution

The following phenolic compounds, Phenol and 2-chlorophenol (CP) were obtained from Merck India. Since Phenol and Chlorophenol were both liquids at room temperature, appropriate volumes of these chemicals were taken to convert to 1 gram. A stock solution of 1000 ppm CP was prepared in 0.1 N NaOH, due to low aqueous solubility.

### Experimental Procedure for Integrated Adsorption and Biological Treatment

Integrated adsorption and biological treatment were conducted in sequential mode. The wastewater was subjected to combined treatment by using adsorption and biological degradation. The adsorbed wastewater was made up to 30 ml by adding the required quantity of media and inoculum. The conical flasks were kept in an orbital shaker at the desired temperature. Neutral pH was maintained by adding acid or alkali. Every 24 hours, chemical concentrations and COD were measured.

The experiments with phenol and CP were conducted for six different initial concentrations ranging from 25 ppm to 400 ppm and 20 ppm to 150 ppm respectively. The glucose concentrations used were 1 gpl, 2 gpl and 3 gpl and the temperatures maintained were 25, 30, 35 and 40°C. We conducted the experiments for seven days, fixing the inoculum concentration at 15%.

### pH

The pH of all the reactors was measured using Water Analyzer (Make: Systronics, Model: 371).

### Determination of Biomass Concentration

The biomass concentration was determined with the help of Systronics spectrophotometer at 600 nm. The obtained value was augmented with its dilution factor to calculate biomass strength.

### Method used for Phenol and Chlorophenol Concentration Determination

Phenols and Chlorophenol were collected from the reactor at fixed intervals and analyzed using HPLC (Make: Shimadzu, Model: 10AS) equipped with UV Detector and a C18 Column. The detection was made at 280 nm with the mobile phase involving acetonitrile and water (50 % v/v). The flow rate was 1 ml/min. The injection volume was 20  $\mu$ l.

### Chemical Oxygen Demand

The final COD values were measured using Colorimeter (Make: HACH, Model: DR 890). The digestion was conducted at 150 $^{\circ}$ C in COD digester (Make: HACH, Model: DR 8200) with the digestion time of two hours.

## RESULTS AND DISCUSSION

### Effect of Glucose Concentration

Figure-1 presents the biodegradation of phenol, whereas integrated treatment is shown in Fig.-2. The processes were compared for the various glucose concentrations (0 g/l, 1 g/l, 2 g/l and 3 g/l) for 400 ppm initial concentration of phenol. The findings were noted for seven days. The biodegradation data implies the prominence of glucose in deciding the degradation rate of phenol. The rise in glucose concentration progressively boosted the degradation rate of phenol.

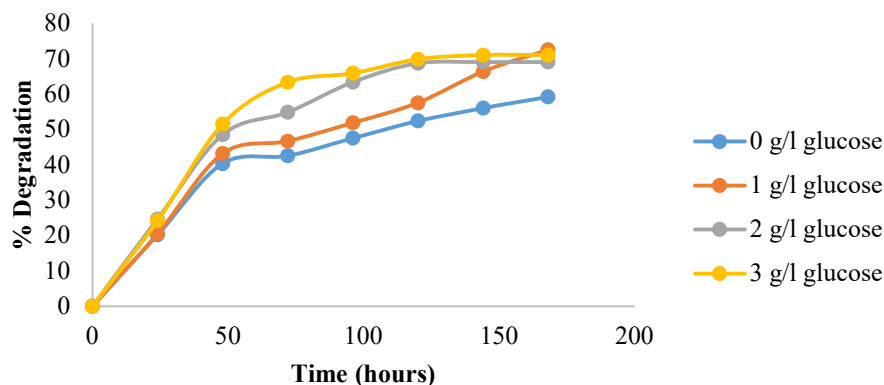


Fig.1: Biodegradation of Phenol at Different Glucose Concentration without Adsorption ( $C_i = 400$  ppm)

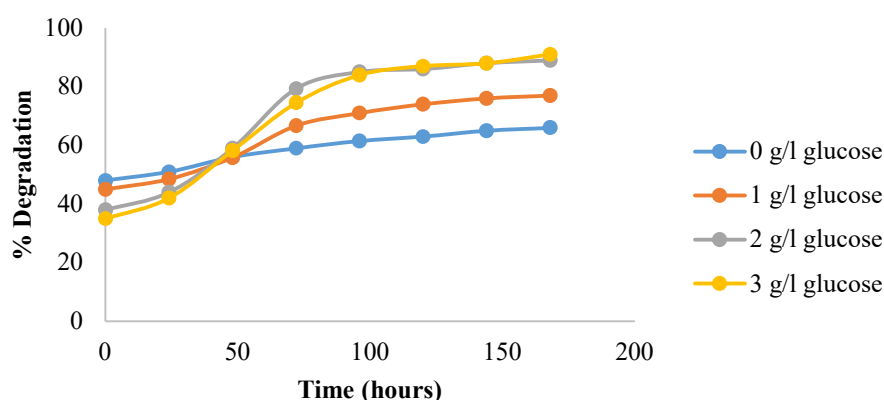


Fig.-2: Biodegradation of Phenol at Different Glucose Concentration in Sequential Mode ( $C_i = 400$  ppm)

The degradation improved from 59% to 71% as glucose concentration rose from 0 g/l to 3 g/l. the sequential degradation, however, yielded 89% removal for cultures with 2 g/l and 3 g/l glucose by the end of the week, whereas cultures without glucose yielded only 66% removal. The rate data shows that glucose

concentrations (2 g/l and 3 g/l) produced comparable trends. 2 g/l glucose was, therefore, selected as the optimal concentration. To further compare the two methods, a new factor, % point change (Pp) was introduced. It illustrates the increase in removal regarding biodegradation alone<sup>20</sup>. With the rise in glucose concentration from 0 g/l to 3 g/l, the Pp value soared from 12% to 28 %. This increase is primarily due to an increase in the biodegradation rate with the rise in glucose concentration. As observed, Pp value was unaffected by increasing glucose intensity from 2 g/l to 3 g/l. Pp value is plotted for different glucose concentrations in Fig.-3.

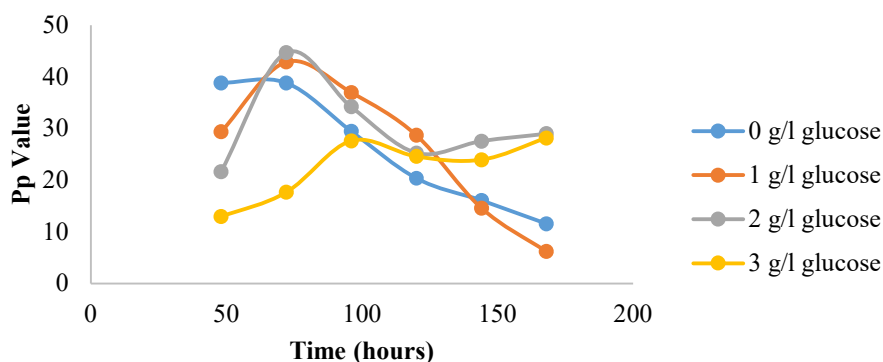


Fig.-3: Percentage Point Change for Phenol at Different Glucose Concentration in Sequential Mode ( $C_i = 400$  ppm)

The results were further confirmed by COD removal data. The COD removal rate increased from 64% to 85% as glucose concentration rose from 0 g/l to 3 g/l. However, it can be noted that adsorption with JDC significantly increased the mineralization capacity of pollutants. Pp value for COD removal improved from 56% to 66 % as the glucose level changed from 0 g/l to 3 g/l. It can be, however, noted that all the values are showing positive changes, i.e. integrated treatment is accomplishing higher COD removal compared to biodegradation alone. It is a significant result, as low-cost adsorbents can complement biological degradation and in fact, can substitute high-priced biogenic substrate.

COD removal for phenol and 2-chlorophenol (CP) by biodegradation and integrated treatment was also studied along with percentage point change values. It was noted that the effect of glucose concentration on COD removal also depends on chemicals. This indicates that an increase in glucose concentration from 2 g/l to 3 g/l reduced the removal rate for both biodegradation and integrated treatment. In the case of CP, both CP removal and COD removal reduced with the rise in glucose concentration. The existence of a biogenic substrate excites the development of microbes. When a contaminated chemical is present, high microbes' concentration facilitates increased removal of these compounds. Some positive enzymes are also encouraged, hastening the treatment of these chemicals. However, this is not always the case. It is therefore important to take substrate interactions into account, whenever two or more carbon sources are present.<sup>21</sup>

### Effect of Initial Concentration

Biological degradations were conducted at various initial concentrations. The result shows that in the case of biodegradation alone, total removal took seven days for the smallest concentration, whereas degradation for the highest concentration was inadequate (69% removal). However, the combined treatment was more effective and successful (Fig.-4 and 5). For an initial concentration of 100 ppm, total degradation was accomplished in four days, 30% less contrasted to biodegradation alone. Interestingly, results were more positive for the solutions with higher concentrations. Integrated treatment was thus found to be more useful as the pollutant concentration increases.

Results for Phenol and CP indicates that there is an upward trend with the concentrations, but interestingly very high Pp value is reported (Fig.-6 and 7). To understand the dynamics, kinetic data is also presented for CP., and it can be seen that the time factor does not have much effect on the efficacy of integrated treatment. At all times, Pp value was positive and higher. It was also noted that at low concentration of CP, Pp value

was very less as indicated by biological degradation at 20 ppm (71%) and 40 ppm (60%). As the concentration increases, biodegradation of such recalcitrant chemicals are more complicated.

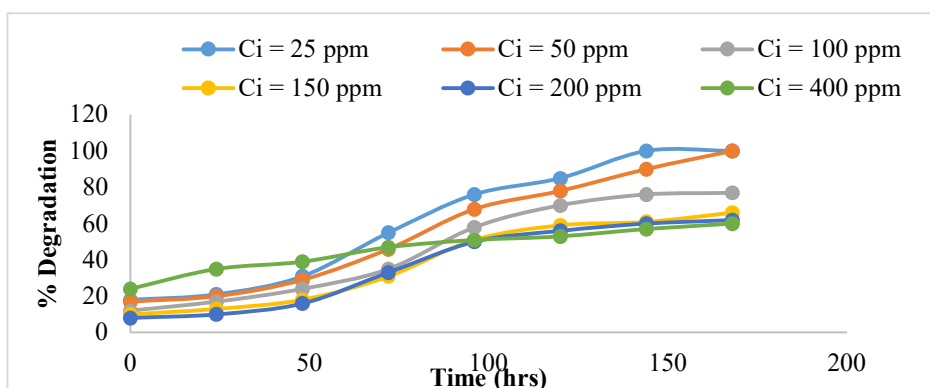


Fig.-4: Biodegradation of Phenol at Different Initial Concentration in Sequential Mode using JDC (Glucose Conc. = 2 g/l)

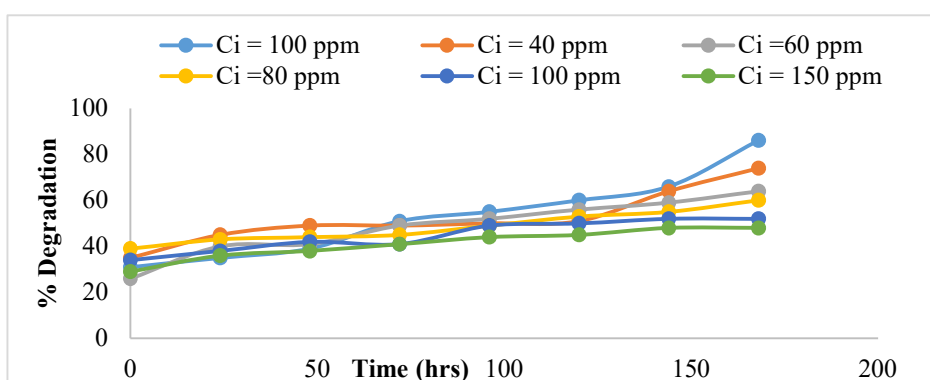


Fig.-5: Biodegradation of Chlorophenol at Different Initial Concentration in Sequential Mode using JDC (Glucose Conc. = 2 g/l)

CP being the most intractable chemical did not get degraded easily by biological degradation alone. Reduction in concentration through adsorption or other pretreatment methods are preferred route for degrading such polluting substances. It was also observed that photolysis, in combination with biological degradation, resulted in higher CP removal. They reported that complete degradation and mineralization of dichlorophenol was accomplished in 96 hours and 144 hours respectively for integrated photochemical and biological degradation.<sup>22</sup>

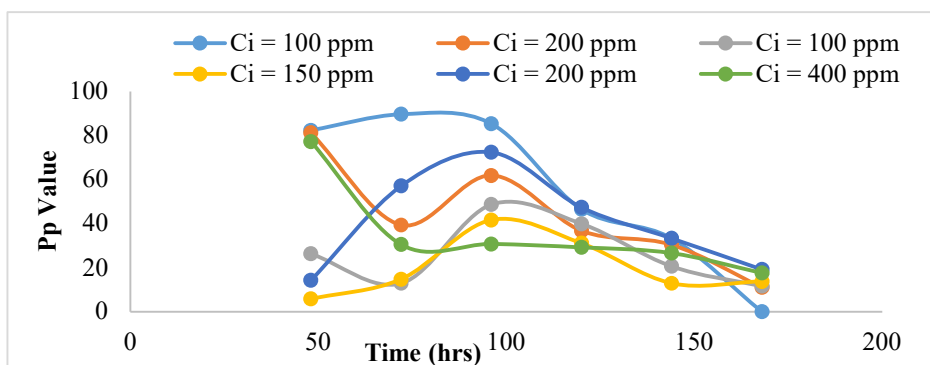


Fig.-6: Percentage Point Change of Phenol at Different Initial Concentration in Sequential Mode using JDC (Glucose Conc. = 2 g/l)

### Effect of Temperature

The effect of temperature was also studied on both biodegradation as well as for the combined treatment. Unlike other processes, the biological degradation rate normally increases with the increase in temperature. Selvakumar et al. studied the textile dye wastewater treatment in a batch reactor and also the effect of various parameters like pH, temperature, agitation speed and concentration of dye effluent on dye decolourization and degradation.<sup>23</sup> Alalewi performed the experiments at different temperatures in the range of 10°C - 40°C. The experiment revealed that decolorization was improved as the temperature increased.<sup>24</sup> The degradation rate increased with the rise in temperature. At 25<sup>o</sup> C, only 67% of degradation was noted which rose to 77% at 40<sup>o</sup> C for biodegradation for 100 ppm. Similarly, combined treatment results demonstrated increased removal with the rise in temperature (Fig.-8 and 9).

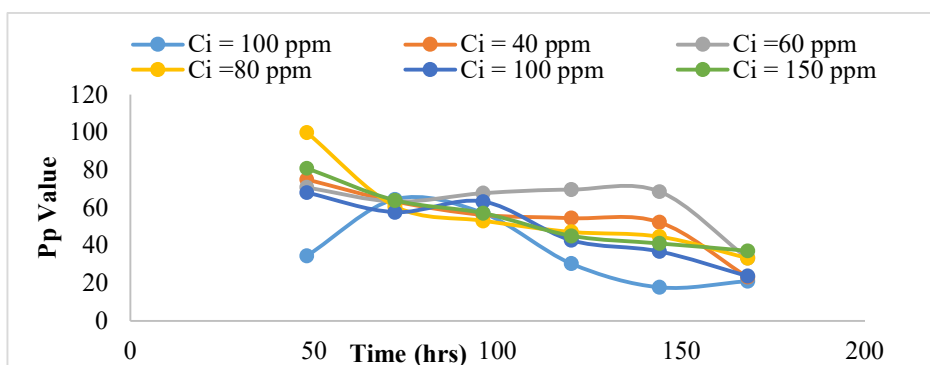


Fig.-7: Percentage Point Change of Chlorophenol at Different Initial Concentration in Sequential Mode using JDC (Glucose Conc. = 2 g/l)

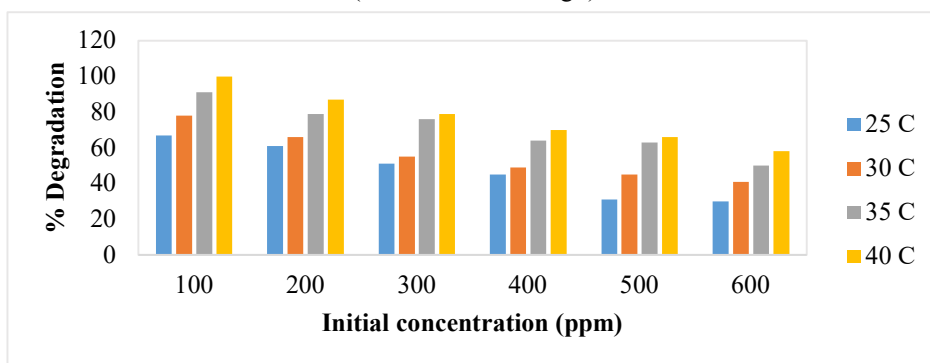


Fig.-8: COD Removal of Phenol at Different Temperature in Sequential Mode

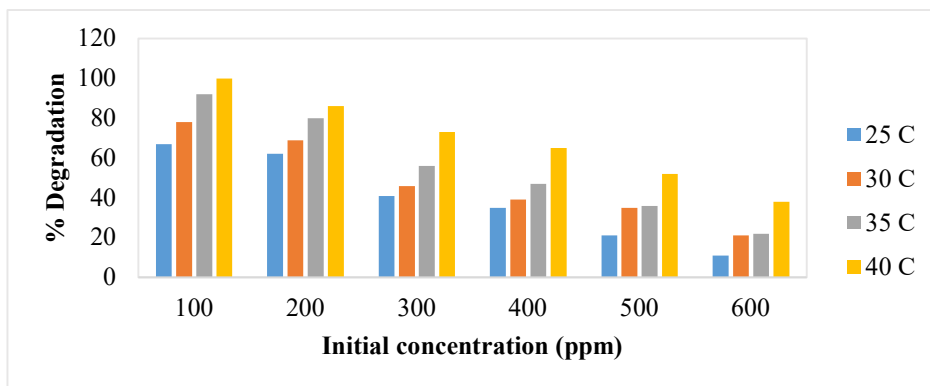


Fig.-9: COD Removal of Chlorophenol at Different Temperature in Sequential Mode

COD removal was also faster at high temperatures. However, COD removal was not showing a clear trend from 25 to 35<sup>o</sup> C. Biodegradation certainly increases at high temperatures. But, it requires high operating costs, and consequently, actual plant design usually involves a trade-off to achieve the safest wastewater treatment opportunities. In this work, therefore, 35<sup>o</sup> C was considered the most optimum temperature.

### CONCLUSION

Sequential adsorption and biological removal were conducted for Phenol and Chlorophenol, and several parameters such as glucose concentration, initial concentration, temperature, etc. were varied. It was observed that a rise in glucose concentration improved the COD removal for both the chemicals. The recalcitrant compounds, Phenol and CP, which yielded very less improvement in biological degradation alone, had been more successful in sequential mode. At all concentrations, COD removal was higher for sequential mode than biological degradation alone. Similarly, COD removal for phenol was 62% in sequential mode, which was 35% higher than biological treatment. In the case of most toxic CP, results were more emphatic. Pp value was more than 100% for all glucose concentrations. Even when compared to biological degradation, sequential mode resulted in very high COD removal. For 150 ppm of CP solution, biological degradation alone could remove only 22% COD whereas sequential mode mineralized 48% of the solution.

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