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Effect of Sequential Treatment of Paper Industry Wastewater using Aluminum Chloride and *Pseudomonas putida*

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ABSTRACT
The effectiveness of a two-step sequential method - chemical precipitation by aluminum chloride and subsequent employment of Pseudomonas putida - was investigated for treatment of paper mill wastewater. Removal of color and phenols was found to be dependent on pH. Maximum color removal (99.8%) was achieved using 4.0 g L^{-1} $AlCl_3$ at pH 5, wherein 39% phenols, 96% total suspended solids (TSS), and 59% chemical oxygen demand (COD) were removed leaving 32 mg L^{-1} residual Al(III) ions in the wastewater. Highest removal of phenols (99%) was achieved at pH 12. The effluent from the treatment with $AlCl_3$ at pH 5, was further processed with P. putida at pH 7 for 48 h, leading to marginal further reductions in color, phenols, TSS, and COD but residual Al(III) ions were sorbed to below disposal level. The proposed sequential treatment resulted in better quality water than chemical precipitation alone.

Key words: *Wastewater treatment, Sequential treatment, Pseudomonas putida.*

1. INTRODUCTION

The paper industry uses a large quantity of freshwater during the production of paper from lignocellulosic materials that generate considerable amount of wastewater. The paper industry wastewater is characterized by dark color, foul odor, high organic content and extreme quantities of chemical oxygen demand (COD), biochemical oxygen demand, and pH [1]. The wastewater has to meet the national standards of discharge limits before disposal onto land or water bodies.

Several physicochemical and biological treatment methods employing variety of chemicals and microorganisms have been proposed in the past to remove phenols and/or coloring matter from wastewaters and the drawbacks of these methods have been reported [2-9].

Chemical precipitation is a widely used technique for reduction of coloring matter from paper industry wastewaters. The treatments employing metal salts of iron, aluminum, calcium, and magnesium for the reduction of coloring matter are already reported [3,10]. However, these treatments failed to check residual metal ion concentrations in treated water. Our group had earlier reported effectiveness of sequential treatment using ferric chloride and *Pseudomonas putida* [11].

This paper investigated the effect of sequential treatment of paper industry wastewater using aluminum salt ($AlCl_3$) and microorganism *P. putida* (MTCC 1194).

2. EXPERIMENTAL SECTION

2.1. Chemicals

Analytical grade chemicals were purchased from Sigma-Aldrich and local suppliers.

2.2. Effluent and its Characterizations

Paper industry wastewater required for the study was collected from a local paper mill and stored at 4°C. The physicochemical characteristics of effluent were determined using American Public Health Association (APHA) methods [12]. The Al(III) metal analysis was performed using inductively coupled plasma.

2.3. Chemical Precipitation Treatment

About 100 ml of wastewater was mixed with predetermined quantity of $AlCl_3$ in the range of 0-5.0 g L^{-1} and solution pH was adjusted, and

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left unshaken for 24 h to facilitate formation and sedimentation of precipitates. Aliquots of sample were analyzed after 24 h.

Effect of pH on removal of color and phenols was investigated by adding 4 g L^{-1} of $AlCl_3$ to wastewater samples maintained at different pH ranges of 2-12. Effect of the metal salt dose was studied by adding $AlCl_3$ (1-5 g L^{-1}) to different 100 ml wastewater samples and adjusting pH to the desired value.

2.4. Sequential Treatment

In the first step of $AlCl_3$ - *P. putida* sequential treatment, the raw wastewater was treated using 4.0 g L^{-1} dose of $AlCl_3$ at pH 5.0. In the second step, the effluent treated with $AlCl_3$ was subjected to microbial treatment with *P. putida*. Modified minimal salt medium (MSM) amended with 0.5 g L^{-1} of glucose and 0.5 g L^{-1} of ammonium sulfate was used [11]. After an initial series of experiments, microbial biomass of 5.0 g L^{-1}, pH 7.0, temperature of 30°C, agitation rate of 180 rpm, and incubation period of 48 h were identified as optimum conditions and employed in the second step of sequential treatment. During incubation, the culture sample was removed under aseptic conditions and analyzed for color, phenols, total suspended solids (TSS), COD, and Al(III) content as described in APHA manual [12]. The culture medium without bacterial inoculum was used as a control in all the experiments.

The biosorption performance of Al(III) ions by *P. putida* cells was compared using linearized Langmuir and Freundlich isotherm models. Biosorption equilibrium isotherms were plotted for metal uptake (Q_e) against equilibrium metal ion concentration (Ce) in the effluent.

3. RESULTS AND DISCUSSION

The physicochemical analysis showed that the wastewater was dark brown in color with pH of 7.18. The estimated color, TSS, total phenols, and COD content in wastewater were 6285 CU, 3263 mg L^{-1}, 79.5 mg L^{-1}, and 4306 mg L^{-1},respectively. Most of the estimated parameters clearly exceed the minimal disposal standards of wastewater (Table 1).

3.1. Chemical Precipitation

Chemical precipitation treatment showed removal of color and phenols from wastewater. However, there was a strong dependence of phenols and color removal on pH (Figure 1). Removal of phenols by $AlCl_3$ was found to be more effective at alkaline pH, increasing from 34% at pH 2.0 to 93% at pH 12 when 4 g L^{-1} $AlCl_3$ was used. Removal of color was effective in acidic pH values (3.0-6.0), with highest color reduction of 99.8% at pH 5.0. Therefore, alkaline conditions were suitable for removal of phenols, whereas acidic conditions were effective for removal of color from paper mill wastewater.

The dependence of phenols reduction on the dose of $AlCl_3$ was studied in pH range of 10-12. The results obtained are shown in Figure 2. The phenols reduction of 78% (pH 10), 89% (pH 11), and 99% (pH 12) was observed with the $AlCl_3$ dose of 5 g L^{-1}, 4.5 g L^{-1},and 4.5 g L^{-1},respectively. The highest phenol removal of 99% was observed at pH 12 for $AlCl_3$ dose of 4.5 g L^{-1}.

Table 1: Wastewater characteristics before and after sequential treatment.

Pollution parameter (unit)	Raw wastewater	After sequential treatment	PL*
pH	7.18±0.1	6.8±0.1	6.5-8.5
Color (Pt-CU)	6285±37	0	Clear
TSS (mg L^{-1})	3263±13	110±12	100
COD (mg L^{-1})	4306±41	1722±38	250
Al (III) (mg L^{-1})	-	1.0±1.0	3.0-5.0
Total phenols (mg L^{-1})	79.5±0.3	47±0.2	1-5

*PL=Permitted limit

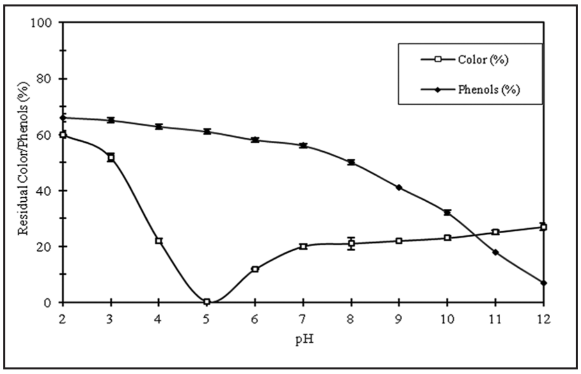

Figure 1: Effect of pH on the removal of phenols and color from paper mill wastewater (applied dose of $AlCl_3$=4 g L^{-1}, initial color=6285 CU, initial phenols concentration=79.5 mg L^{-1}).

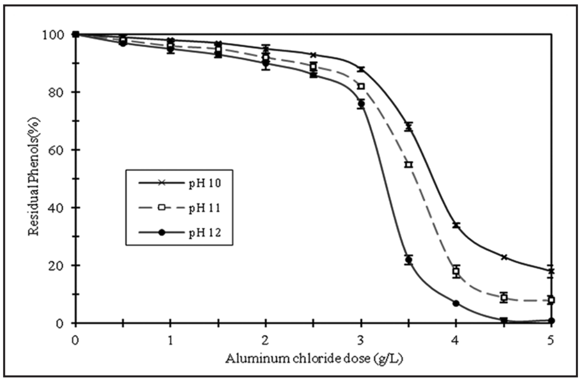

Figure 2: Effect of dose of $AlCl_3$ on the removal of phenols from wastewater at different pH conditions (initial color=6285 CU, initial phenols concentration=79.5 mg L^{-1}).

Under these treatment conditions, 83% of color, 84% of TSS, and 48.5% of COD were removed from the wastewater. However, the treatment induced a residual Al(III) concentration of 43.6 mg L^{-1} to water.

3.2. Sequential Treatment

The bacteria *P putida* (5.0 g L^{-1}) was inoculated into the modified MSM culture media containing $AlCl_3$ treated effluent, and growth of organism was monitored by measuring optical density (OD) at 620 nm. There was no marginal increase in OD indicating the initial attempts of the organism to adapt, whereas the drop in OD later indicates the inability of organism to adapt and survive under the culture conditions.

There were no changes in color and phenol content. However, the concentration of Al(III) ions was reduced significantly from 31.5 to 1.0 mg L^{-1} within the first 2 h of incubation (Figure 3). Controls did not show any change in color, phenols, and Al(III) ion concentrations indicating removal of Al(III) ions through either biosorption or bioaccumulation mechanism. Overall, the results show that sequential treatment removed color, TSS, and Al(III) ions to below maximum permitted levels of disposal.

Previous studies have shown that the pH range of 4.0 to 6.0 is suitable for biosorption or bioaccumulation [13]. Hence, the second step in sequential treatments was performed using *P. putida* at pH 7.0. Experiments on the effect of biomass concentrations were repeated using biomass concentration range of 0-2.0 g L^{-1} to see the detailed biosorption pattern of Al(III) ions, and data were analyzed using Freundlich and Langmuir adsorption isotherm models to understand the nature of biomass adsorption on bacterial cell surface. The Langmuir and Freundlich adsorption isotherm plots are shown in Figures 4 and 5. The linear regression data show that biosorption data of Al(III) ions on bacterial surface fits more to Langmuir's model (R^2=0.9877) than to Freundlich's model (R^2=0.9432), suggesting that biosorption of Al(III) obeys monolayer adsorption on the homogeneous bacterial cell wall surface and the metal binding sites are uniformly distributed on bacterial surface. However, the value of correlation coefficients for the Freundlich isotherm is over 0.9 (R^2=0.9432), and the experimental data does not completely rule out fitment of data to Freundlich type. The recorded maximum sorbate uptake per gram of biosorbent (Q_{max}) for Al(III) on bacterial surface was 50 mg g^{-1} biomass in effluent media.

4. CONCLUSIONS

The effect of aluminum chloride on color, phenols, TSS, and COD of paper mill wastewater was investigated in the present study. Results show that chemical precipitation by aluminum chloride either removes color (pH 5.0, dose 4.0 g L^{-1}) or phenols (pH 12.0, dose 4.5 g L^{-1}) completely but not both of them under the same treatment condition. Chemical precipitation under both treatment conditions left a high concentration of residual Al(III) ion in treated water that poses secondary disposal problems. This

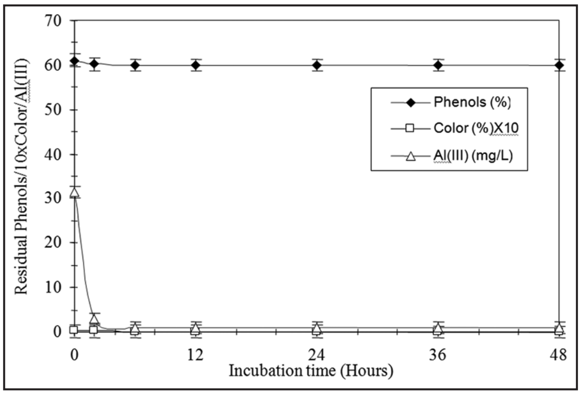

Figure 3: Color, phenol, and Al(III) ion removal during treatment with *Pseudomonas putida*.

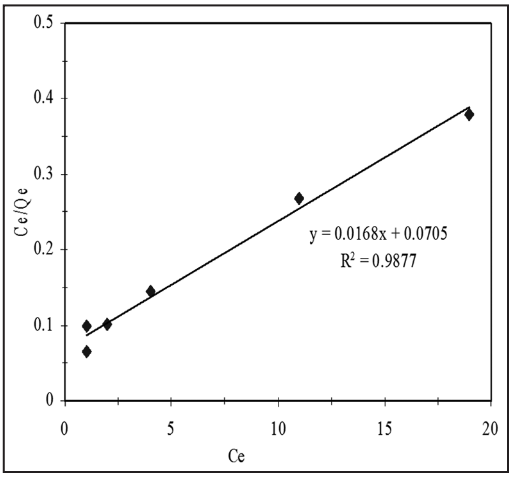

Figure 4: Langmuir adsorption isotherm for the adsorption of Al(III) ions on *Pseudomonas putida* surface.

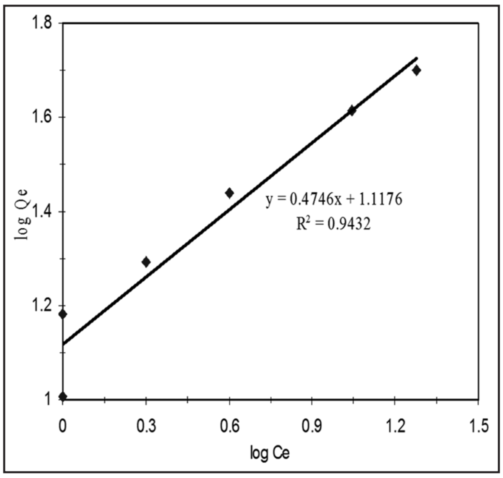

Figure 5: Freundlich adsorption isotherm for the adsorption of Al(III) ions on *Pseudomonas putida* surface.

suggests that chemical precipitation by $AlCl_3$ alone is ineffective. However, after sequential treatment of metal salt-treated effluent with *P. putida*, the metal ions were also removed to below discharge limits. The study concludes that the two-step sequential treatment may be used as an alternative method for the tertiary treatment of paper mill wastewater in the place of chemical precipitation.

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***Bibliographical Sketch**

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