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PRECIPITATION OF PHENOLS FROM PAPER INDUSTRY WASTEWATER USING FERRIC CHLORIDE

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ABSTRACT

The removal of phenols from paper industry wastewater by chemical precipitation using ferric chloride was investigated in the present study. The ferric chloride was able to precipitate out phenols as well as coloring matter from the wastewater. The precipitation was found to be highly dependant on both pH and dose of iron salt used. The phenols removal was effective under highly alkaline conditions above pH 10 and the color removal was effective in the pH range of 3.0-6.0. The chemical precipitation performed at pH 12, using ferric chloride dose of 2.5 g/l, was able to reduce 98% of phenols and 80% of color from the paper industry wastewater. The experiments showed the phenols reduction from 79.5 mg/l to a dischargeable level of 2mg/l after treatment with ferric chloride at pH 12. The study claims that the ferric chloride can be used effectively to remove phenols from paper industry wastewater.

Key Words: Chemical precipitation, Paper industry wastewater, Wastewater treatment.

INTRODUCTION

The pulp and paper industry wastewater is characterized by dark color, foul odour, high organic content and extreme quantities of COD, BOD and pH[19]. The dark color in wastewater is a major environmental concern as the discharge of dark colored wastewater to water bodies inhibits the photosynthetic activity of aquatic biota by reducing sunlight, besides exhibiting the toxic effects on biota[2,3,13,23].

The phenols generated during pulp bleaching stages of paper production are harmful pollutants found in wastewaters that contribute significantly towards the toxicity of paper industry wastewater[1,12,13]. The reduction of dark color and toxic phenols from paper industry wastewater to levels below the discharge limits is important prior to disposal of wastewater onto land or water bodies.

Several physiochemical, electrolytic methods such as electro-coagulation, chemical precipitation, adsorption and various microbial methods have been attempted in the past to remove phenols and or color from industrial wastewaters and the drawbacks of these methods are reported in literature[3,4,6,9-11,14-17,20-22,24-26].

The chemical precipitation of coloring matter and its removal from paper industry wastewaters using lime and salts of iron and aluminum is already reported in literature[4,5,9]**.** However, no systematic study related to removal of phenols from wastewater by ferric chloride ($FeCl_3$) is found in literature and the present study is an attempt in that direction. The major objective identified for this study is to assess the ability of $FeCl_3$ to precipitate and remove phenols from paper industry wastewater.

EXPERIMENTAL

Effluent Samples

The combined effluent of bleaching and pulping stages was collected from local paper mill and it was stored in refrigerator at 4^{o}C until further investigation was carried out.

Reagents and instruments

The chemicals used in treatment were of analytical grade and were obtained from various furnishers. The pH, optical density and Fe(III) concentrations were analyzed using instruments pH meter (ELICO), UV-Visible Spectrometer (Schimadzu) and Inductively Coupled Plasma (ICP) respectively.

Physicochemical characterization

The characteristics of water samples such as pH, color, COD, TSS, TDS and lignin were determined using standard methods of APHA (American Public Health Association)[7].

Total phenol content

The total phenol content was determined by antipyrene method [7]. For the measurement, 100 ml water sample was mixed with 2.5 ml of NH_4OH (0.5N) solution and its pH was adjusted to 7.9±0.1 using phosphate buffer. Subsequently, 1ml of 4-aminoantipyrene and 1 ml of potassium ferric cyanide solutions were added to the sample mixture and was left for 15 minutes. The absorbance of sample mixture was then measured at 500nm and phenol content was determined using standard calibration curves.

Chemical precipitation studies

For the treatment of wastewater with $FeCl_3$, 100 ml of untreated effluent was taken in 300 ml glass stoppered bottles containing predetermined doses of $FeCl_3$. The content in the bottle was mixed thoroughly by repeated inversion and the pH was adjusted to desired value. The bottles were then left unshaken to facilitate the formation and sedimentation of precipitates. During initial runs, the samples were drawn and analyzed for color in the intervals of 30 minutes and the results revealed completion of reaction in first 2-3 hours. However, for the sake of convenience, the batch tests were conducted after 24 hours at room temperature.

The effect of pH on removal color and phenols was investigated by adding 2g/l of $FeCl_3$ to wastewater samples maintained at different pH conditions in the pH range of 2-12. The effect of $FeCl_3$ dose was investigated by adding varying predetermined doses of $FeCl_3$ to 100 ml wastewater and adjusting pH to the desired value.

Table-1: Physicochemical characteristics of paper mill wastewater.

Parameter Measured	Unit	Parameter value
pH	__	7.18
Color	Pt-CU	6285
TDS	mg/l	1046
TSS	mg/l	3263
Lignin	mg/l	4188
COD	mg/l	4306
Fe(III)	mg/l	BD
Total Phenols	mg/l	79.5

* BD-Below Detection Level (<1mg/l)

Table-2: Wastewater characteristics before and after treatment with 2.5 g/l of $FeCl_3$ at pH 12.

Pollution Parameter	Unit	Before Treatment	After Treatment With $FeCl_3$	MPL** (Indian Standard)
pH	__	7.18	12	6.5-8.5
Color	CU	6285	1257	clear
TSS	mg/l	3263	358	100
COD	mg/l	4306	1378	250

Fe(III)	mg/l	BD	30	—
Total Phenols	mg/l	79.5	1.6	1-5

BD-Below Dectection Level (< 1mg/l). ** MPL-Maximum Permitted Level (Indian Standards)

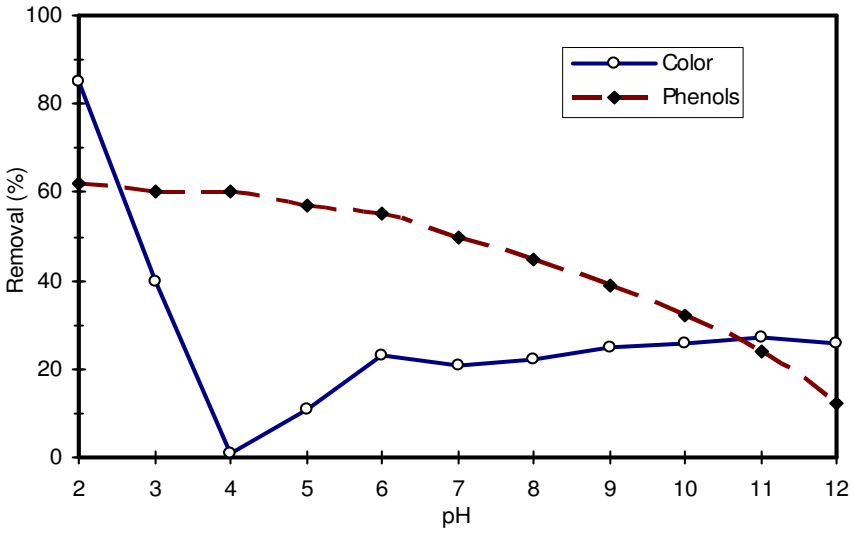

Fig-1: Effect of pH on removal of phenols and color from wastewater after treatment with Ferric chloride

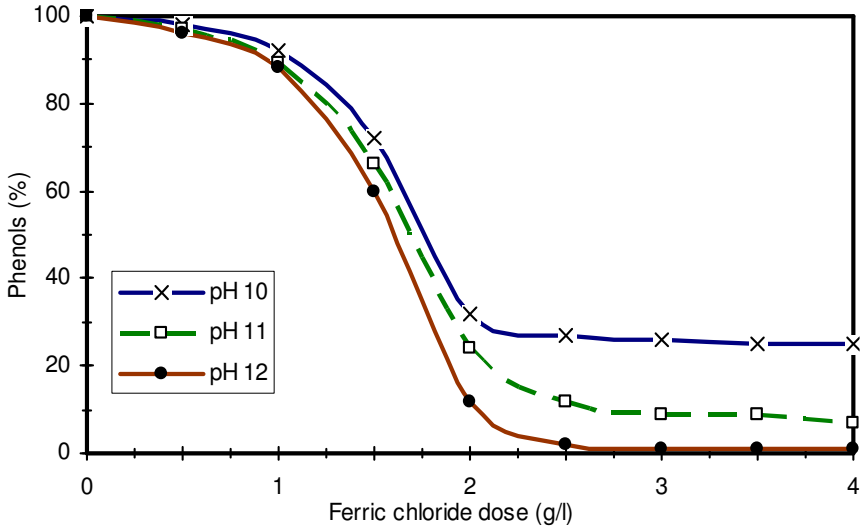

Fig-2: Effect of dose of Ferric chloride on removal of phenols from wastewater at different pH conditions.

RESULTS AND DISCUSSION

Wastewater characteristics

The paper industry wastewater characteristics were analyzed and the results of analysis are shown in Table-1. The wastewater used in the study was dark brown in color and its pH was 7.18. The analysis showed the high presence of color (6285 CU), TDS (1046 mg/l), TSS (3263 mg/l), total phenols (79.5 mg/l) and COD (4306 mg/l) in wastewater. Most of the estimated parameters in wastewater exceed the

Maximum Permitted Limit (MPL) set for the disposal of wastewater by Minimal National Standards (MINAS)(Table-2).

Chemical precipitation

The chemical precipitation was brought about by mixing a predetermined quantity of $FeCl_3$ to 100ml wastewater at a particular pH. The addition of $FeCl_3$ initially produced dark brown flock which eventually formed larger aggregates and settled down as sludge. The supernatant obtained upon centrifugation was clear and lighter in color. It was observed that the addition of $FeCl_3$ reduced the pH of wastewater from 7.18 to 3.0. However, the pH was readjusted to its initial value to facilitate the effective precipitation.

Effect of pH

The experiments on effect of pH showed a strong dependence of phenols removal on pH (Fig-1). The removal of phenols by $FeCl_3$ was found to be very effective in alkaline pH values. The experiments showed increased phenol removal from 38% at pH 2.0 to a maximum of 88% at pH 12 for the dose of 2 g/l. In the same experiments, it was observed that the removal of color was also influenced by pH of wastewater. The color removal was observed to be very effective in acidic pH values ranging from 3.0-6.0. The highest color reduction of 99% was observed in the pH 4.0. These experiments showed that the pH closer to 12 was effective for removal of phenols while pH 4 was effective for the removal of color from paper mill wastewater.

Effect of dose rate

The dependence of phenols reduction on the dose of $FeCl_3$ was studied in the pH range of 10-12 by varying dose of $FeCl_3$. The results obtained are shown in Fig-2. The phenols reduction of 68 % (pH 10), 90 % (pH 11) and 98 % (pH 12) were observed for the $FeCl_3$ dose of 2g/l, 2.5g/l and 2.5 g/l respectively. The highest phenol removal of 98% was observed at pH 12 for the $FeCl_3$ dose of 2.5 g/l.

The most effective phenols reduction was observed at pH 12 for $FeCl_3$ dose of 2.5g/l. Under these conditions, the treatment removed 80% of color and 98% of phenols from the wastewater. The treatment also reduced 89% of TSS and 68% of COD from wastewater. However, the treatment induced 30 mg/l of Fe(III) to water and also resulted in huge sludge formation. The problem of sludge can be overcome through sedimentation and subsequent removal from wastewater.

The characteristics of wastewater before and after treatment with $FeCl_3$ and their respective maximum permitted limits (MPL) for disposal as per Minimal National Standards (MINAS) are shown Table-2. The results indicate that the phenols were reduced to below maximum permitted levels at the end of treatment.

Mechanism of Precipitation

The possible mechanism of removal of coloring organic matter and phenols by precipitation is discussed in literature[4,8,18]**.** Accordingly, in aqueous medium, the trivalent metal cations hydrolyses to form positively charged monomeric and polymeric species that have a very large surface area and they tend to adsorb onto surface of negatively charged coloring organic matter and forms insoluble precipitates which eventually settle down as sludge[5,8].

$$xFe^{3+} + yH_2O \longrightarrow Fe_x(OH)_y^{(3x-y)+} + yH^+$$

The chemical precipitation of phenolic derivatives occurs via adsorption of phenolate ions by metal ions to form metal phenolates[18]:

$$X_nC_6H_{6-n}O-H+OH^- \longrightarrow (X_nC_6H_{6-n}O)^- + H_2O$$

$$3(X_nC_6H_{6-n}O)^- + Fe^{3+} \longrightarrow (X_nC_6H_{6-n}O)_3 - Fe\downarrow$$

The pH influences the type of metal hydroxide formed when the metal salt is dissolved in water. The previous works have summarized the influence of pH on chemical coagulation[4,5]. The phenols precipitation rate increases with increase in pH at very high pH values. This may be due to increased ionization of phenols into phenolate ions under highly alkaline conditions. The higher availability of phenolate ions at higher pH conditions increases the conversion of metal ions into metal phenolates[18].

The chemical precipitation is dependant on dose. The use of high doses of metal salt improves the rate of precipitation by two mechanisms: a) by increasing concentration of metal hydroxide and aggregation rate, and b) by enmeshing organic ligands into large aggregates by sweep floc coagulation[8]. The treatment process is very simple and the cost of chemicals required is also less (~Rs. 5/litre). Another advantage associated with this treatment is the possible recovery of over doses of salts applied during treatment. The over doses of metal ions can be recovered through use of suitable chelating agents.

CONCLUSION

The chemical precipitation of phenols using $FeCl_3$ was investigated in the present study. The iron salt was able to precipitate out phenols as well as color from the wastewater. The precipitation was found to be highly dependant of both pH and dose of iron salt. The precipitation of phenols was effective in the highly alkaline pH close to12 while that of color was effective in the pH range of 3.0-6.0. The precipitation treatment at pH 12, using $FeCl_3$ dose of 2.5 g/l, was able to reduce 98% of phenols, 80% of color, 89 % of TSS and 68 % of COD from paper industry wastewater. This study clearly showed that the phenols from paper industry wastewater can be reduced to below dischargeable limits by treating with $FeCl_3$ under highly alkaline conditions.

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