Tertiary Treatment Option For Pulp And Paper Mill Wastewater To Achieve Effluent Recycling

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ABSTRACT

The pulp and paper industry has traditionally been a heavy water consumer and one of the polluting industries in India. Growing scarcity of freshwater resources and stringent regulatory standards are obligating these units to explore appropriate water management options. The present work is an attempt to achieve water quality suitable for in house re-use by treating the combined wastewater after the biological treatment. The electrochemical oxidation was investigated as a tertiary treatment option, using a batch mode laboratory scale setup. A significant amount of COD (84%) and color (96%) removal is achieved using the above treatment process. Thus, the results presented in this paper support the use of electrochemical process to obtain water of suitable quality which can be recycled in pulp and paper mill at required sections.

Keywords: Tertiary treatment, pulp and paper mill, recycling, color, electrochemical treatment

Introduction

The pulp and paper sector is one of the energy intensive and polluting industrial sectors in India. The manufacture of paper generates a significant quantity of wastewater; India's current average fresh water consumption is 100-250 m^3 of fresh water per ton of paper [Singh, 2004]. The corresponding wastewater generation is also high, reaching the value of 75-225 m^3 per ton of paper [Ansari, 2004]. This figure is far above the global best specific water consumption of 28.66 m^3/t of paper (for large scale wood based pulp and paper mill). This large gap is because of the use of conventional manufacturing and treatment technologies and less water management practices by the industry. In comparison to the international standards Indian paper industry uses 200% more water, 10% more chemicals, around 30% more raw materials and 30% more energy [Roy, 2007].

The fresh water consumption and respective pollutant discharge depends upon the process and type of paper manufacture. The basic wastewater sources from various processes during paper manufacturing are given in Figure 1. Among the various sections, the most significant source of pollution are pulping and bleaching operations. Although, the pulping liquor is recovered, so the problem by this section becomes less. These stages are responsible for most of the color, organic matter and toxicity of the wastewater discharges of this industry

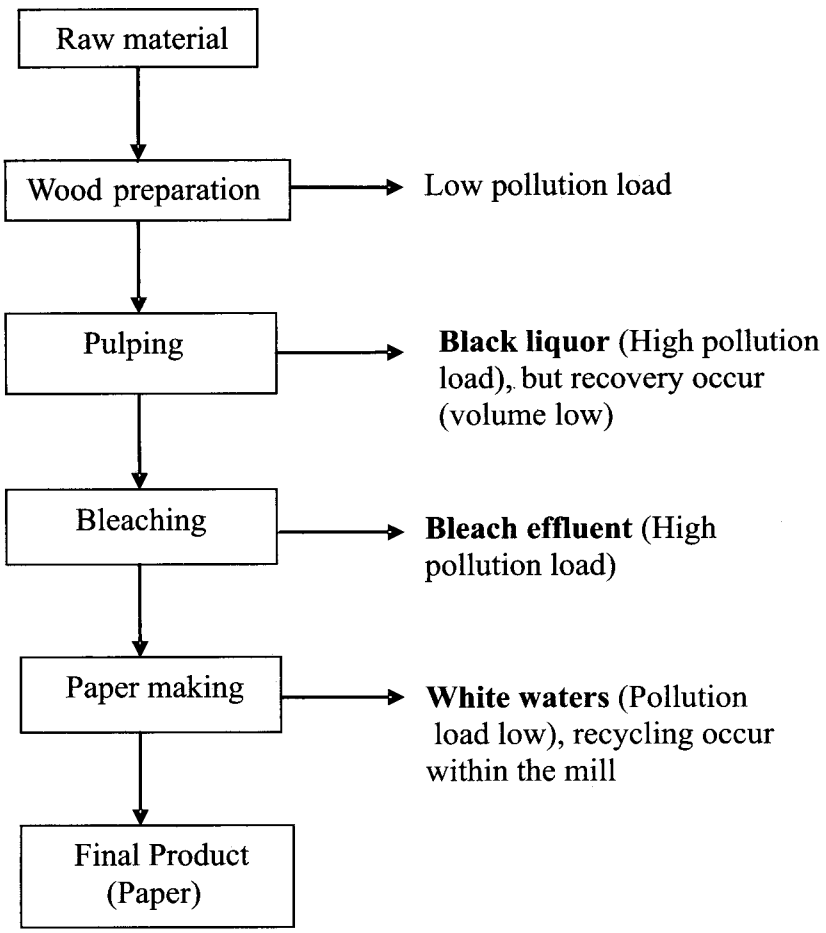

Figure 1: Wastewater sources in pulp and paper industries (CPCB, 2004)

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[Kansal el al., 2008].

The paper industry adopts two stage wastewater treatment processes, in order to treat the effluent. Primary treatment (sedimentation and floatation), and secondary treatment (activated sludge or anaearobic digestion) in order to mitigate the wastewater generated. The activated sludge plants are the most common biological treatment used in our country, but there are numerous problems associated with the process like large amount of sludge is generated which need further disposal and its capacity for removal of toxic and recalcitrant organic material is limited.

Different advanced treatment methods have been employed for the removal of color and toxins from the wastewater. These are activated carbon, membrane filtration, ultra filtration and chemical oxidation [Hillek, et al., 1993]. These treatment methods are expensive and the maintenance cost associated with them is also very high. In recent years, electrochemical degradation has been found to be very effective in treating various types of industrial wastewaters [Chen, et al., 2000; Kobya, et al., 2003; Adhoum, et al., 2004; Daneshvar, et al., 2006]. Electrochemical degradation as a treatment option provides environmental compatibility of treated effluent for disposal and better performance over conventional coagulation methods.

Keeping in view of the environmental norms in India and need for fresh water conservation, there is a requirement for recycling in Indian paper Industry. Figure 2 shows the probability of the recycling in the mill; it may be a direct use or either by regeneration or by giving a tertiary treatment to the wastewater. So, in the present work the objective is to study the electrochemical wastewater treatment as a tertiary treatment option for the paper mill wastewater. This treatment study is performed in order to attain a water quality that can be reuse in the paper mill itself for better water management practices.

Mechanism of treatment

Electrochemical method of treatment is a powerful tool to degrade the organic matter present in the water and wastewater. The main objective of the process is to convert the organics in wastewater to CO_2 and H_2O. Mostly, two different approaches can occur during this process, direct or indirect oxidation mechanism.

- Direct oxidation occurs at the surface of the anode and organics are degraded at the surface. This mechanism is proposed by Comninellis, 1994.

In this case electrode material is an important factor for the oxidation of pollutants. Chemically stable and electrically conductive material must be selected. Usually Ti metal in various combinations of doping is used for the above purpose. which includes: Ti/Ru O_2, Ti/Pt-Ir [Murphy, et al., 1992], fiber carbon [Szpyrkowicz, et al., 1994], Pt-carbon black [Boudenne, 1996}, Stainless steel [Abuzaid, et al., 1999], diamond [Kraft, et al., 2003].

- In the case of indirect oxidation the intermediates (e.g., hydroxyl radicals, ClO^-, Cl^-, Ag^{2+} ozone, hydrogen peroxide, and hypochlorite are generated anodically to destroy the pollutants [Stucki, et al., 1987; Brillas, et al., 1998]

The electrochemical treatment method also involves the process of electro coagulation. The most widely used materials for the electrodes can be aluminium or iron. An aluminium electrode is generally used for water treatment and iron electrodes for wastewater treatment. [Chen, et al., 2007].

In this process, the metal electrodes, by the means direct electric current, produce the metal hydroxide flocculants, these species combine with the organic matter to degrade them. The dissolution of iron for example occurs according to the following redox reaction. The electro coagulation mechanism involves the following redox reactions [Peters et al., 1974];

At anode (oxidation):

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

At cathode (reduction):

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \quad (2)$$

Redox reaction:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 \downarrow + H_2 \uparrow \quad (3)$$

The Al^{3+} or Fe^{2+} ions generated in the reaction are very efficient coagulants for particulates flocculating [Shen et al., 2003]. The gases evolved at the

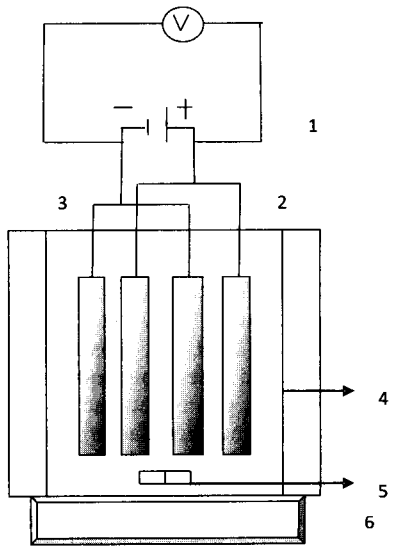

Fig 3: Experimental set up: (1) D.C. Power supply, (2) Anode, (3) Cathode, (4) Reaction vessel, (5) Magnetic bead, (6) Magnetic Stirrer.

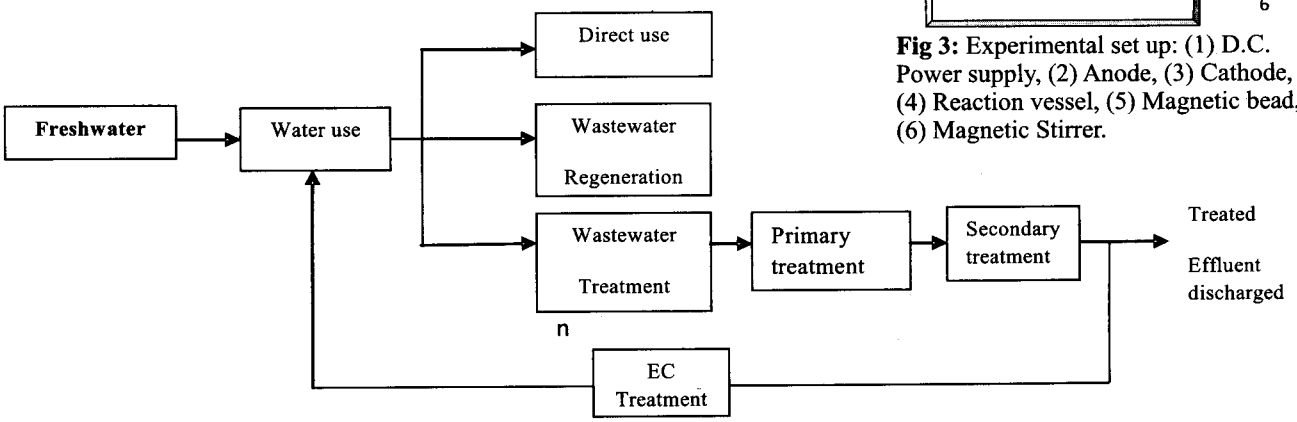

Figure 2: Water recycling probability in pulp and paper mill.

electrodes may cause flotation of the coagulated materials.

Experimental Methodology

Industrial sample tested

The wastewater samples used for the study were collected from a large scale integrated paper mill. The samples were characterized for various environmental parameters; BOD, COD, pH, color, total solids by using standard methods [APHA, 1998].

Electrochemical reactor

The reactor taken for the treatment is very compact and cost effective, keeping in mind the industrial viability of the design. The treatment experiments were conducted in batch mode using treatment vessel of 1 litre capacity. Fig. 2 shows the schematic representation of the experimental apparatus. Two pairs of stainless steel electrodes of area 10 cm × 5 cm each were used. Electrodes were placed vertically and parallel to each other in a mono polar arrangement (a pair of anodes and a pair of cathodes) [Mollah, et al., 2004].

The parallel arrangement is chosen because the cells connected in parallel arrangement leads to lower energy consumption in comparison with the series arrangement [Grøterud, et al., 1986] The inter electrode distance was kept at 1 cm and the electrodes were connected to an external DC power supply. A magnetic stirrer is connected for the uniform mixing of the sample. The wastewater sample was treated under the treatment condition given in Table 1 and kept for 1 hr for the settling of the sludge. The supernatant was tested for the environmental parameters of the treated sample. Final pH and amount of sludge formed were also determined.

Sample Analysis

The wastewater samples were analysed for various environmental parameters before and after the electrochemical treatment, using standard method for the analysis [APHA, 1998]. The COD was determined by the closed reflux titrimetric method [APHA, 1998]. The color was evaluated by measurements of absorbance of the solutions, at the wavelength of 465 nm using a UV-VIS double beam spectrophotometer. A bench scale pH meter is used to measure the pH of the sample. BOD and TDS was determined using APHA standard method.

The treatment efficiency was calculated by using the expression;

$$\text{Degradation}(\%)=\frac{\text{Initial X-Final X}}{\text{Initial X}} \quad (6)$$

Where;

X_o= Initial organic load

X=Final organic load

The current density of the process was determined by following expression

$$CD=\frac{\text{Current applied (I)}}{\text{Area(A)}} \ A/m^2 \quad (7)$$

Where;

CD=Current density applied (A/m^2)

I= Current applied in Ampere

A=area of the electrode in m^2

Table 2: Pollutant reduction under the optimized conditions

Parameters (Units)	Initial value (mg/L)	Residual value (mg/L)	Percent reduction* (%)
pH	7.0	7.6	NA
COD (mg/l)	332.9	63.6	80.9
Color (Pt-Co units)	777.6	40.3	94.6
BOD (mg/l)	32.0	14.0	56.3
TDS (mg/l)	2044	1066.9	52.2
SS (mg/l)	56.0	32.5	58.0

**all the experiments were performed in triplet and average values taken*

Table 3: Pollutant removal at different initial organic load

Samples	COD		Color	
	Initial	Percent removal (%)	Initial	Percent removal (%)
Sample 1	280.3	82.3	766.7	96.0
Sample 2	277.5	82.8	777.6	96.7
Sample 3	332.9	80.9	921.4	94.6
Average	296.9	82.0	821.9	95.8

Table 1: Optimised experimental conditions for EC treatment (Kumar et al., 2010)

Operational Parameters	Conditions/Values
Electrode material	Stainless Steel
Area of Electrode	10 cm x 5 cm each
No. of electrodes	4; 2 anodes, 2 cathodes
Arrangement	Parallel
Distt. between electrodes	1 cm
Effluent volume	1 dm^3
Temperature	Room temp.
Current density	15 A/m^2
Treatment time	2 hrs
pH	7.02

Results and discussion

Wastewater treatment and characterisation

The wastewater samples were characterized before and after the electrochemical treatment for various environmental parameters. The results are shown in Table.2

As industrial samples vary in composition and the organic load also differ under industrial conditions. So, the samples were characterised and treated in sets of three, as shown in Table 3, in order to determine an average values of the results. The highest initial organic load (Sample 3) was selected to present the results.

The waste water samples were treated under the previously optimised condition as mentioned in Table 1 [Kumar et al., 2010]. The treatment conditions which affect the electrochemical method are applied current density, treatment time and pH of the effluent. The EC treatment gives good results towards neutral pH, so it is taken as 7.0 and treatment time of 2 hours was found sufficient to achieve the desired results. The optimum value of current density for present sample was found to be 15 A/m^2, it has been a very important parameter for the electrochemical process, because the supply of the current influences the amount of ferrous ions produced from the electrodes. Current density is the ratio of the current applied per unit area of electrodes and it is expressed in A/m^2, the current density was calculated by using equation (7). Under the above treatment conditions, the color reduction was fast and an increased with time. As it is clear from Fig. 4, there is significant reduction in the value of color, and a very small amount of remnant color is left in the wastewater, which can be suitable for reuse in the mill. The total dissolved solids (TDS) are also reduced to a significant amount.

As can be seen in Fig. 5, a large quantity of COD (80.9%) is reduced during the treatment of wastewater. On the other hand, the reduction in BOD is only 56.2%. The COD contribute to the biodegradable as well as non-biodegradable fraction of the organic matter and during the course of the treatment, the non-biodegradable fraction get converted to the biodegradable fraction leading to the COD reduction to a significant amount. So, it might be the reason for the lower BOD reduction as compared to COD reduction.

Water recycling probability

The treated wastewater recycling probability is studied considering the need in the paper industry. The effluent recycling can be done at the required points in the mill, keeping in mind the damage and corrosion problem and loss in the product quality. A study [Dorica, 1999], gives the concentration of the COD and color for the recycled effluent in the kraft process; according to which the water with COD value of 75 mg/l and color of 40 Pt-Co units, is appropriate for recycling in the paper mill.

On the basis of the above treatment results which shows, a small residual color (40.3 Pt- Co units) and organic matter (63.6 mg/l) in the wastewater. The values reported in Table 2 clearly demonstrate that, the recycling of the treated water can be feasible within the mill itself. This statement is well confirmed by the reference cited previously [Dorica, 1999]. As the results obtained during the EC treatment, there is a favourable reduction in the organic load and color of the wastewater. As far as ion concentration (Ca^{2+}, Cl^- and So_4^{2-} ions) in the treated water is concerned, consideration should be given to a chloride and sulfate ion removal process in order to avoid the corrosion problem. This aspect has to be studied further in detail.

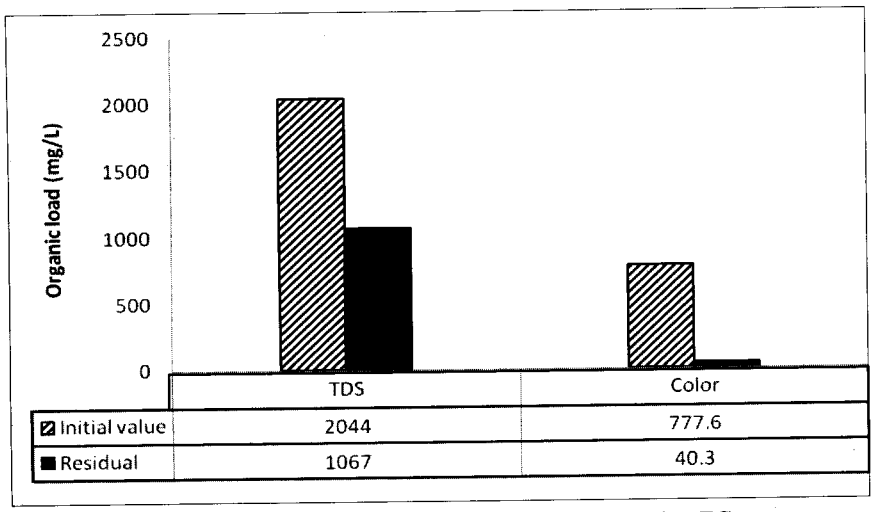

Fig. 4: Removal of TDS and Color from wastewater by using EC treatment

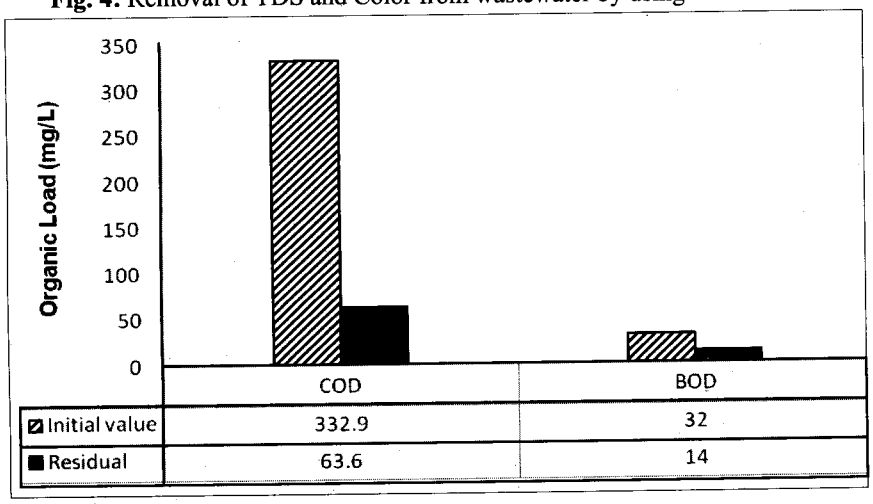

Fig. 5: Removal of COD and BOD from wastewater by using EC treatment

Conclusion

On the basis of results obtained in the above laboratory study, the electrochemical wastewater treatment can be suggested as a viable option for the mitigation of pulp and paper mill wastewater. The electrolytic method that was examined gave satisfactory results for the reduction of the organic load and the color of the wastewater. It must be noted that color reduction is of prime importance for the paper industry effluents. Only with 2 hrs treatment time and current density of 15 A/m^2, COD and color percent reductions exceeds almost from 80% and 90% respectively.

Considering the simplicity of the method, the water treated by electrochemical method may be a promising tertiary treatment option for the paper industry, the recycling of the treated water would not involve any problem. The method can be further optimised in order to take care of the inorganics and to further reduce the cost.

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