Int. Res. Adv. 2017, 4(2), 24-28 Article

Integrated Research Advances

# Analysis of various iron nanoparticles and compounds in pulp & paper mill waste water treatment

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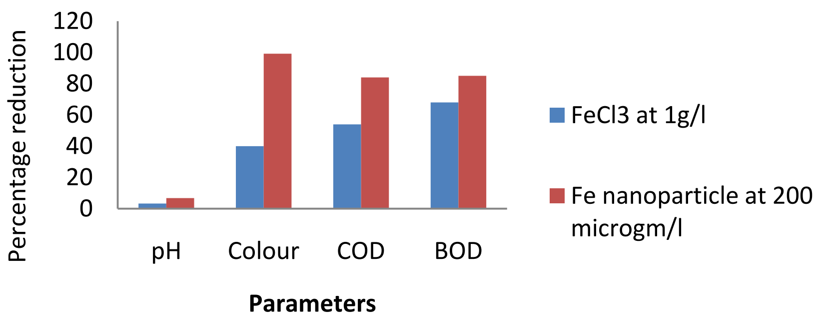
Received on: 14-Jul-2016, Accepted on: 22-Mar-2017, Published on: 23-Mar-2017

## ABSTRACT




The pulp and paper industry waste water is characterized by dark color, foul odour, high organic content & extreme quantities of COD, BOD & chlorinated compounds. These impurities removed by chemical precipitation using ferric chloride and iron nanoparticles. Today iron nanoparticles used for detection and removal of chemical and biological substances include metals, nutrients and chlorinated organic compounds. Iron nanoparticles reveal good result than other chemical techniques used in pulp and paper mill effluent treatment. Iron nanoparticles are widely used in contaminated with chlorinated organic compounds. In present study two samples of pulp & paper mill effluent treated with $FeCl_3$ & iron nanoparticles. It was observed that the concentration of $FeCl_3$ in the sample was high but treatment was less effective while the concentration of iron nanoparticles used in other sample was very low but the treatment was very effective. Iron nanoparticles are highly reactive because of their large surface area, In the presence of oxygen & water they rapidly oxidize to form free iron ions and this treatment process is environmental friendly.

*Keywords: Iron nanoparticle, pulp, water treatment*

## INTRODUCTION

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from nonwood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. The pulp and paper industry is huge, technically diverse, operating a wide variety of manufacturing process on a range of fibre types from tropical hard woods to straw for pulping and bleaching for paper preparation. The effluent of these industries contains stray wood chips, bits of bark, cellulose fibres, dissolved ligneous material (30-45%), saccharinic acid (25-35%), formic acid and acetic acid (10%) and extractives (3-5%). The residual lignin present in wood fibre is major colouring material, and also reacts with chlorine molecules and forms organochlorine compounds in the effluent. About 20% of the organically bound chlorine found in bleaching effluent corresponds to relatively low molecular mass (m.w 4000) products.

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Cite as: *Int. Res. Adv., 2017, 4(2), 24-28.*

Chlorine released after bleaching cross-reacted with lignosulphonic acid, resins, and related compounds and forms chlorinated hydroquinone, phenols, dibenzo-p-dioxin and dibenzofuran in the effluent. These chlorinated compounds are highly toxic, mutagenic and ecoestrogens. They are partly responsible for the high oxygen demand (BOD and COD). In pulp and paper mill, 273-455 $m^3$ of water is required per tones of paper produced that consequently generate 300 $m^3$ as wastewater.[19] Alkali pulp and paper mills provided with soda recovery, discharge about 270-450 liters of water per kg of paper with an average of 305 lt/kg and the amount of lignin discharged being 40-50 g/kg of bleached paper produced. In a small paper mill without soda recovery, all of the black liquor (200-250 g/kg of paper made) is discharged. The pollution load in terms of biological oxygen demand (BOD) from small paper mill is 2-5 times the pollution load from large paper mills with soda recovery. The BOD load discharged per tones of paper by mills varies from 3.45 kg to 6.5 kg.[20]

The dark brown colour is due to the formation of lignin degradation products during the processing of lignocellulosics from paper and pulp manufacture. The undiluted effluents are toxic to aquatic organisms and exhibit a strong mutagenic effect. Further more some compounds in the effluents are resistant to biodegradation and can bioaccumulate in the aquatic food chain. Earlier various physical chemical and biological processes have been done to remove the colour of the pulp and paper mill effluents.[18] Physical and chemical processes are quite expensive to remove only high molecular weight chlorinated lignins, colour, toxicants, suspended solids and COD but BOD and low molecular weight compounds like alcohals, acids appreciably are not removed efficiently. So approach of nanoparticle is feasible for pulp and paper mill effluent treatment. Iron nanoparticles have become a valuable material for its environmental remediation abilities.[3] Iron nanoparticles are strong reducing agent with high reactivity surface area of iron nanoparticles is in the range from 20 to 25 m2/g and average particle size 10 – 100 nm. Reaction products are mostly non toxic iron oxides. Iron in oxidation state O is very unstable, thus reactive one of the strongest reducers.[5] High reactivity & large surface area facilitate to combine processes reduction, sorption & coagulation into the technological step.[17] (). Most widely used chemical method for the synthesis of nano scaled Iron nanoparticles can be synthesized by the reduction of Fe (II) or Fe(III) salt with sodium borohydride in an aqueous medium.[25]

Present research focuses on iron nanoparticles use for paper industry waste water treatment.

## MATERIAL AND METHODS

**Location**

The study was conducted with the effluent released from Pulp and Paper mill, Chattishgarh. The factory uses cane molasses as the raw material. The efflcuent flows out into a 'nala' for about 10 km, which passes through the villages. The villagers use this effluent for the irrigation.

**Sampling:**

The effluent sample from the Pulp and Paper mill were collected at the main outlet point where combined effluents from the factory are being disposed of into mill influent water. Water samples at the point of discharge were collected in clean plastic container from the main outlet. . Immediately after collection the water samples were brought to the laboratory and kept in the refrigerator at $4^0$C till used for analysis.

**Reagent and chemicals**

$FeCl_3$ was procured from Sigma Aldrich and 0.1M solution of Fecl3 was freshly prepared in distilled water. Throughout the experiment distill water was used for dilution.

**Collection of Clove Extract**

Clove buds were obtained from local region. There were washed with distilled water, dried and then crushed with mortar and pestle, 60 ml of distilled water was added to 0.1g of crushed clove and heated for 2 min. Solution was filtered with Whatman's No.1 filter paper to obtain extract.

**Synthesis of Iron Nano particles**

0.1M $FeCl_3$ was diluted in 1:10 ratio using distill water. 200 µl $FeCl_3$solution was added drop wise to the aqueous extrate of clove in a sterilized flask. The change in color, pH and absorbance were observed indicating the formation of FENP, s.

**Effects of different chemicals on pulp and paper mill individually and in combination**

In one set of 100 ml sterilzied Erlenmeyer flasks were filled with 50 ml of sample effluent. In one set of flask $FeCl_3$was added at the rate of each 1 g/l whilst in second set Iron Nano particles of 200 µl concentration was added. All the flasks were shaken at 150 rpm and $25^0$C for 2 hrs. Thereafter, all the samples were centrifuged at 5000 rpm for 10 min. After that pH, EC, TSS TDS, COD and colour were measured.

**Analytical methods**

Electrical conductivity (EC) of the effluent was measured using a pocket type digital EC meter (Hanna Instruments Co.) calibrated at $20^0$C. The reading was taken in milli siemens (ms $m^{-1}$). pH of the effluent sample was measured by a pH meter (model PR 8404) using glass electrode.

For total suspend solids 100 ml of the sample was centrifuged at 2000 rpm for 10 minute. The supernatant was removed and the residue was washed three times by resuspending it in distilled water and recollecting by centrifugation. The residue was finally transferred quantitatively to preweighted dish (X1g). The dish was weighed again after drying (X2g) to a constant weight (X1g). The dish was weighed again after drying (X2g) to a constant weight at $105^0$C. TSS was calculated by using the following formula.

$$\text{TSS (ppm)} = \frac{(X_2 - X_1) \times 1000 \times 1000}{\text{ml of sample}}$$

The TDS was calculated as the difference between the total solids (TS) and total suspended solids (TSS), TDS (ppm), TS (ppm)-TSS (ppm).

COD and Colour unit was calculated by according to the standard method . The sample was centrifuged at 1000 rpm for 30 minutes to remove all the suspended matter. The pH was adjusted to 7.6 with 2 M NaOH (CppA standard method) and then used for the measurement of absorbance at 465 mm. The absorbance values were transformed into colour unit (CU) using the following relationship.

$$CU = 500 \times \frac{A_2}{A_2}$$

where

$A_1$= Absorbance of 500 cu platinum cobalt standard solution ($A_{405}$ = 0.132) and $A_2$ = Absorbance of the effluent sample (N K Swamy, P Singh, I PSarethy, 2011)

## Results and Discussion

Pulp and paper mill Effluent was collected i.e. November 2015 from Century Pulp and Paper mill, Lalkuan, Uttrakhand. The physico chemical analysis of spent wash (raw effluent) was highly acidic in nature with high BOD (32000 ppm), COD (45000 ppm), TDS (9566.66 ppm), TSS (97686.66 ppm), phenol (5.1ppm), sulphate (3800 ppm), nitrogen (299 ppm), phosphorus (767.66 ppm), potassium (481.33 ppm) and low content (Table 4.1). Raw pulp and paper mill effluent contains metal viz. Mn (3.68 ppm), Zn (3.781 ppm), Cu (0.31ppm), Ni (0.86 ppm) Fe (72.07 ppm) and Na (498 ppm). However, the pH of treated pulp and paper mill effluent was acidic and other parameters including metals were high in comparison of MINAS value. Physiochemical characteristics were analyzed and the data are given in 1.

The colour of the effluent was dark brown and colour unit was recorded 6287.87CU, whilst pH was in acidic range 5.1, (Table 1).

All the values are in ppm means (n=3) ± standard error.

Chemical precipitation using $FeCl_3$ and has been studied extensively. This method is cheap but produces a large quantity of sludge and do not completely remove toxicity. Develop a proper chemical method to achieve decolourization and detoxification of effluent water. Decrease in pH was recorded 3.3 on concentration (1 $gl^{-1}$) of $FeCl_3$ (Ferric chloride). Decrease in colour, COD and BOD were also observed with $FeCl_3$. Maximum colour, COD and BOD reduction were recorded 40.76%, 54.16 % and 68.88% with $FeCl_3$ (1 $gl^{-1}$).

The chemical compounds found in pulp and paper mill effluent are mostly degrading products of lignin, cellulose, hemicellulose and wood extractives such as manomeric phenols, enol ethers, mercaptides, stilbene, quinone derivatives, chlorinated phenols, acetic acid, formic acid, acetaldehyde, methanol, furfural and methyl glyoxal. About 300 organochlorine compounds have been identified in effluent while hundred other remain unidentified.

**Table1:** Physicochemical analysis of pulp and paper mill effluent

| Parameters | Mean value |
|---|---|
| BOD | 32000± (577.35) |
| COD | 45000 (±946.48) |
| Nitrogen | 299 (±9.46) |
| Phenolic compounds | 5.1 (±0.06) |
| Phosphorus | 767.66 (±26.26) |
| Sulphate | 3800 (±57.73) |
| Total suspended solids (TSS) | 97686.66 (±566.10) |
| Total dissolved solids (TDS) | 9,566.66 (±88.19) |
| Chlorine | 2800(±26.83) |
| Colour | 6287.87 (± 97.85) |
| Total organic carbon | 2880(±22.30) |
| K | 481.33 (±28.93) |
| Na | 498 (±16.83) |
| Cu | 0.31 (±0.03) |
| Fe | 72.07 (±12.76) |
| Mn | 3.68 (±0.64) |
| Ni | (±0.01) |
| Zn | 3.781 (±0.06) |

**Treatment of pulp and paper mill with IRON nano Particles**

Iron Nanoparticles (FeNPs) has unique magnetic property due to it used to number of environment remediation. When $FeCl_3$ was added color of clove extract immediately turned from yellow to black indicating synthesis of iron nanoparticle (Figure 1). Synthesis of zero valent iron nanoparticle of different shape and size. Iron Nanoparticle (FeNPs) use in pulp & paper mill effluent was kept very low concentration but the treatment was very effective in removal of organic contaminant. Iron nanoparticle resulted in faster degradation of wastewater, removal of color & improving BOD &COD of pulp and paper mill waste water. Maximum colour, COD and BOD reduction were recorded 99.10%, 84.16% and 85.92% respectively with 200 µl concentration of Nanoparticles.

All the values are in ppm mean (n=3) ± standard error

**Table 2** Effect of $FeCl_3$ and Iron Nano Particles on pH,CU,COD and BOD of the pulp and paper effluent

| **Parameters** | **Conc. Of $FeCl_3$ 1g $l^{-1}$** | **Iron Nano Particle (200 µl conc)** |
|---|---|---|
| pH | 3.3±0.31 | 6.8±0.15 |
| Colour Unit | 3724.74±1797.85 (40.76%) | 56.16±4.00 (99.10%) |
| COD ($mgl^{-1}$) | 14666.66±1763.83 (54.16%) | 7128±1763.83 (84.16%) |
| BOD ($mgl^{-1}$) | 14000±881.91 (68.88%) | 4506±1452.66 (85.92%) |

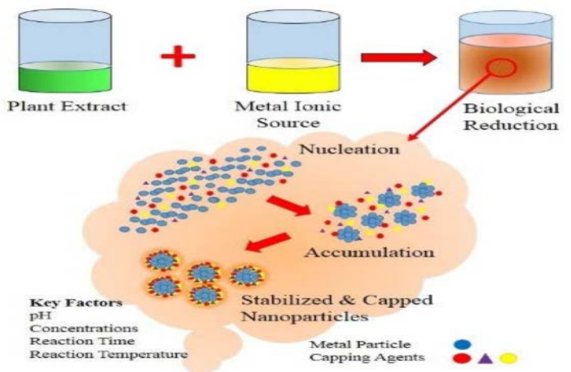


**Figure 1** Iron nano particle generation process

Significant correlation can be seen between colour unit, COD and BOD of the effluent. The result of the study also supports the findings of this study. Linear relationships amongst these parameters were observed. Most of these parameters are found to exceed beyond permissible limit and warrants treatment. The pattern of colour removal by chloride and sulphate salts of aluminium and iron were more or less similar. Per milli equivalent of metal ion for coagulation is based on percentage colour removal.[24]

It was observed that ferrous sulphate alone was not effective in reducing the colour of effluent as it does not form floe with pulp and paper mill waste water.[23] The other flocculant i.e. alum, ferric chloride, lime were found effective for colour removal. But these chemicals also depend on the pH of the waste water. Ferrous sulphate in combination with alum was effective to some extent in reducing colour of effluent due to producing of more acidic chemicals. While COD reduction is comparatively lower.[12]

Thus, initial pH, molecular size and electrical charge have profound influence on the efficiency of colour removal and the chemical dosage required.[13] The coagulant dose required to maximum colour removal was 5000-7000 mg/l in case of ferric chloride and almost double (12000 mg/l) in case of alum. In all cases, colour removal decreased beyond coagulant level (optimum coagulant dose). Percentage colour removal was significantly higher in the case of treated pulp and paper mill waste.[11,29]

Colour causing substances present in pulp and paper mill waste are microcolloids which are hydrophilic in nature like proteins and other biopolymers.[21] Stability of these colloids depends mainly on the hydration shell and high concentrations of colloids naturally required to withdraw the solvent from the hydration shell.[8,9, 27]

Over the last few years, it was reported that iron nanoparticles have several applications in the field of Industrial waste water treatment, removal of xenobiotics and heavy metal remediation.[14,28] Nanotechnology for water remediation will play a crucial role in water security & consequently the food security of the world.[16,25] The applications of nanotechnology in the cleanup of contaminated water could be summarized by Smith, 2006 as Nanoscale filtration Techniques, The adsorption of pollutants on nanoparticle, The breakdown of contaminant by nanoparticle catalyst. Nanotechnology is going to play an important role in addressing fundamental issues such as health, energy and water.[1] Major potential environmental benefit of nanotechnology were reported in the draft nanomaterial research strategy by Savage et al.,[6] including early environment treatment and remediation with Stronger and lighter nanoparticle.

## CONCLUSION

The pulp and paper industries discharge huge amount of industrial waste waters, these industrial effluents are characterized by high BOD & COD levels & contain high percentage of different organic & inorganic materials depending upon the sources of their origin. Pulp and paper mill waste water treatment by both $Fecl_3$ & Iron nanoparticle (FeNPs) respectively the results are in fever of iron nanoparticle (FeNPs) all the parameters of good treatment like BOD, COD & Color are indicate that iron nanoparticle treatment is far better than $Fecl_3$ treatment. Effort should be made to make more research in nanoparticle treatment field so that the process can be commercially viable.

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