Journal of Environmental Pollution and Control
Volume 6 | Issue 1
ISSN: 2639-9288

Research Article Open Access

Treatment of Pulp and Paper Mill Effluent by the Coagulation-Flocculation Process

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Citation: Abdelkader Ltifi, Emna Grami, Ridha Lafi, Chakroun Noussaiba, Neila Saidi, et al. (2023) Treatment of Pulp and Paper Mill Effluent by the Coagulation-Flocculation Process. J Environ Pollut Control 6(1): 102

Abstract

Tunisian mill wastewater analyzed for the first time prove high Chemical Oxygen Demand (COD) and high Turbidity values and deserve treatment. The biodegradability index determined by the biochemical oxygen demand (BOD)/chemical oxygen demand (COD) ratio was only 0.072, suggesting its limited biodegradability. Primarily, settling tank showed a positive effect in COD values reduced from 2490 to 448.2 mg/L. In addition, turbidity was reduced from 140 to 65.8 NTU. The coagulation-flocculation process using chemical coagulants-flocculants prior treatment equilibrate this ratio in range 1-2 promises a feasible biological treatment. Results showed that at the following doses of coagulants (150, 150 and 200 mg/L), COD removal reached percentages of 65, 63 and 60% by using Al_2 $(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_{3x}$ $7H_2O$, respectively. Concurrently, the Tb reduction ranged from 75, 73 and 74% when we apply $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3.7H_2O$, respectively. The performance of $Al_2(SO_4)_3 18H_2O$ as a coagulant was slightly superior to $FeCl_3.6H_2O$ and $Fe_2(SO_4)_{3x}.7H_2O$. The reduction in COD were increased to 90.88 and 87% when the treatment was carried out with polyacrylamide compared the control test without polyacrylamide where the following values 65, 63 and 60% were saved, respectively. Similarly, turbidity ensured 93%, 90% and 91% for $Al_2(SO_4)_3$, $FeCl_3$ and $Fe_2(SO_4)_3$, respectively with polyacrylamide compared to control test without polyacrylamide where was saved only 75, 73 and 74% in turbidity reduction. The best experimental conditions for coagulation were as follow: pH in the range 3–4 with $Al_2(SO_4)$ considered at 150 mg/L associated to polyacrylamide used at concentration of 15 mg/L.

Keywords: Pulp and paper wastewater; Anionic polyacrylamide; Coagulation–flocculation; COD; Turbidity.

Introduction

Manufacturing process of pulp and paper mills consume large amount of water. Each ton of paper produced consumes more than 60 m^3 of freshwater [1]. Untreated mill wastewater (UMWW) rejected in receiving ecosystem such as lakes and rivers without prior treatment present a permanent source of pollution, by causing a degradation in the environment affecting negatively biological diversity and health of surrounding population, even after secondary treatment UMWW remains toxic in nature [2, 3]. The pollution can be vehiculated and spread even beyond the cellulose manufacture [4] and cause harm human, animal, and plant health. In fact, an outburst of cancer and dermatome cases have been reported during the past decades in the vicinity of the manufacture located in Kasserine [5].

The most regular methods applied to treat pulp and paper mills wastewaters is by a secondary biological treatment normally achievable by using indigenous microorganisms [6]. Activated sludge and aerated lagoons are also applied in some cases, depending in the water characteristics and some ratios needed to be verified before starting the treatment. In some cases, filters, and sequences reactors-Mobil-Bed Bioreactor (MBBR) and Membrane Bioreactors (MBR) present interactive methods recommended for paper wastewater treatment. In other cases, anaerobic treatment followed by an aerobic biological stage was showed to be efficient [7]. The crud effluent is not susceptible to receive the biological treatment since the ratio BOD5/COD is over 2. A pretreatment has to be previously applied. Coagulation–flocculation is among the most treatment technologies used in industrial scale [3]. The coagulation-flocculation effect in removal of pollutants is supported by charge neutralization followed by cationic hydrolysis products of colloids negatively charged. This process allows Van der Waals forces to facilitate the initial aggregation of colloidal particles to form microflocs. Coagulation-flocculation is the most common chemical and physical process used for completely removing dye color from waste water, not only partially as occasionally reported with the chemical methods. In the coagulation and flocculation process, the use of inorganic coagulants as aluminum sulfates, ferric chloride or polyelectrolytes, may cause many environmental disadvantages due to the production of a large quantity of metal hydroxide, toxic sludge disposal problem arises and also metal concentration increase in treated water, which may have human health repercussions [8], Other drawbacks of coagulation methods are variations in pH levels, low efficiency in cold water, and very fine particles [9]. Several parameters affect the coagulation-flocculation efficiency such as the type and the concentration of the coagulant, pH, temperature, ionic strength, nature and concentration of organic matter, total dissolved solids, particle size, and distribution of colloidal particles in suspensions [9]. $Al_2(SO_4)_3$ is the most used coagulant in industrial wastewater treatment, via aluminum-polymers interaction. Kinetic of chemical intermediates present in the eventual precipitated metal hydroxides deserve particular attention to ovoid apparition of toxic substances [10].

The present study aims to assess the coagulation floculation process efficiency on pulp and paper mill effluent, and improve effluents quality by the use of $FeCl_3.6H_2O$, $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ via coagulation-precipitation methods: (i) To follow effect of coagulant and flocculant in organic matter discharge (ii) To determine effect/doses of the coagulant and flocculant in water improvement quality (iii) To determine the pH value enhancing the yield coagulation-precipitation methods.

Experiments Design

Samples Characteristics

Five containers of 10L were used for industrial pulp and paper mill wastewater sampling. The cellulose industry is located in Kasserine town situated in the Center of Tunisia, situated at 246 km from Tunis capital. Waster water samples were stored at 4°C after collection until analyses. Thirteen physico-chemical parameters were measured in waster water samples prior and after coasgulation-fluculation treatments. The considered parameters were: as follow: temperature, pH, electrical conductivity (EC), suspended matter (SM), dissolved oxygen (DO), BOD5, COD, chlorides, nitrate nitrogen, phosphate, sulphate and heavy metals [11, 12].

Samples analysis

The pH, conductivity and temperature were analyzed using a multi-parameter analyzer (Consort C860). All other parameters were performed in the laboratory in accordance with standard protocols for collection, transport and processing wastewater [13]. The samples were analyzed for biological oxygen demand (BOD5) by Winkler titration [14]. The suspended matter (SM) was measured by filtering 20 mL of water in pre-dried and weighed Millipore APFC filter paper with 0.45 µm pore size and a diameter of 47 mm. After filtration, the filter paper was dried at 105°C for 24h until constant weight and SM was calculated based on the difference between initial and final filter paper weights [15]. Sulphate and phosphorus were measured, respectively, by the French standards "AFNOR T90: 009 and T90: 023 (1979), on centrifuged samples (2000 rpm for 10 min) followed by settling for 30min to separate any solid particles. All metals Al, Mg, Fe, Mn, Cu, Zn, Ni, Pb and Cd were analyzed by atomic absorption spectrometry according to "AFNOR T90 12 (1979)" on Perkin Elmer 3110 instrument. The standard materials used in the experimental procedures are listed in Table. 1.

Chemicals	Formula	Physical form	Molecular weight (g/mol)	Purpose
Sulfuric acid	H_2SO_4	Liquid	98.01	pH adjustment
Lime	$Ca(OH)_2$	Powder	74.093	pH adjustment
Aluminium sulfate	$Al_2(SO_4)_3.18H_2O$	Powder	666.429	Coagulant
Ferric chloride	$Fe\ Cl_3 6H_2O$	Powder	270.295	Coagulant
Ferrous sulfate	$Fe_2\ (SO_4)_3.7H_2O$	Powder	333.839	Coagulant
Polyacrylamide	$(C_3H_5NO)_n$	Powder	71.07	Flocculant

Table 1: Standard materials used in pulp and paper mill effluent treatment via coagulation-fluculation methods.

Jar-test experiment

The standard technique Jar-test used, evaluated the efficiency of the chemical coagulation–flocculation by measuring the decrease in suspended, colloidal and non-settable matter [11].

Coagulation-flocculation studies used the conventional Jar-test apparatus (ISCO JF-4, Milan, Italy) with four 1L beakers. Brievely, for each trial, 500 mL of wastewater were poured into the beakers. The smalls quantities of each coagulant $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$, $Fe_2(SO_4)_3.7H_2O$ and anionic polyacrylamide flocculant was added to the wastewater and SM determined after each experimental treatment.

Floculant was added at...

Analytical Procedure

The coagulants used in this study were $Fe_2(SO_4)_3,7H_2O$, $Al_2(SO_4)_3.18H_2O$ and $FeCl_3.6H_2O$. Anionic polyacrylamide was used as the flocculant. Sulphuric acid (H_2SO_4) and lime solution (Ca $(OH)_2$) were used to adjust the pH during the treatment process. Different values of pH (3 to 10) were considered. Increasing coagulant doses range 50 to 400 mg/L and increasing anionic polyacrylamide flocculant concentrations (5 to 40 mg/L) were also evaluated. Each coagulant was eluted separately in 500 mL of wastewater and the mixture was magnetically stirred for 2min at 200rpm followed by a second mixing for 15min at only 40rpm. The addition of the flocculant to the mixture solution followed the adequate dose of the coagulant. The formed flocs were allowed to settle for 30 min. After settling, the turbidity and COD removal efficiencies of the supernatant were determined using the following formula:

$$Removal(\%) = 100\frac{(C_0 - C)}{C_0} \quad (1)$$

Where C_0 and C are the initial and final turbidity or COD values of pulp and paper mill wastewater, respectively.

Results and Discussion

Characterization of Water Prior Treatment

The results related to water quality analysis of mill wastewater prior treatment is shown in Table. 2. Pre-treatment turbidity of 140 NTU is considered high, and therefore turbidity needs to be reduced to meet Tunisian effluent water quality (TEQW) standard (7 NTU). COD value of the pre-treated water was 2490 mg/L value over the TEWQ standard fixing COD at 90 mg/L.

Also, the BOD5 of the pre-treated wastewater saved a value of 180 mg/L higher than 30 mg/L value required by TEWQ standard. The other wastewater parameters were as follows in Table. 2. These results showed for the first time that the pre-treated wastewater characteristics were over the required value standards. This supposes that when this effluent will be rejected in receiving waters will affect certainly aquatic ecosystem. All pre-treated water showed characteristics exceeding parameters prescribed standard limits. Thus, a prior treatment has to be applied before discharging it in the environment. The BOD5/COD ratio value of 0.072 indicates that biological treatment is not adequate for the effluent as an initial step [16]. The coagulation-flocculation approach may be an important first step in mill wastewater treatment.

Parameters	Untreated wastewater	Tunisia standard norm
Temperature (°C)	18	25
pH	10.87	6.5–8.5
Conductivity (mS/cm)	2.87	7
Turbidity (NTU)	140	7
SSM (mg/L)	2596	30
COD (mg/L)	2490	90
BOD_5 (mg/L)	180	30
Sulfate (mg/L)	919	500
Chloride (mg/L)	1460	200
Aluminum (mg/L)	0.62	0.2
Manganese (mg/L)	0.56	0.4
Iron (mg/L)	9.73	0.2
Magnesium (mg/L)	0.49	-
Copper (mg/L)	0.99	2
Zinc (mg/L)	8.85	3
Nickel (mg/L)	6.7	0.07
Cadmium (mg/L)	0.41	0.003
Lead (mg/L)	0.04	0.001

Table 2: Pulp and paper mills wastewater characteristics.

Optimization of Coagulant Doses

Effect of Preliminary Settling Time

Since during transport samples, these lasts showed two separately phases due to precipitation of suspended material. Consequently, the raw mill wastewater was allowed to settle in a preliminary settling tank before the addition of the coagulant. Heavier molecules and colloids are removed from the wastewater in this settling process that may be valorized in future experiment. The water quality after discarding the pellet became cleaner expressed by COD and turbidity reduction values. Indeed, after settling tank, the COD was reduced from 2490 to 448.2 mg/L. In addition, turbidity was reduced from 140 to 65.8 NTU. The yield of turbidity removal is approximately 47%. The two parameters remained almost constant after the first 6h settling time (Figure 1).

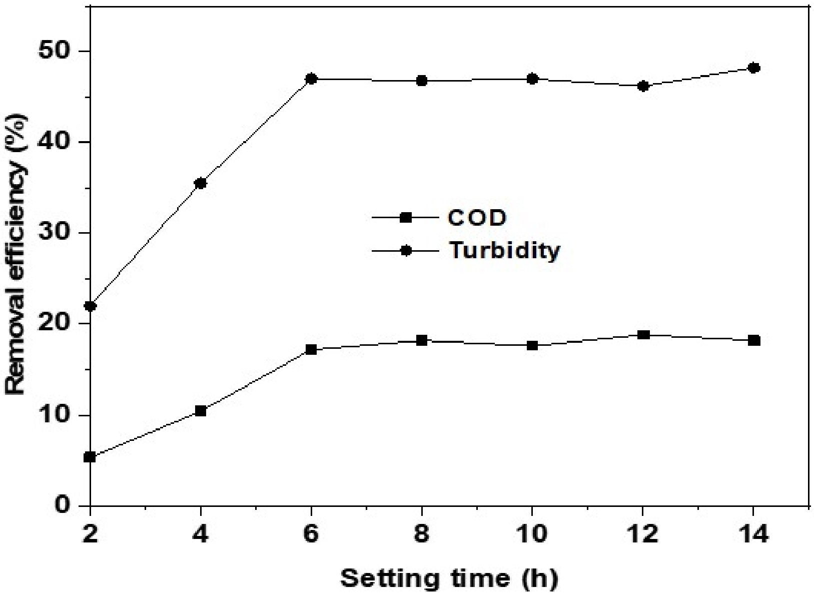

Figure 1: Effect of preliminary settling time on TSS and COD removal efficiency.

Preliminary settling process is a process that requires no chemical addition. Settling ponds are common for industrial effluents, but there is little quantitative information in the literature on the requirements for preliminary settling time aimed to reduce COD and turbidity. Most studies performed in the treatment of mill wastewater were based on diluted pre-settled wastewater [1]. It is well known that raw mill wastewater includes resin acids and resins; that are able to settle quickly due to high mass and complex composition. Evidentially, the accumulated sludge in settlement ponds may be valorized with economical input.

Evolution of COD and Turbidity Related to Coagulant Doses

The coagulant type and dosage effects on the COD and turbidity reduction were investigated by varying the three coagulant doses from 50 to 400 mg/L. Initially, the pH in all experiments was fixed at 6. The results in Figure 2 and figure 3 showed that at lower doses of coagulants 150, 150 and 200 mg/L), COD removal reached percentages of 65, 63 and 60% by using $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3.7H_2O$, respectively. Concurrently, the turbidity reduction increased with increasing coagulant concentrations. The Turbidity reduction yield was 75, 73 and 74% when were used $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3$.7H2O, respectively. The performance of $Al_2(SO_4)_3.18H_2O$ as a coagulant was slightly superior to $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3.7H_2O$ efficiencies. The results showed a fixed value when coagulant dose is above 400 mg/L, with no further COD and turbidity reduction. $Al_2(SO_4)_3.18H_2O$ can be an attractive treatment coagulant based on its efficiency and low cost.

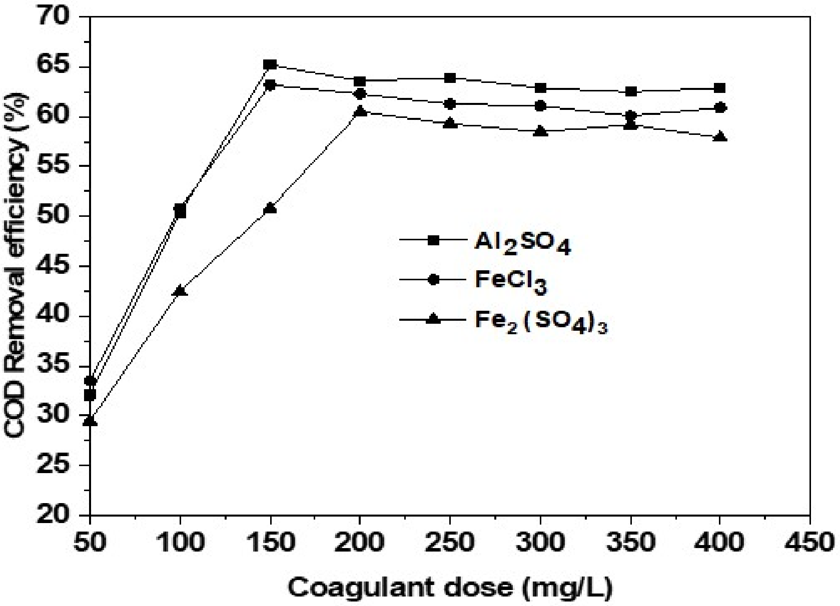

Figure 2: Effect of coagulant concentrations on the COD removal efficiency

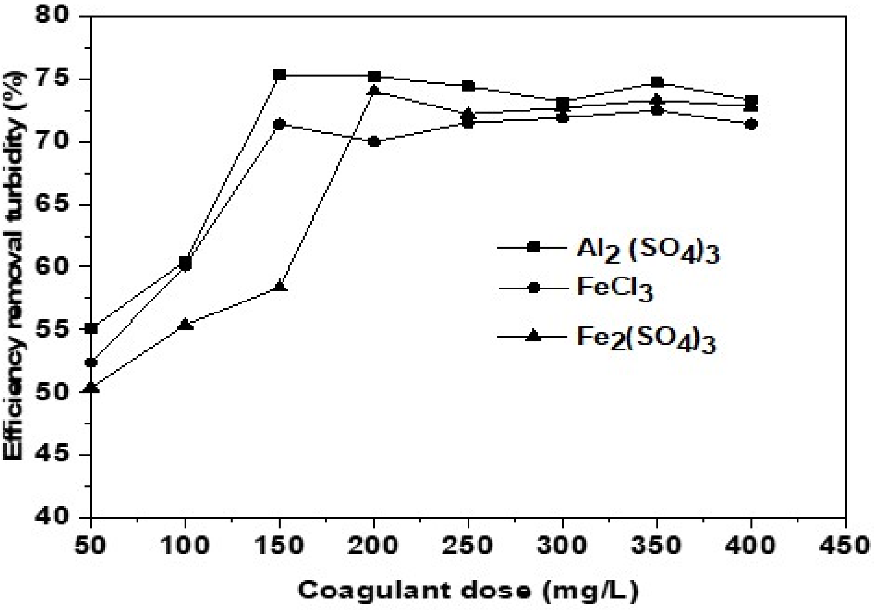

Figure 3: Effect of coagulant doses in on the Turbidity reduction

Precipitation of the metal cations, organic anions and colloids can be attributed to the double layer compression, which reduces repulsive electrostatic force and leads to neutralizing the colloidal charge followed by colloid destabilization [17]. Aluminum has been reported to form insoluble complexes with some of ligands, especially with polar molecules and with oxygen-containing functional groups such as hydroxyl or carboxyl groups, which provide local reacting negative charges [18, 19]. Dissolved organic compounds are removed primarily by sorption onto the hydroxide surfaces.

The removal efficiency for lignin by the tested coagulants is attributed to the lower molar mass fractions (<5 g/mol) of lignin in effluent as well as the amorphous, branched polydisperse macromolecular substance. Lignin contains several functional groups such as, benzylic hydroxyl, carbonyl, phenolic hydroxyl and catechol groups [20]. The ionization of these groups is essential to enhance the lignin water solubility [21]. In addition, lignin was partly degraded during pulping, and became soluble in water in colloidal form [22, 23]. The mass fraction (> 5 g/mol) precipitates almost completely. However, mass fractions (1 - 5 g/mol) precipitates partly. While mass lignin (< 1) remains in the effluent [24]. Metal salts used in chemical coagulation present two inconvenient. The first one is that reaction required high content in salt and the second one is the presence of high levels of dissolved metals in the treated effluent [25].

Evolution of COD and Turbidity Related to the flocculant (Polyacrylamide)

The application of polyacrylamide was investigated to improve the coagulation performance. The effect of polyacrylamide was studied in the presence of $FeCl_3$, $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ to determine the best combination and the optimal concentration. Increasing concentrations of the coagulant (150, 150 and 200 mg/L for $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3$ $7H_2O$, respectively) were tested separately against changes in flocculant concentration from 5 to 40 mg/ L. The reduction in COD were increased to 90, 88 and 87% when the treatment was carried out with polyacrylamide compared the control test without polyacrylamide where the following values 65, 63 and 60% were saved, respectively). Similarly, turbidity decreased to 93%, 90% and 91% for $Al_2(SO_4)_3$. $FeCl_3$ and $Fe_2(SO_4)_3$, respectively with polyacrylamide (compared to 75, 73 and 74% turbidity reduction without polyacrylamide) (Figure 4 and 5). This result suggests that change of flocculant concentration play an important role in treatment effectiveness depending in the nature of the coagulant. The anionic flocculant association with $FeCl_3.6H_2O$, $Fe_2(SO_4)_3$. H_2O or $Al_2(SO_4)_3.18H_2O$ were found to improve COD and turbidity reduction. The associated effect of $FeCl_3$ $6H_2O$, $Al_2(SO_4)_3$ to flocculant gave a 91% COD reduction and 93% turbidity reduction. The three curves obtained showed a minimum value corresponding to coagulation and floc formation (clarification). Once, the optimum conditions were reached, corresponding to the destabilization of the formed flocs expressed by an increase in turbidity and COD values. The destabilization of colloids can be explained by the addition of trivalent cation metal or coagulant, which led to the increase of the water ionic strength, causing compression of the double layer of particles; the energy of repulsion can be neutralized, and the particles can then be agglomerate under the effect of the interactions of Van der Waals. However, the number of bonded ions on the particle depended mainly on the diameter of the whole particle-polymer that exceeds the attraction limit of the central particle. These Me3+ ion-particles then form an electrically neutral particle or "destabilized micelle". In the case of agitation, the polymer folds on the particle itself lead to insufficient neutralization of its charge and its continued state of negative destabilization. However, adding an excess of reagent gave a positive charge and induced re-stabilization. In addition, beyond 15 mg/L, the turbidity reduction started to decrease. The polyacrylamide coated the suspended particles and neutralized their charge by Van der Waals forces [26]. This neutralization allowed particles to come close together and results in agglomeration. This agglomeration reduced the turbidity of the waste particles. The decrease in the turbidity reduction to value under 15 mg/L may be due to the reversal of the particle charge. After complete neutralization, other chains of polyacrylamide will attach or adsorb onto the neutralized particles. These attached chains carry N+, causing change to positive charge of the particles followed by re-stabilization [27].

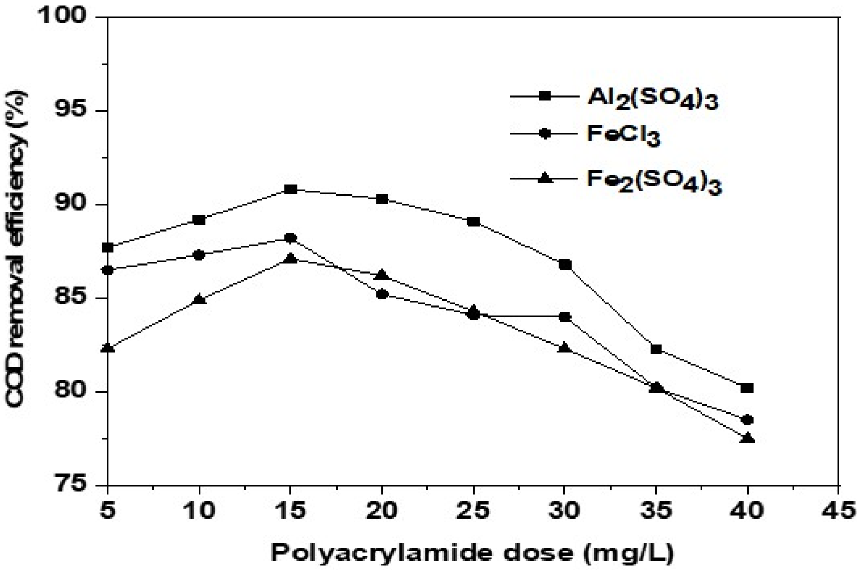

Figure 4: Effect of polyacrylamide (PAC) at various doses on the COD removal.

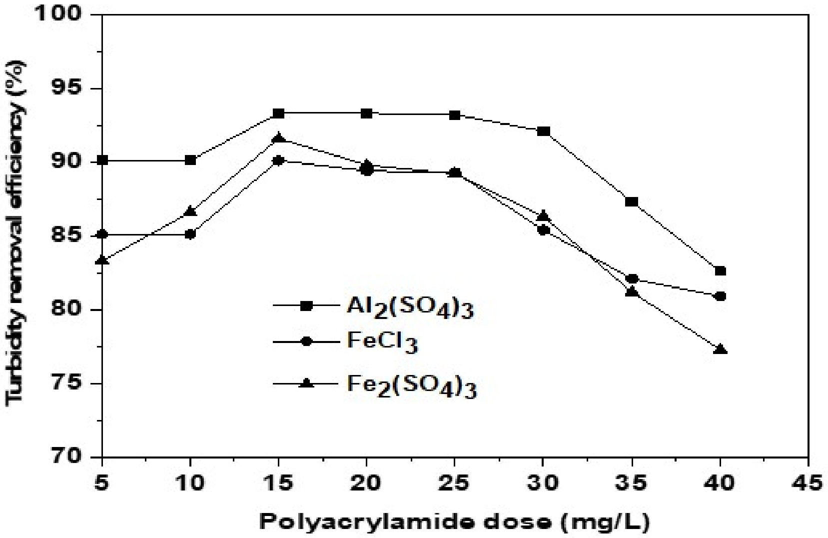

Figure 5: Effect of polyacrylamide (PAC) at various doses on the Turbidity reduction

This series of tests showed that it was possible to achieve an important removal efficiency of 95% for COD and 97% for turbidity. Results showed that the three coagulant doses kept constant with increasing flocculant doses from 10 mg/L to 15 mg/L induce improvement of COD and turbidity removal efficiencies. Even by visual inspection the supernatant became clear following the increase in coagulant and flocculant doses. The experiment considering flocculant and coagulant at 15 and 150 mg/L, respectively have the best results in COD and turbidity removal.

pH evolution

pH is an extremely important parameter, since most of chemical reactions in aquatic environment are pH-modulated. The effect of changing pH values on altering COD and turbidity in wastewater was investigated over changing concentrations of 150, 150 and 200 mg/L of $Al_2(SO_4)_3.18H_2O$, $FeCl_3.6H_2O$ and $Fe_2(SO_4)_3.7H_2O$, respectively. However, each experiment was associated to the use of 15 mg/L of flocculant dose. Results of the previous established coagulant doses with the optimal dose of the flocculant showed that the pH was varied between 3 and 10. In fact, results grouped in Fig. 6 showed clearly that pH could significantly affect the COD removal and the best yield of COD removal was obtained in range pH 3 – 4 where the COD removal yield was in range 90 to 95%. Results also showed a decrease in COD removal yield, when pH increased from 6 to 10 suggesting that this reaction was preferentially realized at pH under 6. Also, the curve related to turbidity evolution showed a similar tendency with turbidity removal yield of 97% and 94% when pH varied from 3 to 4. At pH over 6 resulted showed a decrease on suspended particles removal expressed by low yield (60%). The COD and turbidity removal efficiency was maximized for wastewater treatment was considered at pH included in range 3-4. COD removal for pH 8 was only 73 %, less than the COD removal efficiency of 95 % that was attained at pH 3-4. Also, the turbidity removal for pH = 8 was 80 %, less than the turbidity removal efficiency saving a yield of 97 % obtained at pH 3-4. Because most of the pulp and paper mill effluent is typically alkaline, attaining maximum coagulation efficiency at acidic pH, it would be advantageous to adjust the pH for an efficient coagulation. Furthermore, the final pH of the solution at the end of each experiment was not similar to the initial value. Controlling the pH at an optimal value is critical to achieve maximum performance. However, the results indicated that the adjustment of wastewater pH during coagulation is necessary, to reduce the overall treatment costs. These observations showed that treatment of paper effluents is highly dependent on initial pH value of the effluent sample. The removal of dissolved organic matters during coagulation process at different pH values follows two distinct mechanisms. At low pH, anionic organic molecules interacted with metal cations and form insoluble metal complexes while high pH. However, elevated coagulant concentration led to organics material adsorption onto preformed flocs of metal hydroxides and was precipitated [10]. Similar result was observed by Irfan et al., (2017) who showed that lower pH values are optimal for other natural coagulants [28].

During the coagulation process, the aggregation of colloidal particles occurred through charge neutralization and sweep-floc effects [28]. The pH range 3–4 was appropriate for the charge neutralization between the positively charged coagulant and negatively charged colloids. In addition, as for the metal coagulants $Al_2(SO_4)_3.18H_2O$ or iron salts, the ability of removing turbidity is achieved mainly by the adsorption of the amorphous Al $(OH)_3(s)$. For the formation of amorphous solid-state Al $(OH)_3(s)$, the pH range 6–8 was favorable because the aluminum ions required sufficient alkalinity to be formed. Thus, in the combined action of charge neutralization and flocs sweeping point of view, pH 3–4 was the optimal range for turbidity and COD removal.

As shown in Figure 6 and 7, for turbidity and COD removal, there was a significant correlation between coagulant–flocculant doses and pH. Thus, coagulant dose of 150 mg/L and flocculant dose of 15 mg/L would be the optimal concentration for turbidity and COD removal. This was because the amorphous solid-phase $Al(OH)_3$ was readily formed at pH in range 3–4 and the precipitation of $Al(OH)_3$ reduced the turbidity through adsorbing the colloids into its surface in sweep–floc process.

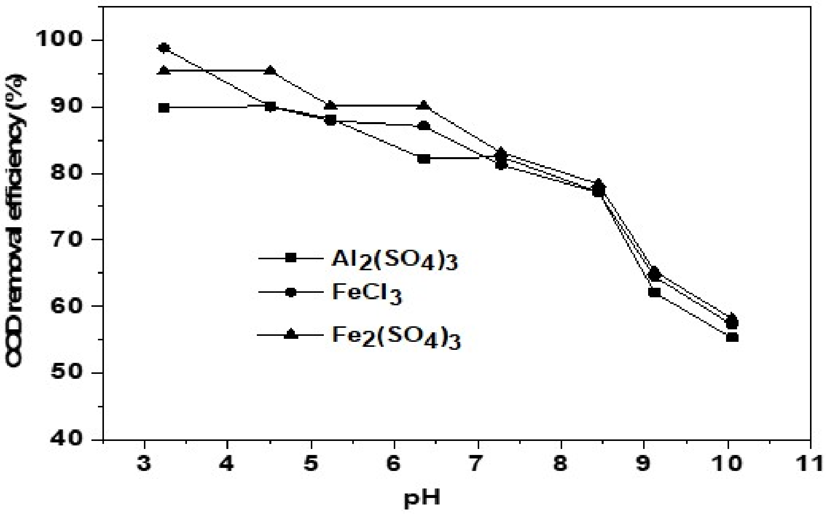

Figure 6: COD removal versus pH using flocculant dose = 15mg/L. Coagulant dose: 150 mg/L for alum, ferric chloride and 200 mg/L for ferrous sulfate.

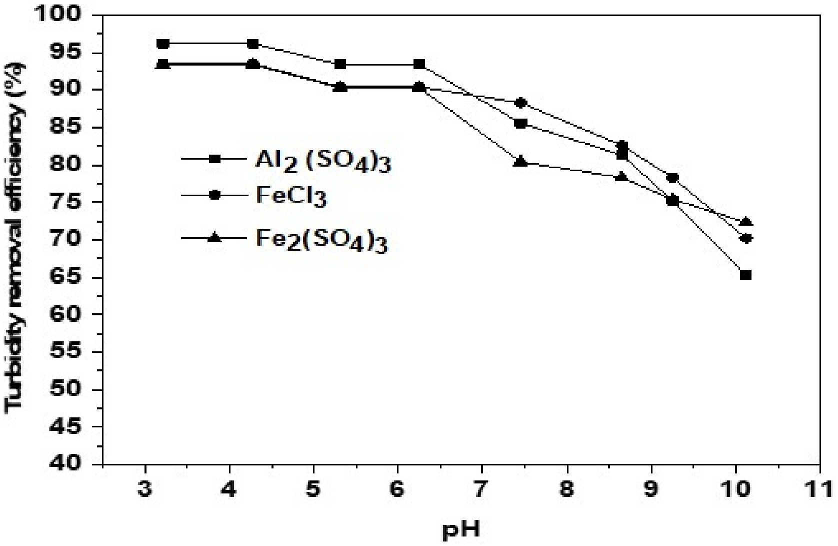

Figure 7: Turbidity removal versus pH using flocculant dose = 15mg/L. Coagulant dose: 150 mg/L for alum, ferric chloride and 200 mg/L for ferrous sulfate.

Characterization of Water After Pretreatment

The pretreatment assessment was affected initially with $Al_2(SO_4)_3$. based on its frequent use in wastewater treatment. $Al_2(SO_4)_3$.is cost effective and available. The wastewater analysis results comparing effluent and treated water in Table. 3 showed that all the metallic elements or minerals studied were reduced at 150 mg/L of coagulant and 15 mg/L of flocculant at pH 4. These values are well below the acceptable values of Tunisian industrial discharge water quality standards. Based on the organic load expressed by BOD5 and COD in the effluent, the treatment results showed a significant reduction up to 95%. Furthermore, the results obtained in the present study were concordant with those obtained by Zouboulis and Traskas (2005) [29] who showed using the same coagulants, a high reduction of organic matter. The discharge of organic and mineral matter from wastewater was in general widely studied by several authors following the same mechanisms based on adsorption, neutralization/destabilization of charges and complexation/precipitation but considering other effluent [30, 31].

During the treatment and under particular environmental conditions, the particles can be effectively destabilized by the surface colloid neutralization with positive species coagulant. After this a close relationship would be established between turbidity levels with the negatively charged particles. Excessive coagulant can absorb or trap the particles suspended in small clumps of floc precipitates. The positive charges of the coagulant species can be complexed with the negative charges of the functional groups forming a floc precipitate that can be eliminated by the separation process. Despite the elevated removal efficiencies, high residual concentration of soluble organic matter indicates that further treatment with biological oxidation must be applied after chemical treatment.

Parameters	Untreated wastewater	Treated water	Removal (%)
Temperature (°C)	18	20	—
pH	10.87	5.5	—
Conductivity (mS/cm)	2.87	3.2	—
Turbidity (NTU)	140	4.2	97
SSM (mg/L)	2596	53	97.95
COD (mg/L)	2490	124.5	95
BOD (mg/L)	180	18	90

Sulfate (mg/L)	919	1270	—
Chloride (mg/L)	1460	1525	—
Aluminum (mg/L)	0.62	2.9	—
Manganese (mg/L)	0.56	0.24	57.14
Iron (mg/L)	9.73	4.66	52.1
Magnesium (mg/L)	0.49	0.18	63.26
Copper (mg/L)	0.99	0.29	70.7
Zinc (mg/L)	8.85	3.79	57.17
Nickel (mg/L)	6.7	2.46	63.28
Cadmium (mg/L)	0.41	0.28	31.7
Lead (mg/L)	0.04	0.01	75

Table 3: Evaluation of mill effluent pre-treatment with aluminum sulfate.

Conclusions

This research on treatment options for mill wastewater led to the following conclusions:

- The effective coagulant $Al_2\ (SO_4)_3$ was utilized to removal of the COD and turbidity from 65% to 75%.
- The optimum dose of $Al_2(SO_4)_3$ for coagulation was 150 mg/L.
- The optimum dose of anionic flocculant for flocculation was 15 mg/L.
- The maximum COD and Turbidity removal was achieved from wastewater at pH =3–4 (95% and 97%, respectively).

Finally, according to the TEWQ standards for industrial discharges, we can assume that the process provided by this research a planning tool to develop a primary treatment plan for mill wastewater prior release into environment. However, the generated sludge needs further research considering the physicochemical and bacteriological characteristics as well as safety assessment for sludge use.

Acknowledgment

This work was supported by the Ministry of Higher Education and Scientific Research of Tunisia. Authors thank (CERTE) staff for their technical support. The authors also are grateful to Pr. Shiva Sreenath Andrali, and Pr Armando McDonald for edition of the manuscript and improving English expression and style.

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