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Coagulation/Flocculation and Aerobic Treatment of Fenton Pre-Treated Phenalkamine Condensate

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ABSTRACT

Phenalkamine is a curing agent produced by the reaction of cardanol, paraformaldehyde, and amine. It has high pH, high COD (Chemical Oxygen Demand), low BOD/COD ratio. In this study coagulation/flocculation and aerobic treatment of Fenton pre-treated Phenalkamine condensate (having COD of 1,50,000 mg/l) was investigated.The optimum operating conditionin the Fenton's oxidation stage was pH-3.5, H_2O_2/COD ratio-1and Fe^{2+}/H_2O_2 -1/30 and achieved COD removal efficiency was 80%. Fenton treated Phenalkamine condensate was subjected to coagulation-flocculation (CF) by using different coagulants like alum, ferrous sulphate, ferric chloride and polyacrylamide (anionic polymer) and the removal of COD at optimum dose of alum (200 mg/L), ferrous sulphate(200 mg/L), ferric chloride(300 mg/L) and polyacrylamide(150 mg/L), were 43.40%, 32.35%, 35.29% and 47.05% respectively. Fenton treated Phenalkamine condensate was diluted and fed toaerobic reactors operated under different hydraulic retention time (HRT-2d,5d,10d) with 3500 mg/l MLSS (Mixed Liquor Suspended Solids). 10 d HRT was found to be suitable for the treatment and the average COD removal efficiency was 75%. Fenton's oxidation followed by coagulation/flocculation or aerobic treatmentis a feasible treatment technique for Phenalkamine condensate

Keywords –Phenalkaminecondensate, COD, HRT, Fenton's oxidation, Coagulation-flocculation, Aerobic treatment

I. INTRODUCTION

During the last decades, the increase in industrial activity demands more fresh water, whereas generated effluent was released into various water bodies, thereby affecting the aquatic life. Untreated industrial wastewater contains a considerable amount of recalcitrant organic pollutants, which are highly resistant to natural biodegradation, when are directly discharged to the surroundings. Growing concern about these problems is pointing towards necessity of better industrial wastewater disposal standards.

Phenalkamines are condensation products of Cardanol, which is a major constituent of the oil obtainable from CNSL (Cashew Nut Shell Liquid), with aliphatic amines such as ethylenediamine, diethylenetriamine, triethylenetetramineorpentaethylenehexamine and formaldehyde. . As a curing agent, the phenalkamines obtained from cardanol have many applications in industrial maintenance, maritime industries and high-performance coating industries.These systems have better curing properties at low temperatures. The great diversity of these Phenlakamine hardeners makes them suitable for many coating applications.Phenalkaminesare generally used in coatings for ships and offshore constructions, tank linings marine and industrial maintenance coatings as adhesives, due to its various advantages likegood chemical resistance and surface appearance, extremely fast and low temperature cure (even below 0°C), excellent water and salt water resistance and good moisture tolerance [1].Cardolite has pioneered new developments in Phenalkamine technology with over three decades of research, such as innovative low viscosity, solvent-free and faster-curing products. The Mannich reaction responsible for the production of Phenalkamines is shown in Figure 1[2].During the processing of

Phenalkamines, 10% of water comes out as waste consists of phenols, aldehyde, and amines which are highly reactive compounds and toxic to the environment and to aquatic system. So the treatment is necessary before discharge. The effluent generated during the production process of Phenalkamine with ethylenediamine was considered for the present study. There is not much research done on the treatment of effluent generated during Phenalkamine production.

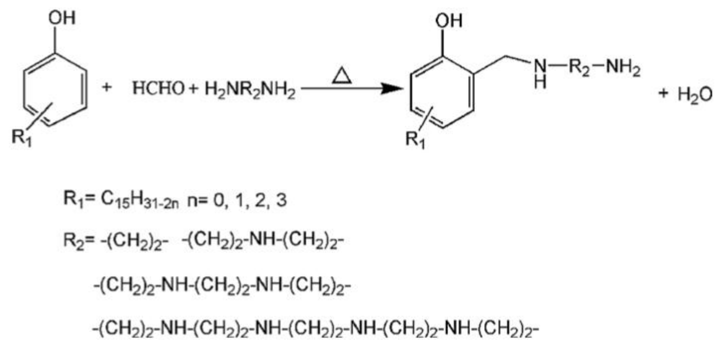


Figure 1: Synthesis route for Phenalkamines with ethylenediamine/ diethylenetriamine /triethylenetetramine/ pentaethylenehexamine

Advanced oxidation processes (AOPs) which are capable of degrading recalcitrant organic compounds, are mostly applied for the treatment of variety of wastewater in recent years. Oxidation with use of Fenton's reagent (Combination of $FeSO_4$ or any other Iron source and Hydrogen peroxide) is quite a common advanced oxidation method of removing undesirable organic compounds as well as transforming non-biodegradable components to a biodegradable fraction, so that it can be used as a suitable pre-treatment for downstream biological process. Catalytic decomposition of H_2O_2 leads to the generation of $OH^{\cdot}$ free radicals, which rapidly oxidizes most organic compounds. The overall reaction is as follows [3].

$$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2\,H_2O \quad (1)$$

The conditions applied in Fenton's treatment will affect the overall sequential treatment techniques. So care must be taken to optimize the parameters to obtain maximum COD removal efficiency.

The conventional industrial wastewater treatment comprises of coagulation-flocculation (C-F) followed by physical (filtration), biological and advanced oxidation process. In this study, the potential application of Fenton's oxidation process sequential with the coagulation-flocculation is considered. The combination of C-F process with Fenton's oxidation can be a suitable alternative for the treatment of industrial wastewater [4]. Destabilization of colloidal and fine suspended particles takes place when a coagulant is added to wastewater and rapidly mixed, causing the agglomeration of destabilized particles under suitable conditions. Flocculation or slow agitation allows these destabilised particles to gather together into bigger aggregates and form visible rapid settling flocs that can be removed easily [5].

The treatment of industrial wastewater by aerobic treatment is quite common and it can be carried out in batch reactors. This process is considered as fill and draw version of the activated sludge process and operates under aseries of periods that constitute a cycle. The cycle is divided into five phases as filling, aeration-reaction, settling, decanting, idle. The biological process is superior to other processes because of its low cost, flexibility and efficient method fortreating dífferent industrial wastewàter, mainly because of its single tank design and ease of automatíon. In thissystem, wastewater is added to one reactor, treated to remove undesírablecomponents, and then released. Ithas been succeśsfully used to treat both municípal and industrial wastewater. Sequential advanced oxidation process and biological process has received attention in recent years as a efficienttreatment method for industrial effluent. The effluent is first treated with an advanced oxidation process to degrade organic matter, generating an effluent with less toxic compounds that can be treated by a biological process [6][7][8].

The objective of the present work is to obtain maximum COD removal efficiency for Phenalkamine condensate using sequential Fenton's oxidation -coagulation flocculation and Fenton's oxidation-aerobic treatment technique.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

II. MATERIALS AND METHODS

A. Phenalkamine wastewater

Phenalkamine wastewater was collected from local Cashew nut processing industry and was stored at 4^0C. Main characteristics of the wastewater are summarized in Table 1.

Table 1: Characteristics of Phenalkamine wastewater

Parameter	Measured value
pH	11.8
Chemical Oxygen Demand (COD)	150000 mg/l
Biochemical Oxygen Demand (BOD_5)	5800 mg/l
Total suspended solids(TSS)	9500 mg/l

B. Reagents

50% w/w H_2O_2 Solution was provided by the Industry. All other reagents are of analytical grade (manufactured by Merck, India) and the materials were used as procured from the manufacturer. The chemicals used include Ferrous (II) sulfate heptahydrate ($FeSO_4.7H_2O$), Sulfuric acid (98–99% pure), Potassium hydroxide (KOH), Potassium iodide (KI), Mercuric sulfate ($HgSO_4$), Potassium dichromate ($K_2Cr_2O_7$), Silver sulfate (Ag_2SO_4), Ferrous ammonium sulfate (FAS), Ferroin indicator, Starch, Sodium thiosulfate ($Na_2S_2O_3$), Alum (Aluminium Sulphate, $Al_2(SO_4)_{3.}18H_2O$), Ferric Chloride($FeCl_3$) and Polyacrylamide.

C. Analytical methods

Closed Reflux Titrimetric method was used for the determination of chemical oxygen demand (COD). Five-day biochemical oxygen demand (BOD_5) and Suspended solids were found out based onstandard methods[9].Digital pH electrode with an integrated temperature sensor (HI763100) was used for pH measurement.

D. Experimental procedure

Fenton's Oxidation

Raw wastewater was subjected to Fenton's oxidation process first. All the experiments were performed in batch reactors at ambient temperature and pressure. 100mL wastewater sample was taken and pHwas adjusted to the desired value with5 Nsulphuric acid and potassium hydroxide (5N). A required quantity of $FeSO_4 \cdot 7H_2O$ and H_2O_2 were added to the sample. Experimental set up for Fenton's Oxidation is shown in Figure 2.$FeSO_4$ used in the process taken in its anhydrous physical form of a commercial grade. Fenton's treatment was conducted for a period of 24 hr.pHwas increased to 7 for decomposition of residual H_2O_2[10].The supernatant was then decanted and filtered using 0.45 μm Millipore filter paper for determination of COD. The optimum Fenton's dosage for maximum degradation was found out by varying concentration of iron and hydrogen peroxide.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Figure 2: Experimental setup for Fenton's oxidation

All the experiments were performed in two sets. COD measurements were done in parallels for each set and the average of two measurements of duplicate set was takes for finding out COD removal. . The formula used for the calculation of COD removal efficiency is as follows.

$$\% \text{ COD removal efficiency} = ((COD_i - COD_f)/COD_i) \times 100 \quad (2)$$

Where,

$COD_i$is the initial COD (mg/l) and COD_f is the final COD (mg/l)

Sequential Coagulation/Flocculation of Fenton treated Phenalkamine condensate

Determining the amount of coagulant to be added to the effluent water sample is essential for the effective and economical removal of colloidal particles. The present work was suggested by adding the powdered type of coagulants in one litre of distilled water to prepare the necessary stock solutions for coagulants. An aqueous solution of alum ($Al_2(SO_4)_3.18H_2O$), Ferrous Sulphate ($FeSO_4.7H_2O$), Ferric Chloride($FeCl_3$) and Polyacrylamide of strength 5g/L was prepared and used for studies.

The conventional 'Jar test' procedure, was employed for coagulation and flocculation processes [11]. Effluent after pretreating by Fenton's oxidation reaction was taken for testing.

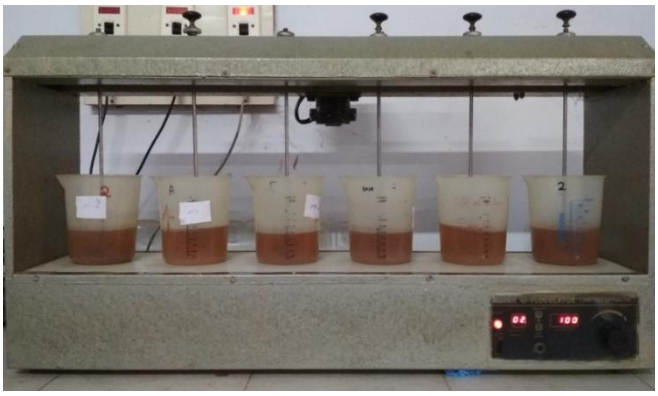


Figure 3: Experimental setup for Jar test

Jar test was carried out with 500 mL Fenton's pretreated effluent in each of 6 beakers of 1L capacity (Figure 3).Coagulants of varying concentrations (increasing dosages) were added, and the mixture was stirred at 100 rpm for one minute and at 30 rpm for twenty-nine minutes. The clarified samples were collected and filtered using a vacuum filter, and the COD was measured.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Sequential Aerobic treatment of Fenton treated Phenalkamine condensate

The aerobic treatment setup consists of four reactors each of total volume two litre with an operàting volume of one litre. It was equipped with air diffuser to keep aerobic condition. The reactor setup is shown in Figure 4. Feeding and decanting were done manually. Thetotal cycle period was dívided into five stages, fill (0.5 h), aeration and reaction(variable), settle(0.5 h), decant(0.25 h) and idle (0.25 h). For the start up, the reactors were fed with aerobic sludge from the NITK wastewater treatment plant. During the initial set up, the sludge had a mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of 20,200 mg/l and 18,200 mg/l respectively. The reactors were seeded with an adequate amount of this sludge so as to maintain an MLVSS of 3500 mg/l. The MLSS and MLVSS were measured periodically to ensure that sufficient biomass was maintained. In order to acclimatize the sludge 1 day HRT was selected and during this period all the reactors were fed with tap water containing starch giving 1000 mg/l COD as the carbon source for a time period of 30 days. After acclimatization Fenton treated water was diluted and fed to three reactors with HRT of 2 d, 5 d, 10 d and one reactor were maintained as a control. The operating volume divided into sludge volume and decanting volume based on HRT and cyclic time.The pH of the Fenton's treatedeffluentwas adjusted to the range 6.8-7.2 using KOH solution.This increased pH results iron precipitation and it was removed by settling. Then the supernatant was taken and fed to the reactors after dilution. During the decanting phase, the supernatant was then decanted and filtered through 0.45 µm Millipore filter paper.COD for both influent and effluent were carríed out.

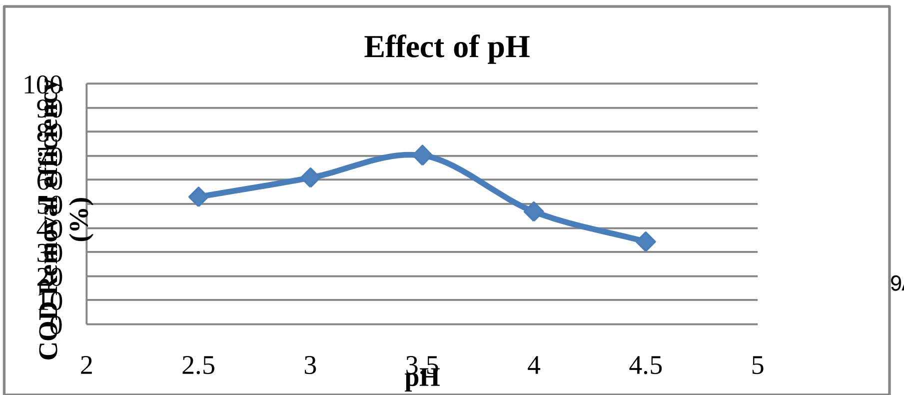
Figure 4: The reactor setup for the aerobic treatment

III RESULTS AND DISCUSSION

A. Fenton's Oxidation

Effect of pH

Among the process conditions affecting efficiency of Fenton oxidation, pH is one of the important parameters and the effect of pH has been discussed in numerous studies [12]. Acidic conditions are favourable for Fenton's reaction and understanding the optimum pH for a particular kind of wastewater is extremely beneficial .In the present study, the initial pH control was performed from pH values 2.5 to 4.5 with an interval of 0.5 pH unit by keeping H_2O_2/COD ratio as 2.13:1 and Fe^{2+}: H_2O_2 molar ratio as 1/20 with initial COD value of 150 g/L. Maximum COD reduction was achieved at pH 3.5 as shown in Figure 5, which is in line with previous studies on Fenton oxidation. Highest COD removal was 70%, and COD removal efficiency decreased with increase in pH. At higher pH (greater than 4), the activity of Fenton reagent was ceased due to the formation of ferric hydroxo complexes. At very low pH values(less than 2), complex iron species $[Fe(H_2O)_6]^{2}+$ and oxonium ion exist, due to which reaction will get slower[3]



ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Figure5: Optimization of pH

Effect of H_2O_2/ COD ratio

The requirement of H_2O_2 for wastewater can be calculated theoretically based on its COD as

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2 \quad (3)$$

$$MW=34 \qquad\qquad 32/2 = (COD)$$

The molecular weight of H_2O_2 is 34 g, so the 2.13 mg/l of H_2O_2 is required to oxidize 1 mg/l of COD (34/16=2.13)[13].In order to maximize the utilization of hydroxyl radical as well as to reduce the quantity of H_2O_2, dosing started from low quantity compared to theoretical calculated H_2O_2dose. H_2O_2/COD ratio was varied from0.6 to 1.6 by fixing the pH as 3.5 and Fe^{2+}/H_2O_2 as 1/20. Maximum COD removal efficiency of 78% was obtained at H_2O_2/COD ratio equal to 1(Figure 6).

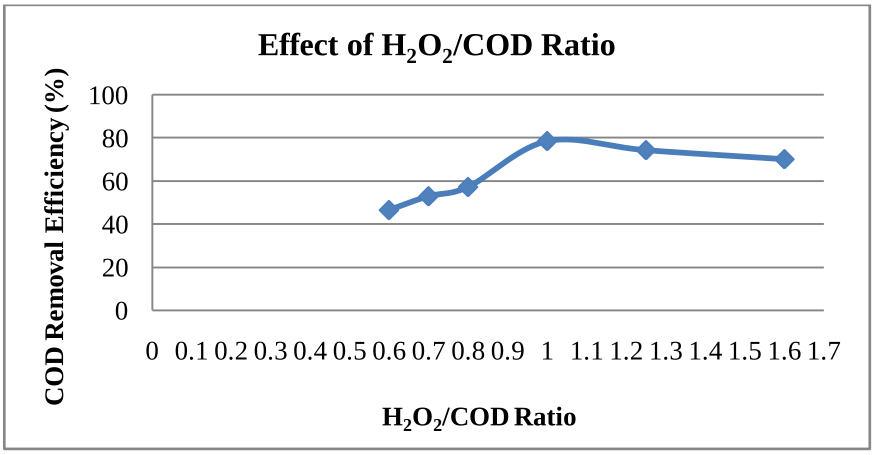


Figure 6: Optimization of H_2O_2 / COD ratio

Efficiency increase with an increase in H_2O_2 / COD ratioto a certain level above that ratio COD reduction will not improve. COD reduction occurs at a faster rate at the initial stage of addition of H_2O_2 on wastewater with high COD and high exothermic effect associated with quick COD oxidation was observed while performing experiments.

Effect of Fe^{2+}/H_2O_2 ratio

H_2O_2 and Fe^{2+} are responsible for the production of hydroxyl radicals, which oxidizes the available organics substances according to the following equation

OH• + organic substances → Oxidation Products (4)

Therefore, It is of greater importance finding out the optimum operational Fe^{2+}/H_2O_2 molar ratio to maximize the effectiveness of the process as well as to eliminate the unwanted reactions of OH• radicals scavenging occurring in the presence of excess H_2O_2 and Fe^{2+}. [12]. The effect of Fe^{2+}/H_2O_2 molar ratio was studied for the ratios 1/125,1/100,1/75,1/50,1/30 and 1/20 by fixing the H_2O_2/COD as 1(Figure 7).COD removal efficiency increased to 80% with an increase in Fe^{2+}.Maximum COD removal efficiency was at the ratio 1/30 and above that slight reduction in COD removal was observed

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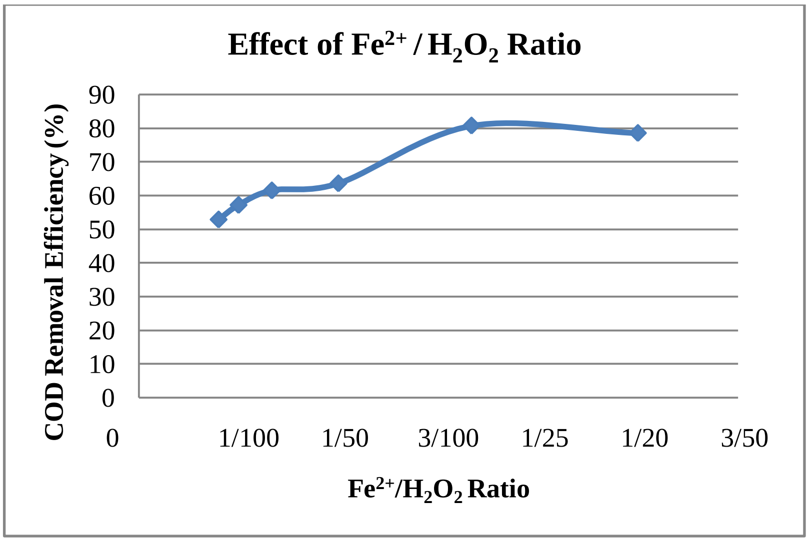

Figure 7: Optimization of Fe^{2+}/H_2O_2 ratio

After optimization for further reduction of COD, the effluent generated from a Fenton's reaction was again treated under the optimized conditions. No significant reduction of COD was observed which indicates that there was no stoichiometric limitation in the Fenton's reaction.

B. Sequential Coagulation/Flocculation of Fenton treated Phenalkamine condensate

After pretreating the phenalkamine condensate using Fenton's reagent, the effluent was treated usingcoagulation-flocculation (CF) method by applying different coagulants like alum, ferrous sulphate, ferric chloride and polyacrylamide (anionic polymer). The study was conducted at various doses of the coagulants for optimization of the coagulants and polymer doses. COD was measured for raw and treated wastewater to fulfil the objective. The COD removal efficiency in each reactor is shown in Figure 8. The removal of COD at optimum dose of alum (200 mg/L), ferrous sulphate(200 mg/L), ferric chloride(300 mg/L) and polyacrylamide(150 mg/L), were 43.40%, 32.35%, 35.29% and 47.05% respectively. Polyacrylamide has higher removal efficiency than other coagulants at lower doses, and thus indicated the better choice of coagulant for the treatment of wastewater. Using polyelectrolyte during the C-F process increases the opportunity for particle collision and joins small floc resulting in a rapid generation of settleableflocs. The enhanced surface activity and improved charge neutralizing capacity of polyacrylamide make them more effective and efficient at a comparatively lower dose than other coagulants. Removal of COD had little variation concerning coagulant type and dosage.

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Vol-22-Issue-16-August-2019

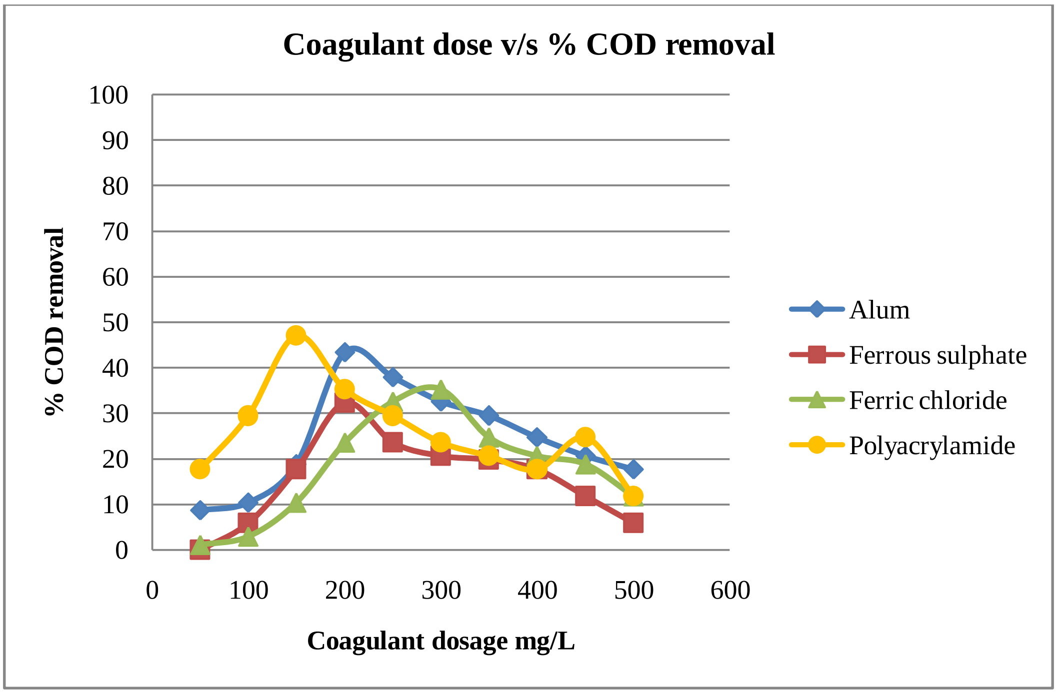

Figure 8: Optimization of coagulant dose

C. Sequential Aerobic treatment of Fenton treated Phenalkamine condensate

The phenalkamine condensate waspretreated by Fenton's oxidation with optimum condition (pH-3.5, Fe^{2+}/H_2O_2 molar ratio 1/30 andH_2O_2/COD ratio 1).Under this operating conditions maximum COD removal was 80% (30000 mg/l). The Fenton treated wastewater was diluted to 10 times and fed to 3 reactors with varying HRT of 2 d,5 d, 10 d. The Figure 9 shows the COD removal efficiency at 2d, 5d, 10d HRT respectively

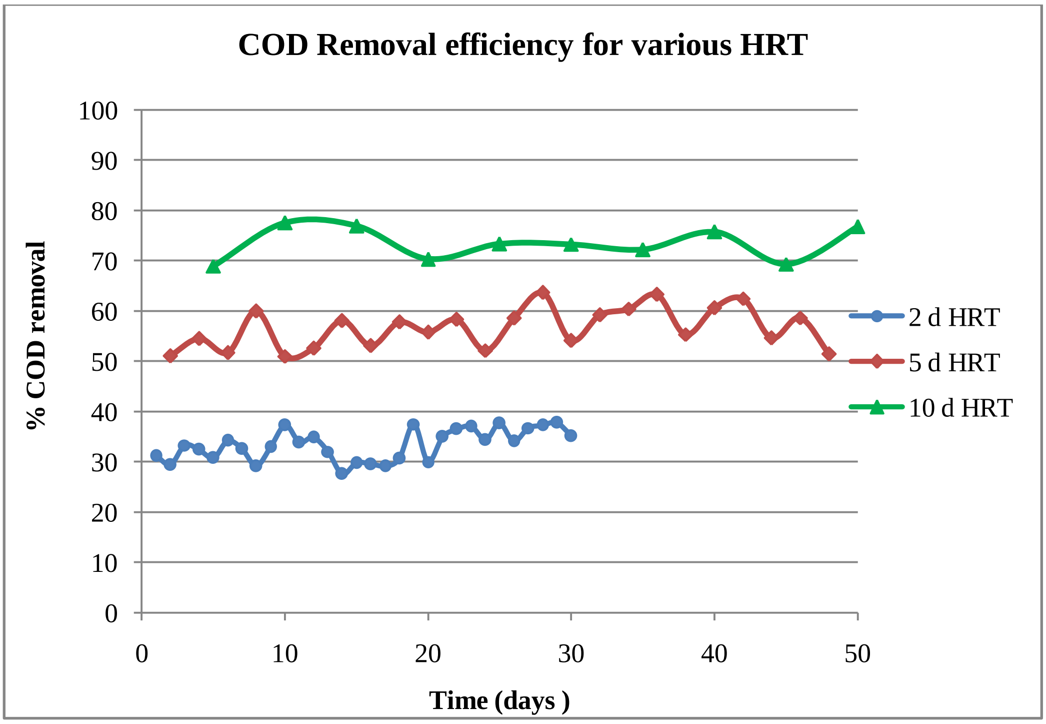

Figure 9: COD removal efficiency for various HRT

According to the figure, the COD removal efficiency for reactor operated at 2 d,5 d and 10 d HRT were 32 ± 5 %, 52 ± 5 % and 75 ± 5 % respectively. The average percentage COD removalwas increased from 32 % to 52 % when HRT varied from 2 to 5d, and it again increased to 75 % when HRT increased to 10 d. So the maximum COD removal was obtained when the reactor operated under 10 d HRT. Less COD removal efficiency at low HRT might be due to the existence of non-biodegradable matter in the effluent. Therefore it is necessary to operate under higher HRT to attain maximum removal efficiency.

IV CONCLUSIONS

- The optimum pH, $Fe^{2+}/H_2O_2$and H_2O_2/COD ratios of Fenton's treatment of Phenalkamine wastewater were 3.5, 1/30 and 1 respectively. Under this condition, maximum COD removal was 80%
- 10 d HRT was found to be suitable for aerobic treatment of Fenton treated phenalkamine condensate, and increased HRT from 2 to 5 d has significantly improved in COD removal efficiency
- The removal of COD at optimum dose of alum (200 mg/L), ferrous sulphate(200 mg/L), ferric chloride(300 mg/L) and polyacrylamide(150 mg/L), were 43.40%, 32.35%, 35.29% and 47.05% respectively and Polyacrylamide has higher removal efficiency than other coagulants at lower doses.
- Sequential Fenton's oxidation-coagulation flocculation or Fenton's oxidation -aerobic treatment is a feasible treatment technique for phenalkamine condensate.

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