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Fenton oxidation: A pretreatment option for improved biological treatment of pyridine and 3-cyanopyridine plant wastewater

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ABSTRACT

The wastewater generated from pyridine and cyanopyridine manufacturing plants is highly complex in nature. It is characterized by high ammonia content, alkaline pH, and extremely high COD values (65,000 and 25,624 mg L^{-1}), making it extremely recalcitrant and virtually non-biodegradable. Therefore it is not usually feasible to directly use biological treatment (BOD:COD < 0.2) for such wastes. However, with a suitable pretreatment option these wastewaters can be made amenable to biological treatment. The study investigated pretreatment of wastewater containing pyridine and 3-cyanopyridine by Fenton oxidation prior to its biological treatment. The results of Fenton oxidation under optimum conditions (3.0 g L^{-1} Fe^{2+}, 900 ppm H_2O_2 dose, pH 3, contact time 180 min) indicated a maximum COD removal of 66% from pyridine wastewater, along with 62.4% pyridine removal. Similarly, for 3-cyanopyridine containing wastewater (2.4 g L^{-1} of Fe^{2+}, 600 ppm H_2O_2 dose, pH 3, contact time150 min) a maximum COD removal of 84% was obtained and total 3-cyanopyridine degradation was 84%. The biodegradation studies of the Fenton-pretreated cyanopyridine and pyridine wastewater were carried out using the isolated *Pseudomonas pseudoalcaligenes*-KPN in batch culture experiments, wherein the residual pyridine and 3-cyanopyridine removal efficiency was observed to be 84% and >99%, respectively.

1. Introduction

The effective treatment of complex wastewaters from pyridine and cyanopyridine manufacturing industries are of severe environmental concern, due to poor biodegradability and presence of a range of complex and toxic components [9]. In this context, the application of advanced oxidation processes (AOP) for priority pollutants like pyridine [1] and its derivatives, which are very recalcitrant to biological treatment has gained much importance and have become a prominent area of research.

Pyridine and its derivatives constitute an important class of compounds with wide applications in pharmaceuticals, pesticide manufacture, chemical manufacture, as industrial solvent, etc. [2]. These compounds occur naturally in the environment, and are also produced in large quantities as a result of industrial activity [2–4]. Once these pyridine compounds enter the environment, they persist for long period of time [5].

The heterocyclic structure of pyridines makes them more soluble than their homocyclic analogues and therefore they can get easily transported through soil and contaminate ground water [6–8].

Biological treatment processes are considered as one of the most techno-economically feasible options for conventional wastewater treatment. However, chemical industries manufacturing pyridines and cyanopyridines (Py-ww and Cp-ww) operate under extreme conditions of temperature and utilize a number of organic compounds for processing. Acetaldehyde, ammonia and catalysts are used for manufacture of pyridines, while ammoxidation of β-picoline at extremely high temperature is carried out for manufacturing 3-cyanopyridine [9]. As a result the wastewater generated from these industries are highly complex and are therefore not amenable to biological treatment.

The Fenton oxidation option has been explored by several workers for treatment of pyridine and its various derivatives [1,10–15]. These reports indicate the effectiveness of Fenton's reagent for reducing the potential strength of the waste either in terms of COD/TOC or mineralization of the target pollutant. However, the main problem associated with this treatment is high reagent cost and generation of sludge, which contain high amount of Fe (III), and needs to be managed by safe disposal methods.

The present investigation was aimed at studying the Fenton oxidation as a pretreatment option to improve the biodegradability of the recalcitrant and complex wastes like pyridine and 3-cyanopyridine contain wastewater generated from a chemical manufacturing industry. The wastewater pretreated with Fenton reagent under optimized reaction conditions was subjected to

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biodegradation using a bacterial species (*Pseudomonmas* sp.) isolated in the laboratory study on pyridine degradation. The results of the study are presented and discussed in this paper.

2. Materials and methods

2.1. Materials

The wastewater obtained from a chemical industry manufacturing pyridine and 3-cyanopyridine was collected and characterized. The characteristics of the pyridine and 3-cyanopyridine wastewater are presented in Table 1.

The chemicals used in the study viz. pyridine, 3-cyanopyridne were procured from M/s Aldrich Co., Germany. Ferrous sulphate ($FeSO_4{\cdot}7H_2O$) from Ranbaxy Fine Chemicals, India and hydrogen peroxide (30%, v/v) from E-Merck, India was used. The pH of the wastewater during Fenton oxidation was adjusted by using 0.5N H_2SO_4/1N NaOH. Furthermore, Fenton reaction was performed in the glass beaker of 1 L capacity. Double distilled water having specifications: pH 7.1, conductivity 140 μm/cm, Cl: 0, SO_4: 0, was used for preparation of all reagents.

Ferroin indicator for COD test was procured from Ranbaxy fine chemicals India, Ltd., Whatman filter paper no. 42 was used throughout the study for general sample filtration purposes, while Gelman membrane filters (0.45 μm, 47 mm diameter) were used for membrane filtration of biological samples obtained from biodegradation studies.

The pH measurements were carried out using control dynamics make pH meter (model no. APX175E/C). The conductivity measurements on the wastewater samples were carried out using a conductivity meter (model CDM3, Radiometer-Copenhagen make). Automatic-Super make incubator was used for incubation of biodegradation samples. IEC centrifuge (Model PR-2) was used during the investigation for clarifying the biological samples for analysis. The glassware and media (growth/nutrient medium for growing the bacterial culture to be used as seed inoculum later) used in the study was sterilized using autoclave (PEIC) at 15 lbs pressure and 121 °C for 20 min.

2.1.1. Seed inoculum for biological treatment

The bacteria *Pseudomonas pseudoalcaligenes* previously isolated in the laboratory in a study on degradation of pyridine and its derivatives [16,17] was used as a microbial inoculum with appropriate initial culture optical density (OD: 0.2) for the Fenton-pretreated wastewater samples.

Table 1
Characterization of wastewater from pyridine and 3-cyanopyridine plant.

Parameter	3-Cyanopyridine plant wastewater	Pyridine plant wastewater
pH	9.43	9.95
Chemical oxygen demand	25,624	65,000
Biochemical oxygen demand	3125	2416
Ammonia-nitrogen	14,175	37,632
BOD:COD ratio	0.125	0.037
Substrate concentration range	700–800	1640–1750
Total dissolved solids	36.74	45.59

All the values except for pH are expressed as $mg\,L^{-1}$. The above values are average of 3 sets of observations. The standard deviation for all the values was observed to be less than 10%

2.2. Methods

The overall treatment was designed as a two-step process, Fenton's oxidation process (FO process) as step I, and aerobic biological treatment (batch culture experiments) as step II.

2.2.1. Fenton oxidation process (F.O. process)

2.2.1.1. Optimization studies for COD reduction. Studies were carried out to optimize the pH, dose of H_2O_2 and Fe^{2+} ions for the pretreatment of pyridine and 3-cyanopyridine wastewater (Table 1). The studies were conducted in a 1 L glass beaker. During pH optimization both H_2O_2 and Fe^{2+} ion doses were kept constant and pH was varied in range of 1–4. The ferrous and hydrogen peroxide dose optimization studies were carried out at optimum pH keeping the contact time constant and finally the contact time was varied under optimum pH and ferrous and hydrogen peroxide concentration conditions.

2.2.1.2. Treatment of pyridine and 3-cyanopyridine wastewater using Fenton's reagent. The Fenton oxidation was used as a pretreatment option for pyridine and 3-cyanopyridine wastewater. The wastewaters having an average input COD 60,000 and 23,000 $mg\,L^{-1}$, respectively, were subjected to Fenton oxidation under optimized condition.

2.2.1.3. Biological treatment of Fenton-pretreated pyridine/3-cyanopyridine wastewater. After the pretreatment with Fenton's reagent, the pyridine/3-cyanopyridine wastewater was subjected to aerobic biodegradation for the removal of residual COD in flask culture experiments. For this purpose, the wastewater pH was adjusted to 7.0 ± 0.2, and supplemented with basic nutrients consisting of $g\,L^{-1}$ dipotassium hydrogen phosphate (K_2HPO_4) 0.615, Potassium chloride (KCl) 0.25, and 0.25 magnesium sulphate ($MgSO_4{\cdot}7H_2O$) [16]. Furthermore, the seed inoculum prepared using *P. pseudoalcaligenes* [17] was used as a microbial inoculum at a minimum OD of 0.2. The flasks were incubated at 30 ± 0.2 °C and the experiments were conducted in triplicates. The results were interpreted in terms of COD removal as well as removal of substrates (pyridine and 3-cyanopyridine).

2.3. Analytical methods

The wastewater under investigation was a highly complex medium, and contained a number of organic compounds apart from the main constituents viz. pyridine and 3-cyanopyridine. UV spectrums of untreated (raw wastewater) and treated (Fenton pretreated) were recorded using a Perkin-Elmer Lambda-900 spectrophotometer for pyridine and 3-cyanopyridine. Similarly the gas chromatographic data was also recorded selectively for pyridine and 3-cyanopyridine removal only and the overall treatability was evaluated based on COD values estimated using standard procedure [18]. A Perkin-Elmer Autosystem GC, with FID and a capillary column was used for analysis of filtered samples. The pyridine analysis was carried out using wastewater samples extracted in solvent dichloromethane, while the 3-cyanopyridine analyses on GC was carried out using samples extracted in benzene. The hydrogen peroxide interference in the standard COD test was eliminated as per the protocol [19]. The metallic content of the wastewater was analyzed using atomic absorption spectrophotometer (Shandon Southern, model A3400) equipped with hollow cathode lamps.

2.3.1. Statistical analysis and optimization

The optimal process parameters for Fenton oxidation were estimated by statistical analysis using MINITAB 14 software (PA, USA) using the response surface methodology (RSM). Multiple regression analysis of the experimentally determined data was used to build an empirical second order polynomial exhibiting quantitative effect of each optimization parameter on the pretreatment of pyridine and 3-cyanopyridine wastewater in terms of the percentage COD removal. Multi-objective numerical optimization was performed on the experimental data using MINITAB 14.

Further, the experimental data (average values of 3 sets of observations) has been used in the study and the same is represented in the figures as y-error bars using Microsoft-Excel.

3. Results and discussion

3.1. Fenton's oxidation process as a pretreatment to biodegradation

3.1.1. Effect of pH

All the studies were carried out on wastewater from pyridine (Py-ww) and 3-cyanopyridine (3-Cp-ww) plant having average input COD of 65,000 and 25,624 mg L^{-1}, respectively. The aqueous pH has a major effect on the efficiency of Fenton's treatment. During the pH optimization study, the pH of the solution was varied in the range of 1–4. The reaction was carried out for 90 min under controlled pH condition with dose of Fe^{2+}: 2 g L^{-1} and H_2O_2 dose of 525 ppm. The results obtained from on the effect of pH on the COD removal are presented in Fig. 1(a) for 3-Cp-ww indicating 70% COD removal. A COD removal of 52% was achieved for Py-ww. It is apparent from fig, that COD removal increases with pH, maximum COD removal was observed for both py-ww and cp-ww at pH 3, after which the COD removal decreases (Fig. 1a). The reduction in COD removal after a pH of 3.0 may be attributed to scavenging of hydroxyl radical with H^+ ions as also reported by Neyens and Baeyens [20]. Also above pH 3, the ferrous ion gets converted to ferric ion, which then combines with OH radical to produce ferric hydroxide, which precipitates and settles down, thereby reducing the ferrous availability in the solution. The observed maximum COD reduction at pH 3 is in agreement with previous studies reported for wastewater containing pyridines [13].

3.1.2. Effect of contact time

The contact time of Fenton's reagent and wastewater in the reaction mixture was varied in the range of 30–240 min (0.5–4 h) and the pH of the reaction mixture was maintained at the observed optimum (pH 3.0) with a Fe^{2+} dose of 2 g L^{-1}. The H_2O_2 concentration was maintained at 525 ppm. The results indicate a maximum COD removal of 79% for 3-Cp ww at 150 minutes and for pyridine wastewater 56% COD removal at 180 min (Fig. 1(b)). The pH was maintained at optimum (3.0) for both the wastewaters. No COD removal was observed with further increase in contact time beyond the optimum. A contact time of little more than 120 min has been reported in literature for Fenton oxidation of 4-tertiary-butyl pyridine for almost complete mineralization [14]. Engwall et al. [13], have reported a contact time of 180 min to be optimum for transformation of creosote-contaminated wastewater. The contact time obtained in the present investigation is therefore well within those values reported previously for wastewater containing heterocyclic nitrogenous pollutants like pyridine and its derivatives.

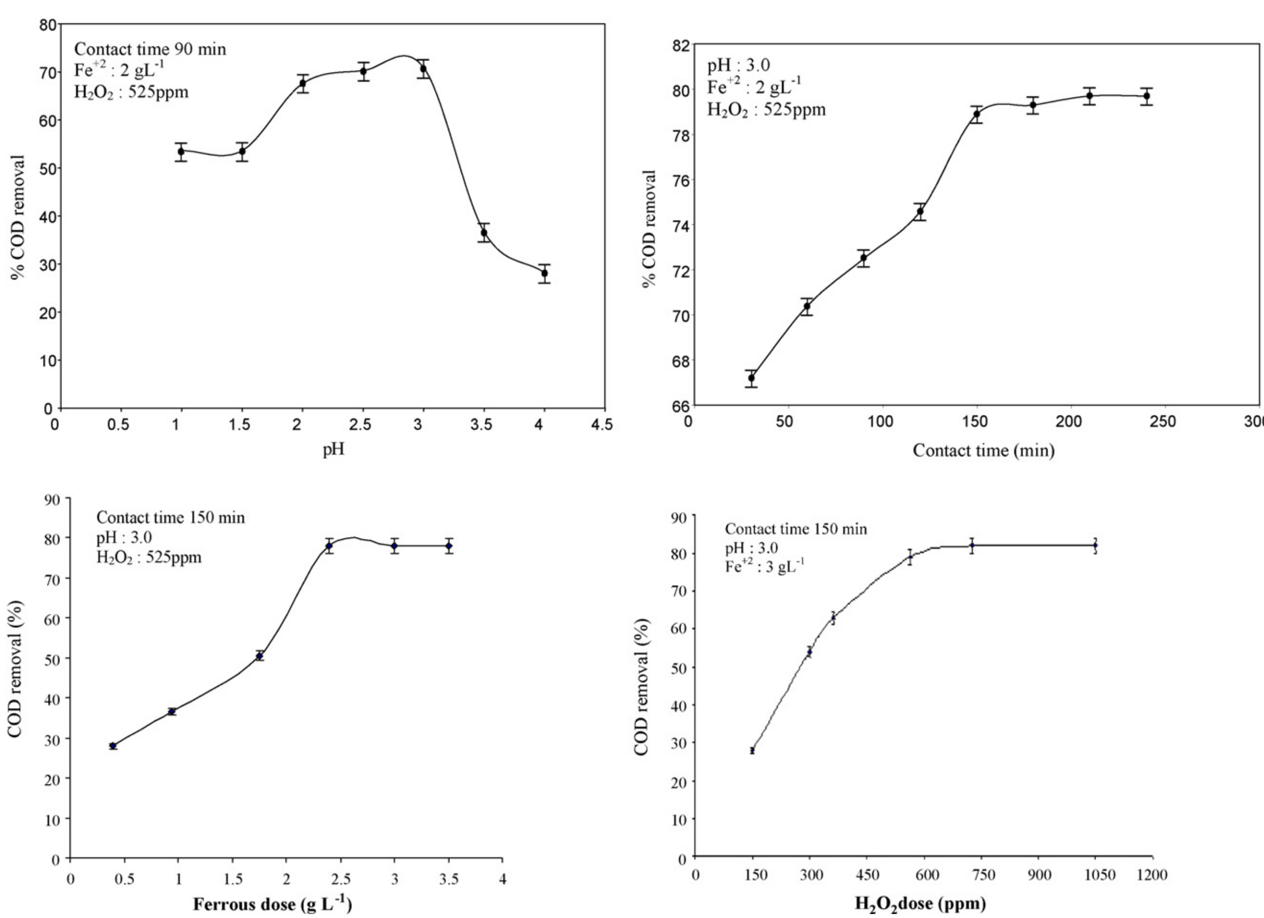

Fig. 1. (a) Effect of pH on COD reduction for 3-cyanopyridine wastewater during Fenton oxidation. (b) Effect of contact time on COD reduction for 3-cyanopyridine wastewater during Fenton oxidation. (c) Effect of ferrous dose on COD reduction for 3-cyanopyridine wastewater during Fenton oxidation. (d) Effect of hydrogen peroxide dose on COD reduction for 3-cyanopyridine plant wastewater during Fenton oxidation.

3.1.3. Effect of Fe^{2+} dose

The ferrous sulphate dose for COD removal for Py and 3-Cp-ww was varied in the range of 0.4–4 g L^{-1}. The contact time for this experiment was maintained at the respective observed optimum (150 min for 3-Cp-ww and 180 min for Py-ww). The pH was maintained at optimum (pH 3.0) and the hydrogen peroxide dose was maintained at 525 ppm. The results on COD reduction with increasing ferrous dose for 3-Cp-ww are presented in Fig. 1(c). The results indicate that the COD removal increases with increasing ferrous sulphate concentration up to a ferrous concentration of 2.4 g L^{-1} for 3-Cp-ww with a maximum COD removal of 80%. The results on Py-ww indicated a ferrous dose of 3.0 g L^{-1} to be optimum with 62% COD removal and above this value the increase in ferrous concentration does not effect COD removal. In the presence of an organic substrate, the –OH radical and both Fe^{2+} ions enter into a series of consecutive reactions that lead to its oxidation and this most effectively occurs in the pH range of 2.0–3.0 [21]. A minimum Fe:substrate/COD ratio must be maintained to allow the reaction to proceed and yield the desired end products. Typically the ratio of 1 part of Fe to 10–50 parts of substrate/COD are reported for compounds like phenols, when treated with Fenton's reagent [22]. In present study the ratios obtained are of the order of 1:8125 (Fe:COD) for treatment of Py-ww and 1:4003 (Fe:COD) for 3-Cp-ww. The iron dose may also be expressed as a ratio to H_2O_2 dose, the typical ratios reported are 1:5–25 (Fe:H_2O_2) [23], however, in the present investigation the ratios are very low 1:1.11 for Py-ww and 1:1.38 for treatment of 3-Cp-ww. These low ratios are indicative of two facts (a) low requirement of H_2O_2, and more economy and (b) extremely remote possibility of residual H_2O_2 in the system after the reaction to interfere with subsequent biological treatment. Moreover, the iron used may even be recycled following the reaction, separating the iron floc and re-acidifying the iron sludge. Typical data on treatment of complex wastewaters like Py/Cp is not available for actual comparison of the obtained ratios/results.

3.1.4. Effect of H_2O_2 dose

The dose of hydrogen peroxide for the reaction was varied from 150–1050 ppm for both Py and 3-Cp-ww under optimum conditions of pH (3.0), contact time (180 and 150 min, respectively) and ferrous dose (2.4 and 3.0 g L^{-1}, respectively). During the optimization studies, it was found that the COD removal increases with increase in H_2O_2 concentration. The effect of H_2O_2 concentrations on COD removal for 3-Cp-ww is presented in Fig. 1(d), the results indicate a 82% COD reduction for a H_2O_2 dose of 600 ppm, similarly for Py-ww a maximum COD removal was observed to be 64% at a H_2O_2 dose of 900 ppm. Further, as the H_2O_2 concentrations were increased, a decrease in COD reduction was observed, which may be due to the scavenging effect of hydroxyl radicals of H_2O_2 according to Eqs. (1) and (2) given below. Hsueh et al. [24], have reported on degradation of azo dyes using Fenton and Fenton like reagent and have reported that degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation of organic compounds was decreased as a result of the scavenging effect. Tang and Huang [25] have also reported the same phenomenon for degradation of 2-4 dichlorophenol using Fenton reaction. A sufficient amount of hydrogen peroxide must be present in the system to avoid build up of undesirable intermediates, which is frequently encountered as a major problem during treatment of complex organic wastewaters. This problem was also encountered in the present investigation. A sufficient H_2O_2 dose not only ensures the COD reduction, but a rapid decrease in wastewater toxicity [23]. The chemical reactions occurring during the Fenton oxidation can be summarized in the form of following two equations:

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \quad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + Fe^{2+} + OOH\cdot \quad (2)$$

A hydrogen peroxide dose more than the optimum does not yield further reduction in the COD of the wastewater. Initially the ferrous ions react with hydrogen peroxide to produce a large amount of hydroxyl radicals (Eq. (1)). Further ferric ions, which are produced, react with more hydrogen peroxide to produce hydroperoxyl radicals ($HO_2\cdot$) and ferrous ions (Eq. (2)). The oxidation capability of hydroxyl radical is much more as compared to hydroperoxyl radicals and that is the reason why the COD removal does not improve even after adding more H_2O_2 after an optimum dose to the reaction system.

3.1.5. Pretreatment of pyridine and 3-cyanopyridine plant wastewater using Fenton's reagent under optimum conditions

The highly complex wastewater containing pyridine and 3-cyanopyridine were subjected to Fenton oxidation as a pretreatment option prior to biodegradation. The Py-ww was treated under the optimized conditions: Fe^{2+} 3.0 g L^{-1}, H_2O_2 900 ppm and a contact time of 180 min (3 h). The results indicate a 66% COD removal with an initial COD of 65,000 mg L^{-1} as well as 62.4% pyridine removal with an initial pyridine concentration of 1700 mg L^{-1}. The 3-Cp-ww was treated under the optimized reaction conditions: Fe^{2+} 2.4 g L^{-1}, H_2O_2 600 ppm and a contact time of 150 min

Table 2
Overall performance of the Fenton followed by biodegradation treatment scheme for pyridine and 3-cyanopyridine plant wastewater.

Type of wastewater	Untreated		Fenton pretreated		Biological treatment	
	COD	Pyridine	COD	Pyridine	COD	Pyridine
Pyridine plant	65,000	1700	22,100	639.28	3978[a]	102.28[a]
% Reduction	–	–	66.0	62.4	82.0	84.0
Pyridine plant	65,000	1700	–	–	57,475[b]	1173[b]
% Reduction	–	–	–	–	11.57	31.0

Type of wastewater	Untreated		Fenton pretreated		Biological treatment	
	COD	3-CP	COD	3-CP	COD	3-CP
3-CP plant	25,000	725	3843	145.0	195.60[a]	0.84[a]
% Reduction	–	–	84.0	80.0	94.0	<99.0
3-CP plant	25,000	725	–	–	9000[b]	275.5[b]
% Reduction	–	–	–	–	36.0	62.0

3-CP: 3-cyanopyridine plant wastewater.
[a] Original wastewater without Fenton pretreatment.
[b] Wastewater pretreated using Fenton oxidation.

(2.5 h). The results indicate 84% COD removal with an initial COD of 25,000 mg L^{-1} and 80% 3-cyanopyridine removal with an initial concentration of 725 mg L^{-1}. The Fenton-pretreated wastewater with an improved BOD:COD (0.037–0.79 for pyridine plant ww and 0.125–0.94 for 3-cyanopyridine wastewater) ratio and residual H_2O_2 < 5% of the initial sample was subjected to biodegradation using isolated *Pseudomonas* sp.

3.1.6. Sludge generation

The production of sludge during Fenton treatment contains high amount of Fe (III), which needs to be managed properly by safe disposal methods [26]. This is considered to be a major problem with the Fenton's oxidation process. In the present investigation, the amount of sludge generated under the optimum treatment conditions was 0.32 and 0.24 g L^{-1} for Py and 3-Cp-ww, respectively, which is far less in magnitude as compared to that produced from conventional coagulants such as ferrous sulphate, zinc sulphate and calcium chloride, for such wastewaters [9]. Hence Fenton oxidation seems to be an economic as well as safe pretreatment option for highly complex wastewaters from pyridine and 3-cyanopyridine manufacturing plants.

3.2. Biodegradation of Fenton-pretreated wastewater

The Fenton-pretreated wastewater was subjected to biodegradation in flask experiments by pH adjustment and supplementation of basic nutrients (Table 2). The *Pseudomonas* sp. isolated earlier in the laboratory for biodegradation of pyridine and its derivatives and reported previously to treat pyridines in bench scale activated sludge unit [17] novel rotating rope reactor [27] and biofilter [28] was used as the seed-inoculum for removal of residual COD and substrates from Fenton-pretreated wastewaters. The results indicate that over a 288 h (12 days) period for 3-Cp-ww with an initial 3-Cp concentration of 145 mg L^{-1} and a COD of 3843 mg L^{-1} (Fenton pretreated) the COD was removed further to the tune of 94% and the cyanopyridine removal was found to be more than 99%. The wastewater which was not pretreated using Fenton oxidation could show only 36% COD reduction during biological treatment in the same time period coupled with only 62% substrate (3-CP) removal. The Fenton-pretreated Py-ww indicated a COD removal of 82% and a pyridine removal of 84% during the 288-h biodegradation study, while the untreated wastewater could show only 11.57% COD removal and 31% substrate (pyridine) removal during the same time period. The results are summarized in Table 2. The chromatograms on pyridine removal are presented in Fig. 2. The results presented in Fig. 2 indicates the initial pyridine concentration in raw wastewater (a) and that after Fenton pretreatment (b) the pyridine concentration is reduced to more than 10 times the original concentration as compared to raw wastewater, which on subsequent biodegradation leads to complete disappearance of pyridine (c).

A number of microorganisms have been reported in the literature for the degradation of pyridine group of compounds. *Nocardia* sp. [29], *Micrococcus luteus* [30], *Bacillus coagulans* [31], *Pimelobacter* sp. [4], *Pseudomonas* sp. [17,30], etc. However, most of these studies have been reported on synthetic wastewaters with defined strength and composition either in batch culture experiments or bench scale reactors and hence cannot be directly compared with the present investigation.

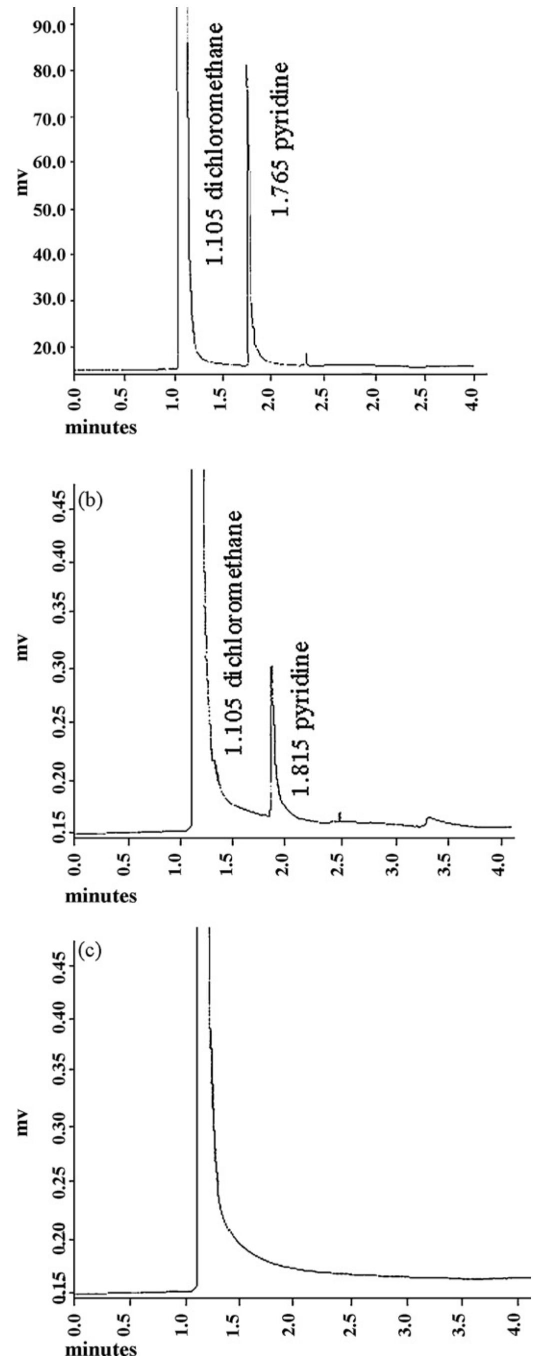

Fig. 2. Chromatograms showing: (a) pyridine wastewater before Fenton treatment. (b) After Fenton treatment. (c) Fenton-pretreated pyridine wastewater after biodegradation.

3.3. Effect of pretreatment on biodegradability of pyridine/3-cyanopyridine wastewaters

The wastewater pretreated with Fenton's reagent under optimum conditions indicated an improved BOD:COD ratio when subjected to subsequent biological treatment. The BOD:COD ratio for Py-ww was improved from 0.037 to 0.79 after Fenton oxidation; the pretreatment could remove 66% COD as well as 62.4% pyridine from the wastewater. The BOD:COD ratio for 3-Cp-ww was improved from 0.125 to 0.94 after Fenton oxidation; and the pretreatment could remove 84% COD. Further, the biological treatment of Fenton-pretreated Py-ww indicated an overall COD removal of 82% and pyridine removal of 84% as compared to 11.57% COD removal and 31% pyridine removal in untreated wastewater. The overall COD removal in Fenton-pretreated 3-Cp-ww was observed to be 94%, whereas more than 99% cyanopyridine could be removed with combined (Fenton + biodegradation) treatment as compared to 36% COD removal and 62% cyanopyridine removal in the case

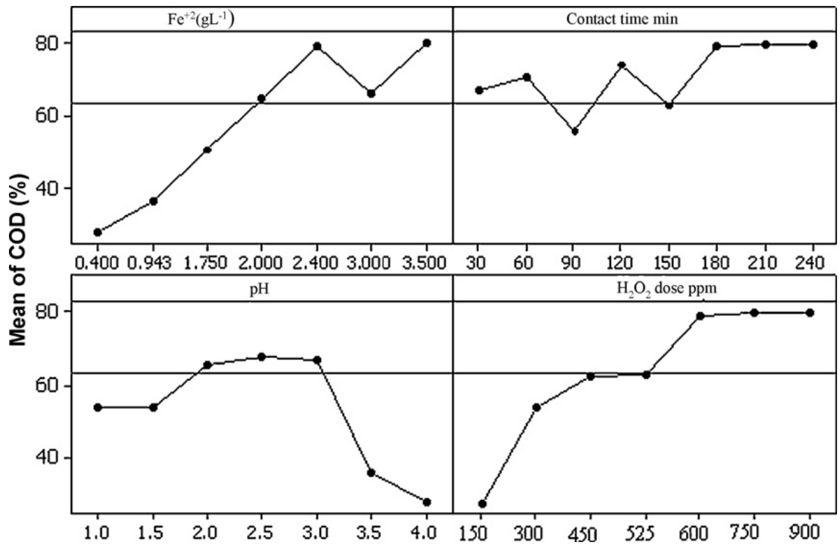

Fig. 3. Main effect plots for % COD removal.

of untreated wastewater. All the results are summarized and presented in Table 2.

The Fenton pretreatment option has been explored earlier by several workers for phenolic compounds prior to biodegradation [11,32] as well as for degradation of wastewater containing azo dyes [33]. These workers have reported the improved biodegradation of wastes when pretreated with Fenton's reagent under optimum conditions, however for complex wastewaters like pyridine and its derivatives the literature reports could not be cited and hence the present investigation can form a significant lead for fur-

Table 3
Data for optimization of Fenton oxidation for 3-CP plant wastewater.

Observations	FE^{2+} ($g\,L^{-1}$)	Contact time (min)	pH	H_2O_2 dose (ppm)	Experimental COD (%)	Predicted COD (%)	% Error
1	0.5	145	2.25	675	91	89.87	1.23
2	0.5	145	2.25	675	89	89.87	−0.98
3	1.5	90	1.5	450	77.09	79.46	−3.08
4	1.5	90	1.5	900	88.54	90.62	−2.35
5	1.5	90	3	900	86.66	88.77	−2.44
6	1.5	90	1.5	450	78.82	79.46	−0.82
7	1.5	200	1.5	450	88.2	89.37	−1.33
8	1.5	90	1.5	900	92.22	90.62	1.73
9	1.5	200	3	450	75.31	78.79	−4.63
10	1.5	200	3	900	83	82.77	0.26
11	1.5	200	1.5	900	88	90.74	−3.11
12	1.5	90	3	450	76.58	75.01	2.04
13	1.5	200	1.5	900	89.23	90.74	−1.69
14	2.5	145	2.25	675	95.47	93.10	2.47
15	2.5	145	2.25	225	75.73	77.97	−2.96
16	2.5	255	2.25	675	82	83.16	−1.42
17	2.5	145	2.25	675	96	93.10	3.01
18	2.5	145	2.25	675	91.23	93.10	−2.05
19	2.5	145	3.75	675	80.5	84.70	−5.22
20	2.5	145	3.75	675	87.63	84.70	3.33
21	2.5	145	0.75	675	89.506	91.62	−2.36
22	2.5	145	2.25	675	94	93.10	0.94
23	2.5	35	2.25	675	76	74.00	2.62
24	2.5	145	2.25	675	89.21	93.10	−4.36
25	2.5	145	2.25	675	91	93.10	−2.31
26	2.5	255	2.25	675	80.12	83.16	−3.8
27	3.5	200	1.5	450	94	93.62	0.39
28	3.5	90	3	900	85.1	83.67	1.66
29	3.5	90	1.5	450	79.27	78.46	1.01
30	3.5	200	1.5	450	94	93.62	0.39
31	3.5	90	3	900	85.1	83.67	1.66
32	3.5	200	1.5	450	90.59	93.62	−3.35
33	3.5	90	1.5	900	77.61	80.01	−3.10
34	3.5	200	3	900	83.61	82.93	0.80
35	3.5	90	3	900	81	83.67	−3.30
36	3.5	200	3	900	80.2	82.93	−3.41
37	3.5	90	3	450	79.01	79.51	−0.64
38	3.5	200	3	450	86.61	88.56	−2.25
39	4.5	145	2.25	675	85.9	89.03	−3.64
40	4.5	145	2.25	675	91.23	89.03	2.41

ther research in improving the treatability of such highly complex wastes.

3.4. Statistical analysis and optimization

Response surface methodology was used for design of experiment and process optimization. Central composite design (CCD) is well suited for quadratic surface response and hence used in the present study. CCD contains a fractional factorial design with center points that is augmented with a group of star (α) points representing new extreme values (low and high) for each factor in the design. The center points are often replicated in order to improve the precision of the experiment. The most important parameters which affect the COD removal from pyridine and 3-cyanopyridine wastewater are pH, contact time, Fe^{2+} dose and H_2O_2 dose. The pH range studied was between 0.75 and 3.75. The contact time was between 35 and 255 min, Fe^{2+} dose between 0.5 and 4.5 g L^{-1}, while the H_2O_2 dose was varied between 225 and 900 ppm. The main effects of each parameter on COD removal are given in Fig. 3 and the data on optimization is presented in Table 3. From Fig. 3, it was observed that Fe^{2+}, pH and H_2O_2dose had significant effect on COD removal; while varying the contact time did not change the COD removal significantly. COD removal increased with increase in the Fe^{2+} concentration up to 2 g L^{-1} and was found to be as high as 80% above 2.4 g L^{-1} Fe^{2+}. A pH range of 2–3 was most favorable for maximum COD removal. An increase in H_2O_2 dose led to an increase in COD removal and reached a constant value of 80% above 600 ppm. Using the experimental results, the regression model equation (second order polynomial) relating the COD removal and process parameters was developed and is given in Eq. (3). Apart from the linear effect of the parameter for COD removal, the RSM also gives an insight into the quadratic effect of the parameters. The regression equation for % COD removal is given by:

$$\begin{aligned}\%\ \text{COD removal} = {} & -5.8527 + 3.9628X_1 + 0.5468X_2 + 5.7596X_3 \\ & +40.5750X_4 - 0.9139X_1^2 - 0.0012X_2^2 \\ & -2.1962X_3^2 - 5.4978X_4^2 + 0.0239X_1X_2 \\ & +1.8360X_1X_3 - 3.2002X_1X_4 - 0.0371X_2X_3 \\ & -0.0593X_2X_4 + 1.1591X_3X_4 \qquad (3)\end{aligned}$$

where X_1, X_2, X_3 and X_4 are Fe^{2+} dose (g L^{-1}), contact time (min), pH, and H_2O_2 dose (ppm), respectively.

The R^2 value of 0.8909 for % COD removal implies that sample variation of 89% is attributed to the factors and 11% of the sample variation could not be explained by the model. The P-values were used as a tool to check the significance of each of the variables, and also their quadratic effects. In general, smaller the value of P (<0.05), the more significant is the corresponding coefficient term. It was observed that the coefficients for the linear effect of time and H_2O_2 dose (P = 0.000) was found statistically significant. Second order and mutual interactions between all the parameters were found statistically significant. The model Eq. (3) was optimized using a multi-objective numerical optimization technique. The predicted values (using the model equations) were compared with experimental result for COD removal and the data are shown in Table 4. The predicted values are close to the experimental values with % error within 10% for most cases. The optimum values of the process variables for the maximum COD removal were found to be 3.49 g L^{-1}, 240 min, 1.077 and 595.5 ppm for Fe^{2+}, contact time, pH and H_2O_2, respectively. The statistical significance of the ratio of mean square due to regression and mean square due to residual error was tested using analysis of variance (ANOVA). According to the ANOVA (Table 5), the F Statistics values for all regressions were higher. The large value of F indicates that most of the variation in the response can be explained by the regression model equation. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. Thus, the form of the model chosen to explain the relationship between the factors and the response can be concluded to be correct. The P-value = 0.000 for the regression model indicates that the second order polynomial model (Eq. (3)) was

Table 4
Predicted optimum values for maximum COD removal from 3-CP wastewater.

Parameter	Predicted optimum value
Maximum COD removal	80%
X_1 (Fe^{2+})	3.49 g L^{-1}
X_2 (contact time)	240 min
X_3 (pH)	1.077
X_4 (H_2O_2 dose)	595.5 ppm

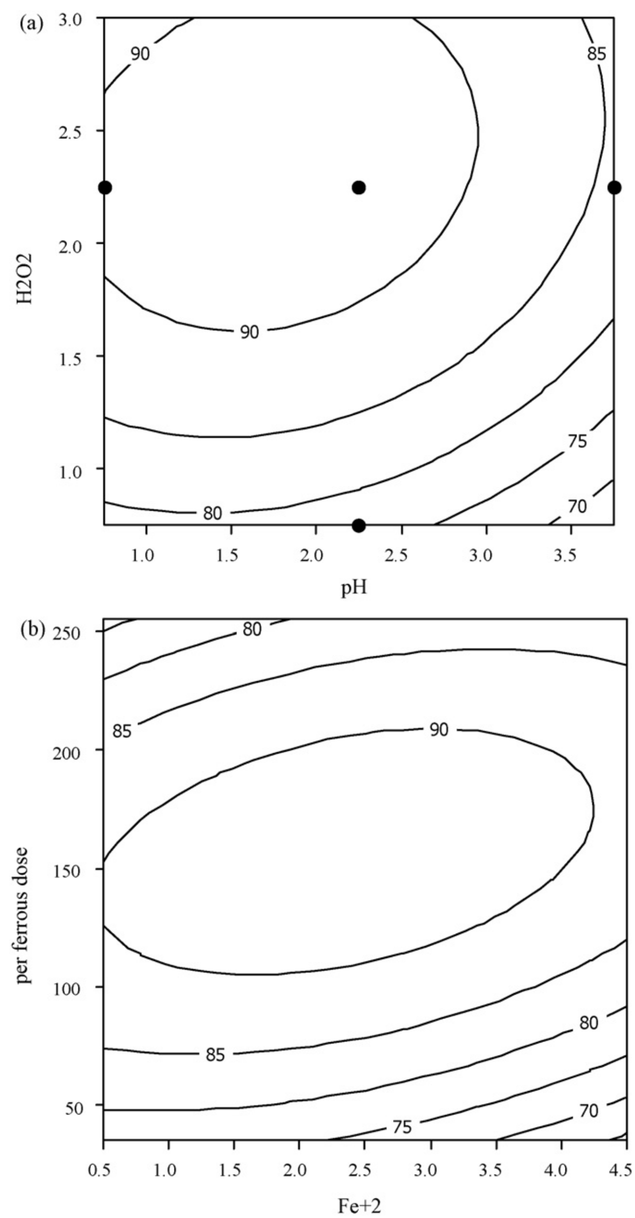

Fig. 4. Contour plots for COD removal in 3-CP wastewater: effect of process parameters. (a) COD removal vs. H_2O_2 dose and pH. (b) COD removal vs. per ferrous dose and Fe^{2+}.

Table 5
Analysis of variance for COD (%).

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	14	1676.16	1676.16	119.726	18.65	0.000
Linear	4	391.88	917.99	229.498	35.75	0.000
Square	4	846.33	828.00	206.999	32.24	0.000
Interaction	6	437.95	437.95	72.992	11.37	0.000
Residual error	32	205.43	205.43	6.420		
Lack-of-fit	9	29.13	29.13	3.237	0.42	0.910
Pure error	23	176.30	176.30	7.665		
Total	46	1881.59				

highly significant and adequate to represent the actual relationship between the response (percent COD removal) and the variables. The response surface plots to estimate COD removal with respect to independent variables is as shown in Fig. 4. These plots were obtained keeping other two variables at constant values obtained during optimization. Similar statistical evaluation was carried out for pyridine wastewater also (data not shown).

4. Conclusion

The wastewaters generated from pyridine and 3-cyanopyridine manufacturing industries are highly complex. The wastewater is not only characterized by the presence of pollutants like pyridine and cyanopyridine, but extremely high COD due to the presence of many organic compounds, high concentration of ammonia and alkaline pH. The BOD:COD ratio is extremely low making it extremely difficult for biological treatment. However, pretreatment options like Fenton oxidation seem to be an attractive and economical option for improving the biodegradability of such complex wastewaters. The reaction time can be as low as 3 h, the dose of chemicals required is also very low in comparison to conventional coagulants and the quantity of sludge generated is also minimal. Further the BOD:COD ratio is improved making mineralization via biological treatment possible. The process has been statistically detailed and optimized using RSM, thereby increasing its efficiency for COD removal. Thus Fenton pretreatment seems to be most feasible and techno-economically attractive pretreatment option for highly complex wastewaters containing pyridine and derivatives

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Appendix A.

Py-ww	pyridine plant wastewater
cp-ww	3-cyanopyridine plant wastewater
RSM	response surface methodology
β-picoline	2 methylpyridine
OD	optical density
AOPs	advanced oxidation processes
SS	sum of squares
Adj SS	adjusted sum of squares
DF	degrees of freedom
Adj MS	adjusted mean sum of squares

References

[1] D.W. Allen, M.R. Clench, J. Morris, Investigation of the products of oxidation of methylpyridines under aqueous conditions by gas chromatography–mass spectrometry, Analyst 119 (1994) 903–907.
[2] S. Fetzner, Bacterial degradation of pyridine, indole, quinoline and their derivatives under different redox conditions, Appl. Microbiol. Biotechnol. 49 (1998) 237–250.
[3] G.K. Sims, E.J.O. Loughlin, Degradation of pyridines in the environment, Crit. Rev. Environ. Control 19 (1989) 309–340.
[4] S.T. Lee, S.K. Rhee, G.M. Lee, Biodegradation of pyridine by freely suspended and immobilized Pimelobacter species, Appl. Microbiol. Biotechnol. 41 (1994) 652–657.
[5] J.E. Rogers, R.G. Rily, S.W. Li, M.L. O' Melley, B.L. Thomas, Microbial transformation of alkyl pyridine in ground water, Water Air Soil Pollut. 24 (1985) 443–454.
[6] E.P. Kuhn, J.M. Suflita, Microbial degradation of nitrogen, oxygen and sulfur heterocyclic compounds under anaerobic conditions: studies with aquifer samples, Environ. Toxicol. Chem. 8 (1989) 1149–1158.
[7] D.H. Stuerner, D.J. Ng, C.J. Morris, Organic contaminants in ground water near an underground coal gassification site in northeastern Wyoming, Environ. Sci. Technol. 16 (1982) 582–587.
[8] J.A. Maya, Pyridines in foods, J. Agric. Food Chem. 25 (1981) 895.
[9] Feasibility studies on treatment of wastewater containing pyridine generated at M/s Jubilant Organosys Limited (JOL), Bhartiyagram, J.P. Nagar, UP, 2004 Technical Report, National Environmental Engineering Research Institute (NEERI).
[10] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.
[11] S.M. Arnold, W.J. Hickey, R.F. Harris, Degradation of atrazine by Fenton's Reagent: condition optimization and product quantification, Environ. Sci. Technol. 29 (1995) 2083–2089.
[12] L.G. Shevchuk, T.A. Boyarskaya, N.A. Vysotskaya, The question of the oxidation of a-hydroxypyridine and nicotinic acid by Fenton's reagent, Chem. Heterocycl. Compd. 5 (1969) 563–564.
[13] M.A. Engwall, J.J. Pignatello, D. Grasso, Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-fenton reaction, Water Res. 33 (1999) 1151–1158.
[14] A. Nedoloujko, J. Kiwi, TiO_2 speciation producing mineralization of 4-tert-butylpyridine accelerated mineralization via Fenton photoassisted reaction, Water Res. (2000) 3277–3284.
[15] S. Yuan, Y. Huang, D. Ren, X. Lu, Degradation of nitrogen-heterocyclic compounds by anodic oxidation and electro-Fenton methods, Water Environ Res. 79 (2007) 759–764.
[16] K.V. Padoley, Treatment of industrial wastewaters containing heterocyclic nitrogenous bases, Ph.D. thesis, Nagpur University, Nagpur, 2003.
[17] K.V. Padoley, A.S. Rajvaidya, T.V. Subbarao, R.A. Pandey, Biodegradation of pyridine in a completely mixed activated sludge process, Bioresour. Technol. 97 (2006) 1225–1236.
[18] American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 20th edition, APHA, AWWA and WEF, Washington, DC, 1998.
[19] I. Talini, G.K. Anderson, Interference of hydrogen peroxide on the standard COD test, Water Res. 26 (1992) 107.
[20] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 35–50.
[21] F. Gozzo, Radical and non radical chemistry of the Fenton like systems in the presence of organic substrates, J. Mol. Catal. A: Chem. 171 (2001) 1–22.
[22] D.F. Bishop, Hydrogen peroxide catalytic oxidation of refractory organics in municipal wastewaters, Ind. Eng. Chem. Process Des. Dev. 7 (1968) 1110–1117.
[23] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.
[24] C.L. Hsueh, Y.H. Huang, C.C. Wang, S. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere 58 (2005) 1409–1414.
[25] W.Z. Tang, C.P. Huang, 2-4 Dichlorophenol oxidation by Fenton's reagent, Environ. Technol. 17 (1996) 1373–1378.
[26] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various oxidation processes and chemical treatment methods for COD and color removal from polyester and acetate fiber dyeing effluent, Chemosphere 55 (2004) 35–43.
[27] S.N. Mudliar, K.V. Padoley, P. Bhatt, R.A. Pandey, M. SureshKumar, S. Lokhande, A.N. Vaidya, Pyridine biodegradation in a novel rotating rope bioreactor, Bioresour. Technol. 99 (2008) 1044–1051.
[28] R.A. Pandey, K.V. Padoley, S.S. Mukherji, S.N. Mudliar, A.N. Vaidya, A.S. Rajvaidya, T.V. Subbarao, Biotreatment of waste gas containing pyridine in a biofilter, Bioresour. Technol. 98 (2007) 2258–2267.

[29] S.K. Rhee, G.M. Lee, J.H. Yoon, Y.H. Park, H.S. Bae, S.T. Lee, Anaerobic and aerobic degradation of pyridine by a newly isolated denitrifying bacterium, Appl. Environ. Microbiol. 63 (1997) 2578–2585.
[30] G.K. Sims, L.E. Sommers, Biodegradation of pyridine derivatives in soil suspensions, Environ. Toxicol. Chem. 5 (1986) 503.
[31] B. Uma, S. Sandhya, Pyridine degradation and heterocyclic nitrification by *Bacillus coagulans*, Can. J. Microbiol. 43 (1997) 595–598.
[32] S. Preis, Y. Terentyeva, A. Rozkov, Photcatalytic oxidation of phenolic compounds in wastewater from oil shale treatment, Water Res. 35 (1997) 165–174.
[33] B. Lodha, S. Chaudhari, Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions, J. Hazard. Mater. 148 (2007) 459–466.