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Novel two stage bio-oxidation and chlorination process for high strength hazardous coal carbonization effluent

Pravin Manekar*, Rima Biswas, Manikavasagam Karthik, Tapas Nandy

Wastewater Technology Division, National Environmental Engineering Research Institute (Council of Scientific & Industrial Research, New Delhi), Nehru Marg, Nagpur 440020, India

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ABSTRACT

Effluent generated from coal carbonization to coke was characterized with high organic content, phenols, ammonium nitrogen, and cyanides. A full scale effluent treatment plant (ETP) working on the principle of single stage carbon–nitrogen bio-oxidation process (SSCNBP) revealed competition between heterotrophic and autotrophic bacteria in the bio-degradation and nitrification process. The effluent was pretreated in a stripper and further combined with other streams to treat in the SSCNBP. Laboratory studies were carried on process and stripped effluents in a bench scale model of ammonia stripper and a two stage bio-oxidation process. The free ammonia removal efficiency of stripper was in the range 70–89%. Bench scale studies of the two stage bio-oxidation process achieved a carbon–nitrogen reduction at 6 days hydraulic retention time (HRT) operating in an extended aeration mode. This paper addresses the studies on selection of a treatment process for removal of organic matter, phenols, cyanide and ammonia nitrogen. The treatment scheme comprising ammonia stripping (pretreatment) followed by the two stage bio-oxidation and chlorination process met the Indian Standards for discharge into Inland Surface Waters. This treatment process package offers a techno-economically viable treatment scheme to neuter hazardous effluent generated from coal carbonization process.

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1. Introduction

Coal is an essential energy source for industrial development, and is pivotal to the growth of Indian economy [1,2]. India is the world's third largest producer of coal with a cumulative production of 431.26 million tonnes for the year 2010 [3]. It produces a wide range of raw materials for basic industries such as fertilizers, coal carbonization, iron and steel plant, nitric acid, soaps, aspirin, solvents, dyes, plastics and fibers. Coal gas is produced through distillation of coal, to generate coke, tar, pitch and other value-added chemicals such as phenol, xylenol, ortho, meta and para cresol in the coal carbonization process. Effluent generated from the coal carbonization process is complex and is characterized with dark brown colour, rich in organic content, phenols, ammonium nitrogen, and cyanide [2,4–8]. Among these phenols contribute to a significant fraction of the chemical oxygen demand (COD) [8].

Heterocyclic and polycyclic aromatic hydrocarbons (PAHs) present in the effluent are hazardous in nature particularly for the aquatic life [6,10–12]. These compounds are also reported to be mutagenic and carcinogenic [13,14] and therefore, it is necessary to remove the pollutants from process effluent to reduce the heath

hazard and negative impacts on the environment [15,16]. Removal of these pollutants from effluent is not achieved in a single stage but requires multiple stage treatment [10]. The effluent from coal carbonization is pretreated through steam stripping process when the ammonia concentration is very high [17]. However, air stripping process has replaced steam stripping where cost effectiveness and simplicity are required.

The conventional post treatment technology for treating the coal carbonization effluents are physico-chemical treatment [18,19] followed by bio-oxidation of carbon and nitrogen. The bio-oxidation process includes single or two stage activated sludge process, sequential batch reactor [20,21], biofilm reactor [22], anaerobic–aerobic (A/O) biofilm [23] and pre-denitrification [24–26]. Some of the industries have tested the possibility of advanced oxidation process such as ozonation [27], wet air oxidation [28], catalytic wet air oxidation [28,29] and microwave radiation for the effluent treatment [30].

In recent times, two-stage C–N bio-oxidation process has gained considerable success, and edge over other treatment process for simplicity in process, design, construction, operation and maintenance (OM) and pollutants removal [31]. In single-stage bio-oxidation process, organic carbon and some of the toxic compounds are oxidized through heterotrophic bacteria. In the second stage, nitrification is achieved through oxidation of ammonia nitrogen in two steps with specific groups of autotrophic bacteria Nitrosomonas and Nitrobacter. Researchers have also reported the

^{*} Corresponding author. Tel.: +91 712 2249763; fax: +91 712 2249900. *E-mail address*: p_manekar@neeri.res.in (P. Manekar).

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Table 1	
Physico-chemical characteristic range of stripped and muster	pit effluents.

Stripped process effluent	Muster pit effluent
8.0-9.1	4.6-8.6
1220-4000	273-1075
24–208	18-106
12,028-22,000	619-5800
10,150-14,500	405-2650
1050-2100	80-520
880–1950	75–357
407-1200	6-230
BDL-235	BDL-88
	Stripped process effluent 8.0–9.1 1220–4000 24–208 12,028–22,000 10,150–14,500 1050–2100 880–1950 407–1200 BDL-235

All values are in mgl⁻¹, except pH. BDL: below detectable limit.

inhibitory effect of phenol and cyanide in nitrification (SSCNBP) [32,33].

The existing wastewater management facility implemented for treating the high strength hazardous coal carbonization effluent comprise ammonia stripper as a pretreatment step followed by SSCNBP. In the SSCNBP, the autotrophic bacteria were observed to be sensitive for the presence of certain chemicals such as phenols, cyanide and high concentration of ammonia. The final treated effluent from the ETP failed to meet the discharge norms of Inland Surface Waters (Table 3). This paper addresses a technoeconomically viable treatment process package for the treatment and management of high strength hazardous coal carbonization effluent. Additionally, it also highlights the design and cost estimation aspect for setting up a full scale effluent treatment facility to render the high strength hazardous effluent.

2. Materials and methods

2.1. Study area

The integrated coal complex plant is a first of its type located in the eastern part of India. It produces smokeless solid, liquid and gaseous fuels through coal carbonization. The production process includes material handling units, retort house, gas producer, gas cleaning and tar distillation unit. The material handling unit handles coal and coke and subsequently supplies to the producer gas unit and retort house. Coal carbonization occurs at 1300 °C generating coal gas and byproducts [34]. The coal gas is purified from residual tar, ammonia, sulfur, napthalene and light oil through gas cleaning. It also produces a series of miscellaneous chemicals such as phenols, cresols, and xylenols which also contribute to value addition of the plant.

2.2. Effluent quantity and quality and treatment

The quantum of process effluent generated from the plant was estimated at $90 \text{ m}^3 \text{ day}^{-1}$. Additionally, effluents were generated from retort house, floor washing, sewage and runoff contribute about $1020 \text{ m}^3 \text{ day}^{-1}$ referred as muster pit effluent. Thus, the total quantity of effluent generated was estimated at $1210 \text{ m}^3 \text{ day}^{-1}$. The process effluent quality was highly organic, toxic and alkaline in nature, where as muster pit effluent was weak compared to the process effluent.

The physico-chemical characteristic range of the stripped and muster pit effluents is presented in Table 1. The hazardous process effluent after ammonia stripping was combined with the muster pit effluent resulting in dilution. The effluent was further treated in the SSCNBP. The sludge from SSCNBP was routed to the sludge drying beds and finally dried sludge was disposed off to a treatment storage and disposal facility (TSDF). The details of the existing ETP are presented in Table 2.

Table 2 Performance of the existing ETP vis-à-vis Inland Surface Waters discharge standard

norms.		
Unit description	Quantity	Dimension ($L \times B \times D$), m
Process effluent tanks	Two	$\begin{array}{c} 15.45 \times 6.65 \times 2.30 + (0.3 FB) \\ 11.10 \times 8.75 \times 1.85 + (0.3 FB) \end{array}$
Master pit tank Equalization tank	One One	$10 \times 5 \times 3.75 + (0.25FB)$ $10.85 \times 6.95 \times 1.0 + (0.23FB)$
Aeration tanks I and II	Two	16.3Dia. × 4.8 + (1.35FB) 16.3Dia. × 4.8 + (1.35FB)
Clarifier Final treated effluent tank Sludge drying beds	One One Two	7.8Dia. \times 2.85 + (0.4FB) 75 \times 20 \times 0.8 + (0.2FB) 12 \times 6.5 \times 0.3 + (0.2FB)

Dia.: diameter; FB: free board.

2.3. Chemicals and laboratory reagents

The laboratory grade chemicals, viz., caustic solution, sodium bicarbonate, phosphoric acid and sodium hypochlorite were used to carry out the studies and were purchased from Merck India Ltd.

2.4. Sampling and analysis of effluents

Twenty-four hour composite samples were collected at each stage of the effluent treatment. The samples were preserved at 4 °C and were analyzed next day for the parameters relevant to the effluent treatment and discharge standards, viz., oil and grease, SS, COD, DO, BOD, phenol, NH⁺₄-N and cyanide. pH was determined in situ by portable pen type meter (with automatic temperature control feature). The parameters like COD and BOD were done by Open Reflux and Winklers Modified method, respectively. Analyses were carried out according to Standard Protocols as referred in the Standard Methods for the Examination of Water and Wastewater [35].

2.5. Performance of ETP

Performance of the ETP under the existing operating conditions was studied with an hourly wastewater sample collection at each stage of treatment and composited for 24 h. Initial assessment, stripper performance as pretreatment was unsatisfactory. Also, equalized flows were not maintained due to variations in the flow rates between stripped and muster pit effluents resulting in shock loading on the SSCNBP. The performance of the existing ETP for effluent discharge vis-à-vis Inland Surface Water discharge standards is presented in Table 3.

The influent to the SSCNBP was low in nutrient ratio BOD:nitrogen:phosphate (BNP) 110:8:0.75 as against a standard protocol of organic and nutrient feeding in the aerobic condition 100:5:1. The equalized effluent was severely deficient in phos-

Table 3

Details of various unit processes of existing ETP.

Parameters	Equalized effluent	Final treated effluent	Discharge standards ^a
рН	6.5-9.1	6.7-8.1	5.5-9.0
Alkalinity	233-1075	10-417	-
SS	26-200	61-140	100
COD	1630-5850	500-900	250
BOD	905-1975	25-230	30
Phenol	180-800	0.5-3	5
NH ₃ -N	220-433	190-400	50
Cyanide	24-210	1-2	0.2
Oil and grease	12-93	4-10	10

 $^{\rm a}$ Indian standards for discharge into Inland Surface Waters; All values are in mg $\rm l^{-1},$ except pH.



Fig. 1. Performance of exiting ETP (SSCNBP).

phate, which became the limiting condition for nitrogen utilization. The DO concentration in the SSCNBP was less than $1 \text{ mg} l^{-1}$ as against the design concentration of $2 \text{ mg} l^{-1}$. The mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) concentrations in the SSCNBP were in the range from 2100 to 2500 and 1452 to 2000 mg l^{-1}, respectively as against 3000 mg l^{-1}.

The microbial analysis of the culture in the aeration tank based on the numbers (Table 4) revealed presence of large number of heterotrophic bacteria (550–650 × 10⁷ CFU/ml) vis-à-vis other bacteria (2–73 × 10⁷ CFU/ml) indicating most favorable conditions for its growth. This resulted in competition between heterotrophic and autotrophic bacteria. The presences of phenolic and cyanide compounds were also inhibiting the growth of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). Thus, results in poor performance of SSCNBP. The final treated effluent concentration for major parameters were in the range SS: 61–140 mgl⁻¹, COD: 500–900 mgl⁻¹, BOD: 25–230 mgl⁻¹, cyanide: 1–2 mgl⁻¹ and NH₄⁺-N: 220–433 mgl⁻¹.

Table 4

Data of microbial sludge in the existing SSCNBP.

Counts (CFU/ml) ^a	Aeration tanks
Total heterotrophic count (HTC)	$550\text{-}650\times10^7$
Total specific count (TSC)	$50-73 \times 10^{7}$
Phenol users	$15-20 \times 10^7$
Cyanide users	$8-12 \times 10^7$
Phenol and cyanide users	$13 - 36 \times 10^{7}$
Ammonia users (nitrifiers)	$5-20 \times 10^7$
Ammonia oxidizing bacteria (AOB) ^b	$2-18 \times 10^7$
Nitrite oxidizing bacteria (NOB) ^b	23×10^5

^a CFU: colony forming unit.

^b Results of most probable numbers (MPN).

The overall performance of the ETP in terms of pollutant removal efficiency was in the range BOD: 75–98%, COD: 63–88%, cyanide: 94–99%, phenols: 95–100% and ammonia: negative–47% (Fig. 1). The performance of the SSCNBP in terms of BOD, cyanide and phenols was good; but failed to meet COD and ammonia reduction. Although, SSCNBP removed a majority of pollutants, stringent regulatory norms have push for higher effluent discharge quality into Inland Surface Waters. Therefore, it was necessary to improve and grow suitable microbial consortia for bio-oxidation of NH₄⁺-N and residual COD to meet the discharge norms.

2.6. Design characteristic for bio-oxidation process

The design pollutant parameters for bio-oxidation were arrived by combining stripped and muster pit effluents in the required flow ratios. The stripped effluent flow was varied against a constant muster pit flow.

2.7. Experimental setup

The experimental setup for ammonia stripping and two stage bio-oxidation process was fabricated in the lab, to carry out the research studies on hazardous coal carbonization effluent. A brief description of the experimental setup is given hereunder:

2.7.1. Ammonia stripper

The lab scale study was carried out on stripper (batch mode) in a packed bed glass column with uniformly packed media (pebbles) to promote a thin feed as a gentle stream. The size of column was 5 cm diameter by 46 cm in height. The column effective height was 31 cm. The laboratory setup of ammonia stripper is shown in Fig. 2. Experiment was initiated with synthetic wastewater at an ambient temperature. The pH of the synthetic wastewater was maintained



Fig. 2. Laboratory setup of ammonia stripper.

at 11.5 using caustic solution. The stripper was fed from the top through a peristaltic pump with the synthetic wastewater and further with process effluent. Counter current air was passed from the bottom of column with a compressor, to facilitate free ammonia transfer from the aqueous to gaseous phase. Compressed air was fed into the stripper at the flow rate of $0.6-1.41s^{-1}$. In all the runs effluent was kept recirculated and the stripping duration was kept for 4 h.

2.7.2. Two stage bio-oxidation process

The two stage bio-oxidation experiments were conducted on the stripped and muster pit effluents in a bench scale laboratory model reactor as presented in Fig. 3. Once a major part of the free NH_4^+ -N removal was achieved through the stripper from the process effluent, the wastewater was neutralized to pH 7.2 by adding dilute phosphoric acid. As the effluent from equalization unit had a high pH (7.5–8.0). The reactor setup consists of a rectangular bio-oxidation vessel and a settling unit provided with a peristaltic pump and diffuser fitted with compressor. The HRT of reactors was maintained by adjusting peristaltic pump (Watson Marlow, make SciQ 323) flow. The compressed air was supplied to maintain the DO concentration 2 mgl⁻¹ in the first and second stage reactors, and to ensure proper contact of substrate with microorganism. The DO was maintained at 30 psi pressure through a compact silent air compressor (Compact 106 FIAC, Italy).

In the first stage, bio-oxidation was initiated with seed obtained from the existing full scale ETP. The seed for second stage biooxidation was obtained from a nitrification unit and enriched with sewage in the laboratory for acclimatization. The first stage bio-oxidation process was fed with proportionate stripped and muster pit effluent at different HRTs, at an extended aeration mode. Whereas, in the second stage bio-oxidation, the pH was maintained at 6.9 using dilute phosphoric acid and sodium bicarbonate as carbon source. The alkalinity to NH₄⁺-N ratio in the second stage bio-oxidation was not less than 5. Maintaining a specific pH in the first and second stage reactors helped in eliminating competition between fast growing phenol oxidizers and slow growing nitrifiers.

3. Results and discussion

3.1. Stripper

The synthetic wastewater was fed in the stripper with ammonia concentration ranging from 800 to $1065 \text{ mg} \text{ l}^{-1}$. The ammonia was oxidized to ammonia gas at pH 11.5 as depicted in Eq. (1).

$$\mathrm{NH_4}^+ \to \mathrm{OH}^- + \mathrm{H_2O} + \mathrm{NH_3} \tag{1}$$

Fig. 4 reveals the free ammonia removal from the synthetic and process effluents. The feed ammonia concentration of synthetic wastewater and air to effluent ratio was kept constant for 5 runs. During these runs, the free ammonia removal was observed to decrease with increase in the feed concentration and air to effluent ratio. A steep drop in free ammonia removal was observed and further it was restored. Free ammonia removal from the synthetic wastewater was in the range between 86% and 94%.

In another set of experiment, the stripper was fed with process effluent with increasing ammonia concentrations ranging from 2000 to 4500 mg l⁻¹ (pH 11.5). Proportionate air to effluent ratio was also increased. Among the 10 runs conducted with process effluent, maximum free ammonia removal efficiency achieved was 89% with the least at 70%. The removal efficiency of ammonia



Fig. 3. Laboratory setup of two stage bio-oxidation process.



Fig. 4. Performance of ammonia removal at different air to effluent ratios.

decreases with increasing ammonia concentration in the process effluent vis-à-vis synthetic wastewater. The difference in the removal efficiency of synthetic and process effluent could be attributed to more impurities present in the process effluent affecting gas transfer from the aqueous phase.

The maximum concentration of NH_4^+ -N 4500 mg l⁻¹ can be treated in the stripper with an optimum air to effluent ratio of 6000 at airflow rate $1.091 s^{-1}$. Maximum ammonia removal through stripping was achieved at $1.11 s^{-1}$ airflow rate (89%) for process effluent. However, researchers have reported achieving maximum free ammonia removal efficiency of 97% at $1.41 s^{-1}$ for the same duration [17]. The fixed ammonia concentration in the stripped effluent ranged between 600 and 1050 mg l⁻¹ and required further treatment.

3.2. First stage bio-oxidation process

Ammonia laden wastewaters prove to be a great challenge for bio-oxidation process even after stripping. Therefore, laboratory studies were carried out in the first stage bio-oxidation process at MLSS concentration 3000 mgl⁻¹ with varying HRTs 24, 48, 72 and 96 h, respectively. The results from this set of experiments are presented in Fig. 5. Capacity of bio-oxidation process depends upon an optimum HRT that yield desired treatment efficiency. A large reactor destroys the economic viability of treatment. Therefore, to ensure cost-effectiveness of the process and desired efficiency yield, selection of an adequate HRT is important.



Fig. 5. Performance of fist stage bio-oxidation process at different HRTs.



Fig. 6. Ammonia removal efficiency at different ammonia loading rates in the second bio-oxidation process.

The removal of major pollutants parameters at HRTs 24 and 48 h was more or less similar and when reactor was operated at HRTs 72 and 96 h the removal of pollutants increased. The optimum removal of major parameters in terms of COD, BOD, phenol and ammonia was obtained at 72 h HRT with MLSS concentration $3000 \text{ mg} \text{ I}^{-1}$. The reported maximum HRT was 58 h [9] for removal of carbonaceous pollutant. The treated effluent concentrations from the first stage bio-oxidation were of the following quality, COD: $\leq 500 \text{ mg} \text{ I}^{-1}$, BOD: $\leq 145 \text{ mg} \text{ I}^{-1}$, cyanide: $\leq 1 \text{ mg} \text{ I}^{-1}$, phenol: $\leq 2 \text{ mg} \text{ I}^{-1}$ and ammonia: $\leq 280 \text{ mg} \text{ I}^{-1}$.

These results were comparatively better than the existing SSC-NBP, although failing to meet the Inland Surface Water discharge Standards. Therefore, further treatment was required to meet the regulatory norms and also to perform consistently well during adverse fed conditions.

3.3. Second stage bio-oxidation process

The treated effluent from the first stage was fed at different loading rates to the second stage bio-oxidation process with MLSS concentration of 3000 mg l⁻¹ and HRT 3 days. The concentration of dissolved oxygen was maintained 2 mg l^{-1} in the second stage for oxidation of ammonia through two consecutive reactions into nitrite and nitrate with the autotrophic ammonia and nitrite oxidizer as depicted in Eqs. (2) and (3).

$$NH_4 + \frac{3}{2}O_2 \xrightarrow{Ammonia \text{ oxidation}} NO_2^- + H_2O + 2H^+$$
(2)

$$NO_2^{-} + \frac{1}{2}O_2^{\text{Nitrite oxidiser}} NO_3^{-}$$
(3)

Fig. 6 shows variation in ammonia loading rate with ammonia removal efficiency. At lower loading rates ($0.0134 \text{ kg m}^{-3} \text{ day}^{-1}$), 90% removal efficiency was obtained. Increasing the ammonia loading rate improved removal efficiency up to a peak of 94%. The peak ammonia removal was obtained at the loading rate of 0.0201 NH₄⁺-N kg m⁻³ day⁻¹ at HRT 3 days with MLSS concentration of 3000 mg l⁻¹ and was considered optimum. Beyond this loading rate, the ammonia removal efficiency dropped.

At low loading rates ammonia removal efficiency was less due to insufficient substrate availability for autotrophic bacteria. The ammonia removal efficiency was enhanced after increasing the loading rates. Increase in removal efficiency was due to the adequate concentration of organic matter and ammonia nitrogen and separation of heterotrophic and autotrophic bacteria that helped autotrophic nitrifying bacteria to transform ammonia to nitrite and nitrate.



Fig. 7. Schematic of proposed ETP for hazardous high strength coal carbonization effluent.

The first stage bio-oxidation resulted in good removal of organic matter, phenols and cyanide through heterotrophic bacteria. Ammonia nitrogen reduction was obtained through autotrophic bacteria in the second stage. Carbon–nitrogen removal was obtained in 6 days HRT (144 h) in the two stage bio-oxidation process, which is quite lower than the 8.33 days HRT (200 h) reported in the study [36] in a three stage treatment process achieving high removal efficiencies for COD, phenols, thiocyanate, total nitrogen and cyanide. The treated effluent concentrations from the second stage bio-oxidation were of the following quality, COD: $\leq 225 \text{ mg l}^{-1}$, BOD: $\leq 18 \text{ mg l}^{-1}$, cyanide: $\leq 0.15 \text{ mg l}^{-1}$, phenol: nil and ammonia: $\leq 12 \text{ mg l}^{-1}$, respectively.

The treated effluent from the nitrification process was further chemically oxidized by sodium hypochlorite. The hypochlorite dosage was varied from 0.1% to 1.0% with a contact time of 1 min and settling of 30 min. The hypochlorite dose of 0.45% was found to be effective in removal of residual COD and colour.

The final treated effluent from the novel two stage bio-oxidation and chlorination process meets the discharge standard for Inland Surface Waters, but can also be reused for coal quenching within the industry. The excess sludge developed from the two stage bio-oxidation process would be pumped to gravity thickener for thickening followed by sludge drying beds. The dried sludge is finally disposed off to the TSDF. The leachate from the bottom of sludge drying beds would be routed to equalization basin for further treatment.

3.4. Design of full scale ETP

The removal of carbon and ammonia nitrogen through biooxidation process has become a matter of great environment concern, because of its toxic effects on the receiving aquatic environment. Operational parameters of the novel two stage bio-oxidation and chlorination process have been optimized and elaborated to design a technically viable treatment scheme for treating the high strength hazardous coal carbonization effluent. The major objectives of the noval two stage bio-oxidation and chlorination process package is to design and implement a full scale ETP, to recycle the treated effluent for coal quenching and to meet the discharge norms for Inland Surface Waters.

The proposed schematic and design concentrations of various unit operations and processes of ETP are presented in Fig. 7. To determine the design concentrations of downstream treatment units, the flow and concentration of the stripped and muster pit effluents were fixed at different ratios based on Eq. (4).

The proportionate flow of process and muster pit effluents required for downstream treatment units were determined keeping muster pit effluent constant (at $1100 \text{ m}^3 \text{ day}^{-1}$) with the following average concentration of parameters, viz., COD: 2400 mgl⁻¹, BOD: 1640 mgl⁻¹, ammonia: 290 mgl⁻¹ and phenol: 300 mgl⁻¹. The stripped effluent flow was varied from 70 to $360 \text{ m}^3 \text{ day}^{-1}$ having the maximum concentration of parameter COD: 22,000 mgl⁻¹, BOD: 14,500 mgl⁻¹, ammonia: 1950 mgl⁻¹ and phenol: 2100 mgl⁻¹. The magnitude of sustainable design concentrations for down stream unit was COD: 5000 mgl⁻¹, BOD: 2600 mgl⁻¹, ammonia: 600 mgl⁻¹ and phenol: 750 mgl⁻¹.

Based on the studies conducted on flow ratio optimization, the profile of the effluents flow ratio vis-à-vis design concentrations of downstream treatment units is presented in Fig. 8. The alone phenol concentration was meeting the design concentration at flow ratio 3.0. At flow ratio 5.7, phenol and ammonia concentrations were satisfied. Other pollutant parameters failed to meet the design concentration, except BOD at flow ratio 6.5. The flow ratio up to 12.0 failed to meet one or other pollutant concentrations. The flow ratio greater than 12.4 meets all the design concentrations of downstream units, but required lesser quantity of stripped effluent. The flow ratio 12.4 of stripped and muster pit effluents was determined



Fig. 8. Profile of the effluent ratio vis-à-vis design concentrations.

to be an optimum for meeting the sustainable design concentration for subsequent treatment.

The optimum flow ratio of 12.4 has the following characteristics, COD: $3864 \text{ mg} \text{l}^{-1}$, BOD: $2600 \text{ mg} \text{l}^{-1}$, ammonia: $481 \text{ mg} \text{l}^{-1}$ and phenol: $435 \text{ mg} \text{l}^{-1}$. The effluent at optimum flow ratio indicated high biodegradability with BOD to COD ratio 0.67. The full scale ETP was design for a flow rate of $1300 \text{ m}^3 \text{ day}^{-1}$. The design and anticipated characteristics at various stages of effluent treatment are presented in Fig. 7 and details of unit operations and processes are presented in Table 5.

The equalization basin volume was determined based on Eq. (5) for efficient operation and to normalize the shock loading on the bio-oxidation process. The full scale two stage bio-oxidation process was design with 6 days total HRT and 3 days at each stage, operating in extended aeration mode. The loading rates for the two stage bio-oxidation were 0.860 and 0.048 kgBOD m⁻³ day⁻¹, respectively. For best operation of the second stage bio-oxidation process, the feed NH₄⁺-N concentration must be less than or equal to 300 mg l⁻¹. Thus, the NH₄⁺-N concentration becomes the limiting factor for the second stage bio-oxidation process. Since, pH affects nitrification in the acidic region [37], a strict pH control was required for the second stage bio-oxidation process.

The oxygen demand (Eqs. (6) and (7)) [38] for the two stage biooxidation process was 6022 and 2000 kgO₂ day⁻¹, respectively. The oxygen demand for the first stage bio-oxidation was 3.0 times the second stage bio-oxidation. The power requirement to meet the oxygen demand (Eq. (8)) [39] was 185 and 85 kW, respectively. The

Table 6

Detail of capital and OM cost for proposed ETP.

Table 5	
Details of	proposed ETP.

Unit description	Quantity	Dimension ($L \times B \times D$), m
Striped effluent collection tank Master pit tank Equalization tank	One One	$\begin{array}{l} 10 \times 5 \times 2 + (0.5 FB) \\ 10 \times 5 \times 3 + (0.5 FB) \\ 10 \times 5 \times 3 + (0.5 FB) \end{array}$
Aeration tank	Two	$\begin{array}{l} 48\times19\times5+(1.35FB)\\ 48\times16.25\times5+(1.35FB)\end{array}$
Clarifier	Two	9Dia. × 3 + (0.5FB) 9Dia. × 3 + (0.5FB)
Collection tank	One	$2 \times 2 \times 1.25 + (0.3FB)$
Gravity thickener	One	4.35Dia. × 3 + (0.5FB)
Chlorination tank	One	2Dia. × 1.5 + (0.3FB)
Treated effluent tank	One	$20 \times 20 \times 3.3 + (0.5FB)$
Sludge collection tank	One	1Dia. × 1.3 + (0.5FB)
Sludge drying beds	Two	$20 \times 13.5 \times 0.3 + (0.2FB)$

Dia.: diameter; FB: free board.

oxygen demand would be met by providing blowers at capacity define above through diffused aeration. An online DO meter will be provided to check the DO concentrations.

$$\frac{Q_1 \times C_1 + Q_2 \times C_2}{C_1 + C_2} \tag{4}$$

where Q_1 and Q_2 are the flow rates (m³ day⁻¹) and C_1 and C_2 are the concentrations of stripped and muster pit effluents (mgl⁻¹).

$$HRT = \frac{V}{Q}$$
(5)

where V is the volume (m^3) and Q is the flow rate $(m^3 day^{-1})$.

$$\frac{Q(S_{\rm o}-S)}{0.53} - 1.42(Y_{\rm obs}Q(S_{\rm o}-S)) \tag{6}$$

where Q is the flow rate $(m^3 day^{-1})$, S₀ is the influent BOD $(mg l^{-1})$, and S is the effluent BOD $(mg l^{-1})$.

$$= 4.57Q(N_0 - N)$$
(7)

where Q is the flow rate ($m^3 day^{-1}$), N_o is the influent NH_4^+ -N ($mg l^{-1}$), and N is the effluent NH_4^+ -N ($mg l^{-1}$).

$$P_{\rm W} = \frac{wRT_{\rm o}}{8.41e} \left[\left(\frac{P}{P_{\rm o}} \right)^{0.283} - 1 \right] \tag{8}$$

where P_w is the power required for blower (kW), *w* is the air mass flow (kg/s), *R* is the gas constant (8.314 kJ/mole K), T_o is the inlet temperature (K), *e* is the efficiency of machine (%), P_o is the absolute inlet pressure (m), and *P* is the absolute outlet pressure (m).

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Particulars	Expenditure		
Capital cost			
Civil	0.55	0.89 million US\$	0.0007 million US\$ m ⁻³
Electrical and Mechanical	0.20		
Piping, laying jointing, value fitting and level indicator, etc.	0.08		
MCC unit, LT and KV cables, including laying in trench, starter and lighting, etc.	0.052		
OM cost			
Chemical	0.284	0.610 million US\$ per annum	\$ 1.32 m ⁻³ wastewater treated
Power	0.278	•	
Manpower	0.035		
Maintenance and repairs			
Civil	0.093		
Mechanical and electrical	0.097		

1 US\$: 44.23 INR.

3.5. Cost estimation

The capital and operation and maintenance (OM) costs play an important role to economically implement and operate the effluent treatment facility for treating the coal carbonization effluent. The cost estimates for the proposed ETP comprises capital and OM costs excluding the cost of stripper and required land. The capital cost includes civil, electrical and mechanical equipments and piping. The OM cost has been arrived based on the expenses incurred on chemical consumption, manpower, energy, labor, maintenance and repairs. The capital and OM costs estimated for the proposed ETP for the flow rate 1300 m³ day⁻¹ are 0.89 million US\$ and 1.32 US\$ per cubic meter of treated wastewater, respectively. The details of capital and OM cost are presented in Table 6. The annualized civil and electrical and mechanical cost estimated are 64,000 and 27,000 US\$, respectively. Thus, the treatment scheme of two stage bio-oxidation and chlorination process is techno economical viable package for rendering the high strength hazardous effluent.

4. Conclusions

Discharges from coal carbonization process are hazardous to the receiving water bodies such as wetlands, lakes, rivers and ocean. The effluent is characterized with high concentrations of organic content, phenols, ammonium nitrogen, cyanides, and is best treated through the novel two stage bio-oxidation and chlorination mechanism. The present study on a two stage bio-oxidation and chlorination process revealed critical interactions and dynamics between engineering parameters and the microbial activity involved in the bio-oxidation of substrate in the effluent. Management of carbon in the first stage and ammonia nitrogen in the second stage helped the respective bacteria to convert the substrate into an environmental acceptable and recyclable form. The treatment process package comprising ammonia stripping (pretreatment) followed by two stage bio-oxidation and chlorination process is the techno-economically viable and effective management scheme for pollution control and meeting the Surface Waters discharge norms.

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References

- M.K. Ghose, S. Roy, Lysimeter test of coal plant effluent disposal to land in India, J. Air Waste Manag. Assoc. 49 (1999) 1245–1249.
- [2] CPCB, Probes, Development of National Emission Standards for Petrochemical Plants, Central Pollution Control Board, Ministry of Environment & Forests, Govt. of India, 2008.
- [3] http://www.worldcoal.org/resources/coal-statistics/ (accessed 17.11.10).
- [4] B.P. Statistical Review of World Energy (site last accessed 16.11.10), http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/ reports_and_publications/statistical_energy_review_2008/STAGING/local_assets/ 2009_downloads/statistical_review_of_world_energy_full_report_2009.pdf, 2009 (accessed 17.11.10).
- [5] Y.M. Li, G.W. Gu, J.F. Zhao, H.Q. Yu, Y.L. Qui, Y.Z. Peng, Treatment of cokeplant wastewater by biofilm systems for removal of organic compounds and nitrogen, Chemosphere 52 (2003) 997–1005.
- [6] I. Vázquez, J. Rodríguez, E. Marañón, L. Castrillón, Y. Fernández, Simultaneous removal of phenol, ammonium and thiocyanate from coke wastewater by aerobic biodegradation, J. Hazard. Mater. B137 (2006) 1773–1780.
- [7] D. Bamelis, Biological purification of coking plant waters, Rev. Metall. (1992) 132-145.

- [8] W. Keith, J. Antil, Biotreatment of coke oven effluent, Steel Time Int. (1991) 26–35.
- [9] E. Maranon, I. Vazquez, J. Rodriguez, L. Castrillón, Y. Fernandez, H. Lopez, Treatment of coke wastewater in sequential batch reactor (SBR) at pilot scale, Bioresour. Technol. 99 (10) (2008) 4192–4198.
- [10] S. Chakraborty, H. Veeramani, Effect of HRT and recycle ratio on removal of cyanide, phenol, thiocyanate and ammonia in an anaerobic–anoxic–aerobic continuous system, Process. Biochem. 41 (2006) 96–105.
- [11] D. Park, Y.M. Kim, D.S. Lee, J.M. Park, Chemical treatment for treating cyanidescontaining effluent from biological cokes wastewater treatment process, Chem. Eng. J. 143 (2008) 141–146.
- [12] Pollution Prevention and Abatement Handbook, World Bank Group, 1998, http://www.ifc.org/ifcext/sustainability.nsf/Content/EHSGuidelines-Integrated steel mills.
- [13] H. Melcer, S. Nutt, I. Marvan, Combined treatment of coke plant wastewater and blast furnace blow down water in a coupled biological fluidized system, J. Water Pollut. Control Fed. 56 (3) (1984) 192–198.
- [14] N.G. Azhar, D.C. Stuckey, The influence of chemical structure on the anaerobic catabolism of refractory compounds: a case study of instant coffee wastes, Water Sci. Technol. 30 (2) (1994) 223–232.
- [15] J.F. Barimo, P.J. Walsh, The effects of acute and chronic ammonia exposure during early life stages of the gulf toadfish, Opspanus beta, Aquat. Toxicol. 75 (3) (2005) 225–237.
- [16] K.R. Lopata, L. Auerswald, P. Cook, Ammonia toxicity and its effect on the growth of the South Africa abalone Haliotis midae Linnaeus, Aquaculture 261 (2) (2006) 678–687.
- [17] X. Quan, F. Wang, Q. Zhao, T. Zhao, J. Xiang, Air stripping of ammonia in a water-sparged aerocyclone reactor, J. Hazard. Mater. 170 (2009) 983–988.
- [18] M.K. Ghose, Complete physicochemical treatment for coke plant effluents, Water Res. 36 (5) (2002) 1127–1134.
- [19] M. Minhalma, M.N. De Pinho, Integration of nanofiltration/steam stripping for the treatment of coke plant ammoniacal wastewaters, J. Membr. Sci. 242 (2004) 87–95.
- [20] R.L. Irvine, A.W. Busch, Sequencing batch biological reactor—an overview, J. Water Pollut. Control Fed. 51 (1979) 235–243.
- [21] P.A. Herzbrun, R.L. Irvine, K.C. Malinowski, Biological treatment of hazardous waste in sequencing batch reactors, J. Water Pollut. Control Fed. 57 (1985) 1163–1167.
- [22] M.R. Morper, Upgrading of activated sludge systems for nitrogen removal by application of the linpor-CN process, Water Sci. Technol. 29 (12) (1994) 167–176.
- [23] Y.U. Zhaoxiang, Q.I. Rong, Y. Yanjun, Treatment of coke plant wastewater by A/O fixed biofilm system, Sci. China Ser. B: Chem. 48 (5) (2005) 489–496.
- [24] M.W. Lee, J.M. Park, Biological nitrogen removal from coke plant wastewater with external carbon addition, Water Environ. Res. 70 (1998) 1090–1095.
- [25] Y.M. Kim, D. Park, C.O. Jeon, D.S. Lee, J.M. Park, Effect of HRT on the biological pre-denitrification process for the simultaneous removal of toxic pollutants from cokes wastewater, Bioresour. Technol. 99 (2008) 8824–8832.
- [26] Y.M. Kim, D. Park, D.S. Lee, K.A. Jung, J.M. Park, Sudden failure of biological nitrogen and carbon removal in the full-scale pre-denitrification process treating cokes wastewater, Bioresour. Technol. 100 (2009) 4340–4347.
- [27] J. Hans, V. Leeuwen, B. Badriya, S. Vaczi, Investigation into ozonation of coal coking processing wastewater for cyanide thiocyanate and organic removal, Ozone Sci. Eng. 25 (2003) 273–283.
- [28] S.K. Bhargava, J. Tardio, J. Prasad, K.I. Foger, K.B. Akolekar, S.C. Grocott, Wet oxidation and catalytic wet oxidation, Ind. Eng. Chem. Res. 45 (2006) 1221–1258.
- [29] M. Yang, Y. Sun, A.H. Xu, L. XY, H.Z. Du, C.Li. Sun, Catalytic wet air oxidation of coke-plant wastewater on ruthenium-based eggshell catalysts in a bubbling bed reactor, Bull Environ. Contam. Toxicol. 79 (2007) 66–70.
- [30] L. Lin, Y. Songhu, C. Jing, X. Zuqun, L. Xiaohua, Removal of ammonia nitrogen in wastewater by microwave radiation, J. Hazard. Mater. 161 (2009) 1063–1068.
- [31] I. Vázquez, J. Rodríguez, E. Marañón, L. Castrillón, Y. Fernández, Study of the aerobic biodegradation of coke wastewater in a two and three-step activated sludge process, J. Hazard. Mater. 137 (2006) 1681–1688.
- [32] N. Shivaraman, P. Kumaran, R.A. Pandey, S.K. Chatterjee, K.R. Chowdhary, N.M. Parhad, Microbial degradation of SCN phenol and CN in a completely mixed aeration system, Environ. Pollut. 39 (1985) 141–150.
- [33] R.A. Pandey, N.M. Parhad, P. Kumaran, Biological treatment of low temperature carbonization wastewater by activated sludge process—a case study, Water Res. 25 (1991) 1555–1564.
- [34] Y. Tüzmen, Effects of coal properties on iron and steel sector, Semin. Coal Technol. Util. (1991) 349–377.
- [35] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, USA, 2005.
- [36] E. Maranon, I. Vazquez, J. Rodriguez, L. Castrillon, Y. Fernandez, Coke wastewater treatment by a three-step activated sludge system, Water Air Soil Pollut. 192 (2008) 155–164.
- [37] J.L. Campos, J.M. Garrido, A. Mosquera-Corral, R. Méndez, Stability of a nitrifying activated sludge reactor, Biochem. Eng. J. 35 (2007) 87–92.
- [38] Metcalf & Eddy Inc., Wastewater Engineering, Treatment and Reuse, III ed., Tata McGraw Hill, New Delhi, 1999.
- [39] S.R. Qasim, Wastewater Treatment Plants: Planning, Design, and Operation, II ed., Technomic Publishing Company, 1999.