Membrane-integrated hybrid bioremediation of industrial wastewater: a continuous treatment and recycling approach

Ramesh Kumar and Parimal Pal

ABSTRACT

A new membrane-integrated hybrid treatment system was investigated to turn highly hazardous coke wastewater reusable. This could protect both air and surface water bodies from toxic contaminants such as ammonia, phenol, cyanide, thiocyanate and other carcinogenic aromatic compounds which are normally released into the environment during discharge of coke wastewater and during quenching of coke by wastewater. Apart from these hazardous substances, oil, grease, other organics and even trace elements could be very effectively removed from wastewater by logical sequencing of chemical, biological and finally nanomembrane-based treatments in an integrated hybrid plant. After almost 99% removal of highly toxic cyanide compounds in a well-optimized Fenton's treatment unit, subsequent biological treatment units could be very effective. All these pretreatments helped achieve microbial nitrification and denitrification of more than 98% of ammonia. Composite nanofiltration membranes selected through investigation could separate ionic trace contaminants from water with a high degree of purification permitting recycling and reuse of the treated water. A selected cross flow membrane module allowed long hours of largely fouling-free operation under a reasonably low transmembrane pressure of only 15 bars while yielding an industrially acceptable flux of 80 L of pure water per hour per square meter of membrane surface.

Key words | biodegradation, hazardous substances, membrane separation, sustainable development, wastewater management, water reclamation

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INTRODUCTION

Coke making units, which are often located within steel making industries or coal-based power plants, generate enormous quantities of wastewater containing quite a number of highly hazardous compounds such as cyanide, phenol, ammonia, thiocyanate and other toxic and pathogenic contaminants represented by high value of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), as analysed by Liu *et al.* (1996). Effective treatment of the organic and inorganic compounds present in coke wastewater has remained a longstanding problem to the industry operators. Failure of the treatment plants often lead to discharge of heavily polluted water into natural water bodies such as river and lakes causing serious

environmental pollution of surface water (Ghose & Roy 1996; Kumar *et al.* 2011). Many coke making industries use hazardous wastewater in quenching hot coke resulting in serious air pollution as carcinogenic aromatics, phenolic compounds, cyanide compounds and ammonia eventually pollute air bodies. The contaminants present in coke wastewater often oppose effective treatment of each other. Considering enormous volumes of coke wastewater, biological treatment is often a low cost option for major contaminants like phenol, ammonia and similar compounds, but the presence of cyanide compounds makes the environment difficult for the survival of microbes and this often leads to failures of such plants (Li & Zhao 2001;

Ghose 2002). Phenol is the organic contaminant which contributes most to the total COD in coke wastewater. Nitrogen compounds (NH_4^+–N, organic bound N and NO_3^-) are other major contaminants in coke wastewater and studies on steam stripping (Minhalma & Pinho 2004), ion-exchange and chemical precipitation (He et al. 2007) have been attempted to reduce ammonia concentration in wastewater. Though several studies have been carried out over the last three decades on chemical, biological and physical treatment for removal of individual contaminants such as phenol, cyanide (CN^-), thiocyanate (SCN^-) and ammonia–nitrogen (NH_4^+–N) from wastewater (Akcil et al. 2003; Roostaei & Tezel 2004; Jeong et al. 2005; Santafe-Moros et al. 2005; Shen et al. 2006; Dash et al. 2008; Justino et al. 2010), studies on an integrated approach for removal of all hazardous substances are very scarce. Some of the methods such as ion-exchange are considered tedious, labour-intensive and expensive and, often, not very effective for large scale treatment. Quite a few studies have reported degradation of cyanide by Fenton's reagents. Pontes et al. (2010) have developed very good kinetic models, also for scale up of phenol degradation by the Fenton method. Ammonia may be removed by a stripping process, but this is often an expensive proposition considering the requirement of chemical feed, stripping tower, pump and liquid spray system, forced air and a carbonization system. In the recent studies of Zhao et al. (2009), Korzenowski et al. (2011) and Kumar et al. (2011), attempts have been made to treat coke wastewater using membranes. Though these studies have indicated the potentiality of membrane use in some stages in reducing individual toxic substances, there is hardly any reported study on a fully membrane-integrated plant that can make highly hazardous wastewater reusable. Moreover, the majority of the reported studies have been conducted with synthetic wastewater whereas the characteristics of real wastewater substantially deviate from such ideal compositions. Thus there is a necessity for developing advanced treatment technology through investigation on real wastewater. If such an advanced treatment option succeeds in treating the wastewater up to the reusable criteria level, then this would lead to two-fold benefits to the water resources in general. On the one hand, hazardous wastewater will be prevented from polluting otherwise clean surface water bodies where wastewater is normally discharged and on the other hand, this will save on fresh water consumption by the same industry. Integration of chemical and biological treatments with membrane separation where each stage can facilitate success of the subsequent stage has the potential of making hazardous coke wastewater reusable. Pressure-driven nanofiltration (NF) followed by microfiltration has the capability of performing finishing or polishing treatment in the integrated advanced treatment scheme. Sen et al. (2010) has shown that NF membranes in appropriate modules can offer a very high degree of purification with reasonably high flux under moderately low transmembrane pressure. Though literature abounds in research on treatment of the major contaminants of coke wastewater, to our knowledge, hardly any integrated approach has been adopted for turning wastewater reusable in a continuous treatment scheme. The majority of the reported studies are on batch mode. Moreover, optimization of chemical treatment using response surface methodology in such cases has not been reported. In the present work, response surface optimized chemical treatment has been integrated with biological and membrane-based treatments leading to a substantial improvement in performance in all the steps. In the absence of such reported studies, the present work intends to fill a major technology gap through integration of chemical, biological and nanomembrane-based treatments with logical sequencing of treatments on real coke wastewater rather than a synthetic one with the purpose of developing a novel scheme of water treatment and reuse that is likely to be sustainable.

THEORETICAL

Chemical treatment

Cyanide oxidation by Fenton's reagent is highly dependent on pH and at high pH cyanide is present as CN^- ions so it reacts easily with H_2O_2 and Fe^{2+} ions, but in acidic conditions, cyanide is present as HCN gas which is very difficult to oxidize. Fenton's treatment has two distinct stages, namely Fenton's oxidation (OH^- generation) and Fenton's coagulation, which is mainly simple ferric coagulation following the oxidation stage and resulting in

sludge. Sarla *et al.* (2004) found that degradation of cyanide using Fenton's reagent follows first-order kinetics.

$$-\frac{d[CN^-]}{dt} = k_{[CN^-]}[CN^-] \tag{1}$$

Bae *et al.* (2004) observed that Fe^{2+} added in the form of $FeSO_4 \cdot 7H_2O$ acts as a catalyst and the peroxide radicals $(OH_2^{\cdot})$ produced are capable of further oxidizing other species including Fe^{2+} present in the reaction medium as below:

$$HO_2^{\cdot} + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^+, \ k = 1.26 \times 10^6 \ M^{-1}S^{-1} \tag{2}$$
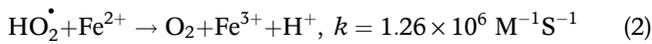
There is a possibility of autoregeneration of Fe^{2+} in this system that may act as a catalyst.

$$Fe^{+3} + H_2O_2 \rightarrow HO^{2\cdot} + Fe^{2+} + H^+ \tag{3}$$
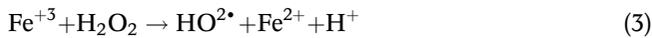
Biological treatment

The degradation kinetics was obtained from the experiments carried out in batches and then making it continuous. The Monod model was selected as the most suitable for this work. In the biological treatment process, the relationship between the rate of growth of microorganisms and the rate of substrate utilization can be expressed by:

$$\frac{dX}{dt} = Y\frac{ds}{dt} - K_d.X \tag{4}$$

where X = microbial concentration; Y = growth coefficient, mass of microorganisms produced per unit mass of substrate utilized; S = concentration of organic food substrate utilized by microorganisms; K_d = microbial decay coefficient, time^{-1}.

Dividing both sides of Equation (4) by X, we obtain:

$$\frac{dX/dt}{X} = Y.\frac{dX/dt}{X} - K_d \tag{5}$$

In the above equation, $(dx/dt)/X$ is the specific growth rate, often represented by μ. The inverse of μ is referred to as the solids retention time or mean cell retention time, θ_c.

$$\theta_c = \frac{X}{\dfrac{dX/dt}{X}} \tag{6}$$

The term $(ds/dt)/s$ is the substrate utilization rate per unit amount of biomass and is called the specific substrate utilization rate. It can be approximated by the following expression:

$$\frac{ds/dt}{X} = \frac{k_s}{k_s + s} \tag{7}$$

where k_s = maximum specific substrate utilization rate, time^{-1}.

Substituting Equations (6) and (7) into (5), we obtain:

$$\frac{1}{\theta_c} = Y\left[\frac{k.s}{k_s + s}\right] - K_d \tag{8}$$

In an activated sludge system, it is assumed that the contents in the aeration tank are completely mixed and that there are no microbial solids in the raw wastewater influent. It is further assumed that the influent substrate concentration, S_0, remains constant and that the system operates under steady state conditions. The solids are wasted from the sludge recycle line, although they may also be wasted from the aeration tank.

For a completely mixed system, Equation (6) can be written in terms of the system parameters. Thus, the solids retention time can be expressed as:

$$\theta_c = \frac{V.X}{[Q_w.X_r + (Q - Q_w)X_e]} \tag{9}$$

An expression for S_e can be obtained by rewriting Equation (8) as:

$$\frac{1}{\theta_c} = Y\left[\frac{k.S_e}{k_s + S_e}\right] - k_d \tag{10}$$

Rearranging this expression, we obtain:

$$S_e = \left[\frac{k_s(1 + \theta_c.k_d)}{\theta_c Y.k - (1 + \theta_c k_d)}\right] \tag{11}$$

The relationship between X and S_e in all tanks can be obtained by first considering a substrate material balance around the tanks. This step gives the amount of substrate utilized per unit time and per unit volume of the aeration tank:

$$\frac{ds}{dt} = \frac{Q(S_o - S_e)}{V} \tag{12}$$

A loading parameter that has been developed over the years is the hydraulic retention time (HRT), q

$$q = \frac{V}{Q} \tag{13}$$

where V = volume of aeration tank, m^3, and Q = sewage inflow, m^3/d; S_o = influent substrate organic matter, pollutants (g/m^3); S_e = effluent substrate organic matter, pollutants (g/m^3).

A similar loading parameter is mean cell residence time or sludge retention time (SRT), q_c,

$$q_c = \frac{V.X}{Q_w.X_r + (Q - Q_w)X_e} \tag{14}$$

Under steady state operation the mass of waste activated sludge is given by:

$$Q_w.X_r = YQ(S_o - S_e) - k_d.V.X \tag{15}$$

where Q = influent flow rate, m^3/d; Q_w = waste sludge flow rate, m^3/d; X_e = concentration of biomass in effluent, g VSS/m^3; X_r = concentration of biomass in the return line from clarifier, g VSS/m^3; Y = maximum yield coefficient.

Membrane separation

NF is a liquid separation membrane technology positioned between reverse osmosis (RO) and ultrafiltration membranes and its performance is predicted in two separate components: the pure water flux and the solute flux are independent from each other; in each of the models the pure water flux can be related to pressure (ΔP). The separation of the solutes from the solution depends on two ways, steric (sieving) and Donnan (electrostatic) (Strathmann

1992) mechanisms, based on whether solutes are charged or uncharged, which can be explained by continuum hydrodynamic models such as that originally proposed by Ferry (1936) and the extended Nernst–Planck model, respectively. In the hydrodynamic models, porous membranes are represented as a bundle of straight cylindrical pores and solute transport is corrected for hindered conversion and diffusion due to solute-membrane interactions. The solvent velocity through the pores of NF membranes may be expressed using the Hagen–Poiseuille equation, as shown in Equation (16) (Bandini & Vezzani 2003).

$$J_w = \frac{r_p^2 \Delta P}{8\mu\delta} \tag{16}$$

where J_w = the pure water permeability; r_p = pore radius; ΔP = the difference in applied pressure across the membrane; δ = the thickness of the membrane; μ = viscosity of fluid. According to Equation (16), increasing the pressure will increase the pure water flux, while the solute flux is proportionally related to the solute concentration gradient across the membrane.

The osmotic pressure difference, $\Delta\pi$, may be calculated using the Van't Hoff equation:

$$\Delta\pi = RT \sum (C_{is} - C_{ip}) \tag{17}$$

where C_{is}, C_{ip} are, respectively, feed and permeate side concentrations of the solute.

Fluxes of permeate and the solute may be computed respectively as:

$$J_v = L_w(\Delta P - \Delta\pi)/\eta \tag{18}$$

$$J_i = VC_{ip} \tag{19}$$

where L_w is pure water permeability determined experimentally.

Solute flux is defined using the extended Nernst–Planck equation as shown in Equation (20):

$$J_i = \left[-D\frac{dc_i}{dx}\right] - \left[D_i z_i c_i \frac{F}{RT}\frac{d\psi}{dx}\right] + [K_i c_i J_v] \tag{20}$$

where J_i = solute flux i; D_i = diffusivity of solute i; c_i = the concentration of solute i at the surface of the membrane; x = mole fraction for solute i; z_i = the valance of solute i; F = Faraday's constant; R = the gas constant; T = temperature; Ψ = the electric potential; K_i = the distribution coefficient of solute i; J_v = the volume flux and can be estimated based on the membrane area.

Three different terms of the Nernst–Planck equation describes a different component of the solute flux. The first term on the right hand side of Equation (20) represents the component of the solute flux that results from solute concentration difference across the membrane. The second term quantifies the flux due to electrostatic forces (as a function of charge gradient) and the last represents the convection of solute i at the surface of the membrane.

Ionic transport through NF membranes has widely been explained by models based on the Donnan equilibrium theory that states the equality of electrochemical potential (Ψ) of the solutions on either side of the solution–membrane interface. Charged molecule transport through NF membranes has been explained by models based on the Donnan equilibrium theory which states the equality of electrochemical potential (Ψ) of the solutions on either side of the solution–membrane interface.

The concentration at the surface of the membrane can be estimated using the Donnan equilibrium as shown in Equation (21):

$$\psi_D = \psi_m - \psi_s \text{ or } c_i = C_i \exp\left[-z_i \frac{F}{RT} \Delta\psi_D\right] \qquad (21)$$

where C_i = the bulk (or feed) concentration of solute i; Donnan potential (Ψ_D) is the difference between the electrical potential of the solution (Ψ_s) and the electrical potential of the membrane (Ψ_m).

The Nernst–Plank equation coupled with the Donnan equilibrium has been shown to accurately predict the rejection of various salts by NF and RO membrane (Afonso et al. 2001; Bandini & Vezzani 2003). Equations (20) and (21) show that solute concentrations at the surface of the membrane determine its passage. If the charge (or electrical potential) of the membrane increases, the concentration of counter ions (ions with the opposite charge) increases. If the ion is neutrally charged, then the concentration at the

membrane surface is unaffected by the charge of the membrane (Afonso et al. 2001; Bandini & Vezzani 2003).

Most of the polyamide composite NF membranes possess negative zeta potential at pH values greater than 7.0 (Schafer et al. 2003). Due to the charged nature of the NF membrane, solutes with an opposite charge compared to the membrane (counter-ions) are attracted, while solutes with a similar charge (co-ions) are repelled. In addition, at the membrane surface, a distribution of co- and counterions will occur, thereby causing more separation.

EXPERIMENTAL

Materials

Reagent grade chemicals were used without further purification. Ammonia and cyanide were procured from Merck (Germany). Methanol and phenol were procured from Sigma–Aldrich and Merck, respectively. All working solutions of different reagent concentrations were prepared using deionized water from Milli-Q (Waters, MA, USA) for calibrating the cyanide and ammonia electrodes and phenyl column. Sodium hydroxide pellets, HCl, ferrous sulphate, hydrogen peroxide and $CaCO_3$ used during the analysis and experiment were purchased from Merck. The set-up was made-up of high grade stainless steel (SS-316) to avoid rusting during long operation. Thin film composite polyamide NF membranes (Sepro Inc., USA) of 165 μm thickness and average pore size of 0.5–1.5 nm (NF1, NF2, NF3, NF20) were used in the flat sheet cross flow membrane module (Table 1) and their basic differences were in membrane surface charge (available as manufacturer's data from Sepro). Polyvinylidene fluoride (PVDF) microfiltration membranes (0.45 μm thickness) were procured from Membrane Solutions (USA). During the experimental investigation in an integrated pilot unit, only real wastewater collected by grab sampling from a coke making industry (Durgapur Projects Limited, India) was used after stabilization.

Methods

The membrane-integrated bioremediation system used for experimental investigations is presented in Figure 1. The

Table 1 | Features of the flat-sheet, polyamide composite NF membranes (Sepro, USA) used

Characteristics	Membranes			
	NF1	NF2	NF3	NF20
Solute rejection, %				
MgSO$_4$:	99.5	97	98	98
NaCl:	90.0	50	60	35
pH	2–11	2–11	2–11	2–11
Max. temp (°C)	50	50	50	50
Max. pressure (bar)	83	83	83	83
Pore radius (nm)	0.53	0.57	0.55	0.54
Thickness (µm)	165	165	165	165

major characteristics of the industrial wastewater as used in the investigations are presented in Table 2 and the final effluent standards in terms of major contaminants are well within emission limit values (ELVs) for wastewater and treated effluent discharged to surface water. Wastewater was recycled after three stages of treatment which included chemical treatment for cyanide, biological treatment for phenol and ammonia and finally a polishing step for the removal of trace elements, mostly in ionic forms by NF membrane. Fenton's reagent (FeSO$_4$·7H$_2$O and H$_2$O$_2$) was used in the chemical treatment unit at a volume of 120 L for removal of cyanide in the first reactor of the series. pH was monitored using a pH probe and was maintained in
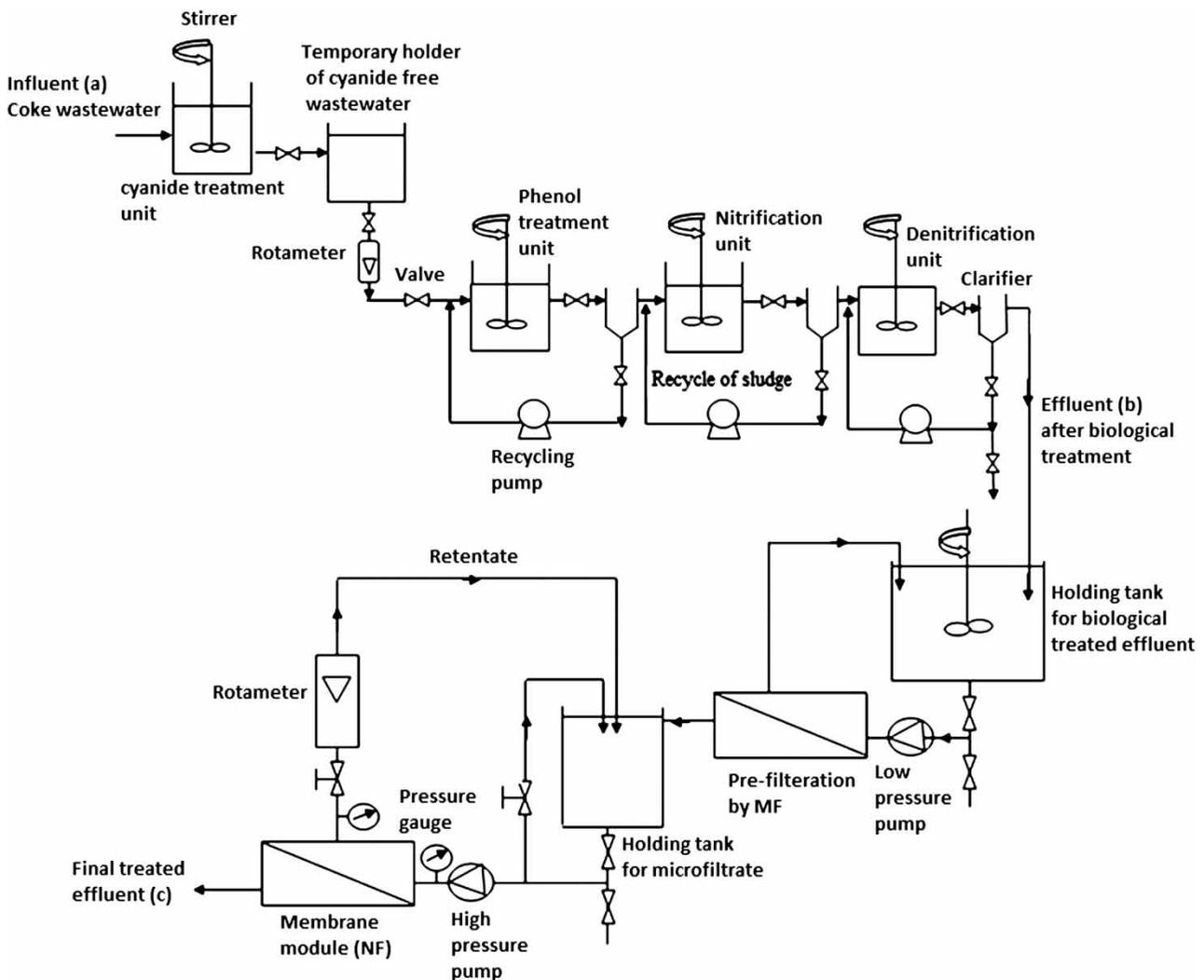

Figure 1 | Flow-sheet of the laboratory unit of membrane integrated hybirid treatment scheme for coke wastewater.

Table 2 | Major characteristics of the water before and after treatment

Parameter	Influent (mg/L)	Effluent 1 after chemical and biological treatment	Effluent 2 after NF (mg/L)	Removal (%)	Permissible limit (mg/L)
Cyandie	121	0.105	ND[a]	100	<0.1
Phenols	159	0.1	ND[a]	100	<0.5
Ammonia-N	2,720	35	15	99.44	<30
COD	1,813	980	11	98.87	<250
TDS	16,470	12,458	880	92.93	–
Conductivity (mS/cm)	14.44	9.25	0.883	92.79	–
BOD	2,445	1,345	6	99.95	<30
Salinity	8.5	5.85	0.2	95.58	–
Oil and grease	51	11.5	ND[a]	100	<10

[a]ND = Non-detectable.

the range of 7.0–8.0 by adding 10 M NaOH or concentrated HCl solution. Clear solution from this unit overflowed to the temporary holding tank with a capacity of 150 L. Microbial treatments were carried out with well-known microbial strains (*Pseudomonas species* (NCIM 2152) for phenol, *Nitrosomonas* (NCIM 5076) and *Nitrobacter* (NCIM 5078) for nitrification and *Pseudomonas aeruginosa* for denitrification) as collected from the National Microbial Collection Center in Pune, India after acclimatization for a sufficiently long time. Continuous experimental investigation was carried out with prior batch studies in a known microbial environment only. Monitoring of microbial growth was conducted following standard methods. Flow of wastewater through the units was maintained by gravity and the attached rotameters indicated flow rates. Recycling was done using centrifugal pumps between the reactors and the settlers. pH was maintained at a range of 7.5–8.5 while temperature was maintained at 30–35 °C by circulating water through the reactor jackets from a thermostatic bath. During nitrification, the food to microorganism ratio (F:M) in the range of 0.10–0.125 kgCOD/(kg MLVSSd) was maintained. The nitrification unit of 70 L capacity was provided with a mechanical stirrer along with an air sparger from a compressor for aeration. Wastewater containing nitrate (1,250–1,300 mg/L) was treated in the denitrification unit containing facultative heterotrophic bacteria *Pseudomonas aeruginosa* (NCIM5032) which reduced nitrate to nitrogen gas at ambient temperature (30–35 °C). Denitrification was carried out with a methanol dosage of 2.4 L/m^3 (equivalent to consumption of 7 mg COD/mg NO_3^--N). Mixed liquor from each biological treatment unit was taken to clarifier units for settling of biomass which was partially recycled back to the respective reactors. The effluent after chemical and biological treatments from the integrated pilot plant was directed to cross the flow microfiltration membrane module followed by a NF membrane module of the same type.

Analytics

Cyanide, ammonia and pH concentrations were determined by Orion 4 Star pH, ISE bench top ion meter (USA) with respective electrodes. The phenol content was determined by high-performance liquid chromatography (Agilent Technologies 1200 series, USA) with Zorbax SB-Phenyl column (Germany) having mobile phase methanol: water (70:30) at a flow rate of 1 mL/min, residence time of 3.567 min and injection volume of 5 μL. After chemical and biological treatments, water was filtered using PVDF microfiltration membranes. Chemical analysis was carried out after this microfiltration for COD and BOD. COD and BOD were measured by COD Vario Tube Test MR (0–1,500 mg/L) of COD analyzer of LoviBond and Oxitop (WTW) kits (Germany) respectively. Total dissolved solids (TDS), conductivity and salinity were measured by InoLab Cond 720, with an electrode TetraCon 325, WTW, Germany. Dissolved oxygen was measured by InoLaboxi 730, with electrode Cellox 325.

Calculations

The influent and effluents were periodically analysed for residual contaminants (i.e. COD) for monitoring performance of the chemical, biological and membrane-based processes. The samples were always kept under refrigeration at 4 °C when immediate analysis could not be done. Nitrate, oil and grease were determined by the cadmium reduction method (4500 NO$_3$E) and partition-Gravimetric Method (5520B) respectively as described in *Standard Methods* of APHA (1998). During NF, the percentage removal of pollutants was calculated using Equation (22) below:

$$\% \text{ removal of COD} = \left(1 - \frac{C_f}{C_i}\right) \times 100 \tag{22}$$

where C_i and C_f were COD in the feed and permeate streams, respectively.

RESULTS AND DISCUSSION

Results of optimization study using design expert software for chemical degradation of cyanide

Experiments were planned and conducted following central composite design (CCD), considering the minimum and maximum levels for hydrogen peroxide (1.50–5.50 g/L), iron salt (1.00–3.75 g/L) and pH (3.0–10.0) and experimental results were incorporated in that design (Table 3). In determining the interrelationships of these variables, a second-order polynomial equation was fitted to the experimental data, and the square root was chosen. From the fit summary section in design, the model *F*-values as obtained for cyanide removal (145.93) implied that models were significant. A value of *P* (0.0001) in this case being less than 0.0500 also indicates that the model terms are significant. The final regression equation made by analysis of variance (ANOVA) shows the empirical relationship among the target variables (cyanide removal) and the three operating conditions or variables and the statistical parameters obtained from the ANOVA for the cyanide removal is listed in Table 4. The equation in terms of coded factors is

Table 3 | Experimental response under suggested operating conditions

STD	Run	H$_2$O$_2$ dose (g/L)	Iron salt dose (g/L)	pH	Response cyanide removal (%)
14	1	3.50	2.38	12.39	36
18	2	3.50	2.38	6.50	99
1	3	1.50	1.00	3.00	7
15	4	3.50	2.38	6.50	99
19	5	3.50	2.38	6.50	99
3	6	5.50	1.00	3.00	26
6	7	1.50	3.75	10.00	59
13	8	3.50	2.38	0.61	4
16	9	3.50	2.38	6.50	99
12	10	6.86	2.38	6.50	100
9	11	3.50	0.06	6.50	28
5	12	1.00	1.50	10.0	18
4	13	5.50	3.75	3.00	51
11	14	0.14	2.38	6.50	33
20	15	3.50	2.38	6.50	99
10	16	3.50	4.69	6.50	100
8	17	5.50	3.75	10.0	98
17	18	3.50	2.38	6.50	99
7	19	5.50	1.00	10.00	83
2	20	1.50	3.75	3.00	35

represented by Equation (23):

$$\begin{aligned}
\text{Sqrt (cyanide removal \%)} &= +9.94 + 1.28 \times H_2O_2 + 1.31 \\
&\times \text{iron salt} + 1.23 \times pH - 0.48 \times H_2O_2 \times \text{iron salt} - 0.14 \\
&\times H_2O_2 \times pH + 0.43 \times \text{iron salt} \times pH - 0.78(H_2O_2)^2 - 0.70 \\
&(\text{iron salt})^2 - 2.07(pH)^2
\end{aligned} \tag{23}$$

It is clear from Equation (23) that the percentage removal of cyanide is linear with respect to H$_2$O$_2$, iron salt and pH and is also quadratic with respect to the same parameters. The quality of the model developed was evaluated based on the correlation coefficient R^2 and standard deviation value. The closer the R^2 value to unity the smaller

Table 4 | Statistical parameters obtained from the ANOVA for the regression models

Response	R^2	Adj. R^2	CV (%)	S.D.	A.P.
Cyanide removal	0.9962	0.9928	3.06	0.23	50.17

A.P., adequate precision; S.D., standard deviation; CV, coefficient of variance.

the standard deviation, the more accurate the response could be predicted by the model. The R^2 value for Equation (23) was found to be 0.9940 which indicated that 99.40% of cyanide removal was attributed to the experimental variables studied. The value of adjusted determination coefficient (adj R^2 for cyanide and removal % = 0.9828) was within reasonable agreement with the predicted R^2 0.9685 (cyanide removal %) and it implies that the model was significant. Effects of H_2O_2, iron salt and pH were highly significant as the P values <0.0001 in both cases. The high significance of the model was also established in the plot of calculated values against the experimental values of cyanide removal % (Figure 2). Clustering of points around the diagonal line indicated capability of the model to predict the experiments in both cases. Figure 3 presents the response surface modelling in a three dimensional representation reflecting the effects of hydrogen peroxide, iron salt and pH on the cyanide removal after 1 h of reaction. As a general trend, it was observed that effects of hydrogen peroxide and iron salt on removal of cyanide was pH-dependent. At low pH, cyanide degradation by hydrogen peroxide and iron salt is very difficult due to the presence of cyanide mainly as HCN gas. At high pH,
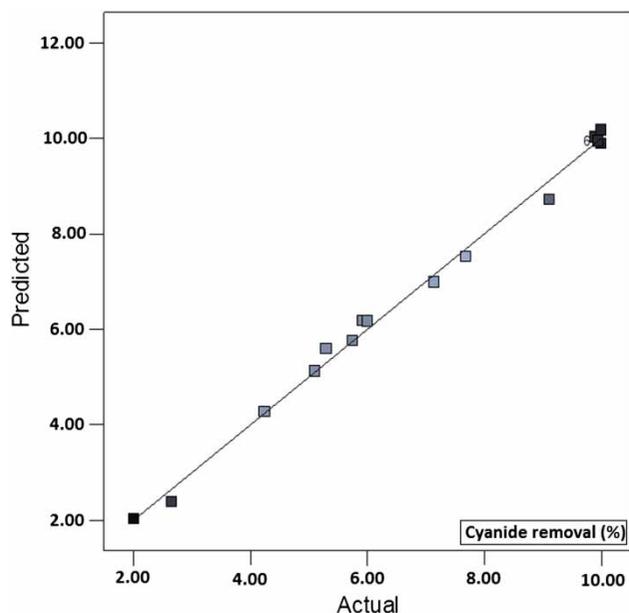

Figure 2 | Distribution of experimentally determined values versus statistically predicted values of cyanide removal (%).
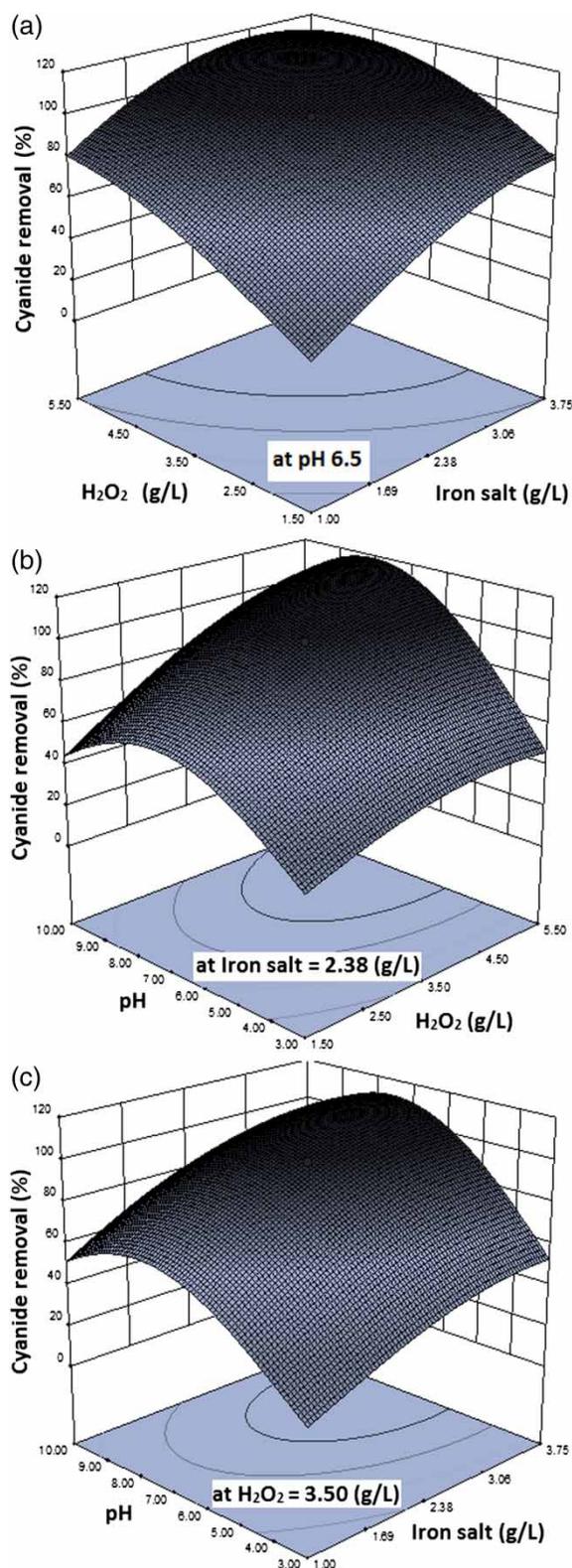

Figure 3 | Response surface plot showing the removal % of cyanide ((a), (b), (c)) with variable parameters pH, iron salt and hydrogen peroxide.

cyanide presents as CN^- ions, so it reacts easily with H_2O_2 and iron salt (Sarla et al. 2004). Using hydrogen peroxide as a powerful oxidizing agent (oxidation potential 1.77 V), cyanide was converted to cyanate and ammonia as intermediate products.

The Fenton's treatment was followed for cyanide degradation uses H_2O_2 and iron salts as basic reagents, where optimization of the concentrations of these reagents and pH is essential for maximum conversion of cyanide with minimum consumption of the chemicals. In the design of the experiments, these aspects were duly considered. Some optimized solutions with different criteria were suggested by the software. From those suggested solutions, one acceptable set of the optimum values of the concentration of the reagents was 5.10 g/L of H_2O_2, 1.52 g/L of iron salt and pH of 7.5 where expected removal of cyanide was 100%. As the selected optimum criteria for variables were not amongst the 20 experiments previously designed by CCD and were rather assumptions, an experiment with selected criteria was performed in a shaker flask and was found that the predicted response was in close agreement with the actual experimental value. The solution was accepted as the complete removal of cyanide with minimum concentration of iron salt which reduced the sludge generation during treatment and avoided iron contamination in the final effluent. Figure 4 shows the result of cyanide
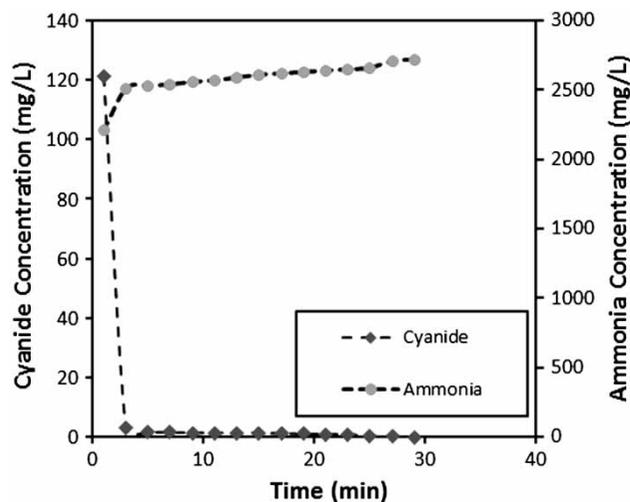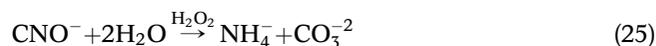
concentration before Fenton's treatment and after treatment with optimized concentration. Cyanide first oxidized to cyanate, which further oxidized to ammonium and carbonate ions as shown following the reactions as shown in Equations (24) and (25) below:

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O \tag{24}$$

$$CNO^- + 2H_2O \xrightarrow{H_2O_2} NH_4^- + CO_3^{-2} \tag{25}$$

Cyanide may also be mineralized to bicarbonate and ammonia following the reaction:

$$CN^- + 2H_2O \xrightarrow{H_2O_2} NH_4^- + HCOO^- \tag{26}$$

Biological degradation of phenol and ammonia

The HRT was optimized for the successful treatment of the phenol and it was found that in 17.5 h, phenol was degraded up to a minimum detection level, as shown in Figure 5.

Phenol was almost completely removed regardless of loading variation and the removal efficiency was always higher than 99%. The influent ammonia concentration was 2,720 mg/L and its removal increased with increasing HRT. After 35 h of retention time, removal almost stabilized. The highest ammonia removal (98.7%) was achieved on operation of the system for 70 h of HRT. The following
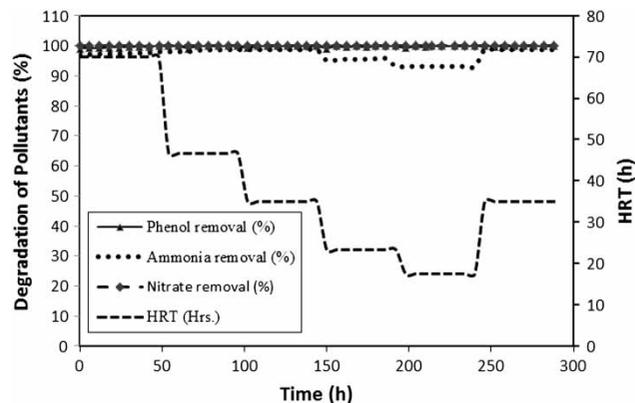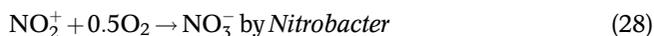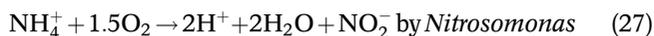
Figure 4 | Cyanide and ammonia concentration profile during chemical pre-treatment. Experimental conditions: influent cyanide concentration 121 mg/L; optimized concentrations of $FeSO_4 \cdot 7H_2O = 1.52$ g/L; $H_2O_2 = 5.1$ g/L; pH = 7.5; temperature: 308 K.

Figure 5 | Phenol, ammonia and nitrate removal efficiencies obtained in the biological treatment of coke wastewater in seperate tank with respective microorganism. Operating condition: influent concentration of phenol = 159 mg/L and ammonia = 2,720 mg/L.

equations describe the nitrification process:

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + 2H_2O + NO_2^- \text{ by } Nitrosomonas \quad (27)$$

$$NO_2^+ + 0.5O_2 \rightarrow NO_3^- \text{ by } Nitrobacter \quad (28)$$

During nitrification, the pH of the medium reduces due to acid produced during nitrification. Hence pH was adjusted by the addition of 5N NaOH. For proper nitrification, the ratio of mass of $CaCO_3$/mass of NH_4^+–N is very important. Alkalinity in the nitrification process was maintained at around 150–200 mg/L of the medium by adding $CaCO_3$ at rate of 5 g/L to achieve adequate buffering, as shown by the following equation:

$$H_2O + CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3 + 2H^+ \quad (29)$$

The initial concentration of nitrate in the nitrification was found to be 1,254 mg/L due to conversion of ammonia to nitrate by two subsequent biological reactions. Nitrate was reduced to free nitrogen in the denitrification unit which was carried out as the last step at a methanol dosage of 2.4 L/m^3 (equivalent to a consumption of 7 mg COD/mg NO_3^-–N) as external organic or inorganic carbon sources are necessary for stable operation of the denitrification unit. By maintaining almost an anoxic condition (0.5 mg/L dissolved oxygen), nitrate was completely converted to free nitrogen at a minimum HRT of 17.5 h.

Nanofiltration of biologically treated coke wastewater

Four different types of polyamide NF membranes (NF1, NF2, NF3 and NF20) were investigated to find out the best possible one in the present treatment. Effects of transmembrane pressure and cross flow velocity on flux as well as on removal of COD, BOD, TDS, salinity and conductivity were studied. Microfiltration with 0.45 μm PVDF membrane in cross flow membrane module was done prior to NF. Suspended solids and microbes were found to be largely screened out during microfiltration paving the way for better NF under a more conducive environment that permitted long hours of largely fouling-free NF.

Effect of cross flow rate and pressure on flux

When pressure was increased from 5 to 15 bars flux at a volumetric cross flow of 750 L/h (L/H), flux through NF2 membrane increased from 158 to 260 L/m^2 h (LMH). A similar tendency of increase of flux with increase of cross flow rate was also shown by other membranes. The highest flux was exhibited by NF2, due to its loosest type, i.e. highest porosity among the four investigated membranes, followed by NF3, NF20 and NF1, respectively. Whereas NF1 was found to be the tightest, meaning the lowest porosity among four types, so flux was the lowest. Adequate crossflow and transmembrane pressure help reduce membrane fouling, optimization of membrane area requirement and maximization of removal of the hazardous compounds.

Effect of transmembrane pressure on the rejection of COD and BOD

Four different types of NF membranes were investigated at different pressures to select the best possible membrane and the optimum operating pressure in removing COD loading, as shown in Figure 6. The first stage of treatment of coke wastewater could remove 45 and 46% of influent BOD and COD, respectively. In all the four membranes, rejection of BOD and COD increased with an increase of applied pressure. NF1 membrane with a flux of 79–80 LMH was
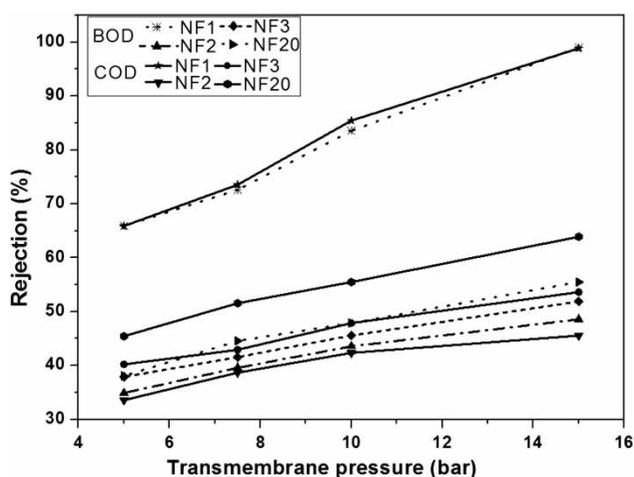

Figure 6 | BOD and COD removal performance by different NF membranes with varying pressure. Experimental conditions: cross flow rate = 750 LPH; pressure = 5–15 bars; pH = 7.6 and at temperature = 308 K.

the best performing membrane in terms of COD reduction (99%) as well as BOD reduction (98%) at a pressure of 15 bars and cross flow rate of 750 L/h. COD and BOD were used to measure the oxygen equivalence of the organic matter content of a sample. When negatively charged organic matter ions come in contact with the negatively charged membrane surface of NF1 membrane, charge repulsion occurs and this culminates in rejection of the organic matters.

Effect of nanofiltration (NF1) on TDS, salinity and conductivity

The NF membrane was very efficient in the removal of TDS, salinity and conductivity more than 90%. All inorganic and organic substances contained in the coke wastewater had created TDS. Microfiltration ($0.45\,\mu m$) of the effluent of chemically and biologically treated wastewater could remove only 24.3% leaving 12,458 mg/L TDS. The charged inorganic and organic molecules were removed by negatively charged NF1 membrane up to 93% due to repulsion and sieving mechanism. A high salinity present in the water and soil would negatively affect the crop yields, degrade the land and pollute groundwater. NF1 removed the salinity by 95–96% at a pressure of 15 bars and cross flow rate of 750 LMH. During chemical and microbial treatment, chemicals and microbes decomposed into ions and also microbial metabolism generated lots of ions which increased the conductivity. In aerobic treatment, oxygen was consumed and CO_2 was released which was subsequently converted into carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^-) decreasing the pH and increasing the conductivity. These charged ions were removed by the charged NF1 membranes up to 93%.

ECONOMIC EVALUATION OF THE TREATMENT SCHEME

Economic evaluation of the treatment scheme was carried out considering the standard size of the plant from which wastewater was used for carrying out the present experimental investigations. Thus for treatment of around $20\,m^3$ wastewater/h, the total annualized cost (investment +

operating cost) was estimated to be around $0.46\,\$/m^3$, which indicates economic viability of such a treatment scheme.

CONCLUSIONS

A sustainable wastewater management strategy was evolved for the coke making industry. The strategy involved the reuse of coke wastewater by integration of chemical and biological treatments with membrane filtration. From experimental investigations on real coke wastewater from a plant, the following conclusions were drawn.

1. Due to the complex nature of the contaminants of coke wastewater, success of the biological treatment steps very much depends on prior chemical treatment of the toxic cyanide compounds.
2. Optimization of the chemical process coupled with logical sequencing of the operations can turn both chemical treatment and subsequent biological treatment in activated sludge processes very effective in reducing the concentration of hazardous substances of coke wastewater.
3. Downstream nitrification and denitrification units could effectively convert 98% ammoniacal nitrogen into elemental nitrogen from the pre-treated water.
4. The use of well-investigated micro and composite NF membranes in the particular flat sheet cross flow membrane module has the potential of offering long hours of fouling-free operation without the need for frequent cleaning or replacement of membranes. The membrane-integrated treatment scheme purifies water to a level that permits its recycling in the same industry. Such a scheme not only saves on fresh water consumption by a highly water-demanding industry but also protects surface water from contamination by discharge of heavily polluted coke wastewater.

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