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Electrocoagulation process to remove contaminants of coking wastewater using aluminum electrode

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ABSTRACT

The removal of phenol, cyanide, ammonia–N and chemical oxygen demand (COD) from coking wastewater was carried out by electrocoagulation process (ECP) in batch mode using an aluminum electrode. Various operating parameters such as pH, current density (CD), electrolyte concentration and electrode gap (EG) that potentially affect the removal efficiency of pollutants were investigated. The optimum pH, CD, electrolyte concentration and EG were found to be 10.5, 37.2 A/m^2, 100 mg/dm^3 and 17.5 mm, respectively. Cyanide, ammonia–N, COD and phenol removal at optimum condition were found to be 82.7%, 52.1%, 91% and 36%, respectively, which indicates that ECP is a promising technology for the removal of these species. Statistical analysis using analysis of variance showed a high coefficient of determination values for COD removal (R^2 = 0.9967) between the experimental values and predicted values by a second-order regression model.

Keywords: Chemical oxygen demand; Electrochemical treatment; Aluminum electrode; Coking wastewater; Phenol; Cyanide; Ammonia–N

1. Introduction

Generation of coking wastewater (CWW) from steel manufacturing industry is a severe problem all over the world. In the world, more than 3,000 coke-oven plants are in operations which produce coke from coal. In these coke-ovens, about 350 million tons of coke are produced, out of which ≈12 million tons are produced in India [1]. Around 4 m^3 freshwater required for production of 1 ton of coal and finally generates about 1 m^3 of CWW, which is composed of complex inorganic and organic contaminants such as ammonia–N, cyanide, thiocyanide, phenolic compound, polynuclear aromatic hydrocarbons (PAHs), polycyclic nitrogen containing aromatics, and oxygen and sulfur containing heterocyclic compounds [2,3]. Most of these compounds are refractory, highly concentrated toxic, mutative and carcinogenic and produce long-term environmental and ecological impacts [4]. Therefore, to bring CWW to recycle or dischargeable limit, efficient and low cost processes are needed for its treatment. The widely used process in coking industries to treat CWW is coagulation followed by biological treatment. In biological treatment selective and efficient micro-organisms are needed to consume highly refractory and inhibitory organic compounds present in high concentration in CWW. This process is not efficient enough to meet the requirement of effluent discharge standard prescribed by central pollution control board (CPCB), India. Many processes have been reported as the advance treatment of CWW. Ozonation of CWW was performed to reduce its contaminant. Significant reduction of SCN and phenol removal was observed, while, CN and of total organic carbon removal was poor [5]. An adsorptive treatment was

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performed using activated carbon. In this process, chemical oxygen demand (COD) and color removal was good but adsorbent dose was high [6]. Anaerobic–anoxic–aerobic membrane bioreactor was also tested for treatment of CWW. In this process up to 90% COD removal and more than 98% phenol and ammonia–N removal achieved in 40 h hydraulic retention time [7]. Coagulation and zero valent iron process applied to treat CWW was found to be not much effective as it gave <50% COD removal [8]. Utilization of heat as vacuum distillation was also tested to remove COD and ammonia–N of CWW. It was found to an effective process for removal of COD, but did not found suitable for large-scale treatment [9]. Recently, electro coagulation (EC) and chemical oxidation using iron as electrode material and H_2O_2 as oxidant for treatment of CWW has been reported [10]. However, detailed study using aluminum has not been reported in electrocoagulation/electrochemical process to treat CWW. Therefore, in the study, the removal of phenol, cyanide, ammonia–N and COD from CWW was carried out by EC process using an aluminum electrode in batch mode and the effect of various operating parameters such as pH, current density (CD), electrolyte concentration and electrode gap (EG) have been investigated.

Table 1
Analysis of treated and untreated CWW

Parameters	CWW	pH 9.5	pH 10.5	pH 11.5
COD	10,100	1,010	909	1,353
TDS	645	37.5	350	360
TSS	20	6.5	5	8
TS	66.5	263.5	355	368
Ammonia–N	110.6	56.2	53	46.01
Phenol	363	259	232	265
CN^-	11.6	3.35	2.0	2.08
Chloride (Cl^-)	4,830	–	2,250	–
Phosphate (PO_4^{2-})	27	–	10	–
Total hardness	225	–	200	–
Color	Blackish brown	Light yellow	Light yellow	Light yellow
Absorbance at 475 nm	1,720	270	340	360
% Color removal	–	84.30%	80.23%	79%
pH	9.5		10.14	11.43

All the values except pH and color is mg/dm^3.

2. Materials and methods

2.1. Wastewater and material

The CWW was obtained from coke-oven plant of Bhilai Steel Plant, Chhattisgarh, India. Laboratory and analytical grade chemicals (Merck Limited, India and Germany) were used in experiments and for analysis of different parameters of CWW. COD, phenol, ammonia–N and cyanide were determined by standard methods (APHA) [11]. COD was determined by close reflux method. Wastewater samples were digested in COD digester (Merck made, Germany) at 140°C for 2 h, and thereafter absorbance was measured using a UV spectrophotometer (Shimadzu, Japan) at 620 nm. The absorbance value was multiplied by 2,248, which gave COD in mg/dm^3. Phenol was determined by direct photometric method. Cyanide and ammonia were determined using selective electrode method (Orion made, Korea). The electrodes were calibrated to measure cyanide in range of 0.1–1.0 mg/dm^3 and ammonia–N in range of 12.2–20 mg/dm^3. The concentrated samples were diluted from deionized water. Electrodes were able to measurement up to three decimals. Chloride was determined by titrimetric Vohlard method [12]. Phosphate was determined by spectrometric method [11]. Sulfate was determined by precipitation method using $BaCl_2$ [11]. Al metal sheet, procured from local market was used as electrode. The composition of CWW before and after treatment is shown in Table 1.

Pyrex glass made electrochemical reactor (ECR), fabricated in the workshop of Bhilai Steel Plant, having a volume of 2.5 dm^3 and a dimension of L × W × H = 120 mm × 120 mm × 160 mm was used in the present study (Fig. 1). A magnetic stirrer with agitation speed 200 rpm was used to agitate the solution. Four aluminum electrode plates (two anodes and two cathodes) were used in the experiment. Electrodes were dipped in CWW to a depth of 8.5 cm with each electrode positioned 12.5–22.5 mm apart. The effective area of each electrode was 0.68 dm^2. The assembly was connected to direct current power source (5 A × 20 V) to constitute an electrocoagulation cell in a galvanic static mode for constant current supply. The electrode and reactor configuration is shown in Table 2.

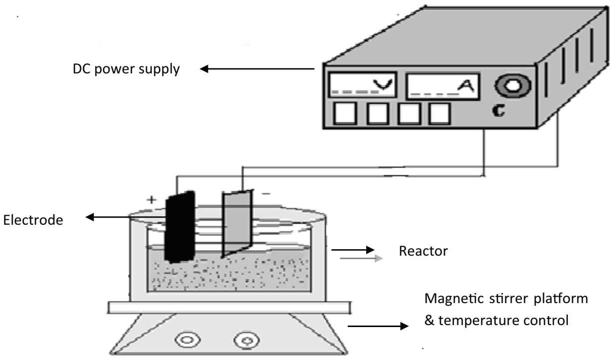


Fig. 1. Experimental setup of the electrochemical process.

2.2. Procedure and analysis

Before each experiment, electrodes were abraded with cotton cloth to remove scales and cleaned with tap water. During each test run, 2 dm^3 of CWW was placed in the reactor. The magnetic stirrer stirred the wastewater at a speed of 200 ppm. The stirrer speed was found to be sufficient for providing good mixing in the electrolytic cell and yet was sufficiently low, not to disrupt the flocks formed during the treatment process. A fixed amount of NaCl in range of 100–200 mg/dm^3 was added to the CWW to increase its conductivity and thus facilitate the EC treatment. The DC power source was operated with constant CD of 18.6–92.5 A/m^2. Each EC test run lasted 100 min. In between after certain interval of time, about 7 mL samples were taken from ECR and analyzed for various parameters like COD. Concentration of phenol, cyanide, ammonia–N and COD was also measured at the end of experiments. Some EC experiments and analysis of

Table 2
Electrode and reactor configuration

Reactor		Electrode	
Make	Pyrex glass	Material (anode and cathode)	Aluminum
Dimensions (L × W × H) (mm)	(120 × 120 × 160)	Shape	Rectangular plate
Volume (dm^3)	2.5	Size of each plate (mm) (W × H)	80 × 100
Electrode gap (mm)	12.5, 17.5, 22.5	Thickness (mm)	3
Type	Up flow	Area (dm^2)	0.80
Mode of operation	Batch	Plate arrangement	Parallel
Stirring mechanism (L × D), (mm)	Magnetic bar (25 × 10)	Submergence area (dm^2)	0.68

Table 3
Concentration of COD, phenol, cyanide and ammonia–N after 100 min treatment at CD 37.2 A/m^2 and different pH as well as different CD (initial COD = 10,100 mg/dm^3, phenol = 363 mg/dm^3, cyanide = 11.6 mg/dm^3, ammonia–N = 110.6 mg/dm^3)

Parameters CD 37.2 A/m^2	pH →	4.5	7.5	9.5	10.5	11.5	12.5
COD	Final concentration	1,464.5	1,914.96	1,010	909	1,353.4	8,888
	% Reduction	85.5	81.04	90	91	86.6	12
Phenol	Final concentration	273.42	264.6	259.5	232.32	264.72	326.7
	% Reduction	23.3	27.1	28.5	36	26.8	10
Cyanide	Final concentration	5.858	5.858	3.35	2.0	2.08	11.13
	% Reduction	49.5	49.5	71.15	82.7	82	4
Ammonia–N	Final concentration	74.39	59.35	56.2	52.98	46.01	97.328
	% Reduction	32.2	45.8	49.2	52.1	58.4	12
Parameters pH 10.5	CD → A/m^2	18.6	37.2	55.8	74.32	92.9	
COD	Final concentration	2,696.7	909	1,111	1,131.2	1,565.5	
	% Reduction	73.3	91	89	88.8	84.5	
Phenol	Final concentration	274.79	232.32	176.05	185.13	192.39	
	% Reduction	24.3	36	51.5	49	47	
Cyanide	Final concentration	7.54	2.0	1.97	1.93	1.99	
	% Reduction	35	82.7	83.1	83.4	82.9	
Ammonia–N	Final concentration	60.6	53	50	48.98	47.56	
	% Reduction	45.2	52.1	54.8	55.72	57	

pollutants were repeated to find its consistency if any deviation in results were found. Maximum errors in COD, phenol, CN^- and ammonia–N estimation were found to be 3%, 2%, 4% and 2%, respectively, which are presented in error bar at figures. Removal efficiency after EC treatment was calculated using the following equation:

$$R\% = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 is the initial (phenol, cyanide, ammonia or COD) concentration (mg/dm^3) and C_t is the concentration after time t (mg/dm^3).

3. Results and discussion

3.1. Effect of pH on removal of pollutants

pH has been found to be a significant factor which affects the treatment of various effluents. Effect of initial pH (pH$_i$) in the range of 4.5–12.5 was studied on removal of phenol, cyanide, ammonia–N and COD at constant CD = 37.2 A/m^2, electrolyte NaCl concentration = 100 mg/dm^3 and EG = 17.5 mm.

3.1.1. COD removal

COD removal data at different pH is presented in Table 3 and in Fig. 2(a). COD removal was fast during initial stages and stabilized with time. In treatment time (t_R) of 20 min and at pH 4.5, 7.5, 9.5, 10.5, 11.5 and 12.5 respectively, COD removal was 81%, 77.2%, 84.4%, 85.5%, 83.3% and 9%, which was increased to 83.4%, 80.7%, 88.08%, 88.8%, 84.4% and 11% in t_R = 60 min. Further increase in t_R = 100 min, COD removal efficiencies reached to 85.5%, 81.04%, 90%, 91%, 86.6% and 12% at respective pH. These observations show that removal efficiency of COD is in order of pH 10.5 > 9.5 > 11.5 > 4.5 > 7.5 > 12.5. It has been reported that initially Al^{3+} ion form in solution due to electrical dissociation. The Al^{3+} further changes into monomeric and polymeric species like $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, $Al_2(OH)_2^{4+}$, $Al(OH)_5^{2+}$,

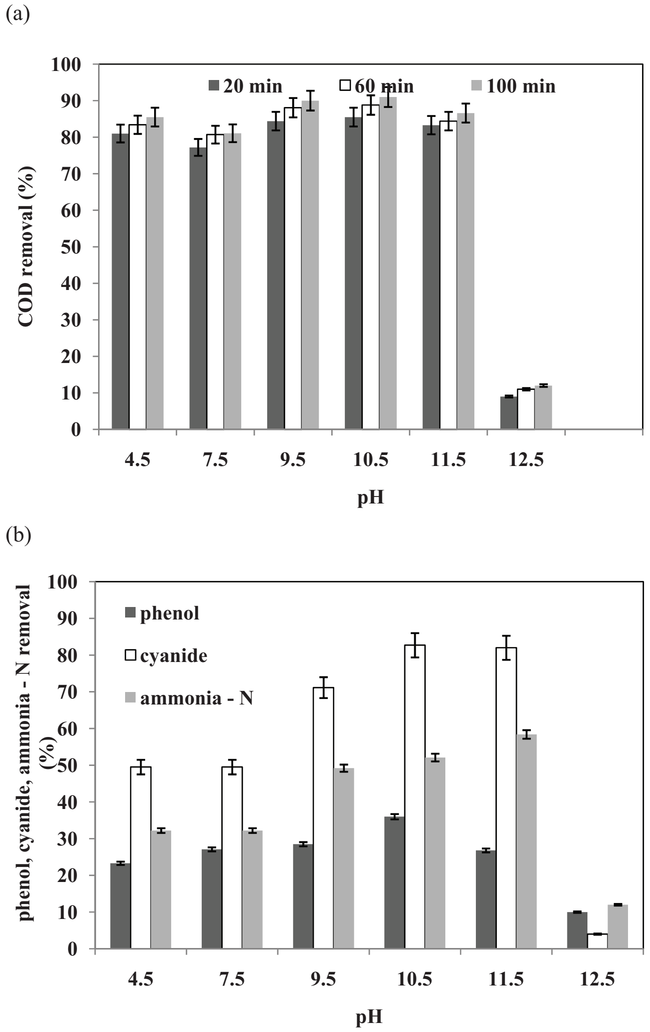
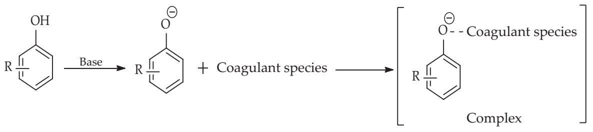


Fig. 2. Effect of pH on (a) removal of COD in 20, 60 and 100 min. (b) removal of phenol, cyanide and ammonia–N after 100 min. CD = 37.2 A/m², NaCl = 100 mg/dm³, COD_i = 9,000 mg/dm³, $phenol_i$ = 363 mg/dm³, $cyanide_i$ = 11.6 mg/dm³, ammonia–N_i = 110.6 mg/dm³.

$[Al_6(OH)_{15}]^{3+}$, $[Al_7(OH)_{17}]^{4+}$, $[Al_8(OH)_{20}]^{4+}$, $[Al_{13}(OH)_{34}]^{5+}$, etc. Formation of these species depends on pH of solution [13,14]. Charges of functional groups of various species that are present in the effluent also vary with pH. At moderate acidic to moderate basic pH (pH 4–11.5) formation of polymeric metal hydroxide cations are expected. As compare with monomeric and metal cations, the polymeric metal hydroxide cations are proved to better coagulant species, due to this, COD reductions are comparatively better in pH range 4.5–11.5. Various species like phenolic compounds, polynuclear aromatic hydrocarbons (PAHs), polycyclic nitrogen containing aromatic compounds, CN^-, ammonia–N, etc., are present in CWW [15]. Color forming agent melonoidin and colloids are also contained in CWW, which have net negative charge. The positively charged metal cations and metal hydroxide cations take part in reaction and consequently removal of pollutants by mechanism of charge neutralization and complex formation take place. Pollutants also get enmeshed in the amorphous complex. The heavy mass of flocs settled down, which also remove pollutants by sweeping. Due to this, high COD removal was obtained at pH 9.5 and 10.5. At highly basic condition it is expected to form $Al(OH)_3$ and $Al(OH)_4^-$. Neutral metal hydroxides and negatively charged metal hydroxides are poor coagulant species, which caused the low COD reduction at pH 12.5 [16,17]. Coagulation process to treat CWW has been reported, in which 32% COD removal was obtained by using 400 mg/dm³ $FeCl_3$ coagulant [8]. Recently, Ozyonar and Karagozoglu [10] performed EC of ammonia pretreated CWW. They were able to reduce only 26% COD at pH 9 by using Al electrode.

3.1.2. Phenol, cyanide and ammonia–N removal

Phenol, cyanide and ammonia–N removal at different pH was estimated and data are presented in Fig. 2(b). The phenol removal was 23.3%, 27.1%, 28.5%, 36%, 26.8% and 10% at pH 4.5, 7.5, 9.5, 10.5, 11.5 and 12.5, respectively. These data show that phenol removal is comparatively more in pH range of 7.5–10.5. Phenol removal mainly takes place by its enmeshment in aluminum hydroxide flocs and by sweeping process. Nature of flocs varies with pH, thus, its removal also varied with pH. Phenol exhibits a neutral species at acidic condition and negatively charged phenoxide ions at basic condition, but phenoxide ions formation varied with various substituted phenols. Seventeen types of phenolic compounds have been identified in CWW analysis [6]. Presence of electron withdrawing groups/substituent favors the formation of phenoxide ions and electron denoting substituent does not favor it. Low % removal of phenol (maximum 35.6%) may be due to the presence of electron denoting substitutes in phenol. Phenol removal in EC at basic condition can be represented as follows:



(2)

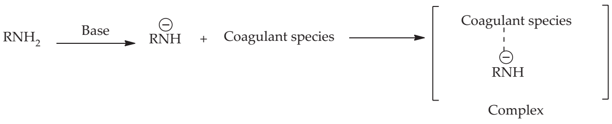
Flocks nature and coagulants species also varies with pH, thus, its removal also varied with pH. At pH 12.5, low % removal of phenol (10%) may be due to the formation of neutral and negatively charged metal hydroxides. In EC process using iron electrode only 16% phenol removal was observed [10].

Cyanide removal at different pH is shown in Table 3 and Fig. 2(b). The removal was found more in neutral and low alkaline pHs as compare with other pH. Cyanide removal increased with an increase in pH up to 10.5 then decreased at pH 11.5 and 12.5. Its removal was 49.5%, 49.5%, 71.15% and 82.7% at pH 4.5, 7.5, 9.5 and 10.5, respectively, which decreased to values 82% and 4% at pH 11.5 and 12.5. Results are better than the maximum 35% cyanide removal and 13% phenol removal at pH 9 reported during simultaneous removal of phenol, chromium and cyanide by coagulation using $FeCl_3$ [18]. In electrocoagulation of CWW, 9% phenol and 9.2% cyanide removal has also been reported [10]. Cyanide is negatively charged species, which is adsorbed in metal hydroxide flocs and neutralized. The neutralized flocs form insoluble heavy mass which settles down. Cyanide is removed by mechanism of charge neutralization as well as sweeping. Charges in coagulant species, that is, in metal hydroxide cations and metal cations vary with pH of solution [19]. In neutral and moderate alkaline pH, metal hydroxide flocks are positively charged and negatively charged chemicals such as cyanides and colloids (COD) contained in the solution gets removed due to charge neutralization by metal species [18]. At pH 12.5, low removal of CN^- may be due to the formation of poor coagulant species at high pH.

Removal of ammonia–N at different pH was also noted and results are presented in Fig. 2(b). Its removal at pH 4.5, 7.5, 9.5, 10.5, 11.5 and 12.5 was 32.2%, 45.8%, 49.2%, 52.1%, 58.4% and 12%, respectively. Removal of ammonia–N increased with an increase in pH up to 11.5, and thereafter it decreased with an increase in pH. Ammonia–N exists in CWW in three forms: free ammonia (NH_3), ammonium (NH_4^+) and amide (RNH_2) [20]. Ammonia–N probably gets adsorbed onto monomeric and polymeric Al hydroxides and gets removed. Organic amine (RNH_2) stay in positively charged species (RN^+H_3) under acidic condition and negatively charged species (RN^-H) under basic medium, due to this, its removal by adsorption and charge neutralization is more at alkaline condition. At very high pH (pH 12.5) its removal decreased due to the formation of ineffective coagulant species like $Al(OH)_3$ and $Al(OH)_4^-$. As already discussed, the complex/monomer polymer hydroxides cations forms in much amount at moderate acidic to moderate alkaline pH, which are active species in coagulation. The mechanism for removal of amine is given as follows:

$$RNH_2 \xrightarrow{\text{Acid}} R\overset{\oplus}{N}H_3 \tag{3}$$

$$RNH_2 \xrightarrow{\text{Base}} R\overset{\ominus}{N}H \tag{4}$$



$$RNH_2 \xrightarrow{\text{Base}} R\overset{\ominus}{N}H + \text{Coagulant species} \longrightarrow \underset{\text{Complex}}{\left[\begin{array}{c}\text{Coagulant species}\\ \vdots \\ R\overset{\ominus}{N}H\end{array}\right]} \tag{5}$$

Mechanism of NH_4^+ removal by EC could be same to heavy metal removal. Removal of copper, zinc and nickel was found to increase when pH was increased from pH 2–10 during ECT of heavy metals containing model wastewater [21]. No data have been reported on removal of ammonia–N by ECT.

Energy consumption and electrode loss was also noted at different pH. Data are presented in Table 4. For the treatment of 2 dm^3 of CWW at pH 4.5, 7.5, 9.5, 10.5, 11.5 and 12.5, respectively, electrode loss were 2.8, 3.1, 3.0, 3.4, 2.8 and 0.2 g; and energy consumption was 13, 24.72, 27.72, 10.69, 39.74 and 15.03 W. At pH 12.5 electrode losses was minimum while at pH 10.5 energy consumption was minimum. At pH 10.5, COD, phenol cyanide and ammonia–N removal was maximum and energy consumption was minimum, where as EL loss was slightly more, thus, pH 10.5 seems to best for treatment of CWW.

At acidic pH, the electrode is attacked by H^+ and EL occurs due to the following reaction:

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2 \tag{6}$$

At basic pH, OH^- attacks the electrode and EL occurs due to the following reaction:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{7}$$

3.2. Effect of current density

CD has been found to highly effluence the performance of EC. Not only metal cations formation rate increases with pH, but also the rate of bubble formation, its size and growth, which influences the efficiency of EC process. Effect of CD on the removal of phenol, cyanide, ammonia–N and COD was studied in the CD range of 18.6–92.9 A/m^2.

3.2.1. COD removal

COD removal at different CD at optimum pH = 10.5, NaCl concentration = 100 mg/dm^3 and EG = 17.5 mm is presented in Fig. 3(a) and Table 3. COD removal of 71.1%, 85.5%, 85.6%, 85% and 81.1% in 20 min; 71.8%, 88.4%, 88.8%, 86.1% and 83.3% in 60 min; and 73.3%, 90.11%, 89%, 88.8% and 84.5% in 100 min was found at CD values of 18.6, 37.2, 55.8, 74.32 and 92.9 A/m^2, respectively. These results reflect that considerable COD removal (85.5%) took placed for CD = 37.2 A/m^2 and treatment time = 20 min., while, maximum 91% removal was observed in 100 min at same CD, which is only 4.5% more. Increase in CD to 55.8 A/m^2, decreased the COD reduction. At high CD, more metal cations and metal hydroxide cations get form, thus, more amount of active coagulant species available, consequently pollutants removal became high [22,23]. However, at much high CD, metal cations and metal hydroxide cations present become more than that of desired, which causes restabilization of colloids, thus, less removal of pollutants [24].

Table 4
Electrochemical treatment data for 2 dm^3 CWW water treatment in 100 min

pH	Current (A)	Voltage (V)	Power (Wh)	Weight loss (gm)	COD reductions (%)
4.5	2	3.9	13.0	2.8	85.03
7.5	2	7.4	24.67	3.1	80.04
9.5	2	8.3	27.67	3.0	91.07
10.5	2	3.2	10.67	3.40	91.18
11.5	2	11.9	39.67	2.8	86.43
12.5	2	4.5	15.0	0.52	10

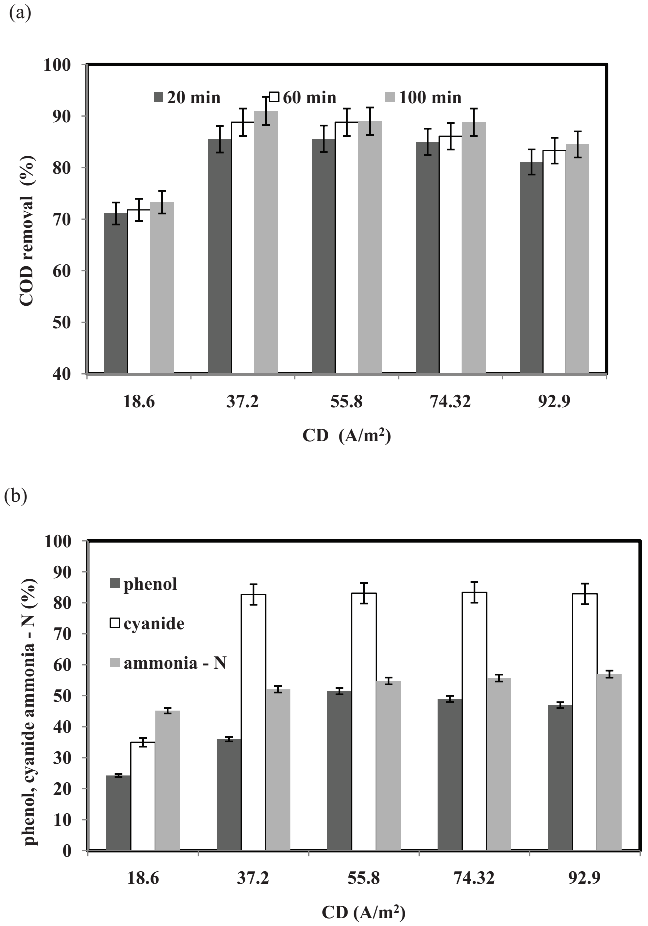


Fig. 3. Effect of CD on (a) COD removal in 20, 40 and 60 min, (b) phenol, cyanide and ammonia–N removal in 100 min. pH = 10.5, NaCl = 100 mg/dm^3, COD$_i$ = 10,100 mg/dm^3, phenol$_i$ = 363 mg/dm^3, cyanide$_i$ = 11.6 mg/dm^3, ammonia–N = 110.6 mg/dm^3.

3.2.2. Phenol, cyanide and ammonia–N removal

Removal efficiency of phenol, cyanide and ammonia–N at different CD was also studied. Results are presented in Fig. 3(b). 24.3%, 36%, 51.5%, 49%, 47% phenol removal; 35%, 82.7%, 83.1%, 83.4%, 82.90% cyanide removal and 45.2%, 52.1%, 54.8%, 55.72%, 57% ammonia–N removal was obtained at CD values of 18.6, 37.2, 55.8, 74.4 and 92.9 A/m^2, respectively. These observations imply that CD = 37.2 A/m^2 is optimum; however, CD = 55.8 A/m^2 looks better for phenol removal. Maximum removal of cyanide and ammonia–N increased by 0.7% and 4.9% only, while, phenol removal increased to 15.5% when CD was increased from 37.2 A/m^2. High value of cyanide removal as compared with ammonia–N and phenol is due to its removal by charge neutralization, adsorption and sweeping. Lower % phenol removal may be due to the presence of electron denoting substituents, which does not favor the formation of negatively charged phenoxides. In a study up to 97% phenol removal has been found in EC of C_6H_5OH [25]. C_6H_5OH contains electron withdrawing group, thus, negatively charged phenoxide formed, which favor the removal through enmeshment in coagulant flocks, charge neutralization and sweeping. Ammonia–N may be in anionic (RN^-H), cationic (NH_4^+) as well as in neutral (NH_4OH) form which were removed by adsorption, charge neutralization and sweep coagulation. Removal of phenol increased from 36% at CD 37.2 A/m^2 to 51.5% at CD 55.8 A/m^2.

Amount of ion generated in electrocoagulation process (ECP) depends on CD and time. Faraday's law relationship between these is presented as follows [26]:

$$m = \frac{M \times CD \times t}{Z \times F} \tag{8}$$

where m is the theoretical amount of ion supplied per unit surface area at CD for time t. Z is the number of electrons transferred in the reaction at electrode, for Al, $Z = 3$. M is the atomic weight of anode material, for Al, $M = 26.98$ g/mol and F is Faraday's constant (96,486 C/mol).

In the EC process with aluminum electrode, number of Al^{3+} increases, when CD increases because m is directly proportional to CD. Since metal ions hydroxide formation also increases immediately, due to this pollutant removal efficiency increases by ion neutralization, precipitation and sweep coagulation mechanism [27]. With an increase in CD, bubble production rate (though reduced in size) also increases due to higher formation of H_2 and O_2 gases [28]. It causes enhanced pollution removal by scum formation at top of the ECR. High CD to that of desired causes restabilization of colloids which produces low removal of pollutant as seen [24].

3.3. Effect of supporting electrolyte concentration

Increase in solution conductivity during ECP could be done by adding a small amount of electrolyte to the wastewater. As concentration of electrolyte increases, the average distance between cations and anions decreases, therefore, there is more interionic interaction. In our study, NaCl was used to increase the solution conductivity. NaCl has been found to low toxic at moderate levels and reasonable cost. Moreover, Cl^- can significantly reduce the adverse effect of other anions like HCO_3^- and SO_4^-. NaCl concentration was varied in the range of 100–200 mg/dm^3 keeping optimum CD = 37.2 A/m^2, optimum pH = 10.5 and EG = 17.5 mm.

3.3.1. COD removal

Table 5 and Fig. 4(a) show the effect of NaCl concentration on COD removal. At NaCl concentration of 100, 150 and 200 mg/dm^3, respectively, COD removed was 85.5%, 84.6% and 83.3%, respectively, in 20 min, which increased to 91%, 87.5% and 86.1% in 100 min. COD reduction was found to decrease by 5.0% with an increase in NaCl concentration from 100 to 200 mg/dm^3.

3.3.2. Phenol, cyanide and ammonia removal

Phenol, cyanide and ammonia–N removal data were also evaluated and results are presented in Table 5 and Fig. 4(b). At NaCl concentration of 100, 150 and 200 mg/dm^3, respectively, after 100 min of EC treatment, 36%, 35% and 34.2% phenol

Table 5
Values of COD, phenol, cyanide and ammonia–N after 100 min treatment time at different concentration of NaCl and different electrode gap at pH = 10.5, CD = 37.2 A/m^2 (initial COD = 10,100 mg/dm^3, phenol = 363 mg/dm^3, cyanide = 11.6 mg/dm^3, ammonia–N = 110.6 mg/dm^3)

Parameters EG – 17.5 (mm)	NaCl concentration mg/dm^3 →	100	150	200
COD	Final concentration	909	1,262.5	1,403.9
	% Reduction	91	87.5	86.1
Phenol	Final concentration	232.32	235.95	238.9
	% Reduction	36	35	34.2
Cyanide	Final concentration	2.01	2.175	2.436
	% Reduction	82.7	81.25	79
Ammonia	Final concentration	52.38	53.64	54.42
	% Reduction	52.1	51.5	50.8
Parameters NaCl – 100 mg/dm^3	Electrode gap (mm) →	12.5	17.5	22.5
COD	Final concentration	1,272.6	909	1,769.5
	% Reduction	87.4	91	82.48
Phenol	Final concentration	252.93	232.32	242.48
	% Reduction	32.8	36	33.2
Cyanide	Final concentration	3.36	2.00	2.919
	% Reduction	71.1	82.7	74.75
Ammonia	Final concentration	55.97	57.62	55.6
	% Reduction	49.4	52.1	49.8

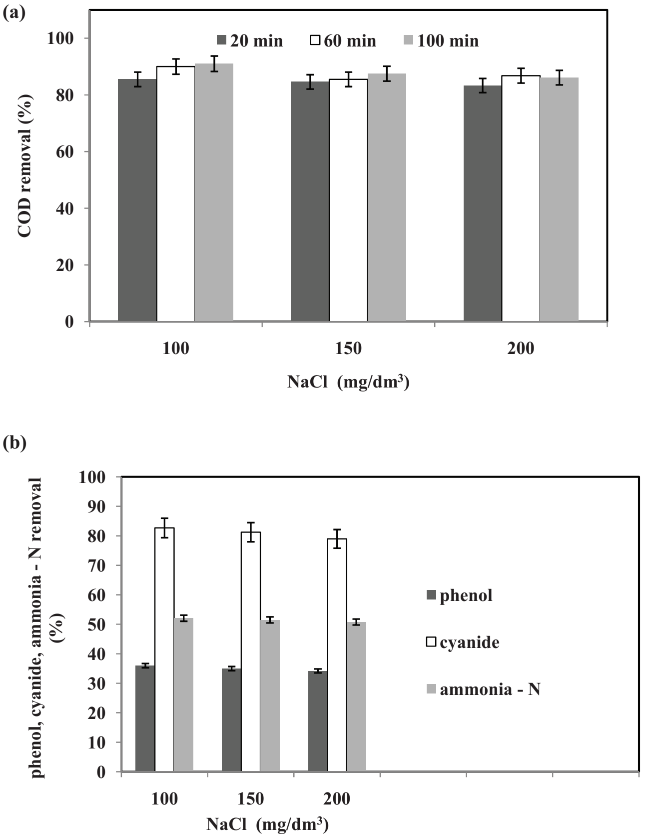


Fig. 4. Effect of electrolyte NaCl concentration on (a) COD removal, (b) phenol, cyanide and ammonia removal after 100 min. pH = 10.5, CD = 37.2 A/m^2, COD$_i$ = 10,100 mg/dm^3, phenol$_i$ = 363 mg/dm^3, cyanide$_i$ = 11.6 mg/dm^3, ammonia–N = 110.6 mg/dm^3.

removal; 82.7%, 81.25% and 79% cyanide removal; and 52.1%, 51.5% and 50.8% ammonia–N removal was obtained. Results reflect that NaCl concentration = 100 mg/dm^3 is good for treatment. Electricity consumption decreases with an increase in electrolyte amount, but weight loss of electrodes increases because Cl$^-$ attacks the anode material [29].

3.4. Effect of electrode gap

EG also affects the treatment up to certain level. It has been reported that in ECR, the solution close to the cathode become more concentrated because of the difference in mobility of the ions present and this effect can be reduced by agitation of the bulk solution. The relationship between EG and resistance R is given by the following equation:

$$R = \frac{\mathrm{EG}}{KA} \tag{9}$$

where A is the electrode surface area and K is the specific conductance of cell. From Faraday's law, at higher values of EG, that is, high cell resistance, the amount of oxidized iron decreased and consequently pollution removal generally decreases. In our experiments, ECT was done at EG values of 12.5, 17.5 and 22.5 mm keeping other parameters like pH = 10.5, CD = 37.2 A/m^2 and NaCl = 100 mg/dm^3 to constant.

3.4.1. COD removal

COD removal efficiency at different EG is presented in Table 5 and Fig. 5(a). At EG = 12.5 mm, 82.4% COD removal occurred in 20 min, which increased to 87.4% in 100 min.

Similarly at EG = 17.5 mm, COD reduction of 91% occurred in 100 min. Further increase in EG to 22.5 mm, COD reduction of 82.48% occurred in 100 min. These data show 17.5 mm EG to an optimum.

3.4.2. Phenol, cyanide and ammonia–N removal

Phenol removal of 32.8%, 36% and 33.2%; cyanide removal of 71.1%, 82.7% and 74.75%; and ammonia–N removal of 49.4%, 52.2% and 49.8% was observed at EG values of 12.5, 17.5 and 22.5 mm, respectively. These data reflects that EG = 17.5 mm is the best for removal of COD, phenol, cyanide and ammonia–N. At EG = 12.5, COD and other pollutants removal was low. It is due to increase in internal resistance with increase in EG, led to the formation of low Al^{3+} and consequently low aluminum cations. It is always not necessary that lower EG gives high removal of pollutants. There should be proper gap and distribution of electrode plate for movement of coagulants and colloids in solution. EG effect the mixing of coagulants and pollutants, thus, its removal varied with EG. Similar trend has been reported in EC treatment of pulp and paper mill effluent [17].

3.5. Statistical analysis and modeling

pH, CD and t_R affect significantly the EC treatment of effluent. Therefore, these variables were used for statistical analysis. Table 6 gives the chosen variable and its level. The encoded values along with set of data used for statistical analysis and corresponding % COD removal are given in Table 7. Set of data were designed as per earlier report [30,31].

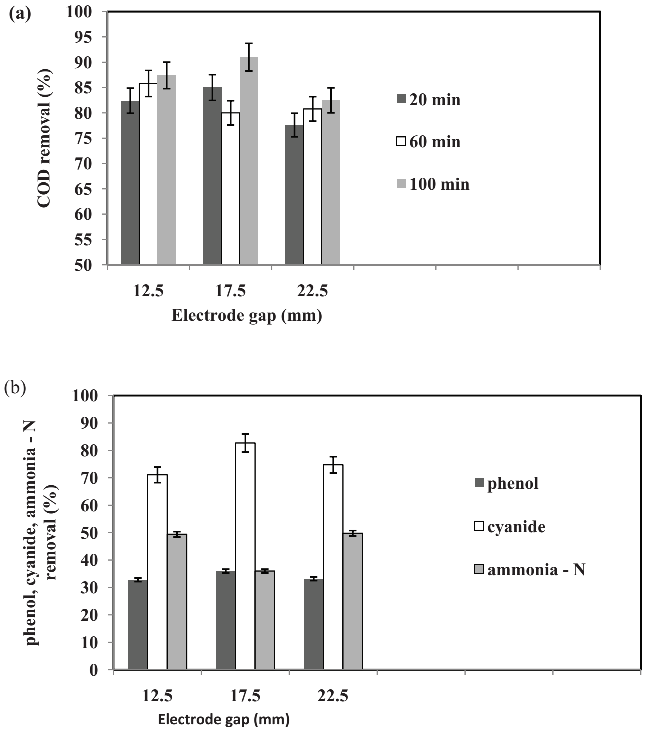


Fig. 5. Effect of electrode gap on (a) COD removal at 20, 60 and 100 min, (b) phenol, cyanide and ammonia–N removal after 100 min. pH = 10.5, CD = 37.2 A/m², NaCl = 100 mg/dm³, COD_i = 10,100 mg/dm³, $phenol_i$ = 363 mg/dm³, $cyanide_i$ = 11.6 mg/dm³, ammonia–N = 110.6 mg/dm³.

Regression method using analysis of variance (ANOVA) was used to fit second-order polynomial to the experimental data. The relation obtained in terms of uncoated factors for COD removal (%) is given by Eq. (10). The model gave significant coefficient of determination (R^2) = 99.67% and adjusted R^2 = 99.07%. These data are quite better than R^2 = 0.9144 reported by Thakur et al. [32]. Predicted values mentioned in Table 7, which was determined from Eq. (10), is very close to experimental values (maximum 5% deviation) also confers validity of model.

$$\begin{aligned}\text{COD removal } (\%) = & -209.764 + 2.195\,A - 47.007\,B + 0.210\,C \\ & - 0.025\,A^2 - 2.24\,B^2 + 0.001\,C^2 \\ & + 0.007\,AB + 0.001\,AC - 0.021\,BC\end{aligned} \tag{10}$$

where A is CD, B is pH and C is t_R.

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using ANOVA. The ANOVA for the second-order equation fitted for COD removal is presented in Table 8. ANNOVA result shows F value of 165.34. F value is the ratio of the mean square of the regression to the mean square

Table 6
Process parameters and their level for the EC treatment using aluminium electrode

Variables	–1	0	1
CD (A/m²), *A*	18.6	37.2	55.8
pH, *B*	9.5	10.5	11.5
Time (min), *C*	20	40	60

Table 7
Design of RSM and its actual and predicted values

Standard order	Current density (CD; A/m²)	pH	Time (min)	%COD removal	%COD removal
				Actual	Predicted
1	55.8	10.5	60	86.8	91.90
2	37.2	10.5	40	87.3	89.31
3	18.6	11.5	40	68.1	65.74
4	55.8	11.5	40	83.6	86.28
5	18.6	9.5	40	69.2	70.82
6	37.2	9.5	60	88.08	90.63
7	55.8	9.5	40	84.2	87.24
8	37.2	11.5	60	85.6	88.57
9	37.2	9.5	20	84.1	85.52
10	55.8	10.5	20	85.2	86.89
11	37.2	11.5	20	83.3	85.14
12	18.6	10.5	20	71.1	70.95
13	18.6	10.5	60	71.8	73.30
14	37.2	10.5	40	87.3	89.31
15	37.2	10.5	40	87.3	89.31

Table 8
ANNOVA for analysis of variance for % COD removal quadratic model

Source	Degree of freedom	Sum of square	Mean square	*F*	*p*
Regression	9	755.054	83.895	165.34	0.000
Linear	3	456.322	20.911	41.21	0.001
A	1	444.020	50.480	99.48	0.000
B	1	3.100	18.178	35.82	0.002
C	1	9.202	0.532	1.05	0.353
Square	3	297.761	99.254	195.60	0.000
A^2	1	278.692	284.958	561.58	0.000
B^2	1	18.907	18.527	36.51	0.002
C^2	1	0.163	0.163	0.32	0.596
Interaction	3	0.971	0.324	0.64	0.623
AB	1	0.063	0.063	0.12	0.740
AC	1	0.202	0.202	0.40	0.555
BC	1	0.706	0.706	1.39	0.291
Residual error	5	2.537	0.507		
Lack of fit	3	2.537	0.846		
Pure error	2	0.000	0.000		
Total	14	757.591			

of error. It is a measure of variation in the data about the mean. For best fit, in ANNOVA analysis, value of *F* should be large. Value of *F* is large, which shows most of the variation in response can be explained by the regression [33]. The associate *p* value is used to estimate *F*. *p* Value is used to evaluate the significance of each selected variable in the experiments. In our case, the value of *p* is 0.0001, which is very less than maximum recommended value 0.05 [33]. This indicates the model is statically significant. In response surface methodology (RSM) studies for COD removal, values of *F* and *p* were 68.74 and 0.0001 [31] and 16.55 and 0.0001 [33] have been reported earlier.

The response surface plot and contour plots for COD removal are presented in Fig. 6. Figs. 6(a) and (b) show the effect of CD and pH on COD removal at constant time of 40 min. In the figure, it can be seen that COD removal increased with an increase in pH up to 10.5 which decreased with further increase in its pH value. COD removal also increased with increase in CD up to certain extent, and then decreased with further increase its value. Maximum COD removal can be seen at CD = 32 A/m^2 and pH = 10.5. Figs. 6(c) and (d) show COD reduction with variation in CD and time at constant pH = 10.5. COD removal is good in the CD range of 30–35 A/m^2. It increased with an increase in time at all CD. Variation in COD removal with change in time and pH at constant CD = 37.2 A/m^2 is presented in Figs. 6(e) and (f). COD reduction was maximum at pH 10.5. The values decreased with deviation from pH = 10.5 for all the treatment time. The treatment time 50–60 min looks good for the treatment. Reasons for variations in COD removal with pH are already discussed.

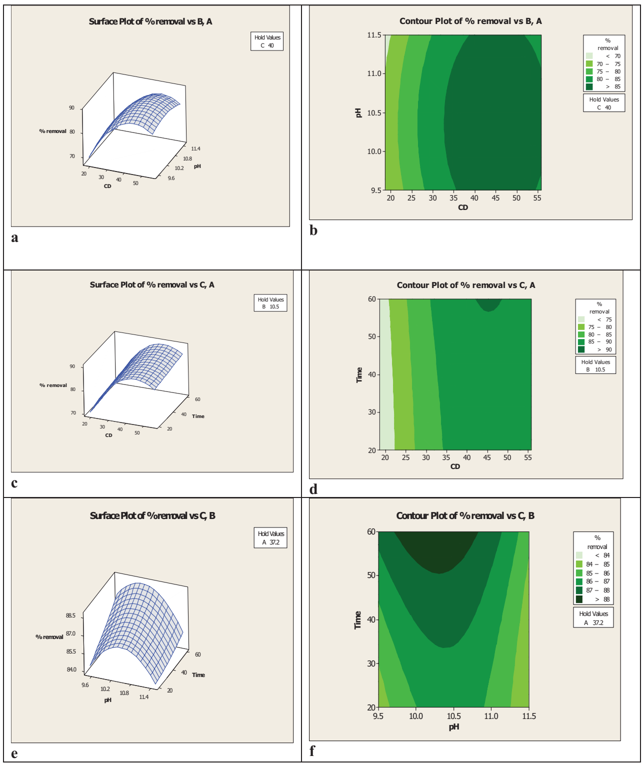


Fig. 6. Three-dimensional response surface graphs for COD removal in ECT using Al electrode. A (CD), B (pH), C (Time).

3.6. Settling characteristics

Settling is known to be one of the low cost separation processes. To separate the solid and liquid of slurry, the treated CWW by EC process was slowly mixed and placed in 1.0 dm^3 cylinder having internal diameter of 61 mm. The height of the interface between supernatant and solid (H/H_i) was noted with respect to time. The liquid–solid interface for different pH, that is, 9.5, 10.5 and 11.5 is presented in Fig. 7. For initial time up to maximum 30 min, steady-state decrease in height of the solid–liquid interface (H/H_i) called zone settling was exhibited. Thereafter, the transition settling zone occurred for short period. Finally, a steady-state compression settling occurred with smaller decrease in height at the interphase. Settling rate was found in order: pH 11.5 > 10.5 > 9.5. At pH = 10.5, removal of COD, phenol, cyanide and ammonia–N are highest and settling characteristics is also good, therefore, pH = 10.5 is the best for the EC treatment of CWW. It should be also noted that pH of coking wastewater varies in range of 9–11. Thus, there is no need to adjust its pH. Various methods have been presented to design a continuous thickener from batch sedimentation data [34,35]. The method proposed by Richardson et al. [35] is most suitable to design a continuous thickeners based on batch study.

3.7. Filterability characteristics

Filtration study was also performed to separate residues content of the slurry. Parameters such as filter media resistance and filter cake resistance for the constant pressure filtration were evaluated using the following filtration equation [36]:

$$\frac{\Delta t}{\Delta V} = \frac{\mu\alpha C}{A^2\,\Delta P}.V + \frac{\mu}{A\Delta P}\,.\,R_m \tag{11}$$

where Δt is the time interval of filtration (s), ΔV is the filtrate volume collected up to that time interval (m^3), C is the solids concentration in the slurry (kg/m^3), V is the total liquid filtrate volume collected up to the time interval t (m^3), μ is the viscosity of the liquid filtrate (Pa s), ΔP is the pressure drop across the filter = ρgh (Pa), A is the filtration area (m^2), R_m is the resistance of the filter medium (m^{-1}), α is the cake specific resistance to filtration, also called as SCR.

Gravity filtration was performed at room temperature (30°C–35°C) and 101.3 kPa using Whatman filter paper supported on a Buchner funnel (75 mm diameter). The volume filtrate was noted at different time intervals. From experimental data, plot of dt/dV vs. V was plotted and it is presented in Fig. 8 and some values evaluated are presented in Table 9. At pH 9.5, 10.5 and 11.5, cake resistance was evaluated to be 1.09×10^{11}, 1.15×10^{11} and 0.953×10^{11} m/kg, respectively; and filter media resistance was found to be 44.63×10^{11}, 48.17×10^{11} and 60.53×10^{11} m^{-1}, respectively. Filterability is measured from the cake resistance. Low cake resistance gives high filterability. Thus, EC treated CWW filterability was found to follow the order: pH 11.5 > 9.5 > 10.5. Filter media resistance is important at the initial period of filtration. Value of α and R_m depends on nature of effluent, treatment conditions and characteristic of sludge. Values of a have been reported in the ranges of (4–12) × 10^{13}, (3–30) × 10^{13}, (2–20) × 10^{11} and (3–10) × 10^{11} m/kg for activated sludge, biodigested sludge, conditioned sludge and conditioned primary sludge, respectively [37]. In our case, a for treated CWW is less than all the three types of sludge indicating its better filterability in comparison with municipal sludge.

3.8. Cost analysis

The cost of EC treatment process depends on nature of the pollutants and the experimental conditions applied. Electricity consumption and EL are considered to be the two major costs in the EC treatment. During the process EL takes place. Coagulants form flocs that may be separated either by filtration and/or by settling. For the treatment of CWW, costs of added chemicals were negligible and thus not considered.

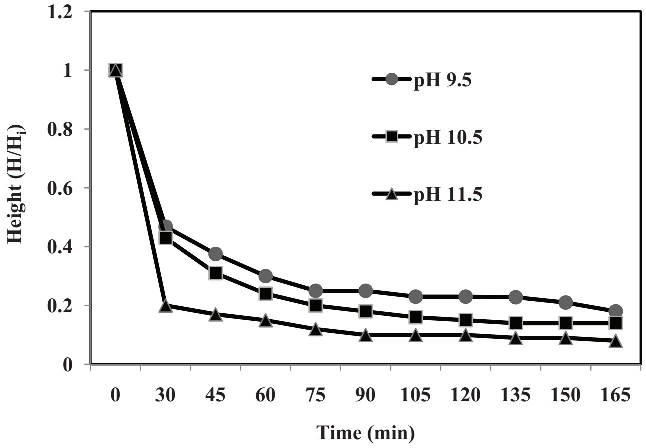


Fig. 7. Settling characteristics of EC treated coking wastewater.

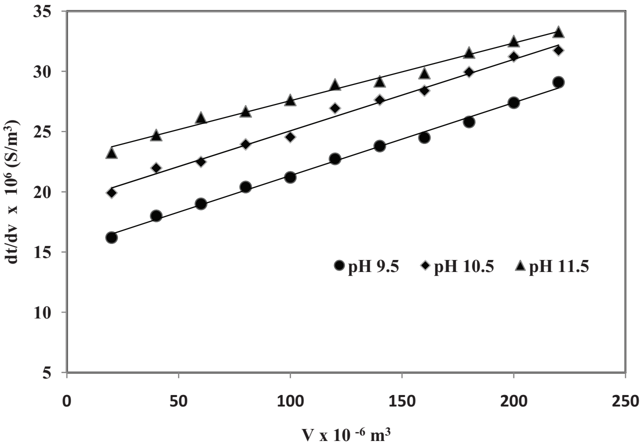


Fig. 8. Filterability of EC treated CWW at pH 9.5, 10.5, 11.5, CD = 37.2 A/m^2, EG = 17.5 mm.

Table 9
Filtration characteristics of treated CWW

S. No.	Initial pH	$K_p \times 10^{-11}$ s/m^6	$\beta \times 10^6$ s/m^3	C kg/m^3	$\alpha \times 10^{-11}$ m/kg	$R_m \times 10^{-11}$
1	9.5	0.60	15.29	4.68	1.09	44.63
2	10.5	0.69	16.48	5.10	1.15	48.12
3	11.5	0.55	20.73	4.92	0.953	60.53

The cost of energy for EC treatment and the cost of Al electrode material consumed can be obtained from the experimental results (without the use of any additive). The sum of energy and electrode material consumption is known as operating cost.

$$\text{Operating cost to treat CWW} = C_{\text{energy}} + C_{\text{electrode}} \tag{12}$$

For the treatment of 2.0 dm^3 CWW, average anode dissolution was 3,400 mg with maximum COD removal of 91% in 100 min at CD = 37.2 A/m^2 (2 A and 3.2 V).

Aluminum electrode cost:

1,700 mg of aluminum gets dissolved per dm^3 of CWW

Aluminum required per m^3 of CWW = 1,700 g

Cost of aluminum sheet = INR 70/kg [38]

Cost of 3 mm sheets on bulk purchase (cleaning, cutting and placing) @ INR 75/kg

= 1.7 × 75 = INR 127.5/m^3

Cost of aluminum sheet per m^3 of CWW treated = INR 127.5/m^3

Cost of energy:

To treat 2 m^3 of CWW, energy consumption was: 6.4 kWh (2 A × 3.2 V)

Energy price in the Indian market for industries are = INR 6/kWh [39]

For 1 m^3 of CWW, energy consumption in 100 min is 5.33 kW

Cost of energy per m^3 of CWW treated in 100 min = INR 6/kWh × 5.33 kW = INR 32

Overall cost:

Cost of electrode + cost of energy = 127.50 + 32.0 = INR 159.50 per m^3 = US $2.41/$m^3$ of CWW (1$ = 66.0 INR)

Also, since COD reduction increased 5.5% only from 85.5% reduction in 20 min to 91% in 100 min, therefore, the treatment cost can be reduced about five times, that is INR 32 (~0.5$) to treat 1 m^3 (1,000 L) CWW with COD reduction of 85.5% in 20 min. The 0.5$ to treat 1,000 L CWW is much less.

4. Conclusions

Following main conclusions are drawn from the present study:

- ECT using aluminum electrode was found to be an effective process to treatment of CWW. Optimum operating condition was at pH = 10.5, CD = 37.2 A/m^2 (2 A and 3.2 V), EG = 17.2 mm and NaCl concentration = 100 mg/dm^3. At this operating condition, electrode loss was 1,700 mg and power consumption was 5.31 Wh for the treatment of 1 dm^3 effluent. Cost of treatment by energy required and electrode loss was calculated to US $2.41/$m^3$ of CWW treated. The treatment cost can be reduced to $0.50/$m^3$ of CWW in 20 min EC with COD reduction of 85.5%.
- At optimum operating condition, pollutants in effluent reduced to COD = 909 mg/dm^3, phenol = 232.30 mg/dm^3, cyanide = 2.0 mg/dm^3 and ammonia–N = 52.1 mg/dm^3 from initial values: COD = 10,100 mg/dm^3, phenol = 363 mg/dm^3, cyanide = 11.6 mg/dm^3 and ammonia–N = 110.6 mg/dm^3.
- Good settling characteristics was found, thus, separation of residue and filtrate of ECT treated CWW is easy. This process is better than various physiochemical process reported by various investigator till present. However, further treatment like adsorption need is required to bring the effluent to recyclable/dischargeable limit, which has been confirmed in laboratory studies.
- The quadratic model developed based on RSM statistical analysis showed a high coefficient of determination (R^2 = 0.9967) ensuring a good representation of experimental data by regression model.

Acknowledgment

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