

Vibha Verma*, Parmesh Kumar Chaudhari and Bidyut Mazumdar

Optimization of multiple parameters of coking wastewater (CWW): catalytic thermolysis (CT) at high pressure reactor (HPR)

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Abstract: Present study deals with the treatment of coking waste water (CWW) for the reduction of pollutants COD, phenol and cyanide using catalytic thermolysis (CT). For screening of catalyst and optimization of pH the CT was performed at 100 °C, pH = 3–11 using catalyst mass loading $C_w = 3$ g/L. In this study $\text{Cu}(\text{NO}_3)_2$ gave best performance. Further, CT was carried out using $\text{Cu}(\text{NO}_3)_2$ catalyst in high pressure reactor (HPR). The investigated parameters range were initial pH (pH_i) = 3–11, $C_w = 1$ –5 g/L, temperature (T) = 100–160 °C and treatment time (t_R) = 6 h. The maximum percentage reduction for COD, phenol and cyanide were 83.33, 80.57 and 97.61%, respectively at pH = 9, $C_w = 4$ g/L, $T = 140$ °C and $t_R = 6$ h. The CT did not give complete reduction of pollutant; therefore it was further treated using adsorption process as second stage treatment. The initial value of COD = 610 mg/L, phenol = 70.58 mg/L and cyanide = 0.45 mg/L were further reduced to 98.85, 100.00 and 55.55%, respectively, when adsorption process was performed at pH = 9, adsorbents dose $A_w = 4$ g/L, $t_R = 2$ h. The response surface methodology (RSM) was performed through central composite design (CCD) for the designing of experiments and optimization of both the process. The kinetics studies of CT at HPR showed first order with respect to COD and phenol, and 0.24–0.608 order with respect to C_w .

Highlights:

- Thermolysis and adsorption process were applied for the treatment of coking wastewater (CWW).

- The parameters like, pH, catalyst amount, time and temperature were studied for removal of pollutants by thermolysis process.
- In adsorption process, the effect of pH, adsorbent dosage and treatment time were studied for removal of pollutants.
- The two stage treated effluent have COD = 8 mg/L, phenol = 0.00 mg/L and cyanide = 0.2 mg/L.
- The treated effluent can be used in same industry for various purposes thus gives zero discharge.

Keywords: adsorption; catalytic thermolysis; COD; cyanide; high pressure reactor; phenol.

1 Introduction

Coking waste water (CWW) is highly polluted organic wastewater generated by quenching of hot coke in coke oven during carbonization of coal (Wu and Zhu 2012). It is a complex mixture of organic and inorganic components like ammonia, cyanide, phenol, sulphate, hydrocarbons, polycyclic aromatics and polycyclic nitrogen (Burmistrz et al. 2014). Due to contained of hazardous chemicals it is very harmful to the environment (Sun et al. 2008; Dhoble et al. 2019); therefore, it is necessary to bring CWW to dischargeable limit using efficient and low cost processes. In most of coking plant the CWW is first treated by coagulation, than followed by biological treatment. In biological process selective and effective micro organisms are needed to consume phenol and cyanide present in CWW (Choudhary et al. 2017). Some other process have been also reported for the treatment of CWW are biofilm reactor (Lai et al. 2009), adsorption (Sun et al. 2008; Dhoble et al. 2019), plasma reactor (An et al. 2011), electro coagulation (Chaudhari et al. 2017), Nano filtration (Korzenowski et al. 2011), sequential batch reactor (Maranon et al. 2008), membrane treatment (Smol et al. 2018), electrocoagulation followed by adsorption (Chaudhari and Choudhary 2019) etc. All these processes are having some limitation as it does not meet the environmental discharge standard prescribed by the pollution control agencies if applied in single

*Corresponding author: Vibha Verma, Department of Chemical Engineering, National Institute of Technology, 492010, Raipur, India, E-mail: desh mukhvibha22@gmail.com

Parmesh Kumar Chaudhari and Bidyut Mazumdar: Department of Chemical Engineering, National Institute of Technology, 492010, Raipur, India

Table 1a: CWW composition before and after treatment in HPR (at $T = 140\text{ }^\circ\text{C}$, $\text{pH} = 9$, $C_w = 4\text{ g/L}$, $t_R = 6\text{ h}$) and adsorption (at $\text{pH} = 9$, $C_w = 4\text{ g/L}$, $t_R = 2\text{ h}$).

| Parameters | CWW | After HPR | After adsorption |
|-------------------------------------|-------|-----------|------------------|
| COD | 1800 | 610 | 08 |
| Phenol | 242 | 70.58 | ND |
| Cyanide | 18.88 | 0.45 | 0.2 |
| Chlorine | 3000 | 1568 | 1428 |
| Phosphate | 10.20 | 6.34 | 0.41 |
| Sulphate | 26.73 | 24.33 | 23.07 |
| Hardness | 300 | 222 | 152 |
| Colour absorbance at 0.432 (475 nm) | | 60.87% | 98.89% |
| % colour removal | | | |
| PH | 9.3 | 9 | 9 |

All values are in mg/L except pH and colour, ND = Not detected.

Table 1b: Operating condition for CWW treatment.

| Operating parameters | Thermolysis (HPR) | Adsorption |
|----------------------------------|-------------------|------------|
| PH | 2–11 | 3–9 |
| Temperature ($^\circ\text{C}$) | 100–160 | 40 |
| C_w, A_w (g/L) | 1–5 | 1–5 |
| Treatment time (h) | 0–6 | 0–4 |

stage. Some processes like plasma reaction, membrane treatment are complex in operation and requires high power consumption and high treatment cost, but gives good treatment efficiency. Some of them like bio treatment, adsorption and electrocoagulation are low cost, but the removal efficiency of pollutants is not good hence second stage treatment is required if applied at plant scale.

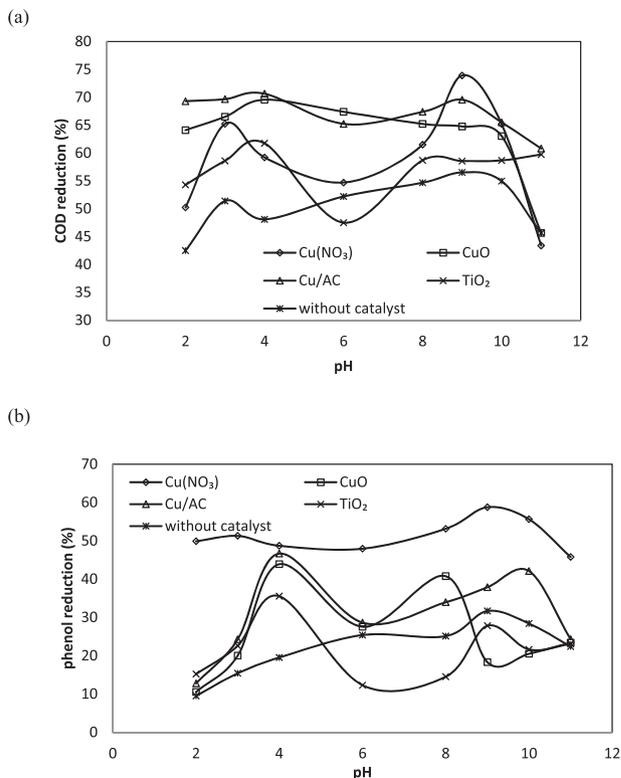


Figure 2: Effect of pH on CT of CWW at $C_w = 3\text{ g/L}$, $T = 100\text{ }^\circ\text{C}$ and $t_R = 3\text{ h}$. (a) COD reduction and (b) phenol reduction.

In present research, catalytic thermolysis (CT) of CWW was performed at atmospheric pressure and high pressure. Atmospheric pressure studies were carried out for screening of catalyst and to optimise the pH. The operating condition was $\text{pH} = 3\text{--}11$, $C_w = 3\text{ g/L}$ and $\text{temp} = 100\text{ }^\circ\text{C}$, in which performance of $\text{Cu}(\text{NO}_3)_2$ catalyst was found best at pH 9. In high pressure reactor (HPR) the effect of various

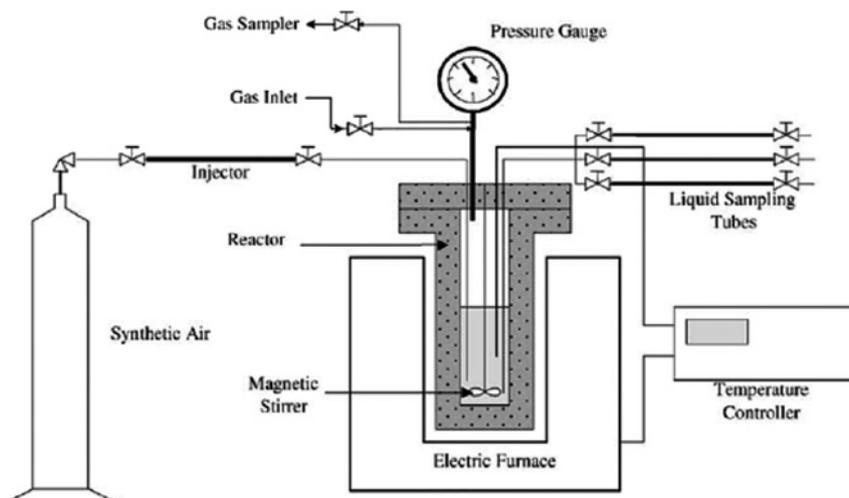


Figure 1: Schematic of catalytic wet air oxidation process.

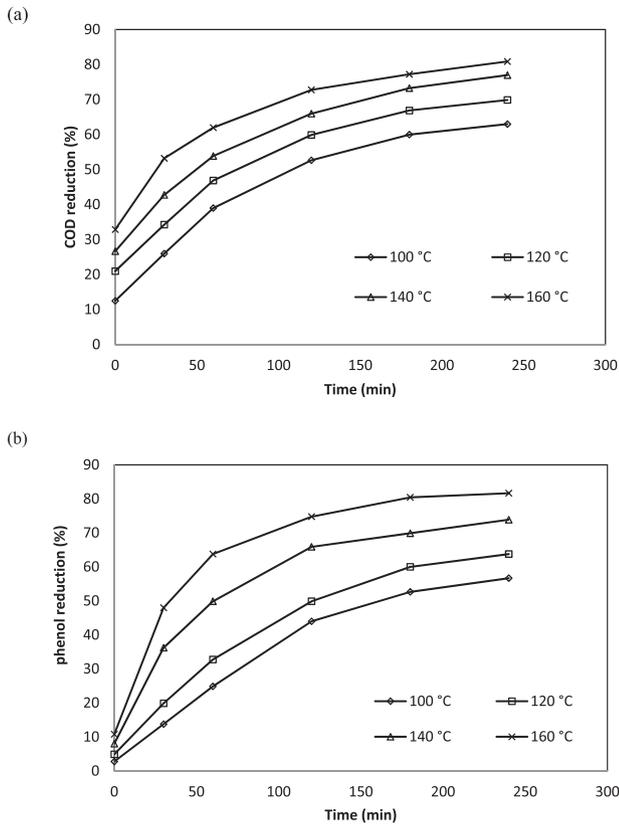


Figure 3: Effect of temperature on CT at HPR of CWW at $C_w = 3$ g/L and $t_R = 4$ h. (a) COD reduction and (b) phenol reduction.

parameters T , C_w and t_R have been explored on COD and phenol reduction using $\text{Cu}(\text{NO}_3)_2$ catalyst. For the complete removal of pollutants present in CWW, the adsorption was performed as second stage process for which operating parameters were pH, adsorbent dose and t_R . Multiple parameter optimizations through response surface methodology (RSM) by using central composite design (CCD) model were developed for both the process. Other parameters like cyanide, chloride, phosphate, sulphate, colour and hardness were also determined at the end of both the processes.

2 Material and methods

2.1 Material

The CWW was obtained from Bhilai Steel Plant, Steel Authority of India Limited, C.G., India. Composition analysis of CWW before and after treatment is presented in Table 1a, b. Analytical reagent grade chemicals for analysis and laboratory reagent grade chemicals for thermolysis and adsorption were used. Chemicals were made of Rankem Ltd Mumbai and Merck Ltd Mumbai. For thermolysis process $\text{Cu}(\text{NO}_3)_2$, CuO , Cu/AC and TiO_2 were used. LR

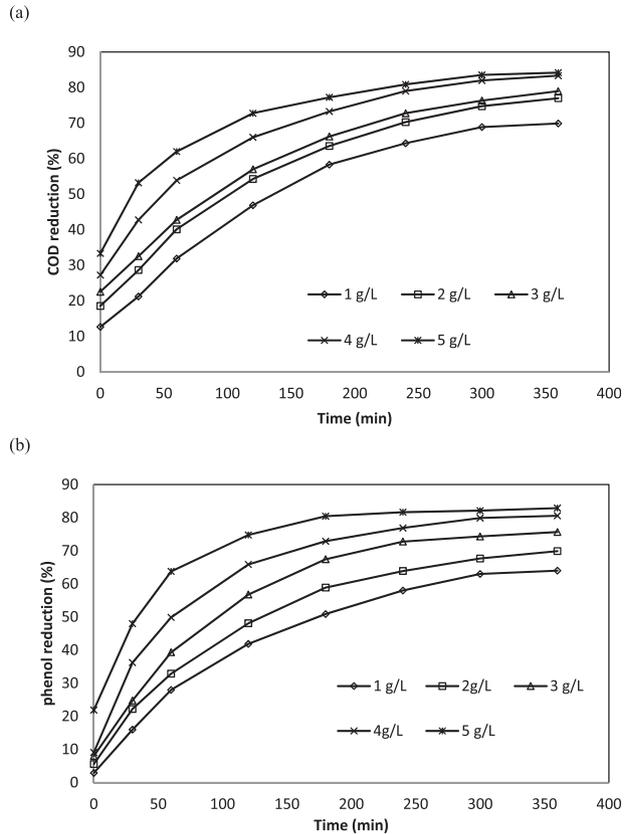


Figure 4: Effect of catalyst mass loading on CT at HPR of CWW at $T = 100$ °C for $t_R = 6$ h. (a) COD reduction and (b) phenol reduction.

grade TiO_2 was used as obtained and CuO was synthesized in laboratory from alkali precipitation followed by calcination at 400 °C for 3 h. Cu/AC catalyst was prepared by impregnation of Cu^{++} in activated carbon.

2.2 Experimental setup

Batch mode CT of CWW was conducted in a 0.70 dm³ high pressure autoclave reactor made by Nano-Mug, India as shown in Figure 1. A stirrer was provided in the reactor to mix the effluent and catalyst. The 400 ml CWW and catalyst (1–5 g/L) was taken in the reactor and heated to experimental temperature. When desired temperature was reached it was considered as zero time. The CWW samples were withdrawn at certain time intervals and analysed for different parameters. The experiments were performed at different pH, T , C_w and t_R . Earlier to high pressure operation, the screening of catalyst and respective pH optimization was carried out. When the best catalyst $\text{Cu}(\text{NO}_3)_2$ was evaluated it was selected for high pressure and high temperature operation.

The CWW treated by CT in HPR gave effluent quality COD = 610 mg/L, phenol = 70.58 mg/L and cyanide = 0.45 mg/L was further treated by adsorption process in a water bath shaker in batch mode. 50 mL of pre treated CWW was taken in a 100 ml of conical flask. The required amount of adsorbent i. e. activated charcoal was added and kept in shaker for adsorption process. About 5 ml CWW samples were taken out at different time intervals between 0 and 2 h, and

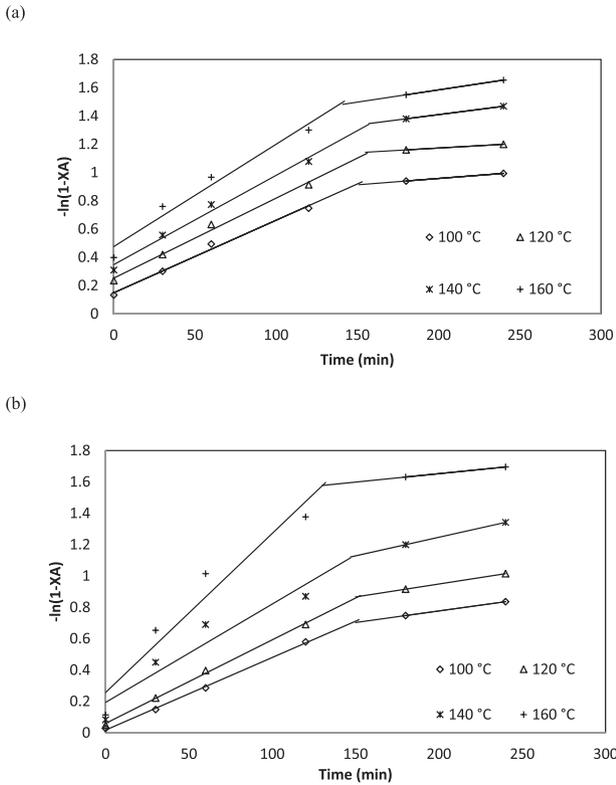


Figure 5: Effect of temperature on first order kinetics of CT at HPR of CWW at $C_w = 3$ g/L and $t_R = 3$ h. (a) COD reduction and (b) phenol reduction.

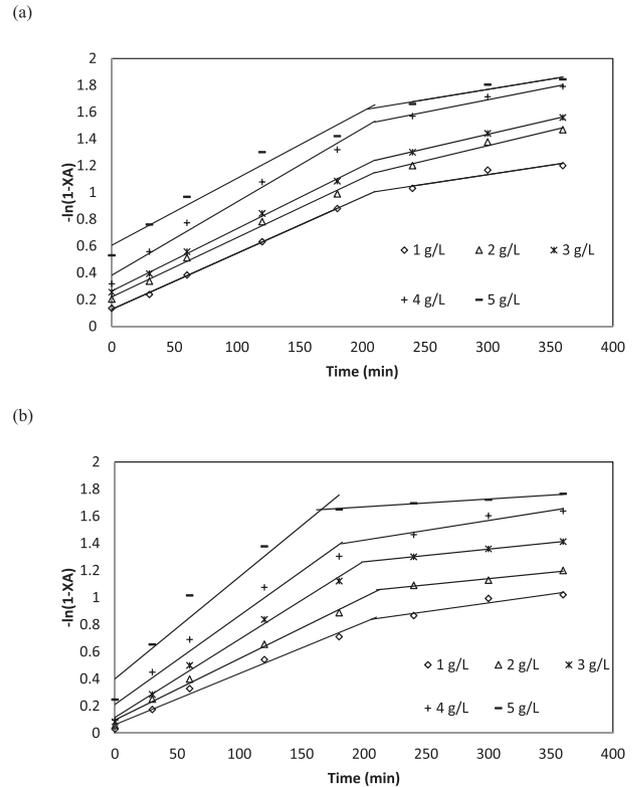


Figure 6: Effect of catalyst mass loading on first order kinetics of CT at HPR of CWW at $T = 140$ °C and $t_R = 6$ h. (a) COD reduction and (b) phenol reduction.

adsorbent were allowed to settle down. The supernatant were tested for the removal of COD and phenol content. Effect of operating parameters in the range of $pH_i = 3-9$, adsorbent dosage $A_w = 1-5$ g/L, $t_R = 0-2$ h were studied for COD and phenol removal. The other parameters like cyanide, chlorides etc. were also determined at the end of experiment.

2.3 Analytical techniques

COD was determined by the standard dichromate closed reflux method. 2.5 mL water sample was taken in COD vials in which 1.5 mL $K_2Cr_2O_7$ reagent was added followed by 3.5 mL H_2SO_4 reagent. The prepared samples were digested for 2 h at a temperature of 148 °C in the COD digester and titrated with standard ferrous ammonium sulphate (Rice et al. 2012). Phenol was determined by colorimetric method for this 10 mL phenol solution was taken in test tube. In this 0.25 mL of NH_4OH (0.5 N) solution was added and immediately pH of sample was adjusted to 7.9 with phosphate buffer. After that 0.1 mL of 4-aminoantipyrine solution and 0.1 mL of potassium ferricyanide was added and mixed well. After 15 min, samples were transferred to cell to read the concentration against the blank at 500 nm using spectrophotometer (Rice et al. 2012).

Cyanide was analysed by using standard kit purchased from Merck Ltd, Mumbai, India. 10 ml wastewater was taken in test tube to which a pinch of citric acid (reagent CN-1) was added and shaken vigorously. The solution formed was heated at 120 °C for 5 min in the

thermo reactor (Merck Made), after that the tube was taken out and cooled. Further, 3 drop NaOH (Reagent CN- 2) was added and its pH was adjusted to 4.5–8. Further, 5 mL sample was taken and in this 1 level micro spoon Reagent CN- 3 and Reagent CN- 4 was added, as a result the colour formed to violet. The CN^- concentration was determined using spectrophotometer (Merck made). Hardness and chloride content were determined by standard titrimetric method (Rice et al. 2012). The percentage reductions of pollutants were calculated by using following equation;

$$\text{Percentage reduction (Y)} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

where, C_o is initial value of COD, phenol and cyanide, and C_t is value of COD, phenol and cyanide at specific time, Y is the percentage reduction of pollutants present in CWW.

2.4 Experimental design and optimization using RSM

RSM is generally used for designing and optimizations of different independent variables. In present case, total 20 set of runs for each CT and adsorption as second stage treatment were performed to evaluate the individual and interaction effects of the independent parameters on the COD and phenol reduction efficiency. The experimental data were analysed using Minitab, and the regression models were developed using three independent process. The experimental results

Table 2: First order data's with temperature and catalyst mass loading at rate constant for COD reduction.

| Temperature (°C) | COD | | Phenol | | COD | | phenol | |
|------------------|---|----------------|----------------|----------------|---|----------------|----------------|----------------|
| | Temperature vs. rate constant (catalyst const. Cw = 3 g/L) | | | | Catalyst mass loading vs. rate constant (T = 100 °C) | | | |
| | K ₁ | K ₂ | K ₁ | K ₂ | K ₁ | K ₂ | K ₁ | K ₂ |
| 70 | 0.0050 | 0.0012 | 0.004 | 0.001 | 0.004 | 0.002 | 0.004 | 0.0001 |
| 80 | 0.0052 | 0.0013 | 0.005 | 0.0012 | 0.0044 | 0.0023 | 0.005 | 0.00012 |
| 90 | 0.0060 | 0.0014 | 0.006 | 0.0014 | 0.0051 | 0.0024 | 0.006 | 0.00014 |
| 100 | 0.0070 | 0.0015 | 0.0061 | 0.0015 | 0.0052 | 0.0025 | 0.007 | 0.00015 |

obtained from the RSM through CCD were written in the form of equation presented below:

$$X = bo + \sum_{i=1}^n bixi + \sum_{i=1}^n biixi^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n bijxixj + ei \tag{2}$$

where, *X* is the predicated response, *bo* is the offset, *bi*, *bii* and *bij* are the first order, quadratic and interaction effects respectively. *n* is the number of factors, *xi* and *xj* are the coded variables, *i* and *j* are the index number for factor, and *ei* is the residual error.

3 Result and discussions

The different homogenous and heterogeneous catalysts like Cu (NO₃)₂, TiO₂, CuO, and Cu/AC were tested for the reduction of COD and phenol at atmospheric pressure. Among these, cupric nitrate gave best performance; therefore, it was further taken for treatment of CWW at high pressure. The effect of Cw (1–5 g/L) and T (100–160 °C) on phenol and COD reduction has been presented.

3.1 Effect of pH

To observe the effect of pH on reduction of pollutants, the experiments were carried out in the pH range of 2–11, at

constant T = 100 °C and Cw = 3 g/L. Optimum pHs were find to 9, 4, 4, 4, and 9 for cupric nitrate, CuO, Cu/AC, TiO₂, and without catalyst. The actual pH of CWW was in between 9.2 and 10. The COD and phenol percentage reduction for Cu (NO₃)₂, CuO, Cu/AC, TiO₂, and without catalyst were 63.65 and 58.76%; 61.98 and 43.90%; 60.34 and 46.65%; 56.98 and 35.52%; 56.52 and 31.67%, respectively, at Cw = 3 g/L and T = 100 °C in 3 h. It shows that cupric nitrate gave the best reduction among the others (Figure 2a, b). It is well known that performance of catalysts in CT depends on pH (Mishra et al. 1995; Garg et al. 2005; Chaudhari et al. 2005). As the CWW has basic in nature, and Cu (NO₃)₂ gave best performance for reduction of pollutants in basic condition,

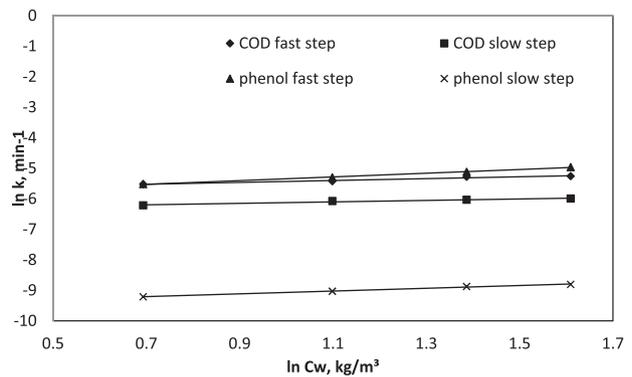


Figure 8: Effect of catalytic mass loading, Cw, on reaction rate constant (*k*) for catalytic thermolysis of CWW, T = 140 °C, pH = 9.

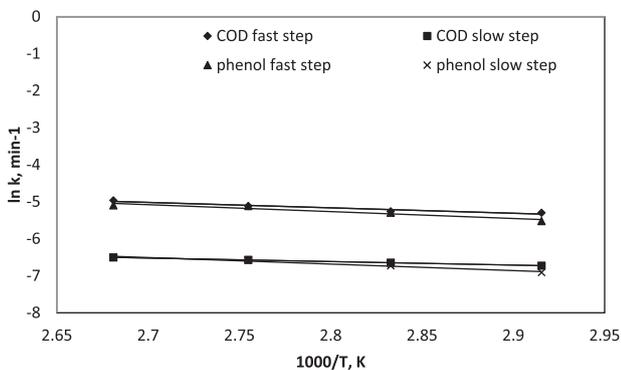


Figure 7: Arrhenius plot for catalytic thermolysis in HPR.

Table 3: Experimental range for independent variables of HPR for CWW.

| Independent variables | Factors | Range and levels | | |
|-----------------------------|---------|------------------|-----|-----|
| | | -1 | 0 | 1 |
| Temperature (°C) | X1 | 100 | 130 | 160 |
| Catalyst mass loading (g/L) | X2 | 1 | 3 | 5 |
| Time (h) | X3 | 2 | 4 | 6 |

Table 4: RSM optimization of COD and phenol for CWW using HPR.

| Run order | X1 | X2 | X3 | %COD observed | %COD predicted | %Phenol observed | %Phenol predicted |
|-----------|-----|----|----|---------------|----------------|------------------|-------------------|
| 1 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 2 | 160 | 5 | 6 | 86.23 | 83.96 | 85.46 | 85.02 |
| 3 | 130 | 5 | 4 | 80.87 | 84.28 | 81.65 | 81.58 |
| 4 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 5 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 6 | 160 | 3 | 4 | 79.87 | 83.04 | 82.32 | 84.36 |
| 7 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 8 | 130 | 1 | 4 | 61.65 | 59.56 | 57.98 | 58.83 |
| 9 | 160 | 1 | 6 | 74.84 | 75.68 | 75.36 | 75.61 |
| 10 | 100 | 5 | 6 | 76.98 | 77.70 | 73.87 | 75.17 |
| 11 | 100 | 1 | 2 | 20.36 | 22.30 | 22.46 | 22.69 |
| 12 | 130 | 3 | 6 | 72.12 | 72.48 | 75.65 | 74.36 |
| 13 | 130 | 3 | 2 | 61.21 | 62.18 | 61.76 | 63.88 |
| 14 | 100 | 5 | 2 | 64.63 | 63.46 | 59.23 | 58.78 |
| 15 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 16 | 130 | 3 | 4 | 72.76 | 72.32 | 72.76 | 72.49 |
| 17 | 160 | 1 | 2 | 70.36 | 69.31 | 72.46 | 70.95 |
| 18 | 100 | 1 | 6 | 40.25 | 40.61 | 41.65 | 41.81 |
| 19 | 160 | 5 | 2 | 82.36 | 81.67 | 83.46 | 83.10 |
| 20 | 100 | 3 | 4 | 58.25 | 56.40 | 56.55 | 55.30 |

therefore pH adjustment of CWW is required very less in case of $\text{Cu}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ catalyst.

3.2 Effect of temperature

Since $\text{Cu}(\text{NO}_3)_2$ performed well therefore it was taken for further studies. To obtain an optimum temperature, the pollutants removal were tested in T range of 100–160 °C, pH 9 and $C_w = 3$ g/L. As the temperature was increased the percentage reduction of COD, phenol and other parameters were also increased, but after reaching to certain temperature the removal did not increase appreciable even further increase in temperature. The COD and phenol reductions at 100, 120, 140 and 160 °C were 63.65 and 58.76%; 69.87 and 63.76%; 76.98 and 73.87% and 80.57 and 81.65%, respectively in 4 h as presented in Figure 3a, b. It is well known that reaction rate constant (k) increases with temperature, thus pollutants reductions also increased with temperature.

3.3 Effect of catalyst mass loading

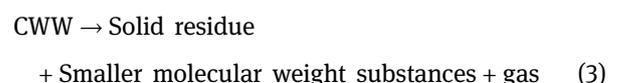
To find the optimum C_w , the pollutants removal were studied in the range of $C_w = 1$ –5 g/L at $T = 140$ °C for 6 h. As the C_w was increased the COD and phenol reduction was also increased up to its saturation point, and then further

increasing on C_w , was not having any remarkable effect on its reduction. Among $C_w = 1$ –5 g/L, 4 g/L was considered as the optimum dose. At $C_w = 1, 2, 3, 4$ and 5 g/L, respectively, the COD reduction were 69.89, 76.98, 78.98, 83.33 and 84.18%, while phenol reductions were 63.98, 69.88, 75.65, 80.57 and 82.88% as presented in Figure 4a, b. Catalyst accelerates the rate of reaction, due to this higher reduction of pollutants were observed at higher catalyst load.

3.4 Kinetics and mechanism

In CT two mechanisms take place simultaneously are thermal and chemical decomposition and complexation. The organic compounds contain large and small molecules which undergo thermo chemical reaction and form insoluble particles, which settle down. Further, the large molecules breakdown into smaller, which are soluble (Chaudhari et al. 2005). The reduction of COD, phenol and cyanide causes due to the formation of insoluble particles and breaking in small molecules. The amount of 0.919, 1.336, 1.361, 1.369 and 1.37 gms of residues were obtained at 100, 120, 140 and 160 °C, respectively.

CT of the CWW thus, can be represented as



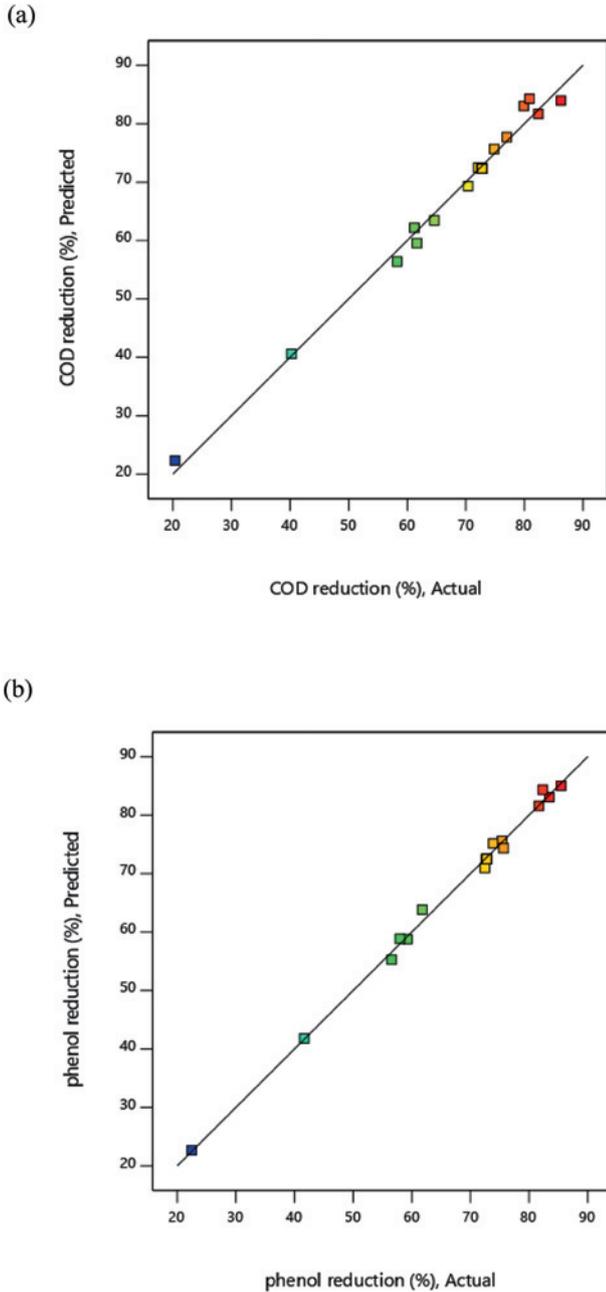
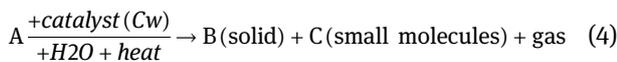


Figure 9: The actual and predicted percentage reduction (a) COD and (b) phenol using HPR process.



The gases formed in small amount thus, it can be neglected.

Rate expression for CT can be written as

$$\frac{-dCA}{dt} = k_c C_A^n C_w^m \quad (5)$$

For constant catalyst load

$$\frac{-dCA}{dt} = k C_A^n \quad (6)$$

$$\text{where, } k = k_c C_w^m \quad (7)$$

Equation (7) can be written as,

$$\ln K = \ln k_c + m \ln C_w \quad (8)$$

All the oxidable organics and inorganics can be lumped into COD, thus, C_A may be taken as COD and phenol. Equation (6) may be written as:

$$\frac{-d(COD)}{dt} = k(COD)^n \quad (9)$$

$$\text{and } \frac{-d(\text{phenol})}{dt} = k(\text{phenol})^n \quad (10)$$

The kinetics in most of the cases for wet air oxidation of organics was found to follow first order for the TOC/COD reduction (Mishra et al. 1995). In a study the thermolysis of sugarcane based distillery was reported to first order with respect to COD (Chaudhari et al. 2008). Equations (9) and (10) can be represented in the form of COD and phenol conversion (X) and for the first order kinetics, it is presented by Equation (11) and Figure 5a, b shows the plot of $-\ln(1 - X_A)$ versus t , which is two step process, first fast followed by slow in second step. Similar, plot for $-\ln(1 - X_A)$ versus t for different C_w are plotted in Figure 6a, b. The rate constant for COD and phenol reduction at different T and C_w are presented in Table 2.

$$-\ln(1 - X_A) = kt \quad (11)$$

The rate constant depends on temperature, and it can be represented by Arrhenius equation as presented in Equation (12).

$$K = k_0 \exp(-E/RT) \quad (12)$$

where, E is activation energy, R is gas constant, k_0 is the frequency factor and T is the temperature, value of E can be determined by plotting $\ln k$ versus $1/T$. The $\ln k$ versus $1/T$ plot is given in Figure 7 which is a straight line relationship. The activation energy were evaluated to 12.18 kJ/mol for fast step and 7.90 kJ/mol for slow step for COD reduction and 15.51 kJ/mol for fast step and 14.63 kJ/mol slow step for phenol degradation reaction. Arrhenius's equation with pseudo first order rate constant indicates that percentage reduction of all the parameters is not controlled by energy

Table 5a: ANOVA regression model for catalytic thermolysis HPR. (a) COD removal.

| Source | Coefficient estimate | Sum of squares | Degree of freedom | Mean square | F value | p value | Remark |
|-----------------|----------------------|----------------|-------------------|-------------|---------|---------|-------------|
| Model | | 4316.42 | 9 | 479.60 | 106.78 | <0.0001 | significant |
| Intercept | 72.32 | | | | | | |
| X1 | 13.32 | 1773.96 | 1 | 1773.96 | 394.95 | <0.0001 | |
| X2 | 12.36 | 1527.94 | 1 | 1527.94 | 340.18 | <0.0001 | |
| X3 | 5.15 | 265.23 | 1 | 265.23 | 59.05 | <0.0001 | |
| X1X2 | -7.20 | 414.86 | 1 | 414.86 | 92.36 | <0.0001 | |
| X1X3 | -2.99 | 71.34 | 1 | 71.34 | 15.88 | 0.0026 | |
| X2X3 | -1.02 | 8.30 | 1 | 8.30 | 1.85 | 0.2038 | |
| X1 ² | -2.60 | 18.53 | 1 | 18.53 | 4.13 | 0.0697 | |
| X2 ² | -0.3959 | 0.4310 | 1 | 0.4310 | 0.0960 | 0.7631 | |
| X3 ² | -4.99 | 68.50 | 1 | 68.50 | 15.25 | 0.0029 | |
| Residual | | 44.92 | 10 | 4.49 | | | |
| Lack of fit | | 44.92 | 5 | 8.98 | | | |
| Pure error | | 0.0000 | 5 | 0.0000 | | | |
| Cor total | | 4361.33 | 19 | | | | |

Table 5b: ANOVA regression model for catalytic thermolysis HPR. (b) Phenol removal.

| Source | Coefficient estimate | Sum of squares | Degree of freedom | Mean square | F value | p value | Remark |
|-----------------|----------------------|----------------|-------------------|-------------|---------|---------|-------------|
| Model | | 4334.28 | 9 | 481.59 | 275.73 | <0.0001 | significant |
| Intercept | 72.50 | | | | | | |
| X1 | 14.53 | 2111.21 | 1 | 2111.21 | 1208.76 | <0.0001 | |
| X2 | 11.38 | 1294.13 | 1 | 1294.13 | 740.95 | <0.0001 | |
| X3 | 5.26 | 276.89 | 1 | 276.89 | 158.53 | <0.0001 | |
| X1X2 | -5.99 | 286.68 | 1 | 286.68 | 164.14 | <0.0001 | |
| X1X3 | -3.62 | 104.62 | 1 | 104.62 | 59.90 | <0.0001 | |
| X2X3 | -0.6813 | 3.71 | 1 | 3.71 | 2.13 | 0.1755 | |
| X1 ² | -2.67 | 19.56 | 1 | 19.56 | 11.20 | 0.0074 | |
| X2 ² | -2.29 | 14.39 | 1 | 14.39 | 8.24 | 0.0167 | |
| X3 ² | -3.40 | 31.74 | 1 | 31.74 | 18.17 | 0.0017 | |
| Residual | | 17.47 | 10 | 1.75 | | | |
| Lack of fit | | 17.47 | 5 | 3.49 | | | |
| Pure error | | 0.0000 | 5 | 0.0000 | | | |
| Cor total | | 4351.74 | 19 | | | | |

barrier (Chen and Huang 2013). The COD, phenol and cyanide all were reduced faster with increasing temperature may be reason for the observed positive effect or due to faster reaching of activation energy (Ogutveren et al. 1999; Oulego et al. 2014). In chemical process much degradation/ consumption of substances take place, because reaction rate constant k increases with time. When temperature is increased, the collision between molecules and catalyst increases with higher rate due to this rate of degradation increases (Ogutveren et al. 1999).

Effect of C_w on k was studied at 140 °C, and its kinetics are presented in Figure 6a, b for COD and phenol reduction. Plot between $\ln k$ versus $\ln C_w$ of equation is presented in

Figure 8 gives the order of reaction with respect to C_w . For COD reduction $m = 0.308$ in first step and 0.240 in second step, and for phenol reduction $m = 0.608$ in first step and 0.453 in second step is evaluated. The values of reaction rate constant for COD and phenol reduction at different C_w (at $T = 100$ °C) is presented in Table 2. From the data it can be analysed that as the C_w increases, k also increases.

3.5 Response surface methodology optimization

RSM was performed for the optimization of COD and phenol removal efficiency. The experiments were designed

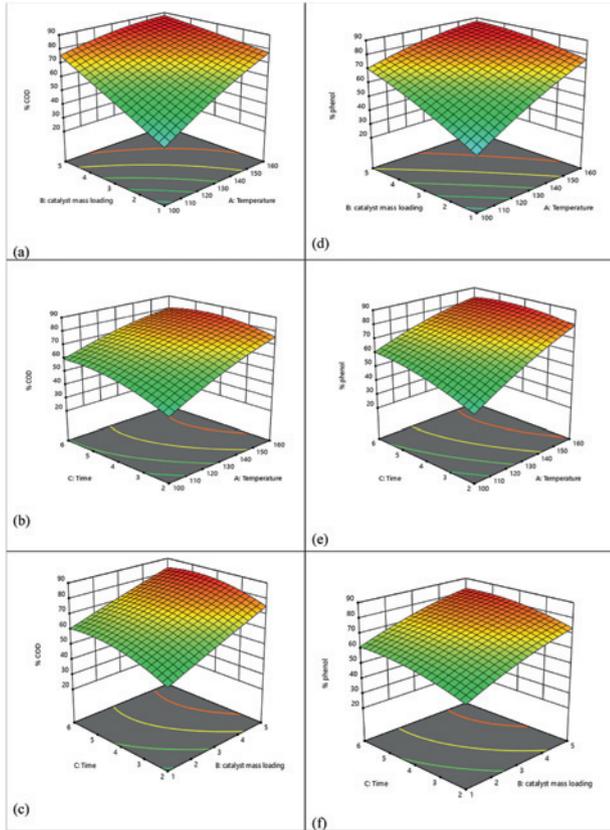


Figure 10: Three dimensional (3D) response surface graphs of COD reduction (a, b, c) and phenol reduction (d, e, f) for HPR process.

using CCD which is one of the most efficient designs for three factors with eight cube points, six central points in cube and six axial points. For statistical analysis three independent variables were coded as X1 (T), X2 (t_R), X3 (C_w) for CT and X1 (pH), X2 (A_w), X3 (t_R) for adsorption are presented in Tables 3 and 6 including its level and ranges (Draper et al. 1988). For CT the CCD was used for designing of experiment by MINITAB version 17.1.0.0. Total 20 experimental runs were designed using three independent variables are presented in Table 4. It also contained the actual (experimental) and predicted COD and phenol reductions, calculated by using quadratic Equations (13) and (14) generated by RSM. The three dimensional plot for COD and phenol removal are presented in Figure 9.

$$\begin{aligned} \% \text{COD reduction} = & -159.58 + 1.753 X_1 + 23.395 X_2 \\ & + 19.791 X_3 - 0.0028 X_1X_1 \\ & - 0.0989 X_2X_2 - 1.247 X_3X_3 \\ & - 0.120 X_1X_2 - 0.049 X_1X_3 \\ & - 0.254 X_2X_3 \end{aligned} \tag{13}$$

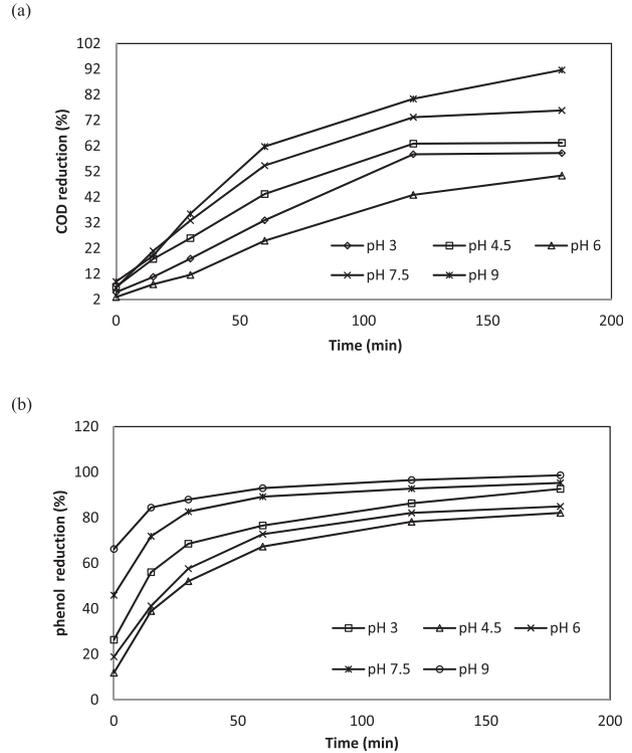


Figure 11: Effect of pH on (a) COD and (b) phenol removal by adsorption process. Adsorbent dosage = 4 g/L, T = 30 °C, t_R = 2 h, COD_i = 610 mg/L, Phenol_i = 70.58 mg/L.

$$\begin{aligned} \% \text{Phenol reduction} = & -159.17 + 1.795 X_1 + 22.77 X_2 \\ & + 17.77 X_3 - 0.0029 X_1X_1 \\ & - 0.5718 X_2X_2 - 0.8439 X_3X_3 \\ & - 0.099 X_1X_2 - 0.060 X_1X_3 \\ & - 0.170X_2X_3 \end{aligned} \tag{14}$$

Analysis of variance (ANOVA) was used to fit the model Equations (13) and (14) for statistical significance. It contains mathematical terms like degree of freedom, mean square, sum of square, R², R²(adj), R²(pred), p (probability) value, F (Fischer’s) value and so on. Model significance are analysed by the values of F and p. F value is a Fischer’s value which must be larger for better fit of the model to the experimental response data, and p value is a probability of independent variable response on the dependent variables which value should be low. Large F (>1) and low p (<0.05) indicates better fit of the model to the experimental data. R² is explained as the degree of fitness of model with the experimental data it lies between 0 and 1. Higher value of R² is important, and the values of R² adjusted (adj) and R²

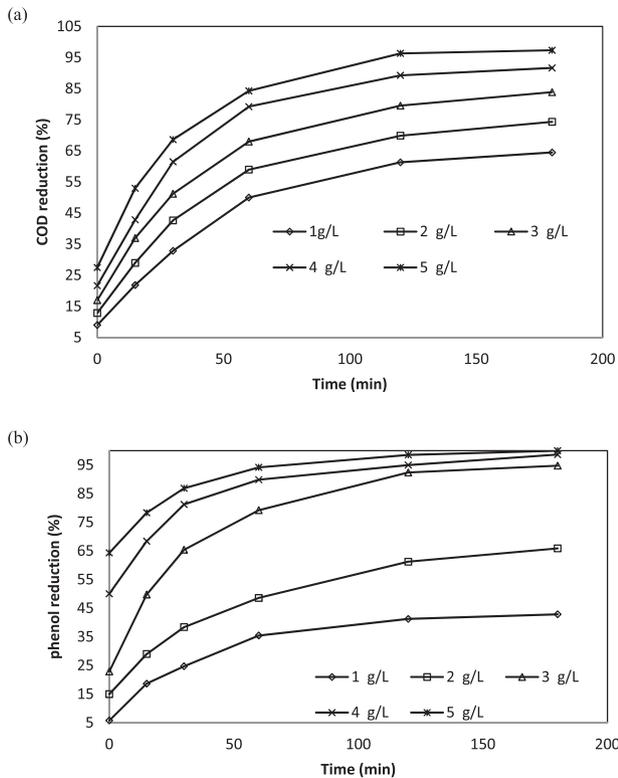


Figure 12: Effect of adsorbents dose on (a) COD and (b) phenol removal by adsorption process. $T = 30\text{ }^\circ\text{C}$, $t_R = 2\text{ h}$, $\text{COD}_i = 610\text{ mg/L}$, $\text{Phenol}_i = 70.58\text{ mg/L}$.

predicated (pred) has smaller than R^2 and nearby values are better.

The ANOVA gave overall F and p value for COD reduction to 106.78 and 0.000, and 275.73 and 0.000 for phenol reduction are presented in Table 5(a) for COD reduction and 5(b) for phenol reduction. The higher value of F and lower low of p suggest the better fit of the model as presented in Figure 10. R^2 values of 0.989 for COD and 0.996 for phenol and $\text{adj } R^2 = 0.980$ for COD and 0.992 for phenol reduction shows the high significance of the models obtained. The predicated R^2 values for both COD and phenol reduction are 0.901 and 0.964, respectively. The R^2 , pred R^2 and $\text{adj } R^2$ are close to each other suggest the high significance and good agreement to experimental and predicted values.

Table 6: Experimental range for independent variables of HPR followed by adsorption for CWW.

| Independent variables | Factors | Range and levels | | |
|-----------------------------|---------|------------------|------|-----|
| | | X_i | -1 | 0 |
| pH | X1 | 3 | 6 | 9 |
| Time (min) | X2 | 15 | 97.5 | 180 |
| Catalyst mass loading (g/L) | X3 | 1 | 3 | 5 |

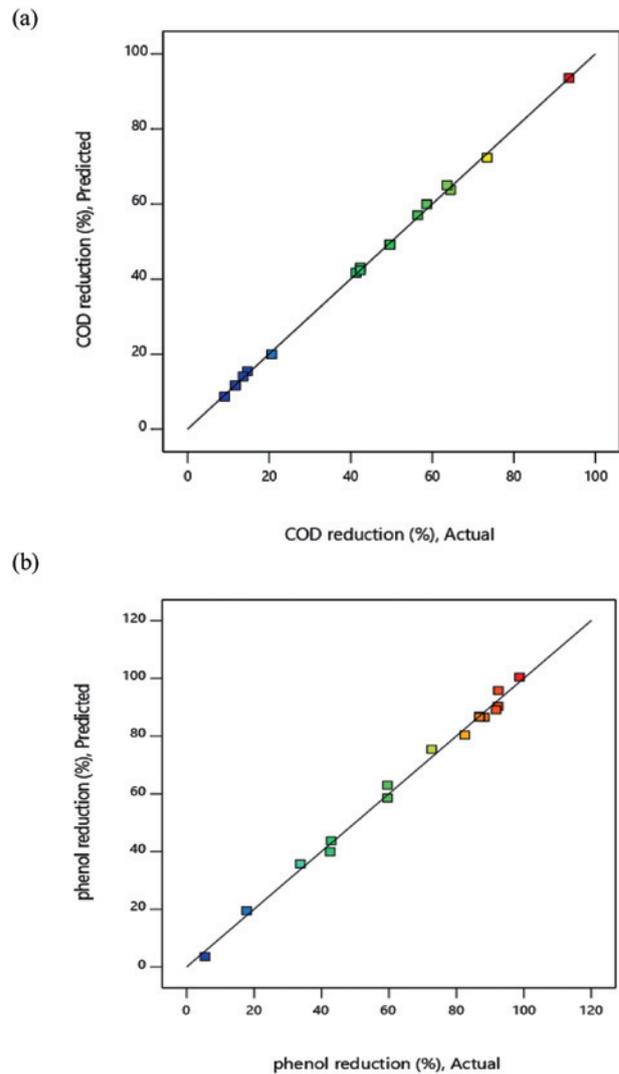


Figure 13: The actual and predicted percentage reduction (a) COD and (b) phenol using HPR followed by adsorption process.

Through the RSM, the optimum condition obtained after examine the response curve and contour plots are $T = 155.62\text{ }^\circ\text{C}$, $C_w = 4.99\text{ g/L}$ and $t_R = 4.75\text{ h}$. At this operating condition, $\text{COD} = 87.48\%$ and $\text{phenol} = 87.01\%$ reduction are achieved.

4 Adsorption as second step treatment process

Adsorption is an effective and commercial process for the reduction of pollutants contained in wastewater. It is a surface phenomenon with having high surface area of various adsorbents available for adsorption. Activated charcoal is mostly used for the removal of pollutants (Rafatullah et al. 2010; Burmistrz et al. 2014). Other

Table 7: RSM optimization of COD and phenol for CWW using HPR followed by adsorption.

| Run order | X1 | X2 | X3 | %COD observed | %COD predicted | %Phenol observed | %Phenol predicted |
|-----------|----|-------|----|---------------|----------------|------------------|-------------------|
| 1 | 9 | 15.0 | 1 | 14.71 | 15.45 | 17.81 | 19.46 |
| 2 | 9 | 15.0 | 5 | 20.66 | 19.96 | 82.51 | 80.36 |
| 3 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |
| 4 | 3 | 15.0 | 1 | 9.11 | 8.72 | 5.43 | 3.57 |
| 5 | 3 | 180.0 | 1 | 41.32 | 41.68 | 33.73 | 35.69 |
| 6 | 9 | 180.0 | 5 | 97.33 | 98.87 | 98.76 | 100.00 |
| 7 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |
| 8 | 6 | 97.5 | 1 | 42.36 | 42.36 | 42.54 | 39.93 |
| 9 | 3 | 15.0 | 5 | 13.67 | 14.07 | 59.59 | 58.55 |
| 10 | 6 | 15.0 | 3 | 11.76 | 11.69 | 59.59 | 62.99 |
| 11 | 9 | 97.5 | 3 | 56.42 | 57.04 | 92.38 | 90.34 |
| 12 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |
| 13 | 3 | 97.5 | 3 | 42.36 | 43.05 | 72.65 | 75.43 |
| 14 | 3 | 180.0 | 5 | 73.45 | 72.37 | 88.33 | 86.50 |
| 15 | 9 | 180.0 | 1 | 64.50 | 63.76 | 42.85 | 43.71 |
| 16 | 6 | 180.0 | 3 | 63.62 | 65.00 | 91.76 | 89.09 |
| 17 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |
| 18 | 6 | 97.5 | 5 | 58.64 | 59.95 | 92.43 | 95.78 |
| 19 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |
| 20 | 6 | 97.5 | 3 | 49.62 | 49.17 | 86.87 | 86.62 |

adsorbent like silica gels, zeolite, coke dust, resins, lignite and bottom ash have been also reported for removal of harmful pollutants from wastewater (Tyagi and Srivastava 1995; Gupta 1998). In the present study, the CWW treated by CT was further treated by adsorption using activated carbon.

4.1 Effect of pH

Effect of pH was studied on COD and phenol removals are shown in Figure 11a, b. A pH of 3, 4.5, 6, 7.5 and 9, respectively, 59.23, 63.22, 50.43, 75.87 and 91.66% COD removal, and

92.65, 82.11, 84.97, 95.28 and 98.65% phenol removal obtained from initial COD value of 610 mg/L and phenol value of 70.58 mg/L. The removal efficiency of phenol was moderately affected by pH, due to its neutral charge.

4.2 Effect of adsorbent dosage

Effect of adsorbent dosage was studied by varying activated carbon dosage from 1–5 g/L. The results are presented in Figure 12a, b. As the adsorbent dosage was increased the reduction of pollutants were also increased,

Table 8a: ANOVA regression model for adsorption. (a) COD removal.

| Source | Coefficient estimate | Sum of squares | Degree of freedom | Mean square | F value | p value | Remark |
|-----------------|----------------------|----------------|-------------------|-------------|---------|---------|-------------|
| Model | | 9239.35 | 9 | 1026.59 | 1153.78 | <0.0001 | significant |
| Intercept | 49.18 | | | | | | |
| X1 | 6.99 | 488.88 | 1 | 488.88 | 549.45 | <0.0001 | |
| X2 | 26.65 | 7103.29 | 1 | 7103.29 | 7983.32 | <0.0001 | |
| X3 | 8.80 | 773.70 | 1 | 773.70 | 869.55 | <0.0001 | |
| X1X2 | 3.83 | 117.66 | 1 | 117.66 | 132.23 | <0.0001 | |
| X1X3 | -0.2125 | 0.3612 | 1 | 0.3612 | 0.4060 | 0.5383 | |
| X2X3 | 6.33 | 320.80 | 1 | 320.80 | 360.55 | <0.0001 | |
| X1 ² | 0.8718 | 2.09 | 1 | 2.09 | 2.35 | 0.1564 | |
| X2 ² | -10.83 | 322.44 | 1 | 322.44 | 362.38 | <0.0001 | |
| X3 ² | 1.98 | 10.80 | 1 | 10.80 | 12.14 | 0.0059 | |
| Residual | | 8.90 | 10 | 0.8898 | | | |
| Lack of fit | | 8.90 | 5 | 1.78 | | | |
| Pure error | | 0.0000 | 5 | 0.0000 | | | |
| Cor total | | 9248.24 | 19 | | | | |

Table 8b: ANOVA regression model for adsorption. (b) phenol removal.

| Source | Coefficient estimate | Sum of squares | Degree of freedom | Mean square | F value | p value | Remark |
|-----------------|----------------------|----------------|-------------------|-------------|---------|---------|-------------|
| Model | | 14,356.45 | 9 | 1595.16 | 222.71 | <0.0001 | significant |
| Intercept | 86.62 | | | | | | |
| X1 | 7.46 | 556.22 | 1 | 556.22 | 77.66 | <0.0001 | |
| X2 | 13.05 | 1703.03 | 1 | 1703.03 | 237.77 | <0.0001 | |
| X3 | 27.93 | 7798.61 | 1 | 7798.61 | 1088.81 | <0.0001 | |
| X1X2 | -1.97 | 31.01 | 1 | 31.01 | 4.33 | 0.0641 | |
| X1X3 | 1.48 | 17.55 | 1 | 17.55 | 2.45 | 0.1485 | |
| X2X3 | -1.04 | 8.72 | 1 | 8.72 | 1.22 | 0.2958 | |
| X1 ² | -3.74 | 38.47 | 1 | 38.47 | 5.37 | 0.0430 | |
| X2 ² | -10.58 | 307.83 | 1 | 307.83 | 42.98 | <0.0001 | |
| X3 ² | -18.77 | 968.86 | 1 | 968.86 | 135.27 | <0.0001 | |
| Residual | | 71.63 | 10 | 7.16 | | | |
| Lack of fit | | 71.63 | 5 | 14.33 | | | |
| Pure error | | 0.0000 | 5 | 0.0000 | | | |
| Cor total | | 14,428.08 | 19 | | | | |

but after reaching its saturation, there was slightly changes occurred in the removal when dosages were further increased. At $A_w = 1, 2, 3, 4$ and 5 g/L respectively, the 64.50, 74.32, 83.87, 91.66 and 98.66% COD removal and 42.85, 65.87, 94.61, 98.65 and 100.00% phenol removal obtained. At $A_w = 5$ g/L complete removal of phenol was

noted, however at 4 g/L 98.65% phenol and 91.66% COD removal obtained looks like to optimum dosage.

4.3 RSM studies

RSM studies were also carried out for adsorption process like CT. Three independent variables were A_w , pH_i and t_R as shown in Table 6. The statistical analysis and modelling were performed using these three variables. Total 20 experimental runs were designed for RSM studies. The actual and predicated removal of COD and phenol were calculated by quadratic models Equations (15) and (16) are presented in Figure 13 and Table 7. ANOVA regression model for COD and phenol are reported in Table 8a, b.

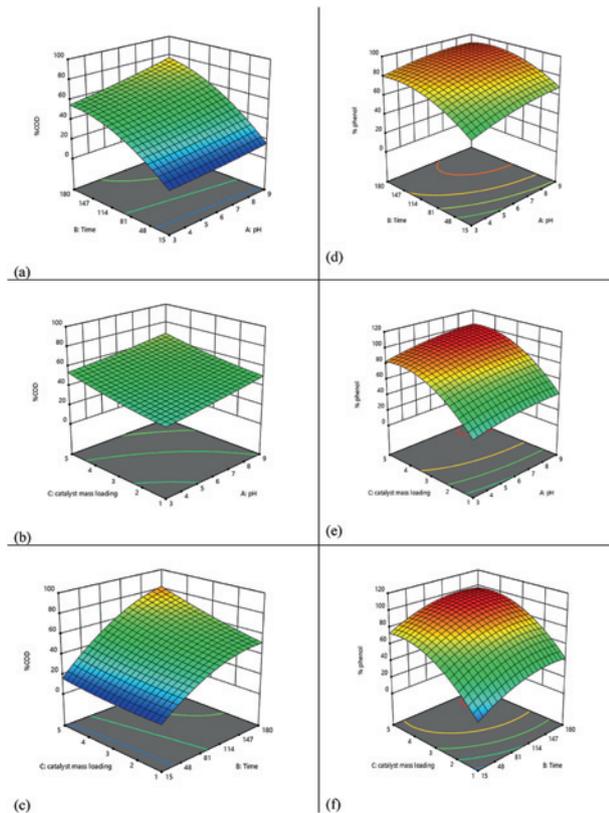


Figure 14: Three dimensional (3D) response surface graphs of COD reduction (a, b, c) and phenol reduction (d, e, f) for adsorption process.

$$\begin{aligned}
 \% \text{ COD removal} = & -26.72 + 2.99 X_1 + 0.4425 X_2 \\
 & + 24.81 X_3 - 0.104 X_1X_1 \\
 & - 0.002187 X_2X_2 - 1.734 X_3X_3 \\
 & + 0.02727 X_1X_2 - 0.869 X_1X_3 \\
 & + 0.01364 X_2X_3 \quad (15)
 \end{aligned}$$

$$\begin{aligned}
 \% \text{ phenol removal} = & -42.78 + 14.642 X_1 + 0.3524 X_2 \\
 & + 18.911 X_3 - 0.6503 X_1X_1 \\
 & - 0.000932 X_2X_2 - 0.562 X_3X_3 \\
 & + 0.00976 X_1X_2 - 1.4867 X_1X_3 \\
 & + 0.00002 X_2X_3 \quad (16)
 \end{aligned}$$

F value of 1153.78 and p value of 0.000 for COD removal and 222.71 and 0.000 for phenol removal are evaluated and

presented in Table 8a, b. Figure 14 shows the 3D response of percentage COD removal and phenol reduction. The experimental results were very well fitted to model, with high R^2 values 0.999 for COD and 0.995 for phenol removal obtained. The (adj R^2) = 0.998 and 0.990, and the (pred R^2) = 0.989 and 0.950 are evaluated for COD and phenol removal, respectively. This shows very high correlation values between the observed and the predicted values.

Interaction between the independent variables can be also understood from ANOVA presented in Table 8a, b. The p value for interaction between pH and t_R is <0.0001 , pH and A_w is 0.538, and t_R and A_w is <0.0001 . It shows that interaction between pH and t_R , and t_R and A_w are significant for COD removal. Similarly, the p values for phenol reductions are 0.064 for pH and t_R , 0.148 for pH and A_w and 0.295 for t_R and A_w . Here, interaction between pH and t_R are more significant to others.

In RSM studies, the optimum operating conditions evaluated are pH = 8.99, t_R = 179.89 min and C_w = 4.99 g/L, at which COD removal = 98.87% and phenol removal = 100.00% achieved at respectively.

5 Conclusions

The CT followed by adsorption process gave significant reduction of pollutants present in CWW. Among various catalysts cupric nitrate gave best performance with maximum percentage reduction of COD, phenol and cyanide to 87.48, 87.01 and 97.61%, respectively at optimum operating condition of $T = 155.62$ °C, $C_w = 4.99$ g/L and $t_R = 4.75$ h. The CWW treated by CT was further treated by adsorption process in which COD, phenol and cyanide were further reduced to 98.66, 100.00 and 55.55% from initial value of COD = 610 mg/L, phenol = 70.58 mg/L and cyanide = 0.45 mg/L. The model developed by RSM studies showed its significance as experimental and predicted value are very close to each other. The kinetic studies of CT showed COD and phenol reduction to first order two step process with respect to pollutants COD and phenol and fractional order (0.24–0.608) with respect to C_w . After two step the treated CWW has COD = 8 mg/L, phenol = 0.00 mg/L and cyanide = 0.2 mg/L. The treated effluent can be used for various purposes where fresh water is required or recycled for quenching hot coke and for cooling purposes in the same plant. Thus, there will be zero discharge of effluent.

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Nomenclature

| | |
|--------|---|
| COD | Chemical oxygen demand, (kg/m ³) |
| C_A | Concentration of organic matter expressed as COD, phenol (kg/m ³) |
| C_0 | Initial concentration of organic matter in the effluent expressed as COD, phenol (kg/m ³) |
| C_w | Catalyst mass loading, (kg/m ³) |
| E | Apparent activation energy, (kJ/mol) |
| k | Specific first-order reaction rate constant, (min ⁻¹) |
| k_1 | First-order reaction rate constant for fast thermolysis step, (min ⁻¹) |
| k_2 | First-order reaction rate constant for slow thermolysis step, (min ⁻¹) |
| k_c | Specific nth order reaction rate constant, (mol ¹⁻ⁿ m ³ⁿ min ⁻¹) |
| m | Order with respect to catalyst mass loading |
| n | Order with respect to organic matter concentration, COD and phenol |
| P | Self (autogenous) pressure |
| pH_0 | Initial pH |
| R | Universal gas constant, 8.314 J/(mole K) ⁻¹ |
| t_R | Treatment time, min, h |
| X_A | Conversion of organic matter = $1 - (COD) = (COD)_0$ |

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