A comparison of Al-Fe pillared Iraqi clays for Catalytic wet air oxidation

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Abstract. Five types of Al-Fe pillared Iraqi clays have been selected depending on a natural clays regions (Anbar- Mosul- Basra- Baghdad- and Erbil) have been used in preparation it, and tested for catalytic wet air oxidation (CWAO) using phenol as target compound at different parameters (temperature, pressure, phenol loading, catalyst loading). The Al-Fe pillared of Anbar- Mosul –and Erbil clay showed a higher activity than Baghdad and Basra for phenol oxidation in Batch reactor. After 8 days continues test for activating AL-Fe PC in PBR, Deactivation appears on catalyst of Anbar in different temperature, but in Erbil with increase temperature, Mosul catalyst has higher activity than other catalyst. Mosul catalyst has higher stability than Erbil and Anbar in blocking of surface area, Leaching Fe was negligible, Fairly different values of apparent activation energy were obtained for this reaction with these five types of catalysts, suggesting that the prevailing pathway in air decomposition is different. From all above discussion, Mosul catalyst in considered the best catalyst.

1. Introduction
Quantities of water is used in industrial processes, which discharged to surface water system before treatment [1], some Organic pollutant load in aqueous wastewaters are toxic [2], such as phenol, polyphenol, and BTEX (benzene, toluene, ethylbenzene, 1, 2-dichlorobenzene, o-, m-, p-xylene) [ 3], Phenol one of these pollutant is awful odor and taste to water, even at concentration in the parts per billion (ppb)[ 4], it is present in the effluent from major chemical and pharmaceutical industries, such as petrochemical industries, petroleum refineries, cool gasification operation, liquefaction process, resin manufacturing industries, dye synthesis units, paper mills [5], some level of phenol has an effect on human, organisms, and water, (10-24mg/l) the level of phenol has an effect on human, (150mg/100ml) that level has an effect on lethal blood [6], also effect on organism, (9-25mg/l) influence on fish [6], and as standard of Environment Product Agency (EPA) for drinking water 0.5μg/l [7], and for surface water less than 1 part per billion (ppb)[8].

Treatment for toxic effluents wastewater by biological process may not be suitable so that, continuous efforts is required to remove phenol from wastewater in order to reduce treatment cost [9], some of these treatments steam distillation [10] Separation by extraction [11] [6], Separation by adsorption [12], Separation by membrane [13], electrochemical oxidation [14], Biochemical abatement [15], Incineration, and advance treatment. (WAO) wet air oxidation is a method for oxide to organic compound with oxygen or air under high temperature and pressure, catalyst wet air oxidation process (CWAO), can speed the reaction temperature and pressure, the organic compound can be partly converted to less toxic intermediate or complete converted to CO₂, and H₂O (16). Two types of solids
have been employed to catalyst for oxidation organic compound in wastewater, metal and noble metal oxide, the later have expansively used as active compounds (17), many advantages from combining two or more metal oxide catalysts, that improved selectivity, activity, and increasing rate of process, to increase the efficiency or process of wet oxidation, which has been modified or used suitable combination of process (18), Sugunan, 2002 [19], show that mixed Fe with Al in different ratio, the Fe –Al0.5 that the best ratio to converted benzoyl chloride.

Also Bankovi, 2009 [20] mixed different contains of Fe with clay shows the composition texture and morphological properties different only in Fe contain according to the Fe amount of Fe added to clay. The CWAO for wastewater carried out in batch or fixed bed reactor to choose the suitable reactor, according to process of selectivity and stability (21). To understand the CWAO process through laws that describe the establishment of both reaction pathway during the oxidation reactions, and design of CWAO units, its important is to correct and safety design chemical reactors [22], [23], because in this reactor the reaction complete conversion to CO2 and H2O [26], apparent kinetic model usually favored for industrial researchers for scale-up of commercial reactor [24]. The oxidation of organic compound in three phase catalytic reactions, gas, liquid phase reactants are in contact with the solid phase [27], when the gas dissolved in liquid phase and diffusion in the bulk of the liquid, it is a physical state, where in the chemical state, both gaseous and liquid phase reactants diffuse into the porous structure of the catalyst and react with active sites, the products diffuse out of the particle in opposite direction [28].

The goal of this research is selecting the five types of Al-Fe pillared Iraqi clay according to Iraqi regions to study the wet air oxidation for phenol degradation from synthesis wastewater and to evaluate the catalyst as activity and stability and to choose the best one.

2. Materials and Methods

2.1 Pillared clay characteristics

Five types of (extrudates 2*8 mm) AL-Fe pillared clays selected according to clays regions (Erbil, Baghdad Anbar- Basra- and Mosul) have been brought to study physicochemical properties, by (XRD) X-ray diffraction, (XRF) X-ray Florescent and BET (Blumauer Emmer Teller) to determinate the surface area.

2.2 CWAO Experiments

The experimental work for phenol degradation by CWAO with different pillared clays were performed in a Basket stirred tank reactor (BSTR), the reactor consists of equipment shown in Figure (1), The experimental work procedure of (BSTR) is shown in Figure 2.

The filtered samples were analyzed by Germany High Performance Liquid Chromatography (HPLC) YL 9100 HPLC System, YL 9101 Vacuum Degasser. And YL 9110 Quaternary pump, YL 9120 UV/Vis Detector with C18 column. A mobile phase H2SO4 of variable composition was programmed at a 1.2 ml/min flow rate. The wave length between 450-550λ detected phenol and low molecular weight Intermediates compound. The (UV –VV-1100, UEBO9025) Spectrophotometer was used to detect phenol concentration. The total organic carbon (TOC) has been measured by Shimadzu TOC-LCSH/CSN Standalone Model TOC analyzer. Residual Fe concentration in the reaction media was also analyzed by Atomic Absorption.
Figure 1. Diagram of the experimental setup of (BSTR)

Figure 2: Diagram of the procedure of experimental work in (BSTR)

2.3 Stability experiments

The experiments of catalyst stability for CWAO of phenol in packed bed reactor with Al-Fe pillared clays for Anbar, Erbil, Mosul regions, the reactor system consist as in Figure (3),

Figure 3. Diagram of the experimental setup of (PBR)
The experimental work was done with different gas superficial velocity between (0.2-0.8 cm/s) and liquid superficial velocity between (0.2-0.8 hr⁻¹) as stated by AL Dahhan (2005) [29] to keep the flow regime in bubble flow. The 500 gm of phenol has been diluted with distilled water to be used as synthesis's wastewater, as ideal wastewater, which recommend (500-1500mg/l) concentration of phenol in typical wastewaters from oil refineries of phenol mixed. The synthesis's wastewater pumped from fed tank to the reactor, in the limited velocity to wetted the catalyst, with Controlled the pressure to limit (3.2 Mpa), than the temperature raised to 150ºC, the pressure and temperature should be controlled along the space time, when the air mixed with liquid after the needle valves, The liquid and gas mixed and preheated in the inert zone before entering the reactor from the bottom through a distributor, when arrived to steady state in 3.2Mpa, 150Cº and in desired (gas, liquid superficial velocity), the liquid cooled in exchanger, and it will be collected in separator to turn off the sign and the liquid is drained after 8 hr till 8 day, samples of liquid collected filtered in micro nylon filter and stored in freezer to time of test, to study phenol and intermediate phenol. Some Instruments perversely used to measure the phenol, intermediate, and TOC.

3. Results and Discussion

Result of physicochemical characteristics of crystalline structure for Al-Fe pillared (Erbil, Baghdad Anbar- Basra- and Mosul) by XRD at 20 between (0-70), show 3 peaks of 2θ appeared between 20 to 27, observed in Figure (4). From XRF the result of concentration iron, aluminum and calcium oxides has been shown in Table (1), Basra has the highest concentration of Fe₂O₃, while Baghdad have highest value of Al₂O₃.

![Figure 4. XRD result for Al -Fe pillared clay for Erbil, Mosul, Anbar, Baghdad, Basra](image)

| Ratio       | Anbar catalyst | Mosul catalyst | Baghdad catalyst | Basra catalyst | Erbil catalyst |
|-------------|----------------|----------------|------------------|---------------|---------------|
| %SiO₂  | 20.26          | 32.35          | 39.04            | 28.7          | 55.36         |
| Fe₂O₃%   | 7.98           | 9.82           | 7.8              | 14.81         | 9.6           |
| Al₂O₃%   | 15.37          | 14.35          | 29.49            | 21.73         | 23.4          |
| CaO%      | 21.44          | 11.3           | 5.21             | 9.28          | 6.51          |
The Result of BET has been shown in Table (2), that is to say that the higher surface area for Erbil pillared clay than Anbar, Mosul, Basra and Baghdad respectively, as well as the pore volume and pore size, according to the International Union of Pure and Applied Chemistry (IUPAC) classification of pore size (Å) as macropore (≥ 500), mesopore (20 to 500) supermicropore (7-20) and ultramicropore (≤ 7) [30]. From the results, obtained Baghdad has the highest value of pore size width 150.4 Å, but Basra has the lowest value 75.1 Å, all regions are mesopore size [31].

| Samples Region   | (BET) Surface area (m²/g) | Average Pore volume (m³/g) | Pore size width (Å) |
|------------------|--------------------------|----------------------------|---------------------|
| Anbar Catalyst   | 97.815                   | 0.0962                     | 78.4                |
| Erbil Catalyst   | 100.74                   | 0.1221                     | 124.2               |
| Baghdad Catalyst | 56.973                   | 0.0907                     | 150.4               |
| Mosul Catalyst   | 93.605                   | 0.1430                     | 89.7                |
| Basra Catalyst   | 61.371                   | 0.1109                     | 75.1                |

### 3.1 Effect of Parameters

#### 3.1.1 Effect of Temperature

Figure (5) shows the result of TOC conversion with different temperature for all catalyst types, the higher TOC conversion for Anbar catalyst reach to 88% than Erbil 79.28%, Mosul 78.2%, Baghdad 66.5%, and Basra 66.46%. The phenol conversion has been shown in Figures (6). The result shows phenol conversion increase with increase temperature with another conditions were constant, the results reveal that a temperature of 150ºC is necessary to obtain an appreciable phenol conversion along the process. The reaction rate is increasing gradually with time and more influence on the reaction rate is at a temperature of 150ºC, Erbil has high value of phenol degradation rate then Mosul, Anbar, Baghdad, and Basra respectively. The highest rate of reaction phenol, from the result phenol conversion is 96.2, 95.44, 93.7, 80, 76.3% for Erbil, Mosul, Anbar, Baghdad, Basra, respectively.

![Figure 5. TOC conversion during 4hr in catalyst loading 7mg/l, pressure 2.5Mpa, 500mg/l phenol concentration, for all regions.](image)

![Figure 6. Phenol conversion during 4hr in catalyst loading 7mg/l, pressure 2.5Mpa, 500mg/l phenol concentration for all regions.](image)

#### 3.1.2 Effect of pH

Figure (7) shows phenol conversion profiles for reaction tests carried out with an initial air concentration. Initial pH of 3.9 and (5.48) and temperature 110ºC to 130ºC, the later corresponds to the natural pH of the wastewater. Without pH adjustment, phenol conversion curves show a sigmoidal profile, which is
typical of radical reactions. Also from the figure show an increase in the decomposition rate when the pH is 3.9, while this rate is less at pH of 5.48 for all regions. Because pH values between 3 and 4 led to the least decomposition of air and higher amounts of available hydroxyl radicals in the solution [32]. The degradation rate in Anbar is higher than that in the rest of the regions, followed by Mosul, Erbil, Baghdad, and Basra, respectively as a result of the nature clay (pore size and surface area) of the pillared clay (catalyst). Figure (8) shows TOC conversion profiles for reaction tests for all catalyst regions.

3.1.3 Effect of Phenol Concentration

The result of phenol conversion is presented in Figure (9) for five regions. It is known that during the CWO of phenol, polymeric compounds can be formed and promoted by acidic sites on the catalyst, which can adsorb at the surface of the catalyst and decrease its activity [33]. Baghdad pillared clay has higher value of degradation, then Mosul, Anbar, Erbil, and Basra. The lower phenol conversion result shows that with high initial phenol concentration of 2000 mg/l, the pillared clay remained active in some region and complete mineralization after 4hr, while in another region uncompleted as Anbar catalyst. Deactivation appears on the surface of pillared clay during the CWO of phenol, the high conversion of TOC is shown in the Figure (10).

3.1.4 The Air Pressure Effect

Figure (11) shows the effect of pressure (0.8-2.0 -3.5Mpa) on phenol conversion at constant temperature 130°C for all catalyst regions. For all regions the high oxidation of phenol at 3.5 Mpa when equilibrium vapor pressure is 0.25Mpa in 130°C. From these figures, the highest phenol conversion was for AL Mosul, Anbar, Erbil, Basra, and Baghdad respectively, while Figure (12) shows the TOC conversion for
all catalyst region. As a result, the highest conversion TOC was in AL Anbar, then Mosul, Erbil, Basra, and Baghdad because these catalyst different in pore size and surface area, so that the result of Anbar, Erbil, and Mosul convergent. The applied air pressure exceeded the vapor pressure of the liquid phase at a given temperature, so that the wet air oxidation was kept in the liquid phase. Corresponding to the temperature range of 90-150°C, the value of equilibrium vapor pressure is from 0.1 to 0.45 MPa [34]. The oxygen is capable to oxide the phenol and substitute oxygen atom an aromatic ring to be quinine or dihydric phenol, and also capable to attract t phenol double bond of Carbone to form carboxylic acid, that represents the very low concentration in aqueous phase.

3.1.5 Effect of Catalyst Loading

The different catalyst loading (0-5-8-10mg/l) investigated in this work for oxide phenol at 110°C and 1.5 Mpa, are shown in Figure (13) as conversion of phenol degradation during 4hr of reaction, From these results, it can be noted that unanalyzed lead (zero catalyst) is gradually increased in phenol concentration removal during 4hr, but considerably less than other value of catalyst loading. As a result, the air or oxygen is not significant on homogenous reaction but has an effect on heterogeneous reaction to oxidation of phenol. During the heterogeneous reaction, the phenol oxidation on active site of catalyst increases the acidity of solution. But for all types of catalysts the deactivation is not significant in these experiments. As a result, it has been noted that the best catalyst load were found in Anbar and Basra (8mg/l) then Mosul (10mg/l). Figures (14) shows the TOC conversion.

The results show that Anbar- Erbil- and Mosul have higher phenol conversion > 90% than other catalyst regions, so that these catalyst used in experimental of packed bed reactor determine the flow regime and to study the stability.

The aromatic intermediates evolve to carboxylic acids, the Hydroquinone, Malonic acid, Formic acid,
Malic acid, Oxalic acid, Acetic acid are intermediate of phenol for Anbar catalyst, and the Hydroquinone is higher concentration of phenol intermediate, while Malic acid is lowest concentration. The three intermediate phenol (Hydroquinone, Formic acid, and Oxalic acid) are appeared for Mosul catalyst, hydroquinone has higher concentration, while formic acid is lowest concentration. The intermediate for Erbil, Baghdad and Basra the two intermediate phenol formic acid and oxalic acid are appeared, the oxalic acid has higher concentration than formic acid.

The result of experimental hydrodynamic was done in packed bed reactor with different gas-liquid superficial velocity shows in the Figure (15) for different gas superficial velocity, but Figure (16) for different gas superficial velocity, from the result the suitable condition (0.2hr⁻¹) for liquid superficial velocity, (0.6 cm/s) for gas superficial velocity, these conditions keep the flow in bubble regime, in that regime the efficient wet is 100%, that refer to the reaction in liquid phase.

From the Leaching Fe test in batch reactor, the result was negligible along the reaction time, which required for practically complete phenol conversion, all result in part per billion. Deactivation appears on samples of Anbar in different temperature as shown in Figure (17), while Erbil Deactivation appear in high temperature as shown in Figure (18), Figure (19) shows result of leaching Fe for Mosul catalyst.

![Figure 15. phenol conversion at different LHSV (Pressure= 3.2 MPa, phenol=500 ppm, and u_G=0.28 cm/s).](image1)

![Figure 16. Effect of gas velocity on phenol conversion at LHSV=0.6hr⁻¹.](image2)

![Figure 17. deactivation in Anbar catalyst during phenol oxidation in Batch reactor](image3)

![Figure 18. deactivation in Erbil catalyst during phenol oxidation in Batch reactor](image4)
The above result shows that Anbar, Mosul and Erbil catalyst have the highest surface area, pore volume in mesoporous and have higher removal of phenol than Baghdad and Basra catalyst.

The three active catalyst (Anbar, Mosul, and Erbil) used to study activity and stability in PBR, from result the Mosul catalyst has highest conversion of phenol reach to (98.7%) at stable condition, LHSV equal to 0.6hr⁻¹ and gas superficial velocity equal to 0.2 cm/s. In the same condition the higher conversion of phenol for Anbar catalyst reach to (98%), while Erbil catalyst shows the higher conversion of phenol reach to (96.7%), that indicate two these catalysts have high activity.

The physical blocking on active sites of catalyst during operation time (192 hr) was observed through the data collection in different operation condition. The physical blocking on active sites not consider in PBR operation of Erbil and Mosul catalyst for phenol removal, due to low leaching Fe value so that these catalyst can be continuously operated, but for Anbar catalyst the blocking appeared catalyst was crashed after 100hr as shown in Figure (20).

The catalyst blocking after PBR also measured by changing the surface area (BET), after testing the surface area of Anbar catalyst is 79.043 m²/g, so that the blocking reach to (19.2%), while for Erbil catalyst blocking equal to (63%) when surface area after test equal to 37.26 m²/g, and surface area for AL-Mosul catalyst equal to 80.17 m²/g, so that the blocking equal to (14.35%), from all above discussion AL-Mosul catalyst is considered the best catalyst stability.

### 3.2 The apparent kinetic models

The apparent kinetic models are generally expressed in terms of either the simple power law or more complex equation based on adsorption–desorption mechanism, i.e. Langmuir- Hinshelwood- Hougen-Watson (LHHW) model, for the heterogeneous catalytic oxidation of aqueous organic pollutants, these models shows in Table (3) [35] [36]. This fact is accounted for in the kinetic model by expressing the catalyst concentration in terms of an empirical correlation [37], thus, the actual phenol disappearance...
rate could be expressed as equation (1).

\[
\frac{dA}{dt} = r_H \; C_{cat}^n
\]  \hspace{1cm} (1)

Where \([A] = [A]_0\) that represent the initial conditions: Power law expressions has been typically pointed out. These equations are of the general form of Eq. 2.

\[
r_{org} = k_0 \exp\left(-\frac{E_a}{RT}\right) [C_{org}]^\alpha [CO_2] \) . \hspace{1cm} (2)

In this study MATLAB is used to solve the kinetic model equations. Figure (21) shows the flow diagram that is used for parameters determinations.

![Flow diagram](image)

**Figure 21.** Schematic diagram for model parameter identification.

**Table 3.** Kinetic models proposed for air CWO heterogeneous reaction

| Types     | Models | Mechanical                  | \(k_0\) | \(E_a\) |
|-----------|--------|----------------------------|--------|--------|
| Power law | M1     | \(r_H = k_1 [A]^q [O_2]^q\) | \(k_1\) | \(q\)  |
| LHHW      | M2     | \(r_H = \frac{k_1 kA ko_2 [A][O_2]}{(1 - kA [A] + Ko_2 [O_2])}\) | \(k_1\) | \(k_1\) | \(k_1\) |
| LHHW      | M3     | \(r_H = \frac{k_1 kA ko_2 [A][O_2]}{(1 + kA [A] + Ko_2 [O_2])}\) | \(k_1\) | \(k_1\) | \(k_1\) |
| LHHW      | M4     | \(r_H = \frac{k_1 kA ko_2 [A][O_2]}{(1 + kA [A] + Ko_2 [O_2])}\) | \(k_1\) | \(k_1\) | \(k_1\) |

The experimental data is fitted with the proposed models M1-M4. The determination scheme was an algorithm coupling the 4th order Runge-Kutta numerical method [38] with the nonlinear Simplex-Marquardt algorithm [39]. Further optimization techniques are implemented to minimize the error between theoretical (computed) results and experimental data by a least-square (equation 7) so that the minimum of residual sum of squares (SQR) could be identified eventually for models M1-M4, respectively.

\[
SQR = \sum_{i=1}^{n} \left( \frac{[A]_{sim} - [A]_{exp}}{[A]_{Exp}} \right)^2
\]  \hspace{1cm} (7)
Where the subscripts \(\text{Exp}\) and \(\text{Sim}\) represent the experimental and simulated values. The previously mentioned models have been tested for \(r_H\) with the kinetic parameter values, in Tables (4) were given the parameter for the best model for all regions Anbar, Mosul, Basra, Baghdad, and Erbil respectively. The actual phenol disappearance rate could be expressed as equation (8) as the average absolute relative errors (AAAR).

\[
\text{AAAR} = \frac{\sum_{i=1}^{N} |y_{\text{Sim}, i} - y_{\text{Exp}, i}| / y_{\text{Exp}, i}}{N}.
\] (8)

The models for all regions can be checked by comparing the simulation data with experimental data. Results of perfect models are shown in Figures (22), (23), (24), (25), (26) for Anbar, Mosul, Basra, Baghdad, and Erbil respectively, exhibits parity plots that compare the calculated with those experimental observations from the suitable models for all regions. From the result of the kinetic models M1, M2, M3, and M4 for all regions.

### Table 4. Rate parameters for CWAO heterogeneous reaction for Anbar

| Catalyst region | Stable Model | Parameter | \(k_1\) | \(q\) | \(p\) | \(n\) | SQR | AAAR |
|-----------------|--------------|-----------|---------|------|------|------|-----|------|
| Anbar M2        | \(K\)        | 1.056E3e(-34213.05/RT) | --- | --- | 0.87 | 1.23 | 0.0811 |
|                 | \(K_{\text{Cph}}\) | 0.5E3e(-32958.38/RT) |         |       |       |       |      |
|                 | \(K_{\text{CO}_2}\) | 3E3e(-30216.8/RT) |         |       |       |       |      |
| Mosul M4        | \(K\)        | 0.7625E3e(-32151.1/RT) | --- | --- | 0.9 | 1.74 | 0.075 |
|                 | \(K_{\text{Cph}}\) | 1.0325E3e(-4638.9/RT) |         |       |       |       |      |
|                 | \(K_{\text{CO}_2}\) | 3.857E3e(-36810.7/RT) |         |       |       |       |      |
| Basra M2        | \(K\)        | 9E5e(-42176.16/RT) | --- | --- | 0.89 | 1.12 | 0.102 |
|                 | \(K_{\text{Cph}}\) | 0.28E5e(-41662.03/RT) |         |       |       |       |      |
|                 | \(K_{\text{CO}_2}\) | 5E5e(-32081.45/RT) |         |       |       |       |      |
| Baghdad M3      | \(K\)        | 1.07E2e(-32346.6/RT) | --- | --- | 0.65 | 1.3 | 0.082 |
|                 | \(K_{\text{Cph}}\) | 1.193E2e(-35177.4/RT) |         |       |       |       |      |
|                 | \(K_{\text{CO}_2}\) | 1.475E2e(-40088.4/RT) |         |       |       |       |      |
| Erbil M2        | \(K\)        | 0.523E4e(-25111.11/RT) | --- | --- | 0.802 | 3.721 | 0.145 |
|                 | \(K_{\text{Cph}}\) | 1.15E4e(-21232.4/RT) |         |       |       |       |      |
|                 | \(K_{\text{CO}_2}\) | 2.564E4e(-20022.9/RT) |         |       |       |       |      |

* Apparent activation energy in J/mol

Figure 22. Parity plot for phenol concentration, (mol/m\(^3\)) for Anbar employing model M1; (b) employing model M2; (c) employing model M3; (d) employing model M4.
The reproductions of some representative experimental data are shown in Figures (27), (28), (29), (30), and (31) for Anbar, Mosul, Basra, Baghdad, and Erbil respectively. The best models with good agreement have been shown in Anbar then Baghdad, Erbil, Mosul, and Basra models respectively. M2 is slightly better in terms of the statistical standard for Anbar, Mosul and Basra. M3 Mode is better in Baghdad models. M4 Model is better in Erbil. Table (5) shows the best models equations obtained for all catalysts in this study.
Table 5. Final kinetic model equation results for five catalyst regions

| Region | Models | Model equations |
|--------|--------|-----------------|
| Anbar  | M2     | \( \frac{dA}{dt} = \frac{k_1 k_2 k_3 [A][O_2]}{(1-K[A]+K[O_2][O_2])} * c_{cat}^{-0.87} \) |
| Erbil  | M4     | \( \frac{dA}{dt} = \frac{k_1 k_2 k_3 [A][O_2]}{(1+K[A])(1+K[O_2][O_2])} * c_{cat}^{-0.82} \) |
| Mosul  | M2     | \( \frac{dA}{dt} = \frac{k_1 k_2 k_3 [A][O_2]}{(1-K[A]+K[O_2][O_2])} * c_{cat}^{-0.75} \) |
| Baghdad| M3     | \( \frac{dA}{dt} = \frac{k_1 k_2 k_3 [A][O_2]}{(1+K[A])(1+K[O_2][O_2])} * c_{cat}^{-0.65} \) |
| Basra | M2     | \( \frac{dA}{dt} = \frac{k_1 k_2 k_3 [A][O_2]}{(1-K[A]+K[O_2][O_2])} * c_{cat}^{-0.89} \) |

Figure 27. Measured and predicted time profiles of phenol removal at different Temperature, employing the best model M2 for Anbar.

Figure 28. Measured and predicted time profiles of phenol removal at different Temperature, employing the best model M4; for Erbil.

Figure 29. Measured and predicted time profiles of phenol removal at different temperature: (a) employing model M2; for Mosul.
4. Conclusions

Five types of Catalysts based on clays regions (Anbar- Mosul- Basra- Baghdad- and Erbil) with Al-Fe have been tested for phenol oxidation with air in different condition of temperature, pressure, phenol loading, and catalyst loading, using phenol as target compound. The catalyst of Anbar, Mosul and Erbil showed a higher activity for phenol conversion and TOC removal for batch reactor test, promotes mainly the generation of OH radicals, in the other cases a substantial percentage of air must be giving rise to O2, with a low oxidation capacity at these mild operating conditions used, Mosul catalyst has higher activity than other catalyst. Mosul catalyst higher stability than Erbil and Anbar in surface area blocking, Leaching Fe was negligible within the reaction time required for a practically complete phenol conversion, all result in part per billion. The best model obtained was for each region as M2 model for Anbar, Mosul, and Basra, M3 model for Baghdad, and M4 model for Erbil, The activation energies of each reactions model with different catalysts are equal to (37114.014 j/mol) for Anbar (37795, 48783.9, 36628, 40785 j/mol) for Erbil, Mosul, Baghdad and Basra respectively. So that Mosul catalyst is considered the best catalyst.

References

[1] Tensel B 2008 Chem. Eng. 1 17 26.
[2] Luck F 1996 Catal. Today 27 195-202
[3] Rubalcaba A M E, Suarez –Ojeda F, Stuber A, Fortuny C, Bengoa I, Metcalf J, Font J, Carrera and A . Fabregat 2007 Water Science & Tecnology, 55 12 221-227
[4] Kulkarni U S and Dixit S G 1991 Ind Eng Chem Res 30 1916-1920
[5] Matatov-Meytal Y I and Sheintuch M 1998 Ind. Eng. Chem. Res. 37 309-326
[6] Sunil J, Kulkarui, Jayant and P.Kaware 2013 Journal Scientific & Reseach Oublication 3 4
[7] Rodriguez I and Liompart M P 2000 Chromatogr 885 291-304
[8] Busca G, Berardinelli S, Resini C, and Arrighi L 2008 Journal of Hazardous Materials 160 265-288
[9] Rubalca A, Suarez –Ojeda F, Stuber A, Fortuny C, Bengoa I, Metcalf J, Font J, Carrera and Fabregat A 2007 Journal Water Science & Tecnology 55 12 221-227
[10] Janda V and Krijt K 1984 J. Chromatography 283 309
[11] Greminger D C, Burns G P, Lynn S, Hanson D N and King C J 1982 Ind. Eng. Chem. Process Des. Dev. 21 1 51–54
[12] Dabrowski A P, Podkoscienk Z, Hubicki and Barczak M 2005 Chemosphere 58 8 1049-70
[13] Xiao M, Zhou J, Tan Y, Zhang A, Xia Y and Ji L 2006 Desalination **195** 281-293
[14] Chen G 2004 *Purif. Technhol* **38** 11-41
[15] Saravanan P K, Pakshirajan and Saha P 2008 *Bioresour Technol.* **99** 1 205-209
[16] Hu X, Lei L, and Chen G 2001 *J. Water Res* **35** 8 2078-2080
[17] Joglekar H, Samant S D, and Joshi J B 1991 *J. Water Res* **25** 2 135-145
[18] Suranjana C, and Krishna G, Bhattacharyy 2006 *Journal of Chemical Technology* **13** 499-504
[19] Sugunan S and Renuka N K 2002 *Ind. J. Chem.* **41A** 304
[20] Bankovic P, Milutionovic A, Nikolic A, Rosic N, Jovic – Jovani and Jovanovic 2009 *Journal of Physical Chemistry* **83** 9 1485-1489
[21] Stüber F, Polaert I, Delmas H, Font J, Fortuny A and Fabregat A 2001 *J. Chem. Technol. Biotecnol.* **76** 743-751
[22] Rob J, Berger E, Hugh Stitt, Guy B, Marin Freek Kapteijn, Jacob A and Moulijn 2001 *EUOKEN* **5** 1 USA
[23] Eftaxias Athanasios 2002 Catalytic Wet Air Oxidation of Phenol in a Trickle Bed Reactor: Kinetics and Reactor Modelling Doctoral thesis in Chemical Engineering of the Rovirai Virgili University
[24] Bos A N R, Lefferts L, Marin G B and Steijns M H G M 1997 *Appl. Catal. A:* General, 160 185
[25] Santos A, Yustos P, Durban B and Garcia Ochoa F 2001 *Ind Eng Chem Res* **40** 2773–2781
[26] Mishra V S V V, Mahajani J B, and Joshi 1995 *Ind. Eng. Chem. Res.* **34** 1 2-48
[27] Kapteijn F, Johan J H, Xander T A N, and Moulijn J A 1999 *Baltzer Science* **3** 24-38
[28] Trunfio G 2008 “Catalyst development for the catalytic wet air oxidation (CWAO) of phenol PhD Thesis, University of Messina
[29] AL-Dahhan Guo 2005 *J. Chem. Eng. Sci.* **60** 735-746
[30] Nicoleta Platon, Ana-maria Rosu, Vasilia Alisa Arua, Denis Ileana nistor, and Ilie Simineanu 2013 *Journal of Engineering Studies and Research* **19** 4 52-58
[31] Lastoskie Christian, Keith E G ubbins, and Nicholas Quirke 1993 *journal phiscal and chemical* **97** 4786-4796
[32] Bishop D F, Stern G, Fleischman M and Marshall L S 1968 *Ind. Eng. Chem. Process Des. Dev.* **7** 110
[33] Pintar A, Levec J 1992 *Chem. Eng. Sci.* **47** 9-11 2395-2400
[34] Lin S H, Ho S J, and Wu C L 1996 *Catal. Today* **29** 317-322
[35] Aurora S, Pedro Y, Beatriz D, and Felix G O 2001 *Ind. Eng. Chem. Res.* **40** 2773
[36] Guo J and Al-Dahhan M H 2004 *Chem. Eng. Sci* **59** 2023–2037
[37] Rubalcaba A, Suarez –Ojeda M E, Stuber F, Fortuny A, Bengoa C, Metcalf I, Font J, Carrera J and Fabregat A 2007 *Journal water Science & Tecnology* **55** 12 221-227
[38] Press H W, Teukolsly S A, Vetterling W T and Flannery B P 1992 *Numerical Recipes, the Art of Scientific Computing*, Cambridge University Press: Cambridge, U.K
[39] Duggleby R G 1984 *Comput. Biol. Med.* **14** 447