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Research paper



Studying the Phenol Degradation in Synthetic Wastewater by Catalytic Wet Air Oxidation Process in Batch Reactor

Ghayda Yaseen AL Kindi [1]*, Faris Hammoodi AL Ani [1],

[1] *Civil Engineering Department /University of Technology/Iraq*
Email:40126@uotechnology.ed.iq:

Abstract

The current paper studies the viability of using a Batch reactor, by five types of Al-Fe pillared clay that prepared from five regions in Iraq for phenol degradation in synthetic wastewater. The operation condition study through variables in (pH, pressure, temperature, pillared load, phenol load). The findings have illustrated that phenol degradation could be increase via incrementing temperature, pressure, pillared load and degrease in phenol load. Phenol good degradation proportion which was 97 %, has been achieved at optimum proportion (pH= 3.9, temperature = 150 °C, pressure = 3.5 MPa, in addition to phenol concentration = 500 mg/l). The two models power-law and Langmuir−Hinshelwood have been used to study the catalytic kinetics of the phenol degradation. From results shown the activation energy for every response equivalent to (37114.014 j/mol) for Anbar (37795, 48783.9, 36628, 40785 j/mol) for Erbil, Mosul, Baghdad and Basra respectively. It was proved that the reaction in this study is under kinetics control.

Keywords: *Batch reactor, catalyst wet air oxidation. Kinetic, packed bed reactor, phenol.*

1. Introduction

Polluting burden of Organic nature in aqueous wastes having the range of only some hundreds to few thousands ppm could be toxic; however it is dilute to incinerate. Therefore, Wastewater treating processes have become a main social, technical, economic, and political difficulty. [1][2]. Phenolic compounds are One of these pollutants that pose a major environmental risk, Because of bioaccumulation and stability, these compounds stay within environment for long times. Also these possess elevated toxic effect; they cause substantial destroy and danger to the ecosystem in water bodies and human health [3]. To understand the CWAO process, the knowledge of the reaction kinetics is fundamental. The kinetic laws can describe the establishment of both the reaction pathways during the oxidation reactions and design. This knowledge, apart from giving a fundamental insight to CWAO can prompt noteworthy changes in the activity and outline of CWAO units.[4].due to the significance of right as well as safe plan of compound reactors [5], however apparent kinetic models cannot
be generally supported for scientific or academic researches, it is often utilized by the industrial scientists for the scale-up of commercial reactors [6], and It ought to be focused on that such kinet
ic approach does not correspond to actual intrinsic kinetics as the and not fine particles have been utilized, according on weather
kinetic, The impact of diffusion limit impediment inside the catalyst particles may mask to the reaction of intrinsic kinetic. Nonetheless, the apparent kinetics can be utilized in scaling up and process advancement thinks about. some studied about the Kinetic parameter obtained in CWAO, of pure organic compounds using Langmuir Hinshelwood Kinetics, Santos et al., (2005) show the Parameter estimation when used activated carbon k1=0.059 e-46600/RT L1.5 g CAT/min/mol 0.5, KO2 =7.30·10-7e41753/RT L/mol, KPhenol= 3.01·106e-76613/RT L/mol, while Wu et al., (2005) show used 10%CuO/AC as catalyst k=8.58 e-35400/RT L2/(mg O2 g CAT s) KO2 not given. The aim of this paper, five types of clay were collected from five regions of Iraq to prepare Al-Fe pillared clay, and the catalytic wet air oxidation of phenol had been evaluated. A kinetics model had also been utilized to investigate the degradability of phenol by CWAO, also to choose the best one.

2.Experimental and method

2.1. Preparation of pillared clay

Five samples of clay were collected out of five region (Anbar, Erbil, Mosul, Baghdad, and Basra), that used as support to pillared clay. The stack clays preeration was made consistent with Professor N. Papayannakos process (A nalysis and plant Design Group at National Technical University of Athens, NTUA). A stock clay suspension (2w %) had been prepared and left to be stirred a long period of 48hr. Suspension had been utilized as support. The cationic solution having AlCL3 (0.18 ,0.16, 0.14, 0.12, 0.10 mol/l) and FeCL3 (0.02 , 0.04, 0.06, 0.08, 0.1 mol/l) (molar ratio 9:1, 8:2, 7:3, 6:4, 5:5) , component had gradually been titrated with NaOH solution at 70C° until the OH/ Cation mole proportion equals to 1.9, the intercalate solution is given to the Al+3/Fe+3 cationic solution under stirring for 1hr and intercalation period and 24hr age time, the intercalated clay had been washed carefully by distilled water to remove chloride ions from that clay surface, as returned by the AgNO3 test according to standard method (4500CL-D). All samples extruded in cylindrical shape 2*8mm, Dried at (60-70C°) for 24hr and finally calcined at 500C° for 1hr according to [13][14], these extradate have been studied the physicochemical properties, by (XRD) X-ray diffraction, (XRF) X-ray

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Florescent and BET (Blumenauer Emmer Teller) instrument to determinate the surface area.

2.2. Description of instrument (Basket stirred Batch reactor):

The experiment arrangement is designed so as to endure elevated temperature (up to 500 C°) as well as much pressure (up to 5 MPa). In a Basket stirred tank reactor (BSTR), the reactor consist of equipment shown within shape (1).

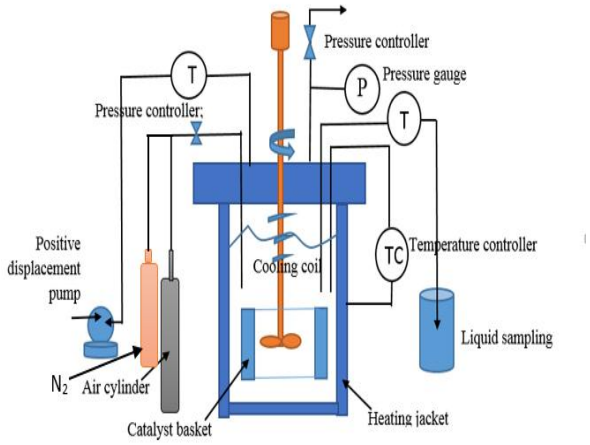


Fig. 1: Diagram of the experimental setup of (BSTR).

3. Experimental procedure

3.1. Basket stirred tank reactor (BSTR):

The 500gm of phenol was liquefied with distilled water to be synthesis's wastewater, as ideal wastewater (500-1500mg/l) concentration of phenol in Typical wastewaters from oil refineries, added sulfuric acid (1N) to reach pH 3.9-4, putting in 600ml reactor, For all kinds of AL-Fe pillared (catalyst), Catalysts is formed in 2*8mm extrudate, and placing in a fixed basket within the reactor, while the basket had been removed for the reactor to replace the catalysts in each test, the rotation speed had been left at 800 rpm. That for minimizing the external-mass transfer resistances, Nitrogen pressured to 1Mpa to inert the reactor , purify air of zero grade or (21% clean oxygen blended to 79% pure nitrogen was continuously provide to the reactor, Five parameters used to study the operation condition and kinetic parameter with different range, Catalyst loadings used in three value (0-5-10 g/L) and the initial phenol concentrations (500- 1000-1500-2000 ppm), whereas the temperatures (90-110-130-150 C°), total pressures (P = 0.8, 2.0, 3.5 MPa) and pH used in (initial pH solution 5.48- 3.9), when the set temperature got achieved (characterized as time zero), fluid example had been pulled back every 30min, every example were pulled back, quickly cooled, filtered and analyzed. Air was introduced and set manually with the required partial pressure for the duration of the test. The airflow rate had been kept up consistent [15]. Each batch was washed to expel all fines, than left to dry overnight, to begin a new test.

4. Result and discussion

4.1. Result of physicochemical properties.

Physicochemical characteristics result of XRD diffraction instrumentfor crystalline structure for Al-Fe pillared (Erbil, Baghdad Anbar- Basra- and Mosul) at 2θ between (0-70), show 3 peaks of 2θ appeared in ranges 20 to 27 that observed in Figure (2).

From the result of XRF Florescent instrument increase in concentration of iron, aluminum but decrease in calcium oxides concentration observed in Table (3), Basra have highest concentration of Fe_2O_3, while Baghdad have highest value of Al_2O_3. Also From The final Results of BET show the higher surface area for Erbil pillared clay than Anbar, Mosul, Basra and Baghdad respectively, as well as the pore volume and pore size as per the International Union of Pure and Applied Chemistry (IUPAC) grouping of pore size measure in (Å) as macropore (≥ 500), mesopore (20 to 500) supermicropore (7-20) and ultramicropore (≤ 7) [25]. From the outcomes, Baghdad has the highest value of pore size width 150.4 Å, however Basra has the least value 75.1 Å, all areas have mesopore size [31], which observed in Table (1).

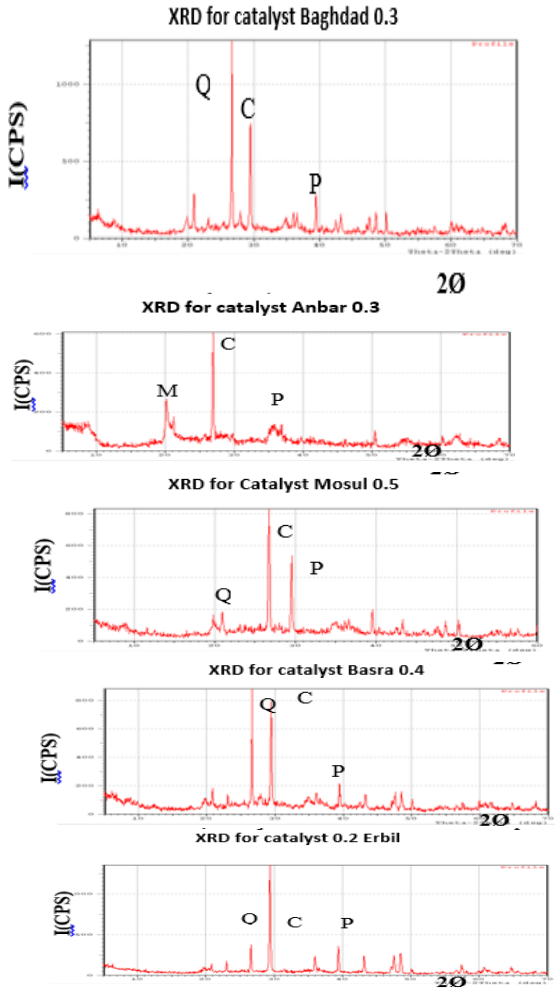


Fig. 2: Result of XRD for Al -Fe pillared clay for Erbil, Mosul, Anbar, Baghdad, and Basra

4.2. Effect of pH solution

The initial pH value of phenol solution between (5.48-5.87), the pH between 3.9-4 it is refer to optimum types of advanced oxidation processes, and this point led to decomposition in higher amount of hydroxyl radical in the solution by air oxidation [22], during the phenol conversion curve show (the two curve in pH 3.9 at130 and 110^{0}C) show inflection point refer to steady state, in present work the figure (3), also show that in pH 4.58 at 110^{0}C only. The result phenol conversion are 91.2, 87.3, 79.1, 70.6, 68.34% for Baghdad, Anbar, Mosul, Basra, Erbil, respectively.

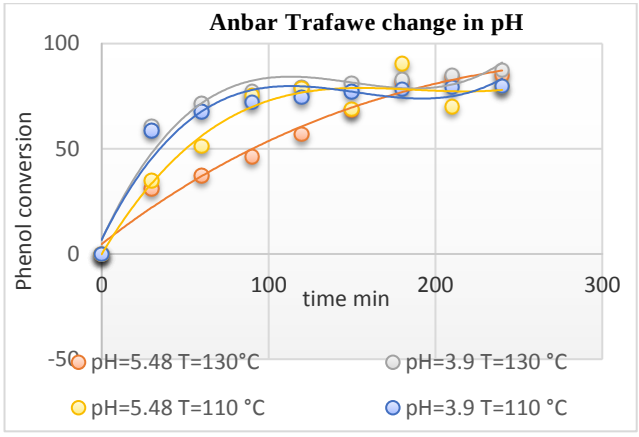


Fig (3): phenol conversion during 4hr in catalyst loading 7mg/l,pressure 1.5Mpa ,500mg/l phenol concentration in Anbar

Table 1: main composition of five types of pillared clays, and the outcome of BET surface area of five types of pillared clays

Samples Region	Anbar Catalyst	Erbil Catalyst	Baghdad Catalyst	Mosul Catalyst	Basra Catalyst
(BEI) Surface area (m^2/g)	97.815	100.74	56.973	93.605	61.371
Average Pore volume (m^3/g))	0.0962	0.1221	0.0907	0.143	0.1109
Pore size width Å	78.4	124.2	150.4	89.7	75.1
%SiO_2	20.26	55.36	39.04	32.35	28.7
Fe_2O_3%	7.98	9.6	7.8	9.82	14.81
AL2O3%	15.37	23.4	29.49	14.35	21.73
CaO %	21.44	6.51	5.21	11.3	9.28

4.3. Effect of Temperature

The influence of the reaction temperature in the action of the heterogeneous catalytic had as well been investigated. Which presented the same effect with all pillared clays region, the temperature is seen to be high effects evaluation of phenol removal, the results reveal that a temperature of 150ºC is be essential to achieve an appreciable phenol conversion with time and more influence on the reaction rate is at a temperature of 150, the highest rate of reaction phenol, from the result phenol conversion 96.2, 95.44, 93.7, 80, 76.3% for Erbil, Mosul, Anbar, Baghdad, Basra, correspondingly, these results shown in Figure (4).

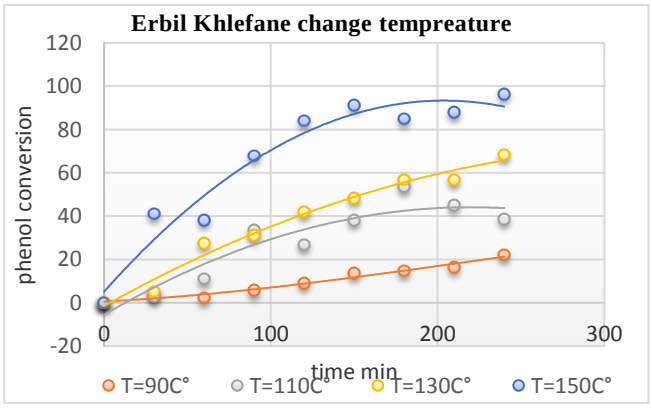


Fig (4): phenol conversion within 4hr in catalyst loading 7mg/l,pressure 2.5Mpa ,500mg/l phenol concentration in Erbil

4.4. Effect of Phenol Concentration

The reaction rate change along the duration time, that effect on kinetic rate law, therefore, in this study investigate the initial phenol concentration in range 500-2000mg/l at 130C°, the pillared clay remained active in some region and completed mineralization after 4hr, and in another region uncompleted as Al Anbar, deactivation appear on the surface of pillared clay within the CWO of phenol, polymeric compounds would be formed and carbonaceous that deposited on surface of pillared prevent the adsorbs on catalyst active sites, From the result phenol conversion 94.3, 93.4, 80, 70.68, 62%for Mosul, Anbar, Erbil, Basra, Baghdad, respectively, these results show in Figure (5)

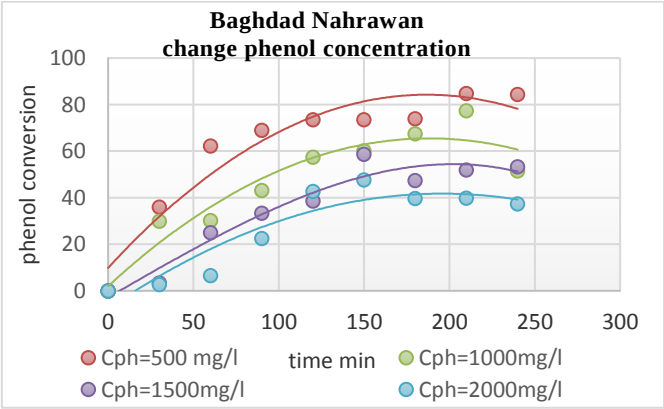


Fig .5: phenol conversion within 4hr in catalyst loading 7mg/l,pressure 2.5Mpa, deferent phenol concentration in Baghdad

4.5 The Air Pressure Effect

The air used for oxidation according to Henry's law, the pressure air should be exceed the steam pressure of fluid stage at temperature provided, thus in this work to stay the wet oxidation in fluid stage at temperature between 90-150C° the vapor pressure range between 0.1-0.45Mpa, the oxygen capable to oxidation the phenol and substitute oxygen atom an aromatic ring to be quinine or dihydric phenol, and also capable to attract the phenol double bond of Carbone to form carboxylic acid, the result of Basra phenol conversion show in figure (6) which presented the same effect with all pillared clays region, for five region, the Basra have high value of degradation phenol,

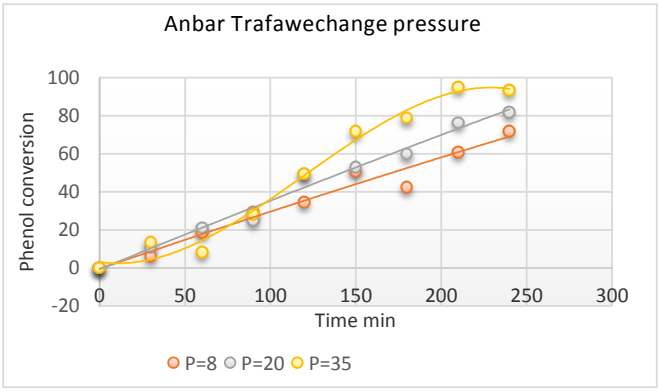


Fig 6: phenol conversion within 4hr in catalyst loading 7 mg/l,tempreature 130C°,500mg/l phenol concentration in Basra

4.6. Effect of Catalyst Loading

The different catalyst loading (0-5-8-10mg/l) investigate in this study to oxidation phenol, from results show the air or oxygen not significant on homogenous reaction but very effect on heterogeneous reaction to oxidation of phenol, during the heterogeneous reaction the phenol oxidation on active site that acidity but for all type of catalyst the deactivation not significant in this study, the catalyst load in Anbar and Basra (8mg/l) beater than in Mosul (10mg/l). From the previously show Mosul, Erbil, and Anbar was very active than Baghdad and Basra, therefore, the continuous study included this area only, these results show in Figure (7).

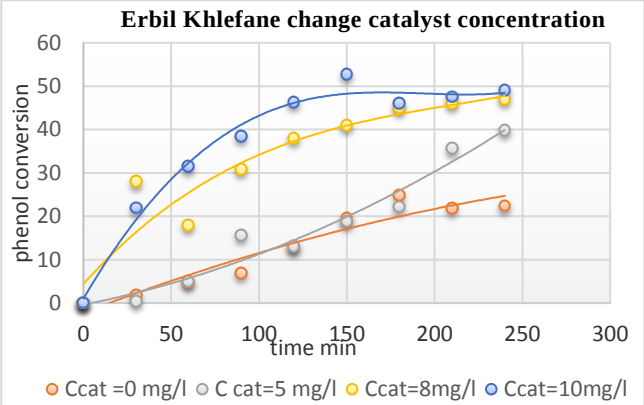


Fig 7: phenol conversion during 4hrin different catalyst loading,tempreture 130C°,500mg/l phenol concentration in Erbil

From these result show Mosul, Erbil and Al-Anbar have the higher ratio in conversion of phenol than Baghdad and Basra, and the operation condition temperature 150ºC, pressure 3.5Mpa, phenol load 500mg/l.

5. Parameter estimation

The obvious proportion law for oxidation phenol is significant to evaluate the technical of phenol removal by catalyst extrudate, it could be utilized in scaling up and raising in treat growth researches. The effect of catalyst loading, when used one concentration of catalyst to do models of kinetic, the response proportion can be presumed to be in a straight line relative to the catalyst concentration. [16], but that variable modified with over the interval concentration. This reality is represented in the kinetic model via correlation, the catalyst concentration as far as an observational relationship [17], in the first step is to consider only the phenol degradation reaction described by equation.

$$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

Thus, the actual phenol disappearance rate could be expressed as equation (1)

$$-\frac{dA}{dt} = rH\ \ Ccat^n \qquad (1)$$

Where the initial conditions are: [A] = [A] $_0$.
Where n: catalyst concentration load in the general proportion of reaction. The simple power law are generally used expressed about apparent kinetic models or more complex equation condition in light of adsorption– desorption component, i.e. Langmuir-Hinshelwood-Hougen-Watson (LHHW) show likewise utilized. Both kinetic models have given sensible simulations of the showing results for the CWAO of reactants [18][19][20][13],

The power law kinetic model (Model 1) associated to the simplest form of surface response proportion. The LHHW rate law is generally used to connect heterogeneous catalyst kinetic. For all models, independent of reactant concentration can be resulted, in rate coefficients and adsorption parameters.

Model 1 $r_h = k_1 [A]^p * [O_2]^q$ (experimental method) (2)

Also based on the LHHW rate law, model (Model 2) consist of changeable on similar site on the catalyst surface for the adsorption of phenol and oxygen molecules as well as of a rate-determining irretrievable surface response phase amid the adsorbed O_2 and phenol,

Model 2 $r_h = \frac{k1\ kA\ ko2\ [A][O2]}{(1-KA\ [A]+KO2[O2])^2}$ single site $O_2 + * \Longleftrightarrow O_2^*$ (3)

The mechanism of the model (Model 3) similar to model (Model 2) that both term have single site for reaction, excluding that oxygen molecules suffer the dissociation along with the surface response happens amid the atoms of the adsorbed phenol and oxygen.

Model 3 $r_h = \frac{k1\ kA\ ko2\ [A]^{0.5}[O2]^{0.5}}{(1+KA[A]+KO2[O2])^{0.5\ 0.5\ 2}}$ single site $O_2 + * \Longleftrightarrow O_2^*$ (4)

The surface response proportion of the model (Model 4) dedicated when the separated oxygen and phenol are adsorbed on clearly dissimilar sites on surface of catalyst,

Model4 $r_h = \frac{K1\ KA\ KO2\ [A]^{0.5}[O2]^{0.5}}{(1+KA[A])^{0.5}(1+KO2[O2])^{0.5}}$ Double site. $O2 + 2* \Longleftrightarrow 2O^*$ - (5)

In all the previous rate the constants define as follows, k1 is the proportion consistent for the surfaces response phase, and K_{O2} and K_A are the adsorption constants for oxygen and phenol on the surface of catalyst, individually. These parameters had been known in view of the heterogeneous test information. The heterogeneous trial information had been estimated at four variables temperatures (90-110-130-150C°), four diverse phenol initial concentration (500-1000-1500-2000mg/l), four diverse O2 partial pressures (0.8-2.0-3.5MPa), and four diverse catalyst load Concentrations (0-5-8-10mg/l).For any kinetic estimations, modeling, and the run in the typical ways to deal with the reactor rate counts, the mass transfer limitation is always assumed to be of less effect that can be negligible [21]. In this study, the fitting of empirical information with the suggested models (Model 1-Model 4) for five region. Mainly the determining scheme system had been an algorithm coupling the 4th order Runga- Kutta numerical method [21] was used in Matlab programs with the nonlinear Simplex-Marquardt algorithm [22], the Schematic diagram shown in Figure(8) the objective function must be minimized during the (equation 6). The kinetic variables had been wide –ranging by a least squares in the scheme therefore the base of remaining aggregate of squares (SQR) could be distinguished in the end for all area Models (Model 1-Model 4), Respectively.

$$SQR = \sum_{i=1}^{n} \left(\frac{[A]_{sim} - [A]_{Exp}}{[A]_{Exp}}\right)^2 \qquad (6)$$

Where the subscripts Exp and Sim are the empirical and simulated values.

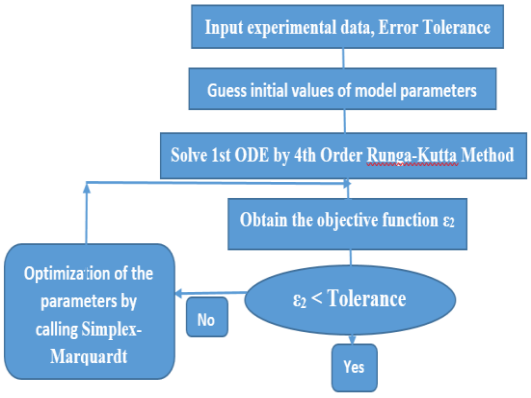


Fig. 8: Schematic diagram for model parameter identification.

This reality is represented in the kinetic model by the catalyst concentration as far as an experimental relationship [17].
The current model parameters had been obtained in previous studies as first guesses for on phenol oxidation and differ broadly. The Converging is succeeded when the model's predicated values of phenol concentration sufficiently are equivalent to the matching

empirical information. The rh with the kinetic parameter values given in in Tables (2), (3), (4), (5), (6) for all region (Anbar, Erbil, Mosul, Baghdad, Basra) therefore, the real phenol vanishing proportion can be stated according to equation (7), the average absolute relative errors (AAAR).

$$AAAR= \sum_{i=1}^{N} \left| (y_{sim,\,I} - y_{Exp,\,I})/y_{Exp,\,I} \right| /N. \quad (7)$$

Table 2: Rate parameters for CWAO heterogeneous reaction for Anbar

Model r_H	Parameter						
	k_1		q	p	n	SQR	AAAR
Model 1		0.11E2e - 37114.014/RT	0.6	0.85	0.82	1.85	0.091
Model 2	K	1.056E3e(-34213.05/RT)	----	---	0.87	1.23	0.0811
	Kc_{ph}	0.5E3e(-32958.38/RT)					
	K_{co2}	3E3e(-30216.8/RT)					
Model 3	K	3.66E2e(-38110.0/RT)	---	---	0.85	2.51	0.0984
	Kc_{ph}	0.5E2e(-38623.54/RT)					
	K_{co2}	2.6E2e(-38382.39/RT)					
Model 4	K	1.65E1e(-32571.6/RT)	---	---	0.86	1.375	0.084
	Kc_{ph}	0.5E1e(-38366.98/RT)					
	K_{co2}	2.7E1e(-38282.39/RT					

* Apparent activation energy in J/mol

Table 3: Rate parameters for CWAO heterogeneous reaction for Erbil

Model r_H	Parameter						
	k_1		q	p	n	SQR	AAAR
Model 1		0.1E4e - 37795/RT	0.65	0.96	0.82	1.52	0. 096
Model 2	K	0.523E4e(-25111.1/RT)	---	--	0.80	3.72	0.145
	Kc_{ph}	1.15E4e(-21232.4/RT)					
	K_{co2}	2.564E4e(-20022.9/RT					
Model 3	K	4.225E4e(-34132.2/RT)	----	---	0.8	1.75	0.098
	Kc_{ph}	1.155E4e(-22361.2/RT)					
	K_{co2}	2.556E4e(-31090.2/RT)					
Model 4	K	0.912E3e(-23465.65/RT)	----	---	0.82	1.42	0.084
	Kc_{ph}	1.132E3e(-33617.88/RT)					
	K_{co2}	0.233E3e(-30783.21/RT)					

Table 4: Rate parameters for CWAO heterogeneous reaction for Mosul

Model rH	Parameter						
	k1		q	p	n	SQR	AAAR
Model 1		0.1E3e - 48783.9/RT	0.57	0.88	0.87	5.12	0.167
Model 2	K	8.0125E3e(-43621.5/RT)	---	---		1.31	0.068
	Kcph	0.5E3e(-38146.623/RT)					
	Kco2	0.026E3e(-38482.7/RT)					
Model 3	K	3.26E3e(-35133.89/RT)	---	---	0.91	1.81	0.091
	Kcph	0.55E3e(-39582.38/RT)					
	Kco2	0.029E3e(-20161.85/RT)					
Model 4	K	0.7625E3e(-32151.1/RT)	-----	----	0.9	1.74	0.075
	Kcph	1.0325E3e(-4638.9/RT)					
	Kco2	3.857E3e(-36810.7/RT)					

* Apparent activation energy in J/mol

Table 5: Rate parameters for CWAO heterogeneous reaction for Baghdad

Model r_H	Parameter						
	k_1		q	p	n	SQR	AAAR
Model 1		0.2E3e(-36628/RT)	0.65	0.96	0.9	1.8	0. 098
Model 2	K	1.075E3e(-43103.34/RT)	----	----	0.74	1.5	0.076
	Kc_{ph}	7.345E3e(-3718.785/RT)					
	K_{co2}	1.4E3e(-43911.7/RT)					
Model 3	K	1.07E2e(-32346.6/RT)	-----	----	0.65	1.3	0.082
	Kc_{ph}	1.193E2e(-35177.4/RT)					
	K_{co2}	1.475E2e(-40088.4/RT)					
Model 4	K	1.075E3e(-33466.6/RT)	---	---	0.76	1.55	0.087
	Kc_{ph}	1.133E3e(-37187.78/RT)					
	K_{co2}	2.605E3e(-40084.43/RT)					

* Apparent activation energy in J/mol

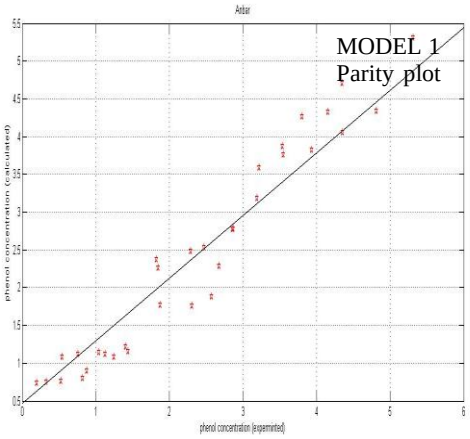
Table 6: Rate parameters for CWAO heterogeneous reaction for Basra

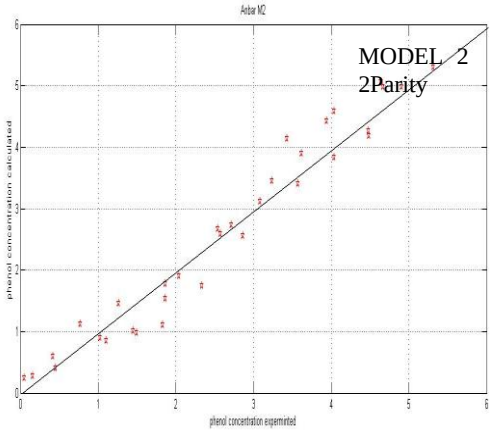
Model r_H	Parameter						
	k_1		q	p	n	SQR	AAAR
Model 1		0.12E5e - 40785/RT	0.6	0.9	0.8	3.90	0. 177
Model 2	K	9E5e(-42176.16/RT)	---	----	0.889	1.12	0.102
	Kc_{ph}	0.28E5e(-41662.03/RT)					
	K_{co2}	5E5e(-32081.45/RT)					
Model 3	K	3.15E4e(-41807.8/RT)	---	----	0.88	2.54	0.095
	Kc_{ph}	0.275E4e(-41550/RT)					
	K_{co2}	0.46E4e(-31864.9/RT)					
Model 4	K	1.15E2e(-42753.66/RT)	---	---	0.86	3.77	0.151
	Kc_{ph}	0.4E2e(-42777.8/RT)					
	K_{co2}	0.44E2e(-36807.7/RT					

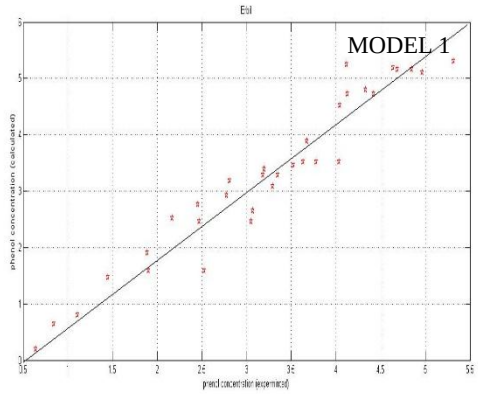
* Apparent activation energy in J/mol

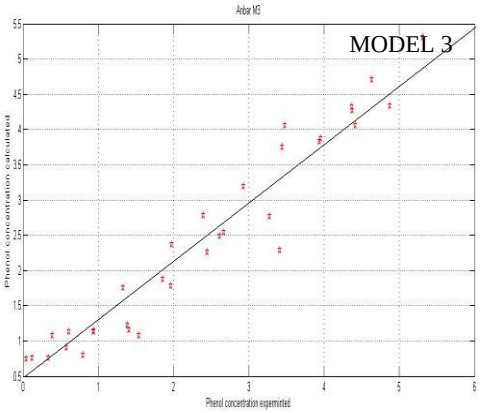
The models quality for all region could be checked through making a comparison between the simulation data with experimental data. The Figures (9), (10), (11), (12), (13) show equivalence plots which contrast the calculated observances with the same experimental ones out of the four models suggested previously for all regions. From the result of the kinetic models (Model 1, Model 2, Model 3, and Model 4) for all region, sufficiently fit the empirical information. No tendency could be noticed also the majority of comparative residuals have been restricted to ± 17.7 % for Basra consider the highest result but ±16.7% for Mosul, ±14.5% for Erbil, ±9.89% for Baghdad, and 9.84% for Anbar, with the average absolute relative errors (AARE) which equals to that in the figures. conversely, model (Model 1), a power-law proportion equation with fixed reaction order, under predicts the phenol concentration of elevated rates, for Basra, Baghdad, Mosul, but the (Model 2) for Erbil and (Model 3) for Anbar of Langmuir-Hinshelwood-Hougen-Watson (LHHW) models

under predicts the phenol concentrations of high values for Erbil and Anbar with the AARE equal to 14.5% and 9.84% respectively. The multiplications of some representing exploratory information are appeared in Figure (14), (15), (16), (17), (18) for Anbar, Erbil, Mosul, Baghdad, and Basra, separately, as the impacts of various temperatures on catalyst phenol expulsion proportion have been tried. At the chose temperatures, all models give agreements satisfactory among the simulated results and the test estimations. In any case, it must be noticed that the physical significance of the mathematical models cannot be over interpreted, on the grounds that different models can be utilized to portray the same experimental notes. The best models have appeared in Anbar Models then Baghdad, Erbil, Mosul, and Basra individually. (Model 2) is somewhat better as far as the measurable standard for Anbar, Mosul and Basra. (Model 3) Mode is better in Baghdad Models, (Model 4) Mode is better ones in Erbil, nevertheless, model (Model 4), signifying to a double site system, can be broadly taken in previous study to depict the response the reaction, irrespective on catalyst types [23][24].









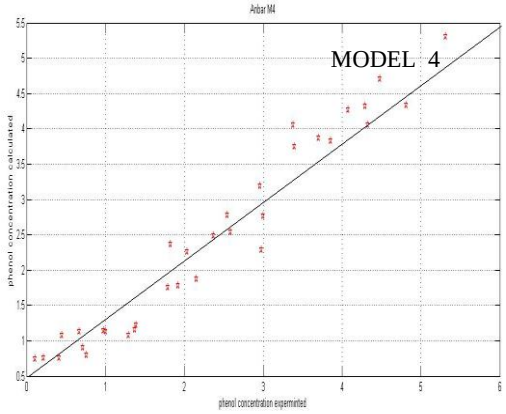
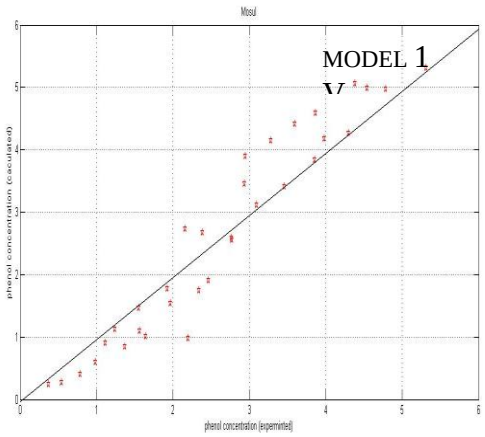


Fig. 9: Parity plot for phenol concentration, (mol/m3): for Anbar using model (Model 1); (b)using model (Model 2); (c) using model (Model 3); (d) using model (Model 4).



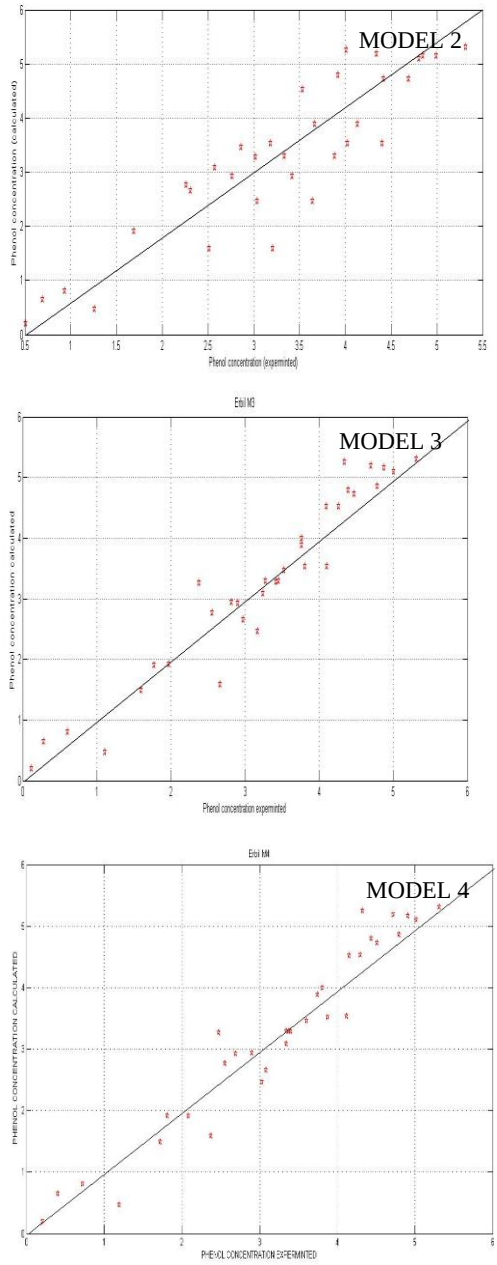


Fig. 10: Parity plot for phenol concentration, (mol/m3): for Erbil using model (Model 1); (b) using model (Model 2); (c) using model (Model 3); (d) using model (Model 4).

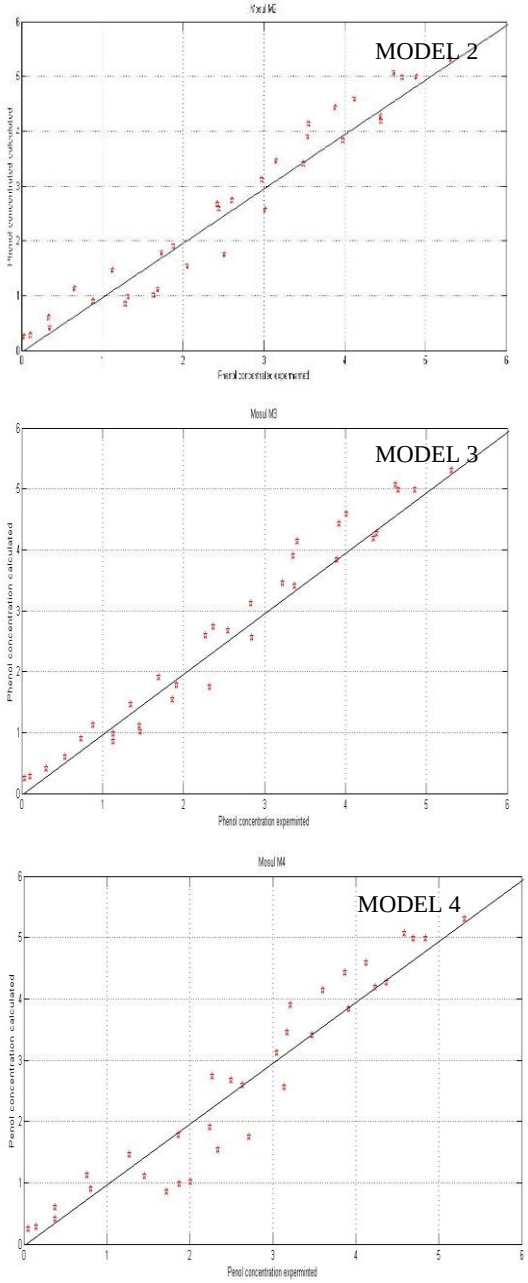
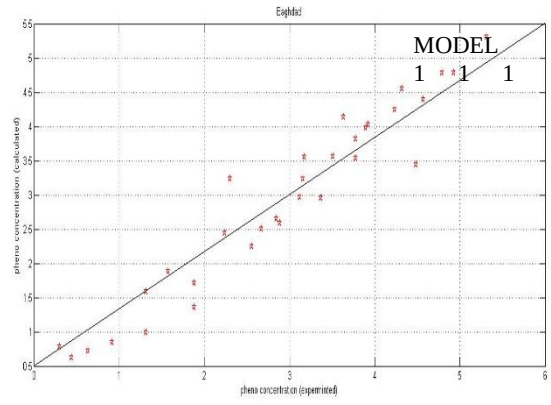
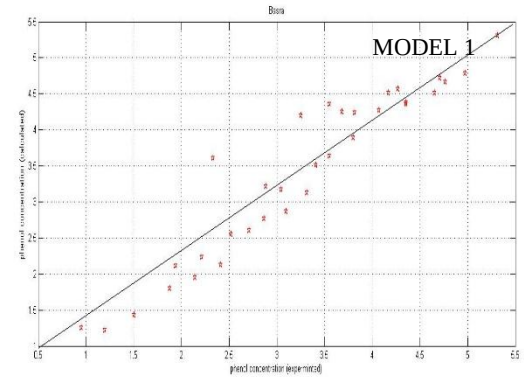


Fig. 11: Parity plot for phenol concentration, (mol/m3): for Mosul using model (Model 1); (b)using model (Model 2); (c) using model (Model 3); (d) using model (Model 4).





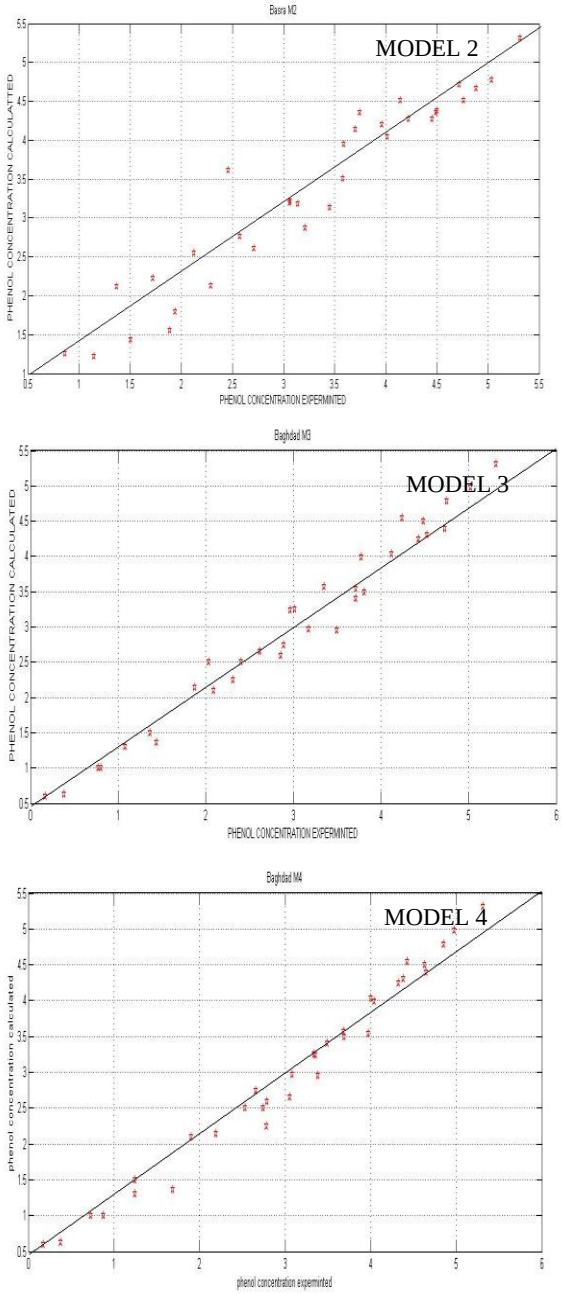


Fig. 12: Parity plot for phenol concentration, (mol/m3): for Baghdad using model (Model 1); (b)using model (Model 2); (c) using model (Model 3); (d) using model (Model 4).

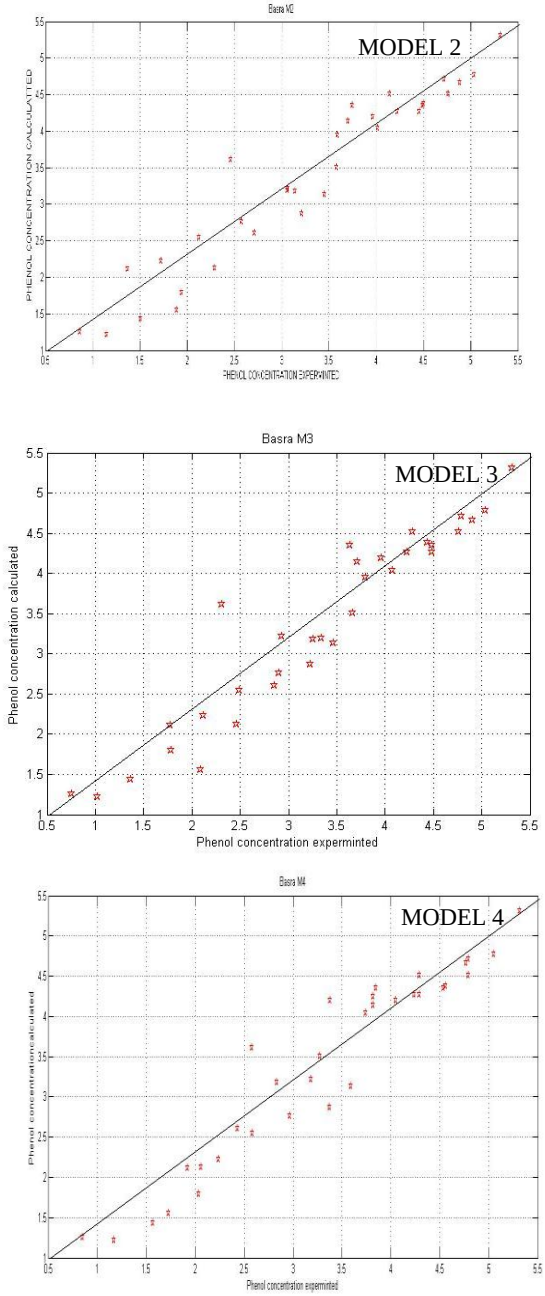
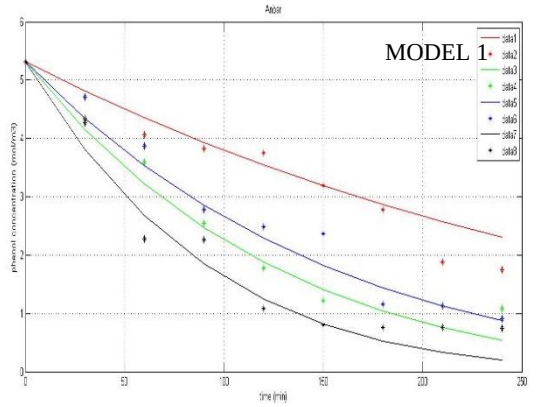
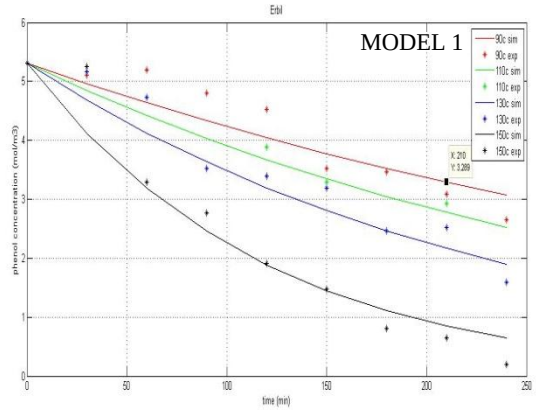


Fig. 13: Parity plot for phenol concentration, (mol/m3): for Basra using model (Model 1); (b)using model (Model 2); (c) using model (Model 3); (d) using model (Model 4).





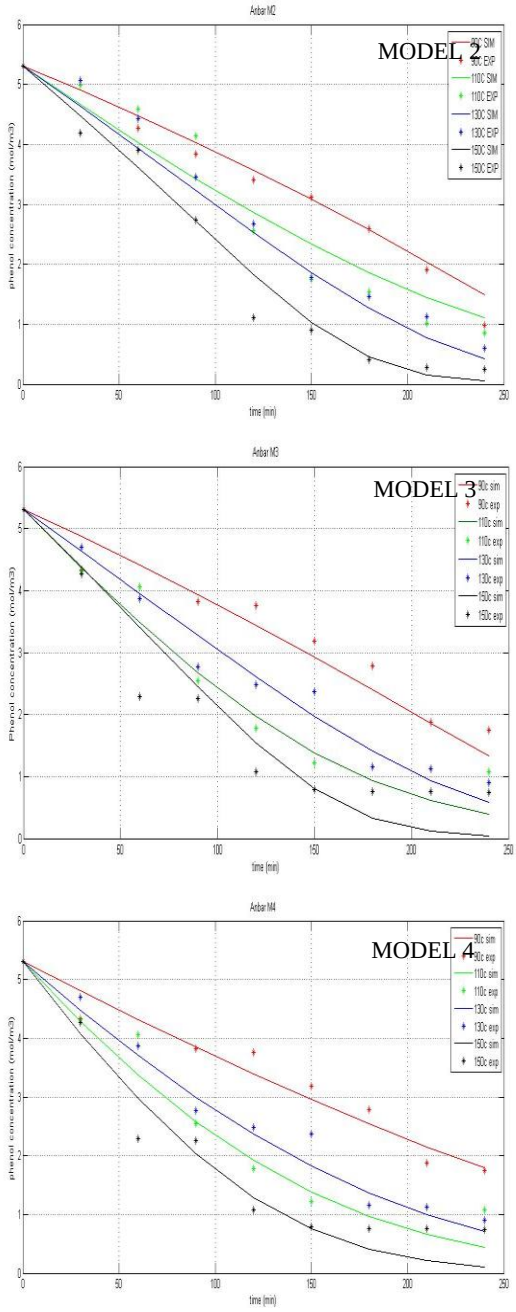


Fig. 14: Measured and predicted time profiles of phenol removal at various Temperature: (a) using model (Model 3); (b) using model (Model 4) (6.6 g/L catalyst, 500 ppm phenol, 1.5 MPa) for Anbar.

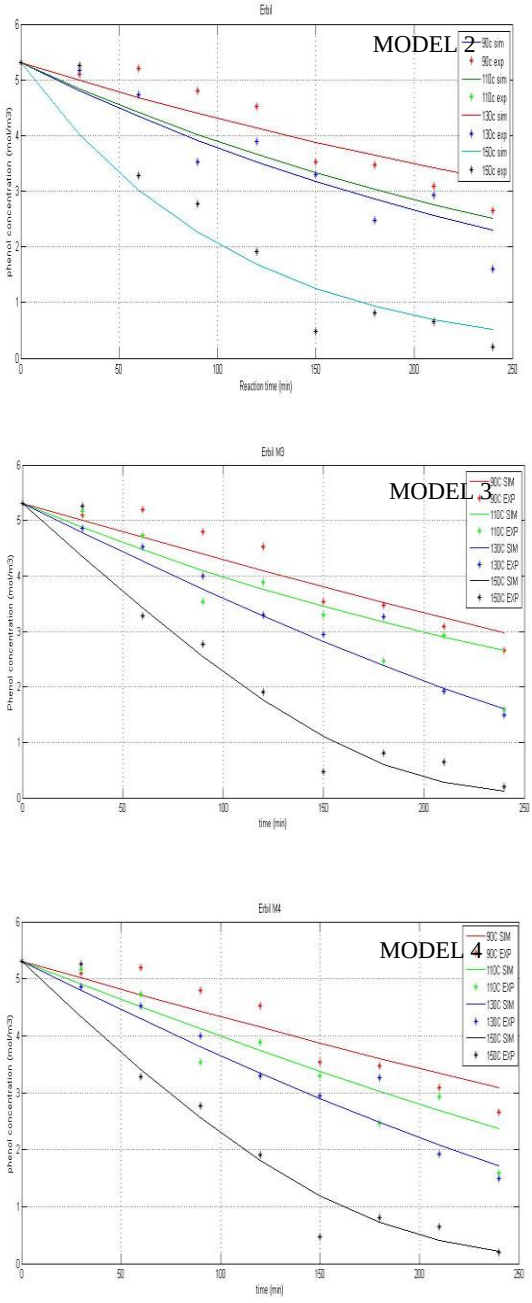
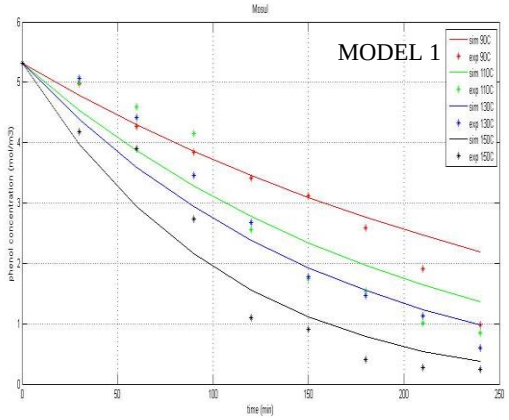
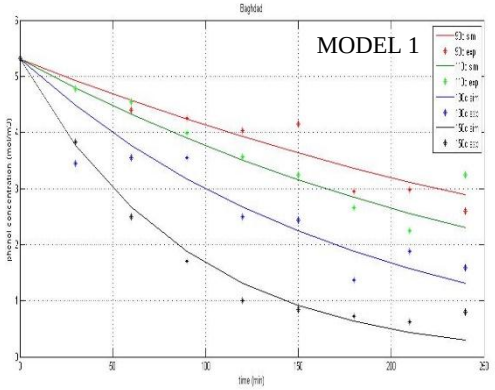


Fig. 15: Measured and predicted time profiles of phenol removal at various Temperature: (a) using model (Model 3); (b) using model (Model 4) (6.6 g/L catalyst, 500 ppm phenol, 1.5 MPa) for Erbil





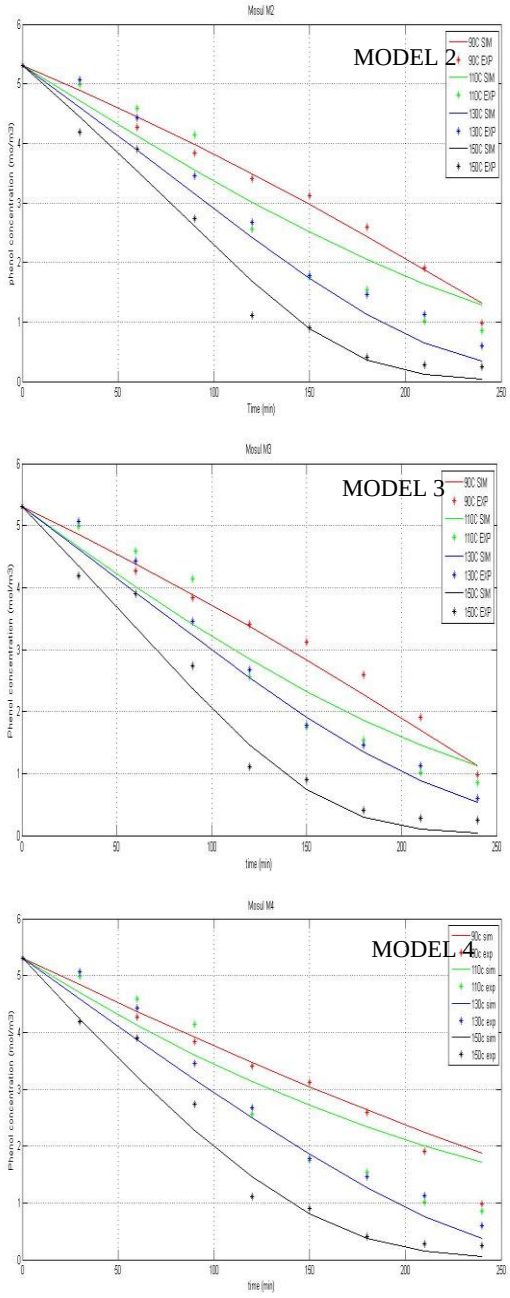


Fig. 16: Measured and predicted time profiles of phenol removal at various Temperature: (a) using model (Model 3); (b) using model (Model 4) (6.6 g/L catalyst, 500-ppm phenol, 1.5 MPa) for Mosul.

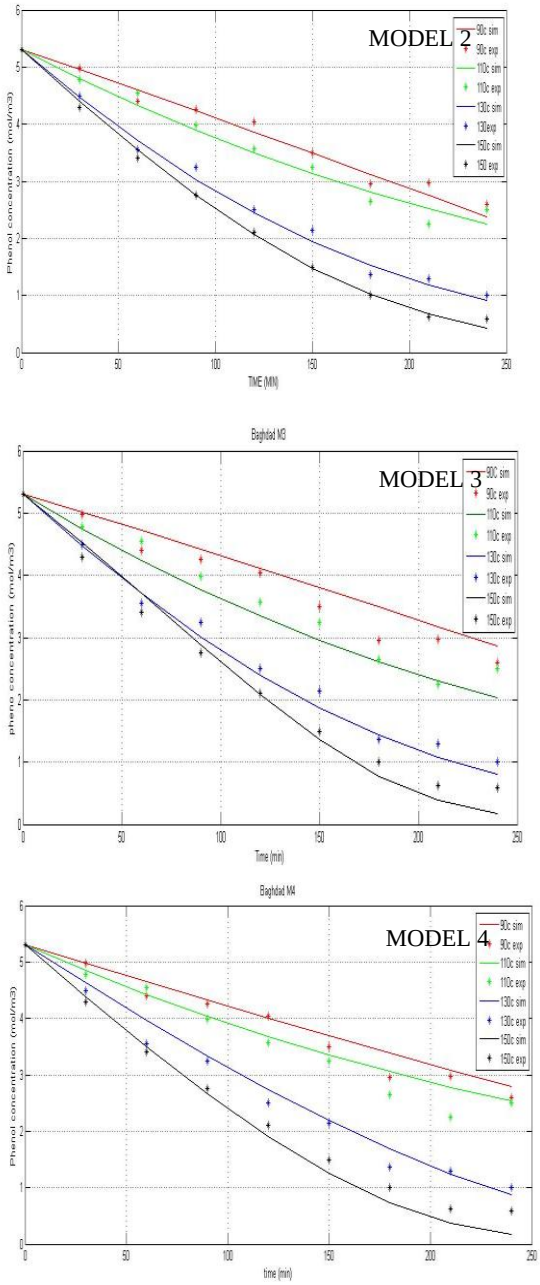
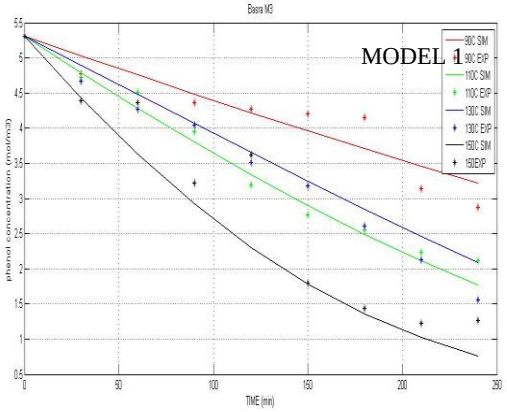
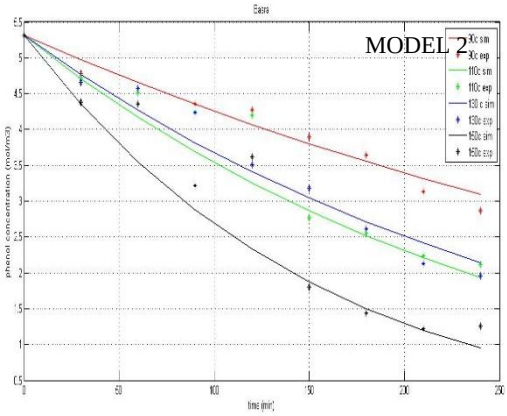


Fig. 17: Measured and predicted time profiles of phenol removal at various Temperature: (a) using model (Model 3); (b) using model (Model 4) (6.6 g/L catalyst, 500 ppm phenol, 1.5 MPa) for Baghdad





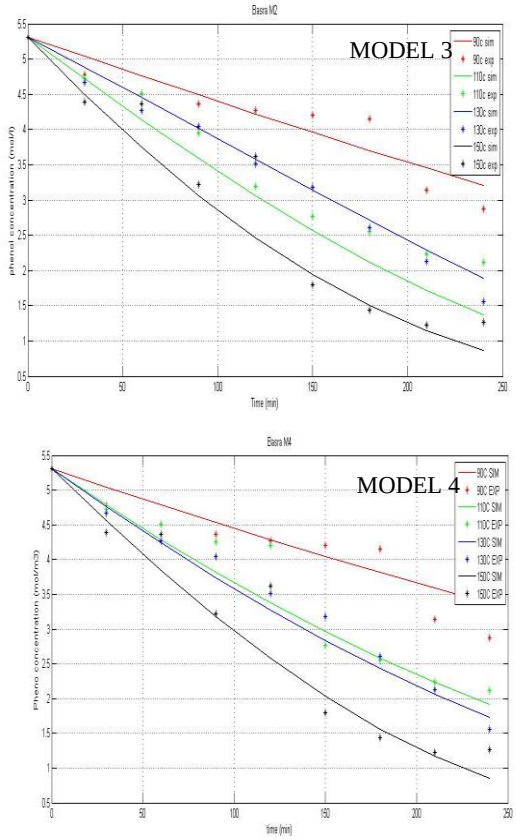


Fig. 18: Measured and predicted time profiles of phenol removal at various Temperature: (a) using model (Model 3); (b) using model (Model 4) (6.6 g/L catalyst, 500 ppm phenol, 1.5 MPa) for Basra.

6. Conclusion

Catalyst can efficiently increase the removal ability of phenol at Fe-AL pillared Mosul and Erbil, Anbar clay than Baghdad and Basra. Catalyst exhibited the best catalytic activity. The operation conditions are 150ºC, 3.5Mpa, 500mg/l phenol loading; the catalyst Fe-AL of Mosul clay is more stable than others catalyst regions.

The catalyst wet air oxidation was Successful for phenol removal from syntheses wastewater. The best model for each region is (Model 2) for Anbar, Mosul and Basra, (Model 3) for Baghdad, and (Model 4) for Erbil, The activation energies of each reaction 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. It was proved that the reaction in this study is under kinetics control. The reproduction of some representing exploratory information, by all models, give acceptable accord among the simulating outcomes and the empirical measurements.

Reference

[1] Matatov-Meytal, Y.I. and Sheintuch, M. (1998). 'Catalytic abatement of water pollutants', Ind. Eng. Chem. Res., 37, 309-326.

[2] Luck, F. Catal. Today, 1996, 27, (1–2), 195 LINKdoi:10.1016/0920-5861(95)00187-5http://dx.doi.org/10.1016/0920-5861(95)00187-5

[3] Kuo-Hua Wang et al. 1999. Photocatalytic degradation of 2nitrophenol by titanium dioxide suspensions in aqueous solution. Applied Catalysis B Environmental. 21: 1- 8.

[4] Eftaxias Athanasios (2002)" Catalytic Wet Air Oxidation of Phenol in a Trickle Bed Reactor:Kinetics and Reactor Modelling" Doctor in Chemical Engineering of the Rovira i Virgili University

[5] Rob. J. Berger, E. Hugh Stitt*, Guy B. Marin, Freek Kapteijn, Jacob A. Moulijn, (2001)" Chemical reaction kinetics in practice"EUOKEN Volume 5, no. 1, USA

[6] Bos A. N. R., Lefferts L., Marin G. B. and Steijns M. H. G. M., (1997) Kinetic research on Heterogeneously Catalyzed Processes: A Questionnaire on the State-of-the–art in Industry. Appl. Catal. A: General, 160, 185.

[7] Al-Dahhan, M., Guo, J., (2005)" Catalytic Wet Air Oxidation of Phenol in Concurrent Downflow and Upflow Packed-Bed Reactors over Pillared Clay Catalyst." *PhD .thesis –school of chemical Engineering, university of Washington.*

[8] Eftaxias, A., Font, J., Fortuny, A., Fabregat, A. and Stuber, F., "Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalys", Journal of Chemical Technology and Biotechnology, 80, 677-687, 2005.

[9] Luma Shihab Ahmed (2012)" Hydrodynamics and Kinetics Study of Phenol Removal Treatment in wastewater in aTrickle Bed Reactor"A Thesis Submitted to the Department of Chemical Engineering of the University of Technology

[10] Mirzaeia, A.A. *, M. Arsalanfara, F. Ebrahimzadeha, H. Atashib and S.H. Mirhoseini Moghaddamc (2013)" Kinetic Study of Fischer Tropsch Synthesis over co Precipitated Iron-Cerium Catalyst Phys. Chem. Res., Vol. 1, No. 1, 69-80, June 2013 www.physchemres.orginfo@physchemres.orgIran.

[11] Ghaidaa, AL-Rawi.., (2015)" Performance Enhancement in Unsteady State Operated Trickle bed Reactor of Organic Compound" Master Thesis University of Technology.

[12] Lamyaa, Adnan, Abdulridha, 2015 "Expermental Study and Simulation of Advanced Oxidation Process for Wastewater Treatment" M.Sc. Thesis in Chemical Engineering Iraq

[13] Santos,A. P. Yustos, A. Quintanilla, F. Garcia-Ochoa, J. A. Casas, J. J. Rodriguez, Environ. Sci.Technol. 38 (2004) 133-138.

[14] Wu, Q., Hu ,X., and Yue, P., "Kinetics study on catalytic wet air oxidation of phenol", Chem.Eng.Sci, 58, 923-928, 2003.

[15] Barrault J., Abdellaoui M., Bouchoule C., Majeste A., Tatibouet J. M., Louloubi A., Papayannakos N. and Gangos N.H,: Catalytic wet peroxide oxidation over Mixed (AL-Fe) pillared clays. APPL.catal. B., Environmental, 2000, 27, 225.

[16] bankovic, P., A. Milutionovic., Nikolic, A. Rosic., N. Jovic – Jovicic , and , Jovanovic: structural and Textural properties of AL-Fe – pillared clay catalysts, Journal of physical chemistry, 2009, vol 83 No. 9 PP 1485-1489.

[17] Pintar, A. and Levec, J., Catalytic liquid-phase oxidation of phenol aqueous-solutions - a kinetic investigation, Ind. & Eng. Chem. Res., 33(12), p. 3070 (1994).

[18] Arora, N., and Biegler, L. T., Redescending estimators for data reconciliation and parameter estimation, Computers and Chemical Engineering, 25, 1585 (2001).

[19] Fortuny, A. C. Bengoa, J. Font, A. Fabregat, J. Hazard. Mater. 64 (1999(181).

[20] Eftaxias, A., Font, J., Fortuny, A.,Giralt,J., Fabregat, A. and Stuber, F., 2001"Kinetic modeling of catalytic wet air oxidation of phenol by simulated annealing", Applied catalysis B:Environmental, 33, 175-190,.

[21] Eftaxias A., Font J., Fortuny A., Fabregat A. (2005)"Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst". J. Chem. Technol. Biotechnol. Vol., 80, 677-687.

[22] Raweewan Klaewkla, Matthias Arend and Wolfgang F. Hoelderich (2011). A Review of Mass Transfer Controlling the Reaction Rate in Heterogeneous Catalytic Systems, Mass Transfer - Advanced Apects,

[23] Dr. Hironori Nakajima (Ed.), ISBN: 978-953-307-636-2, InTech, Available from:http://www.intechopen.com/books/mass-transfer-advanced-aspects/a-review-of-mass-transfer-controlling-thereaction-rate-in-heterogeneous-catalytic-systems

[24] 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

[25] Duggleby R. G., (1984) Regression Analysis of Nonlinear Arrhenius Plots: An EmpiricalModel and a Computer Program. *Comput. Biol. Med*., 14, 447.

[26] Oleta Platon1*, Ana-Maria Rosu1, Vasilica Alisa Aru1, Denisa Ileana Nistor1, Ilie Siminiceanu2 (2013) "Chemically Modified Clays used for Environmental quality" journal of engineering studies and research – volume 19 no. 4, pp. 52-58.