A Kinetic Study of Removal of Some Organic Pollutants from Waste Water

Suada. A. Mohamed

Faculty of Science, Al-Baha University, Kingdom of Saudi Arabia
soada.mokhtar@gmail.com

Abstract

This work deals with removal of some pollutants from waste water, the rate of oxidation of some organic pollutants in water, such as phenol, cresol, toluene that have been oxidized by the reaction with polyoxometals catalyst to activate H_2O_2 have been investigated. The polyoxometals that were used, 10-molybdovanado sodium phosphate $Na_5Mo_{10}VPO_{40}$ (HMoVPA) and 12-molybdophosphoric acid $H_3PMo_{12}O_{40}$ (HMoPA). These reactions have been studied kinetically by varying the reactants concentrations, temperature, catalyst concentrations, pH and solvent. The rate of reaction was found to increase with an increase in concentration of pollutants, H_2O_2, and catalyst and temperature. Toluene appeared to have the highest value of rate constant, while paranitrophenol showed to have the lowest.

In addition, Hammet equation was used to study the effect of the presence of electron donating group (- CH_3), and withdrawing groups (- NO_2, -Cl). Electron donating group increases the rate of reaction while electron withdrawing groups have the reverse effect. Reaction rate ρ was calculated (-1.97) for heterogeneous $H_3PMo_{12}O_{24}$ catalyst and (-1.24) for homogeneous catalyst $Na_5Mo_{10}V_2PO_{40}$.

Eyring equation was also used to calculate the enthalpy of activation $\Delta H^{\#}$ and the entropy of activation $\Delta S^{\#}$ for these reactions (34.323 $KJmol^{-1}$ and -101.3 $KJmol^{-1}$ for heterogeneous catalyst and 41.67 $KJmol^{-1}$ and -78.57 $KJmol^{-1}$ for homogenous catalyst respectively).

$H_3PMo_{12}O_{24}$ has the lowest value of $\Delta H^{\#}$, which means that it is the most reactive catalyst while $Na_5Mo_{10}V_2PO_{40}$ is the lowest reactive among the catalysts studied.

Introduction

Many substances can cause pollution to the environment, some are pesticides, fertilizers, oil, mining, sediment, chemical and industrial processes. Pollutants may be of natural origin e.g. through volcanic eruptions or as a result of human activities such as the spilling of oil or disposal of industrial waste as the fate of these pollutants in concerned. Pollutants are either biodegradable, which can be rendered harmless by natural processes or non-biodegradable. These accumulate in the environment and many appear in food chain[1].

To reduce or prevent the pollution of our environment measures should be taken and strict legislations shall be enforced by some efforts like getting rid of chemical waste in the proper scientific ways, or preventing the atmospheric contamination air contaminants will have distilled in rain water and find their way eventually to ground water or to steam and rivers. Water may be contaminated with high levels of hydrocarbon concentration (up to 50 ppm), of pollutions like chlorobenzene, dichloroethane and vinyl chloride. The concentrations of these compounds in water depend on the type of soil and the extent of its, pollution with industrial waste.[2]

The most harmful organic pollutants are the poly nuclear aromatic hydrocarbons which are carcinogenic. To remove these pollutants activated carbon is used were in particulate or powered from activated carbon adsorbs these substances on its surface.

The volume of the adsorbed material can be calculated using BET (Brunauer-Emett- Teddere) Equation.[3]

The removal of such pollutants can be done by several methods such as chemical oxidation and photolysis.

One of the serious problems now in Sudan is the pollution of drinking water, studies at different cities in Sudan have found that some organic compounds

which are harmful to human health, several methods have been used for water purification, such as ozonation.[4]

Strong oxidation agents such as chlorine gas, perchlorate salts, ozone gas, and uv. radiation is used in this process.[5] Heterogeneous catalysts such as photosensitizers for complete oxidative degradation of organic compounds by oxygen, and polyoxometals, were found to activate O_2 to decompose organic pollutants by oxidation to mineral acids, CO_2 and H_2O.[6]

Activation by per acid formation is the most common industrial use of hydrogen peroxide, in the presence of carboxylic acids produces peroxycarboxylic acid per formic and per acetic acids are the most popular of these pre acids peroxide, can also be reacted with acid to form H_2SO_4.[7]

The most commercial area for the use H_2O_2 is epoxides. Epoxides are used as plasticizers and stabilizers but are particularly use full as synthetic intermediates. The epoxidation of soya been oil is the largest use of H_2O_2 in chemical synthesis.[8] Other oxidants such as dichromate, permanganate is all more expensive than hydrogen peroxide.[9]

Materials and Methods

1. Materials

12- Molybdophosphoric acid $H_3 PMo_{12}O_{40}$ (HMo PA), and 10-molybdovanado sodium phosphate.

$Na_5Mo_{10}V_2PO_{40}$ (HMo VPA) as ployoxometals against organic pollutants, phenol ($C_6H_5 OH$), toluene (m-$CH_3C_6H_4OH$), Parachloro phenol (P-$ClC_6H_4 OH$).

and Para nitro phenol (P-$NO_2C_6H_4OH$), and without purification sample of polluted water. H_2O_2 was used in each kinetic experiment at different concentration and was standardized before the kinetic experiment was done.

2. Methods

2.1 Preparation of Heterogeneous Catalyst

Molybdophosphoric acid was prepared by dissolved 12.36g of ammonium molybedate in 30ml of H_2O, 1ml phosphoric acid was added, and the mixture was stirred for 15minutes. The pH of the resulting solution was adjusted to (4-5) by adding acetic acid and a solution of 5g of tributyl amine in 3ml of glacial acetic acid. The precipitate was collected immediately by filtration.[10] 20ml of 35% H_2O_2 was added to the precipitate formed above, and the mixture was stirred (30-35 °C) for (3-4hrs). The suspended mixture was cooled to room temperature until a yellow precipitate was formed.[11]

2.2 Preparation of Homogeneous Catalyst

Molybdo-venado-phosphate was prepared by dissolving 0.74g of flourooxovandium in 10ml of distilled water at room temperature, 35% H_2O_2 was added which gives yellow color solution, the solution was heated for 1 hr. at 60°C until a brown precipitate formed, which was filtered by vacuum filtration. A clear pale orange solution was heated at 60°C, then 8.64g of MoO_3 was added, and 2.60g of Na_2CO_3. $10H_2O$ was added, then 1ml of H_3PO_4 was added and the mixture was refluxed for 3hrs. the resulting homogeneous red solution was cooled to room temperature and volumetrically diluted with distilled water to a total volume of 400.00 ml giving 0.30 M solution of 10-molybdovenado sodium phosphate.[12]

3. Oxidation of Pollutants

Diluted concentrations of phenol, metacresol, para-cresol, para-chloro phenol, para-nitro phenol and toluene, were added to ployoxometals of different concentration were added to organic pollutants with different concentration and activated with 0.35M H_2O_2, were found to activate O_2 in presence of light to decompose organic pollutants in waste water by oxidation to mineral acids, CO_2 and H_2O.[13] The UV spectra was recorded to each experiment at 5minute time interval, the absorbance of the products of the reaction was measured at different

time intervals at wave length of 380 nm using UV - visible spectrophotometer (UV- 1800 shimadzo –ENG 240 V soft), with path length of 1 cm. In each experiment the absorbance was plotted versus time by using (graphic program origin 61). from graphs each reaction was filled as first order reaction.

And from this equation the slope dA/dt was calculated from the slow reaction and also (initial rate = slope / $\Delta\varepsilon$ was calculated[14].

4. Results and Calculations

Hammet correlation   equation[15] was used to study the effect of substituents on phenol on the rate of these reactions

Log K_x / K_h = $\sigma\rho$

where:

K_x = is the catalyzed rate constant for organic pollutants

K_h = is the catalyzed rate constant for phenol

σ= is the substituent constant

ρ = is the reaction constant

Value of σ is obtain from the literature

The catalyzed rates and the catalyzed rate constants were calculated with variation of temperature. The enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were calculated for these reactions by using Eyring equation.[16]

K_{cat} = K_b T/h$e^{(-\Delta H^{\ddagger}/R)}$ $e^{\Delta S^{\ddagger}/R}$

where

K_{cat} = catalyzed rate constants at temperature T

K_b = Boltzmann constants = 1.38×10^{-23} J/k

h= Planck's constant = 6.6262×10^{-34} JS

T = Temperature (Kelvin = C+273.2)

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$\Delta H^{\#} = enthalpy\ of\ activaiaion$

$\Delta S^{\#} = enropy\ of\ activation$

R = gas constant = 8.31k^{-1} mol^{-1}

= 1.9 87 cal k^{-1} mol $^{-1}$

This equation converted to

$\ln(K_{cat}/T) = (-\Delta H^{\#}/RT) + I(K_b/h) + \Delta S^{\#}/R)$

Plotting of ln (K_{cat}/t) versus 1/T give a straight line with

slope = $(-\Delta H^{\#}/R)$ and intercept = $\ln(k_b/h) + (\Delta S^{\#}/R)$

The absorbance of molobdophosphoric acid (HMoPA) with organic pollutants to activate H_2O_2 was plotted versus time (minute), fig (1) the slope of the resulted straight line was divided by molar absorptive $\Delta\epsilon$ to calculate the initial rate of the reaction equal to slope /$\Delta\varepsilon$.

A=0.17455
B=0.03106
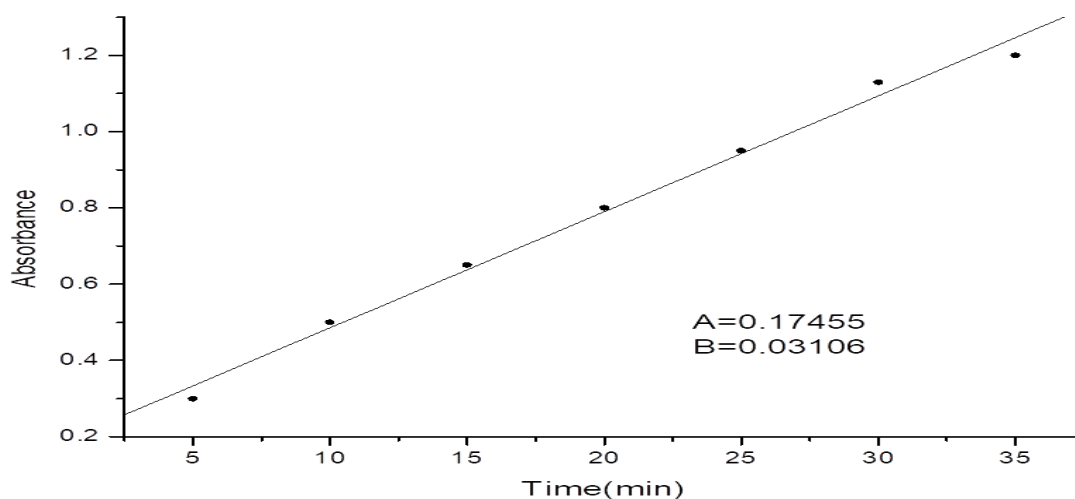
Fig(1):Reaction of HMoPA 0.001 with paracresol 0.0006M

From fig (1) the slope = 0.031 and intercept = 0.175, by using Beer's law ΔE= 900 cm^{-1} dm^{-3} mol and initial rate = 0.0003S^{-1}.

The observed rate constant k$_{obs}$ for each catalytic reaction was calculated by using equation:

$A_t = m_1 + m_2 (e^{-m_3 m_0})$,

Table (1): a reaction was fitted to first order reaction rate law

Organic pollutants	K$_{obs}$
Toluene	0.128
Meta-cresol	0.080
Para-cresol	0.030
Phenol	0.025
Para-chlorophenol	0.020
Para nitrophenol phenol	0.001

by plotting the total absorbance of each reacting versus time (minute), the catalyzed and un catalyzed rate constants, were calculated for each reaction by plotting the values of k$_{abs}$ versus the concentration of HMoPA Fig (2), the slope of the resulted.
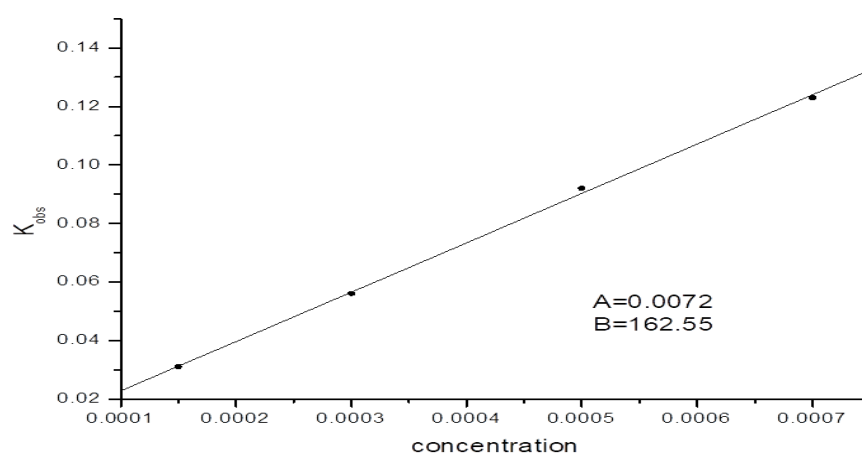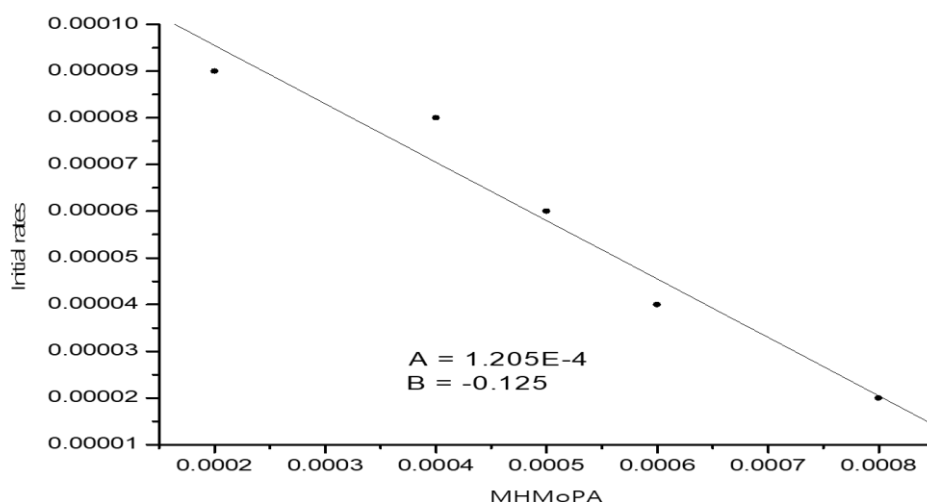

Fig(2):concentration of HMoPA with observed rate constant of parachlorophenol

The straight line is equal to the catalyzed rate constant and the intercept is equal to uncatalyzed rate constant, from fig (2), slope = 162.55 and intercept = 0.0015. the values of catalyzed and uncatalyzed rate constant for the reaction of HMoPA with substituted phenols to activate H_2O_2 are shown in table (2).

Table (2): The values of catalyzed uncatalyzed rate constant

Organic pollutants	K_{cat}	K_{uncat}
Toluene	162.55	0.0015
Meta-cresol	72	0.0020
Para-cresol	60.2	0.0032
Phenol	48	0.0080
Para-chlorophenol	30	0.00010
Para nitrophenol phenol	2.43	0.0008

Effect of concentration of reactants (polyoxometalates) (HMoPA), organic pollutant and H_2O_2 on the rate of reaction was studied by plotting the initial rate of reaction versus the concentration of reactants fig (3) slope = catalyzed reactants = -0.125, and the effect of temperature the catalyzed rate constants

Fig(3):Concentrations of MHMoPA versus initial rates

we calculated for each catalytic reaction by plotting the observed rate constants versus the concentration of HMoPA catalyst at each temperature the slope of the resulted straight line is equal to catalyzed rate constant. Variations of the rat constant values with temperature are shown in table (3) below.

Table (3): Variations of the rat constant values with temperature

TK	K_{cat}	Ln K_{cat}/T	1/T
298	30	-2.9	0.0034
308	44	-1.95	0.0032
318	88	-1.28	0.0031
328	178	-0.61	0.0030

Using Eyring equation,

Ln $(K_{cat}/T) = -\Delta H^{\#}/RT + $ In $k_b/h + \Delta H^{\#}/R$ to calculate the enthalpy of activation $(\Delta H^{\#})$ and entropy of activation $(\Delta S^{\#})$ for these catalytic reaction by plotting Ln K_{cat}/T versus 1/T
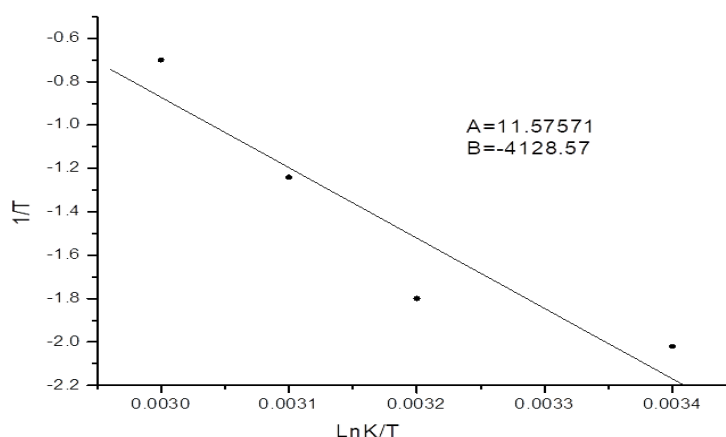
Fig(4):Valus of K_{cat} variated with temperature for the reaction of HMoPA with paracloropenol

where slope $= -\Delta H^{\#}/R = $ -4128.75, R = 8.314 Jk^{-1}

$\Delta H^{\#}$=34.32KJ mol^{-1}

Intercept = In $K_b/h + \Delta S^{\#}/R$ = 11.58

K_b = Boltz Mann's constant = 1.38 x10^{-23} x 10^{-34} Jk

$h = plank's\ constant = 6.63\ x\ 10^{-34} JS$

$\Delta S^{\ddagger} = -101.3\ KJsmol$

Hammet correlation equation was used to study the effect of substituents on phenol on the rate of catalytic reaction values of catalyzed rate constants of the reaction of HMoPA with substituted phenols to activate H_2O_2 are shown in table (4),

Table (4): values of KX variation with Log(KX/Kh)

| Organic pollutants	K_X	$Log(K_X/K_h)$	substituent's constant σ
Toluene	162		
Para-cresol	60.2	0.98	-0.17
Phenol	48	0.00	0.00
Para-chlorophenol	30	-0.204	0.23
Para nitrophenol phenol	2.4	-1.35	0.78

log (k_x/k_h) was plotting versus values of substituent's constant, fig (5) the slope of the straight line was equal to the reaction constant ρ = -1.7952,
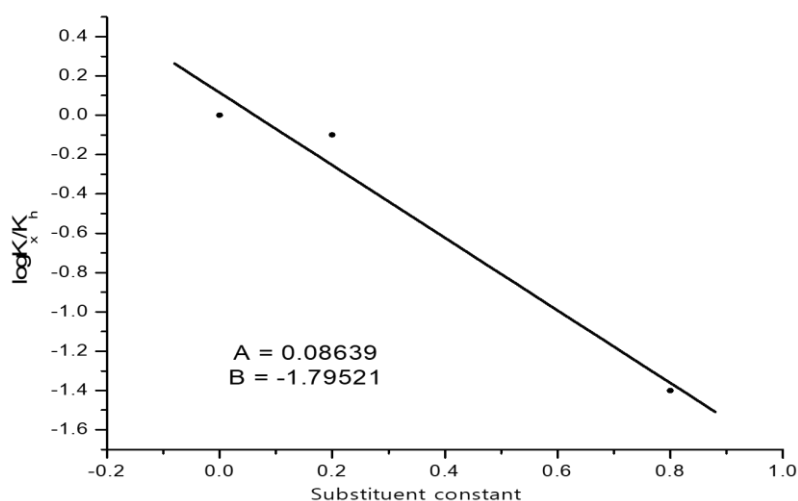
Fig(5):Values of substituentsc constant versus logK$_x$/K$_h$

The initial rate was calculated with variation of the volume percentage acetonitrile as shown in fig (6), the effect of acidity on the rate of reaction was

calculated by plotting the initial rate with concentration of H_2SO_4 the reaction of HMoPA (0.008) with toluene (0.006M) to activate 0.3 5M H_2O_2 at $25C^0$.
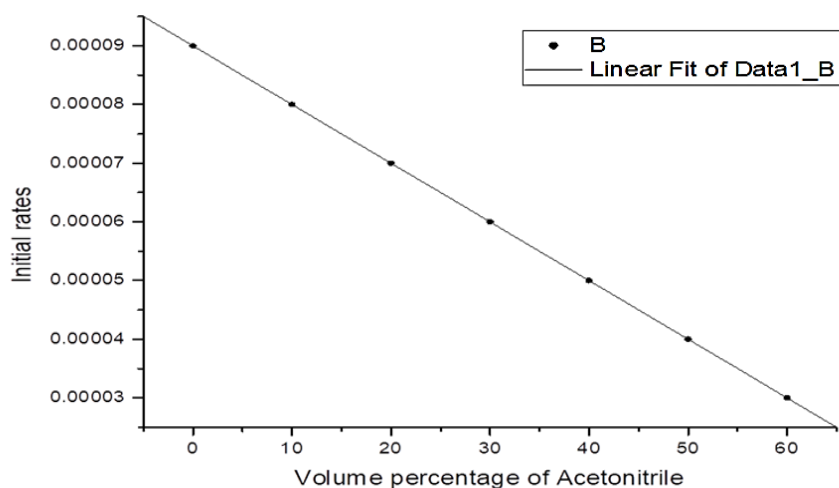
Fig(6):Variaction of initial rates with volume percentageof acetonitrile

5. Discussion

5.1 Oxidation of Some Organic's Pollutants:

Recently many research works have been done on the oxidation of organic pollutants by chemical oxidation.

Many oxidants like iodosyl benzene $C_6H_5IO_2$, permanganate, and thulium-nitrile [16] were used. Other research works used catalytic oxidations where some substances were added to the reaction mixture to activate the oxidizing agent.

Among these polyoxometalates are reported to be good oxidation catalysts. For example, $H_5PV2Mo10O40$ (vanado molybdo phosphoric acid) and 12 tungsto-phosphoric acid $H_3PW_{12}O_{40}$.

Newman's studied the oxidation of alcohols and amines by using $Na_5PV_2Mo_{20}O_{40}$ on activated carbon18.

Hemadneh19 obtained good results on the removal of phenol from waste-water by using tungsto- phosphoric acid as oxidation catalyst.

In this study hydrogen peroxide has been used as the oxidizing agent and HMoPA, HMoVPA used as the oxidation catalysts.

Hydrogen peroxide is the best oxidants and is chosen in this study. Environmentally safe cheap and also good long-term storage stability over a wide range of condition.

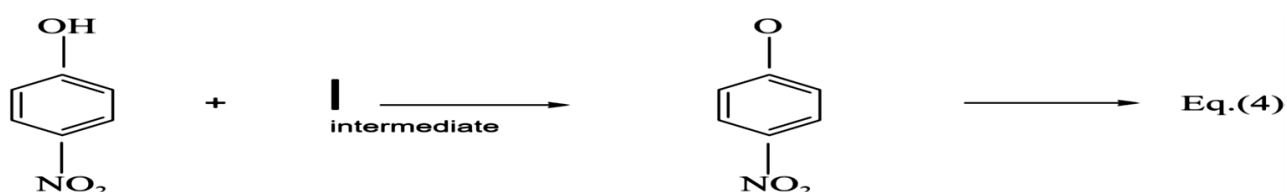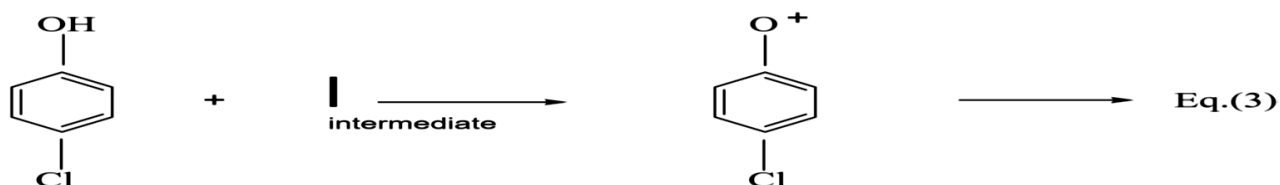## 5.2 Determination of rate constants

The results in the table (1) show that the catalyzed rate constants of toluene are higher than that of another organic pollutant, equation (1),
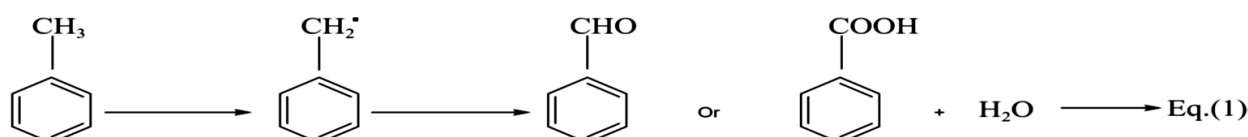
and show that para nitro phenol has the lowest value of observed and catalyzed rate constants while para cresol has the highest values, more than another phenolic compounds which means that toluene is more reactive than other organic pollutants, Para cresol is more reactive than phenol compounds. Methyl group (CH_3-) is an electron donating group which increases the electron density on phenoxy radical and destabilizes it, so its reactivity increases as result as shown in equation (2).
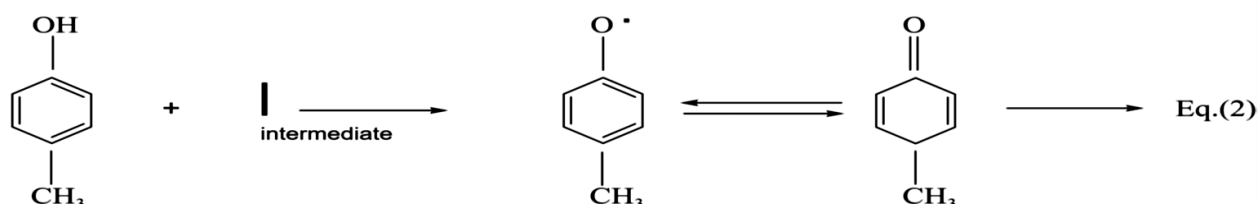
The Paranitrophenol and Parachlorophenol NO_2 and Cl_2 groups are electron withdrawing groups which decrease the electron density on phenoxy radical and stabilize it, so its reactivity decreases as shown in equations (3), (4)

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Result in table (2) show that toluene has the highest catalyzed rate constants, and the values of catalyzed rate constants of HMoPA catalyst is higher than the values of HMoVPA catalyst which mean that HMoPA catalysts is more active than HMoVPA.

6. Summary and Conclusion

In this work the kinetics of the removal of some organic pollutants by polyoxometals activated hydrogen peroxide H_2O_2 was investigated, the kinetic study included the effect of concentration and temperature.

The study concluded, that the rate of the investigated reaction depends on concentration of organic pollutants and the catalysts, and the oxidation processes go with appreciable rate in presence of polyoxometals catalyst of the wise it is quite slow reactions.

Temperature increase the rate reaction; the reactivity of organic pollutants was found studies can be arranged in the following order;

Toluene > Para Cresol > Phenol > Para chloro phenol> Para nitro phenol.

HMoPA is more effective than HMoVPA as a catalyst.

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