Kinetics, Thermodynamic and Mechanism of Ultrasonic Degradation of Ortho-Xylene in Aqueous Solution

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ABSTRACT

Ultrasonic technology, as an innovative technology ,was used for degradation of o-xylene in an aqueous solution under ultrasound frequency of 20 kHz at different temperatures with initial concentration of 100 and 200 mg/L .Kinetic and thermodynamic of o-xylene degradation in aqueous solution were investigated. While the mechanism of o-xylene sonolysis was discussed. The degradation rate of o-xylene increased with increasing electric power, sonication time and by decreasing liquid volume, temperature and initial concentration of o-xylene. The beneficial effect of power on removal rates is believed to be due to increased cavitational activity occurring at higher levels of power. As power increases, the number of collapsing (effective) cavities also increases, which is leading to enhanced degradation rates. Thermodynamic parameters indicated that o-xylene degradation was spontaneous and exothermic in nature. The obtained data was fitted through the pseudo-first order model.

1.Introduction:

Water pollution is one of the serious problem due to technique activities in recent years, especially in developing countries [1]. Xylene is one of the important chemical with a characteristic pungent odor, and has been widely used as a solvent during a variety of many industries and commercial processes, such as chemical production, printing, paint, synthetic resin, rubber, mobile emission [2]. In addition, they are present in many petroleum derivatives, such as fuel oil and gasoline [3]. They are ubiquitous environmental pollutants which can be found in soil, water and air; and they penetrate in humans through ingestion, inhalation or absorption. Healthy it might be could cause problems in liver, kidneys, heart, lungs and nervous system, including neurological diseases or cancer [4]. Therefore, the removal of these pollutants is an important research topics for environmental treatment systems. Since xylene is a volatile organic compound (VOC), conventional VOC control technologies, including condensation, adsorption,

these technologies require high operating costs or secondary disposal treatments, and can be efficient only for high concentration xylene wastewater. Usually, the limit of xylene concentration in ground water is lower than 10 mg / L [5], so it is hard to apply these technologies for the degradation. As an alternative, ultrasonic irradiation has been applied since the 1990 for the degradation of organic pollutants in water, such as phenol [6-8], chlorinated hydrocarbons [9,10] and some other various aromatics [11,12]. This method has been widely investigated and has been proven to be an efficient. It is demonstrated that ultrasonic irradiation has potential for treatment of hazardous wastewater. The chemical effects of ultrasound are due to acoustic cavitation: which means the formation, growth and implosive collapse of bubbles in the liquid. The collapse of cavitation bubbles produces very high local temperatures (>5000 ^oC), and high pressures (>1000 atm) [13, 14]. Under such extreme conditions, water molecules degrade, releasing OH and H radicals. These radicals can also oxidize the solute and causing its degradation. One important advantage of the ultrasonic process is the

extraction, membrane separation and soon, have been

commonly utilized to control its escaping. However,

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fact that it can achieve the mineralization of the solute without producing sludge or another material that must then be discharged. For some organic pollutants, ultrasonic degradation is even efficient without additional oxidants, which can lower the cost of treatment.

In recent years, studies suggest that volatile contaminants could be quickly destroyed by ultrasonic irradiation [10].In this study, an investigation was focused on the ultrasonic degradation of o-xylene in aqueous media. A variety of different operating conditions were examined. The effects of both ultrasonic frequency and power on kinetic rate constants were also examined in order to gain insight into the kinetics of the degradation of o-xylene.

The scope of this work is to study the effect of ultrasound frequency on the removal of o-xylene typically found in wastewaters produced by chemical processes. In particular, the effect of various operating conditions (electric power, liquid volume, liquid bulk temperature, initial substrate concentration) on degradation rates have been investigated.

2. Experimental:





Fig. (1): Experimental setup of ultrasonic probe

2.2. Measurements of pH

The pH value was determined using pH meter of o-xylene solutions before and after degradation.

2.3.*Qualitative tests*

Aromatics and aliphatics were identified. Ignition of aromatics produces a smoky soot while the aliphatic give unsmoky blue flame.

Nitration was used to distinguish between aromatic and aliphatic compounds according to the following reaction

O-xylene supplied by sigma-Aldrich at 99 % of purity was used for degradation. Aqueous o-xylene solutions of 100 ppm and 200 ppm were prepared .Ultrasonic irradiation of the o-xylene solutions were carried out continuously with a sonicator (U.S.A) probe-type sonicator capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz and maximum electric power output of 100w Fig.(1).A sample of 100mlo-xylene solution was placed in 250ml conical flask and placed in water bath at temperatures of (283, 293, 313 and 333K)under a sonication for 150 min. Four milliliters samples were withdrawn every 10 min for kinetic study. The amount of residual concentration of o-xylene in the solution was measured considering the wave length of (215 nm) using a UV-Vis spectrophotometer. The value of the absorbance obtained has been used to determine the equilibrium concentration of calibration curve according to Beer-Lambert law. The degradation percentage(%R) of o-xylene was calculated as follows.

$R = (C_o - Ce) / C_o \times 100\%$

Where C_o and Ce is the initial and remained concentration of *o-xylene*

 $Ar-H + HNO_3 + H_2SO_4 + Ar-NO_2 + H_2O \longrightarrow$ ellow colour compounds

The yellow colour products indicate the aromatic type while the disappearance of the colour reflects the aliphatic one.

Detection of carbon dioxide produced from oxylene after oxidation via clear water-lime gave turbid in the presence of CO_2 according to the equation.

 $CaCO_3 + H_2O \longrightarrow CO_2 + Ca(OH)_2$

3. Results and Discussions:3.1. Effect of initial concentration

Experiments were conducted in various times to see if there was any synergistic effect on the degradation of o-xylene. Increasing the concentration from 100ppm to 200ppm showed a decrease in degradation of o-xylene. Experiments showed that with sonochemical reactor, about 97.88% and 95.52% degradation of o-xylene occurred after 150 min at 283K.But only 86.43% and 78.62% degradation of oxylene was observed within 10 min, as shown in table (1).Therefore, results obtained from the sonochemical

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degradation of o-xylene at various concentrations indicated that removal rates were found to be decreased with increasing of o-xylene concentration.

Table (1): The degradation of *o-xylene* by ultrasonic percentage with concentrationsof100 200ppm at different temperature,

	% of degradation at temperature (K)								
Time	283K		293 K		31 3 K		333 K		
	100ppm	200 ppm	100ppm	200 ppm	100ppm	200 ppm	100ppm	200 ppm	
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
10	86.43	78.62	81.24	76.48	81.00	70.43	74.00	69.12	
20	89.05	83.98	83.71	81.48	83.52	76.98	76.76	71.98	
30	89.57	88.38	86.05	84.50	85.86	78.76	78.33	74.81	
40	90.83	90.62	87.33	86.21	86.62	82.88	78.76	76.71	
50	91.92	91.67	89.10	88.29	88.14	85.64	79.38	78.26	
60	92.59	92.41	89.68	16.08	61.68	87.29	16.67	79.48	
70	92.98	92.91	91.48	90.45	90.57	88.74	80.38	80.10	
80	93.54	93.43	91.81	91.43	91.64	91.05	84.48	81.88	
90	93.98	93.95	92.19	93.55	91.99	92.76	86.33	86.02	
100	94.49	94.21	93.52	94.00	92.99	93.12	86.91	86.88	
110	94.88	94.50	93.95	94.17	93.78	93.52	87.57	87.55	
120	95.48	94.79	94.78	94.38	94.00	93.81	87.91	88.74	
130	95.99	95.17	95.30	94.69	94.15	93.91	88.33	89.19	

140	96.39	95.36	95.92	94.81	94.39	94.07	89.71	89.62
150	97.88	95.52	96.53	94.98	94.91	94.29	93.76	93.05

3.2. Effect of sonication time

In order to observe the effect of sonication time on the o-xylene degradation rate during treatment, sono-degradation (sonication time) for aqueous oxylene concentrations was performed in 150 min. As clearly seen, by increasing of the sonication time, considerable levels of o-xylene degradation, can be expected after150 min. It was observed that the degradation efficiency of acoustic frequency was increased when sonication time increased, as shown in table (1). Therefore, the statistical study indicated that when sonication time is increased, there is an increasing in removal percentage. This effect is due to the increase in the exposure time between the o-xylene solution and the acoustic cavitation process as the time of sonication is increased[15, 16].

3.3. Effect of temperature

Increasing the temperature was causing a decrease in degradation ratios of o-xylene table (1). The reason is possibly coming from the decrease of the surface tension and viscosity of the solution, so that the generation of bubbles becomes easier. However, the increase in solution temperature results in a dramatic increase of the vapor pressure of the liquid, which gives a higher vapor content of the cavitating bubble. In general, increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure. However, the sonochemical effect of such bubbles may be reduced. During the bubble growth, the complete collapse may not occur and the bubble may oscillate in the applied field if some gas or vapor has diffused into the bubble [27, 28, 29, 30].

Experiments showed that pH value has been affected through degradation of o-xylene. The pH values during the sono-degradation are shown in table (2). These values indicated that a surfactant will accumulate on a surface independent of whether it is protonated or deprotonated, the effect of pH value on degradation[21]. Also, this conclusion was confirmed by other researchers [22]who predicted that the pH value was a key parameter affected by the sono-degradation of surfactant.

Time		рН			
(min)	Temp.(K)	100 ppm	200		
(mm)			ppm		
0	Standard	5.694	5.512		
150	283	6.690	6.443		
150	293	5.967	6.367		
150	313	5.715	6.251		
150	333	5.511	6.126		

Table (2): The effect of temperature on pH values for degradation of *o-xylene* by sonication

3.4. Mechanism of o-xylene sonolysis

From the detailed analysis of the intermediate product, we propose that the reaction of o-xylene with the hydroxyl radical might have led to the formation of benzene,methyl benzene, o-methyl phenol, paradioxybenzene, benzoquinone and so on as the primary products. As the sonolysis went on, some carboxylic acids such as formic, oxalic and malonic acids and so on were formed. In the end, all of the carboxylic acids were decomposed into inorganic carbon, which might exist as bicarbonate or carbon dioxide. These results were in agreement with that of Refs.[23,24]. The variation of intermediate products suggests that the degradation of o-xylene proceeded as shown in (Sketch 1).



Sketch (1) Mechanism of o-xylene

3.5. Thermodynamic parameters:

The effect of temperature on thermodynamic constants is determined by using following equations [25].

$d \ln K/dt = \Delta H^0/RT^2 \qquad (1)$

Log K = $\Delta S^0 / 2.303$ R - $\Delta H^0 / 2.303$ RT.....(2)

Gibbs free energy ΔG^0 is given by:

 $\Delta G^{0} = \Delta H^{0} - T\Delta S^{0} \qquad (3) \text{ Where } \Delta G^{0} \text{ is the free energy change (kJ/mol); K is the thermodynamic equilibrium constant, R is the universal constant (8.314 J/mol K), T the absolute temperature (K); <math>\Delta H^{0}$ change in enthalpy; and ΔS^{0} is the change in entropy.

The ΔH^0 and ΔS^0 values were calculated from slope and intercept of the linear plot, of log K vs. 1/T as shown in Fig. (2).The corresponding values of thermodynamic parameters are presented in table (3). The negative values of ΔG^0 indicate that the o-xylene degradation process is spontaneous and feasible, while the negative value of ΔH^0 shown an exothermic degradation process in nature. The positive ΔS^0 indicated the increase in randomness during degradation of o-xylene.

Table (3): Thermodynamic functions of the degradation process using ultrasonic at the concentration of 200ppm

T(K ^o)	К	ΔH ⁰ kJ.mol ⁻¹	ΔS ⁰ J.mol ⁻¹ .k ⁻¹	ΔG ⁰ kJ.mol ⁻¹
283K ⁰	21.341	-7.018	0.658	-7.201
293K ⁰	18.904			-7.160
313K ⁰	16.499			-7.295
333K ⁰	13.384			-7.182



Fig. (2): The plot of Log K vs. the reciprocal of temperature by ultrasonic

3.6.Degradation kinetics:

Degradation kinetic models can be useful to determine the mechanism of degradation and the efficiency of the removal of pollutants. In this study, the degradation data of o-xylene by ultrasonic was fitted through kinetic model including *pseudo-first order kinetic*[26].

$\mathbf{Ln} (\mathbf{q}_{\mathbf{e}} - \mathbf{q}_{\mathbf{t}}) = \mathbf{ln} \mathbf{q}_{\mathbf{e}} - \mathbf{k}_{1} \mathbf{t} \dots \dots \dots (4)$

Where $q_e (mg/g)$ is the amount of o-xylene at equilibrium time while $q_t (mg/g)$ is the amount of o-xylene at any time (t),k, min⁻¹ is the pseudo-first order rate constant, k and q_e was determined from the slope and intercept of the linear plot of ln (q_e - q_t) against t, respectively Figs.(3 and 4).



Fig. (3) Linear relationship between LnCevs. timefor *o-xylenes*olutions at temperature 283K^o and Con. (200mg/L) using ultrasonic.



Fig. (4)Linear relationship between LnCe vs. time for *o-xylene* solutions at temperature 333K° and Con. (200mg/L) using ultrasonic.

4. Conclusion

Results obtained from this research demonstrate that sonochemical reactor at a frequency of 20 kHz and a power of 100 W is capable to some degree of oxylene degradation in aqueous synthetic solutions. The potential of sonochemical reactors for o-xylene degradation are evaluated with emphasis on the effect of sonication time and initial concentration. Experiments showed that sonication time is one of the most important parameters for o-xylene degradation. Sonochemical reactors alone may not be useful for reducing completely complex wastewaters of high surfactant load. Hence, effectiveness may improve coupling acoustical reactors with other treatment processes including ozone, UV, chlorination and H₂O₂. Alternatively, acoustical processor reactor could be used as a pretreatment stage in a sequential chemical and biological treatment process.

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حركية وثرموديناميكية وميكانيكية التحلل بالموجات فوق الصوتية للارثو زايلين في المحاليل المائية

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الخلاصة :

تعتبر تكنولوجيا الموجات فوق الصوتية أحد الطرق المعتمده للأستخدام في تحلل محاليل الاورثو زايلين المائية ، فقد تم أستخدام هذه التكنولوجيا لهذه المحاليل تحت تردد مقداره 20 كيلوهرتز لدرجات حرارية مختلفة وللتراكيز 100و 200 ملغم / لتر . كما تم دراسة حركية وثرموديناميكية تحلل المحاليل المائية للاورثو زايلين. أضافة الى أقتراح ميكانيكية خاصة بهذا التحلل. تشير النتائج الى زيادة مع دل سرعة تحلل الاورثو زايلين مع زيادة القدرة الكهربائية وزمن تعرض المحاليل للموجات فوق الصوتية ، كما أن هذا المعدل يزداد مع الأنخفاض بحجم السائل ودرجة الحرارة والتركيز الاولي للاورثو زايلين . أن زيادة قدرة الموجات فوق الصوتية ، كما أن هذا المعدل يزداد مع الأنخفاض بحجم السائل ودرجة الحرارة والتركيز الاولي للاورثو زايلين . أن زيادة قدرة الموجات فوق الصوتية ، كما أن هذا المعدل يزداد مع الأنخفاض بحجم السائل ودرجة الحرارة والتركيز الاولي للاورثو زايلين . زيادة قدرة الموجات فوق الصوتية سيؤدي الى زيادة عدد الفجوات الفعالة والتي تقود الى زيادة معدل سرعة التحلل . كما تشير النتائج الى زيادة مع أن تحلل الاورثو زايلين يكون بطبيعته تلقائياً وباعثاً للحرارة ، في حين تؤشر نتائج الحركية لهذا التحلل الى أنه تفاعل من الرتبة الاولي الكافري