Kinetics of Organic Dyes Degradation in Water Using Vacuum Ultra Violet Radiation

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Abstaract: In this study vacuum ultraviolet (VUV) radiation (185 nm wave length) was used in the presence of atmospheric oxygen as an advanced oxidation technique. Six organic dyes were examined as model pollutants (methyl violet, methyl blue, brilliant green, malachite-green, Remazole blue B and picric acid). Picric acid as the most persistent one was selected for more detailed kinetic investigations. The influence of each of the related main parameters was studied, Radiation time, salinity, pH, temperature and radiation intensity. Kinetics of the oxidation reaction was studied. COD was also followed up. It follows from the results that vacuum-UV radiation of 185 nm in the presence of atmospheric oxygen is an efficient method for the oxidation process. Four of sex examined dyes were degraded in different rates according to persistency of each pollutant dye. The reaction rates were in the order of: (methyl violet > methyl blue >brilliant green > remazole > malachite green> picric acid). In the case of picric acid; the reaction was promoted by rising the temperature, raising or lowering pH above and below pH 7.0, increasing radiation dosage. The rate was inhibited by increasing salinity and buffering. The present technique was found promising in the elimination of the persistent organic pollutants out of the treated water.

Keywords: Advanced oxidation process - Vacuum ultraviolet - Wastewater treatment, Radiochemistry, Organic pollutants.

1. Introduction

During recent years the **Advanced Oxidation Processes** (AOPs) have become an important group of techniques to the treatment of hazardous water contaminants, with an increasing number of feasible applications. (Ahmed et al. 2011) Normally, the main reason for the use of AOPs is the resistivity and/or the toxicity of pollutants that makes unfeasible the biological treatment. Although AOPs use different reacting systems, all are characterized by the same chemical feature: production of OH free radicals. These radicals are extraordinarily reactive species. (Ahmed et al. 2010)

The oxidation reactions involving hydroxyl radical and organic substrates in aqueous solution may be classified with respect to their character to: (Bossmann et. al. 1998)

·OH +RH	
OH + PhX	>
·OH +RH	
	·OH +RH ·OH + PhX ·OH +RH

AOPs are characterized by a free radical mechanism initiated by the interactions of photons of a proper energy level with the molecules of chemical species present in the solution such as H_2O_2 or with a catalyst surface such as TiO_2 . (US.EPA 1998; Bakardjieva et al 2005; Bakardjieva et al 2004).

Peroxone is another technique including the oxidation of organic pollutants using ozone with H_2O_2 was also reported. (Ben Abdelmelek et al. 2011; Ben Abdelmelek et al. 2010; Chu et al. 2022) Many studies were conducted concerning the elimination of the hardlyoxidized water pollutants by different catalytic methods using hydrogen peroxide as the main source of OH free radicals. Persisting pollutants such as phenol derivatives, (Ben Abdelmelek et al. 2011; Ben Abdelmelek et al. 2010) aromatic pesticides, (Chu et al. 2011; Chu et al. 2010) fuel additives, dyes, and some other pharmaceutical drugs has been treated. (Radjenovic et al. 2009; Gaya et al. 2008)

To date, there are many evidences supporting the idea that hydroxyl radical (OH) are the main oxidizing species responsible for photo-oxidation of the majority of the studied organic compounds. (Ollis et al. 1991; Dodd et al. 2009; Benites et al. 2009; Prevot et al. 1999)

Vacuum-UV irradiation of wavelength <190nm, initiates reactions that produce hydroxyl radicals, hydrogen atoms, and aqueous electrons which play important roles during degradation of organic substrates in water. Depletion rate of organic contaminants depends on the reaction rate of compounds of interest with hydroxyl radicals. Aqueous electrons are powerful reducing agents and act as nucleophiles. They react with substrates with one-electron transfer process. One of the most important reactions of aqueous electrons is with halogenated organic compounds resulting elimination of halide anions.

 $H_2O(L) + hv (< 190 \text{ nm}) \rightarrow H + OH \leftrightarrow H^+ + e^- + OH$

Carbon centered radicals, formed by their reaction with hydroxyl radicals, may result in the formation of higher molecular weight compounds hindering mineralization and TOC (Total Organic Carbon) reduction. This problem may be surmounted by bubbling oxygen gas. (Oppenländer 2003b)

It was reported that (VUV) radiation produced by an immersed Xe-excimer light source (172 nm) was investigated for the oxidative degradation of organic pollutants in aqueous systems. (Hashem et al. 1997; Oppenländer and Gliese 1997; Chong et al. 2010) It was shown that the rates of degradation of the substrate decrease in the order of the applied processes, $VUV/O_3 > O_3 > VUV$.

Influence of the oxygen concentration on the rate and reaction pathway of the degradation of organic compounds in aqueous solution by VUV-irradiation (Xeexcimer: 172 nm) was reported. (Heering 2004) The reaction rate was found to be strongly influenced by the concentration of dissolved molecular oxygen in the volume of primary reactions.

In the present research; 185 nm, VUV, radiation from a low pressure mercury lamp in the presence of atmospheric oxygen will be studied as advanced oxidation technique, the process is thought to be simple, cheap and clean where no chemicals are to be used. Six organic dyes will be tested as model pollutants, the method efficiency and the oxidation kinetic parameters will be investigated on the most persisting one of them.

2. Experimental

2.1 Materials.

Picric acid; (2,4,6-trinitrophenol) was locally prepared by the nitration of phenol, (Brewster et al. 1977) Remazole blue B commercial grade was purchased from (Brilliant Blue Daystar-LP, India), methyl blue, methyl violet and malachite green, Solid sodium hydroxide and Phosphoric acid 85% ~15M were analytical grade of (Merck-Germany). Distilled water of (TDS 60 ppm) was used in all the experimental activities.

2.2 Instruments

The main kinetic investigation system was a semicontinuous system as shown in (fig. 1, a low pressure mercury, VUV, 185 nm lamp (S415 ROL-Rcan- USA) is contained inside of a sealed stainless steel cell (S300-S2R,OZAP-USA) which is protecting the electrical components of the system. The system also includes air pump for the continuous aeration of the reaction media, a thermo-statated water bath, and a circulation system for the treated water. used for the spectroscopic measurements. A Hanna pH meter was used to adjust the pH of different solutions.

2.3 Methodology

The reaction kinetic study was conducted to compare similar samples of different pollutants; the samples have been treated identically under the same conditions of pollutant concentration (mg/l), circulating rate (0.65 dm³/ min), aeration rate (6.0 watt pump), working temperature (25.0 C°) and reaction volume (2500 ml).

Substrates depletion rates were followed spectrophotometrically. For each pollutant separately substrate concentration through the reaction term was determined. Each dye was followed at the proper λ_{max} (picric acid at 355 nm, remazole at 570 nm, methyl blue at 665 nm, methyl violet at 590 nm and malachite green at 625 nm). Absorption bands λ_{max} were obtained practically, Calibration curves of concentration against absorbance were obtained for the six dyes.

Kinetic investigation was performed such that: in each experimental run, reaction vessels were prepared with the proper volume (500 to 2500ml) of the reaction solution. The (observed reaction half-life) $t_{1/2}$ was obtained for each run. The half-life was approved because of the ignorance of the exact reaction order since many reactions are expected to proceed on the same time. Samples of picric acid were read spectrophotometrically with 0.02 mg/L detection limit at 355 nm λ_{max} which was determined experimentally. Reaction parameters such as salinity (ionic strength), temperature, light intensity and reaction pH) were investigated and the resultant halflives were plotted against readings (or values) of each parameter to clarify the relation graphically. Phosphoric acid (0.1M; H₃PO₄), and (0.1M; NaOH) were used to adjust the reaction pH at the values of (5, 6, 7, 8 and 9).

3. Results and Discussion

3.1 Influence of the organic pollutant resistivity.

Six organic pollutant were tested with respect to conversion or degradative oxidation, as shown in (Table 1), it can be observed that the rate of depletion was in the order of (methyl violet > methyl blue > brilliant green > malachite green> picric acid). This order may be due to different persistency of the various functional groups of each pollutant dye or the ease of oxidation. The experimental oxidation process was disturbed in two cases: the first was remazole case where a suspensional colloid appeared after some time (15-30 minutes) of the degradation process and the second was the case of malachite green where polymerization is thought to interfere the degradation process since highly viscous green product was adhering the reaction vessel internal wall. Trinitrophenol (picric acid) was selected for more detailed kinetic study. It was the most persistent pollutant among the six dyes.

Pollutant	Methyl	Methyl	Brilliant	Malachite	Remazole	Picric
die	violet	blue	green	green	blue B	acid
λ_{max} , nm	590	665	523	625	570	355
$t_{1/2}$, hrs	1.5	1.83	1.7	3.11	Colloid	4.73

Table 1: Organic pollutants degradation Half-lives ($t_{1/2}$), (2500 ml total volume, T= 25±0.5 °C, circulating rate, 6.5 dm³/min).

3.2 Effect of salinity

The influence of the treated water salinity on the observed reaction half-life was studied. Salinity of course is mainly proportional to ionic strength. The reaction was conducted under fixed conditions of temperature, circulating power and reaction total volume. In the studied range of [NaCl] the reaction half-life was increasing by increasing [NaCl], direct relation was observed up to 6000 mg/l sodium chloride concentration as shown in (fig. 2), the optimum oxidation rate can be achieved in desalinized treated water. In practical water treatment processes; water salinity is expected to have a negative influence on the rate of degradation. The influence of aqueous NaCl is not clear, wither it is up to free radical scavenging or simply the loss of UV photons by scattering with ions.

3.3 Effect of the volume of the treated water

Degradation rate was lowered by increasing the treated water volume. Reaction half-life was followed. It was increasing directly by increasing the volume of the treated water in the studied range, the relation is plotted in (fig. 3). The conversion rate is decreasing by decreasing the radiation intensity per unit volume of the treated water in the studied range (3.0 to 30.0 Watt per liter).

3.4 Influence of temperature

Increasing temperature has a promotional influence on the oxidation reaction in the range of $(25-60 \ ^{0}C)$. It is clear in (Fig. 4) that an inverse relationship was obtained between ln $1/(t_{1/2})$ and 1/T, where a straight-line was obtained. The result means that the process has an overall Arrhenius type behavior. It was expected according to post studies (Oppenländer et al 2005) that: the radiation intensity is affected by changing the environment temperature. In that case it may affect the UV light intensity and so the reaction kinetics, Arrhenius type relation has been observed in this case, which means a very weak influence of temperature on the radiation intensity under the present reaction conditions.

3.5 Effect of pH

Effect of pH on the oxidation reaction was examined in the pH range (4 to 10). (Fig. 5) shows the values of $T_{1/2}$ corresponding to each pH value. The oxidation rate is increasing by increasing each of OH⁻ and H⁺ concentrations. It means that there are two accelerating roles for each of H⁺ and OH⁻ according to various mechanisms. Comparison of $t_{1/2}$ in buffered and nonbuffered pH 7 reactions which were respectively (14.73 and 4.71 hours) implies that the presence of ions in the treated water again has a retarding influence on the degradation rate.

The last results show that the treatment of basic polluted water is easier and faster than the treatment of neutral and acidic polluted water under the same conditions. It is not recommended of course to increase the basicity of the treated water to get a faster process but at least it should be known that if the treated water was basic by chance the process is expected to be faster. 3.6 COD follow up.

Degradation was followed by measuring chemical oxygen demand COD at different time intervals. One model run was performed. Picric acid oxidation derivatives are thought to go further oxidation by time. After the breakage of aromaticity, ketones, aldehydes and carboxylic acids are thought to precede oxidation (Qian-Rong L. 2006). The final expected products are mostly CO₂ and H₂O. Degradation conditions were (250mg picric acid in 2500 ml, distilled water, 25°C, 6.5 dm³/min circulating rate). (Fig. 6) insures the degradation process, $t_{1/2}$ of the COD depletion was 6.5 where the oxidation process is continuous for the derivatives as well as the starting compound picric acid.

4. Conclusion

The primary goal of this project was to investigate the VUV degradative oxidation of persistent industrial organic pollutants. The method was found efficient for four per six examined pollutants. As expected, the present method is more efficient at higher temperatures and higher intensity of VUV radiation. The present technique can be preferable over other techniques in two ways: it is simple and clean method where no chemicals are needed; only atmospheric oxygen. It can be suggested for practical applications after case study is conducted concerning the real pollutant/s specifically beside the other treated water conditions.

References:

R. Palaniappan, C. Eswaran, Using genetic algorithm to select the presentation order of training patterns that improves simplified fuzzy ARTMAP classification performance, Applied Soft Computing, 9 (2009) 100-106 S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Heterogeneous photo catalytic degradation of phenols in wastewater: A review on current status and developments. Desalination 261 (2010) 3-18. S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewaters: A Review. Water, Air and Soil pollution 215 (2011) 3-29.

S. Bakardjieva, J. Subrt, V. Stengl, M. J. Dianez, M. J. Sayagues, Photoactivity of anatase-rutile TiO_2 nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase. Applied Catalysis B: Environmental 58 (2005) 193-202.

S. Bekkouche, M. Bouhelassa, N.H. Salah, F.Z.Meghlaoui, Study of adsorption of phenol on titanium oxide (TiO₂). Desalination 166 (2004) 355-362.

F. J. Benitez, J. L. Acero, F. J. Real, G. Roldan, Ozonation of pharmaceutical compounds: Rate constants and elimination in various water matrices. Chemosphere 77.1 (2009) 53-59.

F. L. Ben Abdelmelek, E. C. Wert, S. A. Snyder, Evaluation of UV/H_2O_2 treatment for the oxidation of pharmaceuticals in wastewater. Water Research 44.5 (2010) 1440-1448.

S. Ben Abdelmelek, J. Greaves, K. P. Ishida, W. J. Cooper, W. Song, Removal of pharmaceutical and personal care products from reverse osmosis retentate using advanced oxidation processes. Environmental Science & Technology 45.8 (2011) 3665-3671.

S. H. Bossmann, E. Oliveros, S. Gob, S. Siegwart, E. Dahlen, L. Payawan, M. Straub, M. Worner, A. Braun, New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. *J. Phys. Chem* 102 (1998) 5542-5550.

R.Q. Brewster, C.A. Vanderwarvf , W.E. Mcewen, Unitized experiments in organic chemistry, 4th edition, 1977, PP 394.

M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review. Water Research 44 (2010) 2997-3027

T.Chu, S.K. Umamaheshwar, A. Mumper, Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. Chemosphere 79.8 (2010) 814-820.

W. Chu, Y.R. Wang, H.F. Leung, Synergy of sulfate and hydroxyl radicals in UV/S_2O_8 -/H₂O₂ oxidation of iodinated X-ray contrast medium iopromide. Chemical Engineering Journal 178 (2011) 154-160.

M.C. Dodd, H.P.E. Kohler, U. Von Gunten, Oxidation of Antibacterial compounds by ozone and hydroxyl radical: Elimination of biological activity during aqueous ozonation processes. Environmental Science & Technology 43.7: 2498-2504.

Gaya UI, Abdullaha AH. 2008. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. Journal of Photochemistry and Photobiology C: Photochemistry Reviews.9 (2009) 1-12.

T.M. Hashem, M. Zirlewagen, A.M. Braun Simultaneous photochemical generation of ozone in the gas phase and

photolysis of aqueous reaction systems using one VUV light source, Water Science and Technology, 35. 4 (1997) 25–30.

W. Heering, UV bources-basics, properties and applications, International ultra violet association, 6. 4 (2004) 7-13.

D. F. Ollis, E. Pelizzetti, N. Serpone, Destruction of water contaminants. *Environ. Sci. Technol.* 25. 9 (1991) 1523-1529.

T. Oppenländer, Photochemical Purification of water and air, advanced oxidation processes (AOPs): Principles, reaction mechanisms, and reactor concepts. Wiley-VCH, Germany (2003b) 73-91.

T. Oppenländer., S. Gliese, Mineralization of organic micropollutants (homologous alcohols and phenols) in water by vacuum-UV-oxidation (H₂O-VUV) with an incoherent xenon-excimer lamp at 172 nm. Chemosphere, 40. 1(2000) 15-21

T. Oppenländer, J. Burgbacher, M. Kiermeier, K. Lachner, H.Weinschrottin, Improved vacuum-UV (VUV)-initiated photomineralization of organic compounds in water with a xenon excimer flow-through photoreactor (Xe2* lamp, 172 nm) containing an axially centered ceramic oxygenator. Chemosphere 60.3 (2005) 302-9.

A. B. Prevot, M. Vincenti, A. Bianciotto, E. Pramauro, Photocatalytic and photolytic transformation in aqueous solutions. App. Catal. B: Environ; 22 (1999) 149-158.

L. Qian-Rong, G. Cheng-Zhi, D. Yan, y. Hao, Z. Jun-Ying, Photo-degradation of nitrobenzene using 172 nm excimer UV lamp. Materials, 133, Issue: 1. 3 (2006) 68-74

J. Radjenovic, M. Godehardt, M. Petrovic, A. Hein, M. Farre, M. Jekel, D. Barcelo, Evidencing Generation of Persistent Ozonation Products of Antibiotics Roxithromycin and Trimethoprim. Environmental Science & Technology 43.17 (2009) 6808-6815.

Vitae

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Fig. 1. kinetic installation system.



Fig. 2. Effect of [NaCl] on the degradation half-life of picric acid using vacuum UV. (25±0.5^oC, [picric acid]₀=100 mg/l, reaction volume 2500ml, 6.5 dm³/min circulating rate).



Fig. 3. The relation between degradation half-life of picric acid and the amount of the treated water, (25±0.5 ⁰C, [picric acid]_o 100 mg/l, circulating rate, 6.5 dm³/min).



Fig. 4. Effect of temperature change on the VUV oxidative degradation of picric acid, (reaction volume = 2500ml, [picric acid]₀=100 mg/l, 0.65 dm³/min circulating rate).



Influence of changing pH on picric acid degradation Half-live ($t_{1/2}$), (2500ml total volume, T= 25±0.5 0 C, 6.5 dm³/min circulating rate, H₃PO₄/NaOH pH control).



Fig. 6. COD decay with process time, (2500mL total volume, T= 25±0.5^oC, circulating rate, 6.5 L/min). [picric acid]0=100 mg/L, pH=7.0.