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Kinetics based on Mechanism of COD Reduction for Industrial Effluent in Fenton Process

Prabir Ghosh, A.N. Samanta and S. Ray

Department of Chemical Engineering, IIT Kharagpur, Kharagpur 721 302, India

Corresponding Author: Prabir Ghosh, Department of Chemical Engineering, Indian Institute of Technology, Kharagpur-721302, India Tel: +91 9775552387

ABSTRACT

Modeling of Chemical Oxygen Demand (COD) reduction kinetics has been investigated in this study considering hydrocarbon lumps. Traditional approach considers all oxidizable organics as a single lump and a pseudo-first order kinetics for its complete mineralization. Since, single step mineralization is an idealized approach, results from the model have limited matching with the experimental data in narrow ranges. The aim of this study was therefore to develop model forms which will not only match better but will also have greater range of validity, particularly in cases of mixture of pollutants. In this study mathematical models for COD reduction have been developed based on proposition of possible alternate pathways involving more than one lump of degradable. The COD reduction experiments for a typical petrochemical industry effluent by Fenton's reagent were carried out with 150 mL wastewater. Data from these experiments are fitted to the models and the results are discussed. Fitting of literature reported data for these models have also been carried out. It clearly appears that considering the oxidizables as a single lump is clearly an over simplification and models involving either two lumps being oxidized simultaneously or the process occurring in two steps represent the Fenton's process much more closely than the conventional model in case of industrial/real effluents. These multi-lump models represent the progress of COD reduction during Fenton's reaction with much improved accuracy.

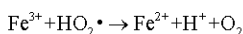
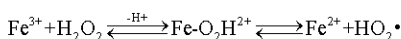
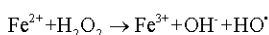
Key words: Advanced oxidation, COD, reduction kinetics, fenton's reagent, multi-lump models, wastewater treatment

INTRODUCTION

Waste water originated from petrochemical plants contains high COD, BOD and toxic pollutants. Almost all wastewater contains several pollutants, some of which are more difficult to degrade compared to others. A local petrochemical industry making primarily polyethylene terephthalate (PET) resins generates raw effluent containing ethylene glycol and 1,4 dioxane apart from other pollutants. The estimated contribution of COD by these two components (ethylene glycol and 1,4-dioxane) is about 75% of the total COD. While ethylene glycol is easily biodegraded and is relatively safe, 1,4 dioxane a group 2B carcinogen with high solubility in water and low vapor pressure is resistant to both aerobic and anaerobic biological degradation. This effluent is currently treated using a different treatment scheme and meets the pollution control standards.

Fenton's oxidation, an Advanced Oxidation Process (AOP), has been proven promising, in terms of cost effectiveness and ease of operation in the treatment of various waste waters (Perez *et al.*,

2002; Guzzella *et al.*, 2002; Alaton *et al.*, 2002; Benitez *et al.*, 2001; Andreozzi *et al.*, 2000). Fenton Process has also been employed for decolorization of dyes (Rezaee *et al.*, 2008; Saif-Ur-Rehman *et al.*, 2008). Fenton's reaction has a short reaction time among AOPs and is used when a high COD removal is required (Sarria *et al.*, 2001). This AOP process has been well studied for its prospective applications in unmanageable wastewater treatment (Prousek, 1996). High efficiency of this process is traditionally thought to be due to the generation of hydroxyl radical (HO_•), which has high oxidation potential (E⁰ = 2.80V) and can oxidize the organic compounds completely to water and carbon dioxide (Huston and Pignatello, 1999; Murugandham and Swaminathan, 2007; Lucas and Peres, 2006; Gogate and Pandit, 2004; Legrini *et al.*, 1993). In acidic medium, this radical mechanism can be described by the following equations:



While, hydroxyl radicals can oxidize most organic pollutants directly, the refractory ones can only be degraded through complex pathways. It can be safely assumed that almost all industrial effluents contain more than one component and often some of those are more refractory.

The mechanism of Fenton's oxidation of organic compounds is very complicated even for single-component solutions. Typically, the oxidation undergoes a complex reaction scheme and leads to the formation of many different intermediates, such as recalcitrant short-chain organic acids (Pintar *et al.*, 2004). In the case of industrial wastewaters, many compounds are present in the waste stream. The oxidation of such a mixture is much more complex than the oxidation of a single-compound solution.

The concentration of organic materials must be expressed by means of a lumped parameter such as Total Organic Carbon (TOC), which accounts for all organic species present in a wastewater, or Chemical Oxygen Demand (COD), which also takes into account oxidizable inorganics. Therefore, the kinetic models that solely predict the disappearance rate of pure compounds are not sufficient: a lumped kinetic model capable of predicting complete conversion of all organic species present in wastewater is needed.

The organic pollutant (COD) degradation kinetics can be expressed by pseudo first order kinetics according to the following rate equation (Kim *et al.*, 1997): $-r = kC_{\bullet\text{OH}}C = k_{\text{exp}}C$ in which r is the rate of degradation, C is the concentration of the organic substances in terms of COD, $C_{\bullet\text{OH}}$ is concentration of $\bullet\text{OH}$ radical, k is the second order rate constant and k_{exp} is pseudo-first order rate constant when $C_{\bullet\text{OH}}$ is supposed to be constant. The pseudo first order of this reaction is based on the assumption that the $\bullet\text{OH}$ radical attains a steady concentration within a short time.

Experiments in connection with an investigation on treatability of the effluent by Fenton's process were conducted to determine optimum process conditions with respect to COD reduction. The present study attempts to develop a kinetic model based on data of COD reduction in the presence of Fenton's reagent with a lumped kinetic description of Chemical Oxygen Demand (COD). This approach is useful when dealing with the kinetics of the reactions with complex mixtures such as waste-waters (Li *et al.*, 1996). The generalized lumped kinetic model proposed by Li *et al.* (1991) has been applied extensively for the different types of wastewaters (Rivas *et al.*,

2001; Lin *et al.*, 1996; Luck, 1996). Apart from the data generated by the authors, the results of fitting the lumped models to data reported in literatures are required to illustrate the generality and applicability of this approach.

MATERIALS AND METHODS

The study reported here was carried out for 3 months from March 15, 2010 to Jun 15, 2010 in the research laboratory in the Department of Chemical Engineering, Indian Institute of Technology Kharagpur, India.

Chemicals or reagents: Characteristics of the raw (untreated) wastewater collected from the petrochemical plant are shown in Table 1.

Hydrogen peroxide solution (50%, w/v), Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Monoethylene glycol (MEG), 1,4-Dioxane, NaOH, H_2SO_4 were all analytical grades. Distilled water was used throughout this study.

Experimental procedure: Fenton's oxidation was carried out in batch mode in beakers of 250 mL capacity with 150 mL of wastewater. Appropriate amount of FeSO_4 was dissolved using part of the liquid in the beaker and then transferring back to beaker. Initial pH of the reaction solution was adjusted by using 1 M H_2SO_4 solution and the beaker was kept in a temperature controlled bath and allowed to attain the preset experimental temperature. Appropriate amount of H_2O_2 were added into the beaker to start the reaction. Small volume of samples were withdrawn after 20, 40, 60 and 80 min using a pipette and filtered through Whatman No. 42 filter paper. The filtrate was analyzed for COD. The optimum process conditions were: initial pH 3, H_2O_2 concentration 3 M, Fe^{2+} concentration 0.06 M. At these conditions, maximum COD reduction (97.5%) was achieved. These experiments were with undiluted as well as diluted effluent. Reproducibility of the results was established to be within 5% by repeating specific experiments several times.

Analytical methods and instruments: The pH was recorded using a digital pH meter (Model: CL- 46, Toshniwal Instruments, India). Conductivity was measured by a digital conductivity meter (Model: 611E, from M/s EI Products, India). COD of the reaction medium were measured by Open reflux method (Clesceri *et al.*, 1998). BOD_5 and total solids were measured according to standard methods (Trivedy and Goel, 1984). Ethylene glycol and Dioxane concentrations were determined using a gas chromatograph (Chemito India Ltd. GC 8610 with a Chemito 10% OV17 column, 6×0.125) with 25 mL min^{-1} nitrogen as carrier gas and $0.5 \mu\text{L}$ sample volume being injected.

Table 1: Characteristics of the waste water used

Parameters	Value
pH	3.2
Conductivity ($\mu\text{mho cm}^{-1}$)	420
COD (mg L^{-1})	11,500
BOD_5 (mg L^{-1})	4,600
TS (mg L^{-1})	7,200
Monoethylene glycol (mg L^{-1})	3,458
1,4-Dioxane (mg L^{-1})	1,316

RESULTS AND DISCUSSION

The COD reduction kinetics considering single lump of pollutants oxidized in a single step Considering 1st order kinetics for COD reduction by Fenton's reaction in a single step for a single lump of pollutant lead to the exponential decay equation:

$$\text{COD}(t) = \text{COD}(0) \times \exp(-k t) \quad (1)$$

Where:

COD (t) = COD after time t min

COD(0) = Initial COD

k = 1st order kinetic constant for COD reduction, min⁻¹

Experimental data of COD vs time (20, 40, 60, 80 min) for same process conditions were fitted to Eq. 1 by minimizing the sum of square of deviations in % error with respect to the experimental data. The minimization program written in MATLAB software used LSQNONLIN routine with Levenberg-Marquardt non-linear optimization algorithm. The best-fit k is 0.04149 min⁻¹. Predicted vales of COD plotted against experimental COD values for different experiments with initial COD of 11500, 9200, 5950 and 3100 mg L⁻¹ are shown in Fig. 1. with a diagonal (45°) line and 10% deviation limit lines. Several predictions can be seen to deviate beyond the 10% limit lines and the average of the sum of the square of deviations % is 2591.1.

COD reduction kinetics considering two lumps of pollutants oxidized simultaneously in single step: Generalized chemical formulae for the two hydrocarbon pollutant lumps are considered to be C_mH_n and C_pH_q. These lumps are assumed to be individually oxidized completely during Fenton's oxidation in single step following 1st order kinetics at different rates. Based on the stoichiometry of complete oxidation in a single step, the COD contribution (α₁ and α₂) from 1 g mol L⁻¹ concentration of C_pH_q and C_pH_q can be written as:

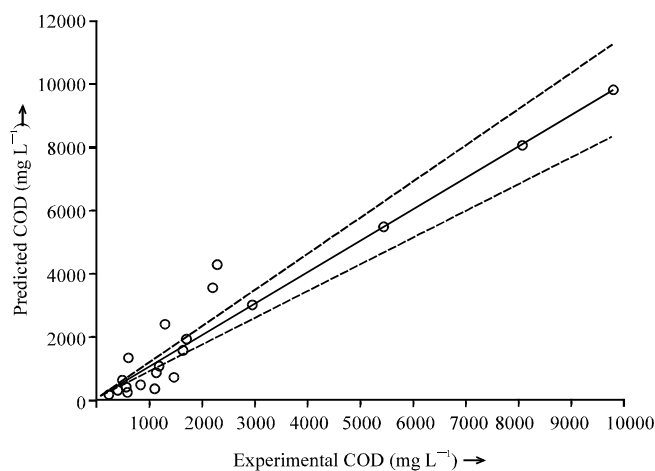


Fig. 1: Predicted COD from model considering a single lump of pollutants oxidized in a single step vs actual COD

$$\alpha_1 = 32 \times (m + \frac{n}{4}) \times 10^3 \text{ mg } \frac{\text{O}_2}{\text{L}} \text{ and } \alpha_2 = 32 \times (p + \frac{q}{4}) \times 10^3 \text{ mg } \frac{\text{O}_2}{\text{L}}$$

COD of the sample having $[C_mH_n]$ and $[C_pH_q]$ g mol L^{-1} of pollutant can be written as $(\alpha_1 \times [C_mH_n] + \alpha_2 \times [C_pH_q]) \text{ mg } L^{-1}$; where the two constituent terms are COD contributions from the individual lumps. Considering two degradation reactions are independent and are both of 1st order, the COD contribution from each lump will have exponential decay but at different rates.

Therefore, the COD of the sample as a function of time can be written as:

$$\text{COD}(t) = f \times \text{COD}(0) \times \exp(-k_1 t) + (1-f) \times \text{COD}(0) \times \exp(-k_2 t) \quad (2)$$

Where:

COD(t) = COD of sample after t min

f = Mole fraction of lump 1 in the sample initially

k_1, k_2 = 1st order kinetic constant for COD reduction for lump 1 and lump 2, min^{-1}

During COD reduction by Fenton's reaction at optimum process conditions, the terms f, COD(0), k_1 and k_2 remain constant with time for Eq. 2. Values of these terms are found by fitting COD of sample vs time to Eq. 2 by minimizing the sum of square of deviations in % error with respect to the experimental data. Previously mentioned MATLAB routines and algorithms are used in this case. The best fit values are:

$$k_1 = 0.0177; k_2 = 1.6753; f = 0.3575$$

Predicted vales of COD plotted against experimental COD values are shown in Fig. 2. with a diagonal (45°) line and 10% deviation limit lines. Fewer predictions can be seen to deviate beyond the 10% limit lines and the average of the sum of the square of deviations % is 334.8.

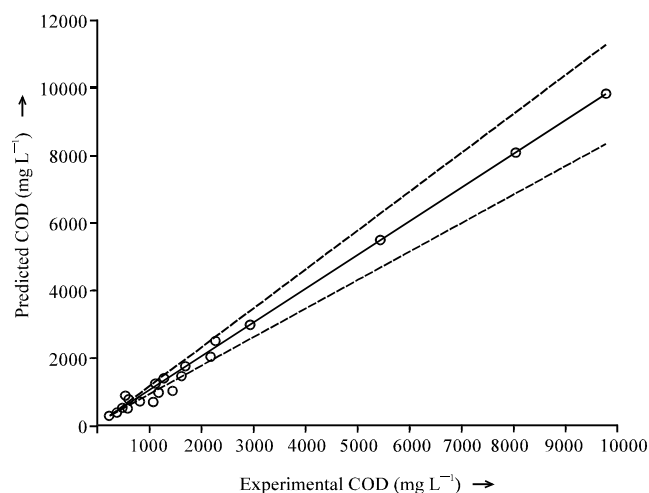
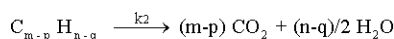
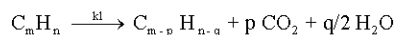


Fig. 2: Prediction from model considering two lumps of pollutants oxidized simultaneously in single step

COD reduction kinetics considering pollutants oxidized in two steps: It is assumed that the general formula of the pollutant lump originally present is $C_m H_n$. This gets oxidized by Fenton's reaction to another product $C_{m-p} H_{n-q}$ along with production of CO_2 and H_2O . $C_{m-p} H_{n-q}$ gets oxidized independently in a single step. In a previous work a lumped kinetic model based on adsorption/electrocatalysis/oxidation mechanism for COD reduction was proposed by Zhou *et al.* (2004). These reactions are also assumed to be pseudo 1st order reactions with rate constants k_1 and k_2 and are shown below:



In the line of treatment presented in previous for single lump of pollutants oxidized in single step, the COD of the sample having $[C_m H_n]$ and $[C_p H_q]$ g mol L^{-1} of pollutant can be written as:

$$(\beta_1 \times [C_m H_n] + \beta_2 \times [C_p H_q]) \text{ mg } L^{-1}$$

where, COD due to 1 g mol L^{-1} concentrations of $C_m H_n$ and $C_{m-p} H_{n-q}$ are:

$$\beta_1 = 32 \times (m + \frac{n}{4}) \times 103 \text{ mg } L^{-1} \text{ and } \beta_2 = 32 \times [(m-p) + \frac{(n-q)}{4}] \times 103 \text{ mg } L^{-1}$$

Based on pseudo-first order decay kinetics of $C_m H_n$, the following expressions can be written as:

$$-\frac{d}{dt}[C_m H_n] = k_1 [C_m H_n]$$

or

$$[C_m H_n] = [C_m H_n]_0 \exp(-k_1 t) \tag{3}$$

Decay of $C_{m-p} H_{n-q}$ follows pseudo-first order, but there is a generation term. Therefore the transient balance of the species is written as:

$$\begin{aligned} -\frac{d}{dt}[C_{m-p} H_{n-q}] &= k_2 [C_{m-p} H_{n-q}] - k_1 [C_m H_n] \\ &= k_2 [C_{m-p} H_{n-q}] - k_1 [C_m H_n]_0 \exp(-k_1 t) \end{aligned} \tag{4}$$

Generalized form of equation Eq. 4 is:

$$-\frac{dx}{dt} = ax - b \exp(-ct), \text{ I.C.: } x=0 \text{ at } t=0$$

and this equation has analytical solution: $x(t) = (b/(a-c)) \times \{\exp(-ct) - \exp(-at)\}$
Therefore,

$$[C_{m-p}H_{n-q}] = \frac{k_1[C_mH_n]}{k_2 - k_1} \times [\exp(-k_1t) - \exp(-k_2t)]$$

and

$$\begin{aligned} \text{COD}(t) &= \beta_1 \times [C_mH_n] + \beta_2 \times [C_{m-p}H_{n-q}] \\ &= \beta_1 \times [C_mH_n] \times \exp(-k_1t) + \beta_2 \times \frac{k_1[C_mH_n]}{k_2 - k_1} \times [\exp(-k_1t) - \exp(-k_2t)] \\ &= [C_mH_n] \times \exp(-k_1t) \times [\beta_1 + \beta_2 \left(\frac{k_1}{k_2 - k_1} \right) \times \{1 - \exp(-k_2 + k_1)t\}] \\ &= [C_mH_n] \times \exp(-k_1t) \times [\beta_1 + \beta_2 \left(\frac{k_1}{k_2 - k_1} \right) \times \{1 - \exp(-k_2 - k_1)t\}] \\ &= \text{COD}(0) \times \exp(-k_1t) \times \left[1 + \left(\frac{\beta_2}{\alpha_1} \right) \times \{1 - \exp\{-(k_2 - k_1)t\}\} \right] \end{aligned} \tag{5}$$

Equation 5 represents the expression for COD of the sample with time involving constants β_1 , β_2 , k_1 and k_2 .

Similar to the procedure followed considering two lump of pollutants oxidized simultaneously in single step, values of these constant terms are found by fitting COD of sample vs. time to Eq. 5 by minimizing the sum of square of deviations in % error with respect to the experimental data. The earlier mentioned MATLAB routines and algorithms are used in this case.

The best fit values are: $\beta_1 = 0.01640$, $\beta_2 = 0.00536$, $k_1 = 0.28068$ and $k_2 = 0.01835$. Predicted values of COD plotted against experimental COD values are shown in Fig. 3. with a diagonal (45°) line and 10% deviation limit lines. Most predictions can be seen to below the 10% limit lines and the average of the sum of the square of deviations % is 247.9.

Validating the models using data reported in literature: In order to check the generality of the model, these models need to be fitted to data from literature. This is done with COD values with

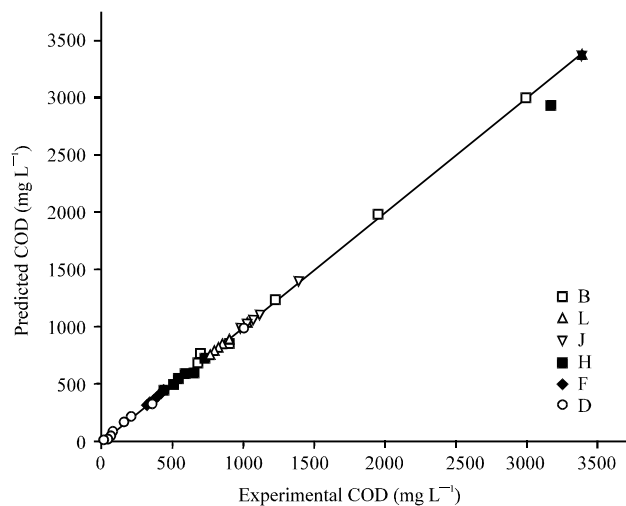


Fig. 3: Prediction from model considering two lumps of pollutants oxidized in two steps

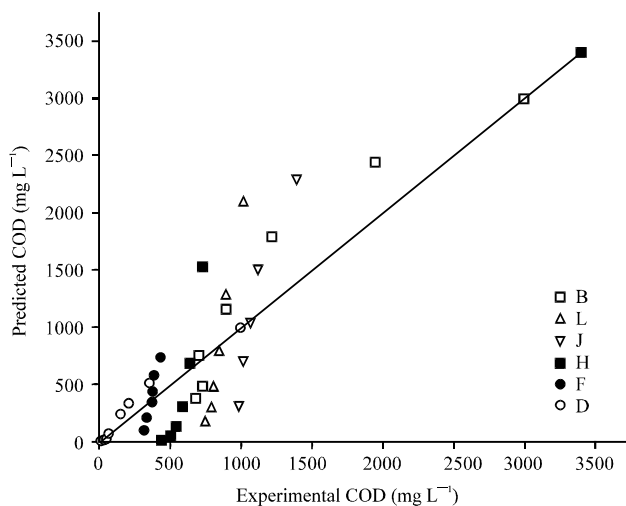


Fig. 4: Prediction from model considering a single lump of pollutants oxidized in a single step for literature data

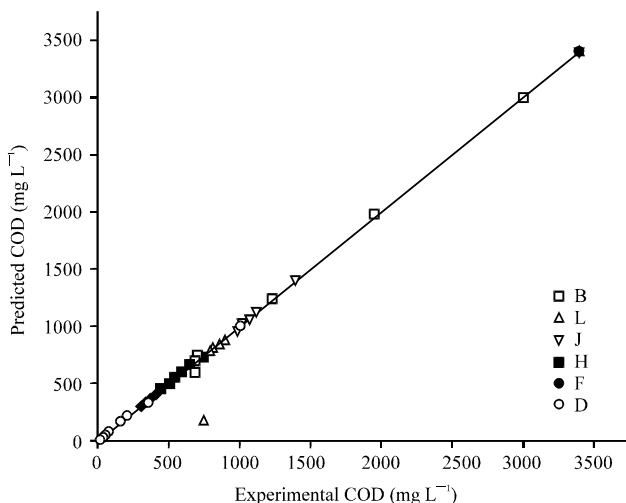


Fig. 5: Prediction from model considering two lumps of pollutants oxidation in parallel for literature data

time during treatment by Fenton's oxidation of leachate streams. The data sets B and D are from the same literature (Zhang *et al.*, 2006), data set F (Zhang *et al.*, 2005) is from the same group of investigators and the data set H, J and L are from a different source (Gotvajn *et al.*, 2009). The above data set from literature are present in the respective publications without relating the same to any mathematical model. Therefore both single and the proposed multi-lump models are fitted to the data.

Figure 4 shows the fit for model considering a single lump of pollutants oxidized in a single step. The average absolute errors in prediction for the data sets (B, D, F, H, J and L) are 26.48, 44.34, 34.84, 59.75, 33.65 and 47.48, respectively.

Figure 5 shows the fit for the model considering two lumps of pollutants oxidized simultaneously in single step. In this case, the average absolute errors in prediction for the data sets (B, D, F, H,

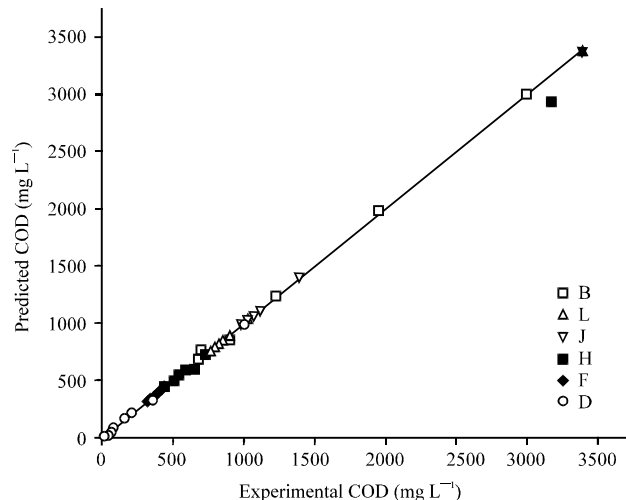


Fig. 6: Fitting of data from literature for considering pollutants oxidized in two steps for literature data

Table 2: Mean square (%) error in prediction for the three models on the literature data

Data set	Single lump of pollutants oxidized in a single step	Two lumps of pollutants oxidized in parallel	Pollutants oxidized in two steps
B	954.23	10.28	10.35
D	2631.80	509.12	509.10
F	1906.71	2.27	1.45
H	5142.67	2.93	3.96
J	1852.56	2.04	1.61
L	3445.38	0.60	1.27

J and L) are 2.57, 16.49, 1.07, 1.45, 1.05 and 0.65 respectively. These errors are markedly lower than the case of fit for model considering a single lump of pollutants oxidized in a single step.

The quality of fit for the model considering pollutants oxidized in two steps is shown in Fig. 6. In this case, the average absolute errors in prediction for the data sets (B, D, F, H, J and L) are 2.63, 16.49, 1.02, 1.66, 1.05 and 0.87, respectively.

Table 2 shows the mean square (%) error in prediction for the three models on the literature data. In all cases the mean square (%) error is practically one order higher in case of the single lump model.

CONCLUSIONS

Although, the chemistry of the Fenton's reaction system involves a complex mechanism of oxidizing hydrocarbons to CO_2 and H_2O , approximations by 1st order kinetic models in various forms can be used to describe the process of COD reduction. In case of the specific effluent from the local petrochemical industry, the model considering a lump of pollutants oxidized in two steps with intermediate product formation fits better than the model considering simultaneous degradation of two lumps of pollutants. It also has an extra constant that allows a degree of freedom more than the other model. Both the said models fit the practical observations markedly better than the classical simplistic model considering single step 1st order kinetics of complete mineralization of a single lump of pollutants present.

Results from fitting these models on literature reported data also suggest that considering the oxidizables as a single lump is clearly an over simplification. Models involving either two lumps being oxidized simultaneously or the process occurring in two steps represent the Fenton's process much more closely, observed as COD reduction with time.

In actual practice the degradation of the complex pollutants involves intermediate formation and degradation of these intermediates. The model considering a lump of pollutants oxidized in two steps with intermediate product formation is more realistic.

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REFERENCES

- Alaton, I.A., I.A. Balcioglu and D.W. Bahnemann, 2002. Advanced oxidation of a reactive dyebath effluent: Comparison of O₃, H₂O₂/UV-C and TiO₂/UV-A processes. *Water Res.*, 36: 1143-1154.
- Andreozzi, R., V. Caprio, A. Insola, R. Marotta and R. Sanchirico, 2000. Advanced oxidation processes for the treatment of mineral oil contaminated wastewaters. *Water Res.*, 34: 620-628.
- Benitez, F.J., J.L. Acero, T. Gonzalez and J. Garcia, 2001. Organic matter removal from wastewaters of the black olive industry by chemical and biological procedures. *Process Biochem.*, 37: 257-265.
- Clesceri, L.S., A.E. Greenberg and D.A. Eaton, 1998. *Standard Methods for the Examination of Water and Waste Water*. 20th Edn., APHA, USA, Washington.
- Gogate, P.R. and A.B. P andit, 2004. A review of imperative technologie for wastewater treatment. I. Oxidation technologies at ambient conditions. *Adv. Environ. Res.*, 8: 501-551.
- Gotvajn, A.Z., T. Tisler and J. Zagorc-Koncan, 2009. Comparison of different treatment strategies for industrial landfill leachate. *J. Hazardous Mater.*, 162: 1446-1456.
- Guzzella, L., D. Feretti and S. Monarca, 2002. Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply. *Water Res.*, 36: 4307-4318.
- Huston, P.L. and J.J. Pignatello, 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. *Water Res.*, 33: 1238-1246.
- Kim, S.M., S.U. Geissen and A. Vogelpohl, 1997. Landfill leachate treatment by a photoassisted fenton reaction. *Water Sci. Technol.*, 35: 239-248.
- Legrini, O., E. Oliveros and A.M. Braun, 1993. Photochemical processes for water treatment. *Chem. Rev.*, 93: 671-698.
- Li, L., P. Chen and E.F. Gloyna, 1991. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.*, 37: 1687-1697.
- Li, L., N. Crain and E.F. Gloyna, 1996. Kinetic lumping applied to wastewater treatment. *Water Environ. Res.*, 68: 841-854.
- Lin, S.H., S.J. Ho and C.L. Wu, 1996. Kinetic and performance characteristics of wet air oxidation of high-concentration wastewater. *Ind. Eng. Chem. Res.*, 35: 307-314.

- Lucas, M.S. and J.A. Peres, 2006. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes and Pigments*, 71: 236-244.
- Luck, F., 1996. A review of industrial catalytic wet air oxidation processes. *Catal. Today*, 27: 195-202.
- Murugandham, M. and M. Swaminathan, 2007. Solar driven decolourisation of Reactive Yellow 14 by advanced oxidation process in heterogeneous and homogeneous media. *Dyes Pigments*, 72: 137-143.
- Perez, M., F. Torrades, X. Domenech and J. Peral, 2002. Fenton and photo-fenton oxidation of textile effluents, *Water Res*, 36: 2703-2710.
- Pintar, A., G. Bercic, M. Besson and P. Gallezot, 2004. Catalytic wet-air oxidation of industrial effluents: Total mineralization of organics and lumped kinetic modeling. *Applied Catalysis B Environ.*, 47: 143-152.
- Prousek, J., 1996. Advanced oxidation processes for water treatment. *Chem. Process. Chem. Listy*, 90: 229-237.
- Rezaee, A., M.T. Ghaneian, S.J. Hashemian, G. Moussavi, A. Khavanin and G. Ghanizadeh, 2008. Decolorization of reactive blue 19 dye from textile wastewater by the UV/H₂O₂ process. *J. Applied Sci.*, 8: 1108-1112.
- Rivas, F.R., F.J. Beltran, O. Gimeno and B. Acedo, 2001. Wet oxidation of wastewater from olive oil mills. *Chem. Eng. Technol.*, 24: 415-421.
- Saif-Ur-Rehman, M., A. Muhammad, A. Shafeeq, M.A. Chughtai, A.M. Ali and F. Ahmad, 2008. Decolorization of turquoise blue dye by ozonation, O₃/H₂O₂ and fenton processes. *Res. J. Environ. Sci.*, 2: 310-315.
- Sarria, V., S. Parra, M. Invernizzi, P. Peringer and C. Pulgarin, 2001. Photochemical-biological treatment of a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone. *Wat. Sci. Tech.*, 44: 93-101.
- Trivedy, R.K. and P.K. Goel, 1984. *Chemical and Biological Methods for Water Pollution Studies*. Environmental Publications, Karad, India.
- Zhang, H., H.J. Choi and C.P. Huang, 2005. Optimization of Fenton process for the treatment of landfill leachate. *J. Hazard. Mater.*, B125: 166-174.
- Zhang, H., H.J. Choi and C. Huang, 2006. Treatment of landfill leachate by fenton's reagent in a continuous stirred tank reactor. *J. Hazardous Mater.*, 136: 618-623.
- Zhou, M., Z. Wu, X. Ma, Y. Cong, Q. Ye and D. Wang, 2004. A novel fluidized electrochemical reactor for organic pollutant abatement. *Separation Purification Technol.*, 34: 81-88.