

Studies on the heterogeneous photocatalytic oxidation of 2,6-dinitrophenol in aqueous TiO₂ suspension

B. Swarnalatha, Y. Anjaneyulu*

Center for Environment, Institute of Science and Technology (IST), Jawaharlal Nehru Technological University, Kukatpally Campus, Hyderabad, Andhra Pradesh 500 072, India

Received 8 June 2003; received in revised form 22 March 2004; accepted 30 March 2004
Available online 21 September 2004

Abstract

Studies on the heterogeneous photocatalytic oxidation of 2,6-dinitrophenol with different catalysts like TiO₂, TiO₂-P25, CdS, WO₃ and ZnO indicated aqueous TiO₂-P25 suspensions exhibit maximum efficiency in photodegradation at the wavelength of 254 nm using an annular-flow type photo reactor with a 8 W low pressure mercury lamp as a UV light source. Operational parameters like variation of catalyst load, initial concentration of 2,6-DNP, irradiation time, pH, oxygen supply and nitrogen supply on the efficiency of degradation was also investigated and optimum conditions were established. All the experiments were carried out in a batch recirculation mode. The possible mechanisms for the photocatalytic degradation of 2,6-DNP are discussed.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Annular-flow reactor; 2,6-DNP; Photocatalytic oxidation; Titanium dioxide

1. Introduction

The elimination of toxic chemicals from waste water is presently of great concern, since their complete biodegradation is usually very slow and requires several days or weeks. These pollutants may originate from industrial applications or from household and personal care areas. The search for effective means of removing these compounds is of interest to regulating authorities worldwide. Recently, it has been demonstrated that semi-conducting materials mediating photocatalytic oxidation of organic compounds can be an alternative to conventional methods for the removal of organic pollutants in water and air [1–3]. Several studies of photocatalytic degradation of dyes have been reported [4–9]. A variety of semiconductor materials (oxides, sulfides and others) acting as photocatalysts have already been used. Titanium (IV) oxide suspended in water has proven to be one of the most active photocatalyst. Extensive work has shown that a wide range of or-

ganic pollutants in aqueous solutions containing UV light illuminated TiO₂ particles are completely oxidized [2,10–13].

Nitro aromatic compounds are highly toxic to humans and animals with LD₅₀ in the range of 25–50 mg/kg [14]. Nitrogen-containing phenols are also of great concern not only because they cause severe health problems but also acts as poisons for catalysts [15]. San et al. [16], studied the photocatalytic degradation of 4-nitrophenol in aqueous TiO₂ suspensions. However, there is a very limited information on the photocatalytic degradation of nitrogen-containing phenols [17,18].

Nitro phenols are common components of industrial effluents and have been detected in urban and agricultural wastes [19]. 2,6-dinitrophenol is one of the six possible dinitro phenol forms used in the synthesis of dyes, picric acid, picramic acid, wood preservatives, diaminophenoldihydrochloride (a photographic developer), explosives and insecticides.

The photocatalytic degradation of 2,6-dinitro phenol in aqueous titanium dioxide slurries was investigated using different catalysts, varying operational parameters like substrate concentration, catalyst load, irradiation period,

* Corresponding author. Tel.: +91 40 23058 731; fax: +91 40 23058 731.
E-mail address: yerramillia@hotmail.com (Y. Anjaneyulu).

pH, oxygen, nitrogen to assess the effects of the variables on the degradation efficiency and the corresponding results are presented in this paper.

2. Experimental details

2.1. Materials

The anatase form of TiO₂, Degussa P25, with a particle size of 30 nm and a surface area of 50 m² g⁻¹, according to the manufacturer's specifications, was used as the photocatalyst without further treatment. 2,6-Dinitrophenol, of AR Grade (Aldrich, Germany) and all other chemicals of extra pure grade were used as received by preparing the solutions in double distilled water.

2.2. Reactor set-up

The annular-flow photocatalytic reactor used for this study was a cylindrical plastic vessel, in which a 8 W low pressure mercury lamp (254 nm), surrounded by a quartz glass tube to protect it from direct contact with an aqueous solution flowing through an annulus between the inner surface of the vessel and the outer surface of the quartz glass tube, located at the axis of the vessel. The study was carried out in a batch recirculation mode. The reactant solution was circulated between the perfectly mixed vessel (1000 ml reservoir), which is covered by aluminum foil to prevent the exposure of the coloured solution to visible light, and the annular-flow reactor at a flow rate of 120 ml min⁻¹ using a peristaltic pump. During the photolysis experiments, reactant solution containing the appropriate quantity of the semiconductor powder was continuously stirred before and during illumination and was bubbled with air except for experiments where effect of oxygen and nitrogen were observed, with a flow of 500 ml min⁻¹ throughout the reaction process.

2.3. Methodology

All the experiments were carried out at ambient temperature (30 ± 3 °C) and at natural pH of 3.0 ± 0.2 of the 2,6-DNP except for experiments where pH values are varied. The solutions were prepared using double distilled water and pH of the reaction mixture was adjusted using 0.01N NaOH/H₂SO₄. In all the experiments, 250 ml of 2,6-DNP solution of appropriate concentration was taken into the reservoir. At specific time intervals samples of 5 ml were withdrawn and analyzed using UV–Vis spectrophotometer and COD digester, respectively, after centrifugation (Remi Research R-24) at 8000 rpm followed by filtration with 0.20 μm (mdi, India), Nylon-66 membrane syringe filters to assess the extent of degradation.

2.4. Analysis

The concentration of 2,6-DNP was measured with UV–Vis spectrophotometer (ECIL GS5703 AT, India) at

432.5 nm. The photodegradation efficiency for each sample are calculated from the expression:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100$$

where η is the photodegradation efficiency, C_0 the concentration of the compound before illumination, and C_t is the concentration of solution after time t .

3. Results and discussion

3.1. Mechanism of photodegradation

The photocatalytic degradation of organic compounds occur on the surface of TiO₂, primarily in trapped holes. •OH and O₂•²⁻ are considered as primary reactive species and O₂ and H₂O are necessary for photocatalytic degradation. Oxygen adsorbed on the TiO₂ surface prevents the recombination of electron–hole pairs by trapping electrons and super oxide ions are thus formed. •OH radicals are formed from holes reacting with either H₂O or OH⁻ adsorbed on the TiO₂ surface. •OH and O₂•²⁻ are also formed from H₂O.

In this process, H₂O₂, O₂ and HO₂• which are suitable for trapping electrons and •OH and O₂•²⁻ are the most important oxidants. The oxidizing power of the OH radicals is strong enough to break bonds of the compound molecule adsorbed on the surface of the TiO₂ leading to the formation of CO₂ and inorganic ions. When the intensity of light was constant, the number of •OH and O₂•²⁻ radicals increase with increasing irradiation period, resulting in the complete photodegradation of organic molecules to smaller fragments like CO₂ and H₂O while the other elements bonded to the organic compounds are converted to anions such as nitrate sulfate or chloride [20].

3.2. Photodegradation efficiency in presence of other photocatalysts

Experiments were performed using 1 × 10⁻³ M 2,6-DNP solution and 1.0 g/250 ml of catalyst in 4 h irradiation period at an optimum pH of 8, with other commercial photocatalysts such as CdS, TiO₂ (Merck), WO₃ and ZnO. The photodegradation efficiency of 2,6-DNP solution in the presence of various semiconductor as photocatalysts are shown in Fig. 1 and it is clear that the photolysis of an air equilibrated 2,6-DNP solution in the presence of the semiconducting oxides leads to the disappearance of the compound. In the presence of TiO₂-P25, complete mineralization of the compound took place after 3 h of light exposure, while for the same time interval CdS, TiO₂ (Merck), WO₃ and ZnO degraded 65.2, 74, 53.1 and 79%, respectively. Generally semiconductors having large band gaps have strong photocatalytic activities. In the present case, TiO₂ and ZnO have band gaps larger than 3 eV and show strong photocatalytic activities. CdS and WO₃ having a smaller band gap show less activity since their conduction bands are much lower than that

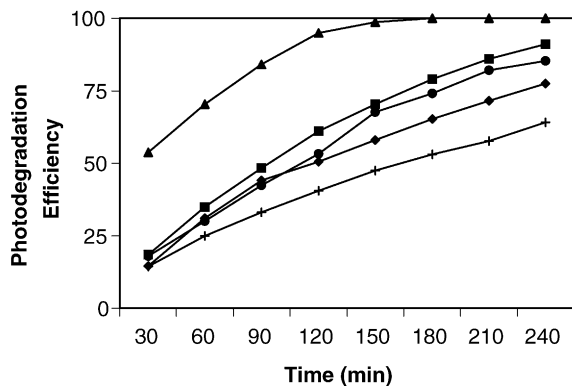


Fig. 1. Photodegradation efficiency using various catalysts: (▲) with TiO₂; (■) with ZnO (Merck); (●) with TiO₂ (Merck); (◆) with CdS; (+) with WO₃.

of TiO₂. Conduction band electron in these semiconductors cannot move into the electron acceptor in the solution rapidly. It should be noted that the activity of the photocatalyst is also affected by the particle size, crystallinity and concentration of impurities included in the catalysts. Thus, many photocatalysts cause partial decomposition of the organic molecules in comparable times. Hence, in the present study attention was given to TiO₂-P25 because of its high photocatalytic activity, its resistance to photo corrosion, its biological immunity and its low cost.

TiO₂-P25 appears to be the most efficient photocatalyst. The superiority of TiO₂-P25 may be attributed to its morphology, which was proposed to be one of the most critical properties for the photocatalytic efficiency of P25 among various grades of TiO₂. Crystallographic study of P25 shows that amorphous, anatase and rutile forms exist. The close proximity of these phases and in some cases the overlapping of forms makes it difficult to differentiate and has been cited to be the reason for long lasting excitation of electrons from the valence band to the conduction band, allowing for efficient and effective degradation of wide range of organic compounds [21].

3.3. Photodegradation efficiency of 2,6-DNP

The percentage of degradation of 2,6-DNP from an initial concentration of 3.2×10^{-3} M under three conditions is shown in Fig. 2. There was no observable loss of compound when the irradiation was carried out in the absence of TiO₂. In non-irradiated suspensions, there was a slight loss, due to adsorption onto TiO₂. However, in the presence of TiO₂, a rapid degradation of 88.1% occurred by irradiation for 240 min.

3.4. Effect of catalyst loading

2,6-DNP solutions at pH 3.0 ± 0.2 and concentration at 3.2×10^{-3} M were used to study the effect of catalyst loading by varying the amount of TiO₂ from 0.5 to 2.0 g/250 ml. It is observed that as the concentration of TiO₂ increases, the

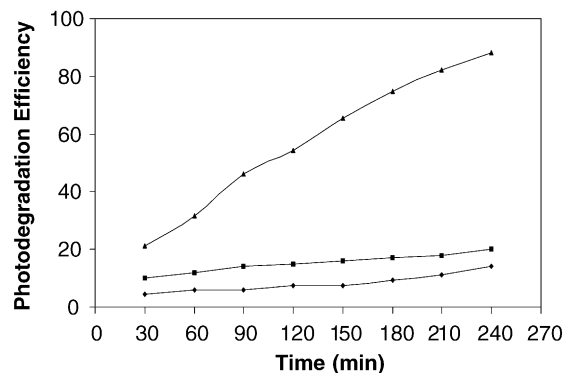


Fig. 2. Photodegradation efficiency at different conditions: (▲) with UV/TiO₂; (■) with TiO₂; (◆) with UV.

percentage of degradation of 2,6-DNP also increases up to a certain point, from there onwards it decreases (Fig. 3) and maximum degradation was observed at the catalyst concentration of 1 g/250 ml. This may be due to the fact that at high TiO₂ concentrations, particle aggregates reduces the interfacial area between the reaction solution and photocatalyst resulting in the reduction in number of active sites on the catalyst surface. The increase in opacity and light scattering by the particles may also be the other reason for the decrease in the efficiency of degradation.

3.5. Effect of initial concentration of 2,6-DNP

The effect of initial concentration of 2,6-DNP on the percentage of photocatalytic degradation was investigated over the concentration range of 0.5×10^{-3} to 3.2×10^{-3} M, since the pollutant concentration is a very important parameter in water treatment. The efficiency of photodegradation was found to decrease with increase in the initial concentration of 2,6-DNP (Fig. 4).

The influence of the initial concentration of compound in the photocatalytic degradation rate of most organic compounds is also described by pseudo-first-order kinetics. This is rationalized in terms of Langmuir–Hinshelwood model modified to accommodate reactions occurring at solid–liquid interface [22,23] and the final form of the expression can be

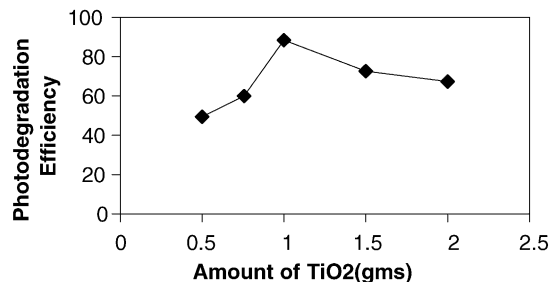


Fig. 3. Effect of catalyst loading on photodegradation efficiency.

Table 1
Effect of 2,6-DNP concentration

Name of the compound	2,6-DNP	
Amount of TiO ₂	1.0 g	
Irradiation time	3 h	
Initial concentration ($\times 10^{-3}$ M)	k^1 (min ⁻¹)	$t_{1/2}$ (min)
0.54	0.0237	29.2
1.08	0.0199	34.8
1.63	0.0135	51.0
2.17	0.0119	58.0
3.26	0.0039	177

represented as

$$\ln\left(\frac{C_0}{C}\right) = k_r K t = k^1 t$$

Therefore, a plot of $\ln(C_0/C)$ versus illumination time should give a straight line whose slope equals the apparent first-order rate constant, k^1 , where k^1 is the apparent rate constant of the photodecomposition (min⁻¹), $t_{1/2}$ values are calculated from the expression:

$$t_{1/2} = \frac{0.693}{k^1}$$

where t is the time in min required for the initial concentration of solute C_0 to decrease to C , K is the equilibrium constant for adsorption of the organic substrate onto TiO₂ particles (M⁻¹), k_r is the limiting rate of the reaction after maximum coverage under the experimental conditions (ML⁻¹ min⁻¹) and k^1 is the apparent rate constant of the photocatalytic degradation (min⁻¹).

In order to study the nature of the photochemical reaction with TiO₂, apparent rate constant, k^1 is calculated from the slopes of the plots for 2,6-DNP (Table 1). The k^1 values depends on the initial concentration of the compounds, which decreases gradually with increase in the initial concentration of the compounds [24,25].

The reason for this behaviour is that, on the surface of TiO₂ particles the reaction occurs between the •OH radicals, generated at the active OH⁻ sites and the 2,6-DNP molecule adsorbed on the surface of catalyst. When the initial concentration is high, the number of these available active sites are decreased by 2,6-DNP molecules, because of their competitive adsorption on the TiO₂ particles. But the intensity of light illumination period is constant and O₂•²⁻ and •OH radicals formed on the surface of TiO₂ are also constant. Thus, the reactive OH and O₂•²⁻ attacking the compound molecules decrease and simultaneously the photodegradation efficiency also decreases.

3.6. Effect of pH

The photodegradation efficiency of 2,6-DNP is represented as a function of the initial pH after 2 h irradiation of the suspension containing 1×10^{-3} M 2,6-DNP and 1 g/250 ml of catalyst (Fig. 5). As can be seen from Fig. 5, when the

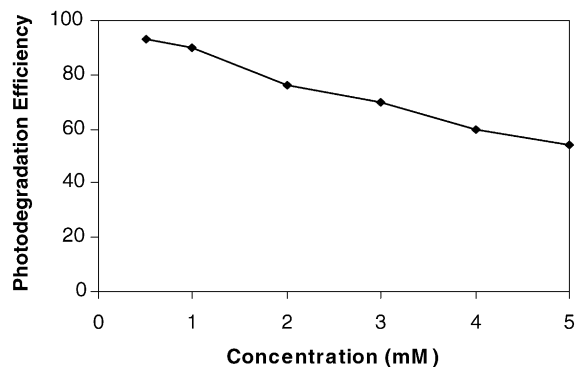


Fig. 4. Effect of initial concentration on photodegradation efficiency.

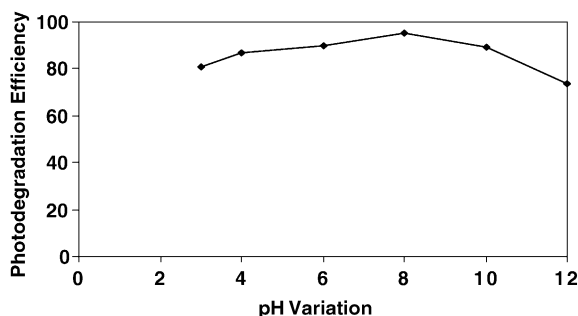


Fig. 5. Effect of pH variation on photodegradation efficiency.

initial pH of the suspension varied from 3 to 12, the photocatalytic activity reached a maximum of 95% at pH 8 and further decrease in the efficiency of photodegradation occurs as pH increases to 12. The inhibitory effect is more pronounced in high alkaline pH range. At high pH values, the hydroxyl radicals are so rapidly scavenged that they do not have opportunity to react with dye molecules [26].

It can be assumed that during irradiation 2,6-DNP may be oxidized by direct reaction with the photo-generated holes in the TiO₂ particles or by reaction with OH radicals, which are also powerful oxidizing agents. The major route of formation of these OH radicals is by reaction between the photo-generated holes with the OH⁻ ions adsorbed onto the semiconductor particles.

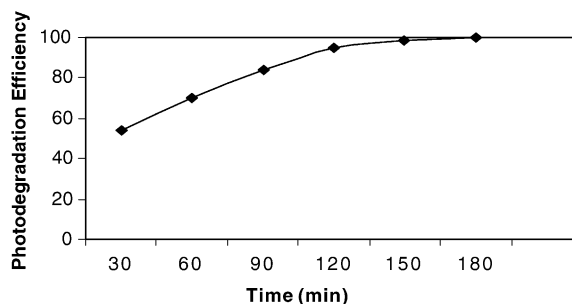


Fig. 6. Effect of irradiation time on photodegradation efficiency.

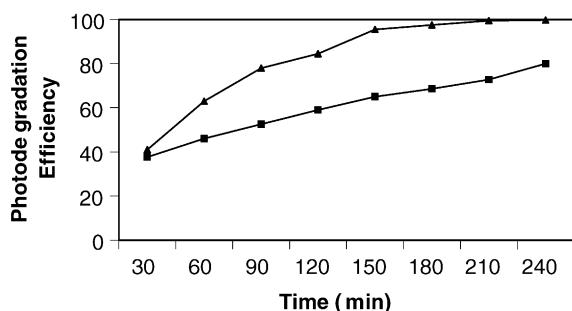


Fig. 7. Effect of oxygen and nitrogen on photodegradation efficiency: (▲) with oxygen; (■) with nitrogen.

3.7. Effect of irradiation period

The 2,6-dinitrophenol degradation in TiO_2 suspension was found to gradually increase with increasing irradiation period at an optimum pH of 8, at a catalyst loading of 1 g/250 ml and a 2,6-DNP concentration of 1×10^{-3} M. Photodegradation efficiency was about 70.3% after 1 h of irradiation. Complete degradation of the compound occurred after 3 h of irradiation (Fig. 6). The chemical oxygen demand (COD) measurements also revealed that the compound which initially showed 243 mg l^{-1} of COD at the initial concentration of 1×10^{-3} M gradually decreased with increasing irradiation period and after 3 h of irradiation it became zero indicating the complete degradation of the compound.

3.8. Effect of bubbling oxygen and nitrogen

The effect of bubbling of oxygen and nitrogen through the aqueous suspension containing 1×10^{-3} M 2,6-DNP solution with 1 g/250 ml of catalyst at an optimum pH of 8 for 4 h of irradiation period on the photodegradation is shown in Fig. 7. Complete photodegradation can be attributed in the case of oxygenated system with in 3.5 h of the irradiation period. For the same time interval in the case of nitrogenated system, 73% of photodegradation is observed.

The molecular oxygen acts as an efficient electron acceptor as it suppresses the electron–hole recombination and forms super oxide radical ion. However, in the case of dinitro compounds their intermediates can serve as an alternate electron acceptors in the absence of O_2 [17] due to which some extent of photodegradation was also observed with nitrogen bubbling also.

4. Conclusions

In the photocatalytic degradation of 2,6-DNP, TiO_2 -P25 is found to be the most efficient as photocatalyst when compared to other catalysts due to its photo stability. The catalyst load, concentration of 2,6-DNP, irradiation time, pH, oxygen and nitrogen mainly controls the rate of degradation for which

optimum conditions for achieving maximum efficiency were established.

Acknowledgements

The authors would like to express sincere thanks to Dr. M. Subrahmanyam, Scientist, Indian Institute of Chemical Technology, for extending his help in carrying out this work.

References

- [1] D. Ollis, E. Pelizzetti, N. Serpone, *Environ. Sci. Technol.* 25 (1991) 1522–1529.
- [2] M.R. Hoffmann, S. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69–96.
- [3] J. Peral, X. Domenech, D.F. Ollis, *J. Chem. Technol. Biotechnol.* 170 (1997) 117–140.
- [4] F. Herrera, A. Lopez, J. Kiwi, *J. Photochem. Photobiol. A* 135 (2000) 45–51.
- [5] D. Chatterjee, A. Mahata, *Appl. Catal. B* 33 (2001) 119.
- [6] T.C.-K. Yang, S.-F. Wang, S.H.-Y.T. Sai, S.-Y. Lin, *Appl. Catal. B* 30 (2001) 293.
- [7] C. Hachem, F. Bocquillion, O. Zahraa, M. Bouchy, *Dyes Pig.* 49 (2001) 117.
- [8] T. Sauer, G. Cesconeto Neto, H.J. Jose, R.F.P.M. Moreira, *J. Photochem. Photobiol. A* 149 (2002) 147–154.
- [9] M.M. Kosanic, J.S. Trickovic, *J. Photochem. Photobiol. A* 149 (2002) 247–251.
- [10] O. Legrini, E. Oliveros, A.M. Braun, *Chem. Rev.* 93 (1993) 671.
- [11] D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993.
- [12] D.M. Blake, *Bibliography of Work on Photo catalytic Removal of Hazardous Compounds from Water and Air*, NREL/T 570-26797, National Renewable Energy Laboratory, Golden, CO, 1999.
- [13] J.M. Herrmann, *Catal. Today* 53 (1999) 115.
- [14] R.B. Leftwich, J.F. Floro, R.A. Neal, *South Med. J.* 75 (1982) 182–185.
- [15] A. Huang, I. Cao, J. Chen, F.J. Spiess, S.I. Suib, T.N. Obee, S.O. Hay, I.D. Freihaut, *J. Catal.* 188 (1999) 40.
- [16] N. San, A. Hatipoglu, G. Kocturk, Z. Cinar, *J. Photochem. Photobiol. A* 146 (2002) 189.
- [17] M.S. Dieckmann, K.A. Gray, *Wat. Res.* 30 (1996) 1169.
- [18] D. Chen, A.K. Ray, *Wat. Res.* 32 (1998) 3223.
- [19] A. Goi, M. Trapido, *Proc. Estonian Acad. Sci. Chem.* 50 (1) (2001) 5–17.
- [20] R.S. Dhodapkar, N.N. Rao, S.P. Pande, S.N. Kaul, in: P.K. Goel (Ed.), *Advances in Industrial Wastewater Treatment*, Techno Science Publications, 1999, p. 453.
- [21] M. Nargiello, T. Herz, Physical–chemical characteristics of P-25 making it extremely suited as the catalyst in photodegradation of organic compounds, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Proceedings of the 1st International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 801.
- [22] C.S. Turchi, D.F. Ollis, *J. Catal.* 122 (1990) 178–192.
- [23] H. Al-Ekabi, N. Serpone, *J. Phys. Chem.* 92 (1988) 5726–5731.
- [24] R.W. Matthews, *J. Catal.* 111 (1988) 264–272.
- [25] M.V. Shankar, B. Neppolian, S. Sakthivel, B. Arabindoo, M. Palanichamy, V. Murugesan, *Indian J. Eng. Mater. Sci.* 8 (2001) 104–109.
- [26] M. Gal Braith, S. Min-Minshu, S. Davis, Masten, *Hazardous Industrial Wastes* 24 (1992) 411.