

CHAPTER V

RESULT AND DISCUSSION

Effect of TiO_2 on the Degradation of dye

Effect of TiO_2 on the degradation of acid orange 7 in solution of 2×10^{-4} M by photocatalysis with TiO_2 shown in figure 5.1. This figure shows that in the absence of TiO_2 , there is very slow degradation and disappearance rate of dye depended on the amount of TiO_2 and illumination time. Next step of this experiment use photocatalytic degradation with 75 mg of TiO_2 . Because of it has high degradation of dye under the condition employed and possible to identification of intermediate products from dye solution.

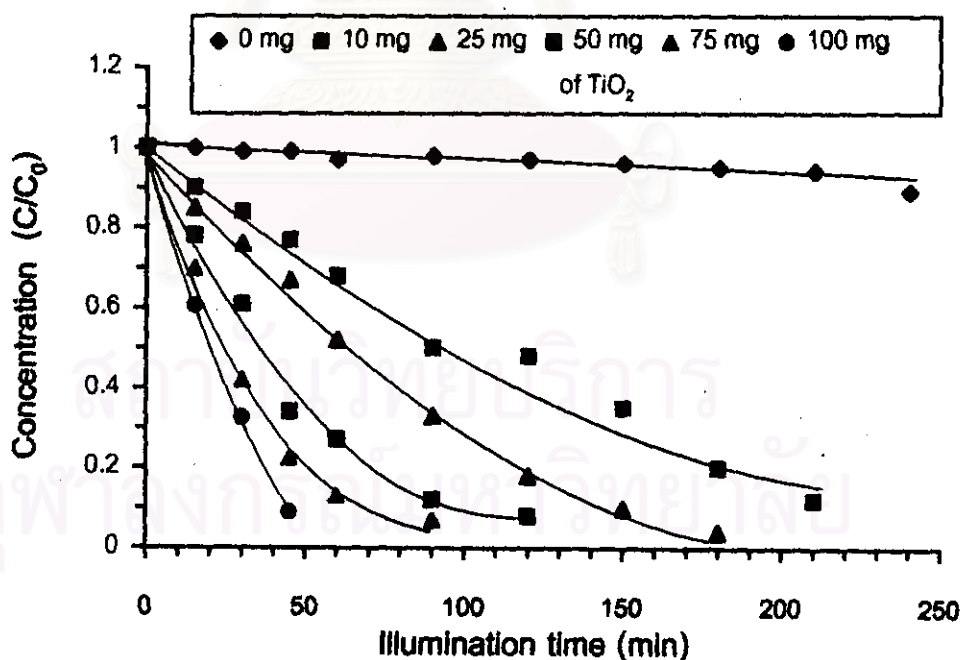


Figure 5.1 Disappearance rate of acid orange 7 in solution of 2×10^{-4} M by photodegradation and by photocatalytic degradation with TiO_2 . (see data in appendix 1)

Effect of Initial Concentration of Dye on the Photocatalytic Degradation

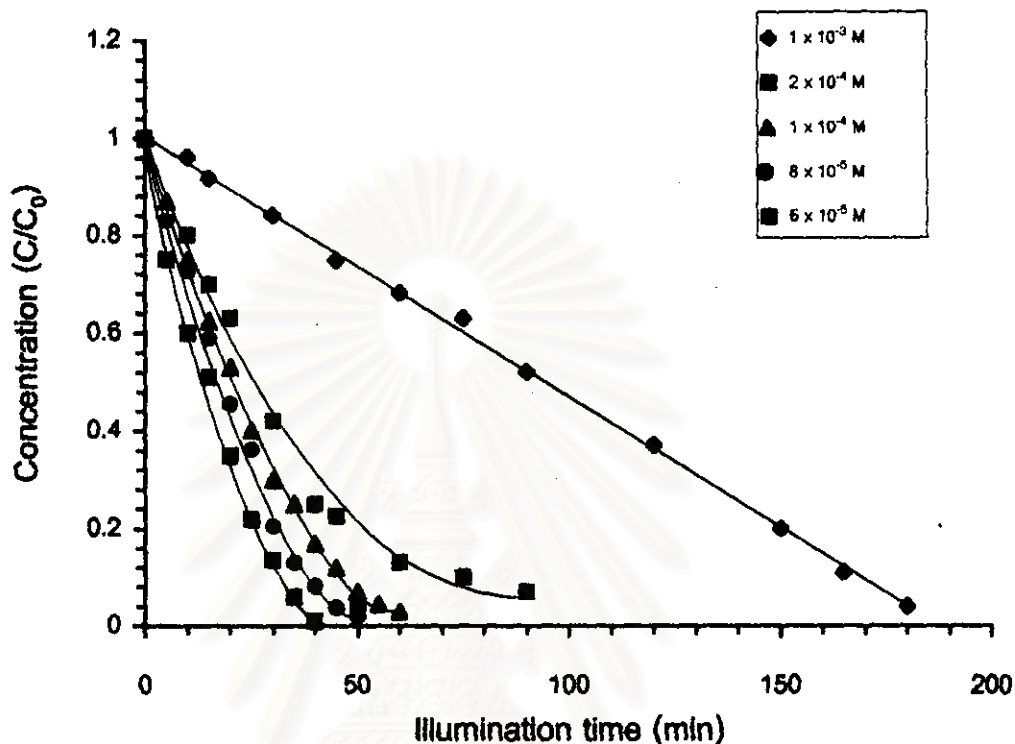


Figure 5.2 Disappearance rate of acid orange 7 on the photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix2)

Disappearance rate of acid orange 7 decrease when increase of initial concentration of dye. acid orange 7 at concentration less than 1×10^{-4} M was completely decomposed within 1 hour.

Effect of Chemical Structure of Dye on Photocatalytic Degradation

Seven azo dyes in this experiment were decomposed by photocatalytic degradation on TiO_2 . Disappearance rate of dyes in solution of 1×10^{-4} M by photocatalysis were compared in figure 5.3. It obvious that structure of dye effects its disappearance rate.

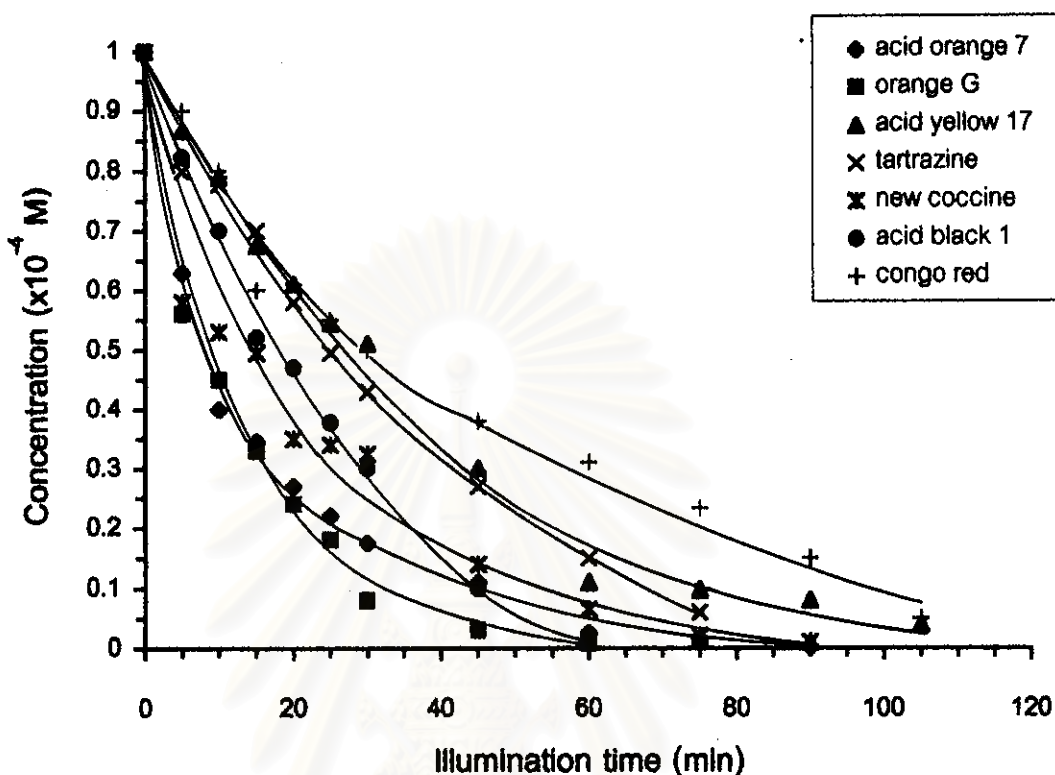


Figure 5.3 Disappearance rate of azo dyes in solution of on 1×10^{-4} M the photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix3)

In the first part of degradation, dyes follow first order kinetics (eq 5.1) and pseudo first order rate constants (k_1) of each dyes calculate by this equation were listed in table 1.

$$\ln C_0 - \ln C = k_1 t \quad \text{eq 5.1}$$

Under the conditions studied, initial rate of degradation depends on the concentration and illumination time. When r_0^{-1} (r_0 is initial rate of photocatalytic degradation calculated for the amount degraded in first 15 min) was plotted as a function of C_0^{-1} (C_0 is initial concentration of dye solution), degradation of these dyes follows Langmuir - Hinselwood equation represented by eq 5.2 where k is photodegradation rate constant, K is absorption coefficient of dyes on TiO_2 (Table 5.1).

$$r_0 = kKC_0/(1 + KC_0) \quad \text{eq 5.2}$$

Table 5.1 Pseudo first order rate constant (k_1) of 1×10^{-4} M of dyes by photocatalytic degradation; photodegradation rate constant(k); absorption coefficient (K) of dyes by photocatalytic photodegradation in range 5×10^{-5} - 1×10^{-3} M.

azo dyes	photocatalytic degradation		
	k_1 (min^{-1})	k ($\times 10^{-4}$ mol/hr)	K ($\times 10^{-4}$ M^{-1})
orange G	0.078	3.058	1.164
acid orange 7	0.058	4.115	0.590
new cocchine	0.044	2.220	1.373
acid black 1	0.040	1.595	4.133
tartrazine	0.028	1.772	1.772
acid yellow 17	0.026	2.924	1.069
congo red	0.020	1.520	0.820

Table 1 shows that the degradation rate of dyes were in the order : acid orange 7 > orange G > acid yellow 17 > new cocchine > tartrazine > acid black 1 > congo red. Diazo dyes were shown to be less degradable than monoazo dyes.

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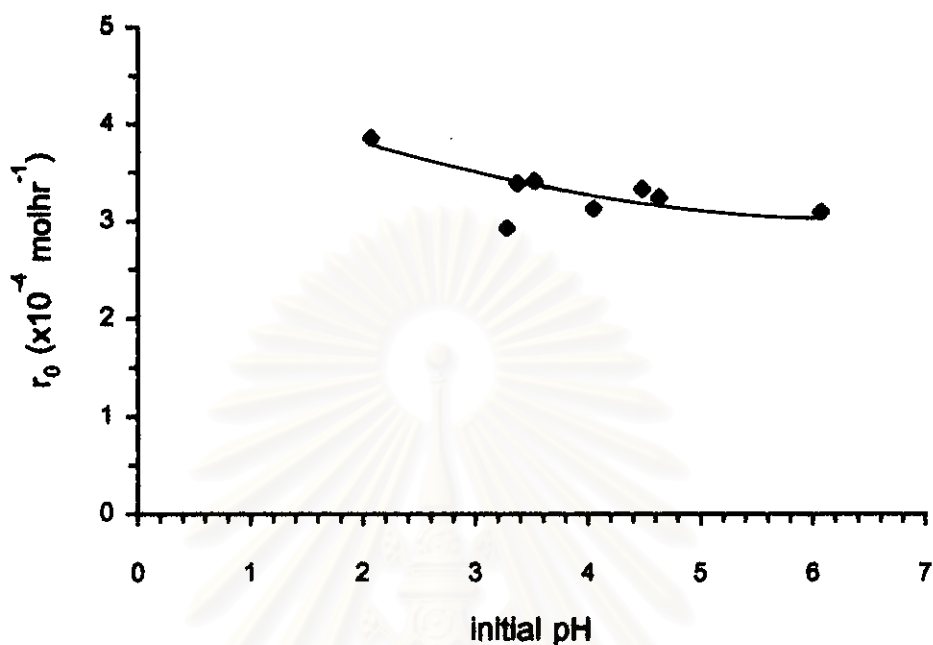


Figure 5.4 Effect of initial pH of dye solution on photocatalytic degradation of acid orange 7, initial concentration = 1×10^{-4} M

Elimination rate of TOC was slower than disappearance rate (figure 5.3, 5.5). This discrepancy indicated the formation of intermediate products. At concentration not exceeding 1×10^{-4} M, azo dyes studied were completely mineralized within 4 hours except congo red which took longer than 7 hours for mineralization.

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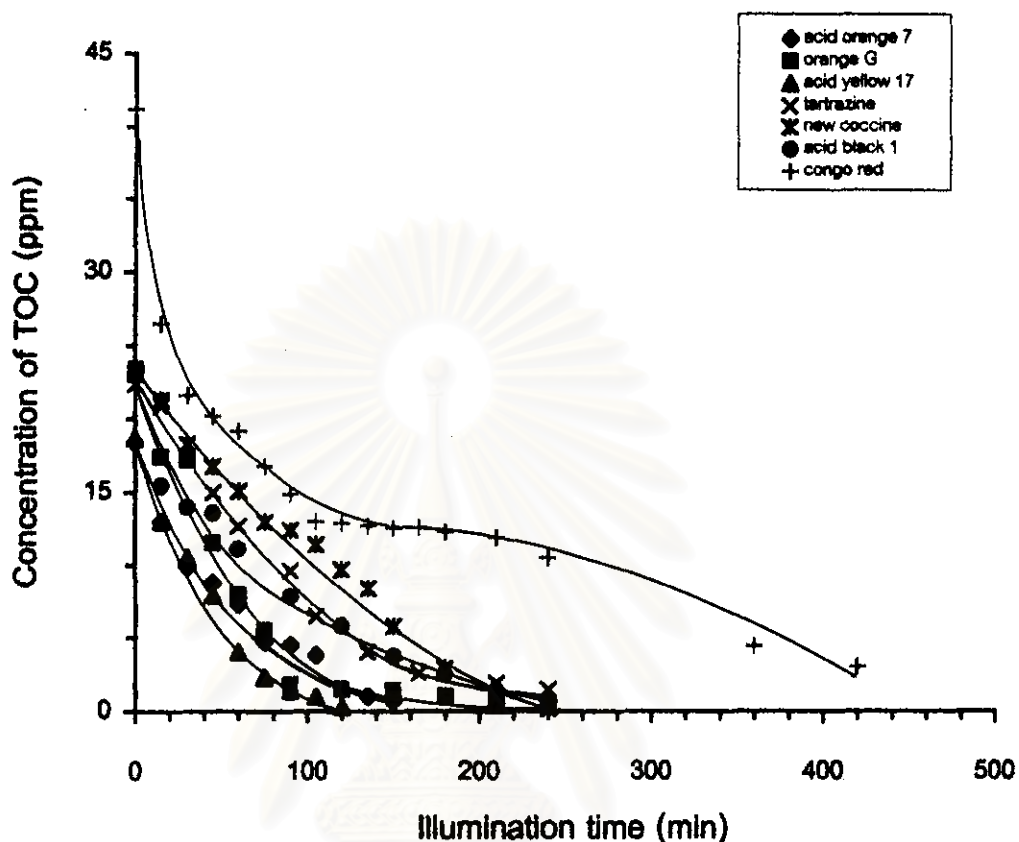


Figure 5.5 Disappearance rate of TOC in 1×10^{-4} M of dye solution during photocatalytic degradation with 75 mg of TiO₂ (see data in appendix4)

Photocatalytic reaction is initiated by photo-excitation of TiO₂, which produces electron and positive hole :



Positive hole forms ^oOH via



H⁺, ^oOH radical thus formed are responsible for oxidation of azo dyes, which led to the formation of several intermediate products such as aromatic compounds and

organic compounds. In this work, phenol (for orange G, acid black 1 and congo red), hydroquinone (for orange G), and sodium sulfanilate (for acid orange 7, tartrazine and acid yellow 17) were identified as aromatic intermediates. The formation curves of organic acids during dye degradation shown in figure 5.6, 5.7, 5.8, 5.9, 5.10, 5.11 and 5.12.

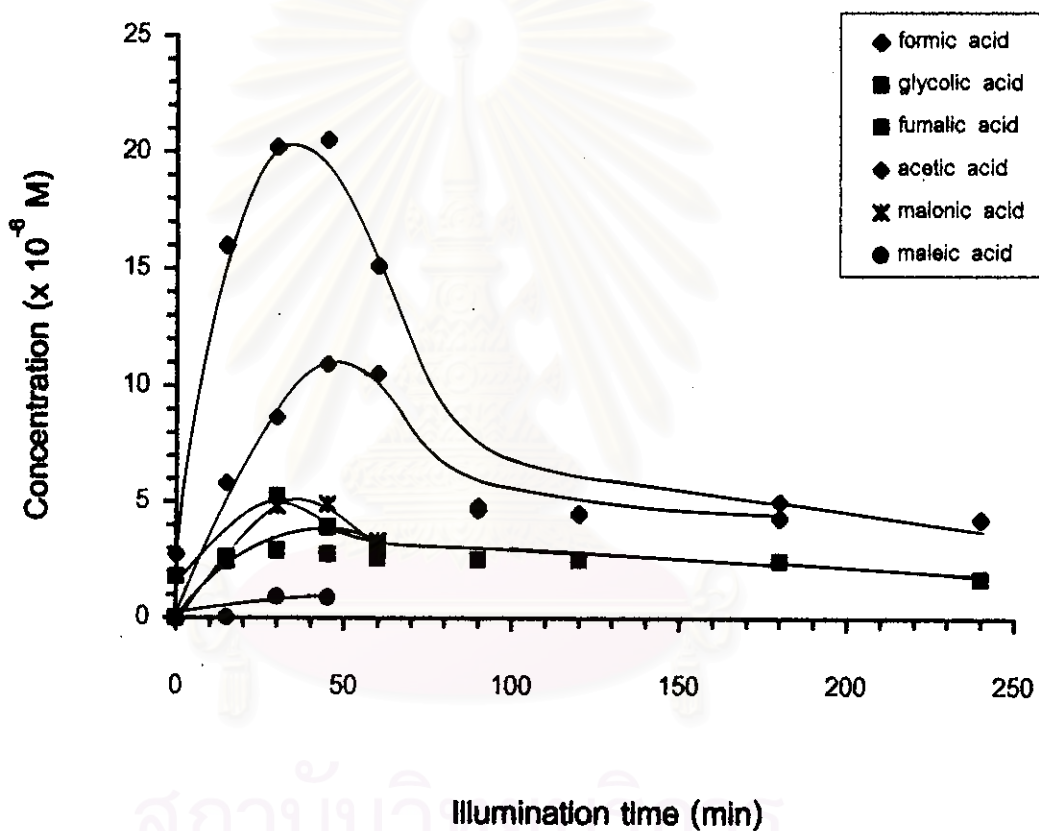


Figure 5.6 Formation of organic acids in 1×10^{-4} M of orange G during photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix 5)

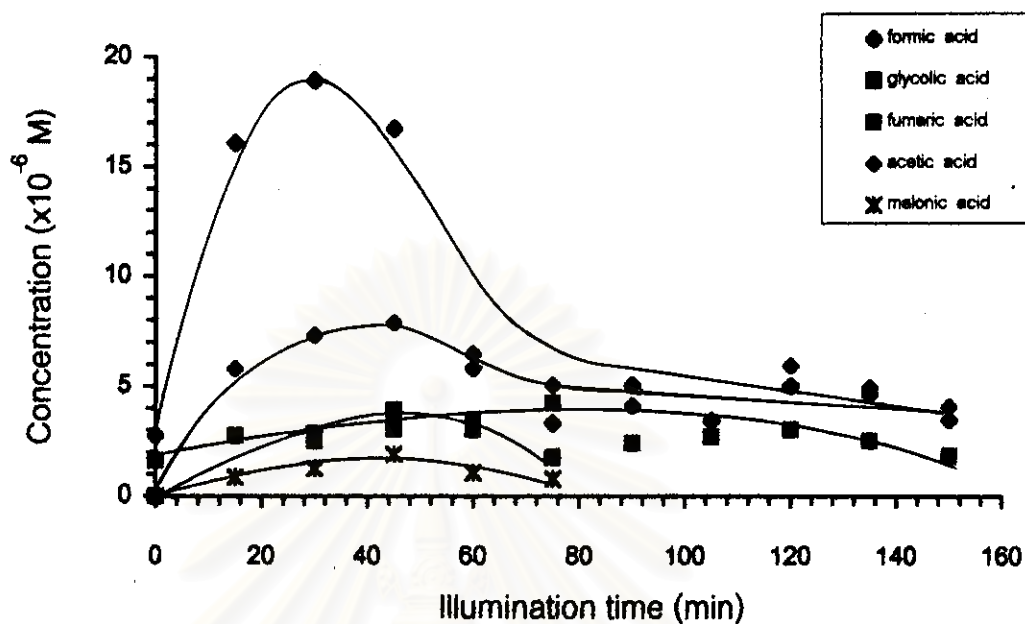


Figure 5.7 Formation of organic acids in 1×10^{-4} M of acid orange 7 during photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix 6)

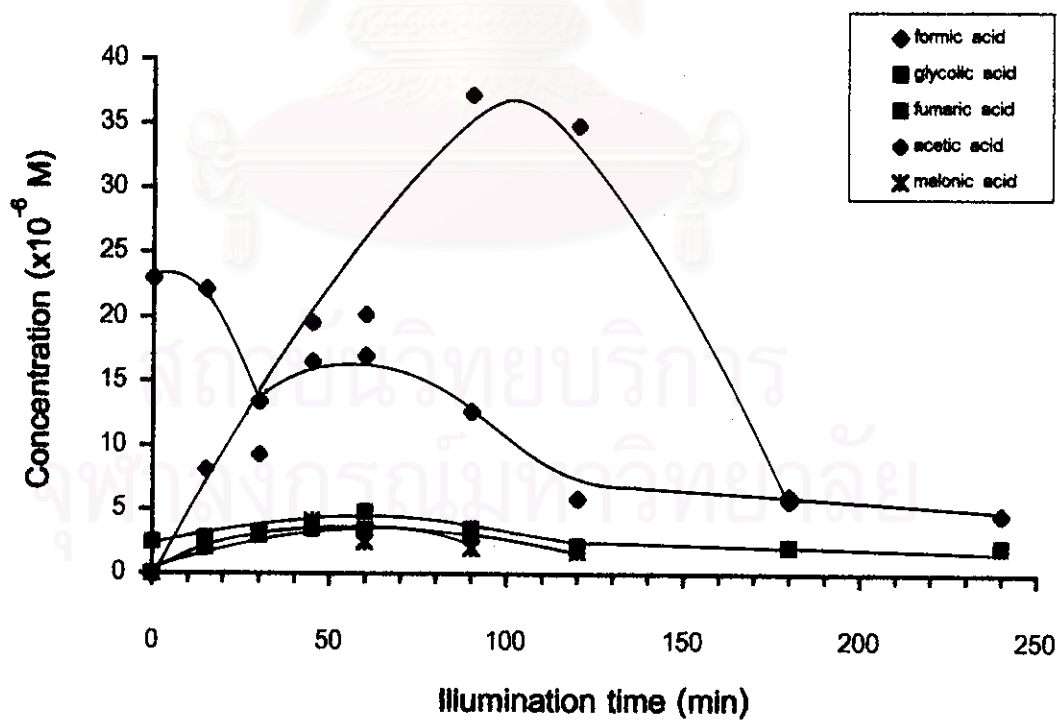


Figure 5.8 Formation of organic acids in 1×10^{-4} M of acid yellow 17 during photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix 7)

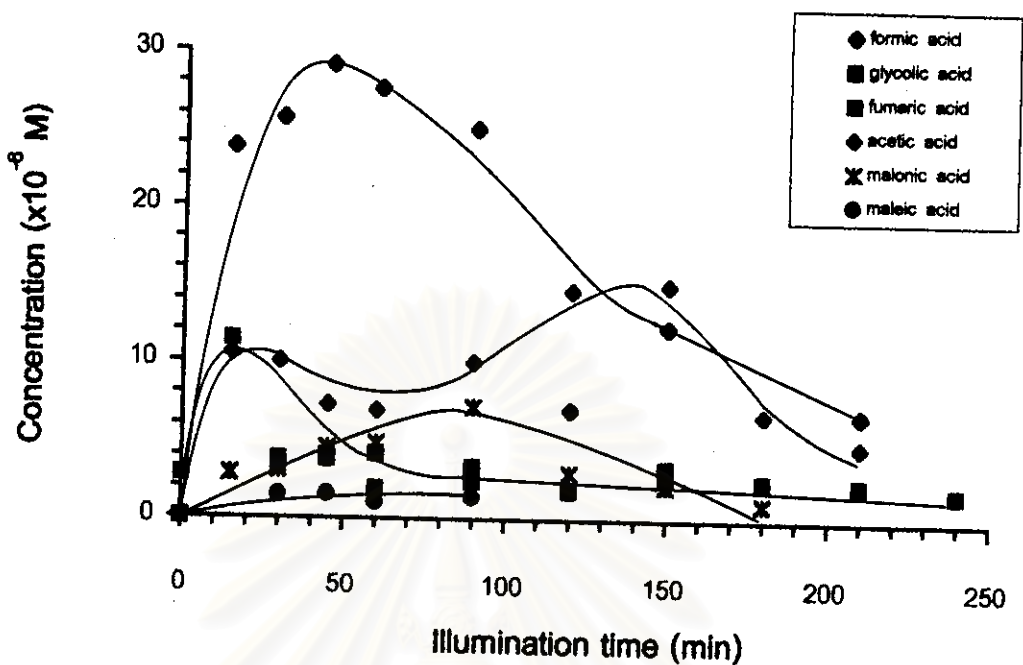


Figure 5.9 Formation of organic acids in 1×10^{-4} M of tartrazine during photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix 8)

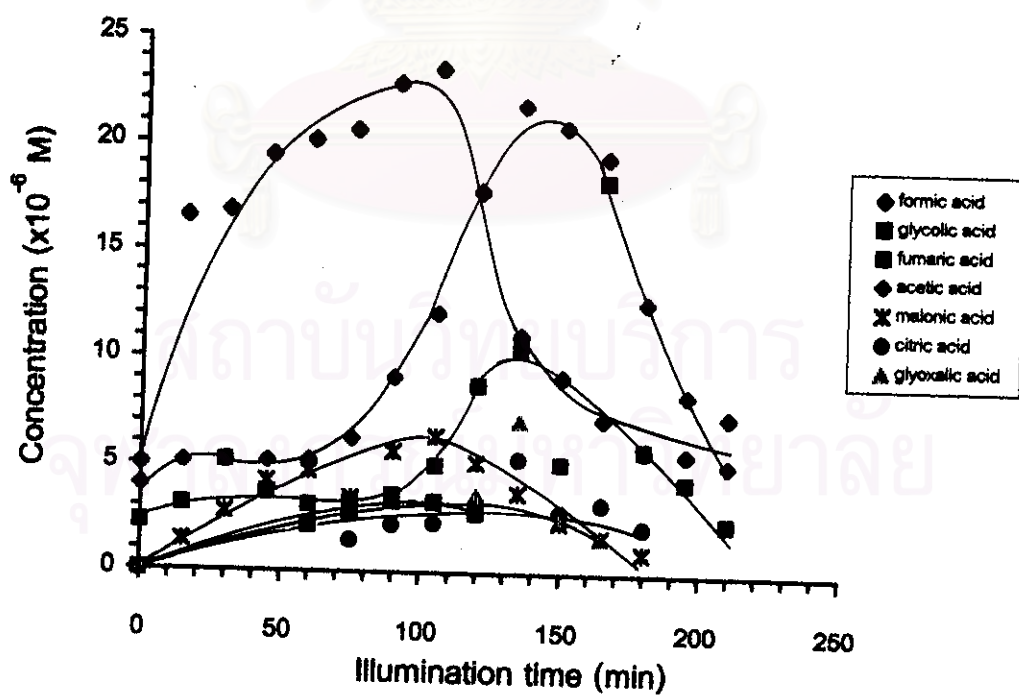


Figure 5.10 Formation of organic acids in 1×10^{-4} M of new coccine during photocatalytic degradation with 75 mg of TiO_2 . (see data in appendix 9)

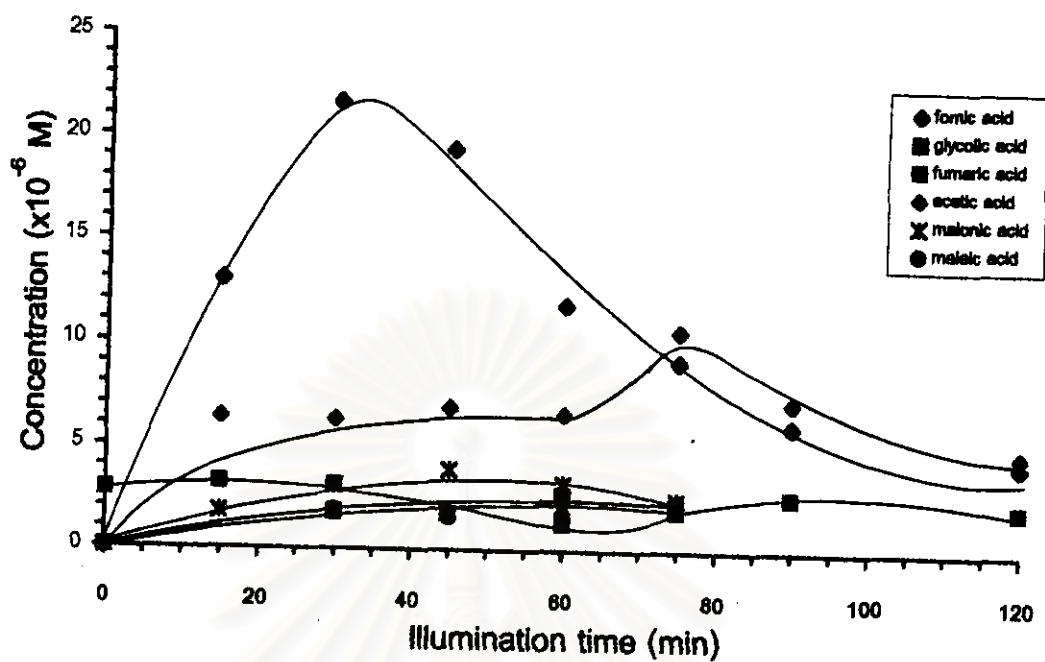


Figure 5.11 Formation of organic acids in 1×10^{-4} M of acid black1 during photocatalytic degradation with 75 mg of TiO_2 (see data in appendix 10)

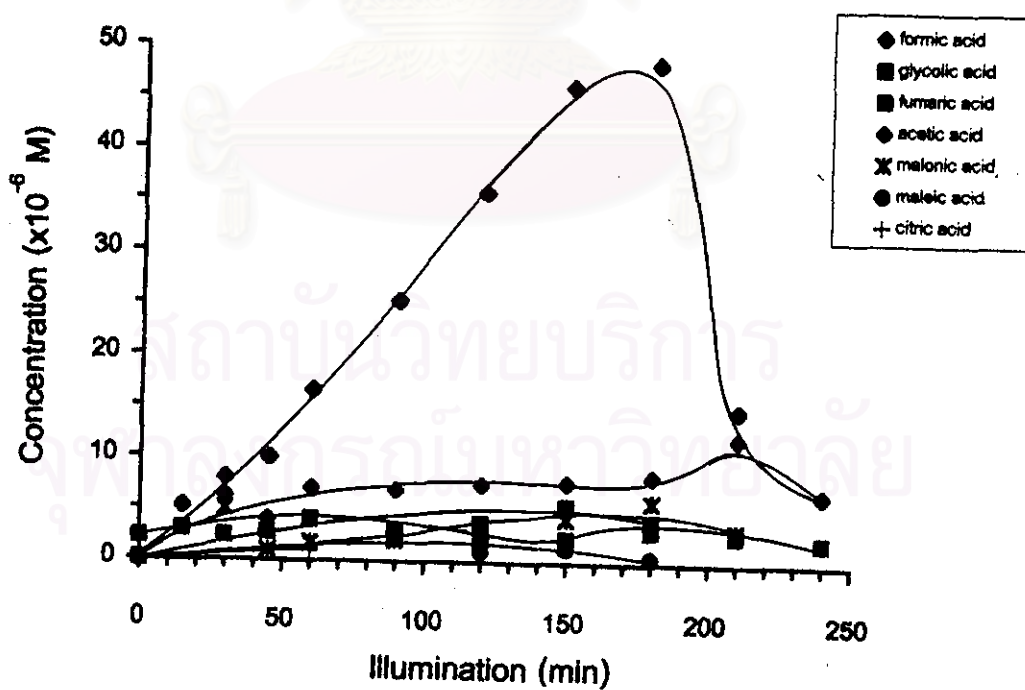


Figure 5.12 Formation of organic acids in 1×10^{-4} M of congo red during photocatalytic degradation with 75 mg of TiO_2 (see data in appendix 11)

Acetic acid (CH_3COOH), and formic acid (HCOOH) were formed in the largest concentration. They are considered to be final intermediate products before degrading to CO_2 . It may be assumed that large part of the dye are mineralized via these acids. NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} were detected as final products. The formation of these ions were shown in Figure 5.13, 5.14, and 5.15.

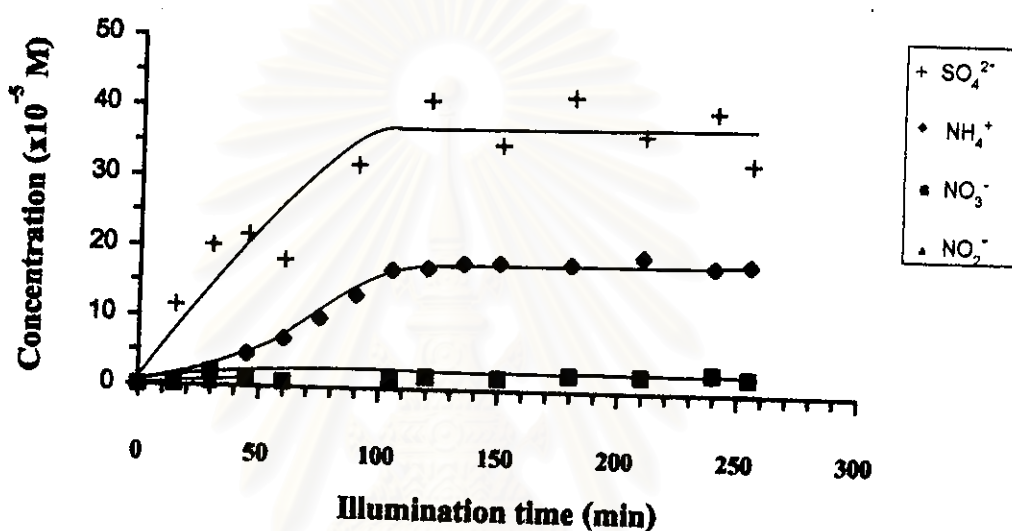


Figure 5.13 Formation of NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} in 10^{-4} M dye solution of acid yellow 17 during photocatalytic degradation with 75 mg of TiO_2 (see data in appendix 12)

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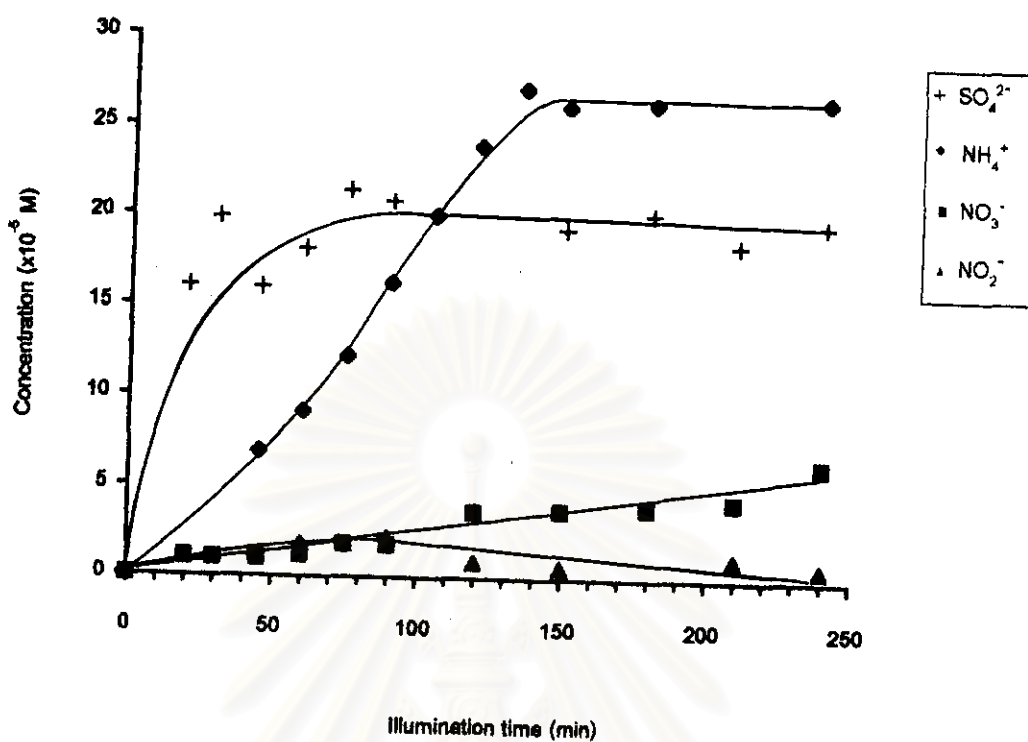


Figure 5.14 Formation of NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} in 10^{-4} M dye solution of acid black 1 during photocatalytic degradation with 75 mg of TiO_2 (see data in appendix 13)

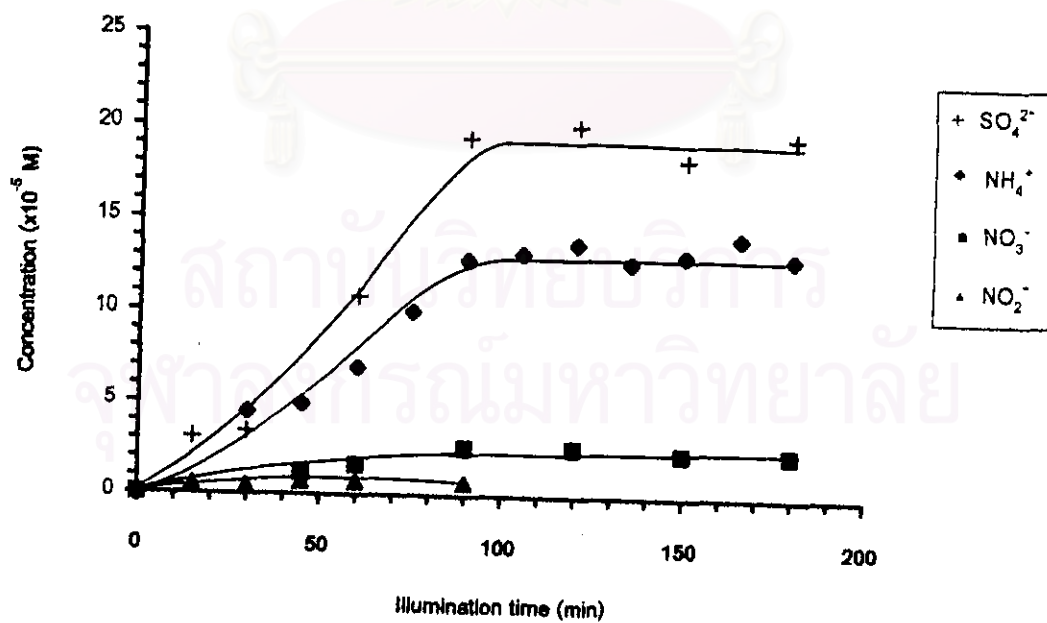


Figure 5.15 Formation of NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} in 10^{-4} M dye solution of orange G during photocatalysis with 75 mg of TiO_2 (see data in appendix 14)

These Figure show that the formation of NO_3^- , NO_2^- and NH_4^+ are less than expected from the concentration of dyes. Whereas the value of SO_4^{2-} from acid yellow 17 is more than expected from the concentration of dye, because the impurity in dye solution may form SO_4^{2-} ions when illuminated (acid yellow 17 powder has about 60 % of dye content). The ratio of NO_3^- , NO_2^- for each dye are 8.17 (acid yellow 17), 5.34(orange G) and 4.29 (acid black 1).

From the intermediate and final products identified, a possible pathway for the degradation of dye by photocatalysis with TiO_2 was propose in Figure 5.16.



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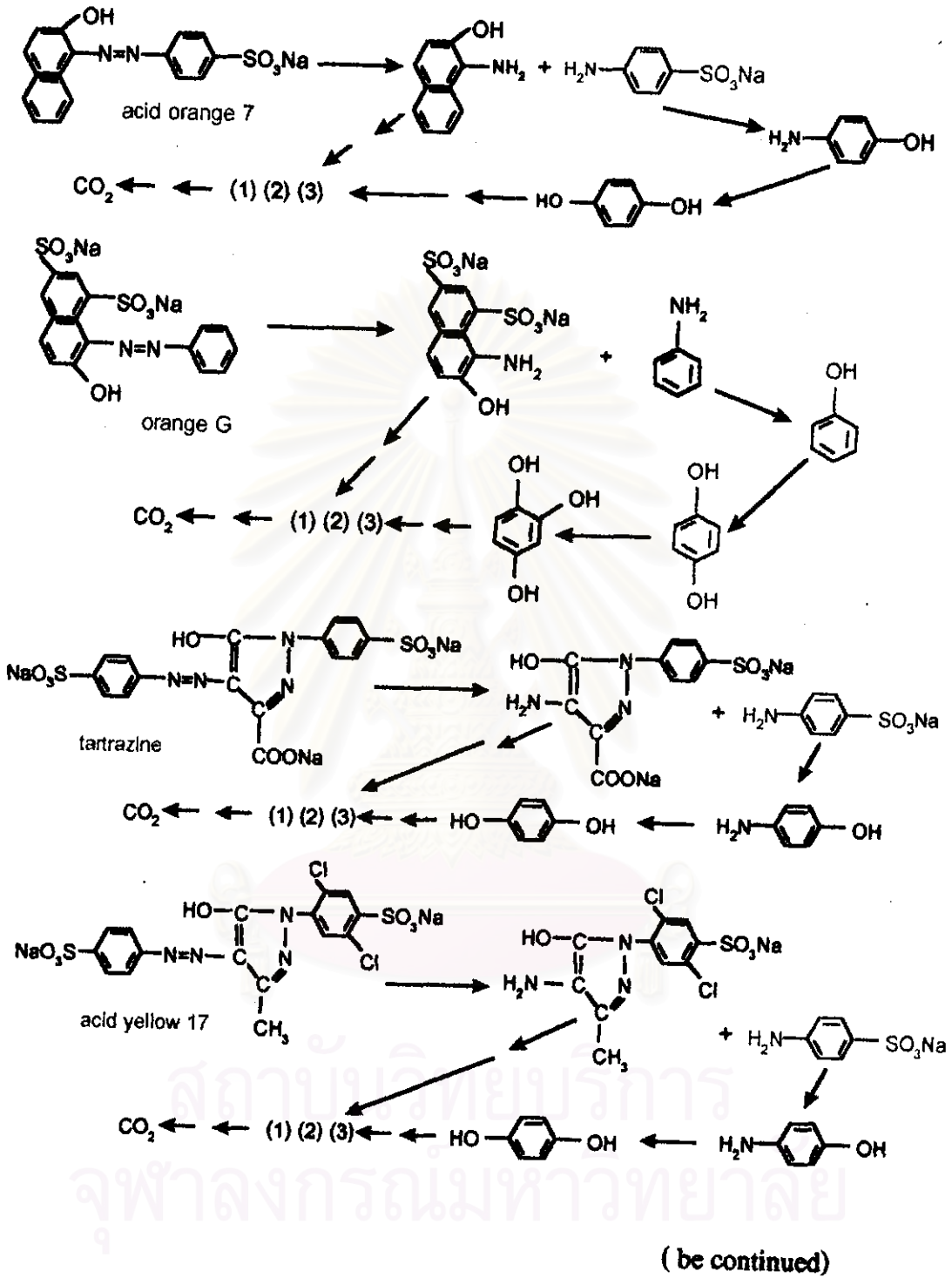


Figure 5.16 Possible degradation pathway of studied azo dyes, red color structure means identified.

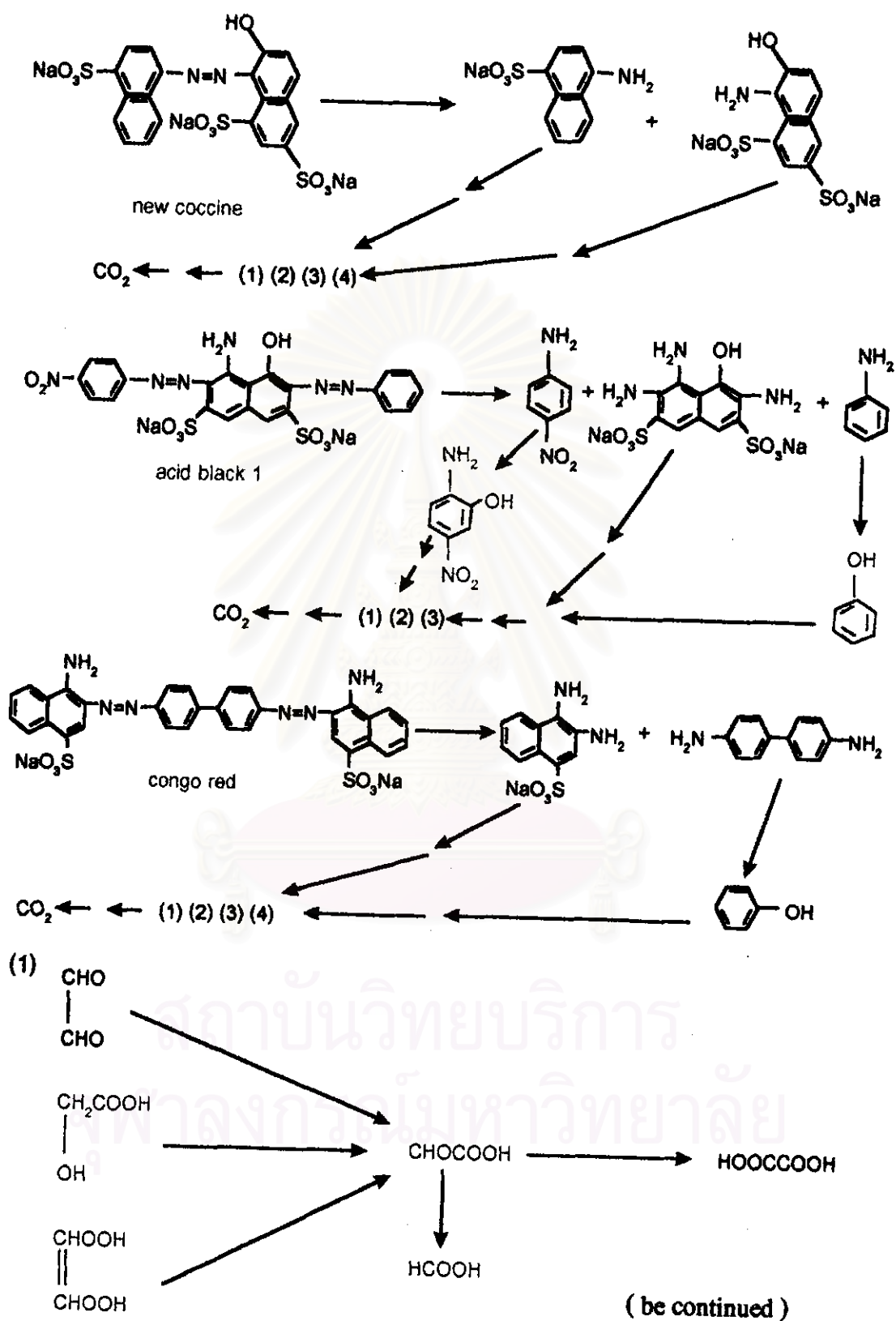


Figure 5.16 (continued) Possible degradation pathway of studied azo dyes, red color structure means identified.

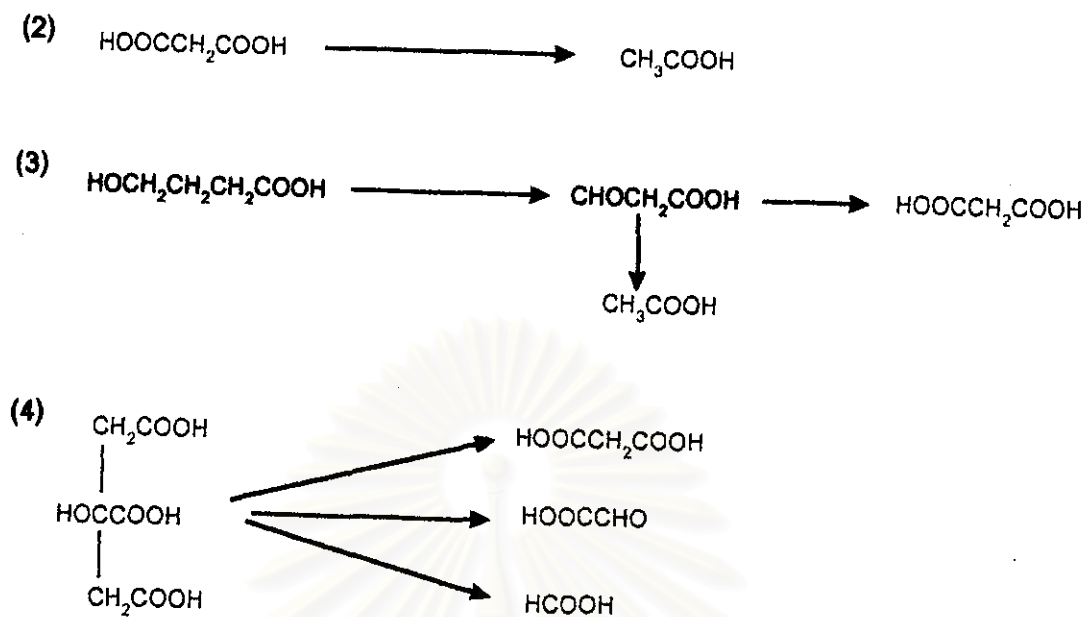


Figure 5.16 (continued) Possible degradation pathway of studied azo dyes, red color structure means identified.

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