DEGRADATION OF NAPHTHALENE BY OXIDANT AND CATALYST IN THE PRESENCE OF GAMMA RAY

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Introduction

Radiolysis is a general class of reaction that uses high-energy radiation for chemical reactions or bond cleavage. Organic molecules can either be degraded through direct or indirect irradiation in radiolysis[1]. Generally, degradation takes place by indirect interaction with irradiation because of the low concentration of molecules in solution (i.e. interaction with hydroxyl radicals and other reactive species by irradiation)[2].So the treatment of wastewater by using the radiation technology has been regarded as a feasible solution[3]. Therefore radiation technology has adopted the non-invasive and non-destructive approaches to conduct the purification of water quality, and it will not cause the secondary pollution after successfully removing the pollutants, which has been also considered as one of the most optimal treatment processes[4].
Recently, the combinations of oxidant such as hydrogen peroxide and persulfate and catalyst such as TiO_2 and Al_2O_3 with radiolysis were studied for enhancement of degraded kinetic constants[5-7]. Especially, potassium persulfate ($K_2S_8O_2$),which is widely applied for wastewater treatment[8], is an efficient oxidizing agent.When combined with gamma radiation,form divalent anions for complexation in aqueous medium and because of their bulkier size can initiate organic molecules[9]. Alsoincreases in the yields were reported for TiO_2because TiO_2 possibly accelerate the reactions induced by ionizing radiation[10-12].
However, there are few reports that directly identify the effect of $K_2S_2O_8$and TiO_2on radiation treatment and no report that investigates the comparison of those two additives. Thus, in this study, the combined processes such as gamma-rays/TiO_2 and gamma-rays/$K_2S_2O_8$were comparatively investigated in terms of their efficiency for naphthalene degradation rate.

Materials and methods

Naphthalene and potassuim persulfate were obtained from Sigma Aldrich, and TiO_2 was P25 by Degussa. All the solutions were made using Milli-Q purified water (Millipore Inc., USA).
The concentrations of naphthalene were1 mg/L and 2 mg/L for the study about effect of initial concentrations. After that, naphthalene concentration was fixed at 2 ppm for other studies. The concentration ranges of persulfate and TiO_2 were 0.1, 0.5, 1 mM and 0.1, 0.2, 0.5 g/L, respectively. 2 mL of 10 M $NaHCO_3$ was added after irradiation for blocking the reaction due to the remained radicals in aqueous solution. The reaction volume was 10 mL without headspace.
Gamma radiation was performed in^{60}Co (Nordion Inc., Canada) at the Korea Atomic Energy Research Institute (Jeongeup,South Korea)at the dose rate of 100Gy/hr. The radioactivity of the source was around 9.85 x 10^{15}Bq (=266,200Ci).
Quantitative analysis was carried out using GC-MSD (Agilent 7890A and 5975C inert XL MSD with triple-axis detector) for measuring the concentration of naphthalene. The samples were analyzed by CombiPALautosampler (CTC Analytics AG) and the column was a DB-5MS with a 30 m length x 0.25 mm I.D. x 0.25 μm film thickness (YW scientific). The GC temperature conditions were initial temperature of 55℃ for 0.4 min, ramping to 300 ℃ at 50 ℃/min and holding for 1 min.
Synergistic effect was calculated by this equation: $\text{synergistic effect} = \frac{k_{combined\ process}}{k_{oxidant}+k_{catalyst}}$ when $k_{combined\ process}$ was usage both of persulfate and TiO_2, $k_{oxidant}$ was usage persulfate, and $k_{catalyst}$ was usage TiO_2 in radiation.

Results and discussion

Effect of initial concentration of naphthalene

The kinetic constantsof naphthalene degradation under various conditions were calculated andit was 5.18x$10^{-2}$and 2.01x10^{-2}/min at 1 and 2 ppm, respectively. It was more efficientat lower initial concentration than at higher initial concentration[13]. The required radiation dose to remove 90% of naphthalene was 74.2 Gy (44.5 min) and

190.93 Gy (114.56 min) at 1mg/L and 2mg/L respectively. The study of initial concentration of other pollutants was observed in the study of trinitrophenol[14] and polychlorinated biphenyls[15]. The results obtainedfor evaluation of initial concentration for 1 mg/L and 2 mg/L of naphthaleneare as shown in Fig.1.The radiolytic degradation of naphthalene at higher concentration decreased the kineticconstants which monitored the experiment to be carried with high concentration at dose rate of 100 Gy/hr.

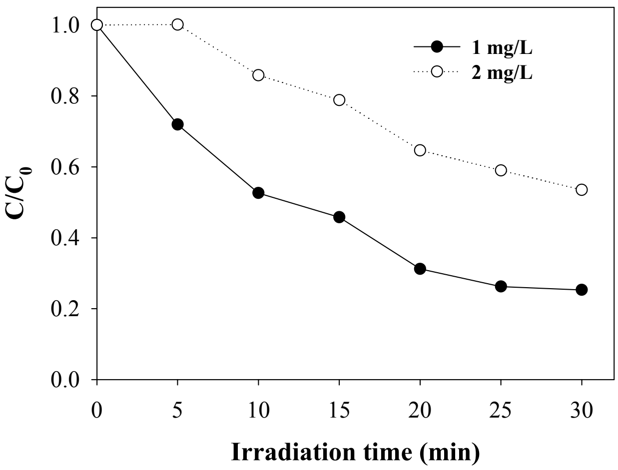

Fig. 1.Effect of initial concentrations of naphthalene at 1 mg/L and 2 mg/L at dose rate 100Gy/hr.

Effect of persulfate concentration

Gamma radiation induced degradation of naphthalene in aqueous solution at different initial $K_2S_2O_8$ concentration with increasing dose was shown in Fig 2.The results indicated that naphthalene was degraded rapidly with increasing dose. When initial $K_2S_2O_8$ concentrations were 0.1mM, 0.5mM, and1.0mM, the kinetic constants were $8.145x10^{-2}$,$9.306x10^{-2}$,$11.631x10^{-2}$/min, respectively.

The relative velocity is defined as the concentration change per unit dose in a selected dose interval. Radiation induced degradation of many pollutants is known to observe pseudo first order behavior[16].In our study it shows that the radiolytic degradation of naphthaleneat different initial persulfate could be fitted with the modified pseudo first order reaction kinetics. The dose constant increased with increasing $K_2S_2O_8$ Concentration.

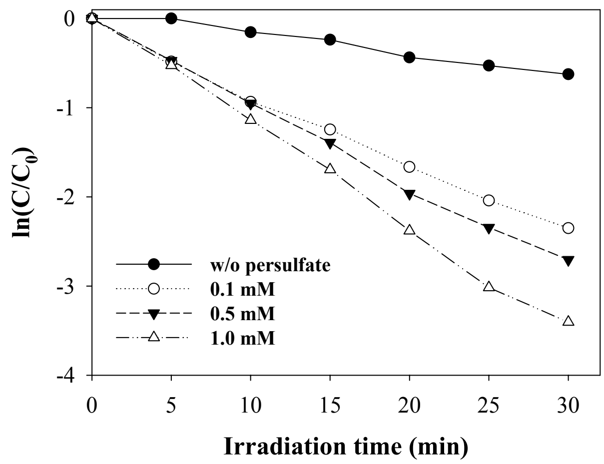

Fig. 2. Effect of persulfate concentration on naphthalene removal 0, 0.1, 0.5, and 1.0mM

Effect of TiO_2 dose

The concentration of TiO_2 was varied between 0.1 to 0.5g/L and Table 1 shows the influence of TiO_2 concentration for the removal of naphthalene by gamma radiolysis .The naphthaleneconcentration increased with decreasing TiO_2.These results represent the characteristics that TiO_2 particlescan inhibit the effect of naphthalene degradation.

The reasons would be since TiO_2 act as a semiconductor; ionizing radiations could form electron-hole pairs inside the particle[17]. The average energy to form a pair is few times as large as the band gap energy in case of many semiconductors[18,19]. Some of the electrons and the holes would recombine and others would move to the particle surface where they could reduce or oxidize solutes.The radiation chemical studies recently reported that surface trapped holes are the main oxidants[20]. The experimentalresult indicates that 0.1g/L would be the optimal dose for the degradation of naphthalene through irradiation.

Synergistic effects of combination of catalyst and oxidant

In the combination system of $K_2S_2O_8$ and TiO_2, the kinetic constants increased with increased concentration of persulfate and the catalyst.

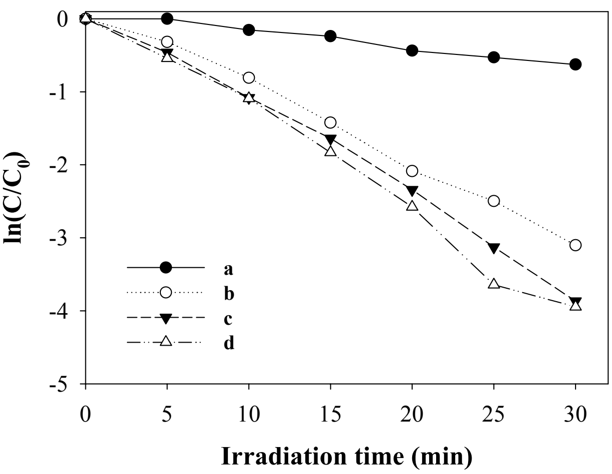

Fig. 3.Degradation of naphthalene with persulfate and TiO_2 combination on gamma radiation; a: radiation only, b: persulfate 0.1 mM and TiO_2 0.1 g/L, c: persulfate 0.1 mM and TiO_2 0.2 g/L, d: persulfate 0.5mM and TiO_2 0.2g/L.

The kinetic constants for the combined system for persulfate 0.1 mM and TiO_2 0.1 g/L, persulfate 0.1 mM and TiO_2 0.2 g/L, and persulfate 0.5 mM and TiO_2 0.2 g/Lwere in the range of 10.03×10^{-2}, 12.25×10^{-2}, 13.28×10^{-2}/min.

When comparing the gamma ray/TiO_2 and gamma ray/$K_2S_2O_8$– as the amount of catalyst dosage increased from 0.1-0.2g/L with 0.1mM of $K_2S_2O_8$and at 0.2g/L of $TiO_2$with high concentration of $K_2S_2O_8$the doserate increased, In the combination of persulfate 0.5 mM and TiO_2 0.2 g/L thek values were most highest.

When comparing the synergistic effect of each combination, the synergistic effect was higher for the high TiO_2 and high $K_2S_2O_8$, the values obtained were 9.5, 1.05, and 1.14.

Table. 1. Effect of TiO_2, $K_2S_2O_8$, combination of $K_2S_2O_8$ and TiO_2, and synergistic effects for the degradation of naphthalene at 100 Gy/hr.

TiO_2		Persulfate		TiO_2+ Persulfate		Synergy
0.1 g/L	2.409 min^{-1}	0.1 mM	8.145 min^{-1}	0.1 g/L + 0.1 mM	10.03 min^{-1}	0.95
0.2 g/L	2.360 min^{-1}	0.5 mM	9.306 min^{-1}	0.2 g/L + 0.1 mM	12.25 min^{-1}	1.05
0.5 g/L	2.005 min^{-1}	1.0 mM	11.631 min^{-1}	0.2 g/L + 0.5 mM	13.28 min^{-1}	1.14

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