

Selection of Supported Cobalt Substrates in the Presence of Oxone for the Oxidation of Monuron

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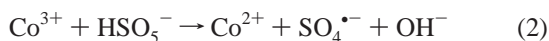
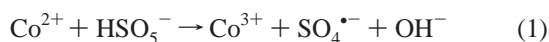
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The immobilization of cobalt ion on different media to catalyze oxone has been investigated. A probe herbicide, Monuron, was effectively degraded by using Co²⁺/oxone systems. For Co²⁺ supported on zeolite, 100% of Monuron could be removed within a 10 min reaction time. However, the recycling of the spent Co–zeolite catalyst using various posttreatments did not give a promising result. This is likely because the zeolite particles in solution have blocked and significantly attenuated the incident UV light from reducing Co³⁺ to Co²⁺. On the contrary, the use of cationic resin has minimized these problems. In the process of Co–resin/oxone/UV, faster Monuron decay could be achieved than that in the dark reaction. In the presence of UV, a significant drop of total organic carbon (TOC) was also observed in this approach suggesting an effective and clean process for Monuron mineralization.

KEYWORDS: Cobalt chloride; oxone; Monuron; oxidation; sulfate radicals

INTRODUCTION

Oxone is a triple salt consisting of 2KHSO₅·KHSO₄·K₂SO₄ and is a good source of generating a strong oxidant peroxy-monosulfate (HSO₅[−]) (1). The coupling of cobalt and potassium peroxy-monosulfate leads to the formation of SO₄^{•−} and SO₅^{•−} radicals as well as hydroxyl radicals through radical chain reactions (2, 3).



Sulfate radicals demonstrate higher standard reduction potential than hydroxyl radicals at neutral pH. Although the reduction potentials of the two radicals are similar at acidic pH, sulfate radicals are more selective for oxidation of target compounds than that of hydroxyl radicals in general (4). The sulfate radical pathway of 2,4-dichlorophenol (2,4-DCP) degradation has been reported (5). Radicals that were generated by the cobalt-mediated decomposition of oxone not only transforms 2,4-DCP but also mineralizes the daughter products and intermediates to carbon dioxide and water eventually.

Despite the fact that cobalt is a promising metal catalyst in the homogeneous Co²⁺/oxone system, it will mostly be discharged with the wastewater after the treatment process. Because of the recycle limitation of catalysts in homogeneous phase, solid catalysts have attracted much attention because of their high stability and durability. They are more cost-effective and easy to handle which make them suitable for the modern wastewater treatment. The recent trend in the development of

heterogeneous catalysis is to immobilize the catalyst or the oxidant on a solid support such as clay, zeolite, and resin (6, 7). For example, the Co-exchanged zeolite has been shown to demonstrate a high activity for the selective catalytic reduction of NO_x with propane (8, 9).

Monuron (3-(4-chlorophenyl)-1,1-dimethylurea), a phenyl urea derivative (as indicated in **Figure 1**), is widely used as a herbicide because of its inhibition of photosynthesis (10), for general weed control of noncrop area, and as pre-emergence on fruit crops. This class of chemicals is characterized by long lifetimes in the environment; Monuron has a lifetime of 8 weeks in river waters (11), and its half-life is about 170 days in the soil (12). Europeans have put it into their black list owing to the possibility of carcinogen to humans (13). Researchers have undertaken many degradation processes of Monuron, and yet the use of cobalt ion and oxone has seldom been reported (14). In this study, zeolite and resin are selected as the potential supports for the loading of cobalt ions on the medium surface. The reactivity and the interaction of such synthetic catalysts with oxone have been studied through the transformation of Monuron.

MATERIALS AND METHODS

Reagents Used. All the chemicals were used without further purification. Monuron (C₉H₁₁ClN₂O; 99%), cobalt(II) chloride hexahydrate (CoCl₂; 98%), and sodium azide were purchased from Sigma Aldrich. Absorbic acid was purchased from BDH while oxone was purchased from DuPont. Acetonitrile in HPLC grade and ethyl acetate, methanol, and acetone in ACS reagent grade were ordered from Tedia. The water used in the preparation of all the solutions was generated from a Millipore Waters Milli-Q water purification system.

Loading Co²⁺ onto Zeolite (Co–Zeo). The zeolite (CBV 100) used in this work was obtained from Zeolyst International, and it was used

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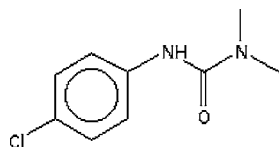


Figure 1. Structural formula of Monuron (15).

as received. To immobilize cobalt ions on zeolite, an aqueous solution of Co^{2+} at 147.33 mg/500 mL was mixed with 5.0 g of zeolite to synthesize Co-zeo. The mixture was stirred for 24 h; the catalysts were then separated by filtration ($0.45 \mu\text{m}$) and were thoroughly washed with deionized distilled water (DDW) until no cobalt ions were detected in the filtrate. To determine the amounts of Co^{2+} exchanged onto the zeolite, the concentrations of aqueous cobalt ions were detected and compared by a Spectronic Genesys 2 UV-vis spectrophotometer before and after the ion-exchange process. Subsequently, the catalysts were dried and stored at room temperature in the desiccator (wrapped in aluminum foil). The cobalt content of the catalyst was $1.17 \text{ mM Co}^{2+} \text{ g}^{-1}$ zeolite.

Loading Co^{2+} onto Cationic Resin (Co-Resin). The cation-exchange resin (CER) used in this work was Amberlite IR-120 (plus) in sodium form purchased from Aldrich. The matrix was 8% cross-linked polystyrene, and the matrix active group was sulfonic acid. The cation-exchange resin was used as received. To immobilize cobalt ions on the CER, an aqueous solution of Co^{2+} at 589.3 mg/200 mL was mixed with 2.0 g of resin to synthesize Co-resin. The mixture was stirred for 24 h; the catalysts were then washed as above. The cobalt content of the catalysts was $3.8 \text{ mM Co}^{2+} \text{ g}^{-1}$ CER. The dominant species that conjugated with the CER-Na in the solution is the CER- Co^{2+} , as indicated below



Experimental Procedures. In each experiment, 0.1 g of either dry Co-zeo or Co-resin was introduced into 200 mL Monuron solution (initial pH was kept at 7). Solution containing cobalt catalyst and 0.2 mM Monuron was mixed by magnetic stirring. The dark experiments were initiated by adding a known amount of oxone. For light-induced reactions, the irradiation source was eight 254 nm phosphor-coated low-pressure mercury lamps placed inside an RPR-200 Rayonet photochemical reactor equipped with a cooling fan. Likewise, the reactions were initiated by turning on the prewarmed UV lamps and by adding the oxone solution simultaneously. The temperature was kept at $23 \text{ }^\circ\text{C}$ throughout the reaction. One milliliter of sample was withdrawn from the reactor at predetermined time intervals, and the Co-zeo was separated from the solution by a syringe filter ($0.45 \mu\text{m}$). On the other hand, the Co-resin was easily separated from the aqueous phase by gravitational sedimentation in a few seconds after the stirrer had been turned off. To quench the reaction, methanol was added at 1:1 (v/v) while in the total organic carbon (TOC) measurement, and excess sodium azide was used.

Finally, the target compound was quantified by a liquid chromatography (LC) analysis with a Restek column packed with pinnacle octyl amine ($5 \mu\text{m}$, $0.46 \times 25 \text{ cm}$), in which, the mobile phase was a combination of acetonitrile and DDW (3:2 v/v) at a flow rate of 1.0 mL/min. The initial concentration of the probe compound at time zero was determined from an unexposed sample, and the decay rate of Monuron was calculated by the pseudo-first-order constant (16). The total organic carbon (TOC) was determined by a Shimadzu TOC 5000 analyzer equipped with an ASI automatic sample injector.

RESULTS AND DISCUSSIONS

Effect of Co^{2+} Dosages under a Constant Oxone Level.

Figure 2 shows the change of Monuron degradation in different $[\text{Co}^{2+}]$ while the level of oxone is maintained at 0.5 mM for the whole batch of tests. When the dosage of Co^{2+} was increased 10 times from 0.1 mM to 1 mM, the pseudo-first-order rate constant doubled, indicating a mild rate improvement within a 30 min reaction time. At fixed oxone concentration, this

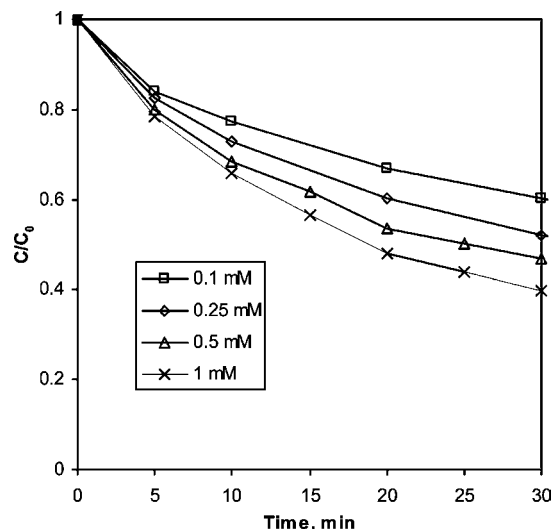


Figure 2. Degradation of Monuron in fixed oxone concentration and various Co^{2+} dosages in homogeneous conditions ($[\text{Monuron}] = 0.2 \text{ mM}$; $[\text{oxone}] = 0.5 \text{ mM}$).

observation has implied that the effect of Co^{2+} dosage is minimal to the degradation of Monuron. Although additional cobalt could assist the initiation of oxone in the production of sulfate radicals (as in eq 1), the side effect of increasing chloride content (the counterion of Co^{2+}) in the reaction cannot be neglected. The effect of chloride has been examined in the oxidation process, and negative results were reported in most cases (17). It has been proven that the presence of chloride in Fenton's process could scavenge the $\cdot\text{OH}$ by forming complex (18). The retardation of sulfate radicals by chloride has also been proposed (19). The researchers claimed that sulfate radicals could be consumed by chloride ions eventually yielding sulfate ion instead of oxidizing the target compound in the solution. Therefore, increasing cobalt concentration may not be a cost-effective way to enhance the degradation rate. In a later section, the effect of oxone dosage is investigated, and this alternative has proven to be much more practical than varying cobalt.

Process Selection. In Fenton's reaction, researchers have suggested that a more efficient organic degradation can be achieved through the addition of UV light and the introduction of oxalate (20). Because Co-zeo/oxone is analogous in nature to Fenton's process (i.e., metal catalyst plus radical precursor), the additive effect was also investigated in the study. Figure 3 shows the results of Monuron removal fraction during a 30 min reaction. There is no significant improvement by adding UV or oxalate to the Co-zeo/oxone process. An enhanced degradation on 2,4-dichlorophenoxyacetic acid has once been reported in the process of homogeneous Co/oxone under UV illumination (2). The level of Co^{2+} could be maintained from the reduction of Co^{3+} with the aid of UV light. Theoretically, the amount of Co^{2+} in the solution is not depleted and is adequate to initiate the remaining oxone generating additional sulfate radicals. In this study, however, light is possibly blocked or scattered by zeolite (present in a cloudy form) rather than promoting the reduction of Co^{3+} back to the Co^{2+} as reactions were carried out in heterogeneous mode. Besides, in a later section, we show that the time required for the reduction process (Co^{3+} to Co^{2+}) is indeed much longer than that of Monuron decay. Therefore, zeolite was believed to be the major obstacle to hinder the recovery of Co^{2+} and to facilitate further enhancement as in photo-Fenton's process.

On the other hand, the addition of oxalate in Co-zeo/oxone could not enhance the Monuron degradation. The use of oxalate

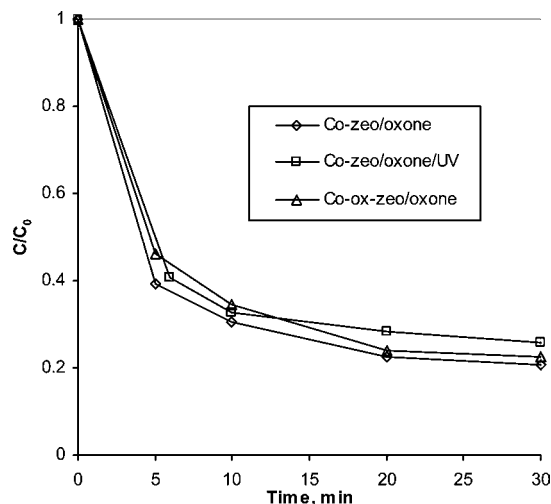


Figure 3. Comparison of different processes (for the reaction involving UV, eight lamps at 254 nm were used; concentration of oxalate was fixed at 16.6 mM; [oxone] was kept at 0.5 mM in all the tests; reaction volume was 200 mL).

to increase the quantum yield of Fe^{2+} in Fenton's reaction has been discussed (20). This is also not applicable in this study owing to the zeolite suspension in the reactor. Even the quantum yield could be increased, and the available light intensity for the reaction is possibly attenuated by the zeolite particle. By comparing the three different processes in **Figure 3**, Co-zeo/oxone is verified to be the most efficient one, and further investigation of this process is carried out in the following sections.

Effect of Oxone Dosages on Co-Zeo. It has been proposed that the use of Co/oxone process could be exempted from precipitation and speciation of iron which has long been the major problems in Fenton's reaction (1). Yet, the oxone dosage could be critical to the organic degradation while overdosing could theoretically be a potential problem to deteriorate the process similar to that of H_2O_2 in Fenton's process (21). To verify these queries, various oxone concentrations therefore were introduced into the Co-zeo system. In general, faster Monuron degradation was observed when more oxone was introduced as shown in **Figure 4**. In the control experiment, zeolite without cobalt has indicated negligible adsorption (<3%) which implies that the generation of sulfate radicals is the dominant reaction pathway causing the Monuron decay. The degradation depended very much on the oxone concentration. The disappearance of 0.2 mM Monuron was only 20% when the dosage of oxone was a quarter (i.e., 0.05 mM) of that of the target compound. When oxone dosage was increased to 2 mM (i.e., 10 times), Monuron completely disappeared within 10 min. Unlike H_2O_2 in Fenton's reaction, the dosage of oxone does not cause any adverse effect on the degradation process.

Reusability of Co-Zeo. Several regeneration attempts were tried to recover Co-zeo by using either DDW washing, ascorbic acid, or UV illumination. After the first run, the spent zeolite was separated and rinsed with DDW before the addition of a second bath of Monuron and oxone solution. As shown in **Figure 5**, a much lower Monuron decay performance was observed when Co-zeo was regenerated by DDW and was reused for the second run. The removal percentage was reduced by 60% for a 30 min reaction. The loss of reactivity is possibly due to the dissolution of Co^{2+} in aqueous phase in the first run and to the oxidation of Co^{2+} into unreactive Co^{3+} . To verify the availability of Co^{2+} after the reaction, the spent Co-zeo was collected after the treatment of Monuron and was rinsed

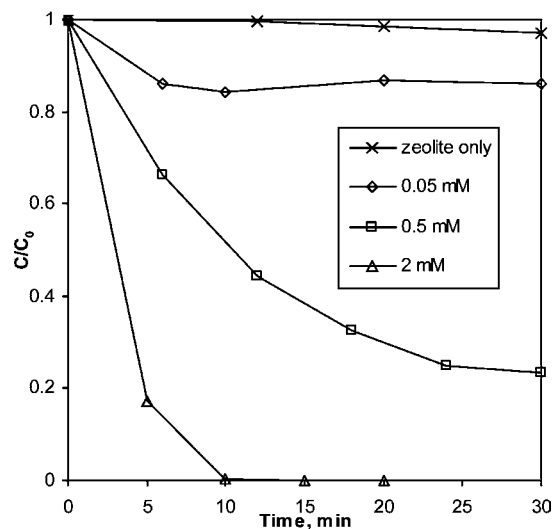


Figure 4. Effect of oxone on the degradation of Monuron at fixed Co-zeo ([Monuron] = 0.2 mM; Co-zeo = 0.1 g; reaction volume = 200 mL).

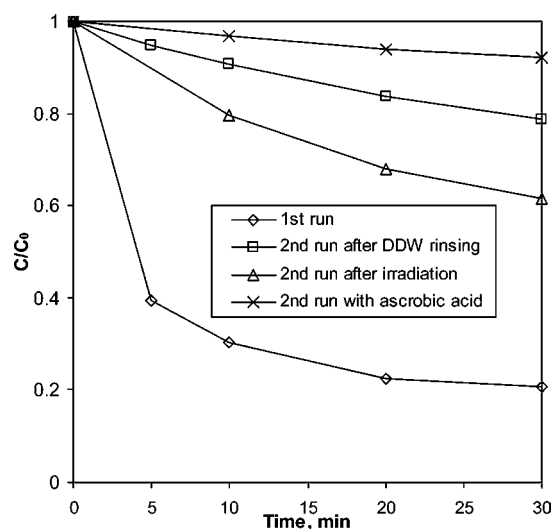


Figure 5. Performance of recovery on Co-zeo by three different treatments (i.e., (1) rinsed by DDW, (2) irradiated by eight lamps at 254 nm for 80 min, and (3) soaked in 4.4 mM ascorbic acid).

thoroughly with DDW. The spent Co-zeo was then suspended into water and was irradiated at 254 nm for another 80 min. It was then separated by filtration and was added to another batch of reaction solution containing the same amount of reactant and oxidant as the first run. The degradation of Monuron with the UV-treated Co-zeo was slower than that with the fresh Co-zeo, but the rate has been improved compared to the DDW-treated sample. This justifies that the UV irradiation process has certain effect to convert part of the Co^{3+} to Co^{2+} through the UV-induced photoreduction process. Similar observation has been reported in Fenton's reaction. It has been proven that the reduction of Fe^{3+} to Fe^{2+} is possible under UV irradiation (20). This could increase the oxidation efficiency by maintaining the level of Fe^{2+} in the solution. Such reaction is believed to be possible and more readily to happen on Co^{3+} as the reduction potential of Co^{3+} (1.82 eV) is higher than that of Fe^{3+} (0.771 eV).

In addition, ascorbic acid was used to further examine the importance of cobalt species on the surface of Co-zeo. The spent Co-zeo was washed and soaked in 4.44 mM of ascorbic acid solution. After Co-zeo was treated by ascorbic acid for

1 h with continuous stirring, it was separated and used in the second run of reaction. An adverse effect on Monuron removal was observed as shown in **Figure 5**. The decay rate with ascorbic acid regenerated Co-zeo was found to be 10 times slower than that with the fresh Co-zeo. It has been reported that the use of ascorbic acid can either function as pro-oxidant or antioxidant (i.e., radical scavenger) depending on the dosage applied and experimental conditions (22). The results have shown that ascorbic acid can work as a pro-oxidant to oxidize Co^{2+} to Co^{3+} in the proposed system. This further reduces the amount of Co^{2+} sites available for the second run and decreases the production of radicals for Monuron degradation. This has further proven that Co^{2+} is the major species that contributed in the Monuron oxidation.

Although Co-zeo has been proven to be effective to degrade Monuron, its posttreatment and the regeneration performance is not very attractive for real application. Therefore, another substrate, cationic-exchange resin, is proposed in the next section.

Effect of Oxone Dosage in Co-Resin. Co^{2+} was exchanged with the cationic resin and was dried before use. Co-resin sank into the solution, and mixing was maintained throughout the reaction. The dosage effect of oxone in 0.2 g resin was investigated, and the pseudo-first-order plot of Monuron degradation was observed and is depicted in **Figure 6a**. The decay of Monuron follows quite well the first-order kinetics with r^2 above 0.95. A linear relationship between reaction rates and oxone concentrations is summarized in **Figure 6b** implying that the degradability was mainly contributed from the oxone with adequate Co^{2+} .

Besides, the reuse of Co-resin is more encouraging than Co-zeo. After the spent Co-resin was washed with DDW, the oxidation of Monuron in the second run only reduced by 18% within a 30 min reaction compared to that of fresh Co-resin (data not shown). A much slower removal of Monuron was observed by the spent Co-zeo in which the removal percentage was significantly reduced by about 58%. Therefore, the use of Co-resin is not only beneficial from an easier separation (i.e., by using sedimentation compared to that of filtration used for Co-zeo), but its higher recovery performance makes it more practicable than using Co-zeo as the catalyst.

UV Irradiation in Co-Resin/Oxone and TOC Measurement. Unlike in Co-zeo/oxone, the use of UV light in Co-resin/oxone has indicated a significant improvement on the Monuron decay. As referred to in **Figure 7**, about 60% removal in 20 min reaction was observed in dark, while in the presence of UV light, a complete removal of Monuron could be achieved at the same reaction interval. The degradation rate was enhanced 4.3 times. This observation is very different from the discussion in Process Selection and has proven that the catalytic process by Co^{2+} and oxone could be sped up by UV if the medium selection is appropriate. Since resin was suspended in the solution in a discrete form compared to that of zeolite (cloudy form), a clear and more transparent solution was observed. Therefore, the light from UV source was not significantly attenuated, and more Co^{3+} is able to convert back to Co^{2+} (via photoreduction) to maintain adequate Co^{2+} sites to activate the catalytic function of oxone.

Simultaneously, the change of TOC was measured in reactions with and without UV light. As shown in **Figure 8**, different TOC profiles were observed. In the dark reaction (without UV), only about 9% of TOC was removed, and it remained at the same level after 3 h of reaction. This suggests that the disappearance of Monuron is possibly transformed into stable

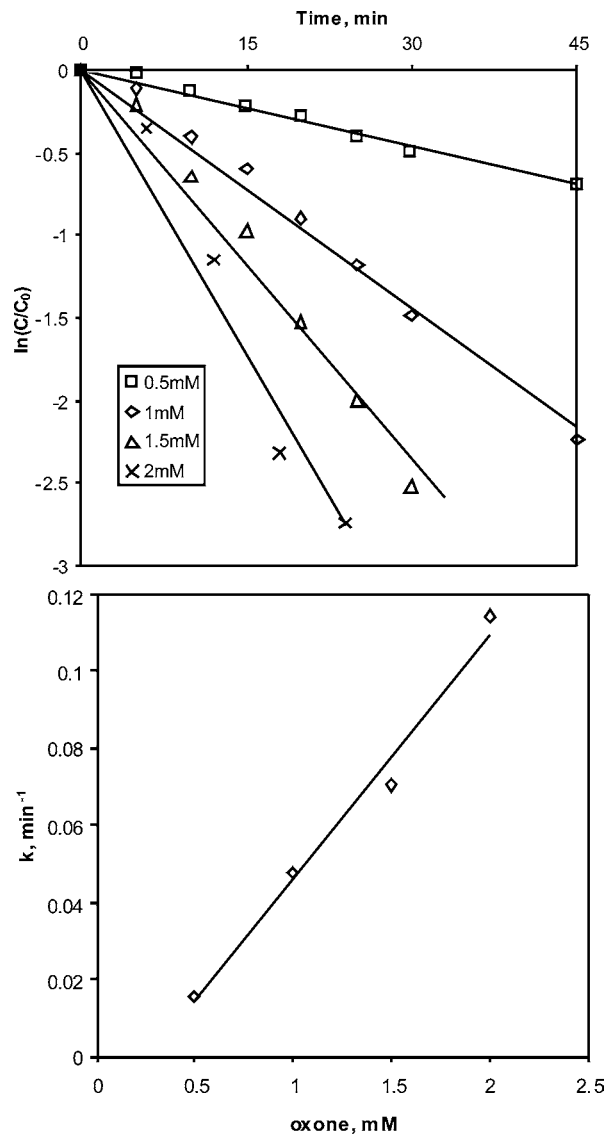


Figure 6. (a) Pseudo-first-order decay of Monuron and (b) comparison of reaction rates in the presence of Co-resin with various oxone dosages.

and refractory intermediates in the solution. On the contrary, an obvious decrease (up to 77%) in TOC was observed when UV was involved in the reaction. Apparently, the high excitation energy from UV did not only enhance the Monuron decay but also enhanced the mineralization of intermediates. From the result of TOC, we can judge that the UV energy is not only able to convert Co^{3+} to Co^{2+} but also is able to assist Monuron break down into smaller intermediates and eventually into CO_2 and water. However, the reduction of TOC slowed down after 1 h of reaction. This could be attributed to two reasons: (1) the available oxone in the solution is depleted after a longer reaction time and (2) the end products such as chloride (from the cobalt source and Monuron) or nitrate species (from Monuron) could be able to quench the degradation as reported elsewhere (23).

In this study, the oxidation process by using cobalt and oxone is successful to degrade Monuron in both homogeneous and heterogeneous phases. Heterogeneous reaction is more convenient and environmentally friendly in the real application. Loading Co^{2+} onto both zeolite and resin is successful to degrade Monuron in aqueous phase by the generation of sulfate radicals. Although higher removal ability was found from Co-zeo/oxone, the postfiltering and recovery would complicate the

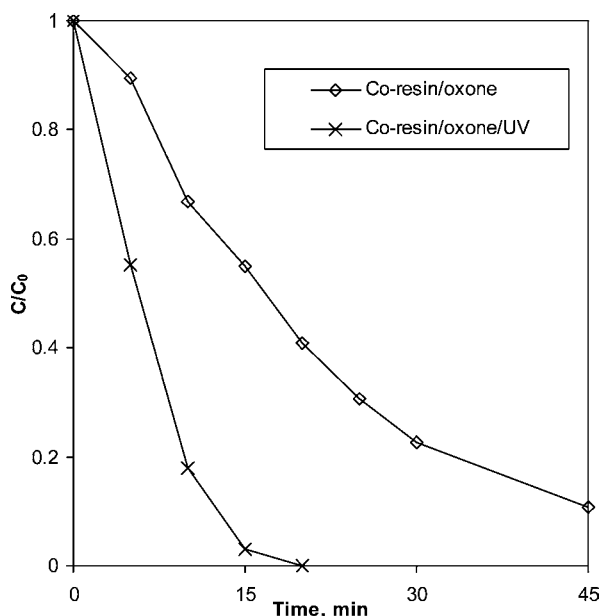


Figure 7. Performance of Co-resin/oxone process in the presence of UV (eight UV lamps at 254 nm were used; [Monuron] = 0.2 mM; [oxone] = 1 mM; Co-resin = 0.1 g; reaction volume = 200 mL).

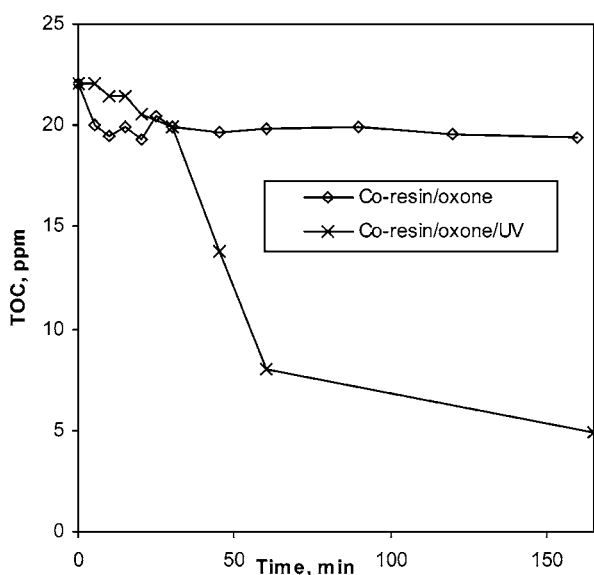


Figure 8. Change of TOC in the removal of Monuron ([Monuron] = 0.2 mM; [oxone] = 1 mM; reaction volume = 200 mL; eight UV lamps at 254 nm were used).

treatment process. While the use of Co-resin was exempted from the problem of light attenuation by the substrate, a more effective degradation is observed in the Co-resin/oxone with the aid of UV. The TOC reduction has also given an insight on the process with UV which is clean and feasible to put into practical applications.

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