

Development of a Biphasic Electroreactor with a Wet Scrubbing System for the Removal of Gaseous Benzene

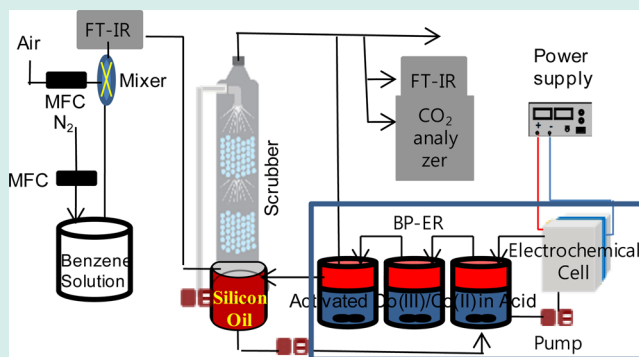
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Supporting Information

ABSTRACT: An efficient, continuous flow electroreactor system comprising a scrubbing column (for absorption) and a biphasic electroreactor (for degradation) was developed to treat gas streams containing benzene. Initial benzene absorption studies using a continuous flow bubble column containing absorbents like 40% sulfuric acid, 10% silicone oil (3, 5, 10 cSt), or 100% silicone oil showed that 100% silicone oil is the most suitable. A biphasic batch electroreactor based on 50 mL of silicone oil and 100 mL of activated Co(III) (activated electrochemically) in 40% sulfuric acid demonstrated that indirect oxidation of benzene is possible by Co(III). Combined experiments on the wet scrubbing column and biphasic electroreactor (BP-ER) were performed to determine the feasibility of benzene removal, which is reside in the silicone oil medium. In semidynamic scrubbing with BP-ER experiments using an aqueous electroreactor volume of 2 L, and an inlet gas flow and a gaseous benzene concentration were 10 Lmin^{-1} and 100 ppm, respectively, benzene removal efficiency is 75% in sustainable way. The trend of CO_2 evolution is well correlated with benzene recovery in the BP-ER. The addition of sodiumdodecyl sulfate (SDS) enhanced the recovery of silicone oil without affecting benzene removal. This process is promising for the treatment of high concentrations of gaseous benzene.

KEYWORDS: biphasic electroreactor (BP-ER), benzene, mediated electrocatalytic oxidation (MEO), sustainable technique, combined process



1. INTRODUCTION

Various processes are being used and developed for the destruction of volatile organic compounds (VOCs), because they are indirect toxic to humans (carcinogenic, mutagenic, or teratogenic) and can cause atmospheric pollution (photochemical smog and destruction of the ozone layer).^{1–4} VOCs are widely used and produced by industrial processes, transport, and during domestic activities,^{5–7} and are commonly used as raw materials for the manufacture of consumer products and as industrial solvents and are usually petroleum derivatives.⁸

In past decade, treatment processes for VOCs have been developed at different stages in divertive way. First, solid sate individual process like solid catalysts in quartz tubular fixed bed flow reactor at atmospheric pressure was used in catalytic oxidation of volatile organic compounds (VOCs) including benzene for partial oxidation of petrochemical materials to minimizing formation of undesirable byproduct.⁹ For the total oxidation of benzene, MnO, Cu-MnO, ZnO, FeO, and CoO high temperature catalysts (400 °C) have been devised in a fixed bed reactor.^{9–11} However, the reactivation procedures required for catalysts are problematic for bulk processing.

Further, an aqueous phase individual treatment process was developed using a bimetallic carbon supported catalyst, particularly for benzene oxidation to increase the removal

efficiency with less working process cost.¹² Though the removal efficiency is high, benzene solubility in aqueous phase limits this process. Other kinds of absorbents like aqueous surfactants were introduced into the aqueous phase to absorb VOCs.¹³ In addition, water–oil emulsion with a polyphasic nature creates homogeneity problems and mass transfer resistances.¹⁴ Consequently, it appeared that pure organic absorbents offer a better solution.¹⁵ Several potential absorbents, such as mineral oil,¹⁶ silicon oil,¹⁷ polyglycols,¹⁸ alkylphthalates, and alkyladipates¹⁹ were investigated. These absorbents were selected for their specific advantages, for example, high absorption capacity, good thermal stability, or possibilities of reuse. Note that these are only absorption.

Pollutants contained in air streams were then aerobically degraded in biofilter columns. However, biofilters were able to treat low concentrations of volatile pollutants.²⁰ Yeom and Yoo suggested a hybrid bioreactor or combined bioreactor comprised of a bubble column bioreactor in series with a biofilter, where a high concentration of gaseous pollutant was fed to the hybrid bioreactor, much of it was degraded in the

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bubble column bioreactor section and the remainder was stripped by aeration and subsequently degraded in the biofilter.^{21,22} In a further advancement, two phase biocatalysis for bioremediation applications in which a second, distinct organic phase was employed, where very large amounts of xenobiotic substrate dissolve in a hydrophobic organic phase, and then partition at an appropriately low concentration by means of equilibrium to bio active cells.^{23–25} In addition, it has been shown that the organic phase can be used to efficiently (i.e., >99%) recover spilled BTX from soil, and then be used in a two-phase system to degrade contaminant species.^{26,27} However, even though this two-phase bioreactor was successful, it has its limitations, such as biocatalyst reuse is hard and the reaction pathway between microorganism and BTX is difficult to determine. Sustainability in the working process is still lacking in the above methods either one way or other.

According to UNEP report, mediated electrocatalytic oxidation (MEO) process can be a future technology for sustainable use.²⁸ In recent years, MEO process hybridized wet scrubbing process, works under physicochemical method, was successfully introduced for the removal of odorous gases and partially water-soluble VOCs at ambient temperatures.²⁹ Moreover, the use of additional chemicals is completely minimized by this process and it works as sustainable way by regenerating the active catalyst using electro-oxidation process.³⁰ Using this MEO hybridized wet scrubbing process, we used Ce(IV), Co(III), and an Ag(II) as active catalyst to remove phenol, acetaldehyde, hydrogen sulfide and NO and SO₂, successfully at ambient temperature.^{31–33} In continuation of our findings, as a further step to removal of water insoluble VOCs, we devised the MEO process through biphasic medium to produce a BP-ER with wet scrubbing system for gaseous VOC removal, especially for the removal of benzene to make sustainable working process.

In this present work, we combined an absorption column with a BP-ER to remove or degrade benzene from a gas stream. In the first set of experiments, the absorption of benzene was examined using different absorbing solutions. Then, a biphasic batch electroreactor was used to understand reaction phenomena by monitoring active catalyst concentration (Co(III)), benzene, and CO₂ evolution. In the third set, combination of absorption (scrubbing) column and BP-ER was developed to get sustainably remove the gaseous benzene under optimized conditions. To enhance the solubility of benzene in the aqueous phase during BP-ER reaction, surfactant was introduced and studied.

2. MATERIAL AND METHODS

2.1. Materials. Cobalt sulfate (Co(SO₄)₂·7H₂O, 99.9%) from TERIO Corporation, China, sulfuric acid (H₂SO₄, 60%) from Sam Chun Chemicals, Korea, SDS from Sigma-Aldrich, U.S.A, sorbitane trioleate (Span 85), methane sulfonic acid (MSA) (CH₃SO₃H), and ferrous sulfate (FeSO₄·7H₂O) from Junsei Chemical Co., Ltd., Japan, were used as received without any further purification. Silicon oil (3, 5,10 cSt) from Sil Tech, Korea, was used as received. Mesh-type Pt-coated-Ti and Ti plate electrodes were from Wesco (Korea). All solutions were made using water purified by reverse osmosis (Human Power III plus, Korea). The oil free air compressor was supplied by Kyungwon Co. (Korea).

2.2. Working Procedures. **2.2.1. For Packed Bed Column.** Absorption of benzene was studied in the continuous flow packed bed column scrubber (used elsewhere), as described in

Figure S11 and its description in Supporting Information (Figure S11).

2.2.2. For Batch BP-ER. A desired silicone oil and benzene amounts (49.5 mL/0.5 mL) were placed in a glass container, stirred using magnetic stirrer, and transferred into a double walled reactor vessel (to maintain temperature) with a capacity of 500 mL, as shown in Figure.1. Then 100 mL of Co(III)/(II)

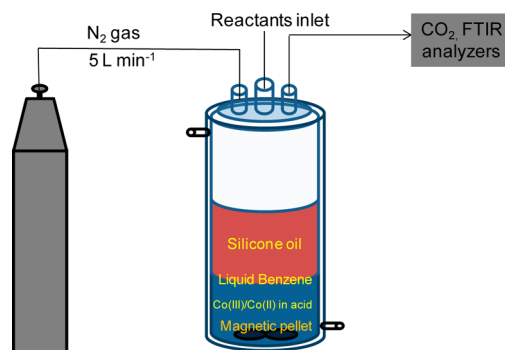


Figure 1. Schematic representation of the batch BP-ER experimental setup for benzene removal.

activated (Co(III) 35%) in 40% H₂SO₄ was added to the double walled reactor vessel. The reaction vessel was stirred using magnetic stirrer and monitor the benzene by measuring Co(III) concentration (using titration with Fe(II)) and exit CO₂ gas using CO₂ analyzer (model MultiRAE-IR(PGM-54), USA). The Co(III) was activated separately (for pictorial information, see ref 29) using a divided electrochemical cell (separated by a Nafion (320) membrane) containing a Pt-coated Ti anode (35 cm²) and Ti cathode (35 cm²) that connected to 700 mL of 0.75 M Co(II) in 40% H₂SO₄ and 300 mL of 40% H₂SO₄ as anolyte and catholyte respectively, in separate containers. A constant current of 2.5 A was supplied to the electrochemical cell at a constant liquid flow rate of 5 L min⁻¹ using a magnetic pump. Oxidation efficiency of Co(II) was calculated by potentiometric titration of an aqueous sample (5 mL) was taken at desired time with FeSO₄, and in addition, oxidation reduction potential (ORP) measurements were also performed.

2.2.3. For Semidynamic BP-ER. The electrochemical cell used in semidynamic process for Co(III) generation contains a narrow gap undivided flow cell configuration with a mesh type Pt-coated-Ti anode and Ti cathode. The interelectrode gap was maintained at 5 mm. The electrode assembly setup was tightly clamped to Ti end plates of thickness 5 mm with the help of Teflon plates (thickness = 5 mm) and rubber gaskets using a filter press technique. A solution of cobalt sulfate in 40% sulfuric acid or MSA (2 L), which comprised a part of the BP-ER in a glass tank (bottom part), was continuously circulated through the electrochemical cell at constant flow rate (5 L min⁻¹) using a magnetic pump (Pan World Co., Ltd., Taiwan). In order to get high Co(III) concentration, electrolysis was performed at 10 °C galvanostatically by applying a constant current (15 A) using a locally made constant current source (from Korea Switching Instruments). The effective surface areas of the anode (280 cm²) and cathode (13 cm²) were exposed to the solution. First, the electrochemical cell was run until Co(II) to Co(III) oxidation conversion attained steady state (35% as Co(III)), as determined by measuring Co(III) levels in the electrolyte solution by potentiometric titration

with Fe(II), before allow it to react with absorbed benzene in silicone oil at BP-ER. Absorption and BP-ER experiments were performed at $25\text{ }^{\circ}\text{C} \pm 1$ and $10\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$, respectively.

The benzene absorbing scrubbing column with the BP-ER reactor system comprised an air supply, a part of BP-ER tank (upper part), the scrubber reactor column, and data logging and gas analysis systems. The scrubbing column, a 5 cm inner diameter and 30 cm high glass vessel, was filled with Tripak packing material (25.4 mm diameter). The benzene-air mixture, obtained by controlled mixing of air, using mass flow controllers (MFC) (model 1179A13CS1BK-S, MKS Co. Ltd., USA), was introduced at the bottom of the scrubber at a 10 L min^{-1} gas flow rate, and the silicone oil was introduced at the top of the scrubber in counter current flow manner at a 10 L min^{-1} flow rate. The outlet silicon oil scrubbing solution containing the benzene was circulated in the active Co(III)/Co(II) containing 40% sulfuric acid solution in the BP-ER.

2.3. Analysis. The outlet gas concentration of benzene from the absorbing column and active Co(III)/Co(II) 40% sulfuric acid solution scrubbing reactor column from the BP-ER tank was measured at regular time intervals using an online FTIR analyzer (1200-MIDAC Corp., Irvine, California). Reproducibility of benzene removals during experiments were measured three times. Outlet CO_2 concentrations from the active Co(III)/Co(II) 40% sulfuric acid solution scrubbing reactor column were measured using a CO_2 analyzer. In particular, to determine the concentration of benzene in silicone oil during the BP-ER process, a GC-MS Shimadzu unit (GC/MS-QP2010, Japan) was used with a DB-5 ms capillary column (60 cm, 0.25 mm, 0.1 μm) at an injection temperature of $280\text{ }^{\circ}\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Benzene Absorption in Packed Bed Column Scrubber. A number of studies have analyzed the volumetric mass transfer coefficients and partition coefficients of VOCs, especially benzene, in silicone oil systems.^{34,35} Here, focused mainly on application part, 10% of three different silicone oils (3, 5, 10 cSt) in 40% H_2SO_4 were chosen for the benzene absorption studies. As depicted in Supporting Information Figure S11, absorption experiments were carried out; obtained results are depicted in Figure.2A. Absorption of benzene get saturated in 60 min in the case of 10 cSt silicone oil. A similar trend was found for the 5 cSt silicone oil but saturation time was slightly extended to 120 min. However, for the 3 cSt silicone oil, saturation of benzene could not attain within the studied time, which means absorption capacity is high in 3 cSt silicone oil. The obtained results correlated well with solute mass transfer change with viscosity of the medium,³⁶ meaning that lower viscosities correspond with high mass transfers or benzene absorption is high at low cSt silicone oil. The low cSt silicone oil (3 cSt) was again analyzed in different percentage solutions, such as 0%, 10%, and 100% on benzene absorption that results shown in Figure.2B. As was expected, 0% silicone oil showed almost no absorption, meaning that benzene is saturated in 30 min. In the case of 10% 3 cSt silicone oil, as expected, benzene absorption decreases sharply and a steady state in absorption is attained in 150 min with keep on absorbing 20 ppm benzene in silicone oil. However, in the case of 100% silicone oil, the benzene absorption decreases very slowly (higher absorption) and attained a steady state in absorption at 320 min with remain 30 ppm benzene in solution and it keeps maintain up to the studied time (Figure.2B, ▲

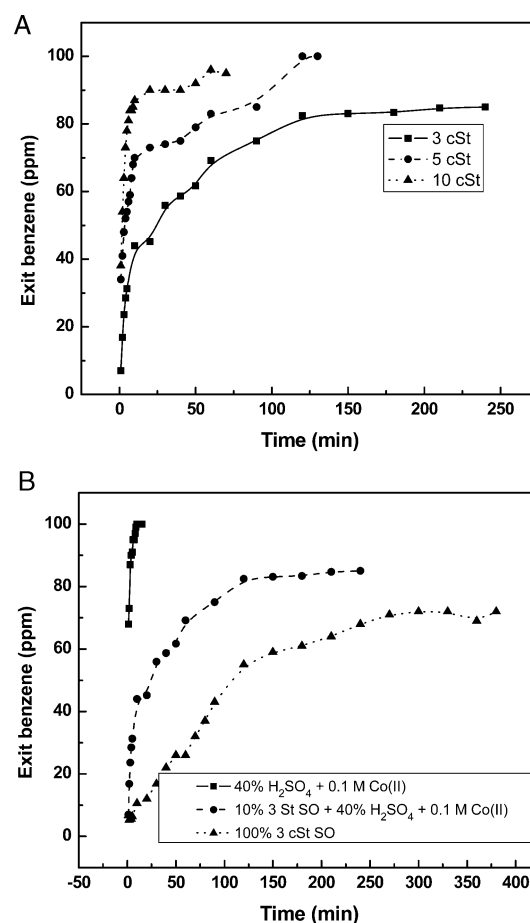


Figure 2. (A) Comparative absorption plot of benzene with respect to time in silicone oil of different viscosity: (■) 3 cSt, (●) 5 cSt, and (▲) 10 cSt. Feed concentration of benzene = 100 ppm, Gas flow rate = 10 L min^{-1} . (B) Comparative absorption plot of benzene with respect to time in different experimental solutions: (■) 40% H_2SO_4 + 0.1 M Co(II), (●) 10% 3 cSt silicone oil in 40% H_2SO_4 , and (▲) 100% 3 cSt silicone oil. The experimental conditions used were the same as those in panel A.

with dotted line). This explains 100% silicone oil is better for the absorption of benzene. It is worth noting that 100% silicone oil effectively absorbs VOCs with minimized practical difficulty.³⁵

3.2. Benzene Removal in Batch BP-ER. As mentioned in the experimental section above, a temperature controlled batch reactor was adopted to minimize the Co(III) auto reduction and to reduce errors in oxidation efficiency calculations, as shown in Figure 1. The collected results of Co(III) concentration changes using the batch BP-ER experimental setup in different experimental solution are depicted as in Figure 3. In pure pre-electrolyzed solution, the concentration of Co(III) decreased gradually with time (Figure 3). It has been well established that the Co(III) is reduced in several ways, such as, by the oxidation of water, self-reduction, or by reaction with any substrates.^{37,38} So, by monitoring Co(III) concentration variation under other experimental conditions kept constant like temperature, applied current etc., one can predict the oxidation effects of silicone oil and benzene indirectly. The square with a solid line for Co(III) concentration variation in presence of silicone oil with time in Figure 3 shows almost no change in Co(III) oxidation trend with respect to only Co(III) in H_2SO_4 (dotted line), which explains no silicone oil oxidation

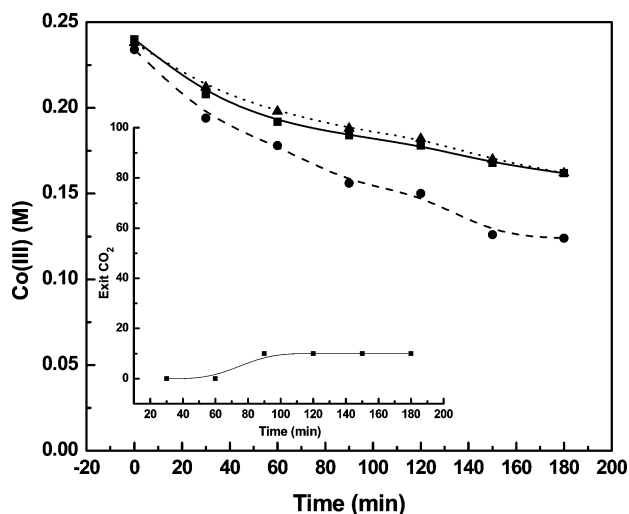


Figure 3. Variation in Co(III) concentration versus reaction time for different experimental solutions in 40% H_2SO_4 : (\blacktriangle) 0.75 M Co(III)/(II), (\blacksquare) 3 cSt silicone oil + 0.75 M Co(III)/(II), and (\bullet) 3 cSt silicone oil + 0.75 M Co(III)/(II) + 1% benzene. Gas flow rate = 5 L min^{-1} . Inset figure shows exit CO_2 concentration variation with time during reaction in batch reactor.

by Co(III) in sulfuric acid medium. However, in the presence of 1% benzene, results showed a prominent change in Co(III) concentration, which decreased to ~ 12.2 M. The consumed Co(III) ions are believed to have been utilized for the oxidation of benzene.

Another way of monitoring benzene oxidation is provided by outlet gas analysis. First, CO_2 analysis was carried in outlet gas by purging N_2 in the head space of the BP-ER batch reactor. The obtained results are shown in the inset in Figure 3. Silicone oil with benzene initially showed 0 and 10 ppm CO_2 after 1 h, which explains the reaction is slow and 10 ppm of CO_2 in 1% feed benzene is almost negligible, detected at the outlet. In other words, the absorbed benzene, around 70% in silicone oil (as in Figure 2B respective curve), may not be transferred (phase transfer) to the electroreactor for further removal, the oxidation rate may be slow in aqueous medium, or some other intermediates products like phenol, catechol, resorcinol, or benzoquinone etc.³⁹ might have formed. It has been well established that the mass transfer of benzene is reasonably rapid in silicon oil.²⁵ Also, intermediates formed are converted to

CO_2 by the Co(III) ion (especially phenol to CO_2). In a previous study, we showed phenol oxidation by Ag(II) and Ce(IV) in a MEO process.³¹ So, we believe that the MEO process in aqueous medium slowly oxidizes benzene.

3.3. New Semidynamic BP-ER for Benzene Removal.

As mentioned above the oxidation of benzene is slow in aqueous medium, and thus, we developed an BP-ER with wet scrubbing process by using three consecutive aggressive mixing tanks to regenerate silicone oil and facilitate the oxidation of benzene, as depicted in Figure 4. First, the benzene gas was introduced under bottom of the scrubbing column, where silicone oil is sprayed on top of the column. The benzene contained silicone oil, after a defined time, is then pumped into the three BP-ER tanks into which 35% Co(III) in 40% H_2SO_4 (H_2SO_4 -MEO solution) is pumped continuously from the electrolysis cell. Through magnetic stirrers, the reaction process continues up to 60 min. Finally, benzene removed silicone oil transfers to the scrubbing column to repeat the absorption of benzene process. In reverse, benzene is oxidized by Co(III) present in H_2SO_4 -MEO solution, which are monitored by CO_2 and FTIR analyzers. In this way, silicon oil is reused and benzene oxidized (results are depicted in Figure 5). The fresh silicone oil absorbs benzene up to 50 ppm of 100 ppm in 15 min. In consecutive batches, the time to reach 50 ppm benzene absorption is decreased from 15 to 8 min. At the same time, benzene concentration in silicone oil at initial time is increased from 15% to 27% upon reuse of spent silicone oil. Thus, the regeneration efficiency of silicone oil is reduced after each batch BP-ER experiments, which means benzene removal is keep reducing or some benzene remains in silicone oil. This phenomenon is well-matched with GC analysis results for benzene in silicone oil during the reaction process, as shown in inset figure in Figure 5. In the pure silicone oil (first batch), benzene presence varies from 56 to 13 ppm in one hour, whereas the benzene concentration increased from 70 to 20 ppm in third reused batch, which means the absorbed benzene was retained more in silicone oil during consecutive batches.

Noel et al. reported that benzene oxidation by Ce(IV) in a batch reactor, did not occur in sulfuric acid medium even after 9 h, but that the same reaction was facilitated to 20% removal of benzene in presence of MSA medium after 9 h.⁴⁰ Given this evidence, benzene removal was carried out using 35% Co(III) in 40% MSA solution (MSA-MEO solution) and the results are depicted in Figure 6A. Fresh silicone oil absorbs benzene up

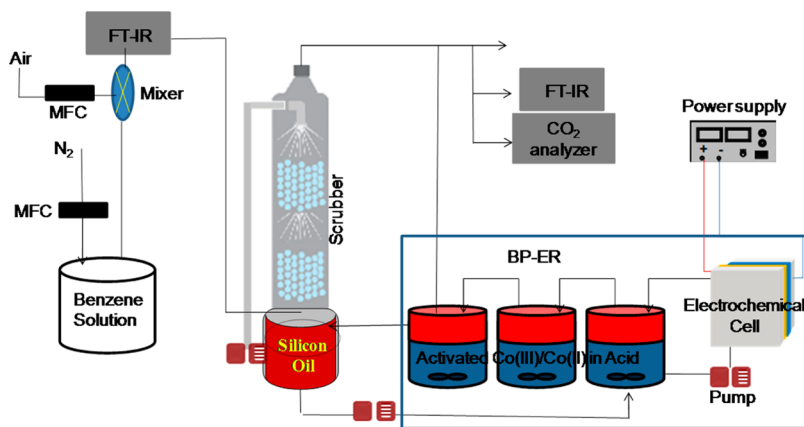


Figure 4. Pictorial representation of the combination of benzene gas generation, scrubbing, and BP-ER with online FT-IR and CO_2 analyzers for the semidynamic benzene removal process.

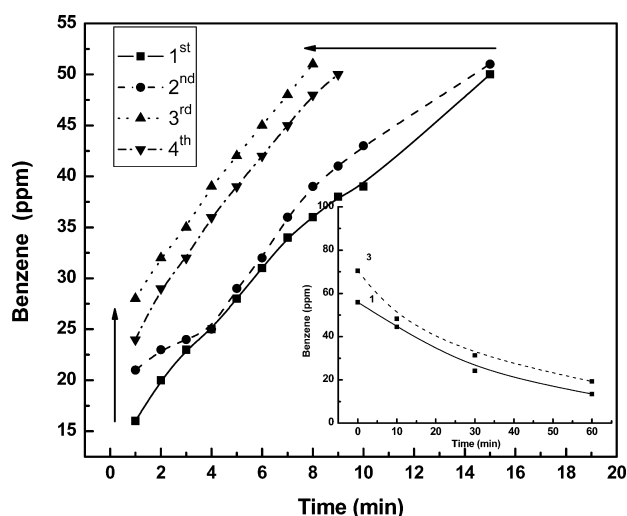


Figure 5. Plot of benzene absorption variation by 3 cSt silicone oil with respect to time when H_2SO_4 -MEO solution and benzene contained silicone oil was used in BP-ER during 1 h reaction: (■) Fresh silicone oil, (●) silicone oil from 1st batch BP-ER, (▲) silicone oil from 2nd batch BP-ER, and (▼) silicone oil from 3rd batch BP-ER. Experimental conditions for absorption were the same as in Figure 2A. Inset figure showing benzene concentration variation in silicone oil during removal process at BP-ER with time for each batch.

to 50 ppm of 100 ppm in 23 min, which is a little longer time than the same process in sulfuric acid medium (Figure 5 first batch), means more benzene is get absorbed. Interestingly, benzene absorption in consecutive batches 2, 3, and 4 showed no variation in benzene absorption time (15 min) to reach 50 ppm of 100 ppm. This results mean that oxidation of benzene by Co(III) in MSA is more efficient or no benzene remains in silicone oil than the same process done in sulfuric acid. These results well correlated with GC analysis of benzene in silicone oil, which is shown in the inset figure in Figure 6A. There observed a benzene concentration difference in silicone oil between the first and second batches, but no concentration difference was observed between the second, third, and fourth batches, which means benzene get removed completely and constantly due to its oxidation by Co(III) in MSA solution. Furthermore, reaction time was increased from 60 to 120 min in the presence of Co(III) in MSA; results are depicted in figure 2 in Supporting Information (Figure SI2). There shows no variation in benzene absorption between first and final batch process, which means complete benzene removal occurred and no benzene remains in silicone oil after each batch experiments. The inset figure of Supporting Information Figure SI2 shows almost no change in benzene concentration differences in silicone oil between the first and third regeneration batch confirms the complete benzene oxidation by Co(III) in MSA solution.

GC analysis showed only the benzene concentration present in silicone oil during the reaction process, but exit gas analysis can be used to determine product conversions and removal efficiencies. CO_2 and FTIR analyses were carried out at the outlet of the final regeneration reaction chamber; the results obtained are shown in Figure 6B. Benzene absorption by fresh silicone oil that used in BP-ER, as first batch, shows 1100 ppm CO_2 evolution initially, it reached to 1400 ppm in 20 min, and then decreased to 850 ppm in 60 min. In consecutive second and third batches, average CO_2 production was about 900 ppm

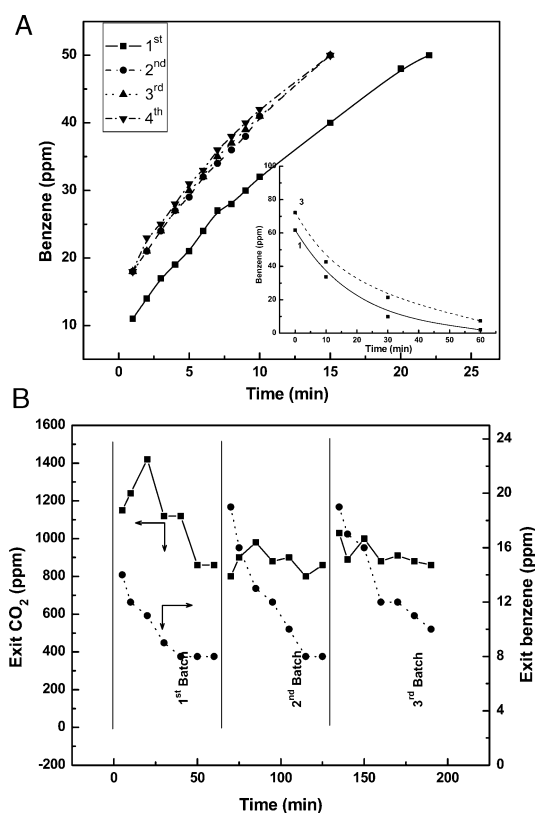
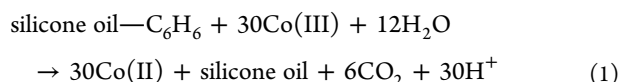


Figure 6. (A) Benzene absorption variation plot versus time using 3 cSt silicone oil when MSA-MEO solution and benzene contained silicone oil was used in BP-ER during 1 h reaction: (■) Fresh silicone oil, (●) silicone oil from 1st batch BP-ER, (▲) silicone oil from 2nd batch BP-ER, and (▼) silicone oil from 3rd batch BP-ER. Experimental conditions for absorption were the same as in Figure 2A. Inset figure shows benzene concentration variation in silicone oil during removal process at the BP-ER with time for each batch. (B) Plot of exit CO_2 and benzene concentrations during removal of benzene at the BP-ER with time for each batch.

in each 60 min. Exit benzene concentrations obtained by online FTIR that varied from 14 to 8 ppm during first batch regeneration and from 20 to 8 ppm during second batch regeneration. CO_2 production and benzene exit concentration trends from BP-ER were well correlated with the benzene absorption trend by used silicone oil (Figure.6A) in scrubbing column, which means fresh silicone oil absorbs more benzene and produces more CO_2 and that consecutive batch absorption and CO_2 production are kept constant. It is hard to compare exit molar ratio with input benzene to calculate exact removal efficiency of benzene. So, based on benzene exit concentrations, we calculated the removal efficiency of benzene by subtracting exit concentration of benzene from totally absorbed benzene then divided this by the totally absorbed benzene ($c_0 - c/c_0$). The removal efficiency of benzene of this semi dynamic-BP-ER reactor was almost 75%. If compare with similar physicochemical process, the obtained removal efficiency is very high in short time. But, biological process showed high removal efficiencies.²⁴ Moreover, we used 100 ppm benzene to check the validity of the present technique. The removal efficiency will improve to nearly 100% if reduce the input benzene concentration to 5 ppm, which is more than emitting level at municipal solid waste disposal.⁴¹ Advantageous of the presently developed BP-ER system is no additional catalyst or worked in

sustainable way. On the basis of our experimental results, the following reaction pathway is proposed:



3.4. Surfactant Effect. It has been well established that surfactants tend to solubilize organic pollutants like benzene in hydrophobic micellar cores.⁴² Accordingly, the anionic surfactant SDS was utilized (to avoid the counterion effect) to enhance the solubility of benzene and facilitate its oxidative removal in the BP-ER system. Along with 0.25% (w/v) SDS in presence of Co(II) in 40% MSA, electrolysis was done until the Co(III) concentration attained a steady state. Then the electrolyzed SDS surfactant contained MEO solution was pumped and mixed in BP-ER reactor with benzene contained silicone oil from scrubbing column for oxidation of benzene and regeneration of silicone oil. The collected results are depicted in Figure 7A. Pure silicone oil absorbs benzene up to 50 ppm of 100 ppm in 15 min. The spent silicone oil using SDS surfactant containing BP-ER process absorbs the same 50 ppm of 100 ppm benzene in 17 min and third and fourth regenerated

batches took 17 and 16 min, respectively. The reasonable explanation for this increase in benzene absorption time effect is that some SDS was retained during the reaction at BP-ER in the presence of SDS contained MEO solution, due to the tendency to form the micelles in aqueous medium and reverse micelles in organic medium, here silicone oil medium.⁴³ This explanation corresponded well with GC results depicted in the inset figure of Figure 7A. The benzene concentration varied from 69 to 7 ppm after regeneration of the first batch of silicone oil. At the same time, the benzene content was a little higher during reaction of the third batch (Benzene concentration varied from 89 to 28 ppm). The increase in benzene concentration in spent silicone oil during consecutive batches might have been due to SDS reverse-micelles solubilized the benzene that was present in the aqueous electrolyzed solution. Note that benzene absorption was not adversely affected, but facilitated, in the presence of SDS.

Figure 7B shows exit CO₂ and benzene trends of three reaction batches of benzene oxidation that occurred in BR-ER by using SDS containing electrolyzed MEO solution. In the first batch, CO₂ exit concentration varied from 2000 to 1300 ppm and then decreased to 1400 and 900 ppm (in average) respectively during second and third consecutive batches. The exit benzene concentrations varied from 16 to 9 ppm during the first batch removal process and maintained the same values during the second batch BP-ER process. A small increase in the exit benzene concentration between 22 and 11 ppm was observed during the third batch BP-ER process. In all batches, benzene exit concentration corresponded well with the CO₂ evolution pattern, that is, that higher CO₂ production levels mean lower benzene exit concentrations. However, as compared with benzene absorption by used silicone oil (Figure 7A), CO₂ and benzene exit concentrations showed contradictory results, that is, CO₂ and benzene evolution should be constant for all batches but they decreased with batch number. It appears that the addition of surfactant does not favor the removal of benzene by the BP-ER process.

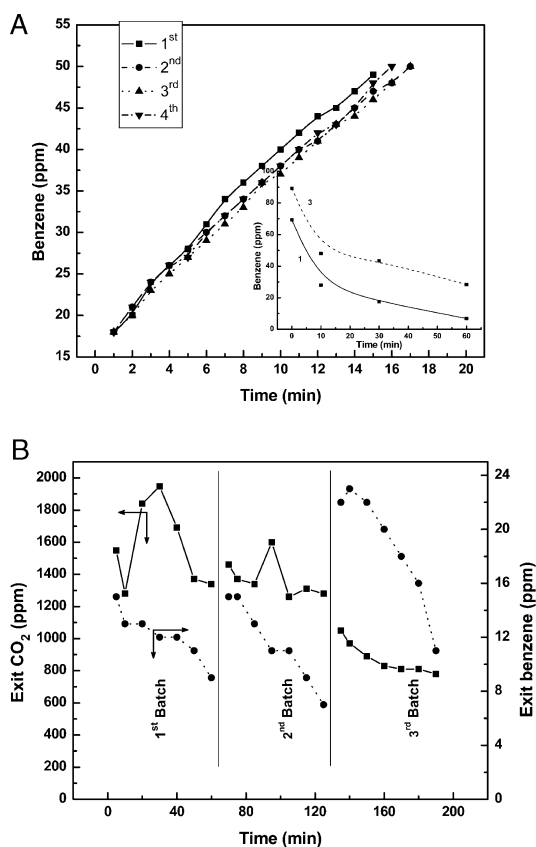


Figure 7. (A) Effect of benzene absorption versus time using 3 cSt silicone oil when 0.25% (wt/v) SDS contained MSA–MEO solution and benzene contained silicone oil was used in the BP-ER during 1 h reaction: (■) Fresh silicone oil, (●) silicone oil from 1st batch BP-ER, (▲) silicone oil from 2nd batch BP-ER, and (▼) silicone oil from 3rd batch BP-ER. Experimental conditions for absorption were the same as in Figure 2A. The inset figure shows benzene concentration variation in silicone oil during removal process at BP-ER with time for each batch. (B) Plot of exit CO₂ and the effect of benzene concentration during the removal of benzene at the BP-ER in presence of SDS with time for each batch.

4. CONCLUSIONS

In this study, combining a scrubbing column with a BP-ER was successfully developed and used to remove gaseous benzene. Initial benzene absorption results using a packed bed column confirmed that the use of pure silicone oil benefits benzene absorption. A decrease in Co(III) concentration in presence of benzene during batch reactor experiments revealed benzene oxidation, but the absence of CO₂ at the outlet of the batch reactor showed that the oxidation rate was slow. Enhanced absorption using spent silicone oil and removal efficiency of benzene at BP-ER were evidenced in MSA medium as compared with H₂SO₄ medium. Furthermore, when BP-ER number and Co(III) concentration were increased, benzene removal efficiency was increased. Also, mixing time was found to enhance the complete removal of benzene and that leaves pure silicone oil for next absorption. In one hour mixing of silicone oil containing benzene in Co(III) containing MSA at BP-ER, 75% benzene removal efficiency was achieved. Given the no additional catalyst and time concerned, this benzene removal efficiency is highly competitive and easily scaled up to industrial levels.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of the packed bed column setup and experiments for benzene scrubbing, and BP-ER results for 2 h reaction time for removal of benzene with GC results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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