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RESEARCH ARTICLE

DEVELOPMENT OF FENTON-LIKE REAGENTS FOR THE DEGRADATION OF PHTHALATE ESTERS

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ABSTRACT

This study involved the development of Fenton- like reagents (Mn^{2+}/H_2O_2 and Cr^{2+}/H_2O_2) for the degradation of phthalates esters - dimethyl phthalates (DMP), diethyl phthalates (DEP) and diphenyl phthalate (DPP). The degradation efficiency of phthalate esters (initial concentration of 20 mgL^{-1}) by the newly developed reagents was conducted at different time intervals, the pH was adjusted to 3.0, the reaction mixtures were extracted and analysed by High-Performance Liquid Chromatography (HPLC). The H_2O_2 concentration was set at 100 mgL^{-1}, and 10 mgL^{-1} for both Mn^{2+} and Cr^{3+}. The results showed that the reagent, Mn^{2+}/H_2O_2 degraded DMP completely within 20 minutes of the experiment, while 3.0 mgL^{-1} of DEP and 4.88 mgL^{-1} of DPP remained. At 30 minutes, DEP was found to be completely degraded with 4.84 mgL^{-1} of DPP remaining. In the same vein, the second reagent (Cr^{2+}/H_2O_2) recorded 100 % efficiency on DMP within 20 minutes while that of DEP did not reach 100 % efficiency until 60 minutes. In this case, the reaction time of 20 mgL^{-1} DMP and DEP with this reagent is 20 minutes and 60 minutes respectively. Furthermore, it could be deduced that 30minutes is sufficient for complete degradation of 20 mgL^{-1} DMP and 20 mgL^{-1} DEP with Mn^{2+}/H_2O_2 reagent while the degradation of 20 mgL^{-1} DPP took 60 minutes. For Cr^{3+}/H_2O_2 reagent, the reaction time for the complete degradation of DMP and DEP was 30 and 60 minutes respectively. These newly developed reagents Mn^{2+}/H_2O_2 and Cr^{2+}/H_2O_2 are very effective and efficient for the degradation of phthalate esters thus, recommended for the degradation of liquid wastes containing these hazardous compounds.

KEYWORDS

Advanced oxidation process, Fenton-like reagents, Dimethyl phthalates (DMP), Diethyl phthalates (DEP) and Diphenyl phthalate (DPP).

1. INTRODUCTION

Organic pollutants are made up of toxic chemicals which are dangerous to the environmental organisms. Many of these chemicals are difficult to degrade to harmless residue, as they stay longer in the environment (Nair, 2008). These chemicals have the capability of travelling very far, bioaccumulating in animal and human organs and systems (Anindita et al., 2008). Among the organic pollutants, phthalate esters have been constantly reported in recent years because of their toxicity (Foster, 2001). These compounds get into the environment as wastes from industries, such as chemical plants, oil refineries, pharmaceutical plants, etc. posing a great risk to environmental ecology and public health (Jiang and Mao, 2012). Also, many Agricultural and industrial processes have contributed greatly to the contamination of water bodies by releasing organic pollutants like phthalate esters in water thereby causing a disastrous effect on the aquatic organisms and human life. (Wang and Gu 2006).

Phthalate esters (PAEs) are organic compounds commonly used as plasticizers in the petrochemical industry and all plastic products. Phthalates are used for the production of common products like paints, dyes, coatings for nutritional supplements and pharmaceutical products, emulsifiers, lubricants, cosmetic products, glue, ink, detergents, and are released into the environment. Phthalates are commonly used in making sex toys, paint pigments, soft plastic fishing lures, floor tiles, food containers, wrappers, adhesives, shower curtains, eyes shadow, moisturizers, liquid soap, hair spray, nail polish, etc (Rudel and Perovich, 2008). Phthalates are also found in blood transfusion devices. The generally used phthalates include diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), di-(2-ethylhexyl) phthalate (DEHP) and dimethylphthalates (DMP).

DEHP is the most used plasticizer throughout the world in manufacturing polyvinyl chloride (PVC) because of its availability and low cost. Benzylbutylphthalate (BBP) is commonly used for producing foamed PVC, which is usually used as material for flooring. The secondary phthalates i.e. phthalates with two alkyl groups in their structures have been tagged as 'endocrine disruptors' because it was discovered that high dosage of it was responsible for hormonal change and birth defect in rodents (Matsumoto et al., 2008; Albert and Jegou, 2013). According to some study, histological modification of testes and reduction in fertility are part of the most disastrous effect of phthalates in the reproductive system (Swan,

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2010; Heudorf et al., 2007; Toppari et al., 2004). It was discovered that the metabolites of dimethyl phthalates (DMP), di-(2-ethylhexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), diethylphthalates (DEP), were found in the urine of humans, reducing the sperm mobility thereby causing low sperm count (Salaza- Matinez et al., 2004). Di-(2-ethylhexyl) phthalate (DEHP) is one of the most abundant phthalate esters (Lin et al., 2009).

Apart from the fact that it is an endocrine and organ disruptor, it has also been found to be carcinogenic, hepatotoxic, and teratogenic (Khan et al., 2015). Generally, phthalate esters are stable compounds that are resilient in the environment, research works have shown that the biodegradation process is very slow and is neither effective nor efficient. Therefore, it has become a matter of necessity to look for effective and efficient methods of degrading these refractory compounds. (Lin et al., 2009). For all these reasons, the development of an effective and efficient method for handling these contaminants is urgently required as this has become a serious concern in all nations of the world. Advanced oxidation processes (AOPs) are potential alternative methods for oxidizing refractory and hazardous organic compounds. The Fenton process (H_2O_2/ Fe^{2+}) is one of the most powerful AOPs that can be used to oxidize organic matter in the water (Beldean-Galea, 2015).

This method generates hydroxyl radicals (·OH), a strong oxidant with an E_0 of 2.8 V. This method is an encouraging process for the degradation of organic pollutants in aquatic media because the reagents are environmentally friendly, easy to handle and cheap. (Litter, 2005). In the same vein, Fenton-like reagents (Mn^{2+}/H_2O_2 and Cr^{2+}/H_2O_2) can also be used since the reactions are based on electron transfers that generate hydroxyl radicals which have the capability of degrading these refractory organic compound via oxidation.

Some researchers have studied the degradation of several phthalate esters by microorganisms under anaerobic and aerobic conditions (Cartwright et al., 2000), while others investigated the fate of phthalates esters by adsorption on solid medium (John and Christopher 2008). However, little work has been done on the study of the degradation of phthalate esters in aqueous medium by Fenton and Fenton-like reagents. Also, the stability of these compounds in the environmental factors is high, many research works have revealed that the biodegradation process is slow and is neither effective nor efficient (Staples et al.., 1997).

Therefore, advanced oxidation processes (AOPs) like Fenton and Fenton-like processes become the potential alternative method for oxidizing these hazardous organic compounds. It is therefore essential, to follow the procedure, set the operating conditions aright that best match the waste that is being degraded to achieve high degradation efficiencies. Thus, this study is aimed at developing an approachable, convenient, simple, and easy to handle analytical reagents for degradation of three phthalate esters (dimethyl phthalates (DMP), diethyl phthalates (DEP) and diphenyl phthalate (DPP)).

2. MATERIALS AND METHODS

2.1 Materials

Glasswares and reagents such as $MnSO_4•4H_2O$, $Cr_2(SO_4)_3•15H_2O$, H_2O_2 (30%w/w), methanol, hexane, sodium hydroxide (NaOH) (0.1M), hydrochloric acid (HCl) (0.1M), phthalate esters: dimethyl phthalate (DMP), diethyl phthalate (DEP), diphenyl phthalate (DPP), all of a high purity obtained from Sigma Aldrich Germany.

2.2 Methods

Oxidation experiment was carried out in a 50 mL brown beaker to prevent the interference of sun radiation according to the modified method described where Fe^{2+} was substituted with Mn and Cr^{3+}, this was equipped with a magnetic stirrer to ensure the homogeneity in the reactor (Esmaeli et al., 2011). 10 mL of water sample containing 20 mgL^{-1} of each selected phthalate was placed into the reactor. The concentration of H_2O_2 was set at 100 mgL^{-1}, and 10 mgL^{-1} for both Mn^{2+} and Cr^{3+} which were subsequently added into the reactor. Before adding the reagent to the reactor, the pH was adjusted to 3.0 using solutions of 0.1 M NaOH and 0.1 M HCl in water to prevent changes in the manganese and chromium form in all experiments.

The pH was measured using a Jenway pH meter. 5 mL of each phthalate ester (100 mgL^{-1}) was added into the reactor for degradation. To estimate the degradation rate of the phthalate esters at different times, the mixtures from the reactor were taken and extracted with 2 mL of hexane in a glass separator funnel as described (Esmaeli et al., 2011). The mixture was then vigorously shaken for 5 minutes and subsequently allowed the aquatic and organic phases separation. Next, the hexane layer was separated in a vial and evaporated to dryness. The residue was then dissolved in methanol and analysed by high-performance liquid chromatography (HPLC). All the experiments were conducted at room temperature (25ºC).

2.3 Analysis of Phthalate Esters

The analyses of the phthalate esters were carried out using an HPLC system CECIL ADEPT 4200 reversed-phase system composed of an auto-sampler coupled with UV-Visible detector all connected to a computer. The analytical column used was a Hypersil Gold C_{18} (30 cm X 4.6 mm i.d, 5 µm particle size) at ambient temperature containing S_5ODS_2 as a stationary phase. The separation was carried out under an isocratic elution condition using acetonitrile and water (90:10) as the mobile phase. Under this condition, separation lasted for about 10 minutes with a flow rate of 1.0 ml/min at ambient temperature. The detection of phthalate esters was carried out at 250 nm wavelength. 20 µL was used as the injection volume. The identification of each phthalate esters was based on retention time.

3. RESULTS AND DISCUSSION

The graph showing the efficiency and effectiveness of degrading reagents, time of completion of reaction, and reaction rate on DMP, DEP, and DPP is given in Figure 1. Likewise, the graph showing the efficiency and effectiveness of degrading reagents, time of completion of reaction, and reaction rate on DMP and DEP is given in Figure 2.

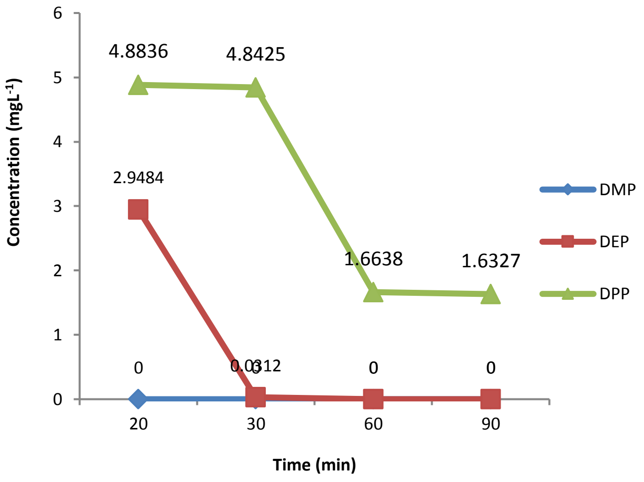

Figure 1: Comparative Degradation of DPP, DEP, and DMP by Mn^{2+}/H_2O_2 Reagent

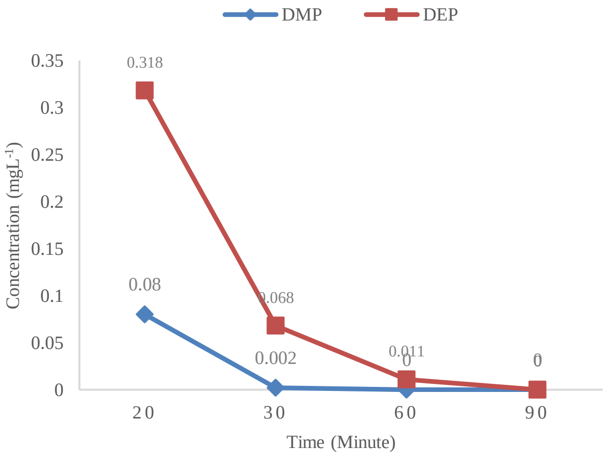

Figure 2: Comparative Degradation of DEP and DMP by Cr^{3+}/H_2O_2 Reagent

3.1 Efficiency and Effectiveness of Mn^{2+}/H_2O_2 Reagent on Phthalate Esters

Previous studies have shown that the efficiency of the Fenton reaction is affected by the concentrations of the reacting reagents (hydrogen peroxide and metal ions), the pH, and the reaction time (Litter, 2005). The importance of hydrogen peroxide as an oxidizing agent in the Fenton process cannot be overemphasized (Kavitha and Palanivelu, 2005). The study have shown that a low concentration of hydrogen peroxide in the reaction mixture did not generate sufficient hydroxyl radical in solution while on the other hand higher concentration was found to enhance the oxidation process as a result of an increase in the generation of the hydroxyl radical (Esmaeli et al., 2011). Similarly, the effectiveness of the Fenton process in the oxidative degradation of organic compounds is reportedly favoured under acidic conditions while the metal ion concentration is maintained at 10 mgL^{-1} (Yang et al., 2005).

Thus, in this study, the optimum hydrogen peroxide concentration of 100 mgL^{-1} was selected against 10 mgL^{-1} of the Mn^{2+}/Cr^{3+} ions at a pH of 3 The degradation of the phthalates was followed at four time intervals. Results from the degradation experiment showed that the reagent, Mn^{2+}/H_2O_2 has a powerful action on the phthalates to the extent that it degraded DMP completely within the first 20 minutes of the experiment, about 2.95 mgL^{-1} of DEP and 4.88 mgL^{-1} of DPP were found to be left in the reaction mixture at this time.

After 30 minutes, DEP was found to be completely degraded while about 4.84 mgL^{-1} of DPP remained and after this time interval, the degradation efficiencies of DPP tend to vary in very small intervals (Figure 1). Furthermore, it could be deduced that 30 minutes is a sufficient reaction time for complete degradation of 20 mgL^{-1} of DMP and DEP with Mn^{2+}/H_2O_2 reagent while the reaction time for the optimum degradation of 20 mgL^{-1} DPP will take at least 60 minutes. This shows that the reagent, Mn^{2+}/H_2O_2 is highly efficient and very effective.

3.2 Efficiency and Effectiveness of Cr^{3+}/H_2O_2 Reagent on Phthalate Esters.

In the same vein, the reagent combination Cr^{3+}/H_2O_2 was reacted with 20 mgL^{-1} of DMP and DEP at different time intervals (20, 30, 60, and 90 minutes). The results showed that the reagent was almost 100 percent efficiency in the degradation of DMP within the first 20 minutes of the reaction while that of DEP did not reach 100 percent efficiency until 60 minutes. In this case, the optimum reaction time for the degradation of 20 mgL^{-1} DMP and DEP with this reagent is 20 minutes and 60 minutes respectively (Figure 2). DPP was however not detected in the chromatogram report at all the tested time intervals, this may suggest a rapid or spontaneous degradation rate within the first few minutes of the reaction.

The efficiency of the degradation of various concentrations of DEP and other related phthalates by the Fenton reagent has been reported to be optimum between the 10 to 60 minutes; this is in agreement with the observation in this study for the manganese and chromium ions used in place of the iron in the Fenton like reagent (Beldean-Galea et al., 2015). The study summarises that Mn^{2+}/H_2O_2 combination in the Fenton reaction was able to degrade 20 mgL^{-1} DMP completely within 20 minutes of the experiment with a 100 % degradation efficiency while Cr^{2+}/H_2O_2 achieved 99.6 % degradation efficiency within the same time and 100 % after 60 minutes. For DEP, Mn^{2+}/H_2O_2 achieved 85.26 % degradation efficiency within the first 20minutes of the reaction and 100 % after 60 minutes while Cr^{2+}/H_2O_2 showed 98.41 % efficiency at the same time with 100 % achieved after 90 minutes. Therefore, Mn^{2+}/H_2O_2 is more efficient and effective for the degradation of DMP while Cr^{2+}/H_2O_2 is more effective for the degradation of DEP.

4. CONCLUSION

The result of this study shows that the reagents, Mn^{2+}/H_2O_2 and Cr^{2+}/H_2O_2 are very effective and efficient in the degradation of phthalate esters at a pH of 3 using the concentration of 1:10 of metal ion to H_2O_2 within a short reaction time. Since the degradation processes with these Fenton reagent combinations recorded high efficiency compared with biodegradation process that is known to be very slow and ineffective, therefore, this method becomes an encouraging and effective method for the removal of hazardous compounds from samples because the reagents are cheap, easy to handle readily available and environmentally friendly. Hence, from the performance of these reagents in the degradation of carcinogenic and mutagenic compounds that are frequently occurring in the aquatic and environmental samples, further studies are needed to investigate the large scale application in the treatment of industrial and agricultural wastes which commonly contain these phthalate esters.

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