Advance Oxidation Process (AOP) of Bisphenol A Using a Novel Surface-Functionalised Polyacrylonitrile (PAN) Fibre Catalyst

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Abstract: Bisphenol A (BPA) is a well-known endocrine disruptor in the environment which is not readily oxidised during wastewater treatment at Municipal Authorities. The aim of this work is to evaluate the environmental value of the wastewater treatment of a novel heterogeneous oxidation catalyst by means of the degradation of BPA, avoiding sewage sludge and its post-treatments. A surface-functionalised polyacrylonitrile (PAN) mesh has been produced by reaction of the cyano group of PAN with hydrazine and hydroxylamine salts. This surface-functionalised PAN is then exposed to iron (III) salt solution to promote the ligation of Fe(III) to the functional groups to form the active catalytic site. The experiments were set up in two different batch reactors at laboratory scale at different temperatures and initial pH. The degradation of BPA was detected by measuring the absorbance of BPA in Reverse Phase High Performance Liquid Chromatography at 280 nm. A total elimination of 75 ppm of BPA in less than 30 min was achieved under 300 ppm H_2O_2, 0.5 g PAN catalyst, initial pH 3 and 60 °C. Almost no adsorption of BPA on the catalyst was detected and there was no significant difference in activity of the catalyst after use for two cycles.

Keywords: bisphenol A; heterogenous Fenton catalysis; PAN mesh

1. Introduction

Endocrine-disrupting chemicals have been mentioned frequently for their deteriorating generative function to a number of living organisms on Earth [1]. Bisphenol A (BPA) is one example in this group and is the subject of increasing focus nowadays. It is widely used as a monomer for the production of polycarbonate (PC) plastics and epoxy resins, and there is a risk that it could be leached from PC products to the detriment of living organisms [2].

Considerable work on the degradation of BPA has been performed using various methods such as thermal degradation [3], electrocatalytic oxidation [4,5], enhanced TiO_2 photocatalytic degradation [6], O_3/UV methods [7,8], photo-Fenton process [1,9], Fenton in soil at high pH [10], biological methods [11,12] and so on. Advanced Oxidation Process (AOPs) are effective and promising methods to eliminate persistent organics pollutants (POPs) in contrast to biological treatment methods because biodegradation may be adversely affected by the toxicity of BPA [13,14].

The heterogenous Fenton process is able to avoid the precipitation of insoluble species, such as metal oxo species ($M^{(n+1)+}$=O) as a metal oxide or hydroxide sludge, because the iron catalyst is bound onto the functionalised PAN to form a solid phase catalyst. Many studies have been performed to produce better heterogeneous Fenton catalysts to oxidise a range of different organic substrate using, for example, silica supports [15], Fe-exchanged pillared beidelite [16], a resin support for Fe(III) [17], immobilisation of Fe(III) cations

by ion-exchange on a protonated microporous silicate known as HY zeolite [18], Fe^{3+}-containing ashes [19] or Fe(III) immobilised on alumina [20] etc. This improvement not only keeps the iron substantially in the solid phase but also adds the advantage of less secondary treatment.

The novel PAN catalyst was prepared by Ishtchenko, Huddersman and Vitkovskaya [21]. As one of the active cations for the decomposition of hydrogen peroxide, Fe^{3+} cations were firmly fixed to the fibre by means of functional groups produced by the reaction of PAN with hydrazine and hydroxylamine salts to produce a mixture of amidrazone, amidoxime, amide and carboxylate groups. The mesh of the catalyst comprises 50% of the polyacrylonitrile supported catalyst and 50% polypropylene fibres. Here, polyacrylonitrile (PAN) is used as a supported material for the metal active centre and the polypropylene is used to enhance the strength and hydrodynamic properties of the mesh [22]. A gram of the mesh contains 0.04 mmol Fe^{3+} [23].

With the modified heterogeneous Fenton's catalyst supported on polyacrylonitrile (PAN) fibre, the oxidation process has been successful in the degradation of organic pollutants in wastewater [21,23–25]. This heterogeneous Fenton catalytic process results in negligible sewage sludge and this avoids post-treatment; also, the openness of the catalytic mesh has excellent hydrodynamic properties and the possibility of working at near-neutral pH to provide better operation conditions for wastewater treatment. It has good performance at ambient temperatures and can be assisted by UV-Vis absorption capabilities, making the PAN mesh catalyst a potential option for solar harvesting applications. The basic principle of the oxidation is the Fenton process using hydrogen peroxide and a heterogeneous ferric catalyst to generate oxidants, which are thought by some to be hydroxyl radicals ($OH^\bullet$).

Whilst fibrous ion-exchangers are fairly well known, they have not been used as catalysts, and they have great advantages in terms of high surface area and ease of handling in comparison to traditional powdered catalysts. Whilst rotating biological contactors [26] are known, it is highly innovative to incorporate this type of catalytic mesh disc in place of the traditional discs to obtain a rotating catalytic contactor. There has been some effort to incorporate catalytic discs [27,28] using TiO2-doped discs under UV radiation with the aim to provide a thin film and better mass transfer conditions; however, the reactor design is substantially different from that used here. This reactor design ensures good mixing thus combing both the reactor design and the catalyst attributes results in a very novel invention.

In the present work, the aim is to demonstrate the potential environmental value of a novel heterogeneous oxidation catalyst for the degradation of Bisphenol A by performing a series of experiments at different reaction temperatures and initial pH. Additionally, oxidation runs at low BPA initial concentration were performed which are more appropriate to the pollutant concentrations found in municipal wastewater. These lower concentrations were carried out in a Rotating Catalytic Reactor, which has excellent potential for industrial scale-up.

2. Materials and Methods

2.1. Chemicals

Bisphenol A (99+%), methanol (HPLC grade), hydrogen peroxide (30% *w/w*) were supplied by Sigma Aldrich, Dorset, UK. Hydrochloric acid (37%) was supplied by Fisher Scientific, UK. The preparation of the PAN catalyst is described in references [21,23]. The mesh of the catalyst after functionalisation is composed with 50% polyacrylonitrile and 50% polypropylene together. A gram of the polyacrylonitrile fibrous catalyst fibers contains 0.1 mmol Fe(III) ions. Typical dimensions of 0.5 g of catalytic mesh are 20 mm long, 23 mm wide and 5 mm depth, containing 0.025 mmol Fe(III) ions. In the case of the Rotating Catalytic Reactor, the catalyst forms 14 discs of 100 mm of diameter (approx. 8.5 g of catalytic mesh each disc).

2.2. Chromatography

Analysis of Bisphenol A was performed using a PerkinElmer 200 HPLC system with Waters 510 HPLC pump with Waters 481 UV detector in the isocratic mode. The eluent of 60% methanol and 40% double-distilled water by volume was degassed by helium sparging and passed through the column at a flow rate of 0.8 mL/min. Hypersil C18 column 5 μm particle size, L × I.D. 15 cm × 4.6 mm was used. The detecting wavelength was set at 280 nm as this was the maximum absorption for BPA as determined by full-scan spectrophotometry and the retention time is around 3.5 min.

2.3. Procedure

The experimental setup consists of a conical flask placed on a magnetic stirrer to provide mixing. This setup provided better conversion of BPA than when the reaction was performed in a vessel connected to a vacuum so as to draw air through the solution to provide bubbling and, hence, mixing.

The BPA powder was dissolved in 25 mL of distilled water and agitated in an ultrasonic bath with warming due to the low water solubility of BPA. The pH of the solution was adjusted using 1 M HCl and 0.1 M NaOH solutions. Experiments were for 2 h and each experiment was replicated twice. During the experiment, at 10 min intervals 20 μL of the sample was injected into the HPLC to determine the concentration of Bisphenol A in the solution.

For the studies varying temperature, the working range was between from 20 °C to 60 °C using a 250 mL round bottom flask in a Radleys Carousel (Radleys Discovery Technologies, Saffron Walden, Essex CBII 3AZ, UK). For the experiments involving the variation of pH, a conical flask was used and thermostatted at 30 °C using a water bath. The reactions were initiated by the introduction of hydrogen peroxide.

The Rotating Catalytic Reactor (RCC) [29] was filled with 1 L BPA solution at pH 3 while the catalytic discs rotated at 2 rev/min and the reaction initiated when the hydrogen peroxide was injected into the closed reactor; samples were taken via a sampling tubing during the reaction.

3. Results

3.1. BPA Degradation

In Figure 1, the ratio of BPA average concentration (C_t) to initial BPA concentration (C_o) is shown as a function of time, the concentration of BPA decreased by up to 92.5% in the presence of H_2O_2 and PAN catalyst after 2 h. On the other hand, almost no conversion was observed for BPA and H_2O_2, and BPA only.

It was noticed that while the concentration of BPA in the sample solution was decreasing, the colour of the sample changed from colourless to yellow. It was very bright yellow at first, and as more BPA was oxidised, the colour of the sample became darker and darker. This phenomenon could be due to the formation of the oxidation products. Moreover, an increase in the pH from 3.02 to 3.45 was noted.

It is not possible to make a direct comparison of the degradation methods used for the mineralisation of BPA with other works. The initial concentration in this work was 75 ppm BPA, 300 ppm H_2O_2 and 1.1 mg Fe^{3+} bound to 0.5 g heterogeneous catalyst. However, investigations by Katsumata [1] using homogeneous photo-Fenton process for the degradation of BPA shows a quick degradation of BPA within 10 min by using 2.2 ppm Fe(II), 13.6 ppm H_2O_2 and 10 ppm BPA as the initial settings.

In the work presented by Chiang [30], using 2.0 wt% Pt-TiO2 in the photocatalytic degradation of BPA, the time required for the complete elimination of BPA was less than 30 min by using UV light (fluorescent black light blue lamp, 20 W NEC BLB with peak emission at λ = 355 nm) with Degussa P25 Titanium Dioxide Nanopowder and 20 ppm BPA at pH 3 as the initial settings.
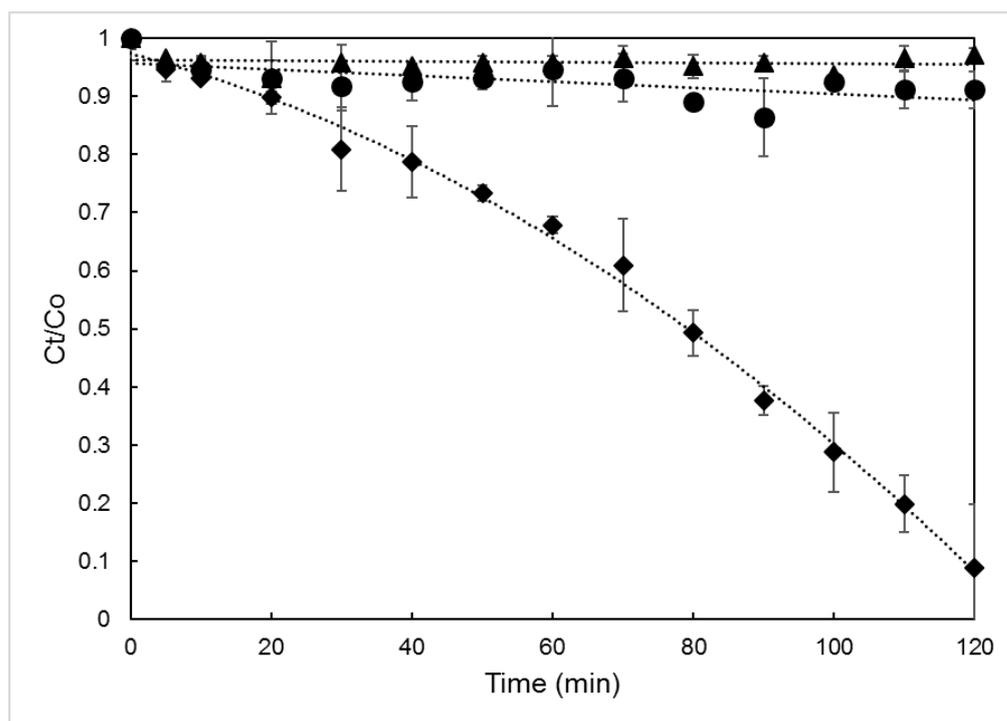
Figure 1. Ratios of BPA concentrations to BPA initial concentration vs. time for 75 ppm BPA initial concentration, pH 3, at the following conditions and at room temperature: (▲) BPA and 300 ppm H_2O_2; (●) BPA and 0.5 g PAN catalyst; and (◆) BPA, 300 ppm H_2O_2 and 0.5 g PAN catalyst.

The aforementioned methods resulted in a faster degradation rate for BPA, however they were using a much lower BPA concentration. The initial concentration of BPA has a major influence on the degradation efficiency. The investigation by both Wang [6] and Zhou [31] shows that with a lower initial concentration of BPA, a higher removal efficiency of BPA can be achieved.

Our work also shows that by raising the temperature, the degradation of BPA can be sped up, for example, the time taken for 50% degradation of BPA decreased from 50 min at 20 °C to 30 min at 40 °C. Moreover, it has to be taken into account that the potential assistance of UV radiation could improve even more the degradation of BPA.

3.2. Effect of the Temperature

The working range of temperature was between from 20 °C to 60 °C using Radleys Carousel (Radleys Discovery Technologies, Saffron Walden, Essex CBII 3AZ, UK) as the batch reactor as can be observed in Figure 2, the conversion increases as the temperature increases. At 30 min, the conversion of BPA at 20 °C is 29%, at 30 °C it is 40% and at 40 °C it is 50%. On the other hand, if the degradation is expressed by half-time, it is 50 min at 20 °C, 40 min at 30 °C, 30 min at 40 °C, 20 min at 50 °C, and 5 min at 60 °C.

From the absorbance areas in the HPLC chromatogram it was seen that, in addition to the faster degradation rate at 60 °C, the reaction is more complete as the peaks arising from the oxidation products greatly decrease. Although organic compounds were still detected in the solution, the peaks were smaller, indicating smaller amounts of compounds in the solution. However, it may also have a negative impact on the reaction, as the higher temperature could influence the activity of the catalyst or the structure of the catalyst during the oxidation process. Therefore, more experiments have to be performed to explore the thermal stability of the catalyst in order to be able to exploit the benefits of high temperature.
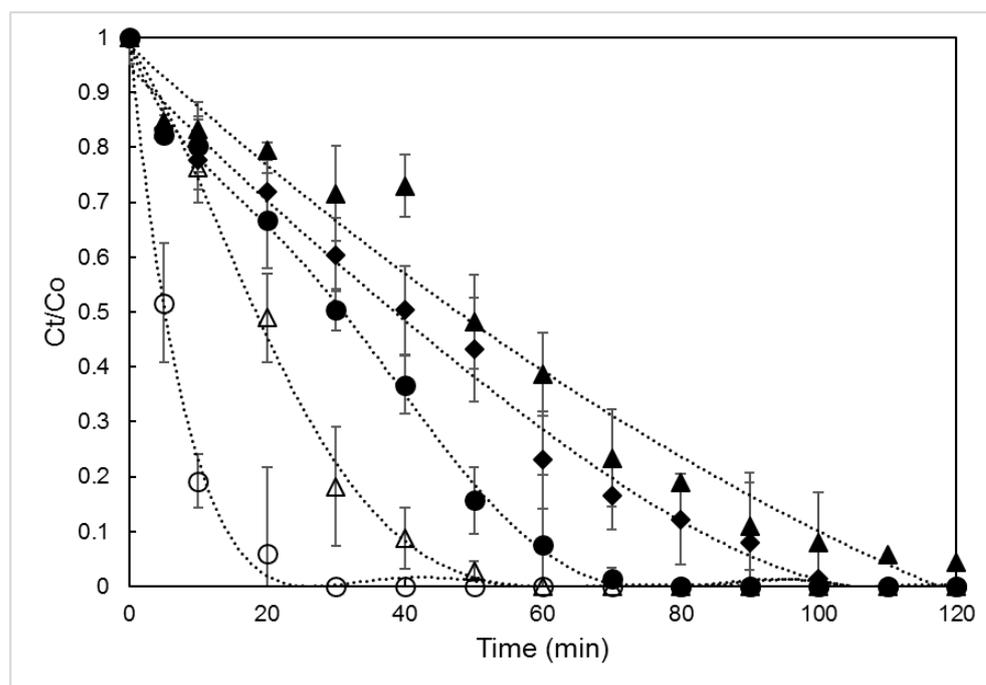
Figure 2. Ratios of BPA concentrations to BPA initial concentration vs. time for 75 ppm BPA initial concentration, 300 ppm H_2O_2, 0.5 g PAN catalyst and pH 3 at the following temperatures: (▲) 20 °C; (◆) 30 °C; (●) 40 °C; (◊) 50 °C; and (○) 60 °C.

3.3. Effect of the pH

Based on the theoretical oxidation condition for the Fenton process, the best pH range for the homogeneous Fenton process is from 2.5 to 4 [32] Wadley, whereas for the heterogenous Fenton process it could be higher at near-neutral [33,34].

In order to achieve the best working condition for BPA, different initial concentration values of pH (pH = 3 to 8) were investigated with two replicates. The initial pH of both the catalyst and the feed was adjusted by using HCl and NaOH in 1 M and 0.1 M solutions, respectively. They were left to run for a period of 2 h, and at 10 min intervals 20 μL of the sample was injected into the HPLC to determine the concentration of Bisphenol A in the solution. The batch reactor (conical flask) in these experiments was placed in a water bath at 30 °C to maintain the temperature.

As can be observed in Figure 3, Bisphenol A conversion increases as pH decreases. It seems that the heterogeneous Fenton process for the catalyst of this work is more efficient in acidic that in alkaline conditions, which is similar to the traditional homogeneous Fenton Process. Unlike the traditional Fenton Process, the novel catalyst of this work is able to operate in alkaline conditions, albeit more slowly. However, this has been shown to be due to the catalyst dropping the pH as the reaction proceeds even though the catalyst is adjusted to the desired pH at the start of the reaction. Thus, both initial and final pH have to be measured. At 70 min, the degradation of BPA at the lower pH 3 is 84%; however, at higher pH it was around 40% at pH 6 and 7, and 29% at pH 8.

3.4. Catalyst Reuse

The Figures 1–3 above have demonstrated that the PAN catalyst has a high activity in degrading BPA. This experiment is aimed at assessing the activity of the PAN catalyst when reused for the same oxidation process.

Three cycles were tested for the PAN catalyst reuses and results of residual BPA after 2 h for the different cycles are presented in Figure 4. It can be observed that, after using the same catalyst over three re-use cycles, there is not significant change in the activity of the catalyst after 2 h. However, the oxidation process seems to have a different kinetic rate. It

can be also observed that the colour of the catalyst was becoming a darker brown after each batch reuse. This could be because of the poisoning of the catalyst by the intermediates during the catalysis [35].
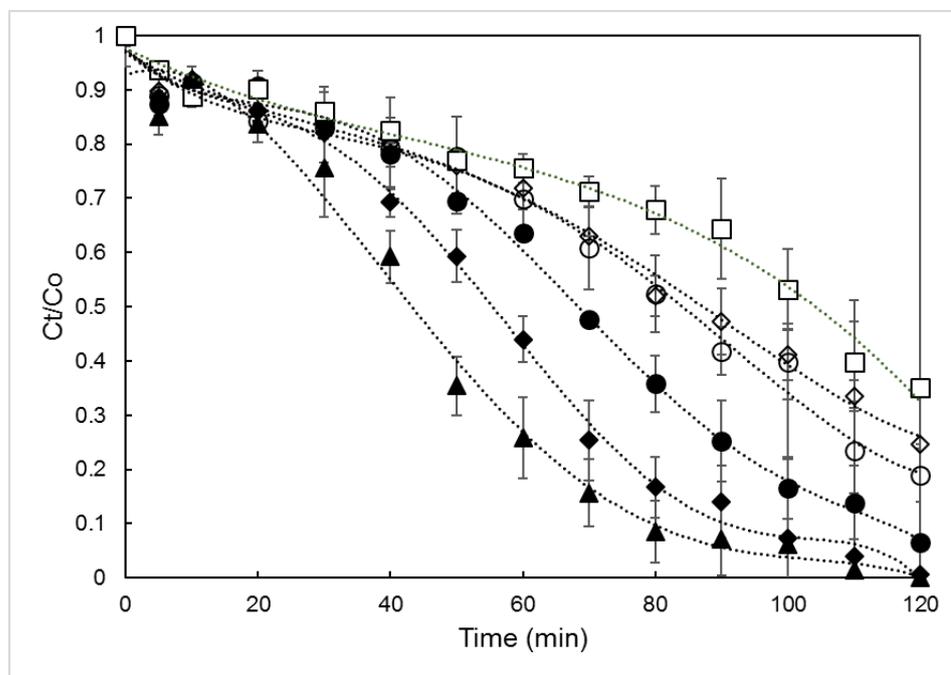

Figure 3. Ratios of BPA concentrations to BPA initial concentration vs time for 75 ppm BPA initial concentration, 300 ppm H_2O_2, 0.5 g PAN catalyst and 30 °C at the following pH: (▲) 3; (◆) 4; (●) 5; (○) 6; (◇) 7; and (□) 8.
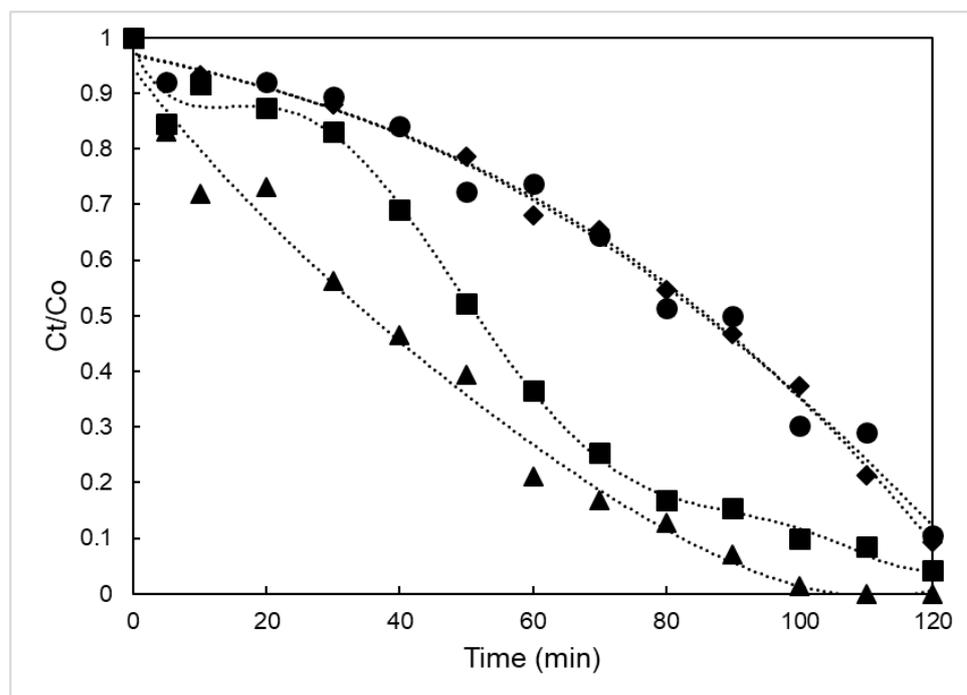

Figure 4. Ratios of BPA concentrations to BPA initial concentration vs. time for 75 ppm BPA initial concentration, 300 ppm H_2O_2, 0.5 g PAN catalyst and 30 °C at the following catalyst reuse: (▲) 1st cycle; (■) 2nd cycle; (◆) 3rd cycle; and (●) 4th cycle.

3.5. Rotating Catalytic Reactor

A series of experiments in a rotating disc catalytic reactor (RCC) have been done to study the elimination of BPA at low initial concentration, more aligned to the pollutant concentrations found in municipal wastewater. Mixing was provided by the rotation of the catalytic discs. The degradation of BPA is shown in Figures 5 and 6. In Figure 5, a very fast degradation was achieved in less than 10 min of the catalytic reaction with an initial concentration of hydrogen peroxide corresponding to the theoretical amount of oxygen needed for the complete mineralisation of the BPA organic pollutant [36].
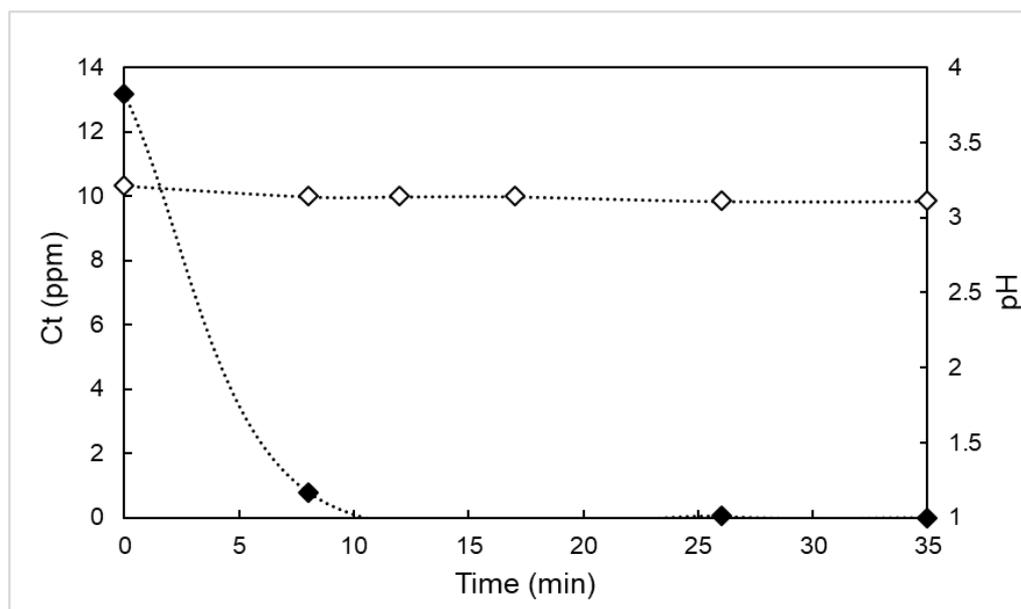

Figure 5. BPA concentrations (◆) and pH (◇) vs. time for 13 ppm BPA initial concentration, 54 ppm H_2O_2, 8.5 g PAN catalyst each disc, solution volume of 1 L and room temperature using the RCC reactor.
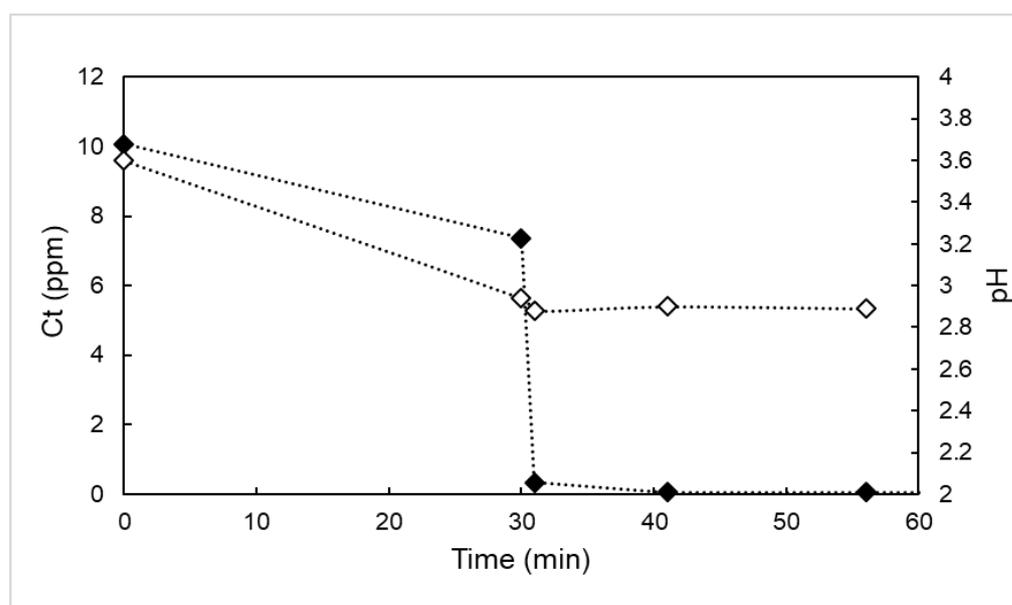

Figure 6. BPA concentrations (◆) and pH (◇) vs time for 10 ppm BPA initial concentration, 54 ppm H_2O_2, 8.5 g PAN catalyst each disc, solution volume of 1 L and room temperature in the RCC reactor.

In Figure 6 the hydrogen peroxide is added after 30 min, so the initial 27% of the concentration drop is due to adsorption of BPA on the catalyst surface. On the addition of the hydrogen peroxide, it can be seen that there is a very fast degradation of BPA. Therefore, at low initial concentration of BPA operating in a batch mode reactor with a considerably higher amount of catalyst a very quick elimination of the pollutant is achieved. There are two possible reasons for this as described below.

When comparing the absolute amounts of reactants the small batch reactor (75 ppm BPA, volume 25 mL, 0.5 g catalyst mesh, 300 ppm H_2O_2) had the following ratios 3.75 mg BPA: 1g catalyst mesh: 7.5 mg H_2O_2. In comparison, the absolute values of reactants in the rotating disc reactor (RCC) (10 ppm BPA, volume 1 L, 8.5 g catalyst mesh each disc, 54 ppm H_2O_2) had the following ratios: 1.176 mg BPA: 1 g catalyst mesh: 54 mg H_2O_2. From previous unpublished work within our wastewater research group [37], it is thought that each g of catalyst mesh will initially leach about 0.05 ppm of Fe^{3+} cations. However, as there is 130 g of catalyst in the reactor, this results in a leaching of 6.5 ppm of Fe^{3+}, which may be sufficient to enable a homogeneous Fenton reaction for such a low initial concentration of BPA. Thus, it is suggested that the very quick removal of BPA in the RCC in comparison to the small batch reactor is because of the combined effects of a higher amount of H_2O_2 and leached Fe^{3+} in the RCC relative to the amounts of BPA.

It Is also noticed that there is a pH drop from pH 3.5 to 3 on adding the catalyst to the BPA solution in the presence of H_2O_2. This could in part be due to leached Fe^{3+} cations, which are well known to hydrolyse in water and to drop the pH, and also in part to the potential production of acidic oxidation products of the Fenton reaction.

4. Conclusions and Future Perspectives

The aim of this work was to investigate the degree of degradation of BPA using a surface-functionalised PAN fiber catalyst. It was found that BPA could be effectively degraded when both hydrogen peroxide and a catalyst were used in the oxidation process. A degradation of up to 95 % of 75 ppm BPA was achieved when 0.5 g PAN catalyst in 25 mL solution volume and 300 ppm H_2O_2 were used for the oxidation, at pH 3 for 2 h at 20 °C.

The investigation of temperature influence on the oxidation process shows that a higher temperature could accelerate the rate of the oxidation process. When the reaction temperature was 60 °C, BPA was completely oxidised in the first 30 min. The effectiveness of the oxidation process decreased as the pH increased from 3 to 8. When the initial pH value of the sample was 3 to 4, more than 99% of the BPA could be eliminated in 2 h, showing an optimum working range of the oxidation process. However, when the pH value was 5, about 90% of BPA was degraded.

The sorption test shows little sorption of BPA on the catalyst, indicating that iron-functionalised PAN fibers work as a heterogeneous catalyst. It was found that after using the catalyst for three reuse cycles in the batch process, no significant deactivation of the catalyst occurred, which shows a potential long-life span for its efficient working.

Our work shows that by raising the temperature from 20 to 40 °C there is a large increase in the rate of degradation of BPA. These raised temperatures are found in many parts of the world where there is an abundance of solar irradiation. Thus, future work involves thermal stability studies of the catalyst, the evaluation of the effect of different initial concentrations of BPA, hydrogen peroxide and PAN catalyst mesh on the degradation of BPA, as well as the determination of intermediates and byproducts. Furthermore, we will explore the degradation of BPA under solar radiation which is not only beneficial in terms of raised temperature, but also by the absorption of UV-Visible radiation both by the Fe(III)-complexes on the catalyst as well as the reactants. The design of the rotating reactor allows UV lamps to be incorporated in the headspace which will promote even faster degradation of BPA as well as overcoming the poor UV penetration when the lamps are held in the bulk of the wastewater tank. The work here also forms the basis for scale-up of the catalyst to liquour ratios to industrial scale.

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