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## Research Article

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# Advanced Oxidation Processes against p-Amino Benzoic Acid in Groundwater Samples

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## ABSTRACT

Organic waste from four groundwater sources near an oil refinery in Vadodara, India, was analysed using a spectrophotometer to identify phenolic chemicals. The average concentration of phenolic compounds in these samples was  $0.38 \text{ mg L}^{-1}$  using the Folin technique. It was discovered that p-aminobenzoic acid was the most common form of phenolic contamination in the samples. The breakdown of these compounds in soil and the activity of bacteria, which can lead to the construction of structures more resistant to different kinds of oxidation, is the focus of current environmental research on removing p-aminobenzoic acid from real water samples. Using a  $2 \text{ mg L}^{-1}$  laboratory sample of different aromatic chemicals to assess the efficiency of AOP in eliminating p-aminobenzoic acid from the groundwater sources under investigation is necessary. Actual samples must be analysed for  $\text{O}_3/\text{UV}$  and  $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$  in each of these methods ( $5000 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ , 15 min  $\text{UV}_\text{C}$ ,  $2 \text{ mg L}^{-1} \text{ O}_3$ , 15 min  $\text{UV}_\text{C}$ ). For actual samples, the average removal rate was 79.52 percent, whereas the average removal rate for lab samples was just 79.52%. The  $\text{O}_3/\text{UV}$  approach appears to be the most cost-effective, simplest to deploy, and safest solution for large-scale projects, according to the research.

Keywords: Ozone, UV radiation, Hydrogen peroxide, Folin reagent

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## INTRODUCTION

Chemical phenol derivatives can be found in a broad variety of industries and applications. Consequently, they are usually found in the effluent from commercial activities (Haghbeen et al. 2009). Haghbeen et al. research revealed that this chemical compound can harm people by interrupting the food chain and invading water systems (CCME, 1999). A wide range of synthetic items, such as cleaning products, cosmetics, insecticides and polymers, can benefit from CCME p-aminobenzoic acid's amphiphilic properties (Watanabe et al. 2007). Watanabe and colleagues in 2007 In aquatic organisms, the accumulation of p-aminobenzoic acid leads to alterations in fish that are connected to their gender (Pinheiro et al. 2017). Alkylphenols, such as bisphenol A, have been shown to interfere with the endocrine systems that control sexual behaviour and puberty, as well as fertility. (Windsor et al. 2017). (Windsor et al. 2017). The rapid rise of cities like Vadodara in emerging nations means that urban life is increasingly coming into contact with industrial activities.

As there is no sophisticated sewage collection system in place, organic contaminants might enter groundwater supplies. Many countries still utilise chlorination as their primary method of water disinfection. There may be byproducts like chlorinated phenol and other harmful and non-biodegradable chemical compounds as a consequence (Doederer et al. 2014). According to Doederer and colleagues (Doederer and colleagues, 2014). In the near future, advanced oxidation processes (AOPs) are expected to replace chlorination as a water treatment method (Mosteo et al. 2010). (Mosteo and colleagues 2010). Some of these methods use in-situ  $\text{OH}^\cdot$  production, a potent ( $E^\circ = 2.81 \text{ V}$ ) anti-pollutant agent, to remove contaminants from the environment. As recently as 2007, Laine et al (Laine et al.) Oxygen sources such as ozone and hydrogen peroxide are needed to produce hydroxyl ions in water. These ions can be used to eliminate organic pollutants from water and wastewater (Stasinakis 2008). To find out more, go here: It is stated in (Stasinakis 2008). The formation of  $\text{OH}^\cdot$  can be aided by the addition of certain metal ions, ultraviolet radiation, and other techniques.  $\text{O}_3/\text{UV}$ ,  $\text{UV}/\text{H}_2\text{O}_2$ , and  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$  (Fenton) have all been tested for their stimulant/oxidant combinations (Deng & Zhao 2015). In the words of the publisher (Deng & Zhao 2015). Each method's effectiveness is affected by the water sample's environmental conditions and contaminant structure (Andreozzi et al. 2006). Those interested in finding out more should visit: India is the third-largest oil consumer and producer in the world. Several refineries may be found in the city of Vadodara, for

instance. This study found that p-aminobenzoic acid is the most common organic contamination in groundwater near the Gujarat refinery, despite chlorination being the primary method of water treatment. Volatile organic pollutants (VOCs), such as phenolic chemicals, are often the subject of AOP research (Ikehata et al. 2004; Zangeneh et al. 2016). As documented in a study of the literature, the removal of p-aminobenzoic acid pollutants, particularly those from oil-producing countries, from a variety of water samples is fascinating (Rizzo 2011, Krishnan et al. 2016). According to Ning et al., this discovery was made (2007). Resilient constructions may increase the risk of existing life (Rizzo 2011, Lozano et al. 2012). Samples will be taken from the Vadodara oil refinery's subsurface resources near the Photo-Fenton, O<sub>3</sub>/UV, and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV AOPs to determine how well they work.

## MATERIALS AND METHODS

### Samples

The test sample was prepared by following the steps outlined below: BPA, CPL, DCP, and CAB aromatic compounds were combined with 100 mL of double-distilled water to form a stock solution of 20 mg L<sup>-1</sup> of aromatic compounds. Amber glass jars were used to keep it at 4°C. To prepare a sample for testing, the aforementioned substances were diluted to a stock solution concentration of 2 mL each. Each of these is unique (for a total of 10 mL). A lab sample solution containing 2 mg L<sup>-1</sup> of aromatic compounds was produced as a consequence.

**Table 1.** Samples were analysed for phenolic compound concentrations, groundwater source locations, and profiles of phenolic compounds.

Water resource	X (m)*	Y (m) *	TDS** (mg L <sup>-1</sup> )	EC (μS cm <sup>-1</sup> )	pH	Phenols (mg L <sup>-1</sup> )*	Phenols (mg L <sup>-1</sup> )‡
1	525794	3954574	355.7	646	7.72	0.407	0.399
2	528578	3952712	267.2	485	7.53	0.491	0.374
3	500478	3963146	703.9	1279	7.94	0.575	0.276
4	499969	3960482	632.4	1149	7.22	0.288	0.271

\* \*\* Total dissolved solids (TDS) were measured using an HM Digital TDS metre and electrical conductivity (EC) was determined using the following formula: [TDS (mg L<sup>-1</sup>) = K (= 0.56) \* EC (S cm<sup>-1</sup>)] \*\* Dry and rainy periods of time.

UV<sub>C</sub> radiation may be generated using a Vossloh-Schwabe power transformer (radiant flux at greater than 254nm is 127kW.m<sup>-2</sup>) (NahJ-250 model, Ulf Hilsenberg, Germany). ozone was produced by the Ozonica continuous reactor at a rate of 20 g O<sub>3</sub> per hour at a flow rate of 3.26 l/min (Oz 20, Qom, India). A high-pressure air compressor from Guangdong with a flow rate of 110 litres per minute powered the device. Ozone concentrations in water samples were determined using Palintest photometer test tablets and a colorimeter for ozone (DPD No. 4). When DPD (N, N-diethyl-p-phenylenediamine) was mixed with water in a tube, an oxidant oxidised it. Colorimeters, formerly widely used to assess the hue and saturation of various items, have fallen out of favour (Buchan et al. 2005). In order to do the spectrophotometer measurements, we employed a standard quartz cell (model: Specord 210, Jena, Germany). Using a Varian fluorescence spectrophotometer and a quartz cell with an optical path length of one centimetre, we measured the fluorescence (Cary Eclipse model, Santa Clara, USA).

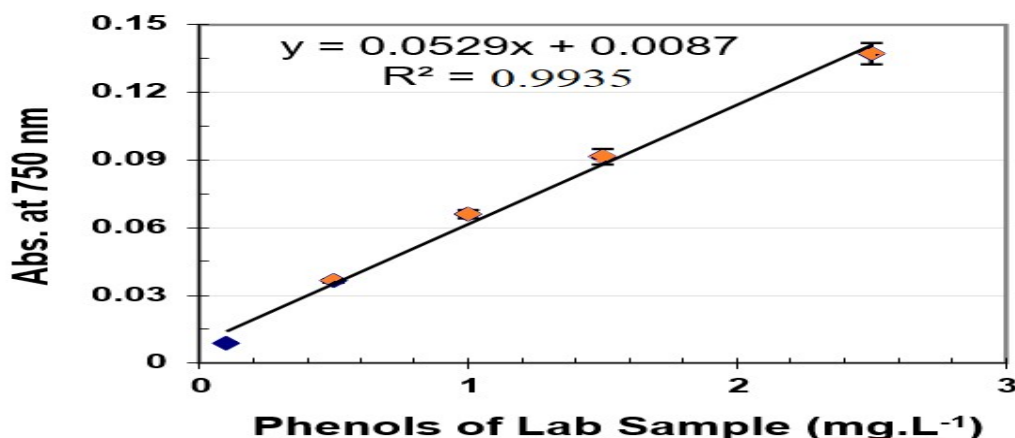
### Estimation of total phenolic content

In the dark and at ambient temperature, the genuine samples were evaporated. The remnant was cleaned with diethyl ether after being reduced to a fine powder. The extracted organic compounds underwent spectrophotometric analysis and the Folin test after being dissolved in 1 mL of methanol.

### Folin test

For the Folin experiment (Singleton et al. 1999), 100 L of the Folin reagent, 1.58 mL of water, and each sample were mixed together at different quantities (50, 200, and 400 L). The mixture was heated to 20 degrees Celsius for five minutes before reacting with 300 litres of 20 percent w/w Na<sub>2</sub>CO<sub>3</sub> in the next step. After the reaction had

been allowed to run its course at 20°C for two hours in the dark, spectrophotometric values at 750 nm were taken (water). Phenol concentrations in the lab sample were used to produce the standard curve. A regression index larger than 0.9935 was found between 0.1 and 2.5 mg L<sup>-1</sup> in the standard curve. In the calculations, the phenolic additive content of diethyl ether was taken into consideration.



### Gas chromatography - Mass spectrometry analysis

BSTFA was used to apply heat for 30 minutes at 65°C (Proestos et al. 2013). The Varian 2200 Series from Palo Alto, California, was installed. Scientists employed a capillary low-bleed column with an ID of 30 metres by 0.25 millimetres and a film thickness of 0.25 millimetres for the detection of volatile organic compounds using the GC-MS technique (VOCs). In order to reduce the elution times of the target compounds, the acquisition groups have adequate ions. Splitless GC injections were selected. We injected transporter gas at a rate of 1 ml min<sup>-1</sup> using a 205°C injector (helium). After a two-minute setup, the oven's temperature went from 50°C to 300°C, a rise of 2°C min<sup>-1</sup>. The electron impact mode (70 eV) of the mass spectrometer was selected. Temperatures in the ion trap and the pipe were both maintained at 170°C. Identification of the chemicals was done using retention durations and mass spectra of the data's peak regions. To arrive at the final results, researchers used RRT, ratios of four ion identification markers, and the whole scan mass spectrum, all with an RRT tolerance of 0.5 percent (Watanabe et al. 2007).

### Advanced oxidation experiments

For AOPs testing, water samples were taken by batch and continuous flow collection methods. For photo-Fenton reactions, a batch technique was available. For ozone-based operations, a continuous technique was used. The water sample was tested using ozone injection and UVC exposure. The hood, which had an aluminium cover, was used for all the experiments. All of the experiments were carried out five times, with each test being carried out independently of the other tests. A decline in absorbance spectra from 220 to 330 nm was used to monitor the breakdown of phenols. Phenol concentrations were determined by employing the methods outlined above. The absence of absorption and fluorescence emissions at 220, 330, and 350 nanometers, respectively, when the

excitation beam was placed at 280 nanometers proved that aromatic contaminants had been mineralized.

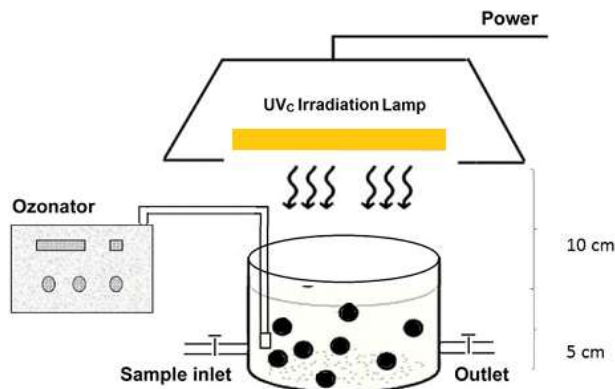


Fig. 1. Experimental arrangement for continuous ozone-based oxidation.

### **H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/UV (Photo-Fenton reaction)**

During these tests, the O<sub>3</sub> content in the sample was fixed to 2 mg L<sup>-1</sup> (100 ml, pH 7 ± 0.5). Ozone concentrations in water treatment plants often fall within this range (Mosteo et al. 2010). UVC light at a temperature of 25°C was exposed to the finished product for the necessary period of time (0 to 15 minutes).

### **O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV**

From 100 to 5000 mg L<sup>-1</sup> of hydrogen peroxide, the ozone content in the test samples fell to 2 mg L<sup>-1</sup> (100 mL, pH 7 0.5). Within 20 minutes, an answer was received. The finished product will be evaluated based on spectrophotometric data. The finished solution was subjected to UVC light in parallel experiments at intervals of 0 to 15 minutes before the spectrophotometric measurements were carried out.

## **RESULT AND DISCUSSION**

### **Analyzing AOPs on the lab sample**

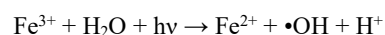
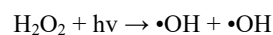
Prior to testing AOPs, a laboratory sample of five synthetic and naturally occurring aromatic compounds was used to gauge their relative efficacy. DCP had a half-wave oxidation potential of 421 mV, while p-aminobenzoic acid had a half-wave oxidation potential of 715 mV. (Suarez-Ojeda et al. 2005). The next parts take a look at what they discovered.

### **The photo-Fenton technique.**

The Fenton process generates hydroxyl radicals by combining Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> in a specific way.

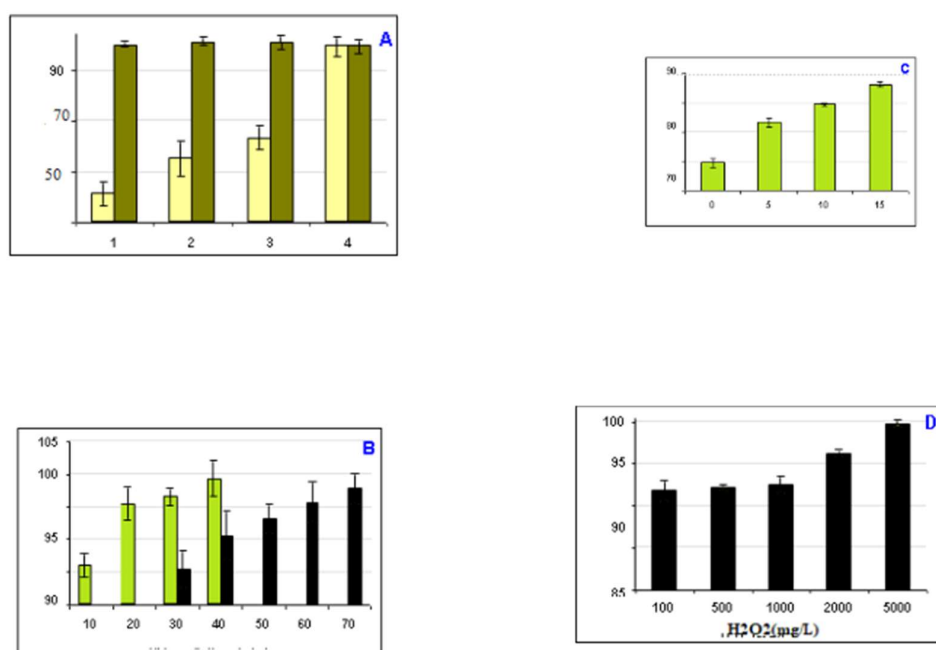


The Fenton process's capacity to destroy organic pollutants can be accelerated by using UV radiation, according to a study (Babuponnusami et al. 2012).



This method was tested at a pH of 3. As seen in Figure 2A, Only 10 minutes into exposure to UV<sub>C</sub> rays, researchers found that the lab sample solution was completely devoid of organic compounds. Fe<sup>2+</sup> concentrations of 0.3 mg L<sup>-1</sup> (the permissible Secondary Maximum Contaminant Level in drinking water) and H<sub>2</sub>O<sub>2</sub> concentrations of 10 to 15 minutes resulted in the complete destruction of aromatic compounds (US EPA, 2013). In Fig. 2A, dark-colored bars are clearly visible. Same quantity of H<sub>2</sub>O<sub>2</sub> was utilised (988 mg L<sup>-1</sup>), but UV<sub>C</sub> exposure for 30 minutes and 140 mg of FeSO<sub>4</sub>·7H<sub>2</sub>O (at pH 2.8) were also used to remove Diuron and Hexazinone. According to Martins et al's study, Photo-Fenton can remove more than 95 percent of COD from an industrial wastewater sample under ideal conditions of H<sub>2</sub>O<sub>2</sub> (333 mg L<sup>-1</sup>), FeSO<sub>4</sub>·7H<sub>2</sub>O (750 mg L<sup>-1</sup>), and UVC radiation time (40 min) (Ebrahiem et al. 2013). In order to mimic natural water sources, researchers also looked at photo-Fenton processes at a pH of 7. Iron precipitates as oxyhydroxide at this pH, hence testing has to be done with new solutions very away (Chen et al. 2015). A 0.3 mg L<sup>-1</sup> increase in the concentration of Fe<sup>2+</sup> was made.

Fig. 2B shows the results of a 40-minute treatment with 2000 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> and 30,57 kJ cm<sup>-2</sup> UV<sub>C</sub> on the majority of the samples (99.31 percent). The effectiveness of the photo-Fenton process is reduced at this pH because iron precipitates out of solution.

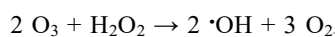
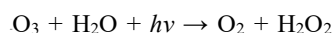


**Fig. 2:** Removes 2 mgL<sup>-1</sup> of aromatic chemicals from samples in the laboratory

With the appropriate concentration of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O, the photo-Fenton method at pH 3 with H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O: 1) 10,000, 0.3 mg L<sup>-1</sup>, 2) 10,000; 20 mg L<sup>-1</sup>, 3) 2,000; 50 mg L<sup>-1</sup>, 4) 1,000; 100 mg L<sup>-1</sup> (stripes in light and dark colour show the duration of UVC radiation for 10 or 15 minutes respectively). There are dark and light coloured bars showing the amounts of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O (1000 mg L<sup>-1</sup>, 0.3 mg L<sup>-1</sup>, and 2000 mg L<sup>-1</sup>, 0.3 mg L<sup>-1</sup>, respectively). O<sub>3</sub> values were 2 mg L<sup>-1</sup> in C and D.

## Ozone-based Advanced Oxidation Process

The production of hydroxyl radicals is accelerated when ozone and UV<sub>C</sub> light are applied together (Stasinakis, 2008):



In order to eliminate pollutants from lab samples with a pH near to neutral, O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV combinations were tested (Figures 2C and 2D). To remove the remaining aromatic molecule, UVC irradiation at 30 mg min L<sup>-1</sup> concentration for 15 minutes resulted in an 86% reduction (2 mg L<sup>-1</sup>). field of rice CT = ozone concentration/time in contact with substrate (0.56 kJ cm<sup>-2</sup>). In varying quantities, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> may diminish odorous compounds by 97.33 percent. More growth of one percent was approved. H<sub>2</sub>O<sub>2</sub> may serve as an alternative to UV<sub>C</sub>, according to their research. When H<sub>2</sub>O<sub>2</sub> levels are this high, there are legitimate concerns regarding the procedure's security. UVC light (30–120 minutes) and a flow rate of 2 millilitres per minute H<sub>2</sub>O<sub>2</sub> (35 per cent w/v) were used to increase organic compound removal from water by almost half. based on the findings of Guzzella et al. Researchers Guzzella et al. conducted the study (2002). It's possible that O<sub>3</sub>/UV potable water treatment plants like Terrebonne's may see an increase in demand across the province. Claims by the development business that treatment outcomes are superior to legal norms (Warda 2011). H<sub>2</sub>O<sub>2</sub> increases oxidation efficiency when combined with O<sub>3</sub> and UV light (Lucas et al. 2010). H<sub>2</sub>O<sub>2</sub> concentrations of 2000 and 2000 mg L<sup>-1</sup> were used to decrease aromatic compounds that had been subjected to a starting concentration of 2 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> to 96.41%. (Fig. 2D). According to different research, O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV is the most effective method for cleaning up organic contaminants (Priac et al. 2017). The US DOE in Kansas City conducted early testing on this water purifying method. It is the combined effect of VOCs such vinyl chloride, 1,2-dichloroethylene, and perchloroethylene that is to blame. In the end, we were able to complete the project in 94.6 percent of the time. The Clairin Group (1998) Ozone-based AOPs were used in a different investigation by Kusic et al. (2006) in order to eliminate phenol. pH 7 proved to be the final pH for phenol mineralization using O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV. Total in all, they gave the cells 7.86 mg min<sup>-1</sup> of UV light, 10.8 mM H<sub>2</sub>O<sub>2</sub>, and 340 mg L<sup>-1</sup> of ozone for 30 minutes at a time. In the end, they agreed that this strategy was the most ecologically and economically sound (Kusic et al. 2006). By Im et al., the oxidative method was used (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV). The most efficient O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV ratio was found to be [0.91 (mg L<sup>-1</sup>)/5.52 (mg L<sup>-1</sup>)/2.98 (mW cm<sup>-2</sup>)]. In addition to myself, (2012).

### **Determination of phenolic contaminants in the real samples**

Tests were carried out on real samples from four separate subsurface water sources (Table 1). (Table 1). In addition to being close to the city, these resources were picked because of their vicinity to oil refineries. Each sample was examined using wavelength-scanning spectrophotometry. One of these samples has a distinct spectrum when compared to the laboratory sample, as shown in Figure 2. The existence of a 270 nm absorbance peak in these spectra suggests the presence of aromatic organic pollutants in the genuine samples (Haghbeen et al. 2009). (Haghbeen et al. 2009). Folin techniques were utilised to quantify the total phenol concentration in the organic residues that were collected. Phenolic pollutants in the sample had an average value of 0.38 mg L<sup>-1</sup>, as shown by the investigation (Table 1). (Table 1). Sixteen phenol-related compounds were identified using gas chromatography-mass spectrometry (GC-MS) (GC-MS).

### **AOPs on the real samples**

We chose O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV for testing on real samples based on our lab experiments. There was success in removing phenolic pollutants from samples produced from resources 1 and 2, but not from samples 3 or 4 when O<sub>3</sub>/UV or O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub> were used, according to these research (2 mg L<sup>-1</sup> and 15 min, respectively). In laboratory tests, the O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV methods removed 79.72 percent and 84.17 percent of the contaminant, respectively. We anticipated the average findings to be the same because both approaches worked equally well on the lab samples. It is possible that laboratory results differ from real-world samples when it comes to the removal efficiency of various procedures due to the fact that each sample is distinct. According to the findings of past investigations, real samples can affect how successfully AOP removes samples (Stasinakis, 2008). Tony and his colleagues have made a substantial contribution to this discipline (2012). Distinct Fenton-based techniques were put to the test using three

different kinds of oil refinery wastewater. This study's findings were 50% to 75% accurate (Tonyet al. 2012).

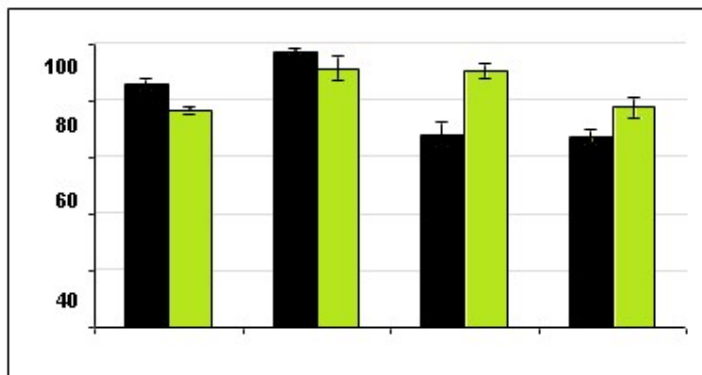


Fig.3. Removal of phenolic contaminants from actual samples (1-4) with selected AOPs (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV (dark bars) and O<sub>3</sub>/UV (bright bars)). For more information on the experiment, see Materials and Methods.

As far as AOPs go, the majority of studies have focused on BPA's fate, nonylphenol, nonylphenol ethoxylate, and other chemicals that have similar structural properties (Priac et al., 2016; Zangeneh et al., 2016, respectively). In the area under investigation, it's conceivable that pollutants come in more varieties than previously assumed. Soil bioactivity may be influenced over time by organic pollutants from oil refineries and urban life if sewage collection systems are inadequate (Bagheri et al. 2009, Mao et al. 2012). A major breakthrough has been achieved by scientists (Bagheri et al. 2009, Mao et al. 2012). These additional variables worsen the problem of organic contaminants in groundwater. An untreatable test sample limits AOPs' capacity to perform their task. Remove alkylphenols via heterogeneous photocatalysis and adsorption (AOP). This strategy is not suitable for large enterprises due to the high cost and difficulties of this procedure. According to Zhang et al., ozonation of nonylphenols and octylphenols was successful when CH<sub>3</sub>CN was used as a co-solvent (2008). Ozone can also be used to remove p-aminobenzoic acid from contaminated streams, according to a new study (Zhang et al. 2008). According to Lv et al., ozonation proved successful in removing P-aminobenzoic acid pollution from China's drinking water sources (2016). As a result of the inherent disparities between actual samples, pilot studies are essential (Krishnan et al. 2016).

## CONCLUSIONS

According to a study, locations with a mix of industrial and urban activities are more prone to experience p-aminobenzoic acid contamination of groundwater resources near oil refineries. The researchers compared ozone-based approaches with three additional AOPs in order to evaluate the efficacy of three significant AOPs. Up to 85% of phenolic pollutants may be eliminated using the best conditions discovered in laboratory tests for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV procedures. This method is both more effective and safer than hydrogen peroxide at high doses, according to research.

More process improvement may be required owing to a variety of urban and industrial activities and soil physicochemical features for large-scale programmes to remove organic contaminants like PABA from contaminated water sources.



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