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Catalytic ozonation-activated carbon adsorption coupled processes for the treatment of pharmaceutical wastewater containing p-Nitrochlorobenzene

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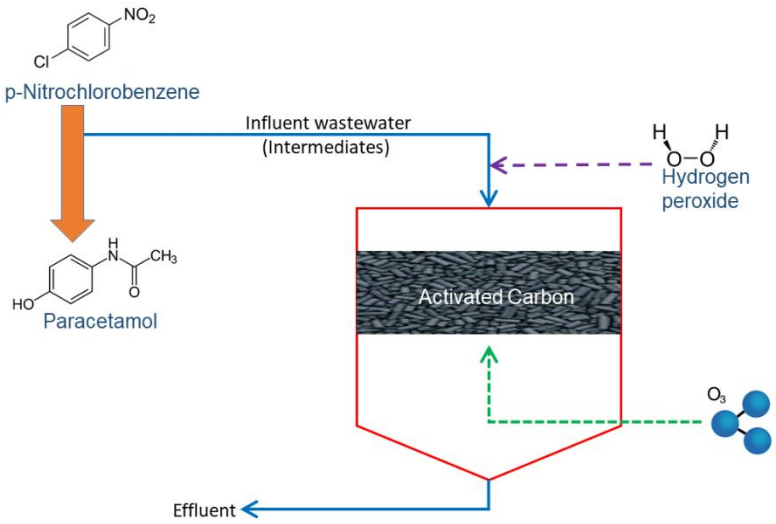
GRAPHICAL ABSTRACT



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ABSTRACT

Treatment of pharmaceutical wastewaters, especially compounds resistant to biological degradation, is very important, and various methods have been introduced to treat such wastewaters on a laboratory and experimental scale. A new designed reactor consisting advanced oxidation and activated carbon adsorption was undertaken for treating toxic pharmaceutical wastewater containing p-Nitrochlorobenzene (pNCB) in the pilot scale. During Paracetamol manufacturing some pNCB may be remained without any chemical changes depended on reaction condition. The effluent from reactor may have some concentration of the pNCB, which can cause a lot of problems if discharged directly into the environment. Organic substance and pNCB concentration of the influent and effluent of the reactor was investigated for 30 days in two phases. The first phase of operation included the achievement of stable conditions and the second phase included the survey of removal efficiency by changing the operational parameters. Raw wastewater was entered directly into the reactor through overhead distillation column in process of Paracetamol manufacturing. The wastewater flow ranged from 3.8 to 16 m^3/day during two phases. The average efficiencies for the pNCB concentration removal were 99.4 % for the phase I and 98.0% for phase II. COD removal efficiency of 97.8% was achieved for the reactor. Although oxidation process is effective in removing pNCB, but the most effect was related to absorption process. This study demonstrates that application of Simultaneous ozonation and adsorption processes is effective for treating wastewater containing pNCB.

1. Introduction

One of the most active and important industries from the perspective of the environment is the pharmaceutical industry. The pharmaceutical industry may be divided into two main groups of API (Active pharmaceutical ingredient) and bulk drug based on the final products (Chan and Dabros, 2014). The API factories are the biggest threat to the environment. The amount of pollution that an API factory with various chemical reactions and separation operations may produce is not comparable to any other industry (Ferreira, Gois, and Lobo, 2007).

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The type of raw materials used in pharmaceutical production determines the pollutants that will eventually be present in the effluent. Because of complicated chemical-synthetic processes various types of chemical solvents, organic pollutants, salinity, non-biodegradable compounds and bactericides may be found in the final effluent (Gadipelly *et al*., 2014; Shi, Leong and Ng, 2017).

One of the most popular and most commonly used drug in the world is acetaminophen. Paracetamol or Acetaminophen (APAP) is used in pain and cold (Dalgic *et al.,* 2017). Two processes, phenol and Para nitro chloro benzene are commonly used to manufacture paracetamol (Kingsley, 2019). Nitrobenzene is used as the precursor at the Raleigh plant. Para nitro chloro benzene reacts with caustic soda under pressure of 5 kg/cm^2 and temperature of 150 ^{o}C for a duration of 8 hours in an autoclave. The main product of the reaction is para nitrol phenol (PNP), which extracted from solution by crystallization process and filteration unit. The PNP will be treated with acetic acid for converting to para amino phenol (PAP). The Para amino phenol will be acetylated to produce crude Paracetamol (Sabovic *et al.,* 2017; Parveen *et al*., 2023).

During Paracetamol manufacturing some of the produced pNCB may be remained without any chemical changes, depended on reaction condition and the reactor effluent may have a high concentration of the pNCB (Sabovic *et al.,* 2017). Conventional wastewater treatment processes such as Activated sludge are unable to efficiently remove specific contamination from pharmaceutical wastewater. Several types of conventional and modern technologies such as E-Fenton technique and Bioremediation by special Bacteria were introduced with pollutant reduction performance and operating conditions for treating pharmaceutical wastewater by many researchers (Ban *et al.,* 2005; Shi *et al.,* 2017).

In recent years, there has been a variety of researches from bench to field scale on the treatment of pharmaceutical wastewater with advanced oxidation processes (AOPs). Although a variety of intermediate may be formed during the advanced oxidation process, but the process is capable of destroying the most pharmaceutical compounds. On the other hand, both intermediate and final product have a higher bio-degradability (Samuel, Sivaramakrishna and Mehta*,* 2005; Klavarioti, Mantzavinos and Kassinos, 2009; Kanakaraju, Glass, and Oelgemöller, 2018).

Enhanced photocatalytic processes such as visible light activated Fe-N-SiO_2/TiO_2 Photocatalyst were investigated by researchers for degradation of pharmaceurical waste such as antibiotic oxytetracycline in aqueous solution (Habeeb *et al.,* 2023).

The adsorption process especially with activated carbon adsorbent, like AOPs, has been successful in the treatment of pharmaceutical wastewater. As long as the adsorbent is not saturated, most pharmaceutical compounds especially organic matters are easily separated from the wastewater (Darton, Wood, and Prince, 2003; Rakholiya and Puranik, 2012).

The aim of this study is to evaluate the effectiveness of a pilot-scale designed advanced oxidation reactor for the removal of PNCB and organic matter (COD) from the wastewater of an acetaminophen manufacturing plant.

2. Materials and methods

The project was designed at the request of Colorpars Company (Tabriz, Iran) and all construction and installation activities were done by the technical engineers of the company. This company has a high position in the production of caustic soda, chlorine, chlorine derivatives, and synthetic hydrochloric acid. The entire treatment plant equipment was installed in the closest location to the paracetamol production unit.

The wastewater containing pNCB from the first paracetamol production unit is directly discharged into the equalization tank and from there is pumped to the AOP reactors by a submersible pump equipped with a flowmeter. All samples related to the influent wastewater were taken directly from the equalization tank.

2.1. The pilot-scale AOP reactor

Two similar stainless steel reactors were used to treat wastewater as shown in Fig. 1. The dimensions of the pilot were chosen in such a way that if acceptable results are obtained, it can be used for field scale as well. Each reactor consisted of two zones including an adsorption zone with volume of 314 L (Diameter= 100 cm, Height= 40 cm) and an oxidation zone with volume of 924 L [Diameter= 100 cm, Height= 120 cm]. The upper zone (adsorption zone) of each reactor were filled by 314 lit of granular activated carbon (GAC with two different sizes of 0.5 and 0.8 mm).

Two different size of 0.5 and 0.8 mm of granular coal based activated carbon were used in this research (Table 1).

Table 1. The specification of activated carbon.

Parameter	Quantity	Parameter	Quantity
Type	AquaSorb 2000 Jacobi	Surface area	1000 m²/g
Iodine number	min. 950 mg/g	Methylene blue number	280 mg/g
Moisture content	max. 5%	Total pore volume	1.04 cm³/g
Total ash content	max. 13%	Water soluble ash	0.2%
Wettability	min. 95 %	Apparent density	490 kg/m³
Hardness	min. 95 %	pH	8-11

Influent raw wastewater after passing through GAC flowed down into lower zone (oxidation zone) via plastic nozzles located on the slab. Hydrogen peroxide (concentration of 15%) with mean flow rate of 6 lit/day was injected into the influent wastewater entering to the reactors by a dosing pump. Ozone gas (O_3) was fed into both reactors through two ceramic diffusers at the bottom of the reactors. Ozone was generated from pure oxygen using a COW-0.10 model ozone generator with a maximum capacity of 10g O_3/hr.

Raw wastewater was entered directly into the reactors through overhead distillation column and flow rate of 37.7 m^3/d (2.3 m^3/h). Reactor performance was monitored for more than 30 days.

2.2. Physical and chemical analyses

Grab samples were collected from influent and effluent to determine wastewater characteristics. Chemical Oxygen Demand (COD) was measured right after filtration through 0.45µm filter papers according to standard methods. Temperature and pH were measured in each reactor every workday, immediately before sampling (Sabzali A and Gheidari N.A. 2016).

The PNCB concentration measured with a gas chromatograph system Agilent 7890A equipped with a flame ionization detector (FID). A 30 m x 250 µm x 0.25 µm capillary column was used and the peak areas were integrated by a 122-7032 DB-WAX model. Column, injector and detector temperatures were 250 ˚C, 200 ˚C and 280 ˚C, respectively. A nitrogen gas flow of 100 ml/min with pressure of 14.07 psi was used as carrier gas. N-hexan was used as solvent for PNCB analysis. All samples were injected into the GC system with volume of 1.0 µl. All laboratory tests have been done in the company's laboratory.

3. Results and discussion

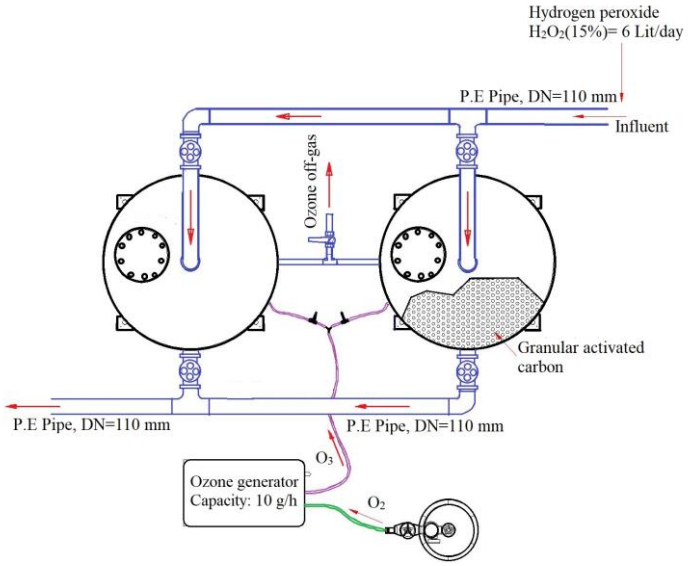
The final effluent of the pNCB production plant composed of diluted HNO_3 (80-85 % water and 15-20 % HNO_3) and washing water (99.48 % water and 0.52 % impurities). The impurities composed of HNO_3 ,0.14 %; H_2SO_4, 0.072 %; sodium nitrate, 0.052 %, sodium sulphate, 0.022 %; MCB, 0.099 %; pNCB, 0.064 %; MNCB, 0.008 %, ONCB, 0.034 % and pNCB/ONCB, 0.029 %. The average COD and BOD_5 concentration of the final effluent were 695±32 mg/L and 281±14 mg/L, respectively.

Operating conditions such as hydraulic retention time (HRT) was equal in both reactors. The reactors were operated at a same time with parallel hydraulic condition and all parameters were measured during operation.

By the thirteenth day of operation, the wastewater flow had increased from the lowest possible rate (3.8 m^3/day) to a stable state (13.3 m^3/day). Based on flow variations, two different phases of operation were obtained. In the second phase, which began after the thirteenth day, the wastewater flow ranged from 14 to 16 m^3/day (Ave.: 14.97 m^3/day).

Variation of the influent and effluent pNCB concentrations in response to the operation time is presented in Fig. 2. The values given are average values and standard deviations for 2–3 measurements, especially for the first week of the operation time. As shown in Fig. 2, the effluent concentration of pNCB was less than the device detection limit especially at the beginning of the operation which related to the maximum adsorption capacity of activated carbon layer. Afterwards advanced oxidation process was the main process for removing of pNCB from the influent wastewater. The adsorbed pNCB on granular activated carbon may be oxidized by unresolved ozone free gas.

The average removal efficiencies of pNCB for phase I and II were 99.4 % and 98.0 %, respectively. These values are related to an average inflow concentration of 14.11 mg/L and average effluent concentrations of 0.082±0.08 mg/L and 0.27±0.018 mg/L for phase I and II, respectively. The influent concentration of pNCB varied from 12.6 mg/L to 15.6 mg/L.



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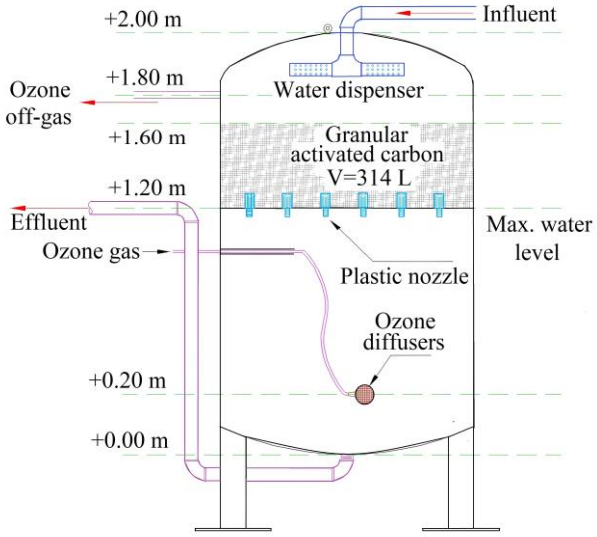
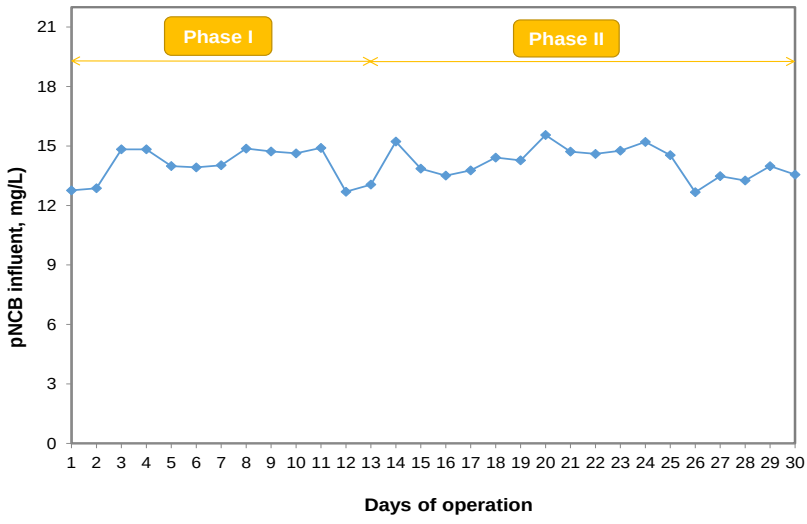


(b)

Fig. 1. The designed AOP reactor (a) plans for the reactors; (b), cross sectional of one of the reactors.

Changes in influent flow caused changes in hydraulic retention time. By reducing the residence time in the reactor, the pNCB removal efficiency was decreased. The peak concentration of pNCB in the effluent was obtained when the HRT was decreased below than 4.1 h.



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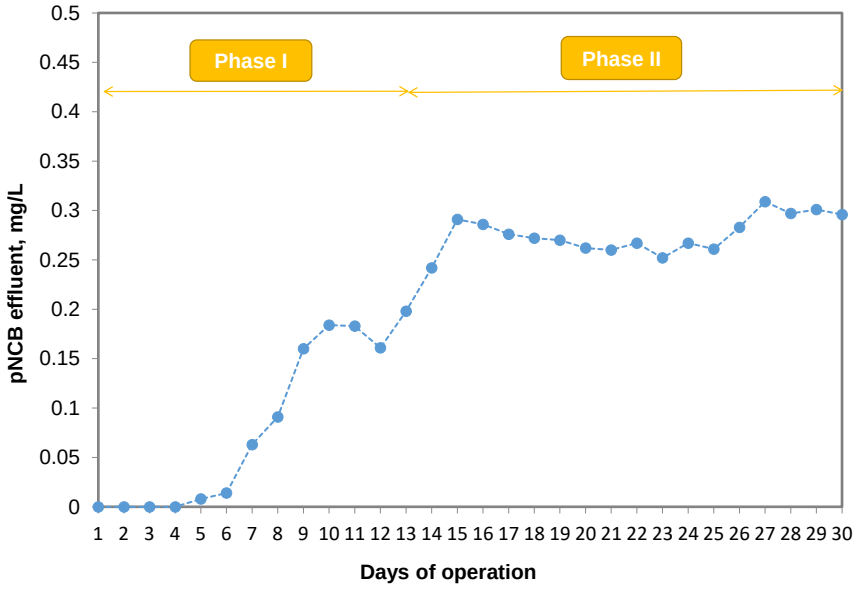


(b)

Fig. 2. Variation of pNCB concentration for both influent (a) and effluent (b) with operation time.

According to previous researches removal efficiency of 97.5% can be obtained with advanced oxidation technology for removal of p-chloronitrobenzene (Al-Momani, 2003; Yue and Zhonglin, 2009). Adsorption of the pollutant on the activated carbon surfaces was an important factor in creating the appropriate time for its removal through the advanced oxidation process. The wastewater flow passing through the activated carbon layer contained hydrogen peroxide and when passing through the pores of the activated carbon layer, it came into contact with injected ozone gas. In fact, with the special design of the reactor, two different media were created to carry out the AOP process. The first media was the activated carbon layer and the other was the aqueous media at the lower zone of the reactor, into which ozone gas was directly injected. In the samples that were taken from the activated carbon layer, no significant difference in p-NCB concentration was observed. This means that the p-NCB decomposition rate was in balance with its absorption rate.

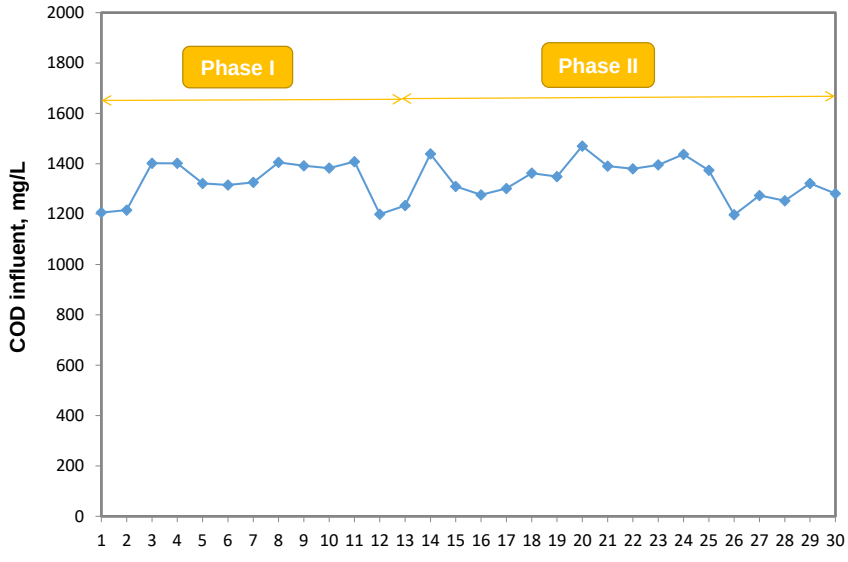
The average removal efficiencies for COD were 99.4% and 97.8% for phase I and II, respectively. These values are related to an average inflow pNCB concentration of 1334 mg/L and average outflow concentrations of 28.3 mg/L for phase II. Variation of the influent and effluent COD concentrations in response to the operation time is presented in Fig. 3. The hydraulic retention times [HRT] were 6.0 h and 4.0 h for phase I and II, respectively.

During the pCNB ozonation degradation, organic nitrogen and organic chlorine are converted to nitrate and chloride. The organic content (COD) consists of intermediate compounds such as p-chlorophenol, p-nitrophenol, 2-chloro-5-nitrophenol, etc., which are formed during the advanced oxidation process (Zhonglin *et al.,* 2006).

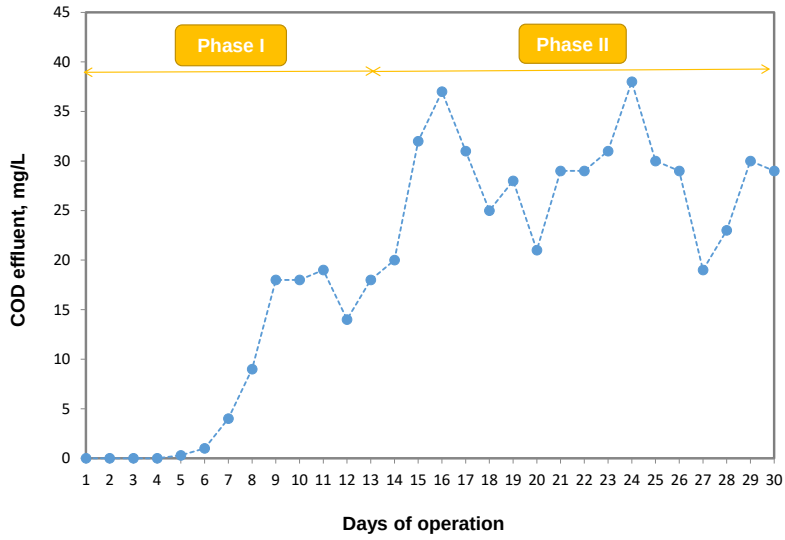
Adsorption of pNCB with low cost adsorbent with contact time of 30 min and COD removal efficiency of more than 45% was exanimated in previous research (Rakholiya and Puranik, 2012). Although advanced oxidation is a powerful tool for decreasing of pNCB, but the most effect was related on the absorption process. Previous researches showed that the adsorption process provides a removal efficiency for 99% removal for phenol and COD. It is completely comparable with removal efficiency of 40% and 30% for phenol and COD removal by continues ozonation (Mariam *et al.,* 2012).

According to similar researches the integrated processes such as simultaneous adsorption and oxidation is more efficient than series different processes (such as adsorption after ozonation) (Mckay, 1988; Zaror, 1999; Mousset and Mousset, 2014). The oxidation of pNCB by persulfate activated with zero-valent iron was investigated by Fu and coworkers through a series of batch experiments. They found that pH, temperature and iron dosage could influence the pNCB removal (Chan, E.J., Gao, Q. and Dabros, M., 2018).

Fenton process with adequate dosage of Iron can degrade pNCB in acidic condition. sAccording to experimental research by Le and coworkers 83.4 % of pNCB can be removed in 7 min. The most problem for degrading pNCB by Fenton process is resistance of nitro function group in pNCB (Le *et al.,* 2014).



(a)



(b)

Fig. 3. Variation of COD concentration for both influent (a) and effluent (b) with operation time.

4. Conclusions

This is the first pilot-scale research reporting the utilization of catalytic ozonation with activated carbon for treatment of pharmaceutical wastewater containing P-Nitrochlorobenzene. With respect to pNCB and COD removal efficiencies we can conclude that combination of ozone and activated carbon with HRT of 4.0 h is an effective process for treating wastewater containing refractory organics. According to our finding application of simultaneous ozonation and adsorption processes is effective for degrading pNCB.

Author Contributions

Ahmad Sabzali: Process design, project management, data analysis, and writing original draft preparation.
Fatemeh Mohammadi: Sampling and laboratory tests
Zeynab Sadghzadeh: Operation of pilot plant and setting up
Mona Eghbali Gharehbelagh: Architectural design of pilot plant and piping

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

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Data Availability Statement

The data will be available on request due to privacy concerns, the data are not publicly available.

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