# Ozonation of Cephalexin Antibiotic Using Granular Activated Carbon in a Circulating Reactor

[1, 2]Javaid Akhtar and [1]NorAishah Saidina Amin*
[1]*Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering*
*Universiti Teknologi Malaysia, 81310 UTM, Skudai Johor, Malaysia.*
[2]*Centre for Coal Technology, University of the Punjab, Lahore, Pakistan.*
noraishah@cheme.utm.my*

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**Summary:** A circulating reactor was used to decompose cephalexin during catalytic ozonation. The effect of ozone supply and granular activated carbon (GAC) catalyst was investigated for removal of CEX and COD. The regeneration of exhausted activated carbon was investigated during in-situ ozonation. According to results, ozone supply appeared as the most influencing variable followed by dosage of granular activated carbon. The BET surface area, thermogravimetric analysis (TGA) and temperature programmed desorption (TPD) curves indicated that solid phase regeneration of activated carbon using ozone gas followed by mild thermal decomposition was very effective. The adsorption capacity of regenerated activated carbon was slightly lower than virgin activated carbon. The overall study revealed that catalytic ozonation was effective in removing cephalexin from solution and the method can be applied for in-situ ozonation processes.

Keywords: Ozonation; Water treatment; Pharmaceuticals; Catalyst regeneration; Circulating reactor; Granular Activated Carbon

## Introduction

Pharmaceuticals active compounds (PhACs) have caught attention as a new class of pollutants harmful to aquatic organisms. PhACs find their way into water streams via urban effluents, community hospitals, and manufacturing sites. Inefficient removal of pharmaceutical compounds at wastewater treatment plants (WWTPs) is believed to be the main source of their exposure to the environment. Some pharmaceutical compounds are even resistant to advanced treatments such as activated carbon adsorption [1, 2]. Many studies have reported the presences of pharmaceutical compounds in rivers and in the effluents of treatment plants [3, 4].

Ozone is extensively being used as an oxidant in disinfection of drinking water suppliers and removal of organic pollutants from both drinking and wastewater [5]. Various researches have investigated the use of ozone and ozone based advanced oxidation processes for removal of wide range of micropollutans such as chloro-phenols, pesticides, pesticides, and toxic medical wastes chemicals etc [6-9]. Advanced technologies have been found to be more effective for removal of micro pollutants from water than simple ozonation [10-12]. Among these include UV/ $O_3$ $H_2O_2/TiO_2/O_3$, metal oxides/$O_3$, GAC/$O_3$, metal impregnated support materials such as silica, alumina, zeolites/$O_3$ etc [13]. Among ozonation processes, catalytic ozonation processes are recommended due to the fact these processes assist the generation of hydroxyl radicals. Hydroxyl radicals can fasten the decomposition rate of organic pollutant species in water and can decompose refractory organic compounds. Among heterogeneous catalysts for ozonation, activated carbon is helpful to act as a catalyst and as an adsorbent for removal of pollutant species [14-16]. Activated carbon has ability to adsorb pollution from solution onto its surface and in a way, helps to enhance the rate of their decomposition. The combination of activated carbon and ozone extends the working life of carbon catalysts. Exhaustion of activated carbon is a common problem in exclusive adsorption processes and often requires regeneration [17, 18]. Combination of activated carbon and ozone may be helpful to prevent quick exhaustion of activated carbon and is expected to increase its operational life by in situ ozonation [19].

CEX is a cephalosporin antibiotic compound usually prescribed for wide range of antibacterial treatments [20]. The molecular weight of CEX is 347.39 g/mol. The values of pKa1 and pKa2 are 2.56 and 6.88, respectively. Few studies were conducted for removal of CEX from water [21, 22]. Liu et al. [23], investigated the effect of Fe (Ferric) and Cu (copper) loading on activated carbon in removal of CEX to find effect of chemisorptions. The amount cephalexin adsorbed according to Langmuir adsorption isotherms was 66.3 mg/g on AC, 78 mg/g on Cu-GAC and 75 mg/g on Fe-GAC. They have proposed that adsorption might be a successful option

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***To whom all correspondence should be addressed.**

to remove CEX from solution. Another study on CEX is relevant to removal of CEX from electrolyte solution using polybenzimidazole nanofiltration membrane [21, 24] and suggested that the role of ionic form of CEX is significant in membrane separation processes. Akhtar, Amin and Junjie [25], investigated the ozonation of cephelaxin and optimization of its parameters using batch stirred reactor and recognized effectiveness of catalytic ozonation to remove cephalexin from solution. The optimized results showed complete removal of cephalexin with 60% of COD was removed.

In this study, circulating reactor was investigated to compare its efficiency with conventional stirred batch ozonation reactor. The scope of the present work includes i) evaluation of the effect of ozone supply and GAC catalyst parameters during ozonation of CEX and ii) regeneration of polluted GAC using ozone as oxidant. For the regeneration study, the GAC was saturated with cephalexin by a set of adsorption experiments. The saturated GAC was regenerated by supplying ozone through GAC bed in the reactor. The properties of virgin GAC (VGAC), saturated GAC (SGAC), and regenerated GAC (RGAC) were estimated using BET surface area, thermo-gravimetric analysis (TGA) and temperature programmed desorption (TPD-$N_2$). Further experiments were performed to compare the adsorption capacity of VGAC with that of RGAC. A comparison of performance efficiency is also made between stirred type reactors with that of circulating type in terms of COD removal and increase in biodegradability of solution.

## Experimental

### *Chemicals*

Cephalexin antibiotic was received from Pharmaniaga Bhd, Malaysia. Cephalexin compound was received from a local pharmaceutical company (Pharmaniaga Bhd, Malaysia). The particle size distribution of GAC catalyst was 0.6-2.35 mm and was dried at 110$^o$C before using in experiments. Chemicals used in study were of chemical grade supplied by QreC. Two HPLC grade chemicals (methanol, acetonitrile) were purchased from Merek.

### *Ozonation Reactors*

Circulating reactor consisted of two cylindrical columns each of 18cm long, 6cm internal diameter. The volume capacity of the reactor was 1100 mL. The reactor was attached with venturi diffuser for gas liquid mixing. A pump recirculated water solution across the reactor columns and was associated with flow control valves to adjust flow rates. Ozone/oxygen mixture was supplied to reactor by venturi mixer and a bubble diffuser. A bubble diffuser was placed at the bottom of the column to supplement fresh ozone to recirculate water in order to extend gas -liquid contact over reactor length. The exhaust gas left from the top of the reactor and was passed through KI washing bottles. Stirred batch reactor was used in several experiments to compare the performance of two reactors for biodegradability increase and COD removal. The stirred reactor was a round bottom three neck flask with capacity of 250 mL. 200 mL of CEX solution of varying concentrations was ozonated each time. Samples were drawn after 30 min and analyzed for BOD or COD analysis.

### *Ozonation Experiments*

The initial experiments were carried out to investigate the effect of input parameters such as ozone supply and GAC catalyst. Stock and working solutions were prepared using deionized water. Initial concentration of cephalexin was 100 mg/L in all experimental runs. The pH was fixed to 6.5-7. The temperature during experiment was set at room temperature (26±1$^o$C). Approximately 1100 mL of cephalexin solution was fed into the circulating reactor. During experiment, solution was circulated across reactor with the help of a circulating pump. Ozonia Lab 2B ozone generator was used to generate ozone ($O_3$) from pure oxygen supply. Mixtures of $O_3/O_2$ were passed through the reactor at two injection points. Approximately 70% of available $O_3$ was injected via venturi mixer in recirculation stream. Remaining supply of $O_3$ was passed through a fine bubble diffuser that was fixed at the bottom of the second column. The purpose of secondary supply of ozone was to extend decomposition of cephalexin or its products in circulating water. In ozonation experiments, effect of operating conditions was investigated for removal of cephalexin and overall COD. For stirred batch ozonation experiments, 200 mL of CEX solution was taken each time using 4 gm of GAC catalyst. The sample was drawn after 30 min of ozonation and collected for BOD and COD analysis. For BOD or COD analysis, the samples were filtered with Wattman filter paper.

### *Regeneration Experiments*

The capability of ozonation for self-regeneration of exhausted GAC was estimated by a set of experiments. Initially, VGAC sample was saturated with cephalexin using conventional adsorption method [26]. A known quantity of VGAC was stirred gently in a concentrated solution of cephalexin (200 mg/L). Samples were drawn after fixed intervals of time for 6 h. Left over concentration of cephalexin in drawn samples was measured using HPLC and COD tests. This gave indirect measurement of cephalexin or COD adsorbed onto GAC sample according to Eq. (1) [27].

$$q_t = \frac{(C_o - C_t)}{W} \times V \qquad (1)$$

where $q_t$ is the amount of cephalexin adsorbed onto VGAC at time t, $C_o$ is initial concentration of cephalexin antibiotic, $C_t$ is concentration of cephalexin at time t, W is weight of VGAC used (g/L) and V is the volume of solution (L). Eq. (2) is a modified version of above equation for measurement of amount adsorbed at equilibrium. Where $q_e$ gives amount of cephalexin adsorbed at equilibrium concentration $C_e$.

$$q_e = \frac{(C_o - C_e)}{W} \times V \qquad (2)$$

Regeneration study was conducted to evaluate the effect of $O_3$ on self-regeneration of GAC catalyst. Saturated GAC (SGAC) was placed in circulating reactor. Saturation experiments gave a saturated sample of GAC i.e. SGAC that was further investigated for regeneration purposes. SGAC was dried in oven at 100°C before being used in regeneration experiments. Gas containing $O_3$ (21 mg/L) was passed through reactor for about 1 h. Flow rate of $O_3$ gas and concentration of $O_3$ were 0.5cm$^3$/min and 35mg/L respectively. After the experiment, RGAC was collected for characterization. Extent of regeneration was estimated using BET surface area test, thermogravimetric analysis (TGA) and temperature programmed desorption (TPD-$N_2$).

### *Analysis*

Samples were drawn from experiments and pre-conditioned to remove particulate matter and dissolved ozone. Particulate matter or other suspended particles were removed from the samples using 0.45µm syringe filters. The samples were put into 2 mL HPLC vials for analysis using Agilent 1200 series HPLC with Synergi hydro C-18, (5 µm, 4.6 x 150 mm) column. The mobile phase was 20 mM ammonium acetate solution: acetonitrile (80:20) passed at 1.5 mL/min. The pH of mobile phase was 4.4 and detected at 254 nm UV. Samples drawn in adsorption study were also tested using HPLC. COD of samples were measured using standard Hach COD vials. For $BOD_5$ analysis, the measured volume of sample was taken in standard Hach bottles according to initial COD values. Samples were mixed with pillow buffer and $MgSO_4$ solution was poured in a porous cork fitted at the opening of the bottles. The bottles were placed in an incubator at 20°C for five days. The difference in values of initial and ozonation samples was recorded as the change in biodegradability according to Eq. (3).

$$\text{Increase in bioderadability} = \frac{BOD_{5f}}{COD_f} - \frac{BOD_{5i}}{COD_i} \qquad (3)$$

### *Characterization Studies*

Three GAC samples (VGAC, SGAC, and RGAC) were characterized using TGA, TPD-$N_2$, and BET surface area. BET Surface area of GAC samples was estimated using surface area analyzer equipment (Thermo Finnigan). The analyzer was preconditioned using $N_2$ degassing at 300°C. Sample size of 0.2 gm was placed in the analyzer port at initial temperature of 77°C using $N_2$ as inert gas. Surface area of samples was calculated using single point method. TPD-$N_2$ test was conducted using gas chromatograph (Perkin-Elmer Sigma 3B) using $N_2$ carrier gas at 20 cm$^3$/cm and 0.2 gm of sample size. Sample was placed in a stainless steel port and heated carefully to 1000°C at heating rate of 5°C/min and was cooled to room temperature in 3 h. Meanwhile TGA analysis gave weight loss of GAC samples using Shimadzu model DT 30 system. Samples were heated to 1000°C at a heating rate of 10°C/min and 20°C/min in presence of $N_2$ inert atmosphere. No significant effect of heating rate was observed on weight loss characteristics of GAC samples. Due to this reason, results for heating rates for 10°C/min are described in this study.

## Results and Discussion

### *BET Surface Area of GAC Catalyst*

Fig. 1 describes the -desorption curves and particle size distribution for granular activated carbon (GAC) at operating temperature of 77 K. Adsorption desorption curves exhibited a semi hysteresis loop and resembled more to type I and type II adsorptions isotherms of IUPAC classification. The developed hysteresis loop indicated the mesoprorsity at high relative pressure. The microporous character was evident in overlapped portion of adsorption desorption curve. The overlapping of lines at low P/Po and developed hysteresis at high P/Po gives an indication about the presence of ink-bottle type and probably be due to slit shaped pores. The appearance of large hysteresis loops at high relative pressure usually has larger pore size in pore body. From Fig. 1, it can be assumed that GAC carbon will have larger adsorption capacity and pore volume at relative pressure from 0.4 to 1.0. The adsorption of nitrogen increases in larger hysteresis loops indicating the larger particle size distribution [28]. Fig. 1 also illustrates the particle size distribution versus volume of pores. The pore size volume decreased sharply for coarser size particles. The majority of particle size distribution was within in 0-50 Å and coarser particles larger than 50 Å were relatively fewer in population. The pore volume of particles varied significantly within 0-50 Å size range. The BET surface area of GAC found (Micrometrics ASAP 2010 Instruments) was 944.0 $m^2$/g. The mesoporous and microporous volume of the pores were 0.1654 $cm^3$/g and 0.0322 $cm^3$/g. The GAC particles with range of 0-50 Å contain more of micropore volume compared to mesopores volume. The dominance of microporous volume, the dominance of surface adsorption can be expected since there is little chance for interactive adsorption or adsorption of bulky cephalexin into microspores of GAC.

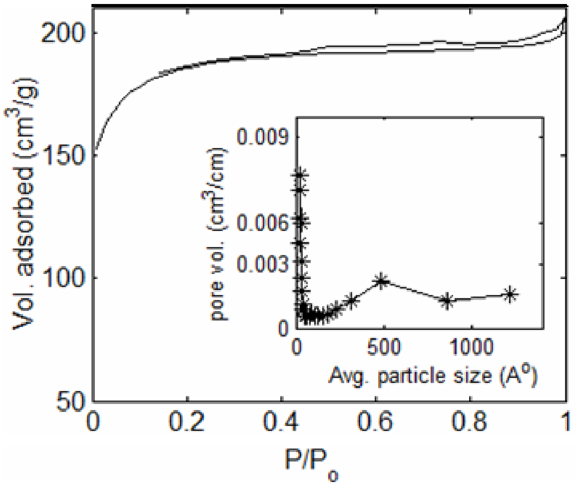


Fig. 1: BET surface area of activated carbon used in this study.

### *Ozonation of Cephalexin*

### *Effect of Ozone Concentration*

The effect of ozone supply on removal of cephalexin from solution was investigated at 16 mg/L, 21 mg/L, and 35 mg/L levels of ozone supply. The ozone gas was passed through cephalexin solution at constant flow rate of 0.5 L/min. All of the other parameters were kept constant that included pH 6.5-7, cephalexin concentration 100 mg/L, GAC 3 g/L, and time 15 min. Fig. 2a describes effect of ozone concentration. The complete removal of cephalexin was observed for $O_3$ supply of 35 mg/L in 5 min of ozonation. However, low concentration of ozone (16 mg/L) in gas did not remove cephalexin completely within 15 min of ozonation. This describes ozone as an important variable during ozonation. The concentration of ozone molecules reflects the probability of reaction between oxidant and substrate [4]. According to mass transfer concept, increase in ozone concentration in bubbles of gas enhances driving force and hence dissolve ozone concentration [29]. The higher the concentration of dissolved ozone; the more is the rate of cephalexin removal.

Fig. 2b gives removal of COD as a function of ozone supply. Ozonation time and gas flow rates were constant at 15 min and 0.5 L/min, respectively. Concentration of ozone was varied by changing the voltage options in ozone generator at fixed gas flow rates. Removal of COD was ~ 40% at 16 mg/L of ozone supply. Removal of COD increased to 80% at 35 mg/L of ozone supply suggesting a synergetic effect of ozone concentration. However, there was not much difference in COD removal at 21 mg/L or 35 mg/L ozone supply. Excessive ozone supply is not favorable from economic point of view. In this scenario, 21 mg/L of ozone supply was regarded as optimum.

Here we compare the removal of parent compound CEX with that of COD of water matrix. The removal of COD was ~ 40% at 16 mg/L of ozone supply i.e. low dosage of ozone managed to remove parent compound mainly. Conceptually, large CEX compound is more prone to ozone attack compared to its byproducts. Initially, at high concentration of CEX compound in water matrix, reaction between CEX/ozone is expected to be the main reaction as evident by the fast decrease in CEX concentration at initial stages (Fig. 2a). During this fast ozonation regime, CEX is expected to convert into its oxidation by-products which kept on accumulating as ozonation proceeded. Increase in concentration of by-products provoked secondary reactions that presumably followed slow reaction kinetics. At the same time, the rate of the main reaction with CEX decreased due to two reasons, i) concentration of CEX decreased in water matrix and ii) ozone being consumed in secondary reactions. Probably due to these reasons, it 16 mg/L of ozone supply did not remove significant quantity of COD. The ozone supply of 21 mg/L is considered optimum for efficient removal of parent compound and COD from water matrix from both efficiency and economic point of view.

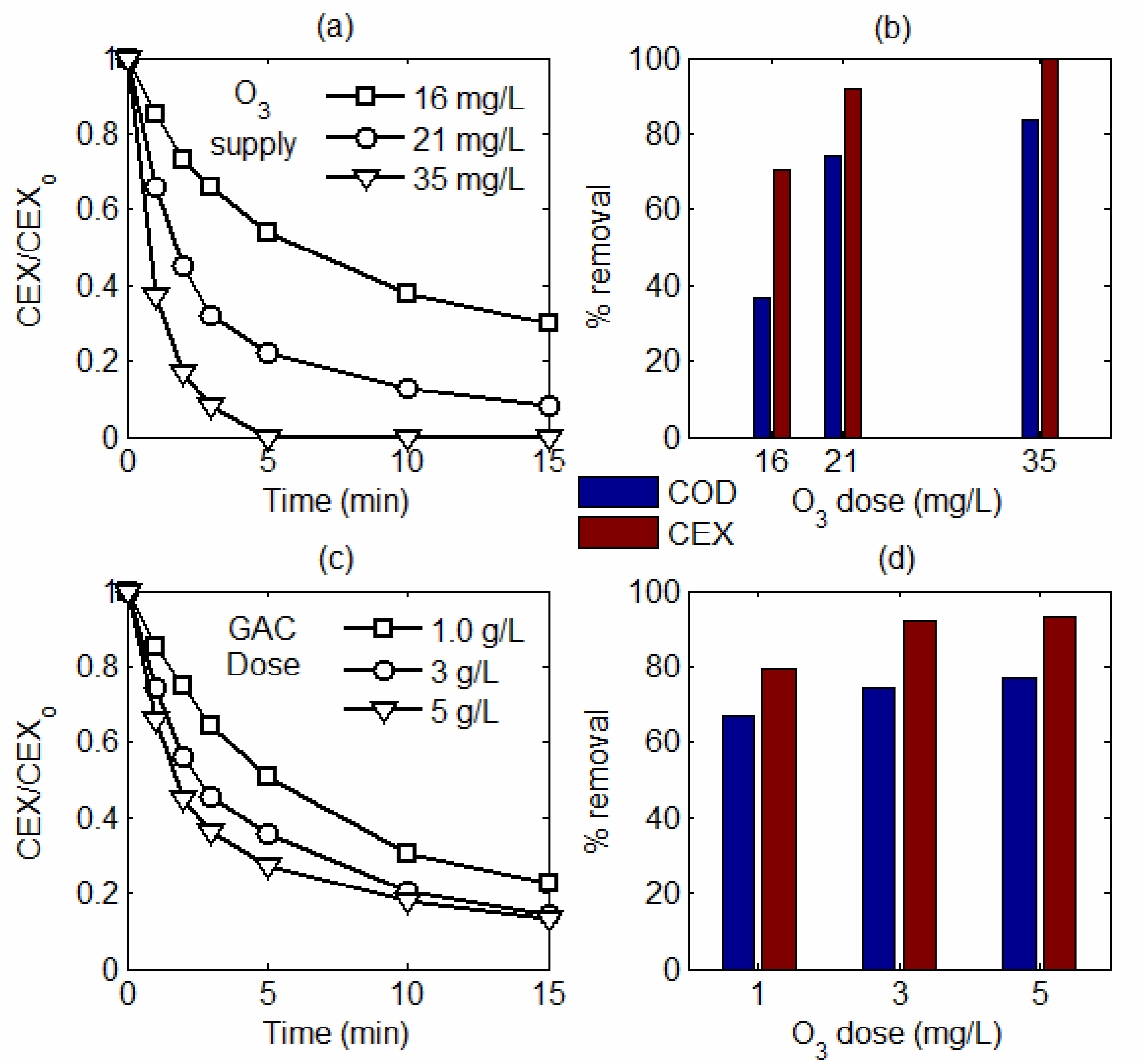


Fig. 2: Removal of CEX and COD from solution a) Effect of $O_3$ supply on CEX removal, b) Effect of $O_3$ supply on COD removal, c) Effect of GAC dosage on CEX removal, and d) Effect of GAC dosage on COD removal. Conditions: pH of solution 6.5-7, CEX concentration 100 mg/L, Temperature 26 ± 1°C.

### *Effect of Granular Activated Carbon Catalyst*

Fig. 2(c) describes the effect of GAC catalyst for removing cephalexin from solution. The constant parameters included ozone concentration 21 mg/L, pH 6.5-7, and cephalexin concentration 100 mg/L. Addition of GAC catalyst is expected to perform dual functions. Firstly, GAC acted as a catalyst surface where ozonation reactions took place between pollutant/ozone [30]. Secondly, GAC surface decomposes adsorbed ozone molecules into powerful radicals (OH/O). These powerful oxidants can decompose any primary or secondary substrates on surface of catalyst or in bulk solution [31]. In a way, addition of GAC may enhance removal of CEX or COD from solution. According to Fig. 2(c), addition of GAC to solution matrix before ozonation slightly increased rate of removal of cephalexin compound. Maximum amount of CEX removal was over 90% in 15 min duration for 5 g/L of GAC dosage. CEX removal at 3 g/L of GAC dosage was slightly lower than 90% and thus not much different from that of 5 g/L of GAC dosage. As illustrated in Fig. 2(d), mineralization increased as GAC dose increased. The role of GAC was less significant in removing COD from solution. The COD of solution increased from 65% to 77% by changing GAC dosage 1-5 g/L.

The by-products formed as result of ozonation are usually less reactive and requires intensive ozone supply [32]. The major byproducts of cephalexin decomposition may be cephalexin sulfo-oxide(s) by nucleophilic attacks and these byproducts decomposed into stable products [33]. The rate of formation of cephalexin sulfo-oxide(s) decreased once significant amount of cephalexin is transformed. The cephalexin sulfo-oxide(s) were not decomposed even at high ozone supply usually sufficient for cephalexin itself [33] indicating the stability of cephalexin byproducts. The plausible reason for such behavior can be decrease of active spots in byproducts that make these less susceptible to ozone nucleophilic attack. That may be a reason for low COD removal in our case compared to parent cephalexin compound.

### *Assessment of Solid Phase Regeneration of GAC Using $O_3$ as Oxidant*

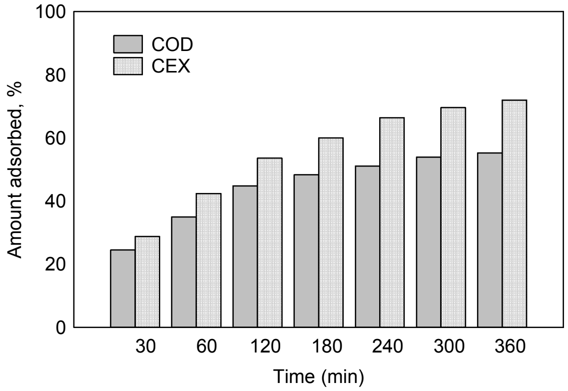


Fig. 3: Saturation curve for adsorption of CEX and COD onto VGAC. Initial CEX = 300 mg/L, gentle stirring, 26 ± 1°C .

### *Saturation Experiments*

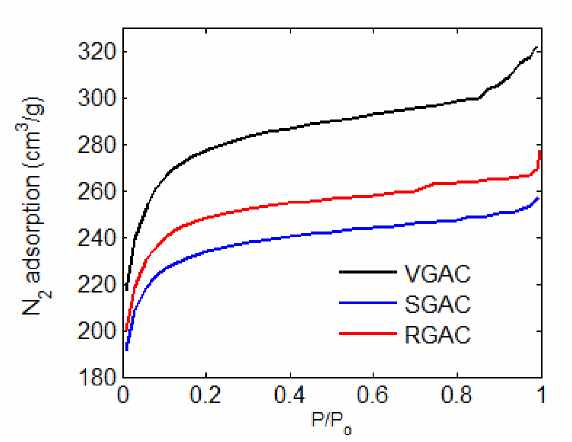
According to Fig. 3, rate of adsorption of CEX onto GAC was higher at initial stages. Approximately 50% of total amount was adsorbed in the first hour of experiment. The rate of adsorption slowed down with passage of time to negligible at the end of 6h. Similar trend was observed for adsorption of COD. The amount of COD adsorbed onto GAC was almost parallel to that of CEX. Total amount of COD adsorbed was nearly 50% of initial value. There was no difference in amount of COD adsorbed at 240 min to that at 360 min. In this view, 240 min can be described as a stage for onset of equilibrium conditions. Fig. 3 also describes that GAC itself is able to remove significant portion of CEX via adsorption. This can be attributed to the fact that GAC has ability to attach significant portion of antibiotics and various studies have reported GAC as an effective adsorbent for antibiotics [34]. Liu et al. [23] found that approximately 70% of CEX was adsorbed onto activated carbon (1031 $m^2/g$), and 90% in Fe-loaded activated carbon. In our study, adsorption was around 75% (944.31 $m^2/g$). This may suggest the importance of GAC surface area for a given pH of solution [35] and role of chemisorptions during adsorption of cephalexin.

### *Regeneration of Exhausted GAC*

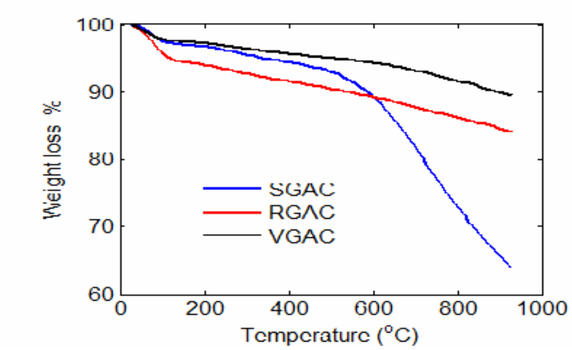
### *BET Surface Area*

Fig. 4 (a) describes the BET adsorption curves for three GAC samples. Accordingly, adsorption behavior of three samples followed type II of IUPAC system of classification [36]. $N_2$-adsorption pattern of all three samples was similar. Adsorption patterns of GAC sample were changed neither by adsorption of cephalexin nor by its regeneration. Amount of $N_2$ adsorbed onto RGAC (red line) was lower than its VGAC sample (black line) possibly due to two reasons. Firstly, $O_3$ gas could not reach into inner spaces of RGAC sample to degrade adsorbed cephalexin. Secondly, decomposition species obtained after reaction of cephalexin and $O_3$ were not desorbed out of GAC pores. The hindrance in regeneration might be associated with the solid phase adsorption of gas onto the activated carbon. Overall, the effect of $O_3$ treatment was evident on solid phase regeneration of GAC. Overall, surface area of RGAC was increased after $O_3$ treatment compared to SGAC.

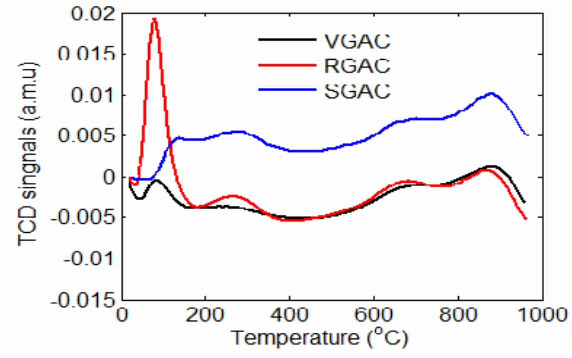
The values of BET surface area and pore volume for all three GAC samples is listed in Table 1. The surface area of VGAC (944.3 $m^2/g$) was much higher than that of SGAC (791 $m^2/g$) or e8RGAC (830 $m^2/g$). Pore volume of samples corresponds to their surface area i.e. VGAC > RGAC > SGAC. The difference in surface area and pore volume for saturated and regenerated samples of GAC was relatively low. The plausible reasons for such a case may be due to i) inefficiency of $O_3$ treatment or ii) incomplete desorption of decomposed species [37].



(a) BET surface area ($m^2/g$)



(b) Thermogravimetric analysis.



(c) Temperature programmed desorption (TPD)

Fig. 4: Regeneration of GAC sample using in situ ozonation for VGAC, RGAC, and SGAC samples a) BET surface area analysis b) Thermogravimetric analysis (TGA) c) Temperature programmed desorption (TPD).

### *TGA Analysis*

$O_3$ treatment may help easier release of decomposed species when sample is heated to a certain temperature. Fig. 4 (b) gives better explanation of the effectiveness of solid phase regeneration of GAC sample. TGA analysis was conducted in $N_2$ environment. Therefore, weight loss of samples is comprised of products of decomposition during TGA. Total weight loss of VGAC was approximately 10% over complete range of temperature. Sharp weight loss was observed at 110°C (initial devolatilization) corresponding to any trapped moisture contents and light volatile matter. Water contents share major portion of weight loss at low temperature. Free water contents escape from solid surface by heating to temperature ~100°C [38]. However, weight loss due to adsorbed water extends up to 150°C [39]. In our study, free moisture is supposed as major cause of weight loss at initial stages. Weight loss increased continuously as a function of temperature for > 110°C. However, weight loss rate decreased to 0.00125% per °C for >150 °C. Therefore, weight loss at high temperature was considered insignificant and was presumed to be due to decomposition of volatile matters present in activated carbon. The porous structure of activated carbon was assumed intact without any distortion [40]. This curve resemble to the weight loss curve for activated carbon given in [40] that may indicate consistent trend for volatilization of activated carbon. SGAC sample followed a similar pattern as original GAC. The weight loss rate in RGAC on the other hand, was much faster up to 125°C compared to other two samples. The extended weight loss in RGAC is attributed to the decomposition products during $O_3$ treatment. Seems like, $O_3$ treatment decomposed major portion of adsorbed cephalexin into smaller products that was devolatilized at initial stage of heating. Weight loss in regenerated sample was gradual from temperature > 150°C and devolatilization pattern was similar to virgin GAC. Total weight loss was approximately 16% in RGAC. This describes that $O_3$ treatment itself had removed significant portion of adsorbed species since total weight loss in saturated GAC was 35% (see Fig. 4b). For saturated GAC sample maximum weight loss occurred between 550-800°C, almost at the rate of 0.1% per °C. The reported weight loss in case of cephalexin complexes Co-cephalexin and Cephalexin-Zn was within 300-600°C that is lower than decomposition temperature range for cephalexin itself (500-800 °C). It is reported in [41] that cephalexin complexes decomposes at lower temperature relatively. This discussion shows that weight loss in SGAC sample can be assumed to be due to decomposition of cephalexin.

Table-1: BET surface area of VGAC, SGAC, and RGAC sample.

| Sample | $T_c$ (°C) | $^aSPS_{BET}$ ($m^2/g$) | $V_{mes}$ ($cm^3/g$) | $V_{mic}$ ($cm^3/g$) | $V_{Total}$ ($cm^3/g$) |
|---|---|---|---|---|---|
| VGAC | 126 | 944.31 | 0.1654 | 0.3217 | 0.4871 |
| SGAC | 126 | 791 | 0.1039 | 0.2890 | 0.3929 |
| RGAC | 126 | 830 | 0.1039 | 0.2972 | 0.4011 |

Comparing BET surface and TGA analysis, it seems cephalexin was decomposed considerably during $O_3$ treatment but was not desorbed. Due to this reason, surface area of regenerated RGAC was smaller than virgin GAC (see Fig. 4(a)). Thermal treatment to ozonated GAC sample was necessary for efficient regeneration of GAC [42]. Therefore, regeneration of GAC may contain two steps i) ozone treatment of polluted sample and ii) thermal decomposition at mild temperature.

### *TPD Analysis*

The thermal decomposition of oxygenated surface groups containing carbon compounds releases $CO_2$ and/or CO. In TPD technique, desorption spectra for CO/$CO_2$ is measured at different temperature.

Type of peaks and decomposition temperature reflect the quantity of oxygenate and type of functional groups to which oxygen is attached. Desorption spectra for carboxylic acid appears at 100-400°C and that for lactones and anhydrides at 190-627 °C [43] Carboxylic acids and carboxylic anhydrides release both $CO_2$ and CO while lactones and phenols release CO only [44]. Fig. 4c illustrates the desorption spectra for TPD analysis for three activated carbons.

Desorption curve for original GAC followed a similar pattern as that of saturated GAC. However, saturated GAC desorbed more of gas reaching a maximum peak at 900°C. Increase in desorption signals in case of saturated sample suggests controlled release of adsorbed cephalexin compound as function of temperature. This also suggested that sufficient amount of cephalexin was adsorbed onto saturated GAC. Desorption signals for RGAC were different reaching a peak between 100-130°C and then followed footprints of original GAC sample. Sharp peak in RGAC is desorption of sufficient quantity of small compounds that originated from decomposition of cephalexin during regeneration. Once these smaller compounds desorbed out due to thermal heating, complete regeneration of GAC was achieved. This fully regenerated GAC followed footprints of virgin activated carbon as shown in Fig. 4(c).

It is notable that all of three graphs in Fig. 4 represented similar conclusion. For example, in case of regenerated GAC, there was sharp decrease in weight loss (Fig. 4(b)) at temperature 100-130°C. Interestingly, within same temperature span, TPD signals represented a similar sharp increase in desorption (Fig. 4(c)). In TPD analysis, we associate this behavior due to desorption of smaller compounds from GAC sample. Presumably, reaction between ozone and cephalexin generated sufficient quantity of smaller compounds called by-products. However, these by-products could not be removed efficiently during regeneration process. Evidence to this statement is relatively low surface area of regenerated GAC sample expressed in $N_2$ adsorption curve (see Fig. 4(a)). Therefore, heating of regenerated GAC sample in $N_2$ environment resulted in release of smaller by-products. After removal of such by-products, regenerated sample, followed footprints of original GAC in both Figures (Fig. 4(b) and Fig. 4(c)). Therefore, it is recommendable that i) solid phase regeneration via ozonation and ii) heat treatment in $N_2$ environment are able to regenerate GAC sample.

### *Adsorption studies for RGAC*

A separate study was performed to observe the uptake of COD on regenerated GAC. Fig. 5 illustrates the amount of COD adsorbed onto regenerated and virgin GAC samples. Approximately 60mg/g of COD was adsorbed onto regenerated GAC sample within 4 h. Significant amount of COD was adsorbed onto regenerated sample that agreed to the results of characterization study. Rate of COD adsorption decreased gradually to saturation level in 4 h duration. Virgin GAC adsorbed 80mg/g of COD for the same time duration. Rate of COD adsorption was clearly higher in virgin GAC. That may hint that adsorption capacity of regenerate GAC was slightly degenerated. The initial COD concentration induced synergetic effect on overall adsorption of COD (Fig. 5b). Amount of COD adsorbed was 20mg/g at 130 mg/L of initial COD that increased to 80 mg/g for 420 mg/L of solution. Similar trend was also observed for regenerated GAC. Maximum amount of COD adsorbed onto regenerated GAC was 60 mg/L at 420 mg/L of initial COD. Probably, this trend is found frequently in adsorption studies [42, 45]. In generally, it is attributed to increase in driving force at solid-liquid interface and enhancement in mass transfer rates [27]. Overall, regenerated GAC adsorbed significant amount of COD and suggested that ozonation was useful way for solid phase regeneration of GAC.

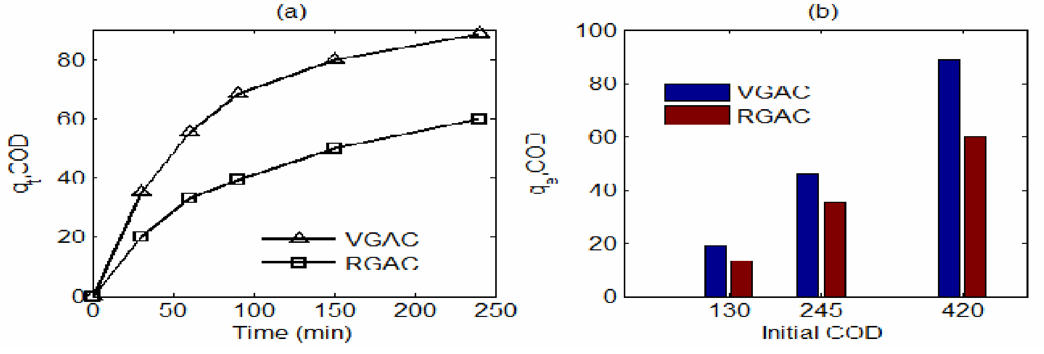


Fig. 5: Saturation curve for adsorption of CEX and COD onto VGAC and RGAC. Initial CEX = 300 mg/L, gentle stirring, 26 ± 1°C.

### *Biodegradability of CEX in Stirred Batch and Circulation Reactors*

The performance of two reactors was compared bycomparing the increase in biodegradability and removal of COD of the CEX samples. Fig. 6 illustrates that the biodegradabilitiy of the two solutions from both reactors was increased after 30 min ozonation. Increase in BOD (BOD$_f$/COD$_f$-BOD$_i$/COD$_i$) in case of stirred reactor was 0.36 and that for circulating was 0.56. Similarly, the removal of COD reached 100 percent during 30 min duration in circulating reactor compared to only 60 percent in stirred reactor. The total volume of solution processed per batch was 1100 mL in circulating reactor much more than 200 mL in case of stirred batch type. Water circulation and gas mixing with the help of a veuntri mixer were the two salient features of the circulating reactor. These provide better ozone consumption resulting in higher degree of pollutant removal. Matheswaran and Moon [46], emphasized the importance of circulating bubble column with venturi injector for phenol wastewater treatment. They highighted the usefulness of circulation rates during ozonation. Houshyar et al. [47], treated tannery wastewater using circulation contactor with venturi injector and observed 88% COD removal with 93% color diminishing. Many other studies also suggested the usefulness of circulating reactor with venturi injector [48]. The stirred reactors used conventional spargers for gas diffusion that are prone to frequent clogging. Venturi injectors seldom face these problems and are cost effective. With this discussion and results we found, it is recommendable that circulating reactor is a preferable choice for advanced oxidation process. Stirred type reactors should be employed in basic ozonation studies only.

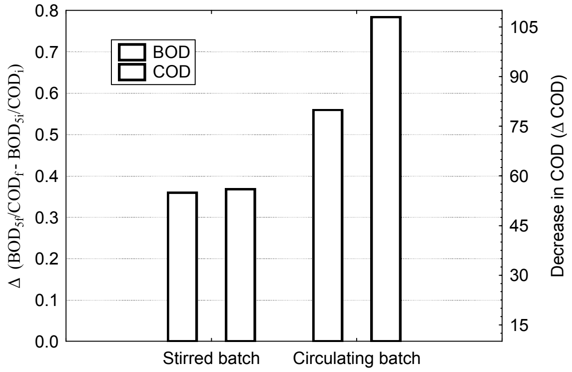


Fig. 6: Increase in biodegradability and decrease in COD values of CEX solution using two reactors. CEX concentration 200 mg/L, pH 7-7.5, Time 30 min, Initial COD 190, O$_3$ dosage 21 mg/L, CEX volume: 200 mL (stirred batch), 1100 mL (circulating batch).

## Conclusions

Catalytic ozonation of cephalexin and regeneration of activated carbon catalyst was investigated using circulating batch reactor. The cephalexin could be removed efficiently in the circulating system. The 100% of cephaelxin was removed within 5 min of ozonation at concentrated supply of ozone and within 10 min at diluted ozone supply. The maximum of 80% COD was removed at 35mg/L of ozone dosage. The GAC catalyst also induced synergistic effect on removal of CEX and COD by 15% and 9% respectively. The ozone based regeneration was very efficient with almost complete regeneration of grannular activated carbon. According to BET surface area, TGA analysis and TPD-N$_2$ analysis, the solid phase ozonation followed by mild thermal decomposotion in inert environment was sufficient for regeneration of activated carbon. The adsorption capacity of regenerated activated carbon was slightly lower than virgin activated carbon. This describes the significance of in-situ ozonation using granular activated carbon for cephalexin or other pollutant removal. Finally, it was found that circulating reactor was more useful in ozonation CEX solution compared to stirred batch type.

## Nomenclature

| | |
|---|---|
| BOD | Biochemical oxygen demand |
| CEX | Cephalexin antibiotic |
| COD | Chemical oxygen demand |
| PhACs | Pharmaceutical compounds |
| RGAC | Regenerated activated carbon |
| SGAC | Saturated activated carbon |
| TGA | Thermogravimetric analysis |
| TPD | Temperature programmed desorption |
| VGAC | Virgin activated carbon |
| WWTPs | Wastewater treatment plants |

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