

A study on the influence of pH changes during catalytic ozonation process on alumina, zeolites and activated carbons for the decolorization of Reactive Red-241

Samra Sajjad, Amir Ikhtlaq, Farhan Javed, Syed Waqas Ahmad and Fei Qi

ABSTRACT

The current study focuses on a prime effect of pH changes in the catalytic ozonation process (COP) by using three main classes of catalysts such as zeolites (alumina-silicates), alumina (metal oxides), and activated carbons for decolorization of Reactive Red 241 (RR-241). The role of pH changes, point of zero charges and the effect of catalyst dose on pH change was studied. The results reveal that the overall removal efficiency of RR-241 in the case of COPs was the highest compared with single ozonation process (at pH = 7 the efficiency was 80, 65.5 and 60% for AC/O₃, Al₂O₃/O₃, Zeolite/O₃ and O₃ respectively). At initial acidic pH 4, the highest pH variations in COPs and ozonation processes were observed. Moreover, the pH changes were not found to be significant near the point of zero charges of materials (pH_{pzc} = 6.8, 8.4 and 8.8 for zeolite, activated carbons and Al₂O₃, respectively). The COP in the presence of activated carbon shows the highest removal efficiency (82%) at pH 7. The material dose effect indicates that increasing the amount of catalyst (from 1 gm to 2 gm) significantly leads to a change in the pH of the solution. Results reveal the prominent effect and significance of pH changes on the efficiency of COP to determine true catalytic efficiency.

Key words | activated carbon, advanced oxidation process, alumina, catalytic ozonation, zeolites

HIGHLIGHTS

- A study on the effect of pH changes in COP by using three catalyst types.
- pH changes can alter the mechanism of COPs and may lead to wrong findings.
- The current study enlightens the significance of pH changes in COPs using various catalysts.

Samra Sajjad

Amir Ikhtlaq

Institute of Environmental Engineering and Research,
University of Engineering and Technology,
Lahore 54890,
Pakistan

Farhan Javed (corresponding author)

Syed Waqas Ahmad

Department of Chemical and Polymer Engineering,
University of Engineering and Technology,
Faisalabad Campus,
Faisalabad,
Pakistan
E-mail: farhan.javed@uet.edu.pk

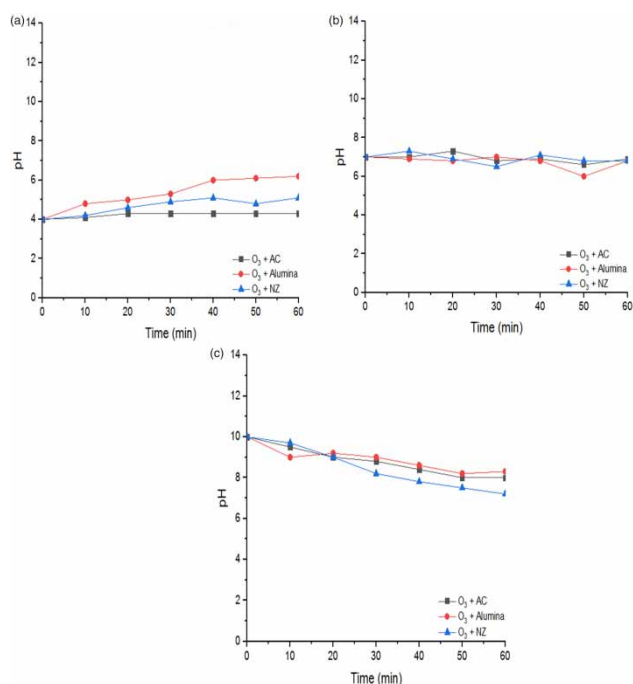
Fei Qi

Beijing Forestry University,
No. 35 Qinghua East Road, Haidian District,
Beijing 100083,
China

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GRAPHICAL ABSTRACT



INTRODUCTION

In the recent few years, catalytic ozonation processes (COPs) have gained much attention in water and wastewater treatment applications, due to the production of highly reactive oxygen species or hydroxyl radicals in such processes. COPs may fall into the homogenous and heterogeneous ozonation process. Due to low cost, high efficiency, lack of sludge formation, and production of hydroxyl radicals (*OH) over a wide range of pH, the heterogeneous catalytic ozonation process may be a good option among the advanced oxidation processes (AOPs) for the removal of toxic and refractory organic compounds present in wastewater (Asaithambi *et al.* 2015). Several materials (such as silica, alumina, zeolites, titanium, activated carbon) have been implied in the COPs with various combinations of metals (Fe/O_3 , Cu/O_3 , Pt/O_3 , Ru/O_3) and metal oxides (CuO/O_3 , MnO_2/O_3 , CeO_2/O_3 , MgO/O_3 , Al_2O_3/O_3). Moreover, activated carbons, zeolites, and alumina were also widely used in COPs (Ikhtlaq *et al.* 2013).

However, some studies reported controversial results with valid reasons (Rosal *et al.* 2010). For example, Jacek Nawrocki *et al.* highlighted the controversies in the catalytic ozonation process and discussed them with possible

reasons. Among those were that the pH changes during the catalytic ozonation process may alter the mechanism and overall effectiveness of the process (Nawrocki 2013). Even in recent years, many research articles were published without considering the pH changes in such processes, which may lead to the wrong interpretation of mechanisms while comparing various materials as a catalyst with the single ozonation process, since both the ozonation and catalytic ozonation processes are pH dependent and their reaction rates depend on the pH of water (Nawrocki 2013). In addition, contaminants present on the surface of such catalysts may alter the pH of water (Nawrocki 2013). Therefore, to resolve the controversies, it is necessary to understand the effect of pH changes on COPs. The controversies in COPs may be due to some experimental errors such as lack of pH control, amount of catalyst, catalyst purity, nature of wastewater, and adsorption of contaminants on the catalyst surface. In the majority of studies, no attention was given to pH control, which is very important at high catalyst concentrations (Kolosov & Yargeau 2019).

In addition, the ozone decomposition in the COP is strongly dependent on pH. Hence, it is necessary to

determine the suitability and ability of catalyst for ozone decomposition as it is important to compare ozone stability in water with and without catalyst at the same pH (Bai *et al.* 2017; Huang *et al.* 2019; Munir *et al.* 2019). It is important to mention here that in some reports buffers were tested to control the pH during the process (Nawrocki & Fijolek 2013). However, buffers may act as hydroxyl radical scavengers and may affect the effectiveness and mechanism of COPs, hence using buffers to study the effect of pH changes in such processes may not be a good idea. Some studies show that the pH was controlled at the beginning of the COPs and not controlled during the process (Li *et al.* 2019).

Similarly, some studies showed the effect of various operational parameters such as the effect of pH, ozone dose, and catalyst dose for the treatment of real wastewater using the COPs; however, the pH during the process was not determined (Alvarez *et al.* 2009). Another study completely highlighted the effect of pH in COP using commercially available aluminum oxide as a catalyst (Nawrocki & Fijolek 2013). The pH effects during COP of carboxylic acids with metal-on-metal oxide catalysts were investigated. However, it lacks the role of a catalyst during the process (Gumus & Akbal 2017; Ghuge & Saroha 2018). It is suggested that contaminants on the surface of the catalyst may be responsible for the pH change. Many reports on COPs have been published in the last decade; however, the role of the type and nature of catalysts in pH change may not be well understood. No extensive comparative study on various catalysts has been conducted to observe the influence of pH changes in such processes.

The current study focuses on the effect of pH changes in COP by using three catalyst types (activated carbon, zeolites, and alumina) for the decolorization of Reactive Red 241 (RR-241). Dyes of different types were used to investigate their removal by different processes (Ahmed *et al.* 2020). In the current investigation, RR-241 was used as a representative dye for its removal by catalytic ozonation process. Various methods have been implied in past for the degradation of various toxic dyes for example photodegradation (Naushad *et al.* 2019a, 2019b), adsorption (Albadarin *et al.* 2017; Naushad *et al.* 2019a, 2019b), electroflocculation (Ikhlaq *et al.* 2018) and Fenton-like degradation (Ikhlaq *et al.* 2019a, 2019b) etc., In the recent few years, catalytic ozonation was also found to be a highly efficient process; however, the mechanisms of such processes are not well understood and monitoring the pH changes due to the catalysts themselves and during catalytic ozonation processes may help to understand these processes (Nawrocki 2013). The effect of catalyst dose on pH changes and the role of pH changes along with the

point of zero charge on the catalyst, which was also playing an important role, were elucidated in the current investigation. To the author's knowledge, the current study is the first report on the role of pH changes with various catalyst comparisons in COP. Hence, the current study involves a comparative approach to investigate pH changes in the catalytic ozonation process by using different types of catalysts comparing with their points of zero charge. Since pH changes can alter the mechanism and efficiency of COPs and may lead to wrong findings in ozonation, the current study may pave the way to clarify the pH changes and their significance in COPs using various catalysts.

MATERIALS AND METHODS

Chemicals

The RR-241 dye was purchased from Archroma, Switzerland, and was used without further purification. A stock solution (1,000 mg/L) was prepared by mixing the dye in ultrapure deionized water. The pH of the solution was adjusted by using analytical grade 1N NaOH and 1N HCl provided by Merck, Germany. All reagents used were available at IEER lab UET Lahore.

Preparation and characterization of catalysts

The catalysts (activated carbon, zeolites, and alumina) were procured from Sigma Aldrich USA. The catalysts were washed with deionized water and then dried overnight at 105 °C in an oven. Afterward, the catalysts were dipped in 0.1N nitric acid, washed, and dried in an oven at 105 °C. The pore size and surface properties of the catalyst were measured by using the Brunauer–Emmett–Teller (BET) analyzer (Micro metrics ASAP 2020). The pH_{pzc} (point of zero charge) was evaluated using the mass titration method (Krishnan *et al.* 2017).

Experimental procedure

The experiments were performed at room temperature by taking 500 ml of RR-241 solution in a flask using the experimental setup shown in Figure 1. The O₃ gas was supplied from the ozone generator (Model, AZCO HTU-5000GE-120). The solution was stirred using a magnetic stirrer. The unreacted O₃ gas was captured using 2% KI traps. Each run was conducted for 1 hour and samples were withdrawn after a fixed interval of time and were subjected to color

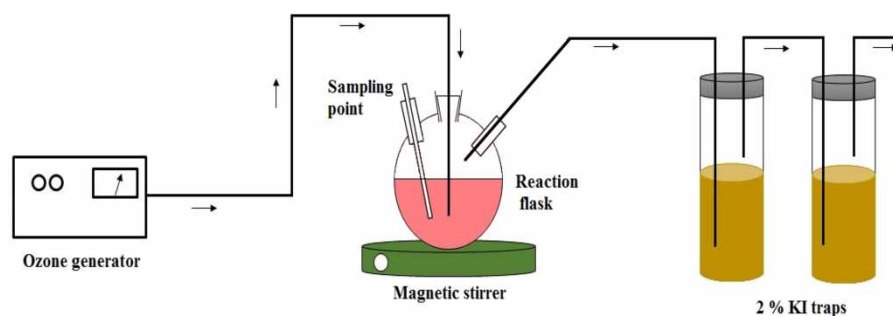


Figure 1 | Experimental setup.

measurement analysis. In the case of COPs, a known quantity of catalyst was added into the reactor. The ozone dose was determined by using the following formula with the help of the Iodometric method (Ren *et al.* 2018).

$$\text{Ozone dose (mg/min)} = \frac{A \cdot N \cdot 24}{T}$$

where, A and N are the volume and normality of $\text{Na}_2\text{S}_2\text{O}_3$, and T is ozonation time.

RR-241 decolorization studies were performed at 542 nm using a UV-vis spectrophotometer (PerkinElmer Lambda 35). Each experimental run was performed thrice to ensure RSD values and accuracy and it was found to be less than 5%. The decolorization efficiency was determined by using the following formula.

$$\text{Decolourization of RR - 241 (\%)} = \left(\frac{A - B}{A} \right) \times 100$$

where A and B are the initial and final absorbance respectively.

RESULTS AND DISCUSSION

Catalyst characterization

The point of zero charge of zeolites, activated carbon, and alumina were found to be 6.8, 8.4 and 8.8 respectively. The activated carbon shows the highest surface area ($205 \text{ m}^2/\text{g}$) compared to zeolites and alumina. The average pore size and surface area of the catalysts are shown in Table 1. The results indicate that the zeolites point of zero charge was on the acidic side while alumina and activated carbons have a point of zero change in the basic range. This confirmed that the nature of materials may play an

Table 1 | Characteristics of catalysts

Material	Surface area (m^2/g)	Average pore size (\AA)	Point of zero charge (pH_{PZC})
Natural zeolite	90	20	6.8
Activated carbon	205	9.3	8.4
Alumina	188	46.9	8.8

important role in their surface chemistry and their ability to attract ions in water.

Decolorization of RR-241 and initial pH effect

The experiments were performed at different initial pH values of an aqueous solution of RR-241. Figure 2 presents the decolorization of RR-241 under these experimental conditions. The pH significantly influences the decolorization of RR-241 during the single ozonation process (SOP). At acidic conditions (pH 4), the single ozonation process (SOP) shows 42% decolorization of RR-241 while this percentage increases to 65% at pH 7. The highest decolorization (82%) was achieved at pH 10. As expected, the molecular ozone directly reacted with contaminants at acidic conditions, while at neutral and basic conditions the ozone degrades the contaminants in two ways: (a) direct reaction with contaminants and (b) O_3 decomposes into hydroxyl radicals, which further react with the target pollutant and degrade it. As a result, the efficiency of the process increases at basic conditions (Manna *et al.* 2017).

Figure 2(a) depicts a comparison of SOP and COPs at pH 4 for the decolorization of RR-241. The SOP has the lowest efficiency compared to COPs. The COP in the presence of activated carbon shows the highest efficiency (70%) at pH 4. This may be due to the high surface area of activated carbons leading to significantly higher adsorption of RR-241 and molecular ozone compared to alumina and

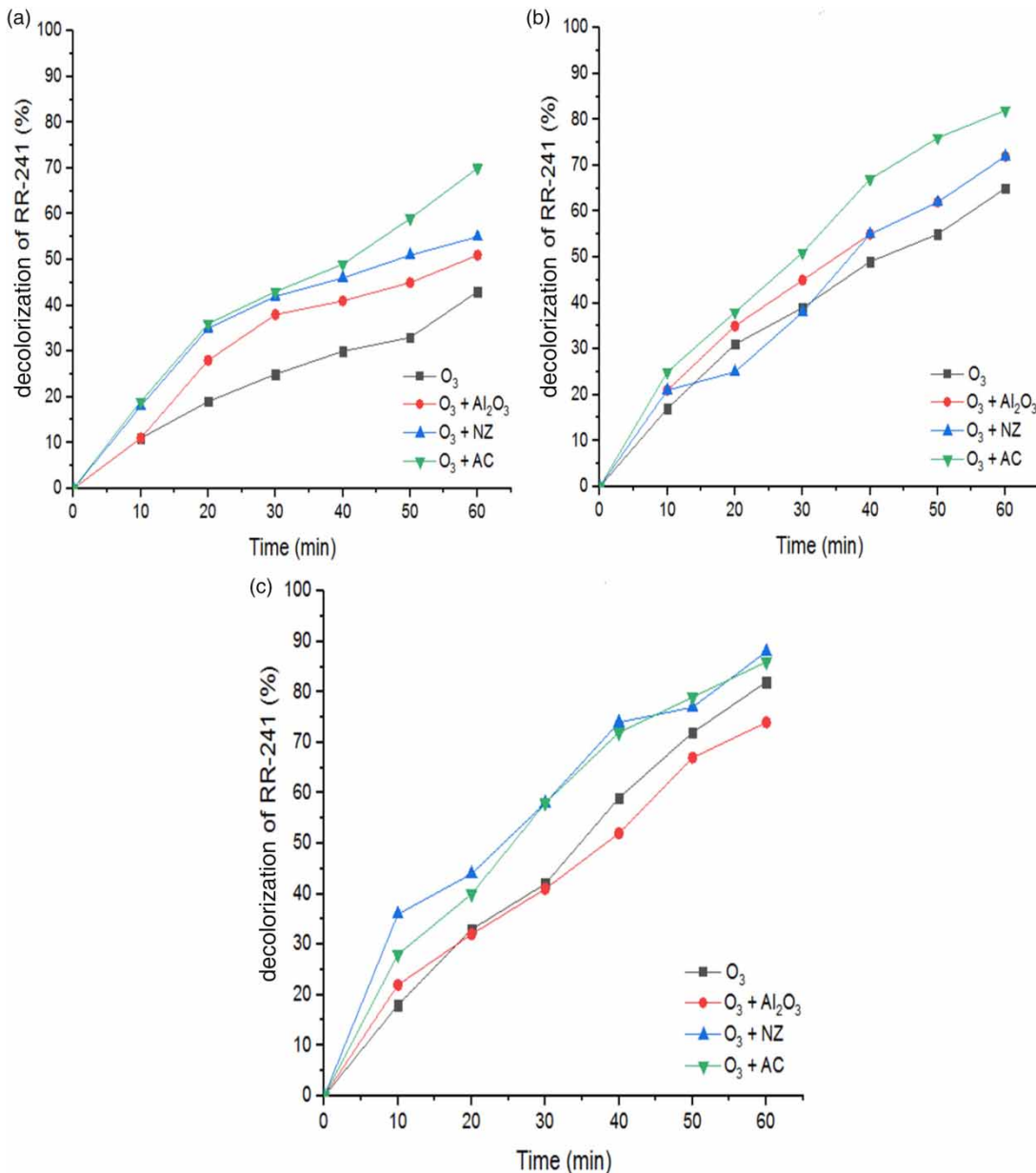


Figure 2 | Effect of initial pH on the decolorization of RR-241 by SOP and COPs (a) pH 4, (b) pH 7, (c) pH 10. ($O_3 = 0.1$ mg/min, $t = 60$ min, $T = 25$ °C, $C_0 = 100$ mg/l).

zeolites (Yong *et al.* 2005; Zhang *et al.* 2013). It is important to note that the addition of catalyst significantly increases the decolorization of RR-241. During SOP, only molecular ozone was responsible for the degradation of the target pollutant at acidic pH (Wang & Bai 2017). However, in the case of COP, the degradation may be increased for several reasons, the target pollutants may adsorb on the surface of the catalyst, the catalyst surface provides a new path for the target pollutant and ozone, where they react with each other, the ozone decomposes on the catalyst surface and

hydroxyl radicals may be generated (Wu *et al.* 2015; Sun *et al.* 2019).

The decolorization of RR-241 was investigated at neutral conditions and a comparison was made between SOP and COPs shown in Figure 2(b). The COPs show higher decolorization efficiency compared with SOP. The increase in efficiency of COPs may be due to the addition of the catalyst, which provides an additional path for the degradation of the target pollutant. In addition, the efficiency of COPs at neutral conditions is greater than the efficiency of COPs at

acidic conditions which shows that the pH has a significant impact on SOP as well as COPs.

Figure 2(c) shows the alkaline pH effect on the decolorization of RR-241 during SOP and COPs. The COP in the presence of alumina shows the lowest efficiency. The COP in the presence of zeolites has the highest efficiency; however, there is a small difference between the efficiency of COP using zeolites and activated carbon. The most important is the significant difference between SOP and COP in the presence of alumina. The lack of catalytic activity in the case in the O_3/Al_2O_3 process at alkaline pH (pH = 10) may be due to the decomposition of ozone itself leading to the production of hydroxyl radicals. The slight increase in decolorization efficiency in the case of O_3/AC and O_3/NZ process compared with O_3 alone may be due to the adsorption of dye on the catalyst surface. The pH changes in the presence of alumina and their effect were studied in some previous findings (Nawrocki & Fijolek 2013); the results obtained indicate that the contaminants on the alumina surface may alter the pH of aqueous solutions, which might affect the catalytic ozonation process (Nawrocki & Fijolek 2013), this was in agreement with the results obtained in the current investigation in the case of the Al_2O_3/O_3 process.

Effect of nature of catalyst on pH changes in catalytic ozonation

The nature of the catalyst is important in COP as it may change the pH of the solution during the process (Xu *et al.* 2019). The surface area of materials plays an important role in the adsorption of pollutants. Since some previous studies suggested that adsorption may play an important role in catalytic ozonation processes, comparing materials with different surface areas may be useful in investigating the role of adsorption on the decolorization of dyes (Ikhlaq *et al.* 2019a, 2019b).

Figure 3(a) shows the pH changes observed during the process for the studied catalysts. The activated carbon shows the least pH changes during the process. For example, the initial pH was 4 and during the experiment, the pH varied from 4 to 4.3 (Figure 3(a)). In the case of zeolites, the pH varied from 4 to 5.2 during a 60 min run (Figure 3(a)), which may be due to hydroxide impurities on zeolite. An alternate explanation may be that the unassociated oxygen on the zeolite surface may absorb H^+ ions from water, leading to an increase in pH (Yu *et al.* 2019). The alumina shows the highest pH variations during the process—the pH varied from 4 to 6.2 (Figure 3(a)), which may be due to the interactions of H^+ ions in solution with

the surface hydroxyl groups on alumina, since alumina may have a basic nature compared with zeolites and a point of zero charge at basic pH, hence the effect of pH was significant in the case of alumina.

Figure 3(b) shows pH changes during the process at neutral conditions. The COP in the presence of activated carbon shows lesser pH variations compared to the other two processes. In the case of O_3/AC , the pH varied from 7 to 6.8 and 7.3. In the case of O_3/NZ , the pH varied from 7 to 6.5 and 7.3. The COP in the presence of alumina shows the highest variations, with pH varying from 7 to 6.

At basic conditions, pH 10, the effect of the nature of materials was investigated (Figure 3(c)). The COP in the presence of AC shows that the pH of the process was varied from 10 to 8. The highest variations were observed in the case of the O_3/NZ process, the pH varied from 10 to 7.2 (almost neutral conditions). The decrease in pH may be due to the nature of the material, as those may try to acquire the point of neutrality, and hence may release H^+ ions on their surface to neutralize some hydroxide ions present in the solution (Li *et al.* 2019). As mentioned earlier and in some previous studies, pH control during the process is an important aspect. Selecting the initial pH cannot guarantee that the pH remains the same during the process. For example, in the current study, at basic conditions, the initial pH was adjusted 7; however, it goes to neutral conditions after 60 min. This proves that the actual performance of the process cannot be estimated by selecting the initial pH. The nature of the material may alter the pH during the process.

pH changes without ozonation

The COPs may result in the production of various byproducts that may affect the pH of the solution, therefore in the current investigation pH changes without COPs were studied (Figure 4). The results clearly show a similar pattern of pH changes, as was in the case for catalytic ozonation processes using zeolites, alumina, and activated carbon (Figures 3 and 4). This clearly suggested that the nature of the catalyst may play an important role in the change in pH once the catalyst has been added to the aqueous solution.

Point of zero charges and pH changes

The point of zero charge (pH_{pzc}) is the pH at which the surface of the catalyst will be electrically neutral; when the pH of water is below the pH_{pzc} the surface will be positively

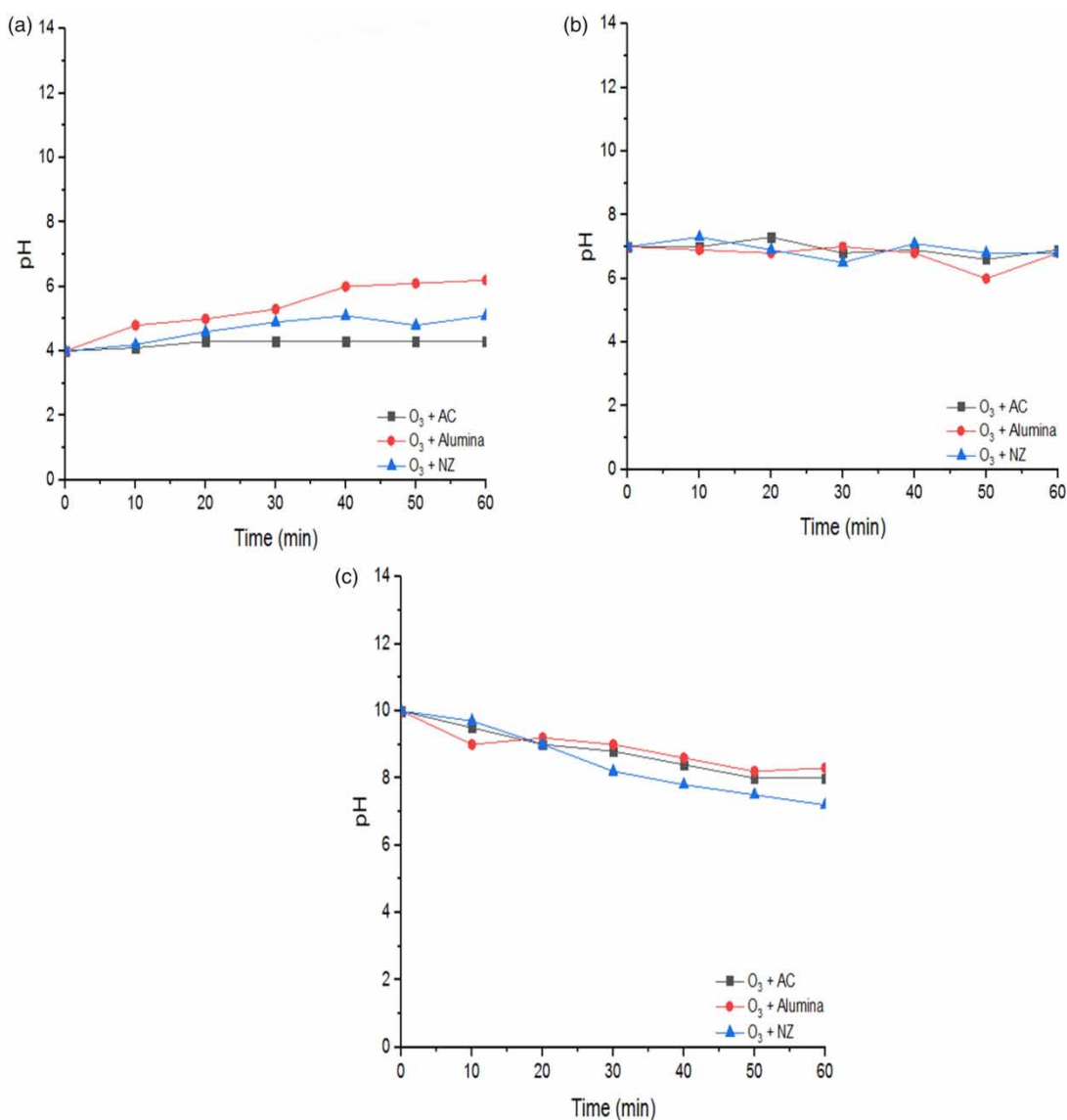


Figure 3 | pH changes during COPs (a) pH 4, (b) pH 7, (c) pH 10. ($O_3 = 0.1$ mg/min, $t = 60$ min, $T = 25$ °C, $C_0 = 100$ mg/l).

charged and when pH is above pH_{pzc} , it will be negatively charged. Since the charge on the catalyst may affect the adsorption of pollutant and ozone interactions with active sites (Lewis or Bronsted acid sites), the point of zero charge may be an important property to study in pH-dependent processes (Ikhlaq *et al.* 2013). Results shown in Figure 5 reveal that while adding subsequent portions of studied catalyst the initial pH either from the acid or basic range may tend to alter up to a certain point known as the point of zero charge (pH_{pzc}) (Ikhlaq *et al.* 2013). This supports our hypothesis that the nature of the catalyst may change the initial pH during the catalytic ozonation process.

While comparing the pH_{pzc} and pH changes with or without COPs (Figures 3–5), it was observed that when the initial pH of catalysts was selected near their points of zero charge, there was no significant change in pH after the addition of catalyst (Figure 4). For example, in the case of alumina and activated carbons, when the initial pH was 7 no significantly higher change in pH was observed (Figure 4(b)). However, in the case of zeolite (at initial pH 10) significantly higher decrease in pH was observed compared with alumina and zeolites, since the point of zero charge of zeolite was towards the acidic side (Figure 5(b)). This may be due to the release of H^+ ions by the protonated hydroxyl

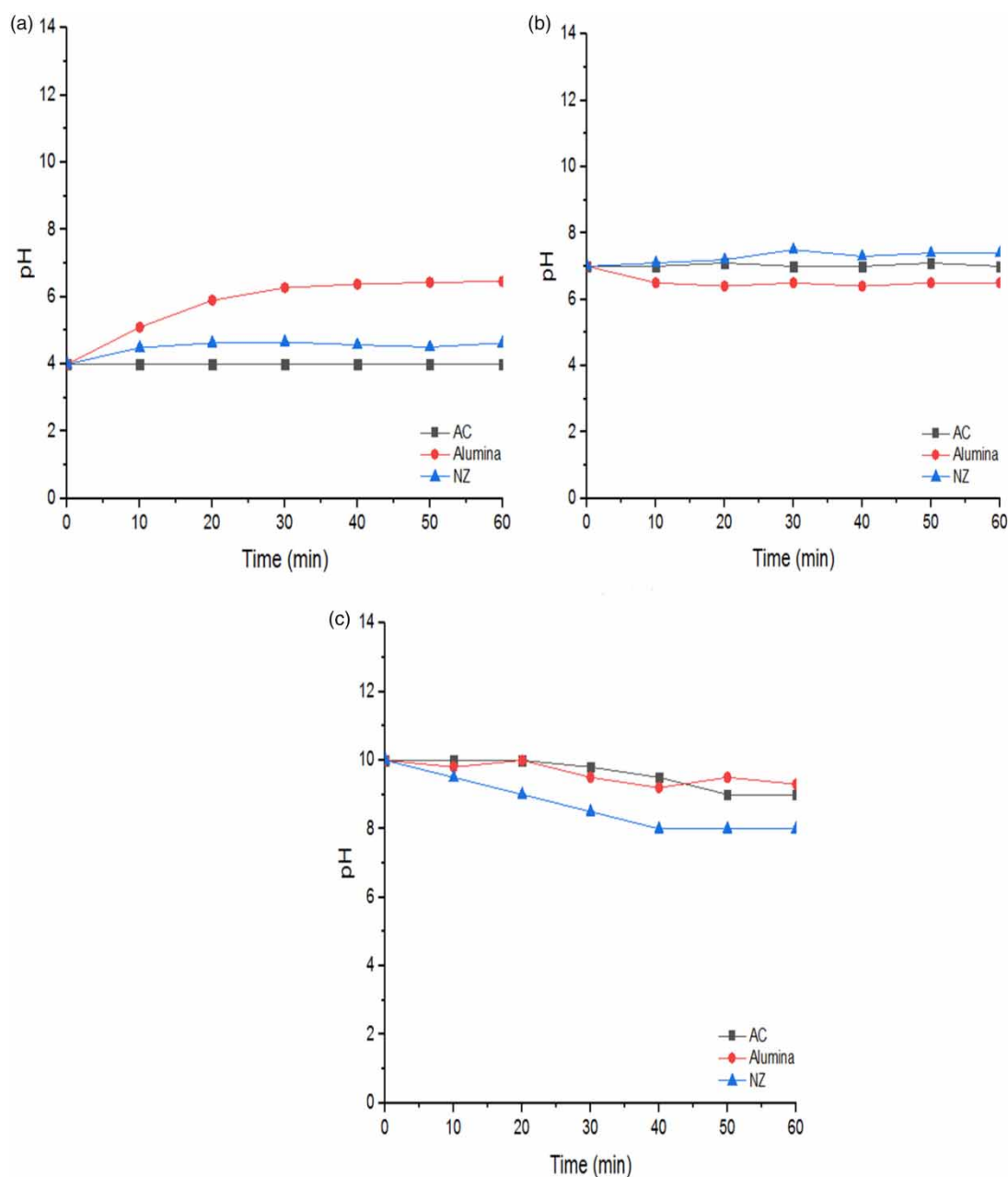


Figure 4 | pH changes in the absence of SOP and COPS (a) pH 4, (b) pH 7, (c) pH 10. (Catalyst = 1 gm, T = 25 °C).

groups of zeolites on the addition to water at such a high pH (pH = 10).

Catalyst dose effect and pH changes

Figure 6 shows the effect of catalyst dose on the pH of the process at acidic, neutral, and basic conditions. The pH variations were significantly observed at pH 4 for all materials,

the alumina shows the highest pH variations during the process. For example, 1 gram of catalyst alumina varied the pH from 4 to 6. The increase in catalyst dose (alumina) also varied the pH of the process. The 2 grams of catalyst (alumina) varied the pH from 4 to 7 (almost neutral conditions). Some previous findings found no significant change during the catalytic ozonation process in the presence of alumina (Ren *et al.* 2018). This may be due to the

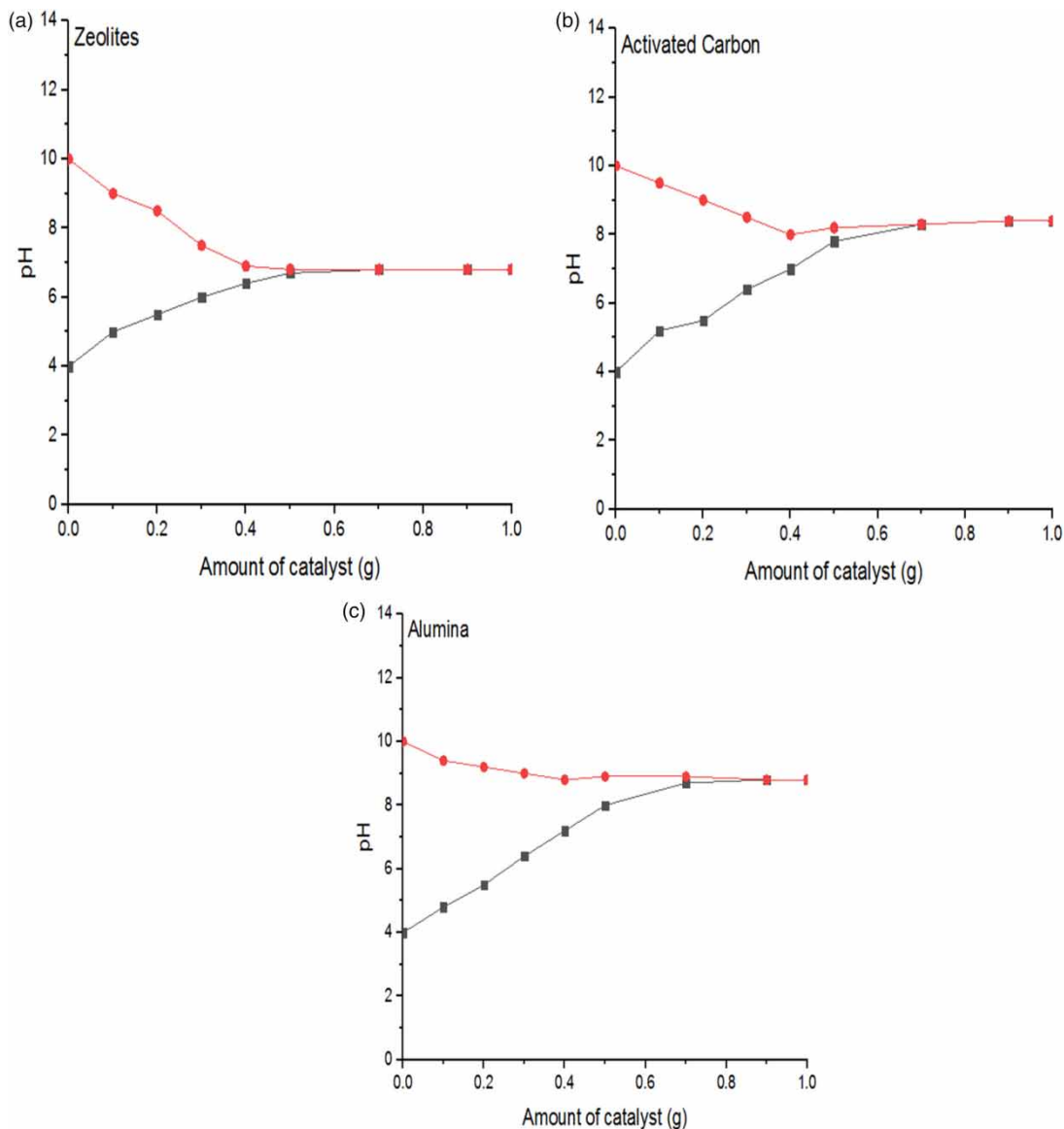


Figure 5 | Point of zero charge of (a) zeolites, (b) activated carbon, (c) alumina.

acidic by-products formed during COPs, which may neutralize the effect of pH change because the catalyst dose may be very low to significantly change the pH during COPs. The activated carbon shows the variation from 4 to 6 as the catalyst dose increases. At neutral conditions, the effect of catalyst dose on the pH of the process was also investigated (Figure 6(b)). At pH 7 with 1-gram catalyst dose of alumina, the pH changes to 6.5 and it reaches 7 when the catalyst dose increases to 2 g. In the case of activated carbon with 1 gram of catalyst dose, the pH was almost 7 and it remained the same as the catalyst dose increased. The effect of catalyst dose on the pH of the process was also investigated at basic conditions (Figure 6(c)). The results indicate that the catalyst

dose significantly changes the pH of the process. When the pH of the process changes, the efficiency of the processes may also change, which may lead to false results while comparing the efficiency of COPs with SOPs. Hence, it is recommended to monitor pH changes in such processes.

CONCLUSIONS

The following conclusions were drawn from the current study:

- (I) The pH changes can affect the COP for alumina, natural zeolites, and alumina.

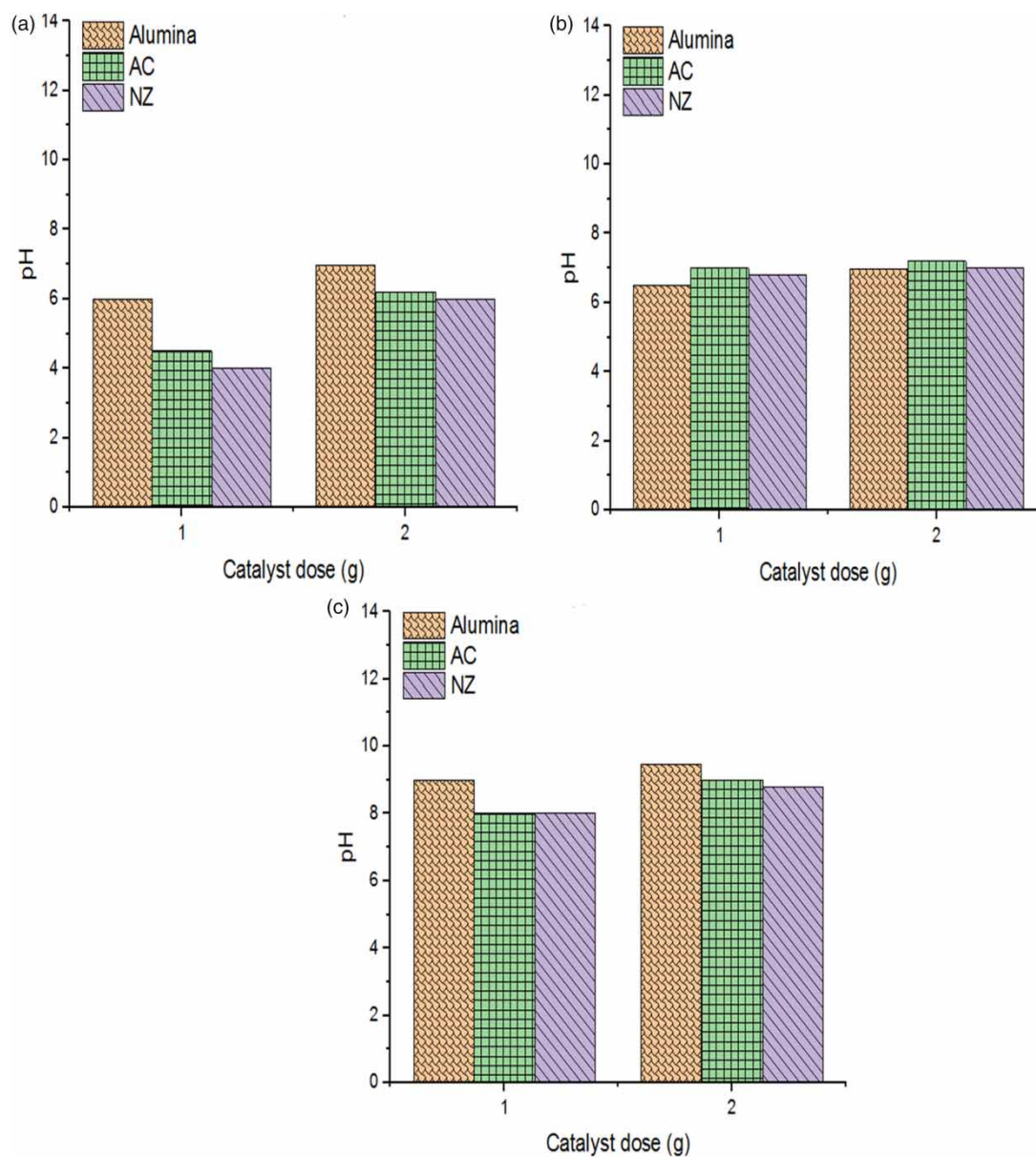


Figure 6 | Effect of catalyst dose on the pH of process (a) pH 4, (b) pH 7, (c) pH 10.

- (II) The AC shows the highest decolorization efficiency (82%) compared with NZ and Al_2O_3 at pH 7. Hence, determination of pH during the catalytic ozonation process is necessary to evaluate the actual performance of the catalyst.
- (III) The catalyst dose and point of zero changes play an important role in pH changes in the presence of materials.
- (IV) The nature of the catalyst is vital as it may change the pH as well as the efficiency of the process.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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