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CATALYTIC OZONATION ON IRON-LOADED RICE HUSK ASH/PEANUT SHELL ASH FOR THE REMOVAL OF ERYTHROMYCIN IN WATER

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Abstract

This study investigates the mechanism and efficiency of catalytic ozonation process on iron-loaded rice husk ash (Fe-RHA) and Peanut shell ash (Fe-PSA) for the Erythromycin removal from aqueous solution. In the current study, the COD removal efficiency of Erythromycin was studied in simple ozonation and catalytic ozonation using Fe-RHA/O₃ and Fe-PSA/O₃ processes. The operational parameters such as pH effect, catalyst dose, and reuse performance of the catalyst were studied. Moreover, the hydroxyl radical scavenger effect and superoxide ion formation were investigated to understand the mechanism of processes. The results revealed the maximum COD removal efficiency of 91 % at pH 4.0 using Fe-RHA catalyst at an optimum dose = 0.8 g, temperature = 25 °C and initial concentration of 50 ppm. While Fe-PSA/O₃ process show high removal efficiency of 83 % at pH = 8.0 (near wastewater pH, 6.0-9.0) at optimum dose = 0.8 g, temperature = 25 °C and initial concentration of 50 ppm. The TBA effect and Superoxide ion formation studies reveal that Fe-PSA operates as an advanced oxidation catalyst as compared with Fe-RHA at pH 8.0. Both the catalysts showed reasonable re-use performance with more than 70 % removal efficiency even after the third cyclic run. Hence, it is concluded that Fe-PSA shows excellent performance as compared with ozonation alone and Fe-RHA/O₃ process at wastewater pH.

Key words: catalytic ozonation, erythromycin, peanut shell ash, rice husk ash, superoxide ion

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1. Introduction

Water resources are being polluted by the industrial, hospital and municipal pollutants during the recent years, with an increasing number of pharmaceuticals and endocrine disrupting chemicals, which has created severe environmental concern. Implementation of safe and environment-friendly techniques are required to maintain and balance the environment and wastewater quality while controlling water pollution (Gomes et al., 2017; Gunten, 2003).

Many methods are used for pharmaceuticals removal in water and wastewater such as ion exchange (Liu et al., 2018), coagulation (Gadekar and Ahammed, 2016), reverse osmosis (Abid et al., 2012), flocculation, ozonation and adsorption (Wang et al., 2018). Catalytic ozonation is the most studied advanced oxidation process in the recent few years (Nawrocki and Kasprzyk-Hordern, 2010). It was found to be highly effective and economically feasible for wastewater treatment (Mehrjouei et al., 2014). Various materials were tested as support in catalytic

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processes in recent studies. For example, activated carbons (Akhtar et al., 2011), zeolites (Chen et al., 2018; Gümüş and Akbal, 2017), minerals (Dong et al., 2007), rice husk ash and reduced graphene oxide (Nidheesh, 2017) etc. These supports were loaded with various metal oxides as active sites. However, less attention was paid to elucidate the role of support in such a catalytic ozonation process. It is indeed important to elucidate the role of adsorption, the pH effect on the active sites on support and role of active sites in the production of active oxygen species, etc (Nawrocki and Kasprzyk-Hordern, 2010; Nidheesh, 2017; Zhang et al., 2008). Therefore, in this paper investigation focuses on the comparative study of two different supports (rice husk ash and peanut shell ash). These supports were loaded with similar active sites (iron), such a study may assist in further understand the mechanism for catalytic ozonation process in to the above-mentioned technique on a larger scale.

Over the past century, environmental pollution has increased exponentially affecting the environment as well as humans and aquatic life in different ways. The main domestic and industrial pollutants include organic and inorganic substances like pharmaceuticals, industrial solvents, food residues, detergent, insecticides, herbicides, disinfection by-products, dyes, heavy metals, fertilizers, nutrients, silts and sediments (Soni et al., 2006). Traces of pharmaceuticals are present in the environment such as surface and groundwater (Kümmerer, 2009). Pharmaceutical compounds become part of water sources after their excretion from humans and animals (Saeid et al., 2018). These may not easily degrade and become part of the environment. Previous studies reveal that the agricultural and food by-products such as almond shells, peanut shells, orange peel, rice husk, straw, date pit, and banana peel are very effective for the removal of pharmaceuticals (Bharathi and Ramesh, 2013). In the current work, the application of iron impregnated rice husk ash (RHA)/peanut shell ash (PSA) was studied as catalysts in the catalytic ozonation process for Erythromycin removal in aqueous solution. This work intends to have a comparison between Fe-PSA and Fe-RHA as heterogeneous catalysts, which may help to understand the nature of two materials and to develop economical and highly efficient catalysts based on agricultural waste products which may bring environmental and economic benefits in the studied area. Furthermore, the parameters like pH, catalyst dose, reuse performance of the catalyst, superoxide ion formation and TBA effect on the removal of Erythromycin in catalysts assisted catalytic ozonation process (Fe-PSA/Fe-RHA/O₃) were studied to understand the process mechanism.

2. Material and methods

2.1. Materials and reagents

Erythromycin was procured from Sigma Aldrich U.K. whereas, rice husk was gathered, and

peanut shell was procured from the market. All the chemicals were used without further purification. The pH adjustments of the solution were done using 1N solutions of HCl and sodium hydroxide. The obtained husk and shells were washed with de-ionized water to separate any dirt, dried in air for 48 hours and burnt in the furnace at 600 °C to obtain ash.

2.2. Stock solution of erythromycin

The stock solution of Erythromycin was first prepared (from which a standard solution of 50 mg/L was prepared for further experimentation). Then the flask was placed in a sonicator for 30 minutes to get a clear and fully dissolved aqueous solution of Erythromycin. The flask was covered with aluminum foil to prevent any interference of light.

2.3. Catalyst preparation

For the preparation of the iron (II) oxide loaded to the RHA/PSA catalyst, the incipient impregnation method (Ikhlaiq et al., 2019) was used, in this method, 6 g of dried RHA/PSA was added to 30 mL of FeSO₄·7H₂O, 0.176 M solution. Reflux was maintained at 60 °C with stirring for about 6 hours. Successively, the RHA/PSA was filtered then residue was washed unless a constant pH is obtained with no color in supernatant remains and then oven-dried at 110 °C.

2.4. Catalyst characterization

The composition of raw catalyst (RHA, PSA) and after iron impregnation (Fe-RHA, Fe-PSA) was elucidated by energy-dispersive X-ray spectrometer (EDX), JSM 6010LA. The surface area and pore size of PSA, RHA, Fe-RHA, and Fe-PSA were obtained by the Brunauer-Emmett-Teller (BET) technique ASAP 2020. The N₂ adsorption-desorption isotherms were developed at 77 K using Micrometrics ASAP 2020 analyser. The sample was first degassed for 6 hours before analysis.

The adsorbate gas was injected into the analyser and the gas pressure was continuously monitored at fixed intervals. The adsorption kinetic data was developed, and nonlocal density functional method was applied to determine the pore distribution using slit pore model.

2.5. Removal efficiency experiments

These experiments were carried out in an ozone bubbler system to elucidate the removal efficiency of Erythromycin in aqueous solution. The COD analysis of the samples was performed before and after treatment by standard open reflux titrimetric method (Eaton et al., 2005). Ozonation experiments were done in two phases with simple ozonation and catalytic ozonation. Ozonation was studied in a semi-batch reactor of 500 mL capacity. In this experiment for each run 450 mL of working solution was taken. The

removal efficiency (Kumar et al., 2016) was evaluated as (Eq. 1)

$$COD\ Removal\ (\%) = [(COD_0 - COD_t) / COD_0] * 100 \quad (1)$$

where: COD_0 and COD_t be the chemical oxygen demand at time 0 and time t respectively.

2.6. Ozone dose quantification

The ozone was supplied from the ozone generator (Sky zone, Pakistan Model DA12025B) with a capacity of 1 g/hr. To determine the ozone dose iodometric method was used. The ozone released from the reaction system was trapped into the two sets of 200 mL solutions of 2% potassium iodide. To liberate iodine, quenching was done with 2N H_2SO_4 . Finally, iodine titration was done against 0.005 N $Na_2S_2O_3$. Ozone dose was determined as (Eq. 2)

$$Ozone\ Dose\ (mg / min) = (V * N * 24) / T \quad (2)$$

where: V -Volume of the titrant used, N - $Na_2S_2O_3$ normality, T -Time of ozonation.

2.7. Analysis of NBD-Cl product and superoxide ion detection

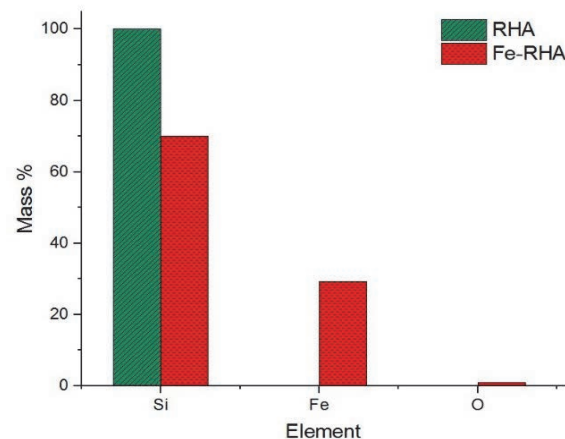
The NBD-Cl formed in each sample was quantified by absorption studies using UV-Vis spectroscopy (Perkin-Elmer Lambda 35) at 470 nm. The samples were filtered and analysed in a 1.0 cm cell. The KO_2 (source of superoxide) and NBD-Cl reaction was used to confirm the NBD-Cl product formation. Finally, a calibration curve was drawn using absorbance (470 nm) versus $^{\circ}O_2^-$ concentration (at various concentrations of KO_2). The concentration of superoxide ion radicals was evaluated from the calibration curve.

3. Results and discussion

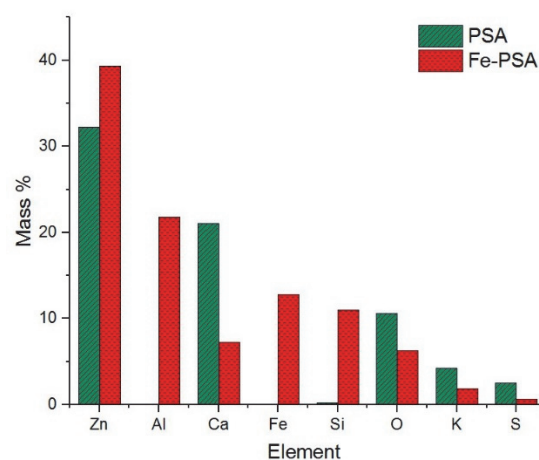
3.1. Catalyst characterization

The EDX spectra of RHA, Fe-RHA, PSA, and Fe-PSA are shown in Fig. 1. EDX results of iron-loaded RHA and PSA confirmed the presence of a minute quantity of Fe. The results of the point of zero charge, the surface area is given in Table 1. The point of zero charge (pH_{pzc}) of Fe-PSA was at basic pH (8.8), while pH_{pzc} Fe-RHA was on the acidic side (3.3).

This may be due to the different nature of both materials, since rice husk is 99% silica, while PSA may contain silica, alumina and trace amount of other metal oxides. Previous findings indicate that alumina has pH_{pzc} on the basic side (Qi et al., 2009). Therefore, it is good to study both supports loaded with iron.



(a)



(b)

Fig. 1. EDX of (a) RHA, and Fe-RHA, (b) PSA, and Fe-PSA

Table 1. Surface area, Pore Size and Point of zero charge of iron-loaded Rice Husk and Peanut Shell ash

Material	BET Surface Area (m^2/g)	Average Pore Size (nm)	pH_{pzc}
Fe- RHA	80.3	19.3	3.3 ± 0.3
Fe- PSA	17.13	14.20	8.8 ± 0.4

3.2. Effect of catalyst dose

Fig. 2 indicates that with the rise in the dose of catalyst (0.2g, 0.5g, and 0.8 g), removal efficiency increases which may be because of increased active sites may present at higher catalyst dose that results in the production of a high amount of hydroxyl radicals. Hence, there was more increased catalytic activity (Benitez et al., 2001). As the chemical oxygen demand efficiency of erythromycin was increased from 49 to 77 % in presence of Fe-RHA (Fig. 2), while COD removal efficiency was 49 to 83 % in the case of Fe-PSA.

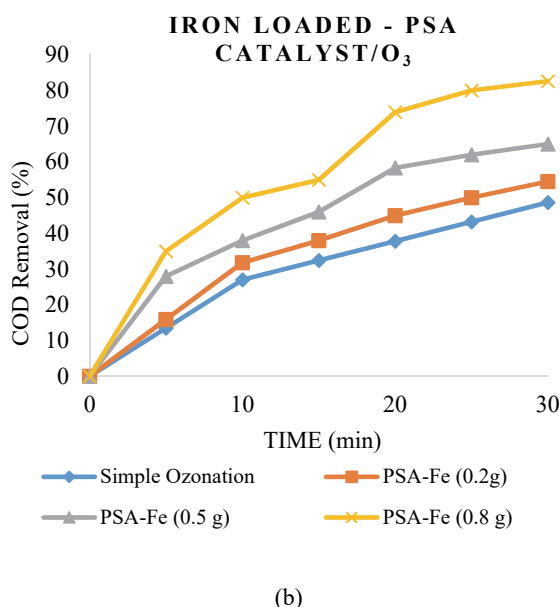
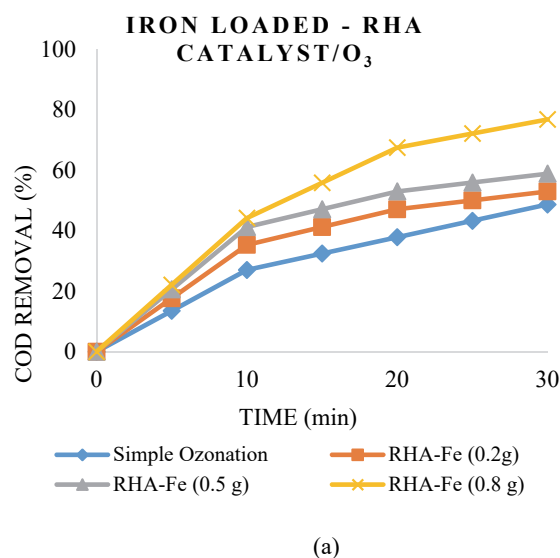


Fig. 2. Effect of (a) Fe-RHA and (b) Fe-PSA catalysts dose effect (pH= 8.0; Catalyst amount = 0.2-0.8 g; V = 450 mL; O₃ = 0.9 mg/min; T = 23 ± 0.2 °C; t = 30 minutes)

3.3. Effect of pH on erythromycin removal

The pH highly influences the removal efficiency in simple and catalytic ozonation (El Haddad et al., 2014). Since the pH of solution and point of zero charge of the material may manipulate the nature of active sites on a catalyst which may affect the performance of a catalyst. Therefore, the effect of pH for removal of Erythromycin was analysed by monitoring the COD removal.

The results (Fig. 3) reveal that Erythromycin removal efficiency was highest at pH value 4.0 ± 0.1 on iron-loaded rice husk catalyst that is 91% as compared to pH values 8.0 (77 %) and 11.0 (82 %). While iron-loaded Peanut shell ash catalyst showed the highest removal efficiency at pH value 8.0 ± 0.1 that is 83% as compared to pH values 4.0 (70 %) and 11.0 (75 %).

This behaviour can be clarified with respect to the various forms of Erythromycin and iron-loaded catalysts at various pH values (Wu et al., 2008). The Fe-RHA may have protonated surface oxygen near its point of zero charge and that may result in high catalytic activity because of surface OH groups interaction with ozone (Wang and Bai, 2017; Wu et al., 2008; Zhang et al., 2008). While at basic pH Fe-RHA surface may be deprotonated and hence results in a lack of catalytic activity. The results obtained from Fe-PSA/O₃ process further confirm our hypothesis that surface hydroxyl groups on catalysts carry the main effect in catalytic ozonation processes (Wang and Bai, 2017; Zhang et al., 2008). Since Fe-PSA highest COD removal efficiency was achieved (as compared with only ozonation, Fig. 3) when pH was near the point of zero charge of Fe-PSA (Wang and Bai, 2017; Wu et al., 2008). In addition to the above reasons, the adsorption of pollutants may also be important in catalytic ozonation processes. At pH 4.0 Erythromycin was present in its ionizable form (positively charged as pKa value of Erythromycin is 8.2) and iron-loaded rice husk was also present in its ionizable form slightly negatively charged to some extent as pH_{pzc} of iron-loaded rice husk was found to be 3.3 which facilitates the interaction between the two oppositely charged species. Whereas, at pH 8.0 and 11.0 both constitutes

Erythromycin and iron-loaded rice husk ash catalyst may possess similar charges that are positively charged surface and negatively charged surface respectively. It will weaken the electrostatic interaction between them. While in the case of Fe-PSA the surface may be slightly positively charged at pH 8.0 (studied pH slightly less than the point of zero charge), therefore, Fe-PSA shows significantly higher catalytic activity nearby its point of zero charge (Fig. 3b).

In this study, two different materials (Fe-PSA and Fe-RHA) were compared as heterogeneous catalysts in catalytic ozonation process and with single ozonation under various conditions for Erythromycin removal in aqueous solution. The results (Fig. 3) indicate that both the catalyst show significant catalytic performance.

For example, the Erythromycin removal efficiency was 91 % with Fe-RHA at pH 4.0 and 83 % with Fe-PSA at pH 8.0. The lack of catalytic activity at pH 11.0 for both catalysts may be due to the significantly high amount of hydroxyl radicals that decompose aqueous O₃ to form hydroxyl radicals and catalyst surface deprotonation. However, it is important to mention here that the studied catalysts were found to be highly effective near wastewater pH ≈ 6.0-9.0.

At highly alkaline pH 11.0, the catalytic performance decreases due to the large availability of hydroxyl radicals which further decompose aqueous O₃ to form HO• which can block the active sites of the catalyst (Ikhlaiq et al., 2019). The reduced availability of catalyst active sites at pH 11.0 reduces the removal efficiency.

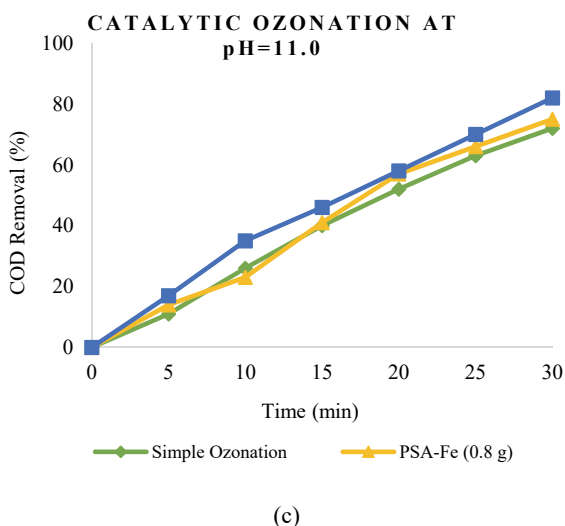
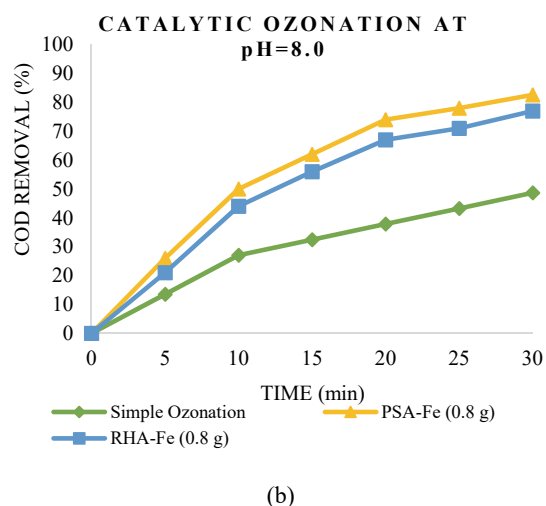
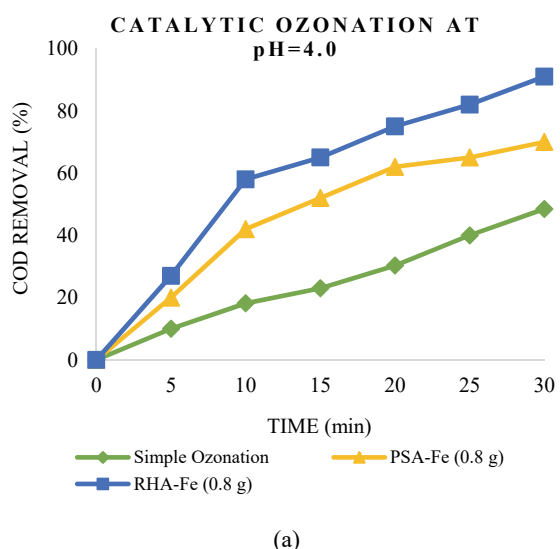


Fig. 3. Effect of pH on Removal of Erythromycin for Simple Ozonation, Fe-RHA and Fe-PSA- (a) pH= 4.0, (b) 8.0 and (c) 11.0; catalyst amount = 0.8 g; V = 450 mL, T = 23 ± 0.2 °C; t = 30 minutes)

3.4. Catalyst reuse performance

In order to determine the stability of both catalysts, their reuse performance was assessed for three successive cycle runs. Catalyst Reuse test was performed to check the ability of RHA-Fe and PSA-Fe for reuse. Iron-loaded peanut shell ash catalyst showed 83% removal when used for the first time and 79% removal even after using it three times (Fig. 4). Rice husk ash catalyst showed 77% removal when used for the first time and 73% removal even after using it three times (Fig. 4). Although, Peanut shell ash was found to be a better catalyst as compared to iron-loaded rice husk ash at studied pH (pH = 8.0). Moreover, a slight reduction in the treatment efficiency of both catalysts may be attributed to the Fe leaching out from the catalyst surface (Ikhlaiq et al., 2018; Kruanak and Jarusutthirak, 2019).

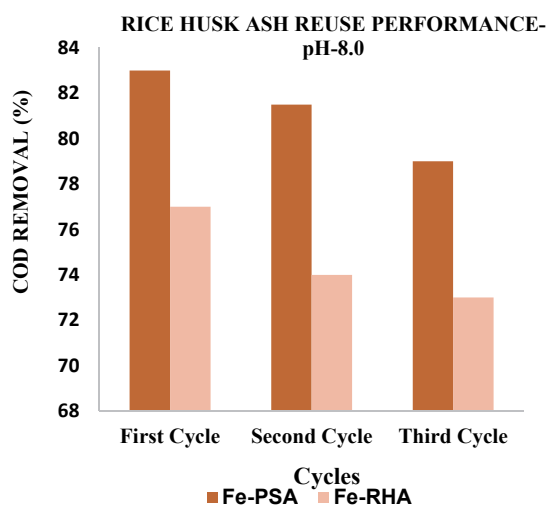


Fig. 4. Reuse performance of iron loaded rice husk and peanut shell ash catalysts. (pH= 8.0; catalyst amount = 0.8g; V = 450 mL, T = 23 ± 0.2 °C; t = 30 minutes)

3.5. Effect of TBA

TBA (Ter-butyl alcohol, 50 ppm) was added to the catalytic ozonation system to elucidate the catalytic activity. TBA acts as a HO[•] radical scavenger due to very high reactivity. Fig. 5 shows that the COD abatement efficiency of Erythromycin was reduced in the presence of the Fe-PSA/O₃ process as compared with only ozonation and Fe-RHA/O₃ process (at pH = 8.0).

It is evident from results that removal efficiency decreased in catalytic ozonation which could be since tertiary butyl alcohol (TBA) acts as hydroxyl radical scavenger at pH 8.0 (Jaafarzadeh et al., 2017). As the COD removal efficiency was reduced from 83 % to 52 % and 77 % to 59 % in the presence of TBA, respectively for Fe-PSA and Fe-RHA.

The results presented in Fig. 5b clearly indicates that difference in COD removal without and with TBA was the highest in the case of Fe-PSA/O₃, which clearly support our hypothesis that at pH 8.0 (near Fe-PSA p*H*_{pzc}), the interactions of surface hydroxyl groups of Fe-PSA with aqueous ozone may result in the hydroxyl radicals generation (Gümüş and Akbal, 2017; Wang and Bai, 2017; Zhang et al., 2008). However, for Fe-RHA at pH = 8.0, the surface of Fe-RHA may be deprotonated hence the hydroxyl radical production may be limited (Gümüş and Akbal, 2017).

3.6. Formation of superoxide ion radicals

Some findings indicate that superoxide ion radicals may form in catalytic ozonation processes (Nawrocki and Kasprzyk-Hordern, 2010; Wang and Bai, 2017; Zhang et al., 2008). In current investigation superoxide ion radical formation was investigated to

understand the mechanism of catalytic ozonation with iron coated materials of different natures. The results presented in Fig. 6 indicates the high amount of superoxide ion radical production in the case of Fe-PSA/O₃ as compared with single ozonation and Fe-RHA/O₃. This may due to the lack of surface hydroxyl group availability at studied pH (pH = 8.0) when Fe-RHA was used as catalyst, the catalyst surface may be negatively charged (Nawrocki and Kasprzyk-Hordern, 2010).

However, on the other side, the Fe-PSA catalyst surface may be protonated that leads to the production of superoxide ion radical while interacting with aqueous ozone (Nawrocki and Kasprzyk-Hordern, 2010; Wang and Bai, 2017; Zhang et al., 2008). It is important to mention here that the reduction in superoxide ion production after first the 10 minutes may be ascribed to the NBD-Cl product reaction with hydroxyl radicals and ozone.

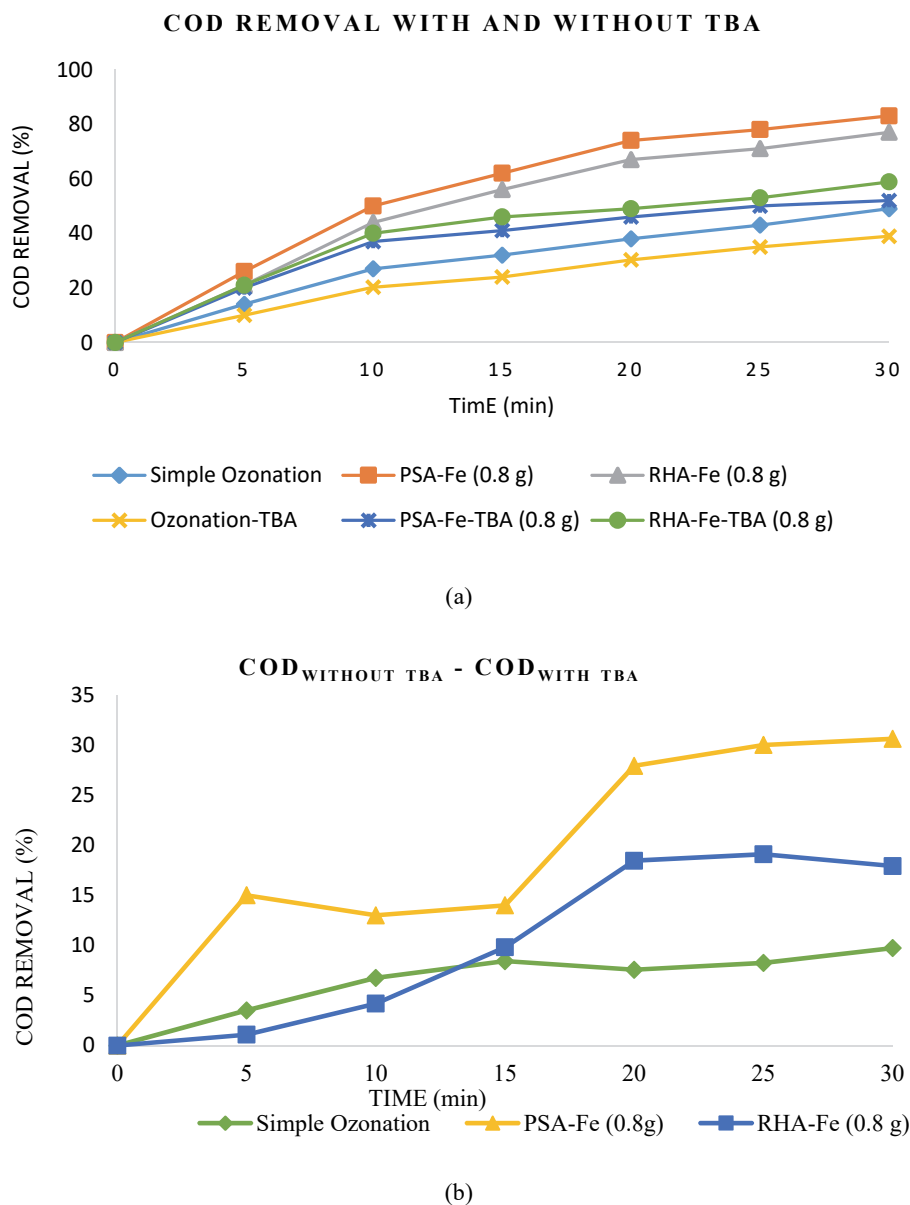


Fig. 5. Tertiary butyl alcohol effect on iron impregnated rice husk (a), Peanut shell ash catalysts and Simple Ozonation (b) (pH= 8.0; catalyst amount = 0.8 g; V = 450 mL, T = 23 ± 0.2 °C; t = 30 minutes)

3.7. Mechanism

The catalytic ozonation processes with Fe loaded peanut shell ash as support or Fe loaded rice husk ash (at pH nearby the point of zero charge) follows the proposed mechanism given in Fig. 7 which shows the production of superoxide ion for catalytic ozonation process and aqueous ozone interactions with surface OH groups on the catalyst surface (Gümüő and Akbal, 2017; Nawrocki and Kasprzyk-Hordern, 2010; Wang and Bai, 2017; Zhang et al., 2008). Moreover, the TBA effect confirms the generation of hydroxyl radicals in both Fe-RHA/O₃ and Fe-PSA/O₃ processes.

It was hypothesized that formed superoxide ion radicals may further interact with aqueous ozone and water molecules to produce hydroxyl radicals as shown in Fig. 7 (Wang and Bai, 2017; Zhang et al.,

2008). It is indeed important that the point of zero charge of the support may play the main role in the mechanism of such processes (Nawrocki and Kasprzyk-Hordern, 2010). For example, in Fe-RHA/O₃ process (Fig. 4) highest catalytic activity was measured at pH 4.0 which was nearby to the point of zero charge of studied catalyst. This may be because at pH higher the point of zero charge, the catalyst surface becomes deprotonated. Therefore, the lack of availability of surface hydroxyl groups may result in a reduction in catalytic activity (Wang and Bai, 2017; Zhang et al., 2008). Moreover, in the case of Fe-PSA and Fe-RHA at pH 11.0 (Fig. 3) both the catalyst was found to be ineffective and COD removal efficiency was nearly similar to single ozonation, this again confirms that at pH above p*H*_{pzc} of catalyst, the involvement of surface hydroxyl groups may be limited.

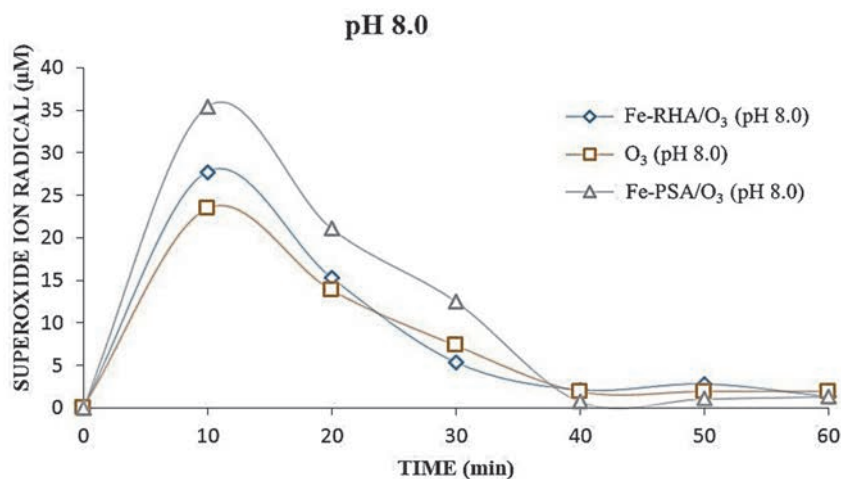


Fig. 6. Superoxide product formation in catalytic ozonation on iron impregnated Rice husk, Peanut shell Ash Catalysts and simple ozonation (NBD-Cl = 20 mg/L; pH= 8.0; catalyst amount = 0.8 g; V = 450 mL, T = 23 ± 0.2 °C; t = 30 minutes)

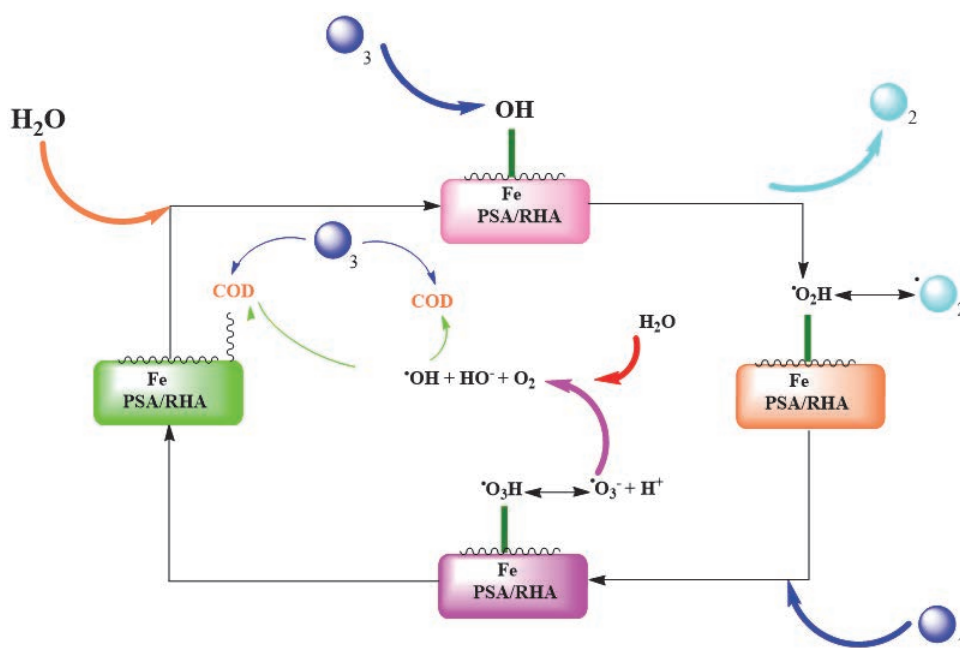


Fig. 7. Proposed mechanism of catalytic ozonation on Fe-PSA and Fe-RHA at pH near their point of zero charge values

4. Conclusions

Following conclusions were drawn based on results obtained:

1. The research concludes the comparative study of two different materials (Fe-PSA and Fe-RHA) as heterogeneous catalysts in the catalytic ozonation process for Erythromycin removal in aqueous solution.

2. Catalytic ozonation on Fe-RHA and Fe-PSA was more effective than simple ozonation.

3. The nature of support, pH, and point of zero charge impart a significant role in catalyst activity.

4. The catalysts were found to be highly effective near wastewater pH 8.0, with 83 % Erythromycin removal efficiency achieved by Fe-PSA and 77 % with Fe-RHA.

5. Both the catalysts showed reasonable re-use performance with more than 70 % Erythromycin removal even after the third cyclic run.

6. The mechanism of both Fe-RHA/O₃ and Fe-PSA/O₃ processes was found to be pH-dependent. Both processes stimulate the production of •OH radicals and superoxide ion radicals.

Acknowledgments

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