



Article Synergistically Improved Catalytic Ozonation Process Using Iron-Loaded Activated Carbons for the Removal of Arsenic in Drinking Water

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Abstract: This research attempts to find a new approach for the removal of arsenic (As) from drinking water by developing a novel solution. To the author's knowledge, iron-loaded activated carbons (Fe-AC) have not been previously applied for the removal of As in a synergistic process using ozonation and catalytic ozonation processes. The As was investigated using drinking water samples in different areas of Lahore, Pakistan, and the As removal was compared with and without using catalysts. The results also suggested that the catalytic ozonation process significantly removes As as compared with single ozonation and adsorption processes. Moreover, a feed ozone of 1.0 mg/min and catalyst dose of 10 g was found to maintain a maximum removal efficiency of 98.6% within 30 min. The results of the catalyst dose–effect suggested that the removal of As tends to increase with the increase in catalysts amount. Hence, it is concluded that the Fe-AC/O₃ process efficiently removes As in water. Moreover, it was established that the Fe-AC/O₃ process might be regarded as an effective method for removing As from drinking water compared to the single ozonation and adsorption processes.

Keywords: As removal; drinking water; ozonation; water purification

1. Introduction

Water is essential for life, and it plays a pivotal role in life. Due to inadequate water supply systems and improper management of resources, developing countries face water deficiency and contamination [1–3]. Pakistan is an example of a developing country. The country has depleted its open water assets; it is considered water-focused and will probably have water scarcity in the near future [4–7]. According to the World Bank Strategic Country Environmental Assessment (WB-SCEA), 2006 per capita water accessibility in Pakistan had fallen from 5000 in 1951 to 1100 m³ per annum. According to national data, only 56% of the total population has access to good-quality drinking water. Water has played a significant role in the economic growth of the country. Water is likewise fundamental for hydropower generation, which is substantial for advancing energy production in Pakistan. Water is likewise essential for the urban and country water supply, modern mining needs,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). sanitation, and water disposal. Hence, the role of water is specifically connected with the quality of life and economic development [8–12].

For drinking purposes, groundwater is considered the predominant source worldwide. However, unprocessed groundwater contains As which is undesirable [13,14]. Drinking water contamination with As is one of the severe public issues people face in developing countries. Such exposure has already been reported in many developing countries such as India, Bangladesh, Argentina, China, Vietnam, Cambodia, etc. The As may enter the drinking water via anthropogenic and/or geological sources [15–18]. In the last few years, chronic exposure to As has been observed in Pakistan. Hence, surface- and groundwaters have been considered a major source of As exposure. This exposure may lead to crepitating in the lungs, chronic cough, hypertension, diabetes mellitus, and weakness [15–18], and the measure of As in drinking water ought to be restricted to extremely low qualities for health reasons. The existence of As in water is harmful to health, applicability, and aesthetics. Neurological indications appear in the human body due to enhanced levels of As in water, especially in immature children. Furthermore, a harmful interactive consequence exists in the accumulation of As [19–22]. Therefore, exploring novel methods to remove the As in drinking water is essential.

Arsenic is one of the significant pollutants that have serious health effects, therefore, in the past, extensive research was conducted to study the removal of arsenic by various processes. Among these are adsorption, electro flocculation, membrane filtration, chemical treatment, oxidation methods, etc.

The following (Table 1) are examples of various processes for arsenic removal that have been examined in previous studies.

Treatment Methods	Material	Removal Efficiency	Reference
Adsorption	Iron oxide-multiwalled carbon nanotube (Fe-MWCNT)	Adsorption capacity; As(III)1723 μg/g and As(V) 189 μg·/g	[23]
Adsorption on Membrane Material	PVDF/zirconia blend flat sheet membrane	21.5 mg/g	[24]
Electrocoagulation	Fe and Al electrodes	Fe electrode (93.5%) and 12.5–15 min for Al electrode (95.7%)	[25]
Coagulation, Flocculation/ Dead-end ultrafiltration	FeCl ₃ /polyetherimide- based membrane	96.9%	[26]
Catalytic ozonation/Adsorption	Iron coated zeolite 4Å	100% in 15 mins	[27]

Table 1. Arsenic removal in drinking water through various processes.

For water treatment, the ozonation process has gained interest all over the world. Ozone was used for water treatment in 1940, and around 119 drinking water treatment plants used this technique for water clarification in 1977. This number has been enhanced to at least 1039 [28]. Adsorption [29–32], membrane filtration [33–35], and electroflocculation [36–38] have been utilized extensively in the past to study the removal of As in water. However, membrane filtration and electroflocculation may be expensive, while adsorption was found to be a bit slower than others. In recent years, the oxidation method was discovered to precipitate out and filter As in water. These methods were found to be more efficient and to possess a rapid rate of As removal [39–42]. Among them, the catalytic ozonation process has recently been shown to remove As in drinking water. Ikhlaq et al. [27] found significant removal of As in drinking water using iron-loaded zeolite along with ozonation. The ozone treatment not only precipitates potentially toxic metals but acts as a disinfectant to kill the pathogens in water [27].

Catalytic ozonation is commonly categorized as a type of advanced oxidation activity. In general, the add-on of catalysts could assist ozone decomposition to make large quantities of operational free radical, which results in a speedy debasement and effectual mineralization of organic pollutants. Moreover, in the presence of catalysts, the effectiveness of O_3 activity can also be increased by several levels [43–46].

This study is the authors' continuation of a previous study to explore novel and efficient methods for the removal of As at the household level. The last study involved iron-loaded zeolites in the ozonation processes for the removal of As [43]. In the current investigation, iron-loaded activated carbon was examined for the first time in the catalytic ozonation process to remove As in drinking water. Activated carbons (AC) possess high surface areas and good adsorption capacities compared with zeolites. Hence, they may be utilized for more efficient treatment based on oxidation and the adsorption of potentially toxic metals. Moreover, in the current study, the effect of various parameters such as catalyst dose, ozone flow, adsorption effect, and reaction time was investigated. This study would help to find an efficient treatment option for the removal of As at the household level.

2. Experimentation

2.1. Materials and Reagents

All the chemicals (FeSO₄ for catalyst preparation, potassium iodide, sodium thiosulfate, and starch solution) for the ozonation experiments were obtained from Merck Germany. The activated carbons were obtained from Sigma Andrich, UK. The NaCl, HCl, and NaOH used in point of zero charge were also obtained from Merck Germany. All the chemicals used in this study were of analytical grade and were used without further purification.

The BET method was utilized in order to investigate the surface area and pore size of the studied catalyst (Fe-AC) using a micromeritics USA ASAP analyzer. For that, adsorption isotherm studies were conducted using adsorption and desorption studies of nitrogen at 77 K. Finally, the Kelvin equation was utilized to quantify the surface area and porosities of Fe-AC.

The point of zero charge (pHpzc) of the studied catalyst was determined by the mass transfer method as described elsewhere [47]. In this method, Fe-AC was subsequently added to a beaker containing an electrolyte solution (NaCl) having a concentration of 10^{-3} mol/dm³ (25 mL). The solution was stirred by utilizing magnetic stirring arrangements, and the pH of the equilibrated dispersion was measured. The experiment was performed at an initial pH of 4 and 10. The pH of the solution was monitored and a gradual change in pH with the addition of catalyst was noted and the point where the pH becomes constant was identified as the point of zero charge.

Fe content on the impregnated catalyst was quantified by utilizing energy dispersive X-ray (EDX) analysis using SEM, model JEOL JSM-6480 LV JSM-6010LA coupled with an EDX unit.

The total As was quantified from water samples by utilizing AAS coupled with a graphite furnace as per the standard method [48]. Calibration curves were prepared before the analysis using standard solutions of arsenic. The linear dynamic range was 1–100 μ g/L with a correlation coefficient of 0.9988. The limits of detection and quantifications were found to be 0.08 μ g/L and 0.91 μ g/L, respectively.

2.2. Sampling Study area and Analysis

Lahore, the capital of Punjab, is known for its great historical importance and is the second-largest city in Pakistan [49]. As we talk about its geographic position, it is extended from 31°15′ to 31°45′ N latitude and 74°01′ to 74°39′ E longitude, having an area of 2260 km² [50]. Various sampling locations of Lahore were selected to quantify the As content in areas where water is supplied by the Water and Sanitation Agency (WASA). The tap water was collected from various locations in Lahore (the Mehmood Booti abad, Saggyian, and Mughalpura areas were selected).

After collection, the samples were labeled with the date, time, and name of the location. On the same day, samples were brought to the laboratory and analyzed on an atomic absorption spectrophotometer coupled with a graphite furnace.

2.3. Catalyst Preparation

The catalyst was prepared by the impregnation method as described elsewhere [27]. In this method, AC was first washed with deionized water and dried in an oven at 103 °C for 6 hours. It was impregnated with iron using 6 g FeSO₄ in 100 mL deionized water containing 20 g of activated carbons. The mixture, as mentioned earlier, was agitated at 100 rpm and a temperature of 103 °C using a magnetic string and hot plate arrangement. After evaporating and drying water in the oven at 103 °C, the sample was dipped in 1 M HNO₃ solution overnight to remove any unreacted iron from the AC. Finally, the Fe-AC sample was washed with denoised water until a constant pH was reached and was later placed in a furnace at 550 °C for calcination (2 h).

2.4. Ozonation and Catalytic Ozonation

Simple ozonation and catalytic ozonation processes were performed using a modified batch reactor (Figure 1). The reaction was performed for 30 min at the natural pH of water and room temperature. The experiments were run by varying iron-loaded AC dose, ozone dose, and reaction time. A 400 mL water sample was introduced into the reactor for 30 min for each experiment. The ozone produced from the ozone generator (Sky zone, DA12025B12L, Karachi, Pakistan) was introduced constantly into the batch reactor. Samples were collected at five-minute intervals, and a few drops of 0.025 M sodium thiosulfate were used to quench for removing the residual ozone. After every 5 min interval, a 50 mL of sample was taken to conduct an As removal study. In order to determine the concentration of gas-phase ozone, 5 mL of H₂SO₄ having the strength of 2N was added to potassium iodide (KI) traps (Figure 1) and was titrated against 0.005 N sodium thiosulfate (Na₂S₂O₃) solution. The samples were filtered through 0.45 μ m PTFE filters prior to analysis; the following equation (Equation 1) was used to determine the percentage removal of As in the water samples.

Percentage removal of As =
$$(C_0 - C_t)/C_0 \times 100$$
 (1)

where C_0 is the initial concentration of As in $\mu g/L$, and C_t is the concentration at time interval t.



Figure 1. Schematic diagram of the process with a modified batch reactor [27].

2.5. Determination of Ozone Dose

In this study, the iodometric method was used to calculate the ozone dose [48]. The ozone produced from an ozone generator was introduced to a flask containing 100 mL of 2% KI solution. In order to free iodide, the solution was quenched with 5 mL of (2N) H_2SO_4 . Finally, by using the starch indicator, the solution was titrated against 0.005 N of $Na_2S_2O_3$. The following formula has been used for ozone calculations:

Ozone dose in mg/min =
$$(A + B) \times N \times 24/T$$
 (2)

- A = Titrant ($Na_2S_2O_3$) used for Reactor (I) in mL
- $B = Titrant (Na_2S_2O_3)$ used for Reactor (II) in mL
- $N = Normality of titrant (Na_2S_2O_3)$
- T = Total time of ozonation.

3. Results and Discussion

3.1. Characterizations

Activated carbon coated with iron was used in this study. Some physicochemical properties of the catalyst are present in Table 2. The point of zero charge of the studied catalyst was towards the basic side. The catalyst has a large surface area, which may be good for the adsorption of pollutants on its surface. The pore size of the catalyst was 9.3 angstrom (Å), and the surface area was $1100 \text{ m}^2/\text{g}$ for Fe-AC and 9.1 Å and $1050 \text{ m}^2/\text{g}$ for AC. The slight increase in surface area in the case of Fe-AC may be due to the Fe loading [51]. While comparing the points of zero charge of Fe-AC and AC, it was observed that there was a negligible change. This may be due to the loading of minute quantities of iron on AC.

Table 2. Some physicochemical properties of Fe-AC.

Material	Surface Area BET (m ² /g)	Pore Size (Å)	Iron Content [%]	Point of Zero Charges (pH _{pzc})
Fe-AC	1100	9.3	5.28	8.8 ± 0.2
AC	1050	9.1	-	9 ± 0.1

The drinking water samples from nine different locations in Lahore were characterized in terms of As presence. The results showed that all points having As concentrations exceeded the World Health Organization (WHO) guidelines. Most of the analyzed samples from the various selected locations (Table 3) also exceeded Punjab environmental quality standards (PEQS). It was found that the parameters studied for drinking water quality in the current study mostly followed the local standards and international guidelines. Moreover, most of the results are in agreement with the previous findings (in the Lahore area) [52].

Table 3. Results of the characterization of nine (9) locations in Lahore.

No	. Sample Name	Sample Code	рН	Arsenic (µg/L)	Turbidity (NTU)	Chlorides (mg/L)	Fecal Coliforms MPN/100 mL	Total Dissolved Solids (TDS) mg/L	Hardness as CaCO ₃
1	Mughal Pura	MU 1	7.6 ± 0.2	58 ± 8	1.6 ± 0.2	48 ± 7	12 ± 4	750 ± 55	383 ± 25
2	Mughal Pura	MU 2	7.8 ± 0.3	45 ± 4	2.6 ± 0.5	52 ± 11	NIL	648 ± 45	590 ± 50
3	Mughal Pura	MU 3	8.0 ± 0.3	55 ± 10	1.5 ± 0.5	75 ± 15	NIL	591 ± 39	423 ± 21
4	Mehmood Booti abad	ME 1	8.1 ± 0.3	75 ± 7	2.3 ± 0.2	32 ± 9	18 ± 7	715 ± 45	517 ± 39

No	. Sample Name	Sample Code	рН	Arsenic (µg/L)	Turbidity (NTU)	Chlorides (mg/L)	Fecal Coliforms MPN/100 mL	Total Dissolved Solids (TDS) mg/L	Hardness as CaCO ₃
5	Mehmood Booti abad	ME 2	7.5 ± 0.2	66 ± 12	2.6 ± 0.2	88 ± 7	15 ± 5	880 ± 55	664 ± 22
6	Mehmood Booti abad	ME 3	7.9 ± 0.1	68 ± 4	2.9 ± 0.5	52 ± 15	NIL	832 ± 35	465 ± 23
7	Saggiyian pull	SG 1	8.3 ± 0.3	44 ± 5	2.6 ± 0.2	39 ± 7	NIL	694 ± 29	396 ± 21
8	Saggiyian pull	SG 2	8.2 ± 0.1	41 ± 6	1.6 ± 0.2	48 ± 3	NIL	731 ± 55	473 ± 25
9	Saggiyian pull	SG 3	8.2 ± 0.1	58 ± 8	0.6 ± 0.3	58 ± 5	10 ± 3	845 ± 55	511 ± 25
W	HO Guidelines/ EPA/ European		6.5–8.5	10	<5	250	NIL	1000	500
	PEQS		6.5–8.5	50	<5	250	NIL	1000	500

Table 3. Cont.

3.2. Treatment of Arsenic

3.2.1. Comparison of O₃, Adsorption, and Catalytic Ozonation Processes

The comparative studies of various processes, such as ozonation, adsorption, and catalytic ozonation, on iron-containing activated carbons suggested that catalytic ozonation results in the highest removal compared with others (Figure 2). For example, the removal efficiency was 98%, 58%, and 51% (in 30 min) for catalytic ozonation, adsorption, and ozonation processes, respectively. These results are in agreement with some previous findings (the catalytic process has the highest removal) where Fe-zeolite was used as the catalyst [27]. As removal through ozonation alone may be due to the precipitation inside the solution (later samples were filtered using PTFE syringe filters) [27,53]. In the case of catalytic ozonation on Fe-AC, it was hypothesized that hydroxyl radicals produced in such processes might lead to an increase in the rate of AS precipitation [27,53].



Figure 2. Arsenic removal in adsorption, single ozonation, and catalytic ozonation processes (As = 75 μ g/L; O₃ = 1.0 mg/min, O₃/Fe-AC = 10 g/L, pH = 7.6 \pm 0.2; t = 30 min; volume = 1 L, T = 25 \pm 2 °C).

In the case of a single ozonation process, the removal of As may result from its precipitation due to the interactions of molecular ozone and hydroxyl radicals in the

solution [27,54,55]. Since iron-loaded materials' Bronsted and Lewis acid sites may interact with aqueous ozone, the decomposition of aqueous ozone may produce hydroxyl radicals that might result in As removal via precipitation [27,56].

It is important to mention here that the comparison of various processes' O_3 , adsorption, and catalytic ozonation in order to observe which process is better may not be fully justifiable, since the different processes may be efficient under different conditions. However, in the current study, the various processes were compared at drinking water pH (real samples) with fixed material dose and time. In order to investigate the applicability of these processes in real conditions.

3.2.2. Fe-AC Dose Effect

In order to investigate the role of the studied catalyst in the removal of As, the removal of As was investigated at various doses of catalyst in the catalytic ozonation processes while keeping other parameters constant. The results presented in Figure 3 clearly indicate that the As removal increased with the increase in catalyst amount, especially when the catalyst dose was increased from 5 g/L to 10 g/L (Figure 3). This suggested that Fe-AC adsorption and catalytic oxidation processes play a vital role in the removal of As in water. The results further indicated that 10 g/L was the optimum dose (Figure 3).



Figure 3. Catalyst dose effect on catalytic ozonation processes (As = $73 \pm 4 \mu g/L$; O₃ = $1.0 \pm 0.2 \text{ mg/min}$; O₃/Fe-AC = 5 g/L, 10 g/L and 15 g/L; pH = 7.6 ± 0.2 ; t = 30 min; volume = 1 L; T = $25 \pm 2 \degree$ C).

3.2.3. Ozone Dose Effect

The ozone dose effect on the catalytic ozonation process (Fe-AC/O₃) was studied in drinking water using 0.5 mg/min, 1 mg/min, and 1.5 mg/min feed ozone flows. The results presented in Figure 4 show that with the increase in ozone flow, the removal efficiency of As was increased. For example, the removal efficiency of As was 61%, 92%, and 99% at 0.5 mg/min, 1.0 mg/min, and 1.5 mg/min, respectively (Figure 4). The optimum ozone flow was considered to be 1.0 mg/min, keeping in view the economic factors. Therefore, the results suggested that the ozone's oxidative capacity plays a key role in As removal [55]. Therefore, the increase in feed ozone flow may enhance the overall precipitation and removal of As [55,57].



Figure 4. Ozone dose effect on catalytic ozonation processes (As = $69 \pm 4 \mu g/L$; O₃ = 0.5 mg/min, 1.0 mg/min, 1.5 mg/min; O₃/Fe-AC = 10 g/L; pH = 7.6 \pm 0.2; t = 30 min; volume = 1 L; T = 25 ± 2 °C).

3.2.4. Removal of As in Fe-AC/O₃ from Drinking Water

The results presented in Table 4 show that under optimized conditions, the removal of As was found to be highly efficient in drinking water samples selected from various locations in Lahore, Pakistan. All the samples after treatment by the Fe-AC/O₃ process were found to be well within the WHO guidelines and PEQS. This suggested that the studied catalytic process was highly efficient in treating drinking water by removing As, even at household levels.

Table 4. Removal of As from nine (9) locations in Lahore through catalytic ozonation processes ($O_3 = 1.0 \pm 0.2 \text{ mg/min}, O_3/\text{Fe-AC} = 10 \text{ g/L}; t = 30 \text{ min}; \text{volume} = 1 \text{ L}, T = 25 \pm 2 \degree\text{C}$).

Sr#	Sample Name	Sample Code	Arsenic before Treatment (µg/L)	Arsenic after Treatment (μg/L)
1	Mughal Pura	MU 1	58 ± 8	5.8 ± 2
2	Mughal Pura	MU 2	45 ± 4	3.5 ± 0.4
3	Mughal Pura	MU 3	55 ± 10	4.1 ± 0.3
4	Mehmood Booti abad	ME 1	75 ± 7	6.5 ± 2
5	Mehmood Booti abad	ME 2	66 ± 12	6.9 ± 2
6	Mehmood Booti abad	ME 3	68 ± 4	4.4 ± 1
7	Saggiyian pull	SG 1	44 ± 5	2.7 ± 1
8	Saggiyian pull	SG 2	41 ± 6	2.6 ± 1
9	Saggiyian pull	SG 3	58 ± 8	5.6 ± 1
WHO C	Guidelines/EPA/European		1	0
	PEQS		5	0

3.3. Arsenic Removal Mechanism on Fe-AC/O₃ Process

Arsenic exists in various forms in groundwater. Among them, the most common is arsenate (As(V)) and arsenite (As(III)). Moreover, the other forms may be organically bounded arsenic (MMA(III), MMA(V), DMA(III), DMA(V), etc.) [58]. The proposed work

was designed to remove various forms of arsenic (organic and inorganic) in a single hybrid reactor. The As(III) form is mostly removed by oxidation, while As(V) may be removed by adsorption to iron-coated activated carbon. The organic forms of arsenic in groundwater may be removed via a two-step mechanism, namely the breakdown of organic compounds via oxidation and adsorption of arsenic on a catalyst. The hydroxyl radicals generated in the catalytic ozonation process may help to promote the oxidation of arsenic (hydroxyl radicals oxidize As(III) to less toxic As(V)) [30,56,57,59,60] leading to its precipitation and adsorption to the surface of iron-coated activated carbon. The following equations explain the transformation of arsenic via oxidation involving various reactive oxygen species, such as °OH, O_2 , and $O_2^{\circ-}$ [30,56,57,59,60].

$$AsIII(OH)_3 + ^{\circ}OH \rightarrow AsIV(OH)_4$$
(3)

$$AsIII(OH)_3 + O_2^{\circ -} + H_2O + H^+ \rightarrow AsIV(OH)_4 + H_2O_2$$

$$\tag{4}$$

$$AsIV(OH)_4 \rightarrow As(III) + As(V)$$
 (5)

$$AsIV(OH)_4 + O_2 \rightarrow As(V) + HO_2/O_2^{-}$$
(6)

$$AsIV(OH)_4 \to HAsIVO_3^- + H^+ + H_2O \tag{7}$$

It is important to mention here that the oxidation process leads to the transformation of arsenic As(III) to the As(V) form. However, the oxidation processes are not very efficient for As(V), since arsenic is in its highest oxidation state; on the other hand, the high affinity of Fe ions towards the As(V) and As(III) forms that have been attached to activated carbons in the current investigation leads to removal via the adsorption process as explained by the following equations [61].

$$\equiv \text{Fe-OH} + \text{AsO}_4^{3-} + 2\text{H} + \rightarrow \equiv \text{Fe-HAsO}_4^- + \text{H}_2\text{O}$$
(8)

$$\equiv \text{Fe-OH} + \text{AsO}_4^{3-} + 3\text{H} + \rightarrow \equiv \text{Fe-H}_2\text{AsO}_4^{\circ}\text{H}_2\text{O}$$
(9)

$$\equiv \text{Fe-OH} + \text{AsO}_3^{3-} + 3\text{H} + \rightarrow \equiv \text{Fe-H}_2\text{AsO}_3 + \text{H}_2\text{O}$$
(10)

$$\equiv \text{Fe-OH} + \text{AsO}_4^{3-} \rightarrow \equiv \text{Fe-OHAsO}_4^{3-} \tag{11}$$

In order to further understand the role of Fe in such processes and to study the stability of catalysts, the reuse performance of the catalyst was studied (Figure 5). The catalyst's reuse performance was evaluated without and with surface regeneration (with NaOH treatment) as described elsewhere [62]. The results presented in Figure 5a clearly suggested that Fe-AC/O₃ process shows excellent performance even after three successive runs when catalyst surface was regenerated with NaOH treatment (removal of adsorbed arsenic). However, in the case of untreated catalyst (Figure 5b), about 16% decrease in As removal efficiency was observed (run 3). This suggested that the adsorption of As on active sites (Fe) of the studied catalyst may also play a key role in the Fe-AC/O₃ process. The NaOH treatment of the already-used samples helps with the removal of adsorbed As on catalyst surface, which leads to the availability of more active sites on the used catalyst for the next run [62].

In addition to the above, Fe leaching tests were also conducted to understand the effect of dissolved, leached-out Fe, if any. The results presented in Figure 5c (average iron leaching in both treated and untreated catalyst) suggested that only a minute quantity of Fe was found to leach out during three successive runs of the Fe-AC/O₃ process. On the other hand, there no significant decrease in As removal efficiency was observed even after three successive runs in the case of regenerated catalyst (Figure 5a). This suggests that even a slight leaching out of iron in such processes may play an important role in the removal and precipitation of iron in ozonation processes [63].



Figure 5. Reuse performance of catalytic ozonation processes (As = $6 \pm 6 \mu g/L$; O₃ = $1.3 \pm 0.2 \text{ mg/min}$; O₃/Fe-AC = 10 g/L; pH = 7.6 ± 0.2 ; t = 30 min; volume = 1 L; T = $28 \pm 2 \degree$ C).

Nishimura et al. (2001) [63] found that the metal ions in water, such as Mn and iron, help to precipitate the As in ozonation processes (Equation 12). Moreover, it was reported that the ozonation leads to the oxidation of metals to a higher oxidation state that reacts with As species in water leading to its precipitation.

$$M^{3+}+H_3AsO4 \rightarrow MAsO_4 + 3H^+$$
(12)

Therefore, in the current process, the leached-out iron and the presence of other metals such as Mn in drinking water may have a positive role in the removal of arsenic in the Fe-AC/O₃ process.

The current process may involve various sub-processes that may lead to As removal, such as adsorption, oxidative precipitation, and breakdown of organo-As complexes in water to facilitate the removal of As in water [63,64].

4. Discussion

It is important to mention here that in the catalytic ozonation processes, not only active sites (Fe in the current study) play a vital role in pollution remediation. In fact, the role of support (base material, such as zeolites, activated carbons, reduced graphene oxide, etc.) is indeed important, since various materials have different properties, natures, and stability under various conditions. Properties such as the point of zero charge, surface area, pore size, binding ability with metals, and hydrophobicity and hydrophilicity are indeed important in both the adsorption and catalytic ozonation processes. Therefore, materials of different natures should be examined to investigate the various pollutants in real conditions. Many materials have been utilized as support in the catalytic ozonation process for pollution remediation. Moreover, metals and metal oxides have been doped as active sites on various materials. Among them, iron-type catalysts have been frequently studied due to their high catalytic activity and relatively low price [25]. Additionally, it has been reported that the loading of iron on activated carbons could further improve the catalytic activity [25,65–70].

The arsenic removal studies were successfully examined by using various processes, among them adsorption, membrane filtration, oxidation, coagulation, flocculation, electro flocculation, and hybrid processes. Each method has advantages and disadvantages [23–27,71–75].

In some recent findings, catalytic ozonation was examined for the first time to investigate arsenic removal in a drinking water sample. Ikhlaq et at. (2021) [27] examined the Fe-Zeolite $4A/O_3$ process, where it was hypothesized that oxidation and adsorption of arsenic in the catalyst was the main reason for arsenic removal in drinking water. In this study, the ozonated samples were finally filtered via 0.45 microns syringe filters to precipitate the arsenic in water. Moreover, the results suggested 100% removal of arsenic (As = 42–68 µg/L). The current findings are in agreement with the previous study, with 100% removal efficiency of arsenic (As = 41–75 µg/L) in the Fe-AC/O₃ process.

Susana et al., (2011) [23] studied the removal of arsenic via the adsorption process utilizing iron oxide multiwalled carbon nanotube (Fe-MWCNT); the results indicate that significantly higher removal was achieved (adsorption capacity; As(III) 1723 μ g/g and As(V) 189 μ g/g). However, it is important to mention here that while comparing the mentioned adsorption process with our recent findings, it was observed that the oxidation/adsorption process results in a more rapid removal of As than the adsorption process. For example, more than 90% removal was achieved in both processes, and in the case of the adsorption process (Fe-MWCNT), removal efficiency was achieved in 200 min. On the other hand, in the case of the Fe-AC/O₃ process, more than 90% removal was achieved in 30 min.

Moreira et al. (2021) [26] studied the ultrafiltration process for the removal of arsenic utilizing FeCl₃ as a coagulant in the pre-coagulation flocculation process and polyetherimidebased membrane in the post-ultrafiltration process. The results revealed that more than 90% removal was achieved in both processes. Therefore, the current investigation is in the agreement with previous findings.

5. Conclusions

From the results, it is clear that catalytic ozonation considerably removes As from drinking water as compared to adsorption and simple ozonation processes. The addition of iron-activated carbons along with ozonation improved the removal of As. The removal efficiency of adsorption was 58%, ozonation was 51%, and catalytic ozonation was 98.6%. A systematic check of water quality can also improve health-related issues connected to drinking water. The Fe-AC/O₃ process was highly efficient in the removal of As in all studied sampling locations.

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