

## Article

# Combined Iron-Loaded Zeolites and Ozone-Based Process for the Purification of Drinking Water in a Novel Hybrid Reactor: Removal of Faecal Coliforms and Arsenic

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**Abstract:** This study was carried out to provide a novel solution to treat drinking water at household levels, specifically removing arsenic (As) and faecal coliforms (microbes). In the current investigation, a synergistic iron-loaded zeolites and ozonation process (O<sub>3</sub>/Fe-ZA) was used for the first time in a modified batch reactor to remove coliform bacteria and arsenic in tap water. Moreover, the study utilizes the human health risk assessment model to confirm the health risk due to As intake in drinking water. The risk assessment study revealed a health risk threat among the residents suffering from the adverse effects of As through its intake in drinking water. Furthermore, the results also suggested that the O<sub>3</sub>/Fe-ZA process significantly removes faecal coliforms and As, when compared with single ozonation processes. Additionally, the ozone dose 0.2 mg/min and Fe-ZA dose of 10 g (in the O<sub>3</sub>/Fe-ZA process) gives the maximum removal efficiency of 100% within 15 min for faecal coliform removal. In 30 min, the removal efficiency of 88.4% was achieved at the ozone dose of 0.5 mg/min and 93% removal efficiency was achieved using 10 g Fe-ZA for the removal of As in the O<sub>3</sub>/Fe-ZA process. Hence, it was concluded that the O<sub>3</sub>/Fe-ZA process may be regarded as an effective method for removing faecal coliforms and As from drinking water compared to the single ozonation processes.

**Keywords:** arsenic; faecal coliforms; ozonation; Fe-Zeolite A; drinking water

## 1. Introduction

Water is essential not only for human survival but for all living beings. Due to rising numbers of the human population and urban expansion, the freshwater resources are under great strain. It is now a challenge to supply safe drinking water to urban areas [1]. It is estimated that globally about 1.1 billion people are deprived of an abundant supply of water. About 675 million people do not have access to improved drinking water resources in Asia [1]. Generally, millions of people from poverty-stricken countries expire every year due to water-related diseases. In the context of an increase in population and water

contamination [1,2], approaches to guarantee fresh drinking water have become a global challenge [1–3].

Drinking water sources are susceptible to contamination by naturally occurring or anthropogenic pollutants and need appropriate treatment to remove disease-causing contaminants. The water sources polluted with human impurities mainly arise due to faecal contamination, which can be a stimulus of many diseases like hepatitis, dysentery, typhoid fever, ear infections, and a variety of health-related illnesses [4]. Among heavy metals, arsenic (As) is a significant contaminant frequently found in various regions of Pakistan [5,6]. The people living in such areas are at high risk due to the high profile of As in drinking water [5,6]. Moreover, its intake through drinking water can cause various diseases like kidney, skin, colon, bladder and lung cancers, diabetes and hypertension etc. [5,6].

Urban water quality deterioration is one of the significant challenges facing by developing countries these days. Lahore (an example of a densely populated city of the developing world) is a metropolitan city of Punjab, Pakistan, at a higher risk due to water quality deterioration. The population increase is putting more strain on water sources; hence, this results in excess groundwater pumping. Water-related health problems are common in Lahore and domestic water in the city is becoming polluted by As, faecal coliforms, and other contaminants [5,6]. The Water and Sanitation Agency (WASA) has installed many As removal filtration plants based on reverse osmosis (RO) processes. However, the majority of them are redundant, old and choked. Because of the lack of resources and affordability issues, RO plants continuous operation and maintenance cannot be possible. However, most of the past studies focused on using conventional methods, but complete purification was not attained with these methods. Moreover, people have to wait for several hours to obtain water and get to filtration plants putting a greater economic burden on them. Under these conditions, it has become challenging for the general population to attain healthy and safe drinking water. Hence, there is a dire need to develop or identify a simple and relatively inexpensive water treatment alternative to treat water at home. Furthermore, this can result in substantial improvements in drinking water quality, specifically in terms of As and faecal coliforms, thus resulting in reduced risk of illness [7,8].

With technological advancement, advanced oxidation processes (AOP) have emerged as an effective technology with the key feature of generating oxidizing species like the hydroxyl radical ( $\bullet\text{OH}$ ), having an ability to decompose and mineralizing the pollutants [9,10]. The disinfection ability of ozonation process can be further increased with a catalyst that increases  $\bullet\text{OH}$  production [11], resulting in effective and faster removal of the contaminants from water [12,13]. AOPs were used to degrade even recalcitrant organic contaminants in wastewater. Many AOPs were successfully studied for the treatment of water and wastewater. Among them are Fenton and Fenton-like processes, photocatalytic processes, electro-Fenton processes, activated persulfate, ionizing radiation and electron beam technology were studied for the treatment of wastewater [14]. Among these AOPs, catalytic ozonation is one of AOPs that was successfully studied for the treatment of various pollutants. Both the homogeneous and heterogeneous catalytic ozonation processes were found to be highly effective even for the treatment of more complex matrix such as real wastewater [14].

Many materials were used in various applications such as renewable energy, wastewater treatment and pollution control [15–36]. In a catalytic ozonation process the addition of a catalyst to ozonation increases the rate of oxidation and decreases contact time, resulting in reduced treatment costs [37]. It has been reported by a variety of research groups that the high performance of catalytic ozonation is achieved to remove organic contaminants in water [10,38,39]. Traditionally, catalytic oxidation processes were based on removing organic pollutants in water; however, in some recent findings, catalytic processes were used to remove microorganisms and heavy metals in drinking water [40–44].

Natural zeolite materials have shown exceptional sorption and ion-exchange properties. They are economically and environmentally acceptable hydrated aluminosilicate materials [45–47]. They have different physical-chemical properties that are connected to

their geological deposits. The effectiveness of zeolites in different technological processes depends on this physical-chemical property [45–47]. Moreover, they have been widely used as an adsorbent or catalyst because of their non-flammability and thermal stability. Fe-based catalysts have shown eminent adsorption activity to eliminate heavy metals from water [48–51]. Moreover, Fe based zeolites (as adsorbents) have shown promising results for the abatement of arsenic from water [48–51]. Therefore, keeping in mind its effectiveness in removing organic pollutants, it has been hypothesized that ozonation using Fe-zeolites will also effectively remove faecal coliforms bacteria from drinking water.

Catalytic ozonation may precipitate arsenic from water [52–54], thus in the current investigation, we adopted a novel batch reactor with a rotatory backed in it, having Fe-loaded zeolite to adsorb precipitated arsenic. This is due to conventional batch reactors having some limitations such as the recovery of homogeneous catalyst/adsorbent, loss in mechanical stirring, mass transfer limitations [55–57], and sludge formation. Hence, a promising approach was adopted in the current investigation, where iron-loaded zeolite was placed in a bucket suspended in the batch reactor. Moreover, in the current investigation, zeolite A was used for the first time to study the removal of faecal coliform bacteria and arsenic in an ozonated environment. The study also compares the effect of ozone and a Fe-ZA dose to determine the effectiveness of the different ozonation processes.

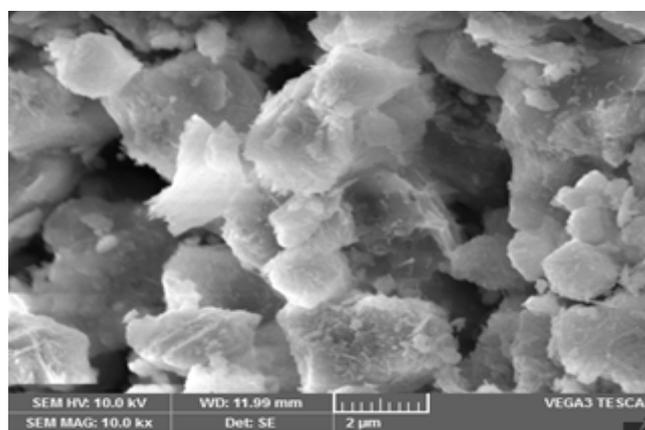
## 2. Results and Discussion

### 2.1. Fe-Zeolite Characterization

The physicochemical properties of zeolite are presented in Table 1. The zeolite 4A type is a sodium zeolite having composition  $2\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-1.75\text{SiO}_2-6\text{H}_2\text{O}$ . The zeolite was loaded with  $\text{Fe}^{+2}$  by the impregnation method [58]. A scanning electron microscope (SEM) coupled with energy-dispersive X-ray (EDX) spectroscopy was used to investigate the surface morphology of Fe-Zeolite and to confirm the presence of iron on the catalyst (Tescan, UK, Vega LMU). The SEM image (Figure 1) indicates the highly porous surface texture of studied catalyst. The EDX spectra clearly indicate the iron coating on Fe-Zeolite when compared with zeolite without iron coating (Figure 2a,b). Moreover, the iron was found to be 10% (Table 1). The Brunauer, Emmet, and Teller (BET) method was used to determine the surface area and pore size. For that, nitrogen adsorption at 77 K, using adsorption isotherms, and using the Kelvin equation and Barrett, Joyner, Helenda (BJH) method, porosities were determined [40]. The surface area of Fe-Zeolite was  $91.21 \text{ m}^2/\text{g}$  and the pore size was  $4 \text{ \AA}$  (Table 1).

**Table 1.** Properties of Fe-Zeolite.

Properties of Zeolite.	Typical Formula	Pore Size (Å)	Thermal Decomposition (°C)	Surface Area ( $\text{m}^2/\text{g}$ )	Fe [%]
	$2\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-1.75\text{SiO}_2-6\text{H}_2\text{O}$	4	700	91.21	10



**Figure 1.** Scanning electron microscope (SEM) image of Fe-Zeolite A.

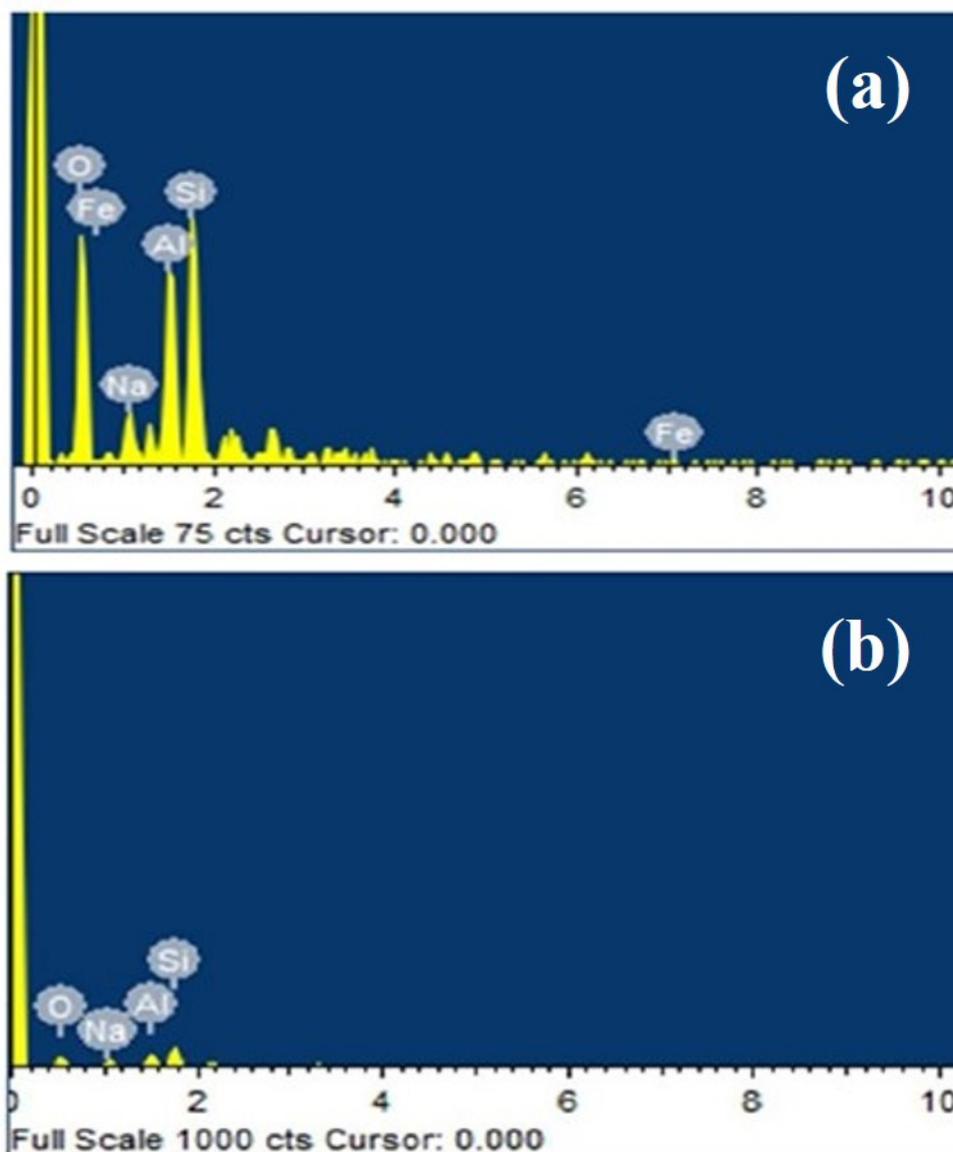


Figure 2. Energy-dispersive X-ray spectroscopy (EDX) of Fe-Zeolite (a) and zeolite without iron coating (b).

### 2.1.1. Drinking-Water Quality Analysis in the Selected Areas

Based on the results obtained (Table 2), this study confirmed that the main concern was As and faecal coliforms in Lahore's given areas. Table 2 shows that all parameters are beyond the guideline values recommended by the World Health Organization (WHO) and national standards for drinking water quality (NSDWQ) except As and faecal coliforms.

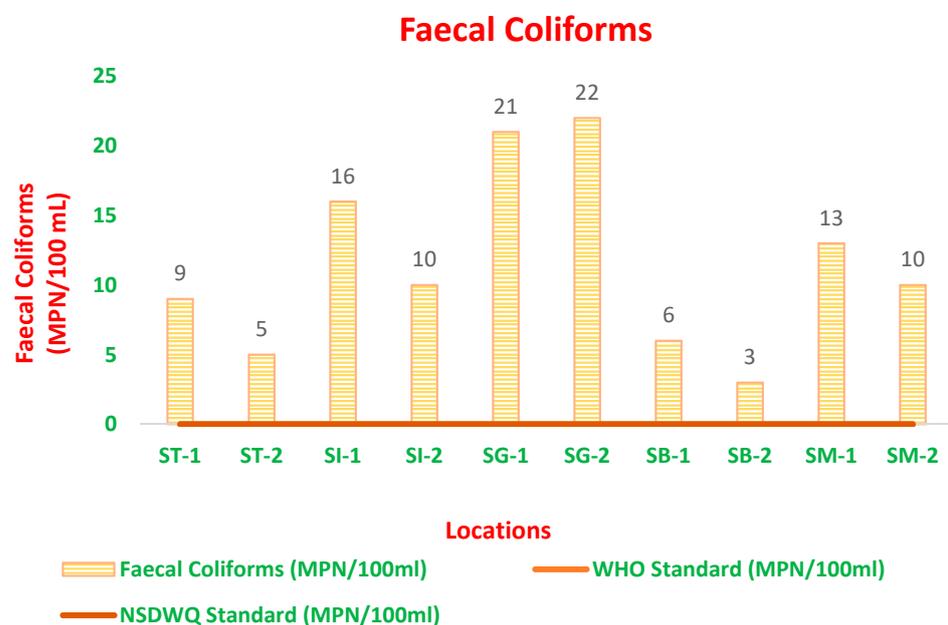
Results confirmed faecal coliforms contamination in all the analyzed samples, i.e., all samples are exceeding WHO and NSDWQ standards at all locations (0 MPN/100 mL) as shown in Figure 3. Usually, faecal coliforms testing is one of the most important drinking water quality parameters of any area. As the name implies, it indicates the presence of viruses, parasites, and bacteria, which can cause cholera, typhoid fever, polio, infectious hepatitis, and dysentery. The results suggest that the quality of water is unacceptable owing to the presence of coliforms. Hence, all analyzed water samples are not safe for drinking purposes without prior treatment to reduce faecal coliforms to permissible levels (0/MPN/100 mL). The previous findings also suggested that in subcontinent region, faecal contaminants were frequently found in various regions of India and Pakistan [3–5]. This may be due to the inadequate sanitary conditions and lack of resources that may pose

a serious threat to many people [3–5]. The As concentrations were also found exceeding in all samples compared with WHO guidelines (10 ppb) of drinking water quality. However, As results with a NSDWQ standards (50 ppb) comparison, four samples (ST-1, SI-2, SG-1, SB-2) from the four studied locations (township, Ichra, Gulshan Ravi and Misri Shah) exceeded the standards (Figure 4). The results of arsenic levels presented in the current investigation are in agreement with previous studies conducted in Pakistan [5,6].

**Table 2.** Results of analysed parameters at selected locations of Lahore.

Sample Codes	Parameters						
	pH	TDS <sup>a</sup> (mg/L)	Turbidity (NTU)	Chlorides (mg/L)	Residual Chlorine (mg/L)	Faecal Coliforms MPN/100 mL	Arsenic (ppb)
<b>Township Area</b>							
ST-1	8.3 ± 0.2	835 ± 15	0.5 ± 0.2	38 ± 11	0.07	9 ± 3	68 ± 8
ST-2	8.3 ± 0.2	829 ± 12	0.6 ± 0.2	39 ± 13	0.07	5 ± 4	45 ± 4
<b>Ichra</b>							
SI-1	8.3 ± 0.1	237 ± 12	0.5 ± 0.1	33 ± 8	0	16 ± 5	44 ± 5
SI-2	8.3 ± 0.3	215 ± 15	0.6 ± 0.1	36 ± 8	0	10 ± 5	69 ± 12
<b>Gulshan Ravi Area</b>							
SG-1	8.3 ± 0.2	209 ± 11	0.5 ± 0.1	24 ± 5	0	21 ± 4	72 ± 8
SG-2	8.3 ± 0.3	212 ± 15	0.5 ± 0.1	22 ± 3	0	22 ± 7	49 ± 6
<b>Bagbanpura Area</b>							
SB-1	8.3 ± 0.1	392 ± 13	0.5 ± 0.3	48 ± 11	0	20 ± 5	41 ± 11
SB-2	8.3 ± 0.1	270 ± 11	0.6 ± 0.4	55 ± 4	0	3 ± 2	58 ± 4
<b>Misri Shah Area</b>							
SM-1	8.1 ± 0.2	340 ± 14	0.7 ± 0.3	40 ± 7	0	18 ± 4	45 ± 4
SM-2	8.1 ± 0.2	330 ± 12	0.7 ± 0.5	37 ± 12	0	10 ± 4	42 ± 2
WHO Guideline	6.5–8.5	<1000	<5	250	0.2–5.0	0	10
NSDWQ Guideline	6.5–8.5	<1000	<5	<250	0.2–5.0	0	50

<sup>a</sup> TDS = Total dissolved Solids.



**Figure 3.** Faecal coliforms in drinking water at selected locations in Lahore, Pakistan.

### 2.1.2. Human Health Risk Assessment Model

The application of health risk assessment is also carried out to quantify the individual health risks in terms of As contamination in the water samples. The threshold limit for HQ was 1. If the HQ value increases more than the recommended limit, it can be harmful and may cause serious health effects [59]. Figure 5 shows that the HQ value of As lies between 0.86–1.39 with 40% of the samples having HQ values greater than 1 (Figure 5). This suggested that the population of Lahore (explicitly residing in the sampling

locations) may be at a severe health risk threat from As contamination in drinking water [59]. Therefore, it is essential to search for novel methods that help treat As at household levels.

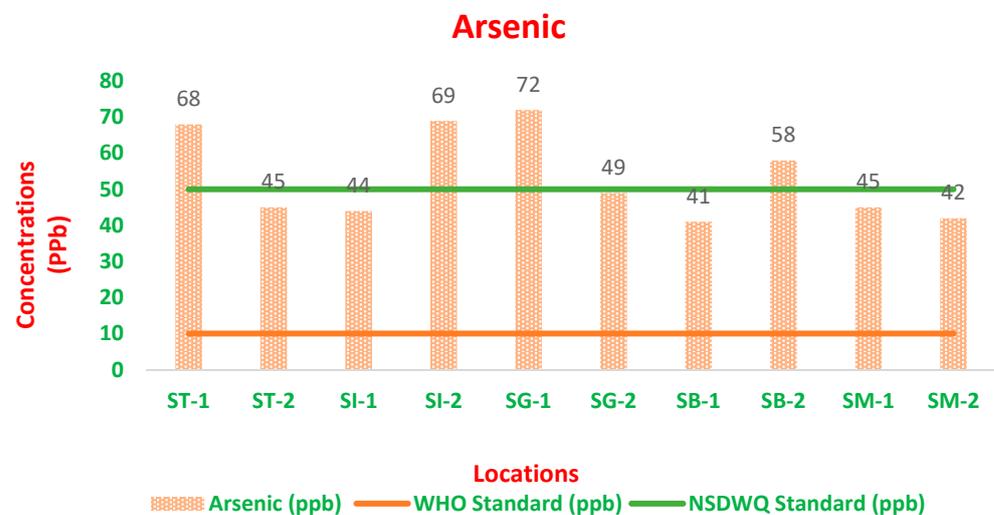


Figure 4. Arsenic in drinking water at selected locations, of Lahore, Pakistan.

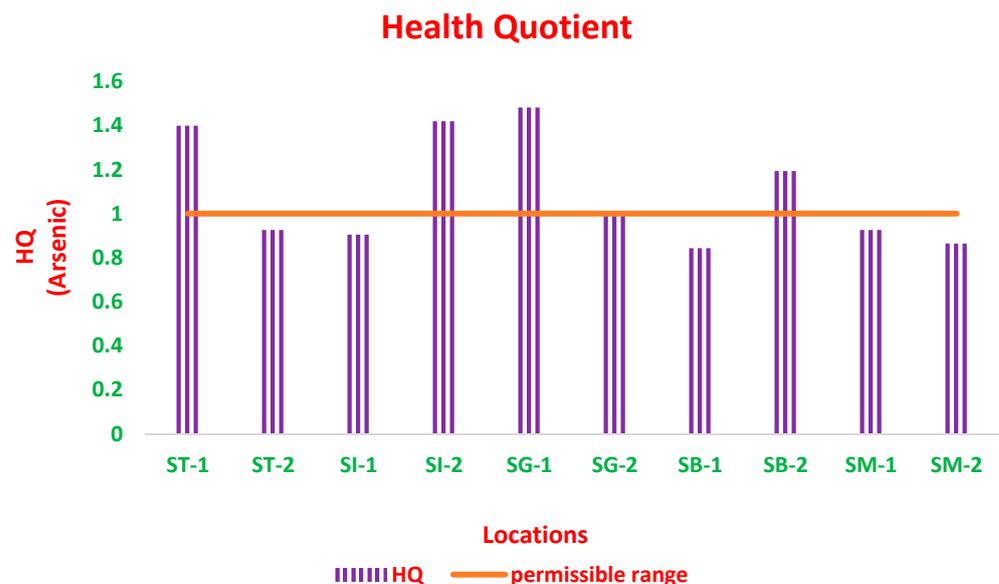


Figure 5. Health quotient in different areas of Lahore, Pakistan.

## 2.2. Treatment of Faecal Coliforms and Arsenic

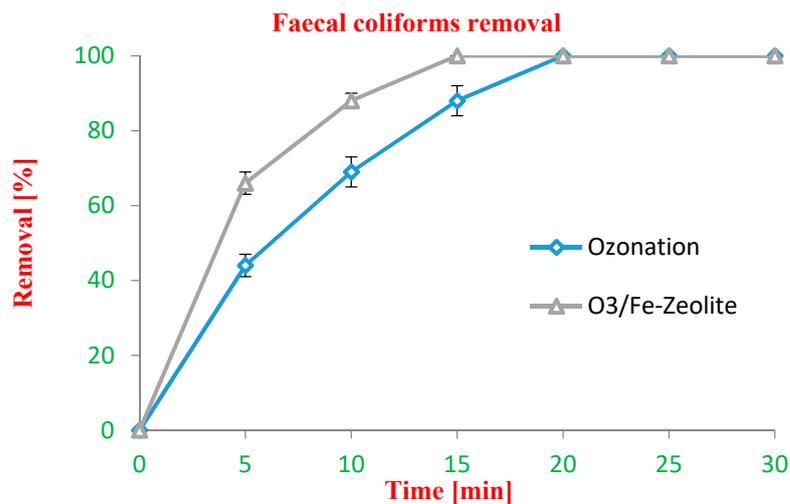
Both ozonation processes (single and catalytic) were carried out for 30 min, aiming toward the disinfection of faecal coliforms and arsenic oxidation in drinking water samples.

### 2.2.1. Treatment of Faecal Coliforms

#### Comparison between Single Ozonation and O<sub>3</sub>/Fe-ZA Process

The results reveal that when water samples were subjected to different ozonation processes (Figure 6), 100% removal efficiency was achieved with O<sub>3</sub> process in 15 min. While in O<sub>3</sub>/Fe-ZA process, 100% removal efficiency was achieved within 10 min. This difference could be due to higher hydroxyl radical production in the O<sub>3</sub>/Fe-ZA process than single ozonation [47,60]. Usually, in the O<sub>3</sub>/Fe-ZA process, more ozone decomposition results in hydroxyl radical's production compared with single ozonation, which can inactivate the cell walls of the faecal coliform group [61,62]. Additionally, the reactions of

ozone and coliform bacteria on the Fe-Zeolite surface may further help in the disinfection process. Mackulak, et al. [43] studied the removal of bacteria and antibiotics from wastewater samples using a Fenton-like advanced oxidation process, it was observed that hydroxyl radicals based on the studied process were highly efficient for the removal of bacteria. However, even after treatment with Fenton-like process bacteria were found in same samples. Interestingly, in the current study where the O<sub>3</sub>/Fe-Zeolite based process was implied to remove bacteria, complete removal of coliform bacteria was observed in all studied samples. Hence, Fe-Zeolite based advanced process may help to effectively remove bacteria in water.

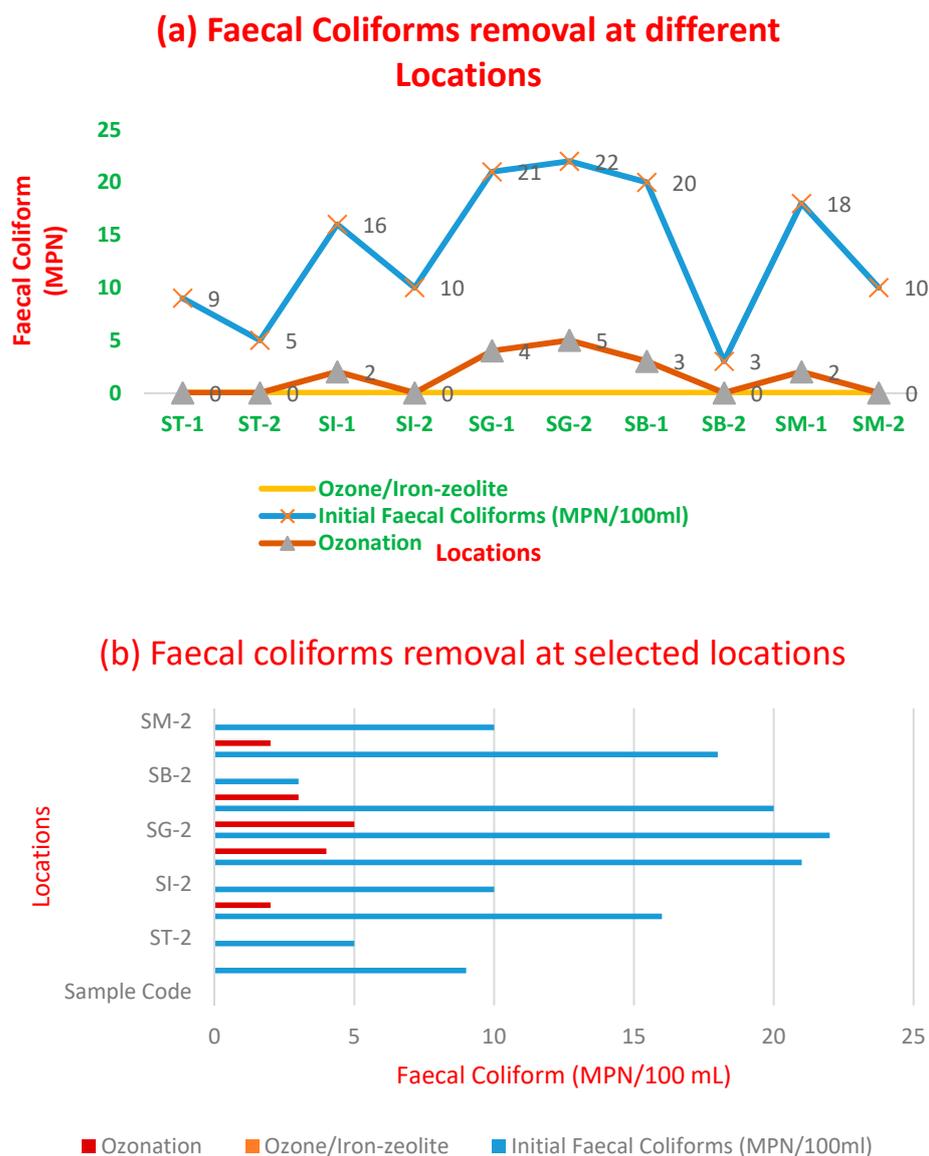


**Figure 6.** Removal of faecal coliforms in ozonation and catalytic ozonation processes (Initial faecal coliforms =  $16 \pm 4$  MPN/100 mL, ozone dose = 0.2 mg/min, Fe-ZA dose = 10 g/L, pH =  $8.2 \pm 0.3$ , volume = 1 L, time = 30 min, T =  $33 \pm 2$  °C).

Figure 7 shows the area-wise results of the faecal coliform with initial MPN compared to both studied processes. The results indicate that the inactivation of faecal coliforms was improved with O<sub>3</sub>/Fe-ZA. Using 15 min as an optimal time with the optimal dose of 0.2 mg/min. Despite this, the results of O<sub>3</sub>/Fe-ZA (Figure 5) maybe not different from the single ozonation at sampling location of low initial coliform number (ST-2, SI-2, SB-2, SM-2), since the dissolved molecular ozone has a vital role in faecal coliform inactivation from drinking water [63]. Moreover, the loading of Fe on zeolites significantly enhances the generation of hydroxyl radicals and the removal of faecal coliforms [64,65].

It is important to mention here that iron loading on zeolite play an important role in the production of hydroxyl radicals [27,40,47], which reacts rapidly with microbes as compared with molecular ozone. Moreover, zeolite A without iron loading may follow molecular ozone-based mechanism in which molecular ozone absorbed on the surface of zeolite reacts with adsorbed species [40]. On the other hand, iron was found to be an effective active site leading to the decomposition of molecular ozone to produce hydroxyl radicals, the hydroxyl radicals formed may interact with target contaminants in bulk and on the surface of catalyst [27,40,47].

Previous studies indicate that when Fe-Zeolite A was used in more complex matrix (wastewater) in catalytic ozonation processes (and found to be quite stable), only a minute quantity of iron was leached out [27,47]. Moreover, the reuse performance of studied catalyst was found to be excellent [27,47]. Since the studied process was based on the generation of hydroxyl radicals by ozone interactions with active sites (iron), even a leach out of minute quantity of iron in bulk, it may behave as a homogeneous catalyst to promote the generation of hydroxyl radicals via interactions with molecular ozone [10,47,50]. Hence, removal efficiency of bacteria and As may not be significantly affected by the leaching of a minute quantity of iron.



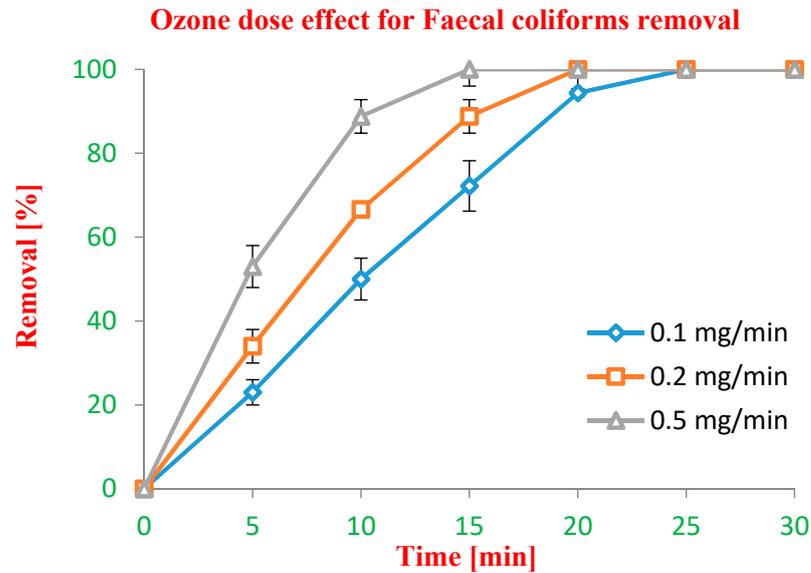
**Figure 7.** Comparison between O<sub>3</sub> and O<sub>3</sub>/Fe-ZA in terms of faecal coliforms removal from drinking water at selected locations of Lahore, Pakistan (ozone dose = 0.2 mg/min, Fe-ZA dose =10 g/L, pH = 8.1 ± 0.3, volume = 1 L, time = 30 min, T = 33 ± 2 °C).

**Ozone Dose Effect**

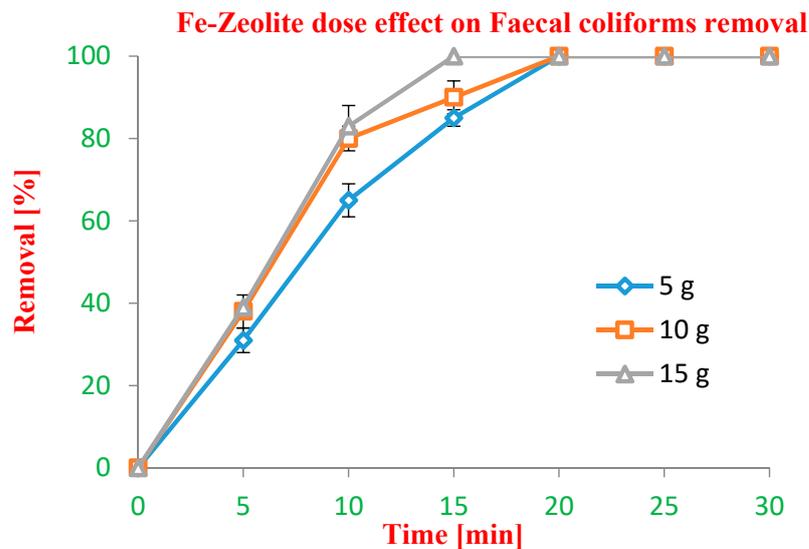
In a single Ozonation process, within first 15 min, 100% removal efficiency (Figure 8) with the ozone dose of 0.2 mg/min and 0.5 mg/min was observed. This may be due to ozone disinfection inactivating or damaging the bacterial cells due to its strong oxidizing properties. Based on Figure 8, an increase in °OH radicals also increases the accumulation of ozone injection, resulting in a higher level of ozone in the system, thus producing more °OH radicals that further result in bacterial inactivation [64,65].

**Fe-Zeolite Dose Effect**

Figure 9 shows faecal coliform removal increased with an increase in Fe-ZA dosage. The production of hydroxyl radicals in solution with an increase in the number of active sites may result in the inactivation of faecal coliform bacteria [64,65]. This further support our hypothesis that hydroxyl radicals along with molecular ozone may play an important role in the deactivation of bacteria. Moreover, Figure 9 shows that the Fe-ZA dose of 10 g/L gives the maximum removal efficiency of 100% within 15 min for faecal coliform removal.



**Figure 8.** Ozone dose effect in faecal coliforms removal studies during ozonation process (initial faecal coliforms =  $16 \pm 3$  MPN/100 mL, ozone dose = 0.1 mg/min, 0.2 mg/min and 0.5 mg/min, Fe-ZA = 10 g/L, pH = 8.1, volume = 1 L, time = 30 min,  $T = 33 \pm 2$  °C).

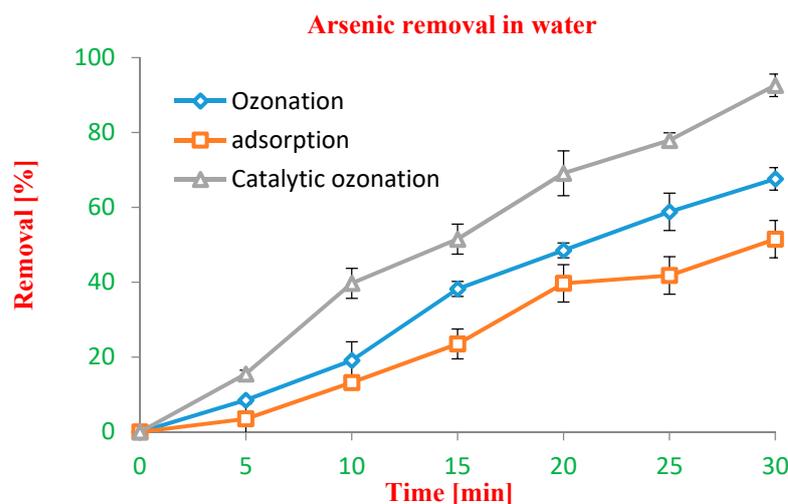


**Figure 9.** Catalyst dose effect (initial faecal coliforms =  $18 \pm 4$  MPN/100 mL, ozone dose = 0.2 mg/min,  $O_3$ /Fe-ZA dose = 5 g/L, 10 g/L and 15 g/L,  $O_3$  = 0.2 mg/min, pH =  $8.3 \pm 2$ , Volume = 1 L, time = 30 min,  $T = 33 \pm 2$  °C).

### 2.2.2. Treatment of Arsenic

#### Comparison between Single Ozonation, Adsorption and $O_3$ /Fe-ZA Processes

The removal rate of As through catalytic ozonation was highest compared with single ozonation and adsorption (Figure 10). The percentage of As removed after 30 min treatment was about 92.6%. While the As removal rate after 30 min of treatment by single ozonation was about 67.6%. Hence, when adsorption is employed, 51.4% of treatment efficiency was achieved. Thus, these results proved that Fe-ZA combined with  $O_3$  was one of the best options for removing As from drinking than the other studied processes.



**Figure 10.** Arsenic % removal in adsorption, ozonation and catalytic ozonation processes (Initial As =  $68 \pm 8$  ppb, ozone dose = 0.2 mg/min,  $O_3$ /Fe-ZA dose = 10 g/L, pH =  $8.2 \pm 0.3$ , volume = 1 L, time = 30 min,  $T = 33 \pm 2$  °C).

The removal of As in single ozonation may be due to the precipitation of As with oxidation, involving ozone and hydroxyl radicals [53–55,66,67]. Similarly, in the  $O_3$ /Fe-ZA process the production of hydroxyl radicals may enhance the precipitation of As. The adsorption of As on Fe-ZA further removes it from water [46,50–52], therefore in the synergic process, precipitation and adsorption on zeolite play an essential role in the overall removal efficiency of As. Previous findings suggested that iron loading on zeolites significantly enhance the overall removal efficiency of As. Moreover, the removal efficiency of As (at low concentrations of As and Fe-Zeolite doses, similar to the current study) was found to be about 30–50% in adsorption process [51,52]. Therefore, the results presented in current study are in agreement with previous finding using Fe-Zeolites for As removal by adsorption process (about 51% As removal in 30 min when Fe-ZA was used). In order to further enhance the As removal efficiency, in the current study catalytic ozonation process using Fe-Zeolites was used for the first time and As removal efficiency was enhanced to about 90% in studied catalytic ozonation process. The As may be precipitated out due to the interactions of molecular ozone and hydroxyl radicals in the bulk in single ozonation process [52,53]. Since Fe-Zeolites may promote the decomposition of aqueous ozone leading to the production of hydroxyl radicals that might help to precipitate As through the oxidation process. Additionally, it is hypothesised that molecular ozone adsorbed on a catalyst surface may also interact with adsorbed arsenic and leads to its precipitation.

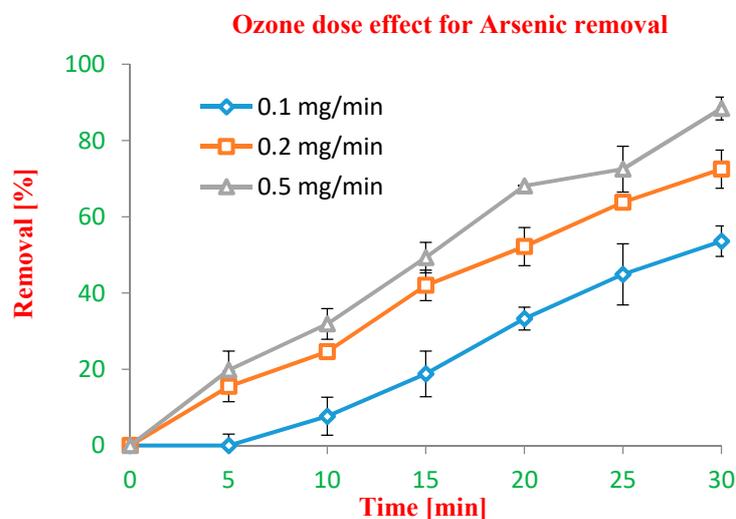
#### Ozone Dose Effect

The ozone dose effect in the  $O_3$ /Fe-ZA process on As removal of drinking water was studied at various doses of 0.1 mg/min, 0.2 mg/min and 0.5 mg/min of ozone in a batch reactor (Figure 11). The maximum removal efficiency of 88.4% was achieved with 0.5 mg/min ozone dose in 30 min, which proved that the ozone's oxidative capacity plays a vital role in As removal. The increase in ozone dose may enhance the overall precipitation of As and they were adsorbed on zeolite and filtered [53].

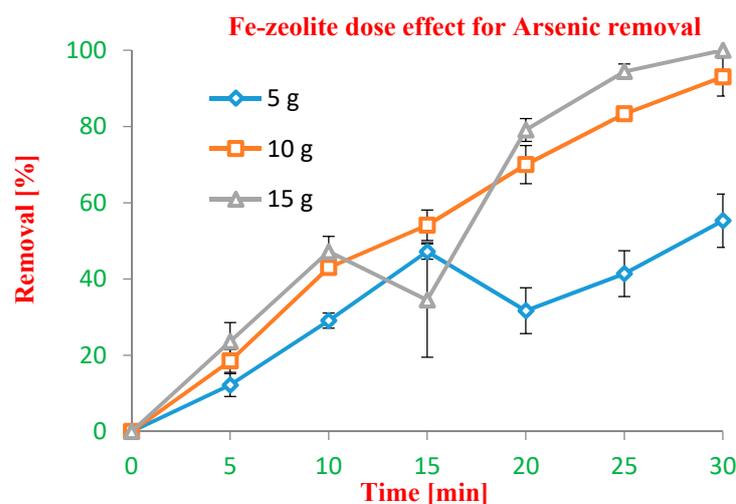
#### Fe-Zeolite Dose Effect

The Fe-ZA dose effect in the catalytic ozonation process on As removal from drinking water was studied at various doses of 5 g, 10 g, and 15 g of Fe-Zeolite in a modified batch reactor. The maximum removal efficiency of 93% was achieved with 10 g of catalyst dose in 30 min (Figure 12). This suggests the importance of Fe-Zeolite in the synergic process. The increase in Fe-Zeolite amount may increase to the active site that further helps to adsorb

and precipitate via hydroxyl radical's generation due to the interaction of ozone with active sites of the Fe-Zeolite [46,49–51,67,68].



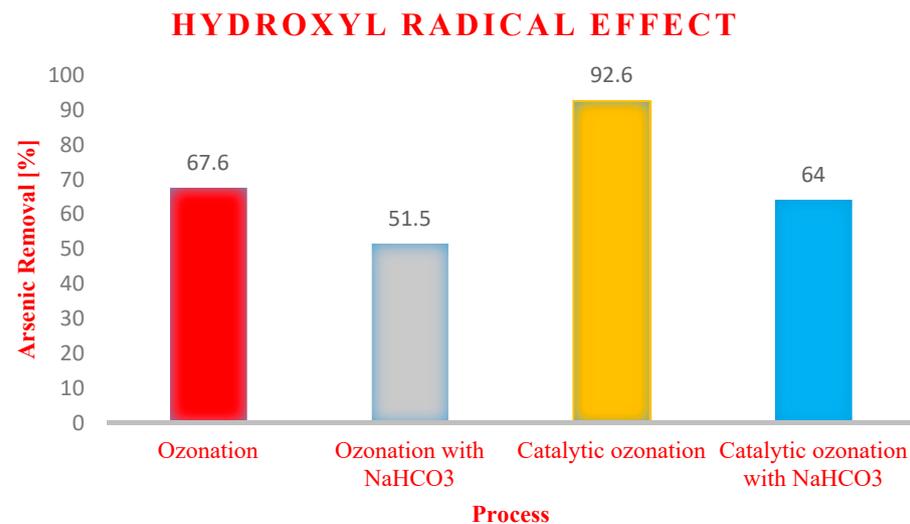
**Figure 11.** Ozone dose effect in arsenic removal studies (ozone dose = 0.5 mg/min, As =  $68 \pm 8$  ppb, 0.1mg/min, 0.2 and 0.5 mg/min, pH =  $8.2 \pm 0.3$ , Fe-ZA = 10 g/L, volume = 1 L, time = 30 min, T =  $33 \pm 2$  °C).



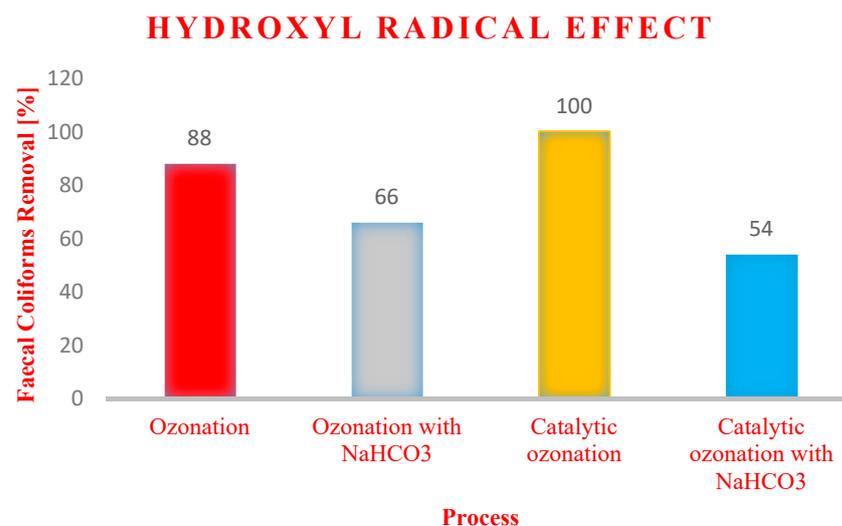
**Figure 12.** Catalyst dose effect in arsenic removal studies during catalytic ozonation process (ozone dose = 0.2 mg/min, As =  $68 \pm 8$  ppb, Fe-ZA dose = 5 g/L, 10 g/L and 15 g/L, pH =  $7.8 \pm 0.3$ , volume = 1 L, time = 30 min, T =  $33 \pm 2$  °C).

#### Effect of Hydroxyl Radical Scavenger on Water Disinfection and Arsenic Removal

In order to understand whether the disinfection and arsenic removal mechanism depends on the hydroxyl radicals in ozonation and catalytic ozonation processes the removal efficiencies were compared in the presence of  $\text{NaHCO}_3$ . The results presented in Figures 13 and 14 clearly indicate that both the removal efficiencies of arsenic and faecal coliforms decreased significantly in the presence of hydroxyl radical scavenger. Moreover, the decrease in arsenic and faecal coliforms was more in the case of catalytic ozonation as compared with single ozonation process. This may be due to the increase in hydroxyl radical's production in the catalytic ozonation process as compared to single ozonation process [27,47].



**Figure 13.** Arsenic % removal in ozonation and catalytic ozonation processes with and with out NaHCO<sub>3</sub> (initial As = 68 ± 8 ppb, ozone dose = 0.2 mg/min, O<sub>3</sub>/Fe-ZA dose = 10 g/L, pH = 8.2 ± 0.3, volume = 1 L, time = 30 min, T = 33 ± 2 °C, t = 30 min, NaHCO<sub>3</sub> = 50 mg/L).

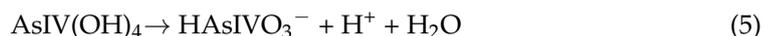
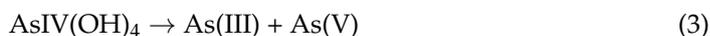


**Figure 14.** Removal of faecal coliforms in ozonation and catalytic ozonation processes with and without NaHCO<sub>3</sub> (initial faecal coliforms = 16 ± 4 MPN/100 mL, ozone dose = 0.2 mg/min, Fe-ZA dose = 10 g/L, pH = 8.2 ± 0.3, volume = 1 L, time = 30 min, T = 33 ± 2 °C, t = 15 min, NaHCO<sub>3</sub> = 50 mg/L).

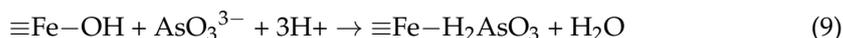
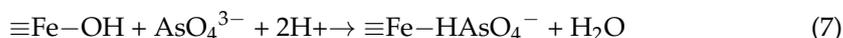
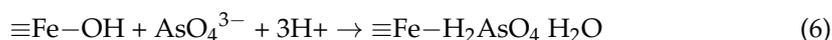
#### Mechanism of Water Disinfection and Arsenic Removal on Fe-Zeolite A

It is proposed that arsenic removal and water disinfection may be enhanced in the presence of hydroxyl radicals formed as a result of ozone with the active sites of studied catalyst. The results presented in Figures 13 and 14 also show that hydroxyl radicals may play an important role in the removal of arsenic as well as removal of coliform bacteria in water. It was further confirmed by the hydroxyl radical scavenger (NaHCO<sub>3</sub>) effect, which clearly suggested that the decrease in arsenic removal and fecal coliforms in the presence of NaHCO<sub>3</sub> in the O<sub>3</sub>/Fe-ZA process as compared with the O<sub>3</sub>/Fe-ZA process without NaHCO<sub>3</sub> and O<sub>3</sub> indicate the significant role of hydroxyl radical in the catalytic ozonation process. Hydroxyl radicals oxidize As(III) to less toxic As(V) [65] (Equations (1)–(3)). The following reactions indicate the transformation of arsenic into various forms in the presence of O<sub>2</sub>, O<sub>2</sub><sup>•−</sup> and °OH

leading to the oxidation of arsenic in water [65] (Equations (1)–(5)). The oxidation may lead to the precipitation and adsorption of arsenic on Fe-Zeolite [48–51].



Myoung et al. [54] found that ozone oxidises the soluble arsenic (AsIII) to As(V) form (Equations (6)–(9)). Moreover, both forms have high affinity towards the adsorption towards Fe ions as proposed by the following equations.



Hence, it is proposed that oxidise arsenic then adsorbed on the Fe-zeolite. The results presented in Figure 10 also show that significant amount of arsenic was removed due to its adsorption on studied Fe-Zeolite.

It was further proposed that in the case of faecal coliform bacteria, hydroxyl radicals are generated in a catalytic ozonation process as a result of interactions of molecules with Fe on the catalyst surface. The role of hydroxyl radicals for the disinfection process was confirmed by the hydroxyl radicals scavenger effect (Figure 14).

### 3. Materials and Methods

#### 3.1. Study Area

Lahore is the capital city of Punjab Province, Pakistan, and a heavily populated city that lies along the west bank of River Ravi. Lahore city expands over 1772 km<sup>2</sup> with an estimated population of around 12,500,000 [69]. Different water utilities are used to supply water. The drinking water source is groundwater and extracted by tube wells installed throughout the city. More than 700 tube-wells are equipped throughout the city to extract freshwater and pump them directly into the distribution system [70].

##### 3.1.1. Sampling Locations

To propose a treatment technology in As and Faecal coliform aggravating locations of Lahore, a total of 5 sampling locations were investigated, which include: Township, Ichra, Gulshan Ravi, Baghbanpura, and Misri Shah. Figure 15 shows the sampling sites of each area under study.

##### 3.1.2. Sample Collection, Storage and Analytical Procedures

The samples were collected from the given five areas of Lahore. From each area, two samples were collected from the consumer ends (tap water). Collection of samples was carried out in dry and sterilized (in autoclave) glass bottles manually and it was ensured that bottles must be free from contamination. Grab samples were collected from each sampling point following the standards and guidelines. Moreover, collected samples were stored according to standard methods described below [71]. The arsenic was analyzed by using an atomic absorption spectrophotometer coupled with a graphite furnace. The faecal coliform bacteria were determined by using the most probable number method (MPN) [71].

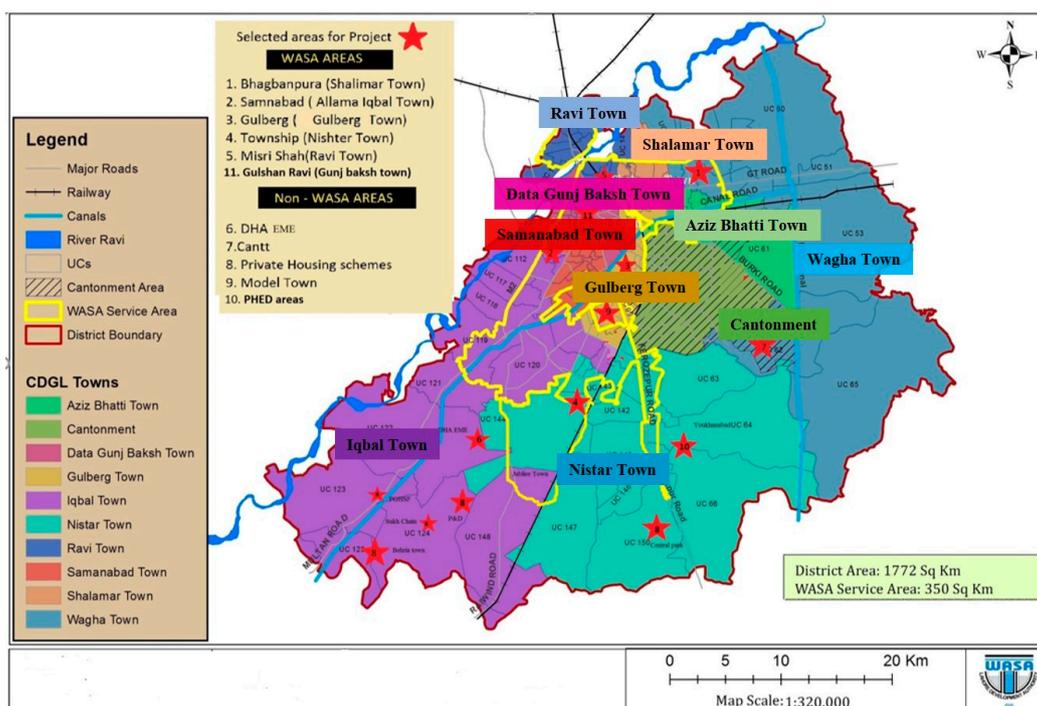


Figure 15. Location map showing sampling sites (WASA = Water and Sanitation Agency) in various towns of Lahore, Pakistan.

### 3.2. Health Risk Assessment Model

#### 3.2.1. Daily Intake of Metals

Daily intake of metals (DIM) was calculated by using the following formula [71,72].

$$\text{DIM} = \text{C metal} \times \text{D food intake} / \text{B average weight} \quad (10)$$

For adults, the daily food intake is 0.345 kg/person/day and the average weight is 55.9 kg [72,73].

#### 3.2.2. Health Quotient

Health Quotient (HQ) was calculated by using the formula given below:

$$\text{HQ} = \text{DIM} / \text{RfD} \quad (11)$$

If the calculated value of HQ was equal to or greater than 1, then the intake of such water was considered to be a health risk [73].

### 3.3. Experimental Setup

#### 3.3.1. Materials and Reagents

All the chemicals (such as EC broth, brilliant green bile broth and lactose broth for coliform identification by the most probable number method,  $\text{Na}_2\text{CO}_3$ , potassium iodide, Sodium thiosulfate, starch solution for ozonation experiments) used in this study were of analytical grade having 99% purity. The reagents were prepared using ultra-pure deionized water and were used without further purification and were obtained from Sigma-Aldrich, UK.

#### 3.3.2. Catalyst Preparation

The zeolites were rinsed in 0.1 M nitric acid for a day and washed with deionized water until constant pH was obtained. Then, placed in an oven at 110 °C overnight. To impregnate iron on zeolites as described elsewhere [47,74], 6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was taken and dissolved into 100 mL of distilled water containing 20 g zeolite. The solution

was then heated on a hot plate (with continuous stirring) at 103 °C until the water gets evaporated. The zeolites were then washed several times with deionized water to remove unreacted iron. Finally, Fe-Zeolite was calcined in a furnace at 550 °C [47,74]. Catalysts are designed by various method and used for specific applications [75–78].

### 3.3.3. Experimental Procedure for Single Ozonation and Catalytic Ozonation

Using the modified batch reactor (Figure 16), the experiments comprising of single and catalytic ozonation was carried out. The reaction was performed for 30 min at room temperature and at the natural pH of water. The experiments were conducted by varying ozone, zeolite dosage and reaction time (the Fe-Zeolite was introduced in a rotatory bucket as shown in Figure 3). For each run, 1000 mL of water sample was introduced into the reactor (203 mm × 152 mm × 152 mm) for 30 min, the ozone produced from the ozone generator (Sky zone, DA12025B12L, Karachi, Pakistan) was introduced continuously into the reactor. Samples were collected at the start of the experiment and 0.025 M sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) was quenched for removing the residual ozone [39]. After every 5 min interval, a 100 mL sample was taken to conduct a faecal coliforms experiment [71,72]. The other 50 mL was taken to analyze on an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 800) to investigate the removal of As. For finding the concentration of gas-phase ozone, 5 mL of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) with a strength of 2 N was added in potassium iodide (KI) traps and was titrated against 0.005 N sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution [71,72]. The samples were filtered through 0.45 µm cellulose nitrate filter paper for the adsorption of As. The calculation of removal efficiency (% removal) was carried using this formula:

$$\text{Percentage removal (\%)} = (Q_o - Q_t) / Q_o \times 100 \quad (12)$$

where Q<sub>o</sub> = quantity at time interval o; Q<sub>t</sub> = quantity at time interval t.

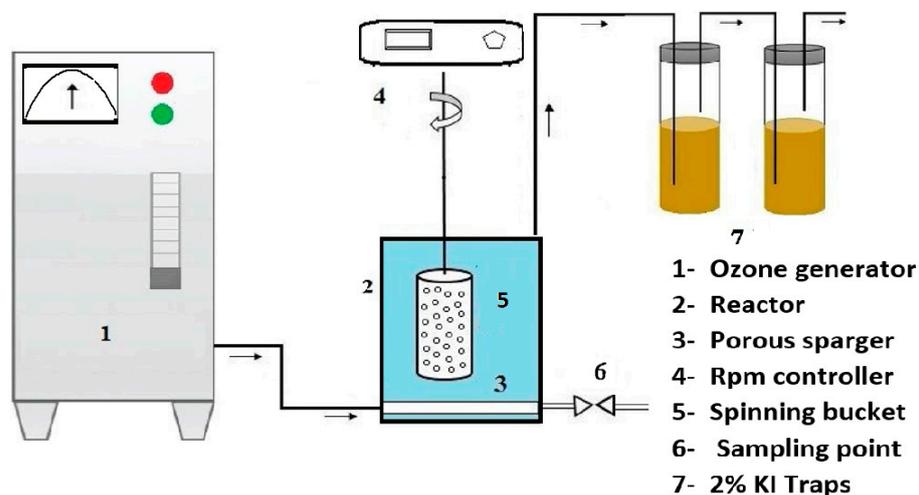


Figure 16. Experimental setup.

### 3.3.4. Ozone Dose

The iodometric method was used to quantify the ozone dose [71,72]. For this purpose, ozone generated from an ozone generator was introduced in a flask containing 200 mL 2% KI solution. In order to free iodide, the solution was quenched with 5 mL of (2 N) H<sub>2</sub>SO<sub>4</sub>. Finally, by using the starch indicator, the solution was titrated against 0.005 N of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> [71,72]. The calculation of ozone dose was carried using this formula:

$$\text{Ozone (O}_3\text{)} \frac{\text{mg}}{\text{min}} = \frac{(A + B) \times N \times 24}{T} \quad (13)$$

A = Titrant ( $\text{Na}_2\text{S}_2\text{O}_3$ ) used for Reactor (I) in mL  
 B = Titrant ( $\text{Na}_2\text{S}_2\text{O}_3$ ) used for Reactor (II) in mL  
 N = Normality of titrant ( $\text{Na}_2\text{S}_2\text{O}_3$ )  
 T = Total time of ozonation

#### 4. Conclusions

The central issue of concern is As and faecal coliforms in Lahore's studied areas and suggests that residents are at risk of suffering from the adverse effects of the long-term intake of As and faecal coliforms in drinking water. Additionally, the combination of ozone with Fe-ZA was found to be an efficient and effective way of removing As as compared with a single ozonation and adsorption process, having As removal efficiency of about 92%. Similarly, the synergic process ( $\text{O}_3/\text{Fe-ZA}$ ) effectively inactivated faecal coliforms from drinking water compared with single processes, where MPN/100 mL was found to be "0" for all treated samples with  $\text{O}_3/\text{Fe-ZA}$  process. Moreover, the ozone and Fe-zeolite dose played a vital role in the inactivation of faecal coliforms and arsenic removal in water for the studied hybrid process. It is therefore concluded that a catalytic ozonation process using  $\text{O}_3/\text{Fe-Zeolite}$  in a novel hybrid batch reactor was highly efficient for the treatment of water.

**Author Contributions:** All the author has contributed to make this study publishable. The authors contribution is as under "Conceptualization, R.F., U.Y.Q. and A.I.; methodology, A.A.; software, R.F.; validation, R.F., U.Y.Q. and A.I.; formal analysis, A.A., R.J.; investigation, A.A.; resources, U.Y.Q. and R.F.; data curation, A.I.; writing—original draft preparation, R.F., A.A. and A.I.; writing—review and editing, F.Q., R.J., U.Y.Q. and A.I.; visualization, S.I.S., A.A. and R.J.; supervision, A.I. and U.Y.Q.; project administration, U.Y.Q. and A.I.; funding acquisition, R.J. and U.Y.Q. All authors have read and agreed to the published version of the manuscript.

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