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Catalytic Ozonation Combined with Conventional Treatment Technologies for the Recycling of Automobile Service Station Wastewater

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Abstract: The ample increase in water scarcity and depletion of natural resources due to their overconsumption and the contamination of water sources becomes more challenging day by day. This challenging situation has pushed the scientific community to cope with it by providing alternative solutions. Therefore, it is indeed important to conduct a sustainable study on recycling wastewater for a particular purpose. Taking this into account, an effort was made to develop a novel hybrid treatment system that applied both conventional and advanced oxidation treatment processes. In this sustainable study, an integrated system was designed for the effective treatment followed by the recycling of automobile service station wastewater (ASSWW) which comprised sedimentation (sed), catalytic ozonation, adsorption, and filtration. In the current investigation, two catalysts/adsorbents, the granular activated carbon (GAC) and rice husk (RH) were employed individually and in combination for the first time in the studied hybrid process and their performance was compared and evaluated. The obtained results revealed that the hybrid system combination-I (Sed–O_3/GAC) was more efficient than combination-II (Sed–O_3/RH); the maximum removal efficiency of COD was 100% and 80%, respectively. In addition, the hybrid system combination-III (Sed–O_3/RH + GAC) was more economical and efficient than others by employing 35% of each absorbent in the adsorption column. Moreover, this efficient Sed–O_3/RH + GAC system has a maximum removal efficiency 99%, 100%, 99%, 100%, (89%, 99%, 100%) and 100% for turbidity, COD, BOD_5, fecal coliform, potentially toxic metals (Cd, Pb, As), oil and grease, respectively, at optimized conditions (O_3 = 82.5 mg/L; contact time = 18 min and catalyst dose of GAC and RH = 200 g each). Furthermore, the treated water sample complied with the WWF-recommended Irrigation Water Quality Guidelines (IWQGs) for class D. The increase in biodegradability (BOD_5/COD ratio) was observed from 0.41 to 0.83. Therefore, the proposed efficacious hybrid system may be employed for the recycling of ASSWW for irrigation purposes.

Keywords: hybrid treatment; rice husk; granular activated carbon; wastewater recycling

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1. Introduction

Worldwide, the water demand exceeds the availability due to three major causes; climate changes, urbanization, and deteriorating water quality. Kahil et al., 2019 [1] declared water scarcity a critical environmental issue globally due to its significantly increased concerns in the last decades in the megacities of the world. As a result, He et al., 2021 [2] quantified the current and future global water scarcity from 2016 to 2050 and applied the climate change and socioeconomic scenarios. It was projected that the water scarcity to be faced by the global urban population will increase from 933 million to 1.693–2.373 billion (one-third to half) between 2016 and 2050, respectively [2]. Due to this alarming situation the achievement of the United Nations' sustainable development goals (SDGs) particularly 6 and 11 are potentially challenging. In addition, the increasing population growth significantly demands clean water for various water sector usages such as domestic, irrigation, manufacturing, and energy [3]. Moreover, water quality especially contributed to water scarcity in the world population portion from an average of 30% to 40% annually. As a result, excessive water consumption sectors not only contributed to water scarcity from a water quantity perspective but also to water quality due to the untreated discharge of wastewater that deteriorates the water quality which further aggravates the water scarcity [4,5].

Car wash stations consume larger volumes of freshwater on daily basis and degrade the water quality by discharging hazardous pollutants such as oils, fats, detergents, and granular material, etc., into the environment [6]. In the past, this high-water consumption sector was overlooked concerning water quantity and quality perspectives. Moreover, car service stations are rapidly growing due to the rising demand for vehicles and everyday pollution, people mostly prefer to tend to wash vehicles regularly.

The car wash stations' wastewater was characterized by various researchers and presented in Table 1; high values of contaminants such as chemical oxygen demand (COD), biological oxygen demand ($BOD_{5)}$, total suspended solids (TSS), fecal coliform, oil and grease (O and G) and wide range of variation was observed. Moreover, the lack of wastewater treatment at car service stations in developing countries produced water quality and quantity issues. To cope with it, treatment is crucially mandatory Moreover, it is important to develop an alternate treatment method for the effective treatment of car service station wastewater.

Table 1. Pollutants characteristics in car wash station wastewater.

Reference	pH	Turbidity (NTU)	Phosphate (mg/L)	Alkalinity (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Coliform (CFU/100 mL)	TSS (mg/L)	Oil and Grease (mg/L)
[7]	7.4–7.7	89–103	-	-	191–241	68–133	$0.47–1.8 \times 10^6$	68–89	6–11
[8]	7.89–8.75	73–772			141–1019			110–5856	1.3–83.7
[9]	7.96–8.33	-	8.35–10.23	108–300	398–490	-	-	268–333	79–89
[10]	-	82.4–93	-	-	-	-	-	-	11–49
[11]	6.90	253	-	-	-	-	-	1000	27
[12]	7.6–8.6	-	-	-	990–1413	297–565	$2.3–4.7 \times 10^3$	1260–3417	-

Over the years, many treatment technologies have been studied by various researchers [13–18] for car wash station wastewater treatment such as coagulation/flocculation [13,14], electrocoagulation [19,20], membrane filtration [14,21], flocculation flotation [16,17], reverse osmosis [22], biological treatment [18,23], electro-oxidation [24], adsorption [25] and the photo-Fenton process [26]. These studied treatment techniques have various limitations such as pH-dependent processes, sludge production, treatment equipment with high electrical energy demands, reactor tanks (stirred, reaction, bioreactor and aeration) requiring large land area and electrical equipment, number of pumps, slow treatment process (time-consuming), cost of membranes, chemical costs (coagulants, adsorbents and catalysts), membrane biofouling and maintenance cost. Ozonation is the most effective method among them [27]. Moreover, car wash stations are small-scale sectors with limited operation in occupied land and are not able to afford the treatment costs of wastewater. Thus, there is a need to provide an effective as well as an economical treatment process.

Advanced treatment technologies (ATTs) were found to be highly efficient for the treatment of wastewater. These treatment processes are based on the generation of reactive oxygen species (ROS) that leads to the degradation of various pollutants [28–32]. Ozonation treatment is currently a more practical technology in various wastewater treatments and is far better than chlorination and does not produce chlorinated byproducts, odors, or trihalomethanes. Rizvi et al. (2022) [33] revealed that ozonation can efficiently remove color and mineralized the organic compounds in more complex wastewaters than conventional treatment. Moreover, a combination of conventional treatment technologies (CTTs)and ATTs was an economical and more efficient treatment method than a single treatment process for the 98%, 89%, 81%, 86% and 84% removal of color, COD, BOD_5, TSS, and turbidity, respectively, in the real textile wastewater, which is more complex and challenging wastewater than car wash station wastewaters [33]. Furthermore, the author previously [34] developed a single hybrid unit comprised of catalytic ozonation followed by filtration with rice husk (RH) and granular activated carbon(GAC) for effective contaminant removal from water. It was found that the removal of fecal coliform, paracetamol, turbidity, and arsenic were 100%, 70%, 98%, and 45%, respectively, and followed the WHO guidelines and NEQS for drinking water quality [34]. In addition, it was also recommended by [35] that a combination of two different treatment technologies can provide recycling of car wash stations' wastewater Therefore, this study is the continuation of the authors' previous studies [34,36] to explore novel, economical, and efficient hybrid technologies for the treatment of water and wastewater.

In this current research, a novel approach was adopted for the efficient treatment and recycling of automobile service station wastewater (ASSWW) for agricultural purposes. In this study, the first time an onsite hybrid treatment system was designed by employing the CTTs and ATTs which are sedimentation (Sed), catalytic ozonation, adsorption, and filtration. Two catalysts/absorbents, the GAC and RH, were employed in three different treatment combinations (Sed–O_3/GAC, Sed–O_3/RH, Sed–O_3/RH + GAC), and their performance was compared and evaluated. The removal of turbidity, COD, BOD_5, fecal coliform, potentially toxic metals (Cd, Pb, As), oil and grease were studied to make ASSWW recyclable. Moreover, the treatment process operational parameters such as ozone dose (mg/L), contact time (minutes), pump speed (rpm), and catalyst dose (g) were also studied for economical treatment combinations. Furthermore, current research may contribute to achieving the UN SDGs of 3, 6 and 11.

2. Material and Methods

2.1. Sampling

The real ASSWW was collected from an automobile service station controlled by Total petrol station located opposite to UET-Grand Trunk Road, Mughalpura, Lahore, Punjab 54890, Pakistan. The sampling point is geographically located at 31.57651 E, 74.35888 N. The sample was collected in a 20 L container and properly labeled. It was stored at 4 °C for the initial characterization of ASSWW.

2.2. Analytical Methods

The ASSWW characteristics such as hardness, chlorides, TSS, total dissolved solids (TDS), COD, BOD_5, fecal coliform, lead (Pb) and cadmium (Cd), arsenic (As) were determined by "Standard methods for the examination of water and wastewater" [37]. The pH of ASSWW was measured by Hanna HI-9811 and turbidity was measured in NTU by HACH 2100 P. The concentrations of potentially toxic metals (Pb, Cd and As) in the ASSWW were determined by an atomic adsorption spectrophotometer (AAS) with a graphite furnace (PerkinElmer Analyst-800, Waltham, MA, USA). The quantification and detection limits were found to be 0.91 µg/L and 0.08 µg/L, respectively. The O_3 was produced from an ozone generator (DA-12025-B12, Pakistan) for the catalytic ozonation process, and the O_3 dose and concentration were calculated by the iodometric method [37]. The flow of ASSWW in the treatment train was controlled by a digital peristaltic pump (Biobase SPP-LabN6, China).

2.3. Chemicals and Reagents

The chemicals used in the current study such as for ozonation (potassium iodide, sodium thiosulfate, and starch solution) and reagents such as HCl, NaOH, H_2SO_4, lactose, EC, BGBB and LB broth were obtained from Merck Germany. GAC was obtained from Sigma Andrich, UK. The RH is the agriculture waste technically known as Oryza sativa that was purchased from a local market. All chemicals and reagents used in the current investigation of analytical grade and applied without further purification.

2.4. Experimental Setup

The hybrid treatment system was comprised of CTTs and ATTs which are sedimentation, catalytic ozonation, adsorption, and filtration. It was established in IEER lab, UET Lahore. The designed hybrid treatment system presented in Figure 1 shows the treatment processes and flow of wastewater. The ozonation treatment was performed in a glass-made reactor with a maximum capacity of 5 L while the adsorption and filtration occurred in the glass-made multi-layered column. This multi-layered column was filled with three layers which are RH, supporting gravel and GAC.

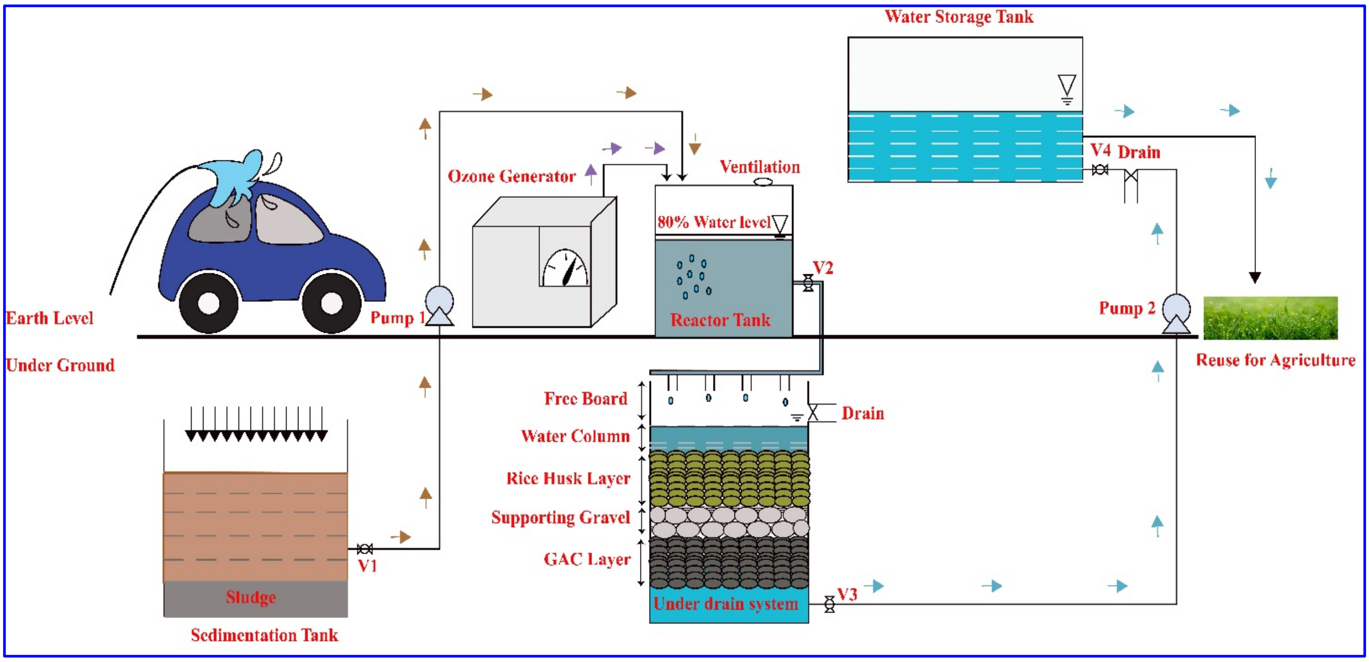

Figure 1. Schematic diagram of novel hybrid system.

2.5. Treatment Procedure

The treatment train involved in the following three stages of treatment;

Stage-I Treatment: Initially, ASSWW allowed for 24 h in a sedimentation tank for the settling of suspended solids.

Stage-II Treatment: After sedimentation, ASSWW is delivered into the reactor with the help of a peristaltic pump for the ozonation treatment.

Stage-III Treatment: Ozonated ASSWW fed into the multi-layered column under gravity for catalytic ozonation, adsorption, and filtration.

In the end, the treated samples were taken for the removal of turbidity, COD, BOD_5, fecal coliform, potentially toxic metals (Cd, Pb, As), oil and grease.

The catalytic activity was suggested since the molecular ozone may be adsorbed on the surface of the adsorbent leading to the reactions with pollutants and leading to the formation of hydroxyl radicals. Besides, the mechanism of catalytic activity of the studied catalyst was explained based on the authors' previous studies [38,39].

It is pertinent to mention here that catalytic ozonation occurred at the same time during filtration/adsorption in the multilayered filtration column, the GAC act as the catalyst itself. When the ozonated sample was fed into the filtration column the aqueous O_3 remained stable for some time [40]; therefore, molecular O_3 attacked the adsorbed pollutants and a breakdown happened. It was studied [40] that the typical half-life of aqueous O_3 is less than one hour due to the reactivity of hydroxyl radicals.

2.6. Ozonation Treatment Optimization

The effect of ozone dose and contact time plays a significant role in the ozonation treatment process for the removal of pollutants. Firstly, the effect of ozone dose was determined with a constant 15 min contact time for the removal of COD. Then, the contact time effect was studied by varying the speed of the peristaltic pump from 100 rpm to 150 rpm to fill the reactor. The contact time in ozonation treatment is highly dependent on the speed of the peristaltic pump for the removal of COD by the following relation;

$$\text{Contact Time} \propto \frac{1}{\text{Pump Speed}} \propto \text{Pollutant Removal} \tag{1}$$

The higher the pump speed, the more electrical energy is consumed to fill the reactor faster and the lower the contact time; the removal efficiency of pollutants is affected. Conversely, the lesser the pump speed takes, the more time to fill the reactor, and again the removal efficiency of pollutants is affected. Therefore, it is essential to optimize and then utilize the optimal peristaltic pump speed and contact time for the efficient removal of pollutants.

2.7. Catalysts Preparation and Characterization

Firstly, the catalyst RH was washed with distilled water and then dried in air for 48 h. Then, it was dipped in nitric acid solution (0.1 M) for 24 h. Filtration was performed with suction filtration assembly and again washed with deionized water thoroughly until a pH of 7.2 was attained [41]. The Brunauer–Emmett–Teller (BET) method by using a micromeritics USA ASAP analyzer was employed for the determination of surface area and average pore size of catalysts GAC and RH. During analysis, the adsorption isotherms were utilized by employing nitrogen adsorption and desorption at 77 kelvin. Finally, the Bopp–Jancso–Heinzinger (BJH) method and Kelvin equation were used for the porosities and surface area determination. Moreover, the point of zero charges (pHpzc) of considered catalysts (GAC and RH) was determined with the mass transfer method [36].

2.8. Treatment Combinations

In the current study, two catalysts/adsorbents were employed in the following three treatment combinations for the removal of pollutants in ASSWW;

Catalytic ozonation of sedimented sample using GAC as a catalyst followed by adsorption and filtration (Sed–O_3/GAC).

Catalytic ozonation of sedimented sample using RH as a catalyst followed by adsorption and filtration (Sed–O_3/RH).

Catalytic ozonation of sedimented sample using RH + GAC as a catalyst followed by adsorption and filtration (Sed–O_3/RH + GAC).

3. Results and Discussion

3.1. Initial Characterization of ASSWW

The real ASSWW characterization is summarized in Table 2. It was observed that the ASSWW sample has a brownish-black color and high values of contaminants such as turbidity, COD, BOD_5, fecal coliform, cadmium, oil, and grease. Moreover, these contaminants exceeded the Irrigation Water Quality Guidelines (IWQGs) for Class D proposed by World Wide Fund, Pakistan [42]. Therefore, the treatment of ASSWW is mandatory by a novel hybrid system to comply with the IWQGs and then recycling for irrigation purposes.

Table 2. Characteristics of real ASSWW and IWQGs.

Parameters	Units	Mean Concentration	IWQGs Class D [42]
pH	-	6.9 ± 0.2	6.5–8.4
TSS	mg/L	217 ± 6	-
TDS	mg/L	1037 ± 35	1000
Turbidity	NTU	669 ± 16	-
BOD_5	mg/L	225 ± 9	8
COD	mg/L	490 ± 11.5	-
Total Nitrogen	mg/L	28 ± 3.5	-
Chlorides	mg/L	150 ± 5.5	100
Total Hardness	mg/L	374 ± 17	-
Fecal Coliform	MPN/100 mL	5170 ± 95	1000
Oil and Grease	mg/L	200 ± 7.5	-
Cadmium	mg/L	0.056 ± 0.001	0.01
Lead	mg/L	0.012 ± 0.001	0.10
Arsenic	mg/L	0.100 ± 0.001	0.10

3.2. RH and GAC Characterization

The physicochemical properties of the studied catalysts are summarized in Table 3. The GAC has a large surface as compared to RH, which may play an effective role in adsorption to adsorb the contaminants on its surface [36]. The pore size of RH of 18.2 angstroms (Å) was higher than GAC of 9.1 Å. It was observed that while comparing the point of zero charges (pHpzc) of catalysts, there was a noticeable difference. The pHpzc of RH and GAC were towards the acidic and basic side, respectively.

Table 3. RH and GAC characterization.

Catalysts	Surface Area (m^2/g)	Pore Size (Å)	pH_{pzc}
RH	90.4	18.2	2.9 ± 0.1
GAC	1080	9.1	8.7 ± 0.2

3.3. Ozonation Treatment

The ozonation dose optimization was performed on the removal of COD by varying the ozone dose at a constant contact time of 15 min. The effect of ozone dose on COD removal in real ASSWW was presented in Figure 2. It was observed from Figure 2 that maximum COD removal efficiency of 89% was achieved at an ozone dose of 116.4 mg/L. While comparing the removal efficiencies at different ozone dosages, it was observed that there was a negligible difference in ozone dose concentrations of 82.5 mg/L and 116.4 mg/L with COD removal of 83% and 85%. The optimum ozone dose of 82.5 mg/L was selected for the current investigation.

For the contact time optimization, ASSWW was ozonated at the optimized ozone dose of 82.5 mg/L at a different speed (100–150 rpm) of the peristaltic pump to fill the reactor. It is important to mention here that the time taken by the peristaltic pump to fill the reactor 4 L (80% of reactor volume) was the contact time of the ozonation treatment process. Moreover, the effect of pump speed associated with the ozonation contact time on COD removal was shown in Figure 3. It was found exposed that the pump filled the reactor in 9, 18, and 21 min at the speed of 100, 150, and 200 rpm, respectively. Then ozonation treatment was performed at an optimized dose of 82.5 mg/L and measured COD removal efficiencies were 60%, 87%, and 89% at contact times of 9 min, 18 min, and 21 min, respectively (Figure 3). There was a negligible difference at 18 min and 21 min of contact time for COD removal. Therefore, the optimized pump speed and contact time were 150 rpm and 18 min, respectively.

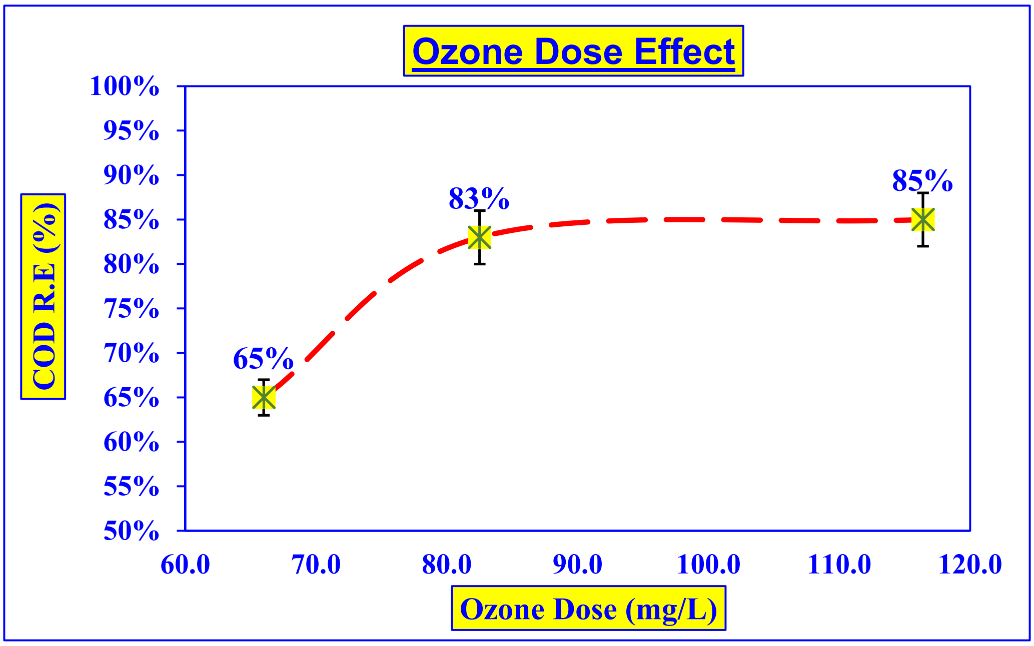

Figure 2. Ozone dose optimization in ozonation process (O_3 = 66.0 ± 1.5 mg/L, 82.5 ± 2.2 mg/L, 116.40 ± 3.6 mg/L; pH = 6.9 ± 0.2; C.T = 15 min; volume = 4 L; T = 25 ± 2 °C).

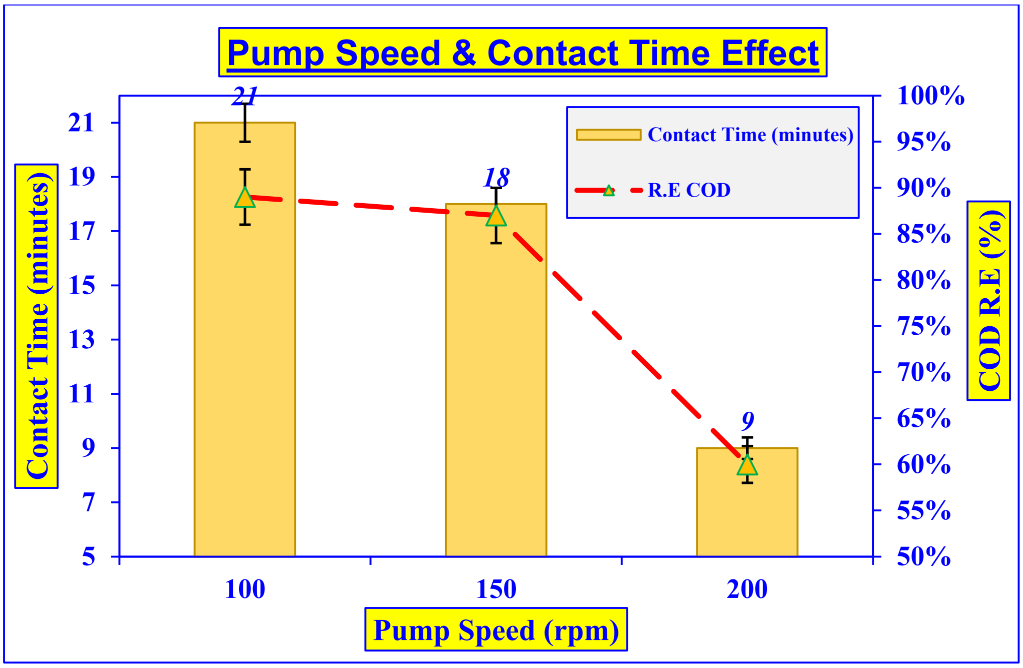

Figure 3. Pump speed and Contact time optimization in ozonation process (peristaltic pump speed = 100 rpm, 150 rpm and 200 rpm; t = 9 min, 18 min and 21 min; Initial COD = 490 mg/L; O_3 = 82.5 ± 2.5 mg/L; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.4. Comparison of Treatment Combinations

The five (05) treatment processes; sedimentation, ozonation, catalytic ozonation, adsorption, and filtration were studied in four (04) different combinations. The combinations of treatments; sedimentation followed by (1) ozonation, (2) catalytic ozonation with RH, (3) catalytic ozonation with GAC, (4) catalytic ozonation with RH + GAC were compared for the removal of a contaminant. The comparison of treatment combinations was presented in Figure 4 for the removal of COD. The results revealed that the removal efficiency of COD achieved by the sedimentation process was 38% due to the settling of suspended solids under gravity at the initial stage, and reduced the pollution load on the next treatment train of ASSWW. Ozonation was performed after sedimentation of the ASSWW sample and 87% COD removal efficiency was attained. Further treatment is required to comply with class D IWQGs for ASWW recycling. Therefore, catalytic ozonation, adsorption, and filtration were introduced with two adsorbents/catalysts RH and GAC. Moreover, while comparing the treatment combinations, it was found that GAC has a higher removal efficiency than RH with 100% and 80% COD removal, respectively, due to the large surface area and pollutants being adsorbed on the GAC surface. The COD removal efficiency was reduced by 7% by Sed– O_3/RH than the Sed-O_3 process (Figure 4) because RH released its color during treatment (Figure 5).

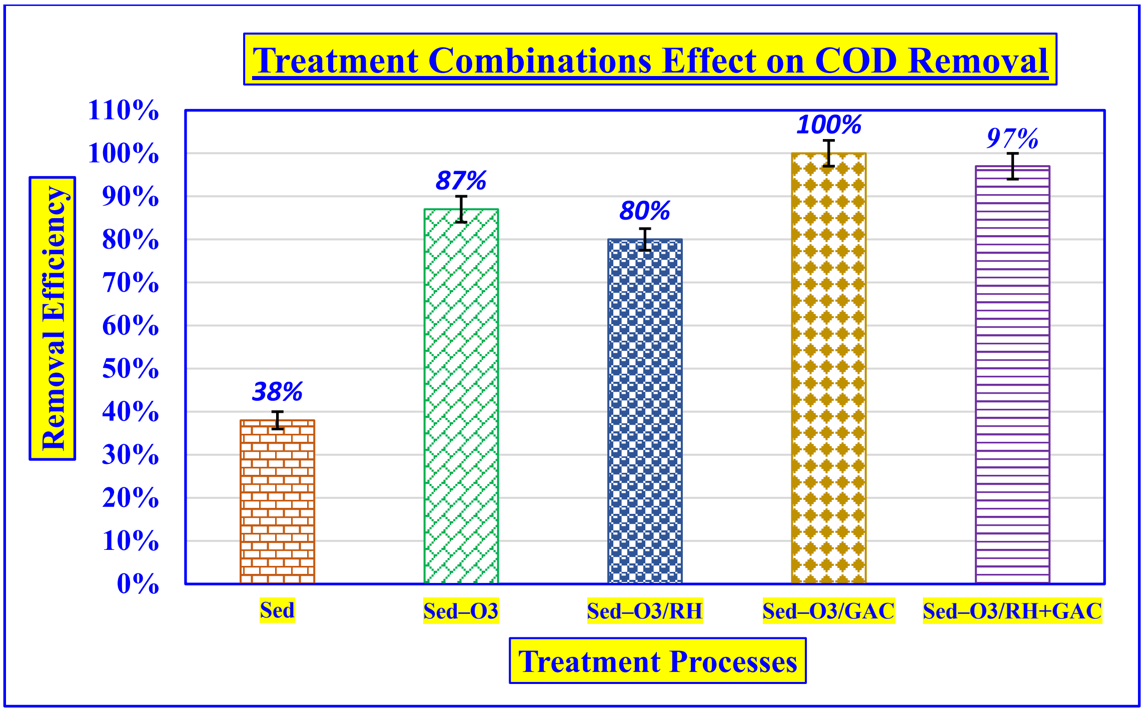

Figure 4. COD removal by different combinations (Initial COD= 490 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C. T= 18 min; GAC= 400 g; RH= 400 g; GAC + RH = 200 g +200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

The maximum 100% removal efficiency was achieved by the Sed–O_3/GAC process with an adsorbent amount of 400 g. To make an economical treatment combination, the combined effect of adsorbents (RH + GAC) was studied due to the higher cost of GAC. The adsorbent quantity was reduced by 50% and 200 g of each catalyst was applied. It was interesting that 97% COD removal efficiency was achieved by the Sed–O_3/RH + GAC process. In this novel treatment combination, the ozonated samples were fed into the multi-layered absorption-filtration column (Figure 1).

Moreover, it was observed from Figure 5 that the treated sample of ASSWW by Sed–O_3/RH + GAC process was more pure and clear water in color than other treatment combinations. It is an efficacious advantage of the Sed–O_3/RH + GAC process other than economical. Thus, Sed–O_3/RH + GAC process was selected for further investigation of other contaminants removal.

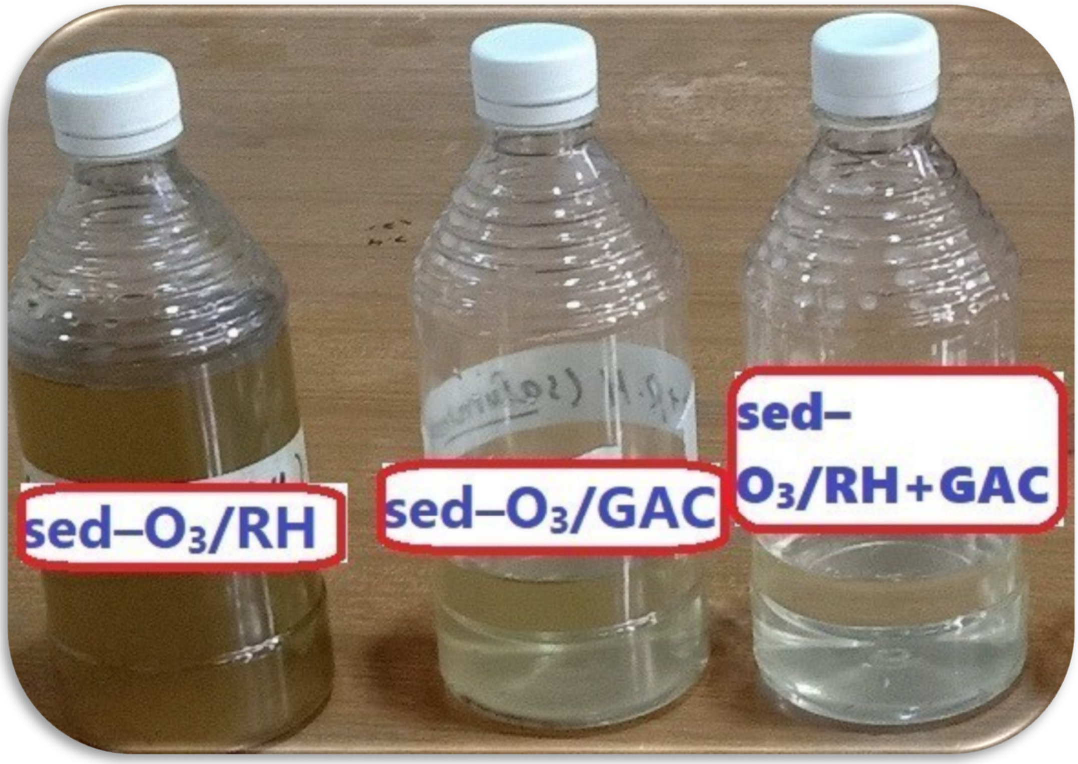

Figure 5. Treated samples of ASSWW by three treatment combinations.

3.4.1. Effect of Turbidity Removal

In this study, a real automobile service station wastewater sample has a high turbidity value of 669 NTU. Figure 6 shows the removal of turbidity by a novel hybrid system; sedimentation followed by catalytic ozonation, adsorption, and filtration. It was found that there was a significant decrease in the turbidity of real ASSWW collected samples. The results revealed that the maximum removal of efficiency of 99% was achieved by the Sed–O_3/RH + GAC process (Figure 6). It is more than the removal efficiency of turbidity (79%) achieved by the Rotating Biological Contactor (RBC) based aerobic biological treatment (RBC) for the treatment of heavy-duty vehicle washing station wastewater [18].

3.4.2. Effect of COD Removal

The removal rate of COD was studied in the current investigation because the ASSWW contained various types of chemical constituents from snow foam, detergents, oil and grease. Thus, the COD must be analyzed in ASSWW as these chemical substances contributed to the COD value. The removal efficiencies of COD were presented in Figure 7, it was revealed that 100% COD removal efficiency was achieved by hybrid combination-III (Sed–O_3/RH + GAC). Moreover, a significant reduction in COD was found in real ASSWW by this efficient hybrid process (Figure 7) as compared to other full treatment units (coagulation/flocculation/sedimentation, sand filtration, ceramic ultrafiltration and reverse osmosis). It was found that 96% of COD was removed by this lengthy and expensive treatment unit; moreover, sludge management involves additional costs [22].

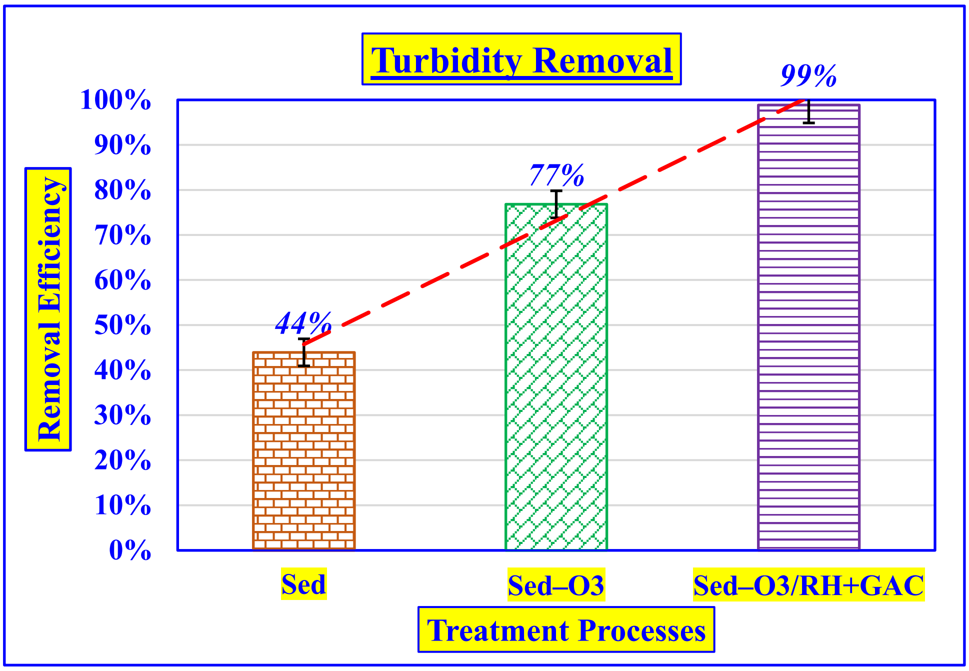

Figure 6. Turbidity removal by hybrid system (Initial turbidity = 669 ± 16 NTU; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

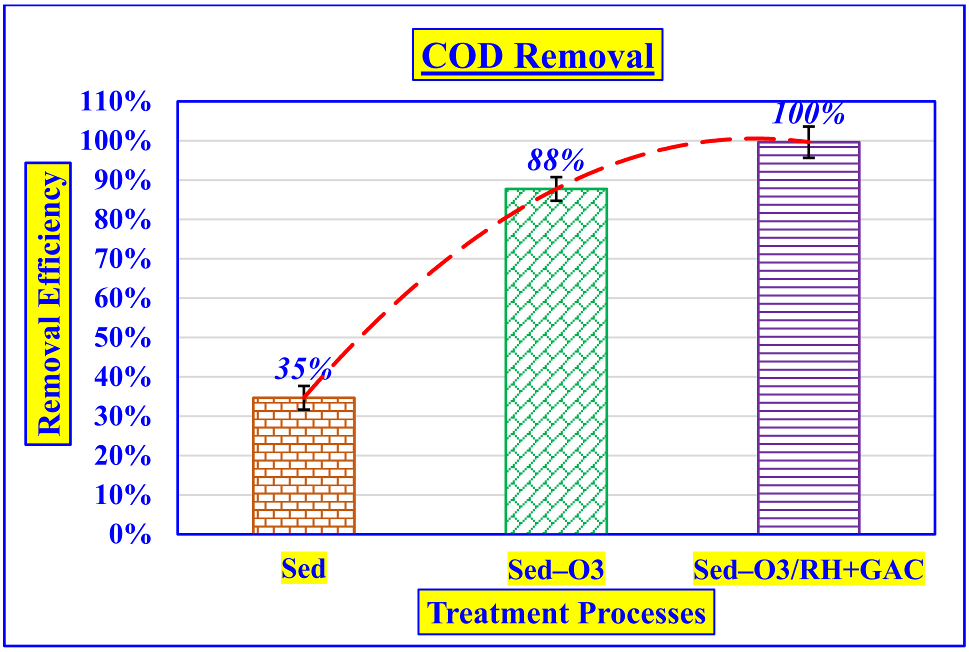

Figure 7. COD removal by hybrid system (Initial COD = 490 ± 11.5 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.4.3. Effect of BOD_5 Removal

In order to treat the car wash service station wastewater and recycling of ASSWW for irrigation purposes, the removal of BOD_5 must be assessed. In the current investigation, the removal rate of BOD_5 by the efficient combination is presented in Figure 8. The novel treatment combination achieved a 99% removal efficiency of BOD_5 and complied with the IWQGs recommended standard value of BOD_5 (Table 4) for Class D proposed by [42]. The integrated method (flocculation flotation, sand filtration, ozonation, and chlorination) was studied by [17] for the treatment of car wash effluent. The results revealed that 26.95% of BOD_5 was removed by flocculation flotation and 84.76% was achieved with the integration ozonation process taking a longer reaction time of 60 min. In the current investigation, the ozonation time was about 18 min, which may save the electrical energy demand and cost of treatment by the Sed–O_3/RH + GAC process.

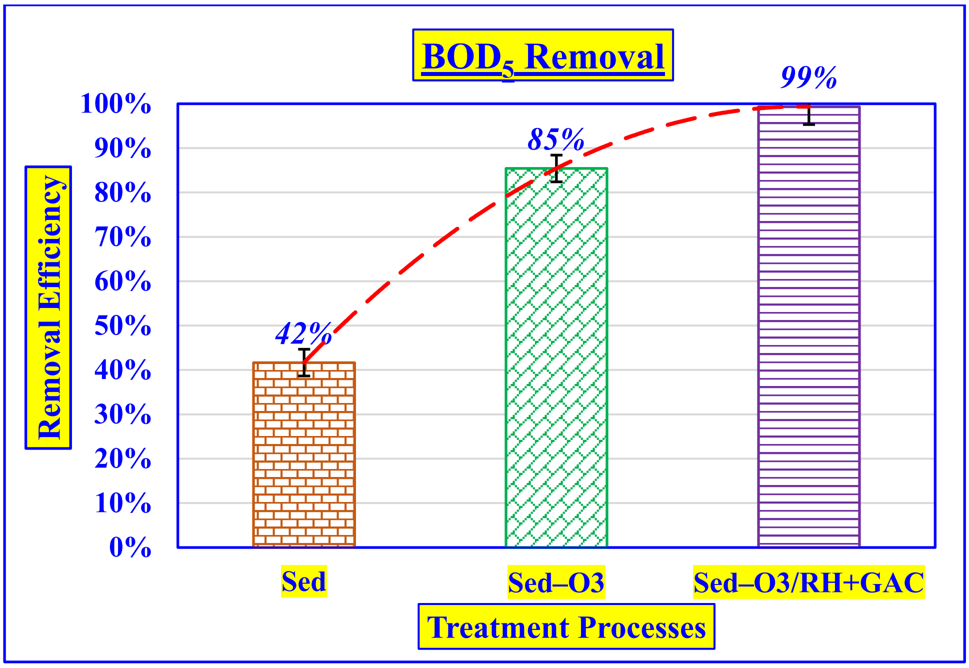

Figure 8. BOD_5 removal by hybrid system (Initial BOD5 = 225 ± 9 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

Table 4. Quality of treated ASSWW sample by a novel hybrid method.

Parameters	Units	Initial Values	Sed	Sed-O_3	Sed-O_3/RH + GAC
pH	-	6.9 ± 0.2	6.9 ± 0.2	7.3 ± 0.2	7.3 ± 0.2
Turbidity	NTU	669 ± 16	375 ± 11	155 ± 4	7.5 ± 0.5
BOD_5	mg/L	225 ± 9	131.3 ± 3.7	32.8 ± 1.5	1.5 ± 0.1
COD	mg/L	490 ± 11.5	320 ± 7	60 ± 2	1.8 ± 0.1
BOD_5/COD	ratio	0.46 ± 0.01	0.44 ± 0.01	0.82 ± 0.01	0.83 ± 0.01
Fecal Coliform	MPN/100 mL	5170 ± 95	3550 ± 69	0.015 ± 0.001	0.007 ± 0.001
Cadmium	mg/L	0.056 ± 0.001	0.055 ± 0.001	0.053 ± 0.001	BDL
Lead	mg/L	0.012 ± 0.001	0.011 ± 0.001	0.010 ± 0.001	BDL
Arsenic	mg/L	0.100 ± 0.001	0.087 ± 0.001	0.07 ± 0.001	BDL
Oil and Grease	mg/L	200 ± 7.5	189 ± 6	52 ± 3	0.9 ± 0.1

3.4.4. Effect of Biodegradability Enhancement

In the current investigation, more than contaminants removal, the efficacy of the novel treatment method was also evaluated by considering the biodegradability (BOD_5/COD ratios) of ASSWW. Figure 9 shows the improvement in biodegradability by Sed–O_3/RH + GAC process from 0.41 to 0.83 and makes the real ASSWW biodegradable for future research. The wastewater is significantly treatable by biological treatment if BOD_5/COD ratio is greater than 0.5 [33,43].

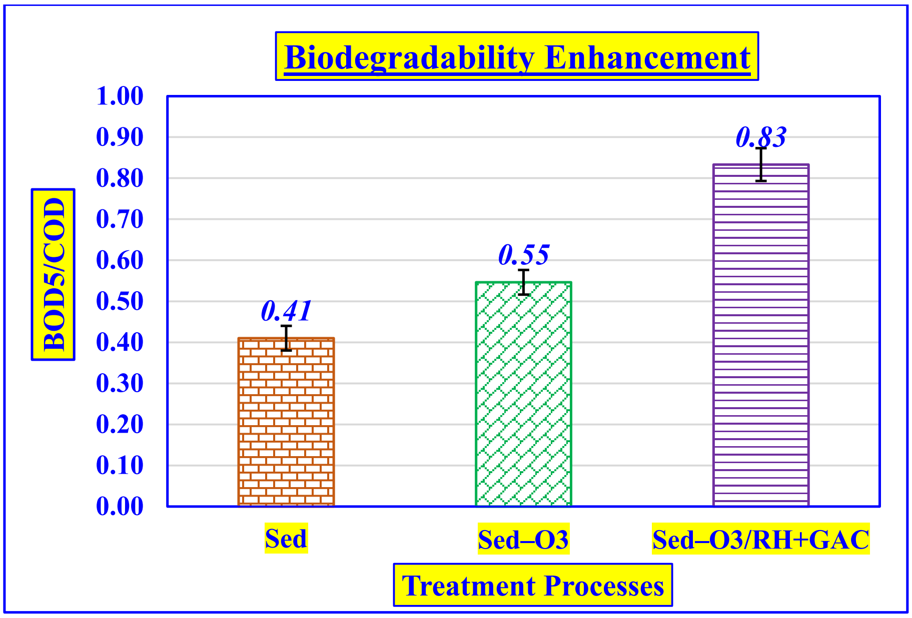

Figure 9. Biodegradability increased by hybrid system (Initial COD = 490 ± 11.5 mg/L; Initial BOD5 = 225 ± 9 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.4.5. Effect of Fecal Coliform Removal

(Kuan et al., 2022) [35] reviewed the 68 studies on the efficacy of various treatment technologies for car wash services station wastewater. Among them, no one studies the removal of coliforms although it is an important parameter for the recycling of vehicle wash station wastewater. Figure 10 shows the 100% reduction in fecal coliform (5 log removal) was achieved by employing the Sed–O_3 and Sed–O_3/RH + GAC process and complying with the IWQGs recommended standard value of fecal coliforms (Table 4) for Class D proposed by [42].

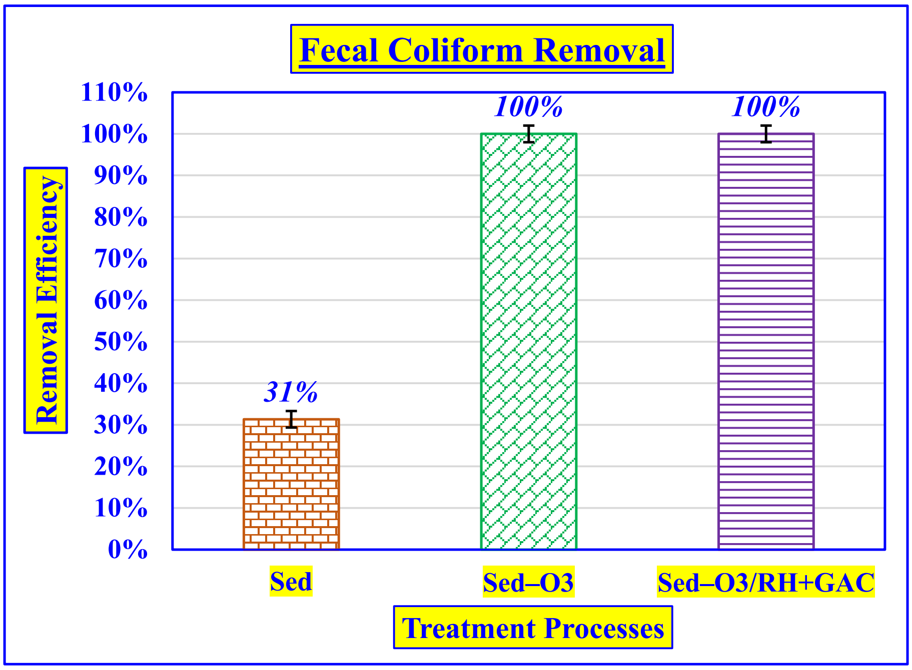

Figure 10. Fecal Coliform removal by hybrid system (Initial Fecal Coliform = 5170 MPN/100 mL; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.4.6. Effect of Oil and Grease Removal

Oil and grease are the most common contaminants present in car wash service station wastewater. The removal of O and G was studied by various research by employing different treatment technologies and integrated methods. The combined two advanced oxidation processes; electrocoagulation followed by nanofiltration using NF 270 and Desal 5DL membranes were studied by [15] for the removal of O and G for car wash station effluent. It was found that 90% removal of O and G was achieved at 30 min of operating time. Moreover, sludge production, high membrane costs, and more electrical energy made it an expensive treatment. In the current investigation, the removal efficiency of O and G was 100% by Sed–O_3/RH + GAC and presented in Figure 11. This suggested that catalytic ozonation of sedimented samples followed by adsorption and filtration (Combination-III) was a more efficient method for the removal of O and G in real ASSWW.

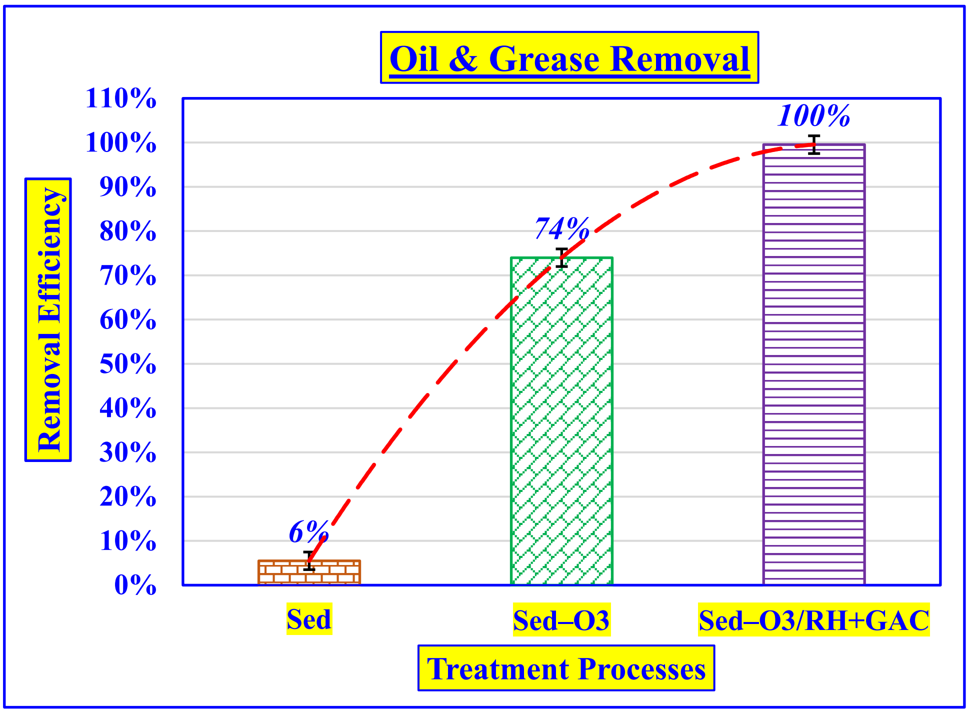

Figure 11. Oil and Grease removal by hybrid system (Initial O and G = 200 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.4.7. Effect of Potentially Toxic Metals Removal

The concentration of potentially toxic metals was also measured in ASSWW collected samples. The concentration of cadmium and lead exceeded the [42] recommended IWQGs standard value for class D (Table 2); however, arsenic was in the accepted range. The removal of Cd, Pb, and As were studied in the current investigation and presented in Figure 12. The obtained results are in support of novel hybrid system effectiveness that removed potentially toxic metals from ASSWW and meets the acceptable range (Table 4). Otherwise, tertiary-stage treatment is required for the effective removal of potentially toxic metals that are mainly comprised of membrane technology [38]. The maximum removal efficiencies of 89%, 99%, and 100% of Cd, Pb, and As were achieved, respectively, by the catalytic ozonation of the sedimented sample followed by the adsorption and filtration process.

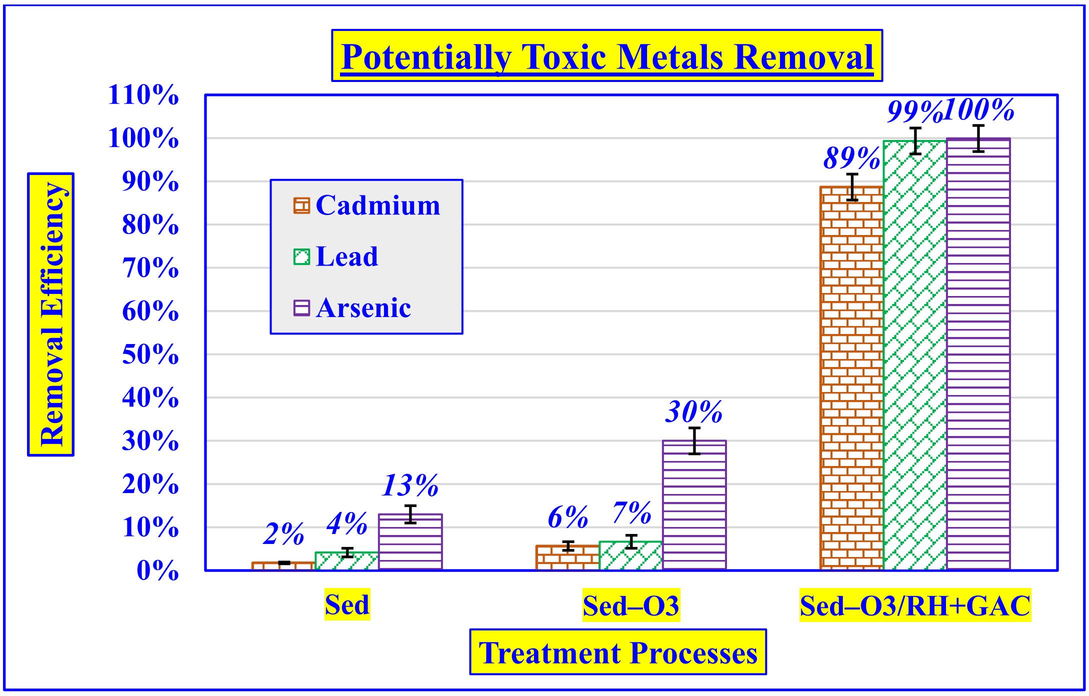

Figure 12. Toxic metals removal by hybrid system (Initial Cd = 0.056 mg/L, Pb = 0.012 mg/L and As = 0.1 mg/L; O_3 = 82.5 ± 2.2 mg/L; peristaltic pump speed = 150 rpm; C.T = 18 min; GAC = 200 g; RH = 200 g; pH = 6.9 ± 0.2; volume = 4 L; T = 25 ± 2 °C).

3.5. Discussion

In the past, many treatment technologies were studied for the treatment of car wash service station wastewater. To have an effective treatment, various treatment methods such as coagulation, flocculation, electrocoagulation, flocculation flotation, membrane treatment, biological treatment, and reverse osmosis were employed individually and in combination for the removal of pollutants. These treatment technologies have advantages and certain limitations [10,11,14–16,20,21,23,35,44].

Table 4 depicted the quality of treated automobile service station wastewater by catalytic ozonation of sedimented sample followed by adsorption and filtration [18]; we proposed a full-scale treatment unit for heavy-duty vehicle washing station wastewater treatment. It was composed of a grit chamber, oil separation tank, high-capacity equalization tank, RBC based aerobic biological treatment followed by ultrafiltration and chlorination for the removal of turbidity, TDS, COD, BOD_5, TOC, and color. The initial turbidity of 62.9 NTU was reduced to 18 NTU (79%) after RBC and 94% after ultrafiltration. In the current investigation, turbidity was reduced from 669 ± 16 NTU to 7.5 ± 0.5 NTU (Table 4) in the real ASSWW sample. This suggested that a novel hybrid process Sed–O_3/RH + GAC may be a highly efficient process for the treatment of real ASSWW.

The approximate COD removal rates of electrocoagulation, flocculation flotation, and coagulation filtration-based treatments were 80%, 70–80%, and 60%, respectively. When these methods were combined with other treatment technologies such as biological treatment, the removal rate of COD may be increased [35]. Moazzem et al., 2018 [22] studied the removal of COD from car wash station wastewater by a fully combined treatment system. It was found that the initial COD 295 mg/L was reduced to 11.5 mg/L (96%) by coagulation/flocculation/sedimentation followed by sand filtration, ceramic ultrafiltration, and reverse osmosis. While comparing with the current study, the initial COD of 490 ± 11.5 mg/L to 1.8 ± 0.1 mg/L by Sed–O_3/RH + GAC (Table 4) from real ASSWW samples, made it the more efficient treatment method.

Etchepare et al. (2015) [17] studied the removal of COD and BOD_5 from car wash effluent by employing an integrated method; flocculation flotation followed by sand filtration, ozonation, and chlorination. It was revealed that the initial COD and BOD_5 683 mg/L and 397 mg/L were reduced to 415 mg/L and 290 mg/L by flocculation flotation and 96 mg/L and 60 mg/L were achieved with the integration ozonation process taking a longer reaction time of 60 min. While in the current investigation, initial BOD_5 was reduced by the Sed–O_3/RH + GAC process from 225 ± 9 mg/L to 1.5 ± 0.1 mg/L (Table 4) at 18 min of contact time which may save the cost of treatment.

Z. B. Gönder et al. (2020) [15] studied the fecal coliform, oil and grease removal from car wash station effluent by employing combined advanced oxidation processes electrocoagulation and nanofiltration (NF 270 and Desal 5DL membranes). The results revealed that fecal coliform, oil and grease were reduced from 1100 MPN/100 mL and 125 mg/L to 0 MPN/100 mL and 13 mg/L, respectively, at 30 min of operating time of electrocoagulation. Furthermore, sludge disposal produced by electrocoagulation, membrane fouling and high electrical energy was involved. While the current hybrid treatment process reduced the fecal coliform, oil and grease from 5170 ± 95 MPN/100 mL and 200 ± 7.5 to 0.007 ± 0.001 MPN/100 mL (5 log removal) and 0.9 ± 0.1, respectively, at 18 min of contact time. This suggested that catalytic ozonation of sedimented sample followed by adsorption and filtration was a more efficient method for the removal of fecal coliform, oil and grease from real ASSWW.

4. Conclusions

It was confirmed in the current investigation that GAC has higher removal efficiency of pollutants than RH due to its large surface area; more pollutants were adsorbed on the GAC surface effectively leading to the reactions with pollutants and leading to the formation of hydroxyl radicals. When hybrid treatments of conventional treatment and advanced oxidation process were performed, it was revealed that the catalytic ozonation of the sedimented sample followed by adsorption and filtration (Sed–O_3/RH + GAC process) was the more efficient and economical method. This novel hybrid process has higher removal efficiencies of pollutants than Sed–O_3/RH and Sed–O_3/GAC processes and no significant pH change was observed. The obtained results showed that the maximum removal efficiencies for turbidity, COD, BOD_5, fecal coliform, potentially toxic metals (Cd, Pb, As), oil, and grease were 99%, 100%, 99%, 100%, (89%, 99%, 100%) and 100%, respectively, at optimum conditions and complied with the irrigation standards. Therefore, the current investigation may significantly contribute to alleviating the water scarcity problem. The implementation of studied onsite novel hybrid treatment systems at an industrial scale may also help in accomplishing the UN SDGs 3, 6, and 11.

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