Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2019.24164

159 (2019) 304–309
August

Combined ozonation and adsorption system for the removal of heavy metals from municipal wastewater: effect of COD removal

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Received 23 October 2018; Accepted 22 March 2019

ABSTRACT

Heavy metals like copper, chromium, cadmium, lead, and zinc are key contaminants of freshwater reservoirs because of their deadly, non-biodegradable, and persistent nature. The work involves the comparison of various single and combined processes such as ozonation (Ozo), adsorption on activated carbon (AC), adsorption on rice husk (RH), ozonation in the presence of rice husk (Ozo/RH) and ozonation in the presence of activated carbon (Ozo/AC) for the removal of chemical oxygen demand (COD) and heavy metals from the municipal wastewater. Various factors such as adsorbent dose reaction time and synchronizing effect of COD removal on the removal efficiency of heavy metals was studied. The maximum removal of both COD and heavy metals was achieved by ozonation in the presence of activated carbon (Ozo/AC) combined process. The results further reveal that COD removal efficiencies have a positive synchronizing impact on the removal efficiencies of heavy metals. It is therefore concluded that (Ozo/AC) combined process may be used for the removal of heavy metals in wastewater.

Keywords: Ozonation process; Adsorption; Heavy metals; Chemical oxygen demand

1. Introduction

The rapid increase in industrialization and urbanization cause serious problem to the environment. The wastewater produced from different industries is heavily polluted by persistent organic compounds, inorganic compounds, and heavy metals. Among these contaminants, heavy metals are more dangerous for the environment [1–3]. The presence of heavy metals such as zinc, lead, cadmium, copper, and chromium is of major concern due to their toxicity and non-biodegradability in living organisms [4–6]. For example, the presence of lead may damage the hematopoietic system which results in liver, kidney and central brain failure leading to hepatitis, encephalopathy, anemia [7]. Similarly, the accumulation of cadmium in human bodies can cause renal abnormalities and diseases like proteinuria and glucosuria [8]. So, the heavy metals must be removed from wastewater in order to protect the environment. The main sources of heavy metals include leather industries, electroplating industries, mining industries, textile industries, municipal wastes, and printing industries etc. The discharge of effluents composing heavy metals causes severe environmental pollution. Methods such as coagulation, reverse osmosis, chemical precipitation, flotation and exchanging ions are used at industrial scale for heavy metals abatement from waste waters. Unfortunately, these methods are moderate efficient, high energy cost, low selectivity in heavy metal removals and also produce large quantities of toxic sludge [9].

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Advanced oxidation processes (AOPs) gain significant importance in recent few years for wastewater and water purification due to high removal efficiencies. These processes involve situ generations of strong oxidants such as hydroxyl radical (•OH) [7]. Several process technologies were used in past as AOPs. Among them, some were already established, especially those involving UV irradiation and ozonation [10,11]. Catalytic ozonation process effectively removes recalcitrant compounds through numerous reaction pathways. Different materials such as activated carbon, zeolites, alumina etc were applied as catalysts in several in catalytic ozonation process for the degradation of recalcitrant compounds [12–14].

A diversity of materials has been used as adsorbents and catalyst supports in catalytic ozonation process. Among them activated carbon has been acknowledged as potential absorbent and catalyst for the removal of organic compounds from wastewater. It is widely used in many industries due to its abundant porous structure, chemical inertness, tenable texture and high-temperature stability [15–18]. Similarly, the rice husk which is the residue of a rice-milling process act as an effective adsorbent for heavy metals and dyes due to a high proportion of cellulose containing several hydroxy functional groups [19,20].

In this study, a comparative study of single and combined processes such as ozonation (Ozo), adsorption on activated carbon (AC), adsorption on rice husk (RH), ozonation in the presence of rice husk (Ozo/RH) and ozonation in the presence of activated carbon (Ozo/AC) for the removal of chemical oxygen demand (COD) and heavy metals from municipal wastewater was performed. To the author knowledge, most of the previous studies on heavy metals are based on synthetic solutions while in the current study, real municipal wastewater was used and the constituents of real wastewater (such as COD) may affect the adsorption, therefore activated carbon and rice husk should be tested in real wastewater matrix, in addition, ozonation was used in combination with adsorption, in which adsorbents like activated carbon and rice husk has not been previously used in comparative study for the removal of heavy metals from municipal wastewater. Furthermore, the synchronizing impact of COD on metal removal efficiencies was investigated in the real effluent of municipal wastewater as a first-time study. This may help to increase the overall removal efficiency of heavy metals and may be practically feasible to the real condition.

2. Materials and methods

2.1. Materials and reagents

Chemicals used in this research study were of analytical grade and all the chemicals were used without further purification. The activated carbon was procured from the Sigma Aldrich and rice husk was purchased from a local market.

2.2. Combined ozonation and adsorption experiments

The experiments comprising ozonation and adsorption were performed in a semi-continuous process. Fig. 1 shows the experimental setup used in the current study. For each run, 3000 ml of wastewater was introduced into the reactor (203 mm × 152 mm × 152 mm), the ozone produced from ozone generator (Sky zone, DA12025B12L, Karachi, Pakistan) was continuously introduced into the reactor for 60 min. The ozone treated wastewater was then fed into an adsorption column (I.D = 50.8 mm, length = 1.5 ft) loaded with the adsorbent (Fig. 1). Samples were collected after every 15 min and were quenched with 0.025 M sodium carbonate (Na_2CO_3) in order to remove residual ozone [21]. 100 ml of the sample was taken out at 15 min of intervals and out of that 50 ml was used to check the COD [22] and the other 50 ml was digested according to the standard method [22] and was analyzed on atomic absorption spectrophotometer (Perkin Elmer AAnalyst 800) to investigate the removal of heavy metals (Zn, Co, Cu, Cd, Pb, Cr). To find the concentrations of gas phase ozone, 5 ml of sulfuric acid (H_2SO_4) having the strength of 2 N was added in KI traps and titrated against 0.005 N sodium thiosulfate solution [21].

$$\text{Percentage removal (\%) [23]} = \frac{\left(C_o - C_t\right)}{C_o} * 100$$

where C_o = concentration at time interval o; C_t = concentration at time interval t.

2.3. Ozone dose

The ozone doses were quantified by using the standard method (Iodometric method) [22]. For that, ozone produced from ozone generator (Sky zone, DA12025B12L, Karachi, Pakistan) was bubbled in 2% potassium iodide solution (250 ml). Finally, the solution was quenched with 5 ml of 2 N H_2SO_4 to liberate iodine. The released iodine was titrated against 0.005 N sodium thiosulphate ($Na_2S_2O_3$) using starch indicator [22]. Ozone dose was calculated by using the following formula:

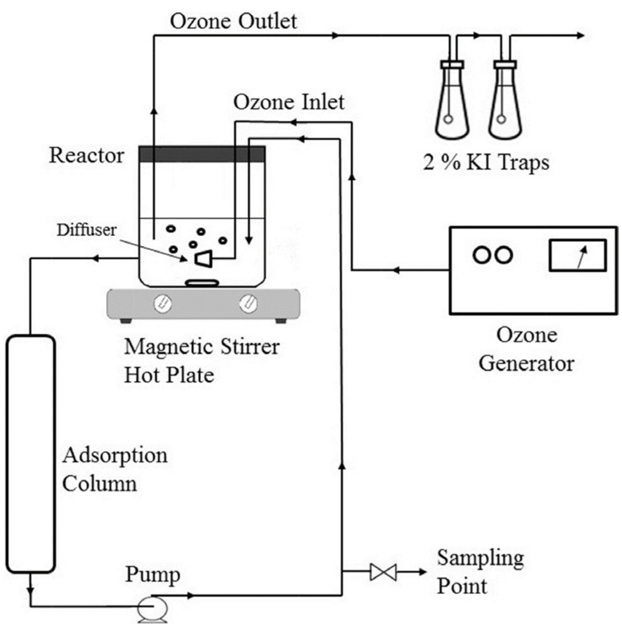

Fig. 1. Experimental setup.

$$Ozone\ Dose\left(\frac{mg}{\min}\right) = \frac{V*N*24}{T}$$

where V: total volume of the titrant used; N: normality of $Na_2S_2O_3$; T: ozonation time.

3. Results and discussion

3.1. Wastewater characterization

The wastewater samples were collected from the main sewage outfall of Saggiyan Bridge Lahore, Pakistan. Samples were filtered after collection and stored at 4°C. Table 1 shows the characterization of various physical and chemical parameters of wastewater. The selected heavy metals for current investigation were significantly found in the wastewater (Table 1). Moreover, the wastewater contains significant COD value which may affect the adsorption process of heavy metals on adsorbents.

3.2. COD removal

The COD removal efficiency was studied under single and combined processes (RH, AC, Ozo, Ozo/RH, Ozo/AC) and the obtained results are shown in Fig. 2. The highest COD removal efficiency of 39.4% was obtained in Ozo/AC process after 60 min. Fig. 2 reveals that the combined processes (Ozo/RH, Ozo/AC) showed higher COD removals as compared to single processes (RH, AC, Ozo). The COD removal efficiencies achieved after 60 min under processes (RH, AC, Ozo, Ozo/RH, Ozo/AC) were 13.1%, 18.6%, 31.6%, 34.3% and 39.4% respectively. The highest removal obtained in the process (Ozo/AC) can be attributed to the fact that the ozonation not only enhances the metal charge by oxidation but also removes the COD from wastewater that ultimately increases the adsorption rate [24,25]. Moreover, the AC provides a high surface area for adsorption and also supports the catalytic effect in the presence of ozonation for pollutant degradation [23,26,27]. The RH showed the lowest COD removal efficiency among the studied processes due to the lower surface area of RH as compared to AC (Table 2) and the absence of the catalytic effect of combined processes.

In combined ozonation and adsorption system, the ozone modifies the surface properties of the adsorbent with the enhancement of active sites for the pollutants degradation [28,29]. The synergistic mechanism of ozonation in the presence of an adsorbent involves two modes. Firstly, the ozone is catalytically transformed into highly reactive oxidants ($OH^{\cdot}$) which readily attack and degrade pollutants at the catalyst surface and in the bulk of the solution [28,29]. Secondly, the acceleration in the catalytic activity due to the regeneration of the catalyst surface by ozone mineralization [28,29]. Fig. 2 shows the highest COD removal efficiency in case of (Ozo/AC) process, which may be explained as the organic matter adsorbed on the surface of AC is oxidized by ozone and AC surface is renewed. The decrease in the COD and the AC surface renewal facilitates the removal of metals as shown in the results (Fig. 4). The results reveal the (Ozo/AC) process as the most efficient and perspective. However, the lower efficiency of the (Ozo/RH) process than that of (Ozo/AC) process may be due to the RH lower surface area as compared to AC.

3.3. Metals removal

The metals removal (Zn, Pb, Cd, Cu, Cr) was studied under single and combined processes (RH, AC, Ozo, Ozo/RH, Ozo/AC). The obtained results for removal studies of metals (Zn, Pb, Cd, Cu, Cr) are shown in Fig. 3 (a,b,c,d,e) respectively. The highest metal removal was obtained in the combined process of Ozo/AC while ozonation was the

Table 1
Characterization of municipal wastewater's sample

Parameters	Value
Temp (°C)	33.1
pH	7.9
EC (dS/m)	1.23
COD (mg/l)	396
BOD (mg/l)	169
TDS (mg/l)	134
TS (mg/l)	571
Cl^- (mg/l)	70
Total hardness (mg/l as $CaCO_3$)	444
Total alkalinity (mg/l as $CaCO_3$)	364
Cu (mg/l)	0.74
Cr (mg/l)	0.56
Zn (mg/l)	49
Cd (mg/l)	1.5
Hg (mg/l)	0
Pb (mg/l)	18.8

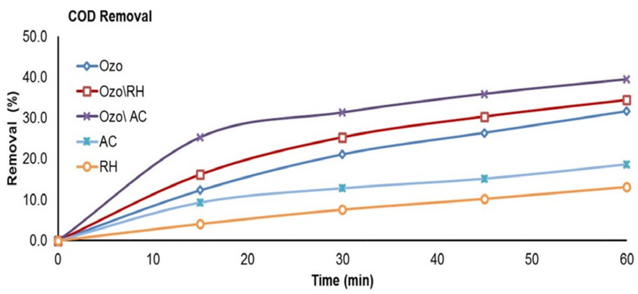

Fig. 2. COD removal at various processes (O_3 dose = 0.98 mg/min; Adsorbent dose (AC/RH) = 10 g/3 L; Volume = 3 L; pH = 7.9; t = 60 min; T = 33 ± 2°C).

Table 2
Properties of rice husk and activated carbons

Material	BET surface area (m^2/g)	Point of zero charge (pHpzc)
Rice husk	90.2	3.2 ± 0.2
Activated carbons	1100	8.9 ± 0.2

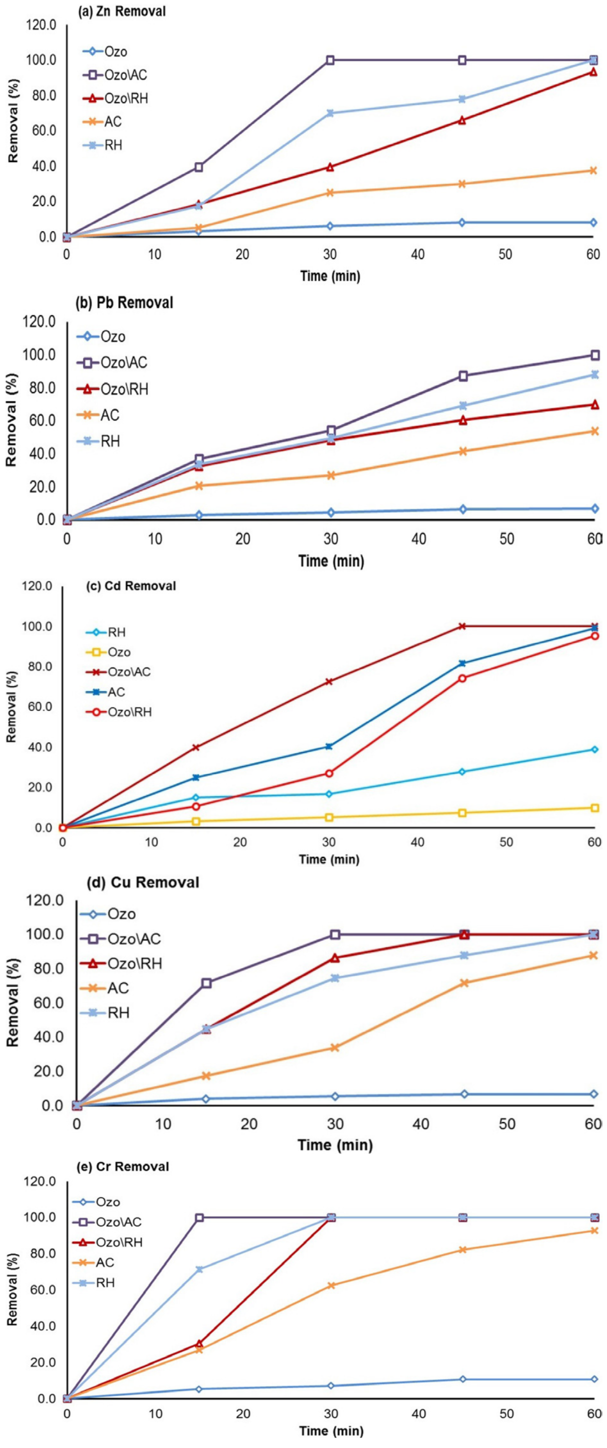

Fig. 3. Metals removal at various processes (a) Zn (b) Pb (c) Cd (d) Cu (e) Cr (O_3 dose = 0.98 mg/min; Adsorbent dose (AC/RH) = 10 g/3 L; Volume = 3 L; pH = 7.9; t = 60 min; T = 33 ± 2°C).

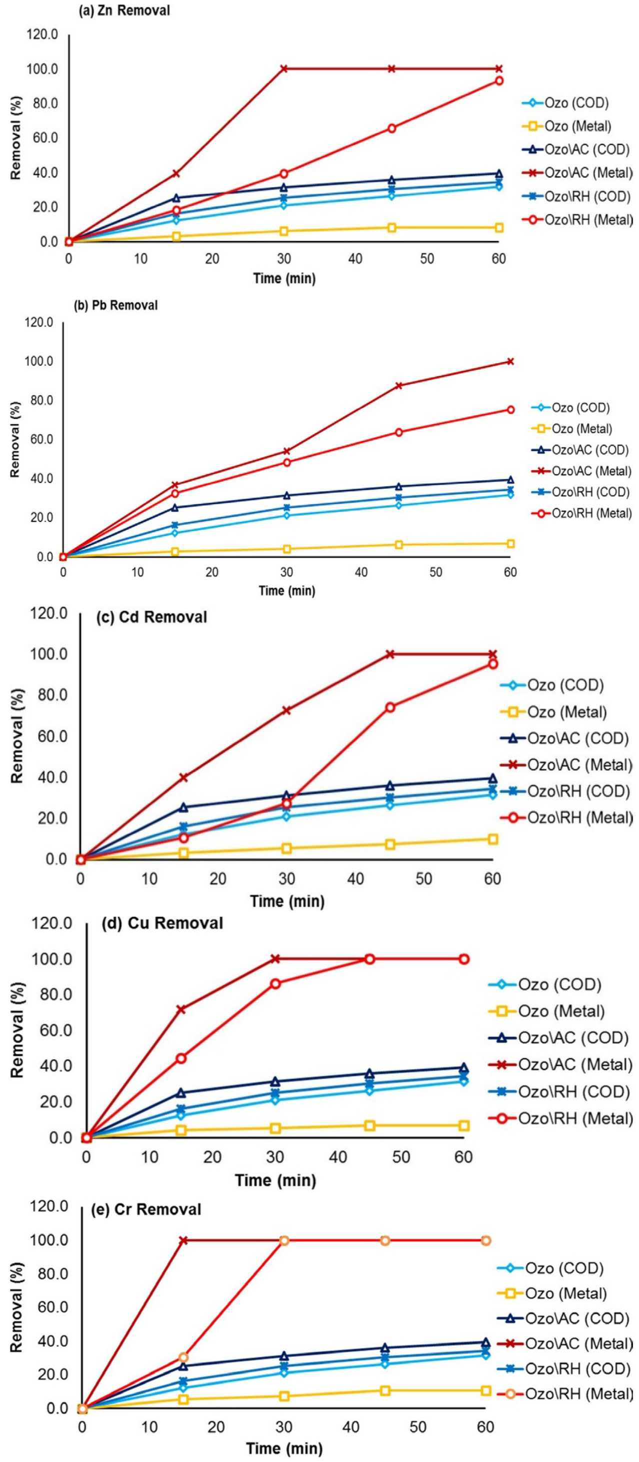

Fig. 4. Comparison between COD and metals removal at various processes (a) Zn (b) Pb (c) Cd (d) Cu (e) Cr (O_3 dose = 0.98 mg/min; Adsorbent dose (AC/RH) = 10 g/3 L; Volume = 3 L; pH = 7.9; t = 60 min; T = 33 ± 2°C).

least effective single process among the studied processes. The fastest metal removal was achieved in the case of Cr while the Pb showed the lowest removal efficiency. After 15 min of treatment (Ozo/AC) the respective metal removal efficiencies were 39.5%, 36.7%, 40%, 71.6% and 100% for the Zn, Pb, Cd, Cu, Cr. The highest removal efficiency of combined processes may be due to the catalytic effect of high surface area activated carbon and availability of adsorption sites due to oxidation of metals in the presence of ozonation [30–32].

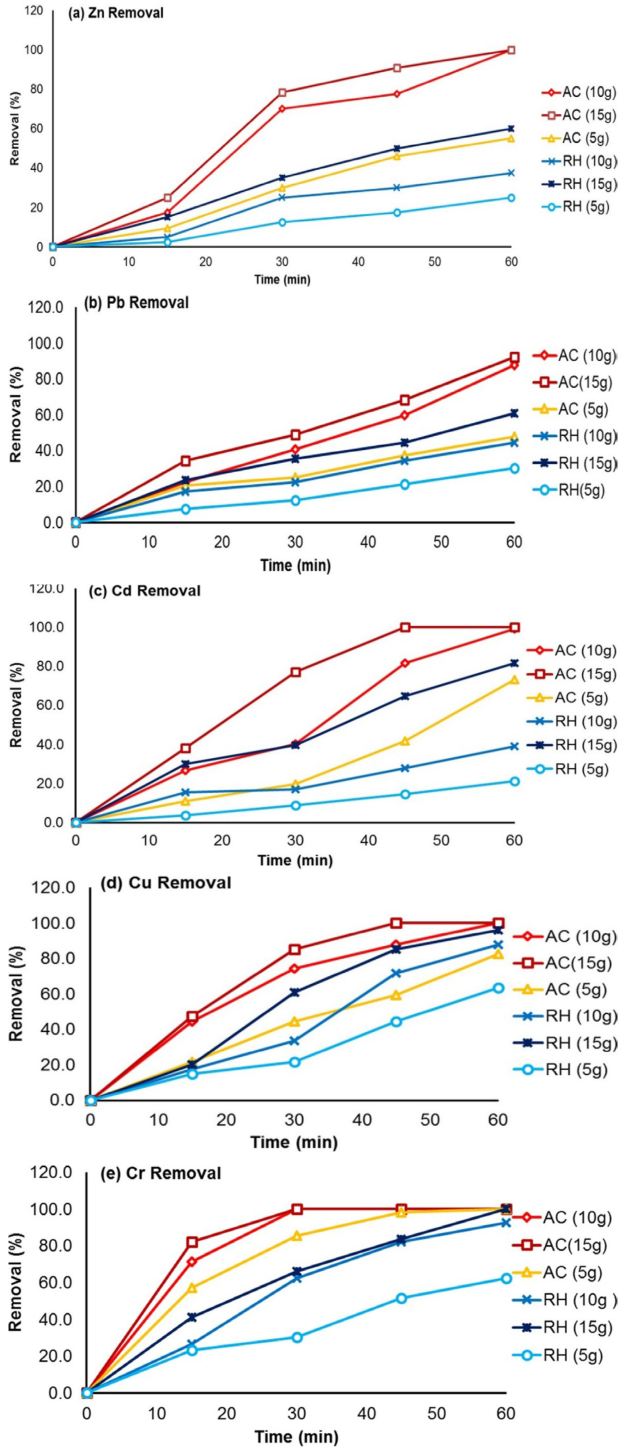

Fig. 5. Adsorbent dose effect on metals removal (a) Zn (b) Pb (c) Cd (d) Cu (e) Cr (O_3 dose = 0.98 mg/min, Adsorbent dose (AC/RH) = 10 g/3 L, Volume = 3 L).

3.4. Comparison between COD and metal removals

A comparison was made between the COD and metals removal discussed in the above sections to enlighten the synchronizing effect of COD removal on metal removal. Figs. 4a–e show the comparison of studied metals (Zn, Pb, Cd, Cu, Cr) under single ozonation and ozonation combined processes (Ozo/RH, Ozo/AC). The highest removal of both COD and metals was obtained in the ozonation combined processes (Ozo/AC) as discussed in the above sections. The results shown in Fig. 4, reveal the synchronizing effect of COD removal on the heavy metal removals as higher COD removals led to enhanced heavy metal removal efficiencies. This may be explained as the COD removal or the organic removal decreases the competition among the metals and organics at the adsorption sites of the catalyst. Therefore, effective adsorption and catalytic activity of AC was observed in the presence of low organics in the wastewater [27,28,33]. Moreover, the oxidation of metals in the wastewater may increase the charge on metals which may lead to the higher adsorption rates of metals as compared with adsorption alone process.

3.5. Adsorbent dose effect

The effect of adsorbent dose was studied on the heavy metal removal efficiency in the absence of the ozonation process. Figs. 5a–e shows the results of heavy metal removal Zn, Pb, Cd, Cu and Cr as a function of adsorbent dose. The metal removal was significantly increased with a rise in adsorbent dose from 5 to 15 g, in both adsorption processes (RH, AC). The adsorption using activated carbon showed high removals as compared to that of rice husk. The availability of more adsorption sites at high adsorbent doses and enhance surface area causing high removal efficiency [34,35]. The better performance of Activated carbon as compared to rice husk may be due to the higher surface area and porosity (Table 2)

4. Conclusions

I. The combined process of ozonation with activated carbon (Ozo\AC) shows the highest removal efficiency for metals, among the studied processes.
II. COD removal influences the adsorption of metals as the higher COD removal efficiencies enhance the adsorption of metals.
III. The oxidation of wastewater has an overall positive effect on the removal of heavy metals.

Acknowledgment

The finical support from the Institute of Environmental Engineering and Research, University of Engineering and Technology Lahore (Pakistan) is gratefully acknowledged.

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