

Eco-technological Treatment of Hattar Industrial Wastewater in Constructed Wetland through Different Arrangement of Anaerobic Conditions

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ABSTRACT

Hattar Industrial Estate discharged effluent without any treatment into Jarikas drain. Present study was an endeavor to evaluate the contaminant in Hattar Industrial wastewater by appraising the physico-chemical and heavy metal analysis which showed that pH, COD, Cu, Ni, As and Fe were above the standards for industrial liquor discharge. Treatment through natural processes like anaerobic digestion and constructed wetland more appealing option for in the context. Different arrangement in the units affect the treatment efficiency and quality of effluent. Current study evaluated the different arrangements of natural processes, in T1 ABR Post-treated in Constructed Wetland whereas; T2 ABR Pre-treated in Constructed Wetland. Compared the effluent of both the treatments with permissible limits for irrigation and observed that most of the water quality parameters were under the permissible limits in T2 as compared to T1. Also higher percentage removal conducted in T2 as rivaled with T1.

Keywords: Hattar Industrial Estate, constructed wetland, anaerobic conditions

1. INTRODUCTION

Today world's civilization expressing one of the major threat of environmental pollution¹⁻². The load of pollution from industrial water streams increased³ which has a magnificent destructive effects on rivers water quality, having consequential health risks through direct ingestion for drinking or bathing in the river water⁴. The quality of river water effected by the discharge of contaminated and untreated domestic sewage, storm water, agriculture runoff, industrial effluent and other sources, which have short and long stint tremendous ruthless effects⁵. Industries directly discharge their effluent and waste into the surface water⁶ which lead not only the foremost threat to the environment but also distressing condition for humanity approaching disaster⁷. There are number of different wastewater treatment units and methods available, the choice for process of treatment i.e. chemical or biological, determined by wastewater characteristics, economic and environmental condition⁸. Limited world's water source, reuse and recommencement of sewage is an exigent way but public health and environment must be unspoiled⁹.

In developing countries anaerobic biological treatment process is most suitable, practical and realistic approach because of limiting and scarce economical resources which they put on for the treatment of the wastewater. The benefits of this process describe in a study conducted by Ward¹⁰ *et al.*, (2008) is to reduce environmental pollution in two main ways: Enclose system prevent the atmosphere from the methane gas exit, while¹¹ burning of CH₄ gas will release carbon-neutral CO₂ (no net effect on atmospheric CO₂ and other greenhouse gases). For industrial wastewater treatment most widespread technology used is the up-flow anaerobic sludge blanket (UASB)¹². Low temperature adversely influenced the UASB treatment¹³⁻¹⁴ and the predominantly perplexing is the maintenance of well-settling granules at low temperature¹⁵. Wastewater treatment in CW are engineered structures particularly designed for the treatment of the wastewater¹⁶ by enhancing the physical, chemical, and biological processes¹⁷ that occur in natural wetland ecosystems¹⁸. Aquatic plants stored nutrients and contaminants into their tissues, so the removal concentration of nutrients by these plants depends on the type of plants used, their biomass and concentration of nutrients present in tissues¹⁹. In constructed wetland the most common plant for the treatment of wastewater used is *Phragmites australis*²⁰. Wastewater from municipal and industrial sectors containing high level of heavy metals, so the treatment of that wastewaters performed by the reed which is extensively purposed²¹⁻²²⁻²³.

2. MATERIALS AND METHODS

2.1 Study Area

The Hattar industrial estate is located at Kot Najeebullah district Haripur in Khyber Pakhtunkhwa (KPK) Province of Pakistan. Hattar Industrial Estate (HIE) is the largest industrial Estate of the KPK, consists of more than 360 industrial units²⁴. The industrial waste then passes through from more than 100 villages of Haripur and Attock; a part of the waste is absorbed by the cultivated land, while the rest ends up in ditches and ponds²⁵.

2.2 Sample Collection

Collection of wastewater samples carried out from Jarikas drain, where effluent discharged by different industries like steel mill, ghee mill, paper and pulp, textile, chemical industries, drugs and food processing etc. combined passed from Jarikas drain to Attock basin.

2.3 ABR and CW Experimental Setup

Research work was conducted in the laboratory of COMSATS Institute of Information Technology, Abbottabad, Pakistan. A lab scale ABR was operated which is made of Perspex with a working volume of 5 liters. Peristaltic pump used for pumping nutrients into the reactor. Inoculation of the reactor seeded with anaerobic bacteria obtained from biogas plant, Haripur. Allow to stand reactor in that position about 2 weeks, so that to stable the growth of microbes in the reactor. Influent was directly ejected into the reactor, with retention time of one week. The lab scale experimental constructed wetland consists of two independent rectangular basins (length: 44.5cm, width: 10cm, and depth: 30cm). The basin was filled with gravel, sand, and soil. Wetland was constructed at the Department of Environmental Sciences, COMSAT Abbottabad. The constructed wetland systems had *P. australis* with vegetation which was collected from a river Dor near village Changi Bandi, Haripur. The constructed wetland lab model was made up of glass.

2.4 Experimental Design

Two different arrangements were used in the experiment. In first arrangement ABR Post-treated in Constructed Wetland named (T1) whereas; in second arrangement ABR Pre-treated in Constructed Wetland that was (T2).

2.5 Analytical Procedures

Wastewater and treated water analyzed for physicochemical (pH, EC, TDS, Turbidity, COD and Na) and heavy metal analysis (Ni, Fe, As and Cu). Digital pH meter (HANNA, HI 991003 Sensor Check pH) used for the measurement of pH and TDS and conductivity by HANNA, HI9835 Microprocessor for conductivity and TDS. Heavy metals were analyzed through atomic absorption spectrophotometer. For COD determination closed reflux, calorimetric method include digestion at 150°C for 2 hour in COD vials go by spectrophotometer reading at 530nm. Heavy metals were analyzed through atomic absorption spectrophotometer. At least three readings were taken for each parameter each time and then mean value was recorded. Samples were taken at an interval of 7 days. The analysis was done as per APHA standard method for the examination of water and wastewater (21st edition). American / held association Washington.

2.6 Statistical Analysis

Analysis of collected data was done by MS Excel 2010. For descriptive statistics and means SPSS 21.0 was used for analysis of variance.

3. RESULTS AND DISCUSSIONS

Physicochemical analysis of Intel and Outlet of treatment T1 presented in Table (i) reveal that pH, EC, TDS, Turbidity, COD and Na decreased to (8.2 units), (532 $\mu\text{S}/\text{cm}$), (339 ppm), (92 NTU), (147 ppm) and (34.52 ppm) respectively. While heavy metals Ni, Fe, As and Cu reduce to (0.053 ppm), (0.548 ppm), (1.457 ppm) and (0.094 ppm) respectively. Physicochemical analysis of Intel and Outlet of treatment T2 indicated that pH, EC, TDS, Turbidity, COD and Na decreased to (7.8 units), (526 $\mu\text{S}/\text{cm}$), (338 ppm), (8.5 NTU), (125 ppm) and (32.05 ppm) respectively. While heavy metals Ni, Fe, As and Cu reduce to (0.012 ppm), (0.457 ppm), (1.37 ppm) and (0.198 ppm) respectively as shown in Table (i).

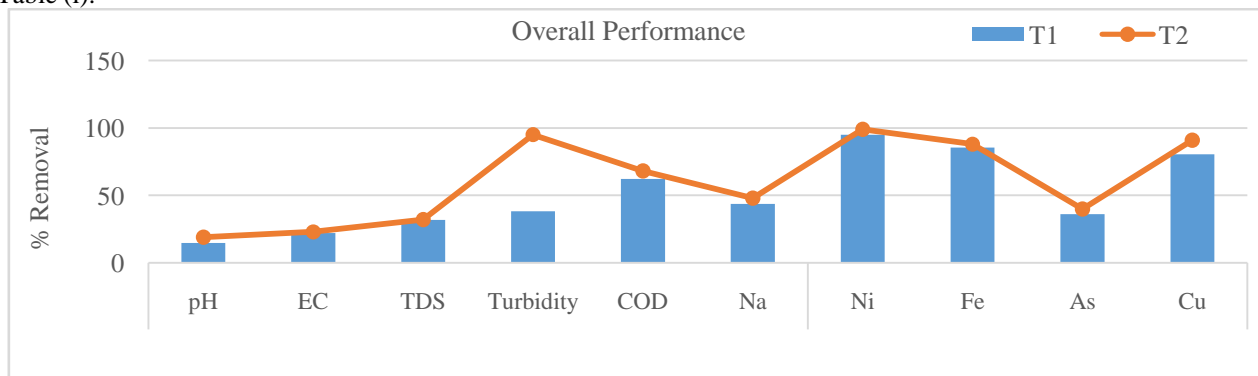


Fig.1: Overall Concert Evaluation of Both the Treatments (T1 and T2)

3.1 pH

In T1A CW decreased pH from 9.62 units to 7.78 units neutralizing the pH²⁶. But pH in ABR dramatically increased. In a study Goncalves²⁷ *et al.* (2007) relate generation of H₂S due to reduction in sulfate which increased in pH in ABR. Bad odor is also due to H₂S. In another study Mtembu²⁸, (2005) relate the increased in pH due to increase in buffering capacity from increasing feed. Effluent from ABR contain anaerobic microbes²⁹ may also increase the pH. But overall, pH of T1 was under the permissible limit of (6.5-8.4) for irrigation. Further analysis for soil quality and crop agronomic parameters also indicate that high pH from ABR increased the soil fertility and increased the crop yield as compare to T2 which having comparatively low pH.

In treatment T2 slight decreased in pH occurred in ABR from 9.62 units to 9.3 units. Slight decreased in the pH of ABR effluent due to presence of methanogenic process³⁰. The pH of the reactor be contingent with influent pH, Mtembu²⁸, (2005) documented the slight decrease in pH (0.3 units) due to VFA production. But in wetland pH decreases significantly 9.3 to 7.8 units. Wetland act as buffer zones neutralizing the pH (Higgins²⁶, 2004) consequently pH decreased by the wetland. CO₂ production in the wetland ensuring decrease in pH³¹.

Overall concert evaluation of both system indicated that removal efficiency for T1 and T2 was 17.76 and 18.65 percentage respectively. Irrigation water from treatment T1 and T2 was under the permissible limit (8.4-6.5), whereas; effluent from T2 exhibited performance better than T1, ideally neutral pH is consider best, so in treatment T2 more close to the pH as compare to T1. There was significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.2 EC

In treatment T1A, CW decreased EC extent of 23% whereas, in T1B (ABR) EC increased to extent of 1.33%, not significant removal of EC occurred in ABR. Same results observed in treatment T2B (ABR), but T2A (CW) decreased the EC 23.98%. Significant removal of EC only possible in wetland in this experiment. Process of evapotranspiration loss of molecules of water from the aerial part of plant is also interlinked with uptake of macro and micro nutrients, ion and elements by the plant and adsorption with roots and particles used in wetland³². Bouallagui³³ *et al.* (2005) suggested that effluent from ABR not meeting with permissible limit so post treatment is required.

Overall concert evaluation of both system indicated the removal efficiency for T1 and T2 was 21.99 and 22.87 percentage respectively. Non-significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.3 TDS

In treatment T1A, TDS decreased form 497 ppm to 346 ppm, but in T1B (ABR), TDS only decreased 44 ppm. Overall decreased was significant in Wetland, with removal efficiency of 30.38% but not much removed by T1B that was 11%. In treatment T2B (ABR) increased TDS form 497 ppm to 513 ppm, mean no significant removal is taken place in ABR due to high concentration of influent concentration which may cause inhibition of the bacterial growth by direct feeding with high concentration contaminants. Microorganisms were more sensitive toward high concentration of contaminants. But in T2A (CW) decreased TDS from 513 ppm to 351 ppm. 31.5% removal performed by wetland.

Overall performance of both the treatments (T1 and T2) non-significantly varied. TDS removal by T1 and T2 was 31.79% and 31.99% respectively. Although TDS concentration within permissible limit but continuous application of high TDS water may cause soil salinity³⁴. TDS represent the measurement of organic matter, inorganic salts and other dissolved substances in water. It is the sum of anions and cations, main constituents of TDS includes (Mg⁺², Ca⁺², Na⁺, CO₃⁻, HCO₃⁻, Cl⁻, SO₄⁻ and K⁺). Salinity causes osmotic stress, toxicity of specific ion and distorted the nutrient balance³⁵⁻³⁶.

3.4 Turbidity

In treatment T1A turbidity decreased extent of 96%. Highly significant decreased in turbidity occurred in CW. But removal efficiency in T2A was lower than T1A. In T2A, 90% turbidity decreased in (CW) of Treatment T2. Current results also very closed to Vipat³⁷ *et al.* (2008) documented that wetland removed turbidity 88%, which posed significant removal. But in T1B (ABR) turbidity increased (94%) due to presence of anaerobic bacteria in the effluent from ABR. High TDS, EC and SAR values also contributing towards turbidity. In treatment T2B turbidity decreased 42.9%. Turbidity in the effluent from T2B was due to presence of anaerobic bacteria in the effluent²⁹.

Overall concert evaluation of both system indicated that removal efficiency for T1 and T2 was 38.25 and 94.92 percentage respectively. Irrigation water from treatment T1 was above the permissible limit (10 NTU), whereas; effluent from T2 within limits. There was highly significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.5 COD

The effluent from treatment T1A contained 133 ppm of COD means highly significant ($p < 0.05$) removal occurred in CW. Same results obtained by a study performed by Ong³⁸ *et al.* (2009) but slight difference which was non-significant (62%) but increase the value of COD removal reported by Ladu³⁹ *et al.* (2014) that was (77%). *P. australis* increased the DO level in the root zone which help aerobic bacteria to degrade the contaminants and enhance the removal of COD from the system. Phragmites transfer the atmospheric oxygen to the root bed (Ong⁴⁰ *et al.*, 2009). Removal of BOD executed in the wetland outstanding by aerobic bacteria which was faster than anaerobic BOD removal by anaerobes⁴¹.

But effluent obtained from outlet of T1B increased COD (9.5%). Significant influence of temperature on microbes and methane production remarked by many scientists^{33,42}. Lowering of temperature decreased the growth and biogas yield⁴³. Requirement for post treatment must be needed to meet the effluent discharge quality in UASB even in warm climate^{42, 43}.

Treatment T2B increased COD (3.2%) during study. But again T2A decreased COD (68.98%) more significant as compared to T1A. Ong³⁸ *et al.* (2009); Ladu³⁹ *et al.* (2014); Randerson⁴¹, (2006) all studies was line with current findings for CW. Low temperature was also linked with less removal efficiency acquired in ABR. Studies of different researchers (Bouallagui³³ *et al.*, 2009; Riau⁴² *et al.*, 2010; Trzcinski and Stuckey⁴³, 2010; Chernicharo⁴⁴, 2006; Foresti⁴⁵ *et al.*, 2006) also argument with present findings.

Overall concert evaluation of both system indicated that removal efficiency for T1 and T2 was 62.30 and 67.94 percentage respectively. Irrigation water from treatment T1 and T2 was under the permissible limit (150 ppm) whereas; effluent from T2 exhibited low COD compared with T1. Significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.6 Sodium

In treatment T1A (CW) significantly decreased the Na concentration extent of 28.9%, removal efficiency in T2A was slight higher than T1A. In T2A, 29.23% Na concentration decreased in (CW) of Treatment T2. A study by Zingelwa and Wooldridge⁴⁶, (2009) pointed towards observation that Na, Ca and Mg concentration in outflow from wetland (*P. australis*) is lower than inflow. Strong affection shown by aquatic Macrophytes shown toward nutrients and carbon.

In treatment T1B, significant removal observed, 20.8% decreased occurred in ABR of treatment T1. Whereas; high decreased experienced in ABR of treatment T2, that was 29.2%. There is a membrane of semi permeable protoplasm that confine the freed propagation of ions, but restrict the water. High concentration of sodium dehydration occurred so prevent from dehydration microbes accumulate the Na into cells⁴⁷. High concentration of Na effect the activities of anaerobic bacteria, whereas; Na concentration in the range of 100-200 ppm enhance the growth of anaerobes⁴⁸.

Overall concert evaluation of both system indicated that removal efficiency for T1 and T2 was 43.7 and 47.7 percentage respectively. Effluent from T2 exhibited low Na concentration compared with T1. Significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.7 Nickel

In treatment T1A (CW) highly significantly decreased the Ni concentration extent of 81.5%, but removal efficiency in T2A was higher than T1A. In T2A 97.63% Ni concentration decreased in (CW) of Treatment T2. In a study conducted by Kamel⁴⁹, (2013) reported Ni accumulation in the stem of *Phragmites* was the highest as compare to other aquatic plants. Also present study agreement with Kamel⁴⁹, (2013) for the effective and highest removal of Ni about 81% from the wastewater. For the development and growth of aquatic macrophytes concern likewise other higher plant they also required micronutrients such as Ni, Zn, Fe and Cu⁵⁰.

3.8 Iron

In treatment T1A (CW) significantly decreased the Fe concentration extent of 81%, but removal efficiency in T2A was higher than T1A. In T2A 84% Fe concentration decreased occurred in (CW) of Treatment T2. A study conducted by Ayeni⁵¹ *et al.* (2012) on metal concentration and photosynthesis in *Phragmites australis* signify toward greater concentration of Fe accumulation into roots than shoots. Result from current study reveal that Fe removal or uptake by *Phragmites* was 81% and 85% for T1A and T2A respectively. For the development and growth of aquatic macrophytes concern likewise other higher plant they also required micronutrients such as Ni, Zn, Fe and Cu⁵⁰.

In treatment T1B, significant removal observed, 21.37% decreased occurred in ABR in treatment T1. Whereas; low decreased experienced in ABR in treatment T2, that was 19.71%. Effluent from HIWW contained high concentration of Fe received by T2B as compared to T1B which received effluent from CW containing less concentration of Fe. Findings by⁵²Kavamura and Esposito, (2010) also strengthen the above argument. Microorganisms were not able to absorb HM and store into their biomass due to toxicity, so that why treatment of industrial wastewater are still in trial⁵³. Current research pointed that only Ni and Fe removal is significant but rest of the other having removal capacity less than 5% (Cd, Pb, As, Cu, Cr, Hg and Zn). Present study indicate that Ni and Fe used by anaerobic bacteria, also correlated with the findings of Zheng-Bo⁵⁴ *et al.* (2007) that these metals were required at trace level for the stimulation of bacterial growth.

Overall concert evaluation of both system indicated that removal efficiency for T1 and T2 was 85.39 and 87.82 percentage respectively. Water from treatment T1 and T2 was under the permissible limit (5.0 ppm) whereas; effluent from T2 exhibited low Fe concentration compared with T1. Significant differences ($p < 0.05$) for removal efficiency endure between both systems.

3.9 Arsenic

In treatment T1A (CW) significantly decreased the as concentration extent of 33.8%, but removal efficiency in T2A was higher than T1A. In T2A 39% as concentration decreased in (CW) of Treatment T2. According to study by Verma⁵⁵ *et al.* (2014) *Phragmites spp.* having ability to accumulate as up to some extent. But when concentration exceeds from 1400 ppb (1.4 ppm) intolerable by the plant examined. So these results also responding to current study that was 33.8% and 39% for T1 and T2 respectively. As removal done by wetland.

In treatment T1B, non-significant removal observed, 3.38% decreased occurred in ABR in treatment T1. Whereas; lowest decreased experienced in ABR in treatment T2, that was 0.877%. Effluent from HIWW contained high concentration of Fe. Findings by Kavamura and Esposito⁵², (2010) also strengthen the above argument. Microorganisms were not able to absorb HM and store into their biomass due to toxicity, so that why treatment of industrial wastewater are still in trial⁵³. Methanogenic bacteria are extra irritable towards toxic substances in the treatment of waste. Relative high concentration of heavy metals causing cytotoxicity⁵² and change the biochemical performance. Heavy metals also exhibit biological importance such as manganese and iron at trace level not causing toxicity. But As, Hg, Pb, Cd and Ag restraining the growth⁵².

3.10 Copper

In treatment T1A (CW) highly significantly decreased the Cu concentration extent of 90%, whereas low removal efficiency in T2A was marked. In T2A 80% Cu concentration decreased in (CW) of Treatment T2. Many studies concluded that the removal of *P. australis* perform better accumulation of HM in their root as compare to shoot, because roots of *P. australis* having cortex parenchyma together with huge intercellular spaces. Cu determination by different aquatic Macrophytes reported as high by Kumar⁵⁶ *et al.* (2013). Kamel⁴⁹, (2013) also relate the *P. australis* with the most effective removal of Cu. For the development and growth of aquatic macrophytes concern likewise other higher plant they also required micronutrients such as Ni, Zn, Fe and Cu⁵⁰.

Table.1: Physicochemical and Heavy Metal Analysis of HIWW and Treated Water T1

		Water Quality Analysis									
		Physicochemical Analysis					Heavy Metals				
		pH	EC	TDS	Turbidity	COD	Na	Ni	Fe	As	Cu
		-----	µS/cm	ppm	NTU	ppm	ppm	ppm	ppm	ppm	ppm
T1A CW	Inlet	9.62	682	497	149	390	61.39	1.047	3.753	2.278	1.011
	Outlet	7.78	525	346	5.465	133	43.63	0.193	0.697	1.508	0.095
	% Removal	----	23.02	30.33	96.33	65	28.92	81.56	81.42	33.8	90.6
T1B ABR	Inlet	7.78	525	346	5.465	133	43.63	0.193	0.697	1.508	0.095
	Outlet	8.2	532	339	92	147	34.52	0.053	0.548	1.457	0.094
	% Removal	----	↑1.33	2.02	↑94.05	↑9.5	20.88	72.53	21.37	3.38	1.05

In treatment T1B, non-significant removal observed, 1.05% decreased occurred in ABR in treatment T1. Whereas; low decreased experienced in ABR in treatment T2, that was 0.09%. Effluent from HIWW contained high concentration of Cu received by T2B as compared to T1B which received effluent Cu. from CW containing less concentration of Findings by Kavamura and Esposito⁵², (2010) also strengthen the above argument. Relative high concentration of heavy metals causing cytotoxicity and change the biochemical performance⁵².

Table.2: Physicochemical and Heavy Metal Analysis of HIWW and Treated Water T2

		Water Quality Analysis									
		Physicochemical Analysis					Heavy Metals				
		pH	EC	TDS	Turbidity	COD	Na	Ni	Fe	As	Cu
		-----	µS/cm	ppm	NTU	ppm	ppm	ppm	ppm	ppm	ppm
T2B ABR	Inlet	9.62	682	497	149	390	61.39	1.047	3.753	2.278	1.011
	Outlet	9.3	692	480	85	403	43.44	0.057	3.013	2.258	1.012
	% Removal	3.32	↑1.44	3.42	42.95	↑3.22	29.23	51.57	19.71	0.877	↑0.09
T2A CW	Inlet	9.3	692	480	85	403	43.44	1.047	3.013	2.258	1.012
	Outlet	7.825	526	338	8.5	125	32.05	0.012	0.457	1.37	0.198
	% Removal	15.86	23.98	29.58	90	68.98	26.22	97.63	84.83	39.32	80

Heavy metals also exhibit biological importance such as manganese and iron at trace level not causing toxicity. Cu concentration least removed by the anaerobic bacteria. Means no accumulation occurred by the microbes. Some studies

relate the growth of anaerobic bacteria with Cu and Zn concentration with the inhibition of anaerobic bacterial growth which poses the threat to the digester⁵⁷.

Table.3: Physicochemical and Heavy Metal Analysis of Both Treatments (T1 and T2)

		Water Quality Analysis									
		Physicochemical Analysis				Heavy Metals					
		pH	EC	TDS	Turbidity	COD	Na	Ni	Fe	As	Cu
		----	µS/cm	ppm	NTU	ppm	ppm	ppm	ppm	ppm	ppm
T1	Inlet	9.62	682	497	149	390	61.39	1.047	3.753	2.278	1.011
	Outlet	8.2	532	339	92	147	34.52	0.053	0.548	1.457	0.094
	% Removal	14.76	21.99	31.79	38.25	62.30	43.76	94.93	85.39	36.04	80.41
T2	Inlet	9.62	682	497	149	390	61.39	1.047	3.753	2.278	1.011
	Outlet	7.825	526	338	8.5	125	32.05	0.012	0.457	1.37	0.198
	% Removal	18.91	22.87	31.99	94.92	67.94	47.79	98.85	87.82	39.85	90.70

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