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Performance evaluation of the Martaş Port Waste Reception Facility Treatment Plant (Tekirdağ, Turkey)

Emre Subaşı, Neslihan Doğan-Sağlamtimur*

Department of Environmental Engineering, Faculty of Engineering, Niğde University, 51245, Niğde, Turkey Tel. +90 388 2252229; Fax: +90 388 2250112; email addresses: nds@nigde.edu.tr, neslihandogansaglamtimur@gmail.com

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ABSTRACT

The establishment of adequate waste reception facilities is a necessary step to reduce and eliminate ship-generated pollution. This study aims to evaluate the performance efficiency of the Martas Port Waste Reception Facility (WRF) Treatment Plant as well as to determine whether the quality of effluent complied with the discharge standards/criteria to the seawater, the receiving environment. This plant is one of the predecessors among the mid-scale and multifunctional WRFs in Turkey. Samplings both in the influent and in the effluent of the WRF were analyzed monthly between September 2009 and April 2010 for pH, total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), oil and grease, total phosphorus (TP), metals (As, Cd, Cu, Cr, Fe, Hg, Ni, Pb, and Zn), and total petroleum hydrocarbons, considering the pollution parameters stated in the Turkish Water Pollution Control Regulation (TWPCR). On an average, the removal efficiency of the treatment plant was found to be 98% for total petroleum hydrocarbons, 86% for TSS, 80% for BOD, 79% for oil and grease, and 75% for COD. The effluents of the WRF exceeded the discharge standards of the receiving environment that were stated in the TWPCR standards for TP and the German and the European Commission Directive 91/271/EEC standards for COD and TP. On the other hand, the Cr concentrations of the effluents exceeded only the British standards.

Keywords: Marine pollution; Ship-generated waste; Oily wastewater; Port waste reception facility; Pollution parameters

1. Introduction

Maritime transportation at continental scale has an increasing importance due to its cost efficiency even though it brings severe environmental problems. Marine pollution originating from various sources is increasing throughout the food chain due to the contamination of all living systems and its mitigation is of great importance for the sustainability of natural resources, protection of communities and future of society [1–4]. A series of measures and decisions are taken in many countries under the coordination of the United Nations International Maritime Organization (IMO) [5]. It is vitally important that appropriate facilities are established and services are provided for

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^{*}Corresponding author.

the implementation of measures arising from both the international and the national regulations [6–13].

The International Convention for the Prevention of Pollution from Ships (MARPOL 73/78) prepared by the IMO is one of the international conventions applied to prevent contamination of the seas from ships [14]. Turkey signed MARPOL (73/78) Convention in 1983 together with countries bordering the Mediterranean and the Black Sea in order to prevent pollution from oil (bilge water, sludge and slop, etc.), noxious liquid substances in bulk, harmful substances, sewage, and garbage disposals. This Convention was entered into force by the 90/442 decision of the cabinet on 3 May 1990 [15]. As for the MARPOL (73/78), "Reception of Wastes from Ships and Waste Control Regulation" was prepared by the Ministry of Environment and Forest and the Ministry of Transport and published in the Official Gazette on 26 December 2004 and numbered 25,682 [16]. They provide policy actions to minimize routine and accidental marine pollution resulting from ships, waste reception in terms of quality and quantity and waste treatment, in order to establish an adequate national policy for waste reception facilities (WRFs) in Turkey. WRFs in Turkey are facilities where ship-generated wastes of Annex I, Annex IV, and Annex V of MARPOL (73/78) are stored, treated, and disposed in.

Table 1

Comparative table of discharge standards/criteria to the seawater, a receiving environment

Parameters (mg/L)	Discharge standards/criteria to the seawater			
	Turkey [17]ª	Germany [18]	UK [19]	91/271/ EEC [20]
pН	6–9		6–9	
TSS	200			35
COD	400	120		125
BOD		25		25
Oil and grease	20			
ТР	2	1.5		1
Hydrocarbons ^b	6	2		
Cd	0.01		0.003	
Cu	0.01		0.005	
Ni	0.10		0.03	
Pb	0.10		0.03	
Zn	0.10		0.04	
Fe	10		1	
As	0.10		0.03	
Cr	0.10		0.02	
Hg	0.004		0.0003	

^aThis column was prepared by using Tables 4, 11, and 19 of the Turkish standards (TWPCR) [17].

^bTotal petroleum hydrocarbons.

Capacity of these facilities and treatment methods may vary because of regional-economic reasons. WRFs started to be established a few years ago. Nowadays some of them are operational, whereas some of them stay idle due to adaptation problems on developing technology and vessel traffic.

In this study, the performance evaluation of the Martas Port WRF is performed for the first time. The aim of the study is to determine whether the quality of effluent complies with the discharge standards/criteria to the seawater, the receiving environment stated in the Turkish Water Pollution Control Regulation (TWPCR) [17], the German [18], and the British [19] standards (Table 1). These three standards are the most appropriate in evaluating the performance of WRF treatment plants; but we also included the European Council Directive 91/271/EEC [20] standards concerning urban waste water treatment into the analysis. In particular, the operational differences and performance efficiencies are determined and the effluent concentrations considering discharge standards for the period September 2009-April 2010 are discussed.

2. Materials and methods

2.1. Information about the facility

Martaş Marmara Ereğli Port Facilities, located along the coast of the Sea of Marmara (Tekirdağ, Turkey, Fig. 1), is chosen for the study because it is one of the predecessors among the mid-scale and multi-functional WRFs in Turkey. This facility was licensed (59-AKTL-002) on 8 February 2007 to serve for general cargo, loading, discharge, handling, storage, general warehousing, and storage services established and operated by the private sector. Ships arriving at this port carry bulk and general cargo. The Martaş Port WRF consists of storage, heating, separator and control units, and treatment plant [1] (Fig. 2).

Ship-generated wastes of oil (MARPOL 73/78 Convention, Annex I) are taken to the Martaş Port WRF; whereas garbage and sewage (MARPOL 73/78 Annexes IV and V) are sent to landfill and treatment plant of Municipality of Marmara Ereğli, respectively. Wastes transferred from the vessels by the waste collection vehicle are delivered to the Martaş Port WRF through a waste reception collector and a pump [1]. The storage unit consists of two carbon steel tanks, having capacities of 30 and 50 m³, respectively, where the waste is stored and preliminary preparations are performed prior to treatment. The waste is kept for minimum 5h here, and the waste oil products are stabilized. As the waste is stored by means of both the pumps of



Fig. 1. The location of the Martaş Port WRF.



Fig. 2. Flow diagram of the Martas Port WRF.

waste collection vehicle and the WRF, it is in emulsion form. Storage tanks are heated for physical decomposition of water-oil mixture. Because wastes are variable, there is no certain ratio of aqueous and oil phases. However, the average volume comprises 10-50% for the oil phase and 50-90% for the aqueous phase. The aqueous taken from the bottom of tanks is sent to the treatment plant (Fig. 2) directly. The aqueous phase also contains the oil phase which is not separated by physical methods (generally, 10-40% for the oil and 60-90% for the aqueous). The aqueous sent to the plant is treated in corrugated plate interceptor oil separator, stabilization pool, neutralization tank, and coagulation and flocculation tanks, respectively. Treated water is discharged into the sea through pipeline from the top of chemical clarifier through weirs. Flocks settling in the chemical clarifier of the WRF accumulate over time and remain as sludge at the bottom of the tank. This sludge is transferred to sludge thickening tank and then it is sent to filter press for dewatering and solid and liquid separation. The aqueous discharging from the filter press is given to equalization basin of the treatment plant again, whereas the sludge is packed and deposited in the landfill of the Municipality of Marmara Ereğli. Whether the sludge may contain several harmful constituents is not clear at this stage because examining its level of environmental safety was beyond the scope of the present study.

When the dispersion of the aqueous flow from the WRF storage tanks is completed, what remains in the tanks is a mixture of the aqueous and the oil. Although the aqueous has been extracted from the tanks, there is still some emulsified waste. The proportion of the water in this waste is lower than the proportion of the water in the aqueous, while the proportion of the oil is higher. However, it is not possible to state something definite. The emulsified water-oil mixture left over in the storage tanks after the removal of the aqueous is pumped, respectively, to equalization basin with mixer and separator unit to be processed. The dispersed aqueous is transmitted to water chamber and then to the treatment plant with the help of a pump, while the oil is transferred to the oil chamber and then on to dewatered bilge water tank by means of a pump. In this process, the sludge occurring in the separator was transferred first to sludge chamber and then sludge tank by pumping. The sludge separating from the separator of the WRF is not dry sludge

2.2. Information on sampling and analyses

The Martaş Port WRF Treatment Plant, having a capacity of 10 m³/h, includes physical and chemical treatment processes. Sampling was performed for 8 months from September 2009 to April 2010. Requirements of the TS EN ISO 5667-3 "Water Quality-Sampling-Part 3: Guidance on the Preservation and Handling of Water Samples" which came into force in 2007 were met [21,22]. Pollution parameters stated in the TWPCR [17], which are pH, total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD)₅ (BOD thereafter), oil and grease and total phosphorus (TP), metals (As, Cd, Cu, Cr, Fe, Hg, Ni, Pb, and Zn), and total petroleum hydrocarbons (hereinafter referred to as hydrocarbons), were analyzed in the influent and in the effluent of the Martas Port WRF to evaluate the performance efficiency of the treatment plant and to determine and monitor compliance of the effluent with the discharge standards/criteria of the seawater, a receiving environment [17-20]. Additionally, Al, Ca, and Cl were measured in the influent and in the effluent to determine the effects of chemicals (polyaluminium chloride that is PAC and hydrated lime) used in coagulation and flocculation processes.

In the study, analytical grade reagents (E. Merck, Darmstadt, Germany) were used. Standard methods (4500-H⁺ B/electrometric method for pH, 2540 D/total suspended solids dried at 103–105 °C for TSS, 5220C/ closed reflux, titrimetric method for COD, 5210 B/ 5-Day BOD test for BOD, 5520 B/liquid–liquid, and partition-gravimetric method for oil and grease) were performed [23]. Metal, TP, Al, Ca, and Cl analyses were done by using ICP-ES and ICP-MS in Acme Analytical Laboratory (Vancouver, Canada). Hydrocarbon oil index (TS EN ISO 9377-2) [24] was used for the determination of hydrocarbons using GC 6890 N (Agilent Technologies, CA, USA).

3. Results and discussion

The pH values of the influent and the effluent of the Martaş Port WRF varied from 5.4 to 7.7 and from 7.2 to 8.4, respectively, during the study; the lowest level was observed in December 2009 with the values of 5.4 and



Fig. 3. Variation of some pollution parameters in the influent (\bullet) and in the effluent (\circ) of the treatment plant of the Martaş Port WRF during September 2009–April 2010.

7.2, respectively (Fig. 3). The pH values of the effluent complied with the discharge standards (Table 1) of the receiving environment stated in the TWPCR [17] and in the British standards [19] are between 6 and 9; so it is not seen any problems in operation.

TSS concentrations of the influent and the effluent of the WRF varied from 146 to 317 mg/L and from 21 to 40 mg/L, respectively, thus the influent and the effluent ratio is around six (Fig. 3). TSS concentrations of the effluent are complied with the TWPCR standards (200 mg/L; Table 1) [17] and exceeded the 91/271/EEC standards (35 mg/L; Table 1) [20] only during November 2009. TSS concentrations of the influent and the effluent were high (202 mg/L) and low (21 mg/L), respectively, in December 2009 due to high treatment performance (90%) of the treatment plant. While the highest TSS removal efficiency of the plant (92%) was determined in April of 2010, its average was 86% during the measurement period.

From September 2009 to April 2010, COD concentrations varied from 794 to 1,737 mg/L in the influent 3044

and from 118 to 467 mg/L in the effluent of the Martaş Port WRF; thus, the influent and the effluent ratio is around four (Fig. 3). COD removal efficiency of the treatment plant was 75% on average, and it was below the average value (60-74%) for November-December 2009 and April 2010. COD concentrations of the effluent of the WRF were above the TWPCR [17] discharge standards (400 mg/L; Table 1) only in November–December 2009 $(463 \pm 33 \text{ and } 467 \pm 26 \text{ mg/})$ L) and April 2010 $(403 \pm 23 \text{ mg/L})$. They were also above the German [18] and the 91/271/EEC [20] standard values in the studied period due to the stringent limits of these standards (120-125 mg/L; Table 1). The low COD removal efficiency in November 2009 could be due to an operational failure since the other parameters measuring performance of the plant were within the acceptable discharge standards during the same month.

The low COD removal efficiencies in December 2009 and April 2010 were also reflected in BOD. Concentrations of BOD varied in the range 124-330 mg/L in the influent and 14-78 mg/L in the effluent (Fig. 3). BOD concentrations were the highest in the influent and in the effluent of the WRF in October and December 2009, respectively. The BOD removal efficiency of the plant was 80% on average. The plant was able to operate at an efficiency that is either close to or above the average during September-November 2009 and January-March 2010 periods. The BOD removal efficiencies for December 2009 and April 2010 were at 57–59% level that is well below the average. Therefore, the effluent of the WRF for BOD exceeded general quality criteria (25 mg/L; Table 1) of the receiving environment stated in the German [18] and 91/271/EEC [20] standards in these two months. As indicated in Table 1, there is no standard value for BOD in the TWPCR [17].

The facility's influent COD/BOD ratio varied in the range of 4–9; this ratio changed in a range of 6–12 in the effluent and increased to 22 due to low operation efficiency of the plant in November 2009 (Fig. 3). Because this ratio is higher than the range 1.5–3, biodegradation of this waste was difficult. Additionally, the oily waste reaching the treatment plant was contaminated by various chemicals used for cleaning tanks, wastes of chemical loads, etc. For these reasons, being a physico-chemical treatment type of this plant was an appropriate decision. The fact that the COD/ BOD ratio of the influent and effluent of the WRF was generally lower than 10 shows that the majority of the organic materials received can be easily degradable.

Oil and grease concentrations were 71-329 mg/L and 10-175 mg/L, respectively, in the influent and the effluent of the WRF achieved highest values in October 2009 (Fig. 3). The oil and grease removal effi-

ciency of the treatment plant was 79% on average. The efficiency decreased to 47% in October 2009, but close to the average during the rest. Thus, the effluent of the WRF for oil and grease exceeded the TWPCR [17] discharge standards (20 mg/L; Table 1) for only a limited period of the year.

The Martaş Port WRF Treatment Plant inclu -des physical and chemical treatment processes. Physico-chemical treatment is an approriate method, but it is mostly incapable of complete elimination of COD and oil-greases of ship-generated oily wastes, resulting in average destruction efficiencies of 75% of initial COD and 79% of oil-greases content. All of these disadvantages have promoted the usage of alternative treatment methods for this oily wastewater treatment [25-28] with better removal efficiency for COD and oil-greases. For example, wet air oxidation of oily wastes from ships, in oxygen excess conditions, proves to be an effective method to eliminate oilgreases and to reduce COD content. At 350°C and 200 bar, oil-greases elimination is 99.9%, while COD reduction reaches approximately 91% [29]. Application of a membrane bioreactor to treat surfactant containing oil-water emulsions appears to be a feasible method as it may remove more than 90% of the influent COD [30]. The microfiltration process may provide 98% reductions of oil and grease contents as well [31].

The average TP concentration of 1.65 mg/L in the influent increased to 2.95 mg/L in the effluent. This unexpected situation may be due to the operational failure. For TP, the effluent of the WRF exceeded the discharge standards (Table 1) of the receiving environment that were stated in the TWPCR (2 mg/L) [17], the German (1.5 mg/L) [18], and the 91/271/EEC (1 mg/L) [20].

The average concentration of hydrocarbons in the influent of the Martaş Port WRF was 11.09 mg/L, and it dropped to 0.22 mg/L in the effluent. The hydrocarbons removal efficiency of the treatment plant was 98% on average. The effluent in terms of hydrocarbons complied with discharge standards (Table 1) of the receiving environment was stated in the TWPCR (6 mg/L) [17] and the German standards (2 mg/L) [18].

The average Cd, Cu, Ni, Pb, and Zn concentrations were almost at the same levels (<0.0005, 0.006, 0.013, <0.001, and 0.017 mg/L, respectively), both in the influent and in the effluent. The Fe concentrations showed an increasing trend from the influent to the effluent with the values of <0.100-0.331 mg/L. Conversely, As, Cr, and Hg concentrations showed a decreasing trend, as expected, from the influent to the effluent with the values of 0.047-0.033, 0.016-0.005, and 0.003-<0.001 mg/L, respectively. For the metals, the effluent complied with the discharge standards

and general quality criteria (Table 1) of the receiving environment was stated in the TWPCR [17] and the British standards [19] (except Cr). Their TWPCR and British standard values comprise Cd (0.01 and 0.003 mg/L), Cu (0.01 and 0.005 mg/L), Ni (0.10 and 0.03 mg/L), Pb (0.10 and 0.03 mg/L), Zn (0.10 and 0.04 mg/L), Fe (10 and 1 mg/L), As (0.10 and 0.03 mg/L), Cr (0.10 and 0.02 mg/L), and Hg (0.004 and 0.0003 mg/L).

For coagulation and flocculation processes in the neutralization tank of the Martaş Port WRF, 500 mg/L PAC and 300 mg/L hydrated lime were added as chemicals. The Al, Ca, and Cl concentrations varied from 0.302 to 0.308, 322 to 394, and 11,13 to 10,91 mg/L, respectively, in the influent and in the effluent of the treatment plant. The Ca concentrations increased 0.8-fold, whereas Cl concentrations decreased 0.98-fold in the effluent but no significant change was observed in Al concentration.

4. Conclusion

In this study, the efficiency of the treatment plant of the WRF is evaluated in terms of the removal efficiencies of TSS, COD, BOD, and oil-grease. On average, the removal efficiency of the treatment plant was found to be 98% for total petroleum hydrocarbons, 86% for TSS, 80% for BOD, 79% for oil and grease, and 75% for COD. The effluents of the WRF exceeded the discharge standards of the receiving environment that were stated in the TWPCR standards for TP and the German and the European Commission Directive 91/271/EEC standards for COD and TP. The Cr concentrations of the effluents exceeded only the British standards. Because some soluble organic components go untreated in the physical and chemical treatment and result in increased levels of BOD and COD in the plant effluent, the conventional physico-chemical treatment method appears to be incapable for complete elimination of COD and oil-greases of ship-generated oily wastes, resulting in average removal efficiencies of 75% of initial COD and 79% of oil-greases content. Conventional oily wastewater treatment methods that include gravity separation and skimming, dissolved flotation, de-emulsification, coagulation, air and flocculation have several disadvantages such as low efficiency, high operation costs, corrosion, and recontamination problems. Also, these methods are not effective in removing smaller oil droplets and emulsions. Therefore, implementation of an alternative method with higher removal efficiency is desired for the oily wastewater treatment.

The data further implicate importance of avoiding short-term operational failures in order to increase treatment efficiency of the WRF. Personal mistakes and operational conditions that are incongruent to waste load and variable characteristic of oily wastewater may be possible causes for the observed inefficient removal efficiencies of the treatment plant and the operational failure during certain months. On the longer term basis, alternative technologies which are not affected by variations in characteristics of influent need to be investigated. Membrane treatment technologies may be the most suitable choice for these types of waste to effectively remove pollution parameters and obtain effluent concentrations complying with the international discharge standards.

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