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Characterization and removal of phenolic compounds from condensate-oil refinery wastewater

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ABSTRACT

Phenols are present in discharge effluents of many heavy industries such as refineries. The refinery at Emirates National Oil Company (ENOC), UAE, processes condensate oil and produces wastewater that is treated at the refinery wastewater treatment plant (ENOC-RWTP). Characterization of phenol level at ENOC-RWTP and assessment of the effectiveness of employed pollution control technologies in reducing phenol level at the treatment plant have been conducted in this study. It was found that the main sources of total phenols in the received waste streams at ENOC-RWTP are the tank water drain (average 11.8 mg/l), the desalter effluent (average 1.4 mg/l), and the neutralized spent caustic (average 234 mg/l) waste streams. However, there are large fluctuations from the average phenol level within each waste stream. Also, the level of total phenols and its derivatives (substituted phenols) in these streams vary significantly with straight phenol, combined m- and p-cresols, o-cresol, tri- and tetra-chlorophenols and to a lesser extent 4-chloro-3-methylphenol are common among these streams. The study further showed that the sequencing batch reactor system employed at the plant was effective in the removal of total phenols from the waste streams, with an average removal efficiency of about 98%. Meanwhile, the employed activated carbon bed has an additional removal capacity in reducing the level of total phenols to the regulatory discharge limit, with an average removal efficiency of 30%. It was further found that statistically significant relationships exist between the level of total phenols in the discharged treated effluent and the levels of the chemical oxygen demand, biochemical oxygen demand, and sulfides.

Keywords: Phenolic compounds; Oil refinery; Wastewater; SBR; Pollution; Removal; Characterization

1. Introduction

Pollutants are common waste by-products in petroleum processing and in the manufacture of chemical, pharmaceutical, and agricultural products. A high percentage of phenols are found from wastewaters of coal gasification, chemical industries, textile, pulp and paper industries, petroleum and petrochemical plants [1–4]. If these wastewaters are not treated adequately, they can cause damage to the environment by

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contaminating surface and groundwater where they are discharged [5].

The development of petroleum and petrochemical industry in the Arabian Gulf region has been growing rapidly. In the last 50 years, exploration, drilling, extraction, refining, and chemical engineering activities of oil and gas industry have all become an essential component in the economy of many of the Arabian Gulf countries. This speedy development has resulted in many changes such as landscape, economy, human development, and interactions with other regions of the world as well as having impacts upon the environment and society. In fact, "one of the most serious challenges facing the modern Middle East is the protection of its environment and the need to balance sustainable development with environmental security" [6].

Water pollution is a serious concern in the UAE. This critical problem is made even more serious with the fact that water is very scarce in the region. Like most industries, oil refineries generate enormous quantities of wastewater. Such wastewater may contain several pollutants including phenols. Because of its toxicity [7–10], phenol became a wastewater quality parameter that the regulators closely look at in the effluents of heavy industry such as refineries. For example, Jebel Ali Free Zone Authority in Dubai, UAE, stipulates a maximum phenol level of 0.1 mg/l in industrial effluents discharged to marine environment [11].

In oil refineries, the typical ranges of phenol concentration are from 50 to 185 mg/l for catalytic cracking wastewater to sour water streams, respectively [12]. Similar levels of phenols in waste streams of a full-fledged oil refinery have also been reported by Patterson [13]. The author reported that the level of phenols typically falls in the range of 80–185 mg/l for raw outlets sour water, 40–80 mg/l for general waste stream, about 80 mg/l for post-stripping, 40–50 mg/l for catalytic cracker, and 10–100 mg/l for general wastewater. It should be noted that industrial wastewaters originating from oil production processes may contain phenols in high concentrations [14].

There are various methods based on physical and chemical processes for removal of pollutants especially phenolic compounds from waste streams containing them [5,13–17]. In addition, several studies have been reported in the literature on the use of biodegradation for removal of phenols from wastewater [18–33]. In many of these studies, *Pseudomonas putida* (Pp) strain-type bacteria have been found to be effective for the degradation of phenols [14,26,28]. The efficiency of biological methods employed for the treatment of phenol-contaminated wastewater varied with operating process variables such as pH, temperature, dissolved oxygen, and nutrients [34,35]. It was further found that anaerobic degradation is typically more effective in removing phenol than degradation under aerobic conditions [21,24]. Sequencing batch reactor (SBR) has been found to successfully degrade phenol in petroleum wastewater within a reasonable treatment time [36–38].

Phenol levels in most of the previously mentioned studies ranged between 100 and 1,000 mg/l. At high phenols levels, however, the inhibitory nature of phenol has been observed in the system with *P. putida* and *Trichosporon cutaneum* strains for phenol degradation in batch experiments with an initial phenol concentration above 100 mg/l [39]. The authors found no phenol degradation at concentrations > 1,300 mg/l. Also, the lag phase increased with the increase in initial phenol levels for concentrations < 1,300 mg/l. Meanwhile, it was reported that biodegradation follows substrate inhibition kinetics at higher concentration [39].

Most of the studies conducted on the removal of phenol from wastewater were limited to laboratory conditions. Transfer of laboratory results to field conditions may not be straightforward, as the latter could be subject to several variables including differences and changes in waste characteristics. Thus, assessment of phenol removal under field conditions becomes important. To our knowledge, no investigation has been made on the effectiveness of the commonly employed treatment processes for the removal of phenols from condensate refinery wastewater. So, the main objective of this study was to investigate the efficiency of treatment processes employed at ENOC-RWTP in reducing phenol concentration. Another objective was to identify and quantify individual phenols in waste streams that contain these chemicals.

2. Site description

ENOC is the first oil refinery in the Emirate of Dubai, UAE. The company is a condensate splitter refinery with various plants including Merox sulfur removal and sulfur recovery units. Due to the nature of the condensate, the plant has little environmental emissions when compared to crude oil refineries, which have other units such as hydrocrackers, vacuum distillation, and coking units. The crude received at ENOC refinery is at times varying in basic quality due to oil nature, and use of different injected anti-corrosive chemicals and drilling mud. Wastewater generated from oil processing at ENOC is treated at the ENOC-RWTP before discharge into the harbor of Jebel Ali Free Zone, UAE.

The wastewater treatment plant receives incoming wastewater from 18 streams. These streams include the following: wet slop, sour-water-stripper bottoms (SWS bottoms), desalter effluent, boiler blowdown, cooling water blowdown, utility water caustic soda pumps flushing, LPG vaporizer polluted condensate, fuel oil heater polluted condensate, Merox plants caustic soda, caustic heater condensate, pre-treated neutralized spent caustic wastewater, oily water from Merox plants, pad drainage, naphthenic neutralized spent caustic, tank drain water, storage area stormwater, waste sludge from a locally operated sanitary wastewater treatment plant, and clean stormwater.

As shown in Fig. 1, many of the streams are first directed into a diversion box, which feeds into corrugated plate induced separators (CPI) for oil removal. The CPI enhances coagulation of emulsified oil particles and flotation of these particles. After having floatable oil removed by the CPI, the flow goes into induced gas floatation (IGF) units, where air and a polyelectrolyte/strong cationic additive polymer are injected to further reduce the oil content. The outlet from the IGF is directed to biological SBRs for further removal of dissolved organic matter.

The SBRs are a fill-and-draw type system involving a single complete-mix reactor, in which all the sets of the activated sludge process occur under extended aeration conditions. Mixed liquor remains in the reactor during all cycles, thereby eliminating the need for separate secondary sedimentation tanks. The processes of sedimentation and clarification take place sequentially in the same tank (not simultaneously as in the activated sludge process). The SBR system is a batch operated system and is primarily used for removal of soluble biodegradable organics through biodegradation. To allow for continuous operation, more than one reactor is used, each with a capacity of about 500 m^3. The SBR is nearly filled with wastewater in the presence of pre-settled activated sludge but in the absence of supplied aeration (anoxic fill period). The SBR is then filled to its operating capacity with the initiation of aeration (aerated fill period). The filling period (under anoxic and aerobic conditions) takes about 25% of the total cycle time (about 24 h). Biodegradation takes place under aerobic conditions over a period of 35% cycle time, but could be extended with higher pollution loading. After that, formed bioflocs are allowed to settle (quiescent settling period) and then clarified supernatant is pumped to a skimming basin. Once decanted, the SBR becomes ready to receive more feed wastewater and repeat the batch cycle.

The pH in the SBRs is controlled in the range of 7–9 because biological systems operate better within this pH range. Meanwhile, phosphorus (as phosphoric acid) and ammonia (as urea pellets) are added, if needed, to support the metabolic activities of the organisms. The microorganisms are normally acclimatized through a long process of slow concentration increases in feed to deal with high chemical oxygen demand (COD) and phenol effluents. Periodically, excess sludge generated in the process is drawn off from the SBRs and transferred to the sand drying beds.

There are four SBR units (SBR A through SBR D Fig. 1) at ENOC-RWTP. SBR A and B receive treated waste streams leaving the IGF unit, while SBR C and D receive a mixture of treated wastewater from the IGF unit, neutralized spent caustic, and treated wastewater from the skimming pond. Typically, the proportion of neutralized spent caustic is about 1 part to 35 parts of the whole mixed streams.

The skimming basin acts as a settling tank of escaped active sludge and is also used to remove some of the floatable solids. Effluent from the skimming basin is pumped through a sand filter to further reduce the level of suspended solids. Effluent from the filter goes into an activated carbon bed, which acts as a polishing step for the removal of remaining organic substances. Effluent of the carbon bed is then sent to a final storage pond before it is discharged into the harbor.

Fig. 1 also shows the average processed flow rates by the unit processes. The flowing streams usually come with different flow rates as well as different constituents. However, a major fraction of the processed wastewater comes from the desalter effluent. The average processing rate of the CPI and IGF units is 25 m^3/h. The majority of water processed by the IGF unit goes to SBR A or B, and a small fraction is directed to SBR C or D, which is mixed with wastewater coming from the neutralized spent caustic wastewater and the skimming basin as indicated before. The average processed flow rate through the sand filter and carbon bed is about 35 m^3/h.

3. Sample collection and analysis

Samples were taken from eleven locations within the treatment plant as shown in Fig. 1. Three of these (1–3) are of the waste streams including desalter water, tank drain water, and neutralized spent caustic. Location 4 represents an average characteristic of all waste streams excluding the neutralized spent caustic (which is sent to a storage tank and added directly under controlled conditions to the SBR). This location is referred to as raw mixed inlet. The other 8 locations (5–12) are located at the outlets of processes within

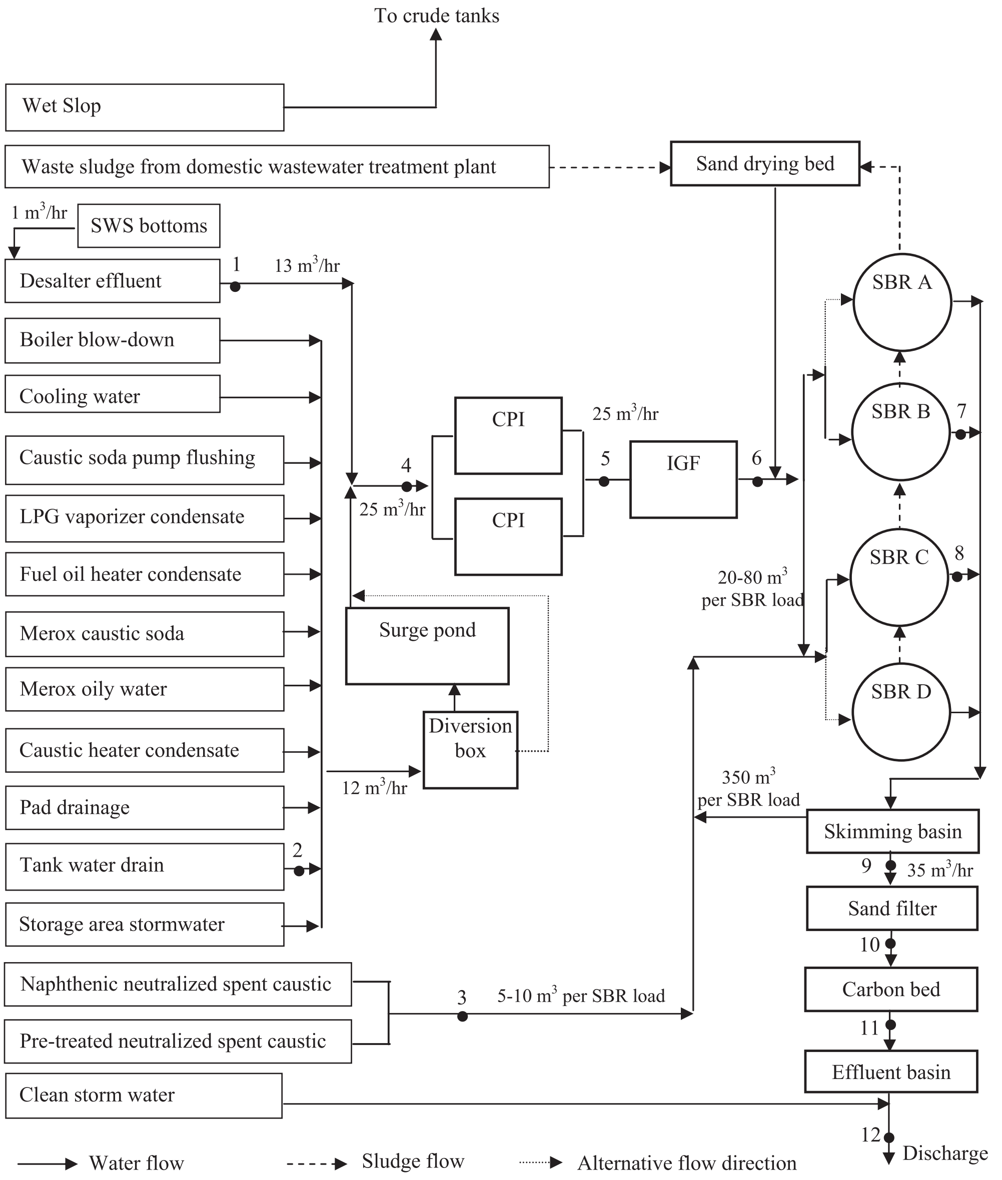

Fig. 1. Waste streams and process flow diagram at ENOC-RWTP.

the treatment plant. Two locations at the outlet of the SBRs were chosen (7 and 8). The other sampling locations (9–12) include the outlet of the sand filter, the outlet of the activated carbon reactor, and the effluent pond, respectively.

Phenol in the waste streams was determined as both total phenols and as individual phenols. Some individual phenols in the waste streams were quantified by a gradient high-performance liquid chromatography (HPLC) system as outlined in the US EPA Method 555 [40]. Phenols were separated on a Symmetry ODS column (250 mm length, 4.6-mm ID, and 10-μm particle size) and detected using fluorescence (λ_{Ex}: 224 nm and λ_{Em}: 320 nm) and photodiode array (280 nm) detectors. Other phenolic compounds were analyzed (as pentafluorobenzyl derivatives) by gas chromatography (GC) coupled with an electron capture detector following the US EPA Method 604 [41]. Individual phenols in the GC method were separated on a CP-Sil 8 capillary column (30 m long 0.32 mm ID and 1 μm film thickness). Individual phenols that were determined by the HPLC method include 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, phenol, combined m- and p-cresol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol, 2,3,4-tetrachlorophenol, and 4-chloro-3-methylphenol. The remaining phenols (i.e. 2,4-dimethylphenol, o-chlorophenol, 2,6-dichlorophenol, o-nitrophenol, p-nitrophenol, and pentachlorophenol) were determined by the GC method.

The concentration of total phenols was determined by spectrophotometry using a HACH photometer located at ENOC-RWTP. Testing procedure for total phenols was based on the American Public Health Association (APHA) Method 5530 D [42]. The validity of total phenols data was ensured through cross-checking, using the same sample, on a Varian Cary spectrophotometer (located at the UAE University campus) using a different set of standards. Other parameters in the water samples have been analyzed following the recommended methods by APHA [42] which include the following: temperature (Method 2550), pH (Method 4500H, using Metrohm pH meter), total dissolved solids (TDS) (Method 2540 C), dissolved oxygen (DO) (Method 4500 O, using an Orion DO meter), oil and grease (O&G) (Method 5520 C, using an Infracal TOG/TPH analyzer), COD (Method 5220 C), 5-d biochemical oxygen demand (BOD_5) (Method 5210B), total organic carbon (TOC) (Method 5310 B, using a TOC-1200 analyzer), and sulfide (Method 4500 S2).

Samples were collected from the sampling locations on different days as shown in Table 1. Collected samples were analyzed for the parameters that are listed in the footnotes of Table 1. Samples of the continuous-flow units (CPI, IGF, sand filter, and carbon bed) were drawn at the same time without consideration of hydraulic retention time. However, testing was further conducted over a 48-h period using 6-h samples in order to determine fluctuation in the inlet characteristics of these units.

4. Results and discussion

4.1. Highly polluted waste streams

Based on the levels of phenols used in the design of ENOC-RWTP, the streams that are considered highly polluted in terms of phenol loading are the desalter effluent, the neutralized spent caustic, and the tank water drains. Samples from these waste streams were collected for the analysis of phenol and phenol individuals as well as other water characteristics. The results are summarized in Table 2 and are further discussed below.

The desalter effluent water is characterized by heavy brownish light particles in suspension with a relatively pungent mixture of petroleum odor. The desalter effluent water shows a neutral pH and low TDS (Table 2). Meanwhile, the organic matter content (COD, TOC, and O&G) is relatively low compared to the other two streams. Also, the phenol level obtained during the analysis (average ≈1.4 mg/l) is lower than the level found in the other two streams.

Samples from the neutralized spent caustic have dark greenish-yellow color with black floating and settleable particulate matter. This waste stream, which is a mixture of many different compounds is generated in the Merox processes, has a blend of very strong, pungent petroleum and sulfide-type odor. As shown in Table 2, neutralized spent caustic stream is characterized by high TDS and high organic matter content (COD, TOC, and O&G). The phenol level in this stream (average 233.5 mg/l) is the highest among the other streams and fluctuates in the value as depicted by the range of parameter values observed (Table 2).

Samples from the drain water of the condensate tanks have dark yellow to brownish color with black floating and settleable sediments. As is the case with the neutralized spent caustic, this stream has a blend of very strong, pungent petroleum, and sulfide-type odor. The tank drain water is generally discolored due to the presence of high iron. This stream also has higher organic matter than that associated with the neutralized spent caustic. However, the phenol level (average 11.8 mg/l) is almost 20 times lower than what has been found in the neutralized spent caustic stream but again fluctuates widely as depicted by the listed range values (Table 2).

4.2. Phenols characterization in waste streams

Finger prints of phenols in the main troublesome streams are shown in Fig. 2. Results presented in Fig. 2 for the desalter effluent are the average of two analyzed samples that were collected from the two existing deslater units. Meanwhile, results presented for the tank drain are the average of two samples each taken from the two existing drain water tanks.

Analysis of individual phenols in the desalter effluent indicates that straight phenols and cresols are the highest in the stream at nearly equal levels (Fig. 2). Also, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol, 2,3,4-tetrachlorophenol, and 2,4,-dimethylphenol all exist in nearly equal concentrations. Furthermore, 4-chloro-3-methylphenol, and 2,6-dichlorophenol could be present in this waste stream. It is evident, however, that the levels of phenol derivatives in the desalter waste stream are generally less than the corresponding levels in the drain water and the neutralized spent caustic streams.

The level of individual phenols in the tank drain varies significantly with certain types of phenols such

Table 1
Sampling dates and locations[a]

Location	30/12/03	6–7/1/04	14/1/04	8/2/04	14/2/04	3/3/05	4/3/05	5/3/05
1	X[b]	–	X[b]	–	X[b]	X[b,c]	X[b,c]	X[b]
2	X[b]	–	X[b]	–	X[b]	X[b,c,d]	–	–
3	X[b]	–	X[b]	–	X[b]	X[b,c]	–	–
4	X	X	X	X	X	X[e]	X[e]	X[e]
5	X	X	X	X	X	X[e]	X[e]	X[e]
6	X	X	X	X	X	X[e]	X[e]	X[e]
7	X	X	X	X	X	X[e]	X[e]	X[e]
8	X	X	X	X	X	X[e]	X[e]	X[e]
9	X	X	X	X	X	X[e]	X[e]	X[e]
10	X	X	X	X	X	–	–	–
11	X	X	X	X	X	–	–	–

[a] X means samples were collected on the indicated date and location and were analyzed for temperature, pH, TDS, DO, O&G, COD, BOD_5, TOC, sulfide, and total phenols unless otherwise mentioned.

[b] Analysis included all water parameters except BOD_5 and sulfide.

[c] Analysis included quantification of individual phenols.

[d] A sample was collected and analyzed from each of the two existing tank drains, and the results were averaged and presented later.

[e] Samples were taken every 6 h from 3–5/3/05 and were analyzed for temperature, pH, TDS, COD, and total phenols.

Table 2
Average characteristics of the three troublesome waste streams[a,b]

Parameter	Desalter effluent (Location 1)	Tank drain (Location 2)	Neutralized spent caustic (Location 3)
pH	7.3 (6.5–7.8)	5.8 (5.6–6.1)	7.0 (6.8–7.1)
Temp. (°C)	39.1 (23.5–55)	23.5 (23–24)	23.9 (23.5–24.2)
TDS (mg/l)	129 (20–310)	28,860 (5,900–86,570)	35,954 (7,732–65,230)
COD (mg/l)	754 (552–916)	34,608 (5,250–108,100)	11,093 (5,220–17,100)
Total phenols (mg/l)	1.4 (0.25–2.89)	11.8 (0.63–15)	233.5 (112–375)
DO (mg/l)	3.7 (1.8–5.5)	1.3 (0.3–2.5)	2.1 (1.1–3.2)
O&G (mg/l)	<5 (NA)	125.8 (8–217)	87.3 (56–110)
TOC (mg/l)	118 (114–122)	22,215 (5,250–39,180)	5,212 (3,200–6,820)

[a] Tabulated results are based on analysis of six samples collected from the desalter effluent, five samples collected from the tank drain, and four samples collected from the neutralized spent caustic waste stream.

[b] Values in parenthesis represent the range of values based on the results of the analyzed samples.

as cresols, 2,4-dimethylphenol and 2,6 dichlorophenols. Furthermore, the level of straight phenol seems to be the highest followed by o-cresol + 2-cyclohexyl-4,6-dinitrophenol and combined m- and p-cresol, which are almost at equal levels followed by 4-chloro-3-methylphenol. These compounds are probably found due to added chemicals during exploration and pre-treatments, which are undertaken on the crude condensates prior to arrival at the refinery. Other nitro- and chlorophenols are evident in this stream but at lower levels.

Phenol compounds present in the neutralized spent caustic waste stream include 2,4,6-trichlorophenol, combined m- and p-cresol, 2,3,4-tetrachlorophenol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol, and straight phenol. In this waste stream, o-cresol + 2-cyclohexyl-4,6-dinitrophenol and combined m- and p-cresol were detected in concentrations nearly equal to that of straight phenol. The detected phenol compounds in this waste stream are probably products of the Merox and subsequent neutralization reactions that take place in the plant operations. These are found due to possibly the violent catalysis oxidation reactions and subsequent acid-base reactions (neutralization) that take place which are undertaken on the final raw products prior to final product storage and export from the refinery. Again, straight phenol and combined m- and p-cresol seem to be the highest in concentration among other phenols.

Comparison among the three waste streams based on the results presented in Fig. 2 shows that the level

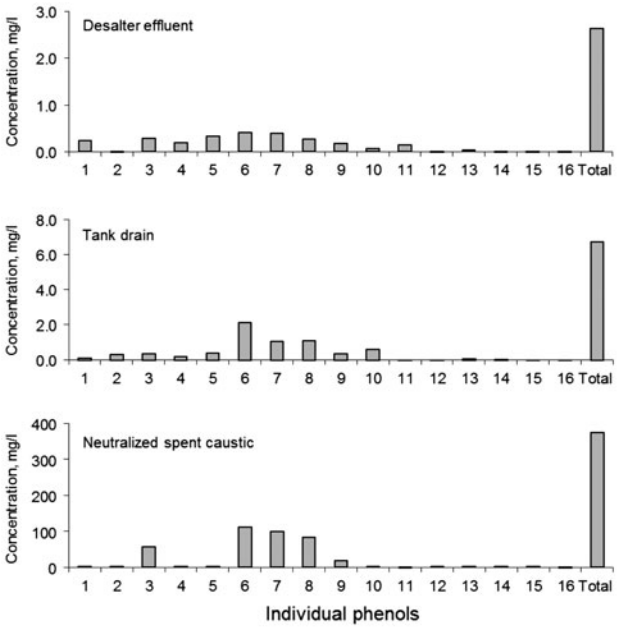

Fig. 2. Characterization of phenols in the troublesome waste streams. 1 = 2,4-dinitrophenol, 2 = 2-methyl-4,6-dinitrophenol, 3 = 2,4,6-trichlorophenol, 4 = 2,4-dichlorophenol, 5 = 2,4,5-trichlorophenol, 6 = phenol, 7 = combined m- and p-cresol, 8 = o-cresol + 2-cyclohexyl-4,6-dinitrophenol, 9 = 2,3,4-tetrachlorophenol, 10 = 4-chloro-3-methylphenol, 11 = 2,4-dimethylphenol, 12 = o-chlorophenol, 13 = 2,6-dichlorophenol, 14 = o-nitrophenol, 15 = p-nitrophenol, and 16 = pentachlorophenol.

of total phenols is the highest in the neutralized spent caustic (375 mg/l), followed by tank drain water (6.7 mg/l), and followed by deslater effluent (2.6 mg/l). This is generally consistent with the trend observed in the previous section, but the levels are different due to the variability of total phenols of each stream. Further comparison reveals that commonly found phenols in these steams include 2,4,6-trichlorophenol, combined m- and p-cresol, 2,3,4-tetrachlorophenol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol, and straight phenol. These 5 phenols contribute to about 60–80% of the total phenols in the three waste streams. On the other hand, the phenol compounds that have been detected or detected at very low levels in the three waste streams include 2-methyl-4,6-dinitrophenol, o-chlorophenol, 2,6-dichlorophenol, o-nitrophenol, p-nitrophenol, and pentachlorophenol.

4.3. Changes in phenol level with time and throughout processes

Fluctuations in phenol levels and other wastewater parameters were investigated by taking samples from the inlet of unit processes every 6 h for 48 h. Fig. 3 shows variations of phenols in the incoming and treated effluent of each unit process. As the figure shows, the level of phenol in the incoming flow to the unit processes varies over time from about 0.2 to about 1.3 mg/l, except for the wastewater entering the sand filter and the carbon bed where the level retains a value of about 0.1 mg/l.

Fig. 4 shows changes in other wastewater parameters (temperature, pH, TDS, and COD) in the inlet of unit processes at ENOC-RWTP. Changes in temperature (22–28˚C) reflect the effect of ambient conditions, with lower temperatures during night and higher ones during daytime. Temperature, however, does not differ much among different processes at a certain time during the day. The pH, on the other hand, falls in the range of 6.5–7.5 with no particular changes with time or process. The pH at the inlet of the sand filter and carbon bed remains almost constant (pH 7.2) due to homogenization of the incoming streams in the SBRs.

TDS variations at the outlet of the CPI, IGF, and SBR seem to be related to variation in the TDS of the inlet to the treatment plant especially those of the tank water drain (see Table 2). Moreover, TDS at the outlet of the SBRs, sand filter, and carbon bed does not fluctuate much but is at a higher level compared to that of the CPI and IGF. Slight fluctuation in TDS at the outlet of the SBRs is due to homogenization of the incoming waste streams to the SBRs. However, higher TDS at the outlet of the SBRs is due to dosing of nitrogen and phosphate compounds through addition of urea and phosphoric acid in addition to processing neutralized spent caustic waste that is characterized by a high TDS (Table 2).

Fig. 4 shows significant variations in the COD of the influent of the CPI, IGF, and SBRs, with no partic-

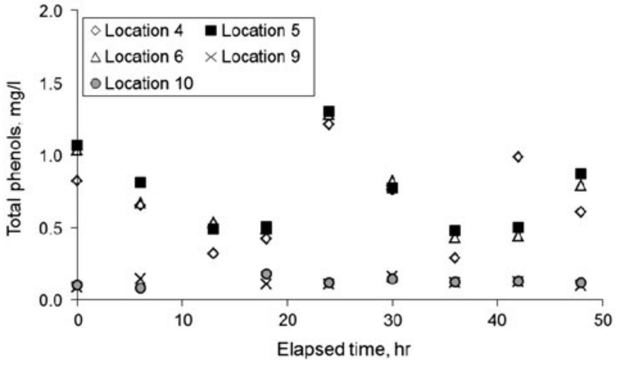

Fig. 3. Changes in total phenols level at the inlet of unit processes at ENOC-RWTP.

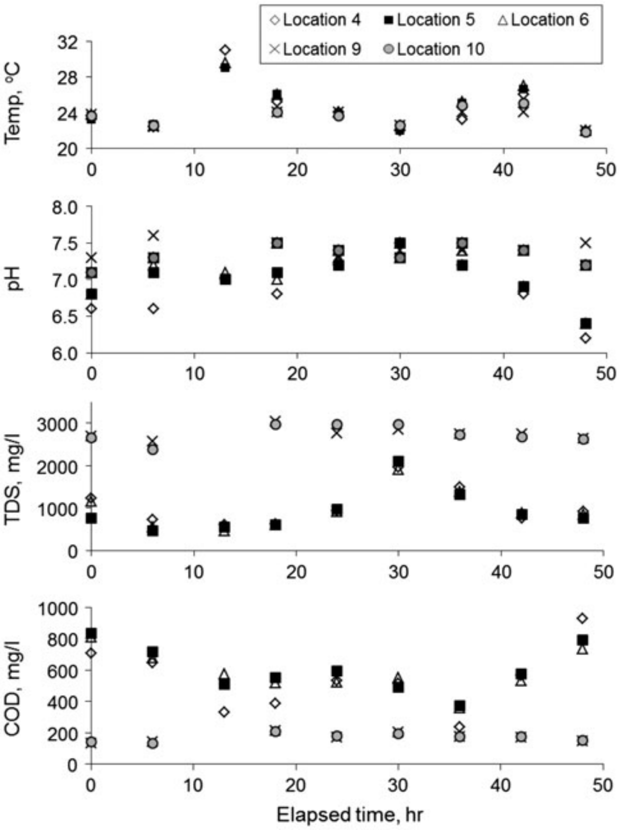

Fig. 4. Changes in temperature, pH, TDS, and COD at the inlet of unit processes at ENOC-RWTP.

ular trend of increase or decrease in COD level within the monitoring duration. The inlet of the IGF has generally higher COD than that in the inlet of the CPI due possibly to dissolution (emulsification) of organic matter in the CPI that was originally not dissolved when the stream entered the CPI. The figure also reveals that the SBR process is very effective in removing COD as demonstrated by the significant drop in COD at the inlet of the sand filter as compared to the levels at the outlet of the IGF. COD also temporally fluctuates at the inlet of a certain process in addition to its variation among different processes. Such behavior is similar to that observed for phenol (Fig. 3).

Fig. 5 shows phenol removal across the unit processes at ENOC-RWTP. The figure clearly depicts the effect of the SBRs on phenol reduction. The removal efficiency of total phenols and COD by the different unit processes was determined based on the average concentration in the stream entering and leaving each unit process. For all the reactors except the SBR C and D, such data were available from the analysis of the collected samples. Since the SBR C and D receive a mixture of different streams (neutralized spent caustic, IGF outlet, and skimming basin) and no samples were taken in this study directly after filling these reactors, then the initial average level of total phenols (4.3 mg/l) and COD (517.3 mg/l) in the SBR C or D was calculated by mass balance using the input volume of each stream (see Fig. 1) along with the average level of the target pollutant in each stream.

Table 3 lists the values of the calculated removal efficiency of total phenols and COD by the different unit processes. The CPI process results in negative removal efficiency for phenol due to possible emulsification of oil droplets in the reactor, causing a release of some phenols in solution. On the other hand, both the IGF and the sand filters do not have any significant effect on phenol removal as almost similar phenol levels, compared to the level in the entering waste stream, are observed in the outlet of these processes. Among the different employed processes in the treatment plant, the SBRs are the most effective ones in removing total phenols with an average removal efficiency of about 98%. As can be noticed, SBR A and B perform better in terms of phenol removal than that of SBR C and D due possibly to an inhibition effect caused by higher initial phenols levels processed by the latter SBRs or due to the higher salinity level (average 3,250 mg/l) as compared to the processed waste stream in SBR A and B (average 870 mg/l). As for the carbon bed, it shows a positive effect on the removal of total phenols with an average removal efficiency of 30%.

The results shown in Table 3 compare very well to those mentioned in the literature. The removal efficiency was reported in the range 56–99% for pure phenol feed in a SBR (of small size, 1.65 L), and the efficiency decreased with the increase in phenol concentration (in the range 516–1,135 mg/l) [43]. The

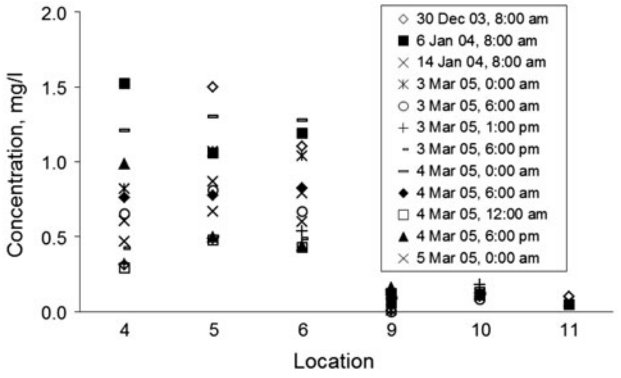

Fig. 5. Changes in total phenols concentration across the unit processes at ENOC-RWTP.

Table 3
Removal efficiency of total phenols and COD by the different unit processes[a]

	Total phenols			COD		
Process	Inlet level (mg/l)	Outlet level (mg/l)	Removal efficiency	Inlet level (mg/l)	Outlet level (mg/l)	Removal efficiency
CPI	0.70	0.82	−18.2	520	616	−18.5
IGF	0.82	0.80	2.3	616	610	1.0
SBR A or B	0.80	0.01	98.8	610	19.7	96.8
SBR C or D	4.33[b]	0.10	97.6	517[b]	133	74.3
Sand filter	0.123	0.12	2.6	173	171.6	0.8
Carbon bed	0.12	0.08	30.3	171.6	104	39.4

[a] Concentration values are average of the values for the samples collected in this study unless otherwise mentioned.

[b] Determined by mass balance of mixing 50 m^3 of water from the outlet of the IGF unit, 7.5 m^3 of water from the neutralized spent caustic stream, and 350 m^3 of water from the skimming pond.

removal efficiency reported [44] for a feed of phenol and o-cresol was 99% and 94%, respectively, in the concentration range 100–800 mg/l. Similar values of removal were reported in a SBR study for treatment of wastewaters with various influent phenol concentrations [45]. The removal of total petroleum hydrocarbons in other types of reactors was reported in the range 78–98% [46,47]. Considering the fact that our analysis was for samples from an industrial-size plant that contains various phenols at different concentrations, the overall removal of total phenols achieved in the combined SBR and carbon bed processes can be considered very good.

The removal efficiency of COD by the unit processes follows almost the same trend as that of total phenols. Possible emulsification in the CPI resulted in an increase in the average COD level in the stream leaving the reactor and consequent negative removal efficiency. Meanwhile, the IGF and sand filters do not appear to significantly remove COD from the processed streams. However, the SBRs and to a lesser extent the activated carbon reactors are the main contributors to COD reduction in the processed waste streams. Again, SBR A and B perform much better than SBR C and D in terms of COD removal, possibly due to the salinity effect of the processed waste, which could have resulted in a lesser degradation ability of the active microorganism in the SBR C and D. The COD removal reported in the literature is in the range 80–94% for treatment of phenolic wastewaters and other wastewater containing toxic chemicals [48,49]. The COD removal efficiency of 74% in SBRs and additional 39% in carbon bed achieved in this study for an industrial-scale plant is considered to be satisfactory.

4.4. Relationship between phenol and other water parameters

Previous records available at ENOC-RWTP for the effluent (treated wastewater) allow comparison between parameter values. It should be noted that previous data represent monthly averages from daily final effluent pond readings. Fig. 6 shows plots of effluent BOD, COD, and sulfide vs. total phenol levels. The figure also shows the best fit line between phenol and the other water parameters. The best linear equations along with the coefficient of determination (r^2) and the 95% confidence interval (CI) of the slope are also presented in Table 4. The CI for the slope was determined according to the method described by Anderson [50].

As shown in Table 4, the r^2 values associated with the linear relationships between phenol and the other water parameters are relatively low (especially for COD) due to the scatter of the data as depicted in Fig. 6. Nonetheless, the established relationships are statistically significant on a 95% confidence level since the slope is different from zero. These relationships could be used to estimate effluent BOD, COD, and sulfide based on an already determined effluent phenol level. Meanwhile, by meeting a phenol value of 0.1 mg/l or less in the final effluent prior to discharge, one can estimate based on these relationships whether the effluent limit of BOD_5, COD, and sulfide is met or not.

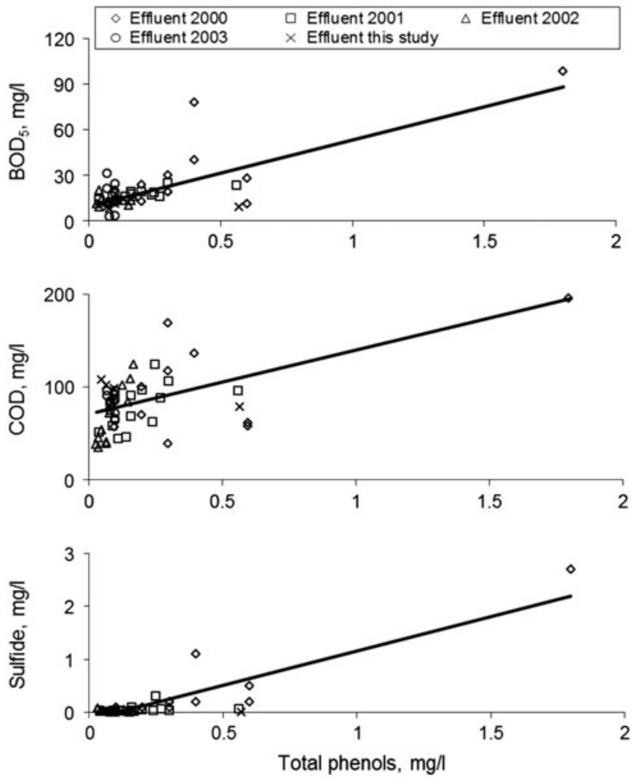

Fig. 6. Correlation between total phenols and other water parameters in the discharge water.

Table 4
Relationships between phenol and other parameters of treated wastewater

Relationship	Equation	r^2	Confidence interval (CI)
Phenol–BOD$_5$	BOD$_5$ = 43.7 × phenol + 9.7	0.56	43.7 ± 15.3
Phenol–COD	COD = 68.6 × phenol + 71.3	0.25	68.6 ± 37.2
Phenol–sulfide	Sulfide = 1.29 × phenol − 0.13	0.76	1.29 ± 0.38

5. Conclusion

The following conclusions are drawn based on the data collected in this study and those collected from the refinery testing records:

- Phenol in refinery wastewaters at ENOC-RWTP comes from the tank water drain, the desalter effluent, and the neutralized spent caustic waste streams. The latter has the highest total phenol levels of 234 mg/l, but large deviations from the average level exist within each stream.
- The concentration of phenols in the troublesome waste streams varies between certain types of phenols with straight phenol and combined m- and p-cresol are the most dominant in the waste streams. Other phenols that are common among the waste streams include o-cresol, tri- and tetra-chlorophenols and to a lesser extent 4-chloro-3-methylphenol.
- The existence of 7 out of 16 phenol compounds in the different waste streams indicates that the source of phenol is probably the processed condensate crude oil and is not a by-product of oil processing at the refinery.
- The waste stream at the inlet of unit processes at ENOC-RWTP varies in its total phenols concentration and other water characteristics over time, but variations become less pronounced after the SBR.
- The main unit operations responsible for the removal of total phenols from the processed waste streams are the SBR at an average removal efficiency of 98%, followed by sorption by activated carbon at about 30% removal efficiency.
- A statistically significant relationship exists between total phenols concentration in the discharged effluent and other water parameters such as COD, BOD$_5$, and sulfides.

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