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Bioaugmentation for improving the activated sludge process of treating refinery spent caustic: laboratory and field pilot-scale studies

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ABSTRACT

In this work, successful treatment of refinery spent-sulfidic caustic was achieved in activated sludge system bioaugmented with three specific bacterial strains (including *Bacillus thuringiensis*, *Bacillus cereus*, and *Acidovorax ebreus*) at both laboratory and pilot scale. After 18-fold dilution by volume, the diluted wastewater was treated aerobically. The volumetric loading rate of chemical oxygen demand (COD) was studied by treating variously diluted samples of high-strength wastewater (COD 3,100–3,600 mg/L). The results obtained with the raw wastewater were remarkably good, with an average COD removal of around 80%. The addition of peptone and trace elements improved the performance of the process. The mixed liquor suspended solids (MLSS) concentration in the reactors could be increased from the 2,500–3,000 mg/L MLSS level of general activated sludge processes to 6,000–8,000 mg/L after installation of draft tubes. These results showed that activated sludge process may be a powerful tool for treating refinery spent caustic by bioaugmentation and nutrient amendment.

Keywords: Spent-sulfidic caustic; Di-*n*-butyl phthalate; Bioaugmentation; Draft tube

1. Introduction

Refinery spent caustic is a waste stream originated from petroleum sweetening and hydrocarbon washing in refinery plants, which is characterized by strong alkalinity (pH > 12) and elevated salinity ([sodium]) of 5–12 wt.% [1]. Depending on the source, spent caustics may contain high concentrations of phenols, hydrosulfide, sulfide, amines, mercaptans, and other organosulfur compounds that are soluble or emulsified in the caustic [2]. Spent caustics have been classified as hazardous waste according to the US Resource Conservation and Recovery Act

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because of its noxious odor, toxicity, and hazardous characteristics [3].

Conventionally, spent-sulfidic caustics have been disposed of by ocean dumping or deep-well injection [4]. However, those options are currently prohibited due to stringent environmental regulations [5]. Currently, chemical oxidation, such as Fenton oxidation, and electro-Fenton process, is usually applied to the treatment of spent-sulfidic caustics, often leading to an incomplete oxidation of the dissolved sulfide to thiosulfate and thus in a residual chemical oxygen demand (COD) of the treated effluent [1,4,6]. In addition, physicochemical treatment technology, such as ultrasound-Fenton reagent process, was also researched to treat spent-sulfidic caustics [5]. Wet air oxidation is generally used for the physicochemical treatment of spent caustics. This process is characterized by high investment and operational costs due to operation at high temperature and pressure.

Onsite biological treatment could be an inexpensive and safe alternative to the currently employed physicochemical treatment processes. However, many refineries do not have the specific treatment system to treat the entire amount of spent caustics produced, and concerns regarding odors and toxicity frequently prohibit this practice. Some refineries dispose of spent caustics in their activated sludge treatment systems by blending small amounts of spent caustics with refinery wastewater. Nevertheless, these biological processes can be disturbed by fluctuating pH conditions, increasing salt concentrations, accumulation of toxic compounds, and sludge bulking [1]. Thus, specific biological treatment systems are needed to treat spent caustics with high efficiency and low cost. Recently, some studies have been reported on the biological treatment of spent caustics on laboratory scale [1–4,7,8]. Seok-Young and Dong-Sik studied the removal of total dissolved solids in spent caustic using biochar as a pretreatment method for subsequent biological treatment [9]. However, research on the successful application of biotechnology for spent caustic remediation on pilot scale is still very scarce.

It has been well documented that environmental adaptability of micro-organisms and biodegradation ability could be improved by addition of organic nutrients, such as yeast extract, glucose, and even maize powder [10,11]. In view of this, the proper addition of appropriate nutrient may be beneficial for maintaining good performance of the spent caustic treatment system, because that sulfide is toxic to micro-organisms and may inhibit several enzymatic systems at already low levels [12].

Bioaugmentation of wastewater treatment systems with specialized bacterial strains has been known to be a powerful tool to improve the removal efficiency of recalcitrant and/or toxic compounds [11,13,14]. In spite of several successes of bioaugmentation in laboratory scale [14,15], its application to a pilot or full-scale wastewater treatment is still scarce.

In this study, three di-*n*-butyl phthalate (DBP)-degrading bacteria were isolated and identified by 16S rDNA sequence. Both laboratory and field pilot-scale experiments was conducted to evaluate the feasibility of bioaugmentation application for the rapid upgrade of the activated sludge process to treat refinery spent caustic. A mixture of inorganic and organic nutrients was used to enhance the treatment performance. The outcome of this work was expected to provide a basis for developing environmentally friendly and economically competitive approaches for refinery spent caustic treatment.

2. Materials and methods

2.1. Refinery spent caustic

Refinery spent caustic was provided by a refinery plant in Yueyang, China. The spent caustic was strongly alkaline and had high concentrations of COD, phenol, and sulfide (Table 1).

2.2. Activated sludge

Raw aerobic activated sludge was collected from the wastewater treatment plant of a petroleum refinery in China. At this refinery, the activated sludge unit occasionally received spent caustic as a component of the feed to the unit. This system was, therefore, expected to contain spent caustic degraders. The activated sludge was washed three times with NaH_2PO_4–Na_2HPO_4 buffer (0.1 mol/L, pH 7.0), harvested by centrifugation, and resuspended in the same phosphate buffer before use.

2.3. Isolation of DBP-degrading bacteria

The consortium was enriched from activated sludge sampled from a pharmaceutical factory, China.

Table 1
Characteristics of refinery spent caustic used in this study

Parameter	Value (mg/L)
Dissolved solids	200,000–240,000
Alkalinity	14,500–18,300 as $CaCO_3$
COD	56,000–64,000
Volatile phenol	1,400–1,750
Sulfide	43,500–48,200
Oil and grease	750–1,320

Activated sludge (50 mL) was domesticated for one month under the pressure of a DBP gradient from 100 to 1,000 mg/L with a changing period of three days in a 250 mL Erlenmeyer flask at 30˚C and 150 rpm. Sterile Bushnell–Haas mineral solution (BHM) [16] was added to the domesticated liquid to a total liquid volume of 100 mL. The BHM contained (per liter of distilled water): KH_2PO_4 1.0 g, Na_2HPO_4 1.0 g, $(NH_4)_2SO_4$ 0.5 g, $MgSO_4{\cdot}7H_2O$ 0.2 g, $CaCl_2{\cdot}2H_2O$ 0.02 g, $FeCl_3$ 0.002 g, and $MnSO_4{\cdot}2H_2O$ 0.002 g, pH 7.0. After one month, 5 mL of the supernatant from the enrichment solution was inoculated into the BHM supplemented with 1,200 mg/L DBP in a 250 mL Erlenmeyer flask, cultured at 150 rpm and 30˚C. The consortium was serially subcultured for 20 generations for stabilization over a period of two days. Finally, three isolates were obtained and named B-4-9, BS-3-12, and JF-3, respectively.

2.4. Characterization of DBP-degrading strains

The DNA of the three strains was extracted with a commercially available kit (Dingguo, China). The V6 and V8 regions of 16S rDNA genes were amplified by polymerase chain reaction (PCR) in a Techgene thermocycler (FTGENE 5D, 112757-4, Techne Combridge Ltd. DUXFORD Cambridge UK), using the bacterial universal primer F8 (5′-AACGCGAAGAACCTTAC-3′) and R1510 (5′-ACGGGCGGTGTGTACA-3′). The sequence was determined on an ABI Prism 310 genetic analyzer (Vilber Lourmat, France). The 16S rDNA sequence of the three strains was made against the sequences in the GenBank using the BLAST program on the NCBI website (http://www.ncbi.nlm.nih.gov).

2.5. Inoculum preparation

The three bacterial strains were used as bioaugmentation inoculum. The strains were separately cultured using 100 mL BHM solution, supplemented with liquid paraffin (0.1%, v/v), peptone (0.2 g/L), and the refinery spent caustic (0.1%, v/v) at 30˚C and 150 rpm. Late-exponential phase cultures were harvested by centrifugation (10,000 g, 10 min at 4˚C), washed three times with NaH_2PO_4–Na_2HPO_4 buffer (0.1 mol/L, pH 7.0), and finally suspended in 50 mL phosphate buffer as inoculant.

2.6. Laboratory experiment

A laboratory-scale reactor with a volume of 7.0 L was operated in continuous flow mode. Fig. 1(A) shows a schematic representation of the activated sludge system. Temperature was maintained constant at 30 ± 2˚C using an electric heating element connected to a temperature controller. Air was introduced into the reactors through diffusers placed at the bottom of the aeration zone. The spent caustic was diluted with water and the pH was adjusted to 7.5 using H_2SO_4, which was then fed using peristaltic pumps.

The reactor was inoculated with the activated sludge, which served as indigenous micro-organisms in the activated sludge systems. The initial activated sludge concentration in the two reactors was 1.5 g/L. Then 50 mL bacterial suspension of the three strains was introduced to the reactor, respectively. After inoculation, the diluted spent caustic was introduced into the reactor to obtain a working volume of 5.0 L. Air was diffused in order to supply oxygen to the biomass. After aeration for 12 h, one-half of the mixed liquid was drained off and then the same volume diluted spent caustic was introduced for the next 12 h of the operation. This procedure was repeated during the first week of the startup. After that, the feed mode of wastewater was changed into continuous flow mode. As required, the influent of the reactor was supplied with nutrients which contained (mg/L): KH_2PO_4 126, peptone 800, $MgSO_4$ 60, $FeSO_4$ 20, $ZnSO_4$ 0.6, $CuSO_4$ 0.025, H_3BO_3 0.6, Na_2MoO_4 0.025.

2.7. Field experiment

The field pilot-scale study was performed in Changling Petroleum Refinery Plant, Yueyang, China. The schematic diagram and photo of the experimental system are shown in Fig. 1(B) and (C), respectively. The bioreactor had a working volume of 1.5 m^3. After installation of draft tubes, the reactor could be operated at mixed liquor suspended solids (MLSS) concentration of 6,000–8,000 mg/L, which was significantly higher than the 2,500–3,000 mg/L MLSS level of general activated sludge processes. The inoculation and acclimatization procedures were the same as in the laboratory test. The influent was diluted and neutralized in the acidification tank. The floated oil was separated in the oil separator. The influent flow rate was controlled at 60 L/h. The temperature was controlled at 28 ± 2˚C and dissolved oxygen concentration was controlled around 2.5 mg/L during the operation. The pH of the wastewater was controlled at about 7.5 by addition of H_2SO_4 and NaOH.

2.8. Analytical procedures

Wastewater parameters were regularly monitored according to standard methods [17]. Briefly, COD was

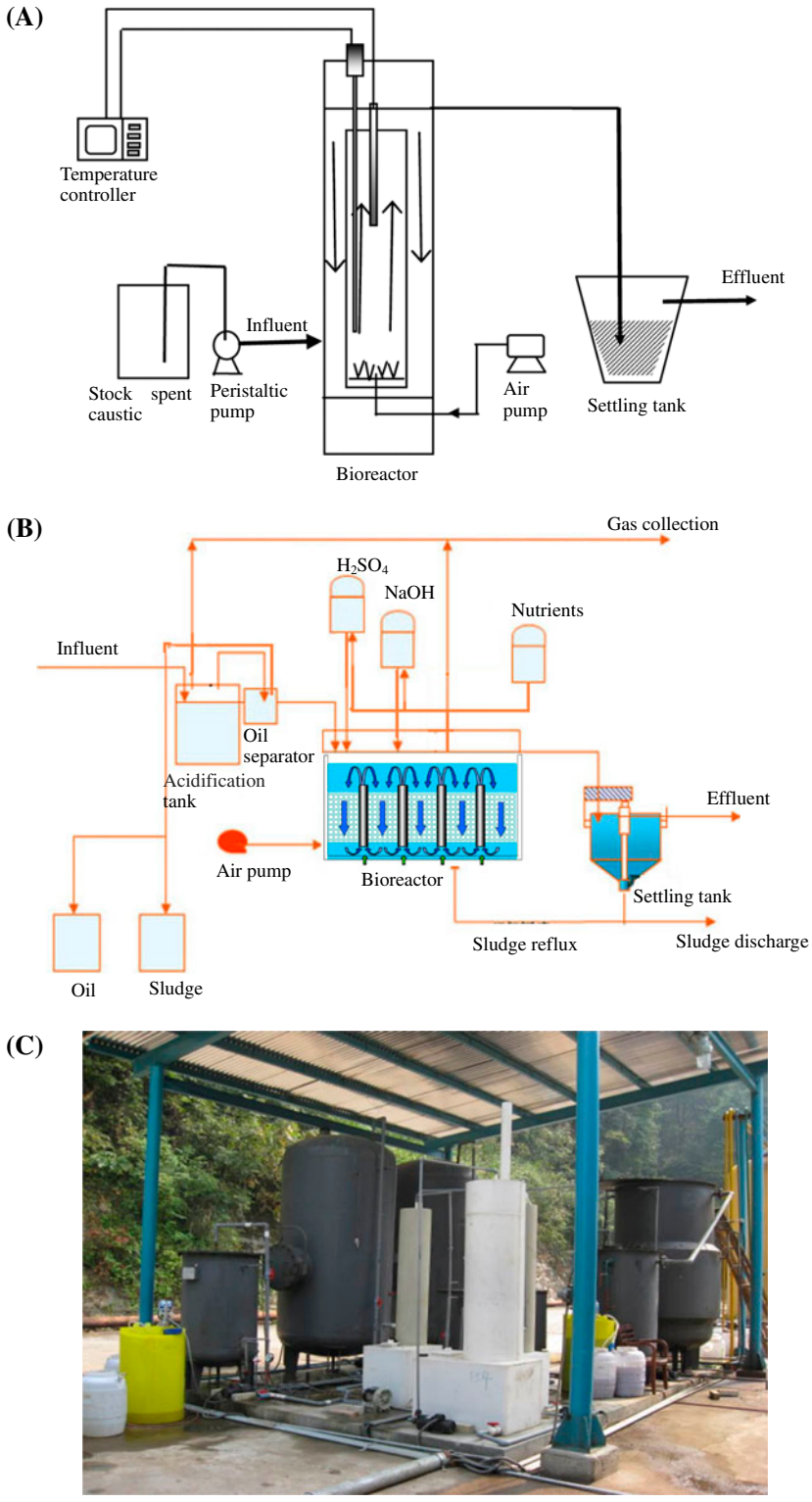

Fig. 1. (A) Schematic overview of the laboratory-scale gas-lift bioreactor, (B) schematic representation of the field pilot bioreactor system, and (C) the photo of the field pilot experimental system.

determined with $K_2Cr_2O_7$ and H_2SO_4 in a 1:1 ratio by the open reflux method with $AgSO_4$ as a catalyst and $HgSO_4$ to remove Cl^- interference. Sulfide was analyzed using the iodimetric method. Volatile phenol was determined using bromizing titration method. The content of oil and grease was measured by an infrared spectrophotometry oil-measuring instrument (H3-OCMA-350, Japan). All experiments in this study were performed in triplicate to get reliable data, and the results are presented the average of three parallel experiments.

2.9. GC–MS analysis

The gas chromatography–mass spectrometry (GC–MS) analysis was conducted on day 30 during the field test. A 50 mL aqueous sample was adjusted to pH 2 and extracted by 5 mL dichloromethane three times. The three extract layers were combined and dried using nitrogen, and the residue was dissolved in a 1 mL solution of *n*-hexane and then was analyzed by an Agilent 7890–5975c GC-MS equipped with an Agilent HP-5MS fused silica capillary column (60 m × 0.25 mm × 0.25 μm). The injection volume was 1 μL. The carrier gas was helium at 37 kPa. Flow velocity was 1 mL/min. The analytical conditions were: initial temperature of 50°C, with isothermal operation for 1 min; heating to 120°C at a constant rate of 20°C/min; heating to 250°C at a constant rate of 4°C/min; and heating to a final temperature of 310°C at a constant rate of 3°C/min, with a 30 min isothermal. Mass spectrometer conditions were: electron impact, electron energy 70 eV; filament current 100 μA; multiplier voltage, 1,047 V; full scan.

3. Results and discussion

3.1. Isolation and identification of isolates

In present study, three different bacterial strains (B-4-9, BS-3-12, and JF-3) were isolated as dominant DBP-degrading strains. The three strains with size of 0.3–0.6 μm × 1.0–2.7 μm were Gram-negative and short rod shape. The 16S rDNA sequence analysis showed that the closest relative of B-4-9 was *Bacillus thuringiensis* strain AMB 6 (GenBank accession no. JX971523.1) (99% similarity). The closest relative of BS-3-12 was *Bacillus cereus* strain A16 (GenBank accession no. KC434970.1) (98% similarity). The closest relative of JF-3 was *Acidovorax ebreus* strain TPSY (GenBank accession no. NR 074591.1) (100% similarity). Thus, strains B-4-9, BS-3-12 and JF-3 were assigned to *B. thuringiensis*, *B. cereus*, and *A. ebreus*, respectively.

3.2. Laboratory test

3.2.1. Effect of dilution ratio

Test 1 was performed to investigate the effect of dilution ration on treatment performance of the system under hydraulic retention time (HRT) of 84 h. As shown in Fig. 2, it is obvious that decreasing the dilution ratio from 1:18 to 1:12.5 increased the effluent COD. The average COD removal efficiencies were 80.2 and 77.0% in the case of 1:18 and 1:12.5 dilution, respectively. This observation revealed that the treatment performance of the system was not altered significantly by higher concentration of influent. Nevertheless, the effluent COD was relatively high (830–1,200 mg/L) when 1:12.5 dilution was applied. Thus, 1:18 dilution was employed in the subsequent experiment. The dilution ratio had difference among the spent caustic from different sources. For instance, the dilution multiple of spent caustic from Wuhan petrochemical company was 12 times for biotechnology treatment [5].

3.2.2. Effect of nutrient addition

Fig. 3 demonstrates that the addition of the nutrients had significant positive influence on COD removal efficiency of the treatment system. With or without nutrient amendment, the average COD removal was 80.2 and 63.9%, respectively. One of the reasons for the enhanced degradation with addition of nutrients can be attributed to the attenuation of spent caustic toxicity by peptone and the buildup of more cell mass formed as a result of the additional carbon

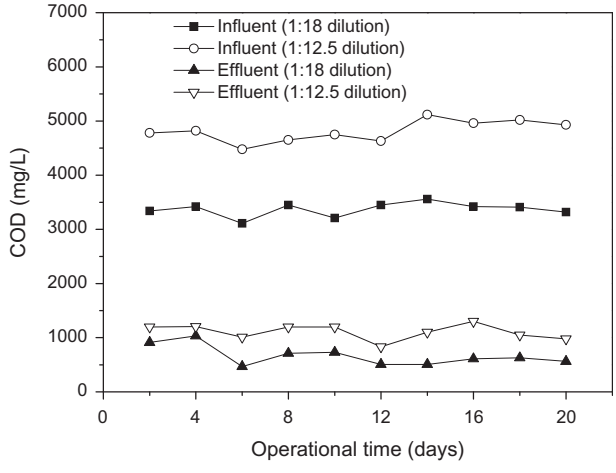

Fig. 2. Effect of dilution ratio on COD removal of refinery spent caustic HRT = 84 h.

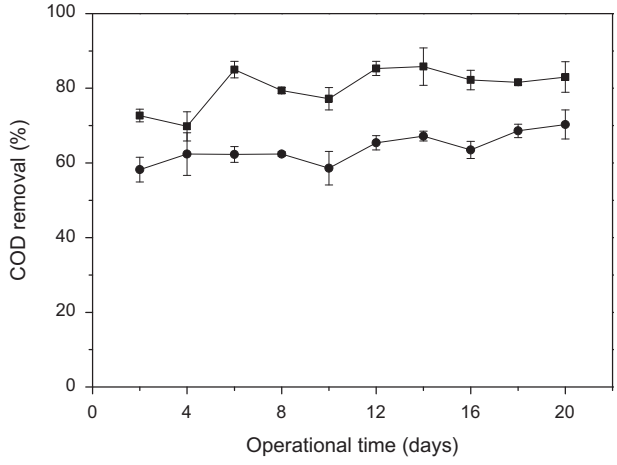

Fig. 3. Effect of nutrients on the efficiency of the activated sludge treatment system. Symbols: ■: 18-fold diluted spent caustic with nutrients; ●: 18-fold diluted spent caustic without nutrients HRT = 84 h.

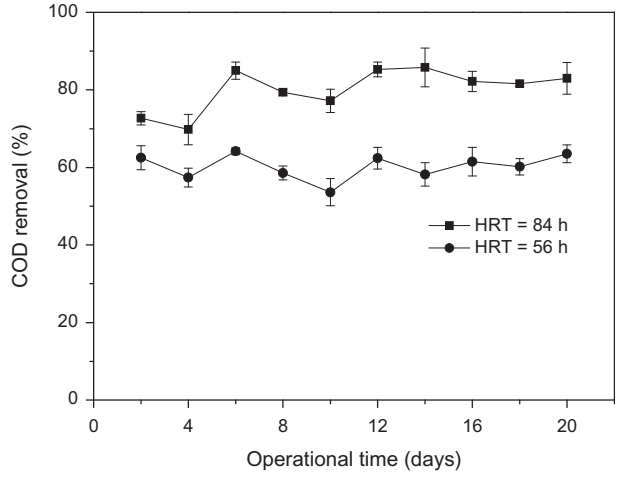

Fig. 4. Effect of HRT on the efficiency of the activated sludge treatment system.

source. It is known that a possible method of increasing the tolerance of the cells to substrate inhibition is to supplement the growth medium with conventional organic nutrients, such as yeast extract, peptone, or glucose [18]. Peptone is typically rich in carbohydrate, nitrogen, and microbial growth stimulants, such as amino acids and vitamins. Therefore, peptone is often used in medium for microorganism cultivation. Additionally, the degree of degradation has been shown possible to increase by the addition of trace elements [19]. The positive effects of trace elements are likely correlated to the essential function of metals as cofactors in enzyme systems active in the biodegradation process.

3.2.3. Effect of HRT

The average COD removal efficiencies at different HRTs are shown in Fig. 4. The results showed that at an HRT of 84 h, the average efficiencies for COD removal were consistently higher than 70%. When the HRT decreased from 84 to 56 h, however, the COD removal efficiency decreased significantly from average 80.2 to 60.5%. This indicated that the activated sludge system had a low capacity to resist shock loading caused by the change in influent flow rate. In general, conventional activated sludge process is characterized by low cost and easy operation; however its resistance to shock loading is inferior to immobilized biological treatment system [20]. To obtain relatively high COD removal, 84 h was taken as the optimum HRT.

3.3. Field trial

Based on the results of laboratory experiments, field trial was conducted over a period of five months. The raw spent caustic was diluted 18 times using the discharge water from the refinery wastewater treatment plant. Design treatment capacity of the pilot system was 1.0 m^3/d, and the HRT of the bioreactor was maintained at 84 h. The temperature of the wastewater during operation was 27–32 ˚C. Before entering the biological system, the wastewater mentioned above was pretreated by neutralization and primary sedimentation. Table 2 lists the content of specific organic pollutants before and after acidification. As shown, the three dominant compounds in the raw spent caustic were 4-methyl-phenol, dimethyl sulfide, and phenol. The concentrations of these compounds were greatly reduced by acidification and flotation.

For simplicity, only the 48th day COD results are listed. As shown in Fig. 5, when the COD of the influent varied between 2,570 and 5,200 mg/L, the COD of the discharge water was in the range of 233–650 mg/L, corresponding to an average removal of 87.8% which was much higher than that of single Fenton oxidation (34.3%) and ultrasound-Fenton reagent process (42.2%), and a little higher than that of bioaugmentation treatment studied by Wang (87%) [5]. However, the experimental data obtained from the literature showed maximum COD removal of general petroleum refinery wastewater by electro-Fenton process was 82.55% [6].

The effluent could be discharged into the wastewater treatment plant for further treatment. Though the effluent COD did not meet the national emission

Table 2
Content (mg/L) of organic pollutants in the spent caustic during the field experiment detected by GC–MS

Pollutant	Content	
	Before acidification	After acidification
Dimethyl sulfide	80.1	7.25
Dimethyl trisulfide	1.32	0.83
Toluene	0.35	0.20
Tetrachloroethylene	1.52	1.06
Methyl ethyl disulfide	8.29	0.32
Phenol	46.2	35.1
1,1-bis(methylthio)-ethane	6.89	0.21
4-methyl-phenol	87.3	51.4
C2-phenol	11.6	2.5

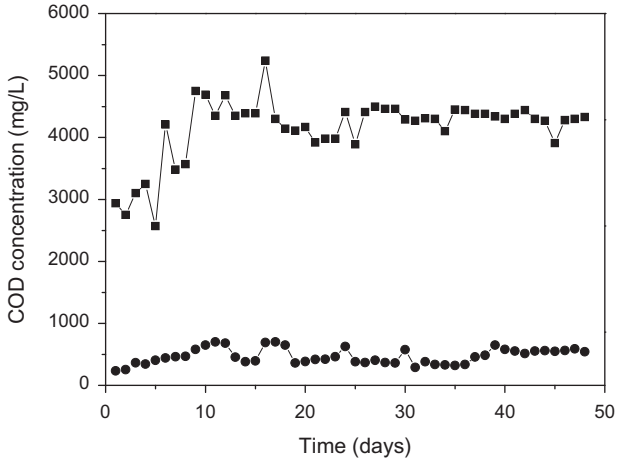

Fig. 5. Time course of COD concentration and removal efficiency during the field pilot trial. Symbols: ●: influent COD of 18-fold diluted spent caustic; ■: effluent COD.

standard, it was still quite encouraging considering the low biodegradability and great toxicity of the refinery spent caustic. This demonstrated that bioaugmentation was a powerful tool to enhance the performance of the biological system.

4. Conclusions

Refinery spent-sulfidic caustic has been successfully biotreated at both laboratory and pilot-scale tests. Nutrient amendment and augmentation exhibited positive effect on treatment performance of the biological systems. A preliminary economic analysis showed that the caustic could be treated for roughly $30 per ton. Based on the results obtained, the potentials are very promising.

Acknowledgments

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References

[1] M. de Graaff, M.F. Bijmans, B. Abbas, G.-J. Euverink, G. Muyzer, A.J. Janssen, Biological treatment of refinery spent caustics under halo-alkaline conditions, Bioresour. Technol. 102 (2011) 7257–7264.
[2] M. de Graaff, J. Klok, M.F. Bijmans, G. Muyzer, A.J. Janssen, Application of a 2-step process for the biological treatment of sulfidic spent caustics, Water Res. 46 (2012) 723–730.
[3] M.D. LaGrega, P.L. Buckingham, J.C. Evans, Hazardous Waste Management, Waveland Press, Long Grove, 2010.
[4] J. Sipma, A. Svitelskaya, B. van der Mark, L.W. Hulshoff Pol, G. Lettinga, C.J. Buisman, A.J. Janssen, Potentials of biological oxidation processes for the treatment of spent sulfidic caustics containing thiols, Water Res. 38 (2004) 4331–4340.
[5] G. Wang, Experimental study on pretreatment of alkaline wastewater in oil refining process, Wuhan University of Science and Technique, (2012).
[6] R. Davarnejad, M. Pirhadi, M. Mohammadi, S. Arpanahzadeh, Numerical analysis of petroleum refinery wastewater treatment using electro-Fenton process, Chem. Prod. Process Model. 10 (2015) 11–16.
[7] R. Potumarthi, G. Mugeraya, A. Jetty, Biological treatment of toxic petroleum spent caustic in fluidized bed bioreactor using immobilized cells of thiobacillus RAI01, Appl. Biochem. Biotechnol. 151 (2008) 532–546.

[8] D. Sorokin, P. van den Bosch, B. Abbas, A. Janssen, G. Muyzer, Microbiological analysis of the population of extremely haloalkaliphilic sulfur-oxidizing bacteria dominating in lab-scale sulfide-removing bioreactors, Appl. Microbiol. Biotechnol. 80 (2008) 965–975.
[9] O. Seok-Young, S. Dong-Sik, Removal of total dissolved solids in spent caustic using biochar: Pretreatment for subsequent biological treatment, Clean—Soil Air Water 43 (2015) 92–95.
[10] S. Yuan, C. Yu, B. Chang, Biodegradation of nonylphenol in river sediment, Environ. Pollut. 127 (2004) 425–430.
[11] M. Lu, Z. Zhang, W. Yu, W. Zhu, Biological treatment of oilfield-produced water: A field pilot study, Int. Biodeterior. Biodegrad. 63 (2009) 316–321.
[12] T. Bagarinao, Sulfide as an environmental factor and toxicant: Tolerance and adaptations in aquatic organisms, Aquat. Toxicol. 24 (1992) 21–62.
[13] D. Park, D.S. Lee, Y.M. Kim, J.M. Park, Bioaugmentation of cyanide-degrading microorganisms in a full-scale cokes wastewater treatment facility, Bioresour. Technol. 99 (2008) 2092–2096.
[14] M. Wang, G. Yang, H. Min, Z. Lv, X. Jia, Bioaugmentation with the nicotine-degrading bacterium *Pseudomonas* sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms, Water Res. 43 (2009) 4187–4196.
[15] M. Head, J. Oleszkiewicz, Bioaugmentation for nitrification at cold temperatures, Water Res. 38 (2004) 523–530.
[16] R. Wyndham, J. Costerton, Heterotrophic potentials and hydrocarbon biodegradation potentials of sediment microorganisms within the Athabasca oil sands deposit, Appl. Environ. Microbiol. 41 (1981) 783–790.
[17] State Environmental Protection Administration of China, GB8978-1996: Integrated Wastewater Discharge Standard, 1996, pp. 9–13 (in Chinese).
[18] G. Briceño, G. Palma, N. Durán, Influence of organic amendment on the biodegradation and movement of pesticides, Crit. Rev. Environ. Sci. Technol. 37 (2007) 233–271.
[19] A. Karlsson, P. Einarsson, A. Schnürer, C. Sundberg, J. Ejlertsson, B.H. Svensson, Impact of trace element addition on degradation efficiency of volatile fatty acids, oleic acid and phenyl acetate and on microbial populations in a biogas digester, J. Biosci. Bioeng. 114 (2012) 446–452.
[20] N. Seetha, R. Bhargava, P. Kumar, Effect of organic shock loads on a two-stage activated sludge-biofilm reactor, Bioresour. Technol. 101 (2010) 3060–3066.