Application of sequencing batch reactor (SBR) for treatment of refinery wastewater containing nickel

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Abstract

A petroleum refinery is a complex combination of interdependent industrial processes that generate wastewater effluent containing hydrocarbons, heavy metals and dissolved minerals which cause harmful effects to human and environment. While physicochemical systems are widely accepted as effective methods for treatment of industrial wastewater, biological processes are beginning to play an increasing role in the treatment of metal containing effluents. The objective of the present study is to investigate the biological treatment of refinery wastewater containing nickel. The SBR performance was assessed by measuring Chemical Oxygen Demand (COD), Mixed Liquor Suspended Solid (MLSS), Mixed Liquor Volatile Suspended Solid (MLVSS) as well as nickel concentrations. The SBR was operated on a 12-hour cycle basis which consisted of five distinct modes: fill, react, settle, draw, and idle. The wastewater was brought from an equalization tank of a refinery plant and was fed to the reactor after characterization. The nickel concentration ranged from 2.3 to 2.6 mg/L. The experimental results demonstrate COD and nickel removal efficiencies of 70–90% and 77–80%, respectively.
Keywords: refinery wastewater, sequencing batch reactor, nickel.

1 Introduction

Large amounts of water are being utilized in petroleum refinery industry for cooling, desalting and dehydration processes [1, 2]. Refining process generate wastewater 0.4-1.6 times the volume of crude oil processed [1]. The most important pollutants are hydrocarbons, phenol and dissolved minerals that are

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referred as priority pollutants [3], 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals such as nickel even at very low concentrations [2, 4].

Nickel is one of the toxic heavy metals present in petroleum refinery wastewater [4, 5]. Nickel is commonly found in crude oils and need to be removed due to its ability to poison the catalysts activities in refining process [6]. In addition, residual feedstock at fluidized bed catalytic cracking units have higher metals content especially nickel and greater coke forming potential than distillate feeds. This contaminant reduces catalysts activity, promotes coke and hydrogen formation and leads to decrease gasoline yield due to its deposition on the catalyst [7]. Discharge of untreated petroleum refinery wastewater containing nickel into water bodies results in environmental and human health problems [5]. Accumulation of nickel in the body can cause lung fibrosis, cardiovascular, kidney diseases and act as carcinogenic agent [8–10]. Excessive concentrations of nickel in water affect the living organism's growth such as algae [10].

Studies conducted on wastewater treatment containing heavy metals using chemical precipitation, coagulation-flocculation, flotation, membrane filtration and ion exchange indicated that these technologies are costly and produce excessive sludge [3, 4, 12]. Biological wastewater treatment systems are rapidly gaining support as the option is being shown to be technologically and economically feasible [11, 12]. Biological system is simple to operate and cost effective due to the use of microorganisms. Microorganisms play an important role in oxidizing dissolved and particulate carbonaceous organic matter into simple end products.

SBR is a biological method that has several advantages compared to the activated sludge process. Application of SBR is feasible since the system operates in a simple tank and the need of a clarifier is eliminated. Moreover, SBR system is also flexible in operation, controllable in reaction time and has perfect quiescent settling [13–15]. SBR gives high efficiency in Biochemical Oxygen Demand (BOD) and Suspended Solid (SS) removal (89–98% and 85–97%, respectively) [14].

The objective of this research is to evaluate the performance of SBR in presence of nickel in refinery wastewater treatment.

2 Materials and methods

2.1 Sampling procedures

Refinery wastewater was collected from equalization tank unit. It was then brought to the university Environmental Engineering Laboratory and stored in a cool room at 4^{o}C. A portion of the sample was brought to room temperature and analyzed for COD, BOD_5, TSS, pH, turbidity, alkalinity, colour, nitrate, phosphorus, ammonia nitrogen, phenol, sulphide, sulphate and nickel. Analyses were conducted based on Standard Method for the Examination of Water and Wastewater [16]. pH and turbidity were measured using a pH meter (HACH sension 4) and a turbidimeter (HACH 2100P). Dissolved oxygen (DO) was measured using a DO meter (YSI Incorporated, Model: YSI 5000, USA). The performance of SBR was monitored by measuring the COD, MLSS, MLVSS and nickel concentrations. Analyses were carried out in triplicate and the standard deviation was calculated respectively.

2.2 Seeding materials

The SBR was started with the adding of seed sludge collected from treatment facility of same refinery plant for faster start-up. The volume of seed sludge added to the system was based on *F/M* ratio as in eqns (1) and (2).

$$Q = V_{in} \cdot N_{cycle} \tag{1}$$

$$F/M = \frac{Q.COD_{in}}{V.MLVSS} \tag{2}$$

where Q is the wastewater flow rate (L/d), V_{in} is the influent feed volume per cycle (L/cycle), N_{cycle} is the number of cycle per day, V is the volume of the SBR (L) and *MLVSS* is the sludge concentration in the reactor (mg/L).

2.3 Experimental setup

SBR was operated using a fill and draw periodic system with a total working volume of 4 L. The reactor was seeded with sludge and fed with wastewater from the equalization tank. The SBR was operated on a 12 h cycle basis which composed of fill (15 min.), reaction (585 min.), settle (60 min.), draw (15 min.) and idle (45 min.). An aquarium pump (Hailea ACO-9610, China) was used in the system to supply sufficient air to the reactor with an air flow rate of 4.5 L/min. All experiments were carried out at room temperature. Fig.1 illustrates the schematic diagram of the SBR.

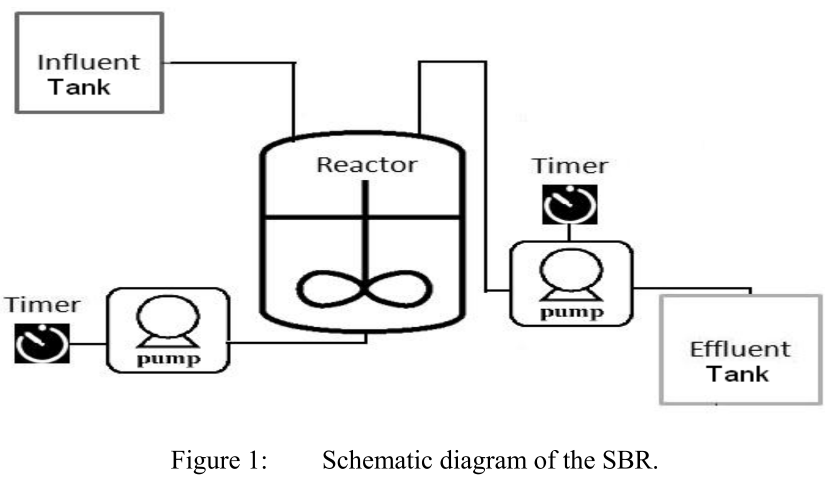

Figure 1: Schematic diagram of the SBR.

3 Results and discussion

3.1 Refinery wastewater characteristics

Table 1 shows the petroleum refinery wastewater characteristics. The results indicate a low BOD_5 of 94.1 ± 3.80. BOD_5 for refinery wastewater is lower than municipal wastewater due to small concentration of organic materials that are partially biodegradable [17]. A study conducted by Misbahudin *et al.* also reported low BOD_5 in petrochemical wastewater [18]. Both COD and nickel concentrations (405 ± 11.59 and 2.3 ± 0.01, respectively) exceeded Standard B by Department of Environmental Malaysia (DOE); stipulated in Environmental Quality Act 1974 and the Environmental Quality Regulations (Sewage and Industrial Effluents) 2009 [19]. According to DOE Standard B, the allowable concentrations for COD and nickel are 100 and 1.0 mg/L respectively. In addition, other parameters such as ammonia nitrogen, colour, sulphide and phenol also exceeded DOE Standard B.

Table 1: Petroleum refinery wastewater characteristics.

Parameters	Units	Values	Standard B
BOD_5	mg/L	94.1 ± 3.80	50
COD	mg/L	405 ± 11.59	200
pH	-	9.4 ± 0.01	5.5-9.0
Turbidity	NTU	38.2 ± 0.81	-
Alkalinity	$CaCO_3$	657 ±13.01	-
Color	Pt Co	133 ± 3.05	200
TSS	mg/L	104.3 ± 2.08	100
Nitrate	mg/L	3.7 ± 1.10	-
Ammonia nitrogen	mg/L	13.8 ± 0.42	20
Phosphorus	mg/L	1.7 ± 0.03	-
Sulphide	mg/L	0.163 ± 6.66	0.5
Sulphate	mg/L	43 ± 5.77	-
Nickel	mg/L	2.3 ± 0.01	1.0
Phenol	mg/L	5.73 ± 1.15	1.0

3.2 COD analysis

SBR was operated and its performance was monitored for 77 days based on COD analyses. At start-up of SBR, wastewater was mixed with seed materials and being acclimatized. Acclimation period is necessary in order to expose the microbial community to the potentially inhibitory or toxic organic compounds present in wastewater [20]. Moreover, acclimatization period is important for development of metabolic systems such as appropriate enzyme-producing genes that are essential to encourage biodegradation [11, 20, 21]. The final COD concentration and COD removal efficiency are shown in fig. 2.

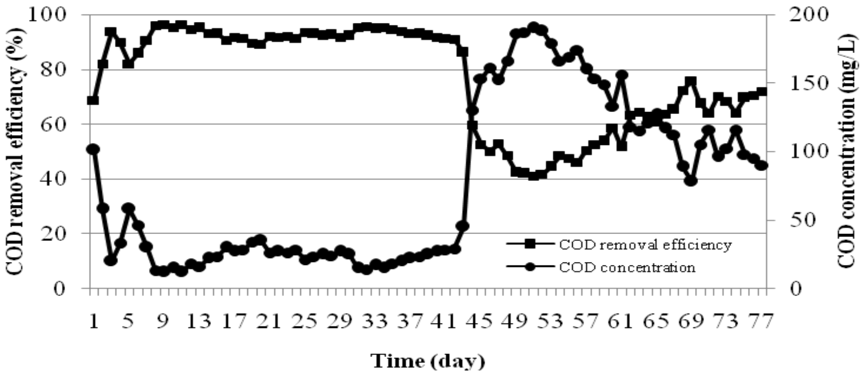

Figure 2: Final COD concentration and COD removal efficiency (%).

From the beginning until day 9, the system was unstable based on fluctuation of COD concentration. This shows that the microorganisms were still not able to adapt with the new environment. From day 10 to 42, COD removal efficiency started to gradually reach constant values. Adaptation of microorganisms to the system can be indicated by monitoring effluent COD which is reaching constant values [13]. This indicates that microorganisms in the system have acclimatized after day 9 and the SBR is ready to receive higher nickel dosage. Therefore, nickel concentration which was 2.3 mg/L at the beginning was increased to 2.4 mg/L on day 43 and 2.6 on day 60 after achieving steady state conditions in the system. Addition of 2.4 mg/L and 2.6 mg/L higher nickel dosage leads to decreased COD removal efficiency in both dosages. Relatively low concentration of heavy metals may serve to stimulate biological systems. However, any increase in concentration of toxic materials may decrease stimulation and eventually result in the system becoming inhibited [15, 22]. While, nickel with concentrations of 2.4 and 2.6 mg/L were introduced to the system, acclimatization was achieved based on COD removal efficiency after each increment in nickel concentration. However, the system was not able to produce less polluted effluent as compared to the duration where it was operated with lower nickel dosage. It shows that after receiving a higher dosage, the system becomes inhibited and decreases COD removal efficiency. Overall, the final COD concentration met DOE Standard B.

3.3 MLSS and MLVSS analysis

MLSS and MLVSS were analyzed to measure the microorganism's concentration in the system. MLSS indicates the presence of volatile and inert solids in the sludge. MLVSS closely approximates the biologically active portion of the solid in the sludge [11]. Chan *et al.* [13] reported that the acclimatization phase might be achieved when the MLVSS concentration is increased steadily. This trend reflects the active growth of bacteria which indicates the success of adaptation [13]. The bacteria utilize organic matters and multiply to form new cells. An adequate MLVSS concentration has to be maintained to ensure sufficient biomass concentration for biological reactions. Process operations with low MLVSS will lead to poor bio-flocculation, inadequate entrapment of particulate organic matter and bad settling of activated sludge [23]. Results shown in fig. 3 indicate stable MLVSS concentration throughout the experiment. It was due to proper selection of *F/M* ratio and perhaps high concentration of acclimatized microorganisms in the collected sludge from refinery wastewater treatment plant. However, decrease in MLSS and MLVSS concentration at certain days on nickel addition to the SBR affects SBR system performances.

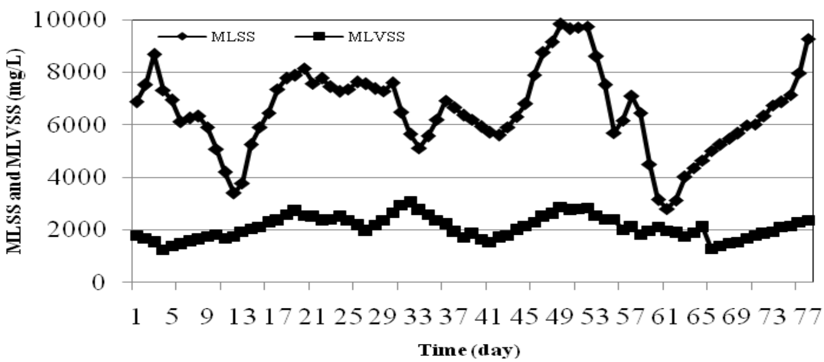

Figure 3: MLSS and MLVSS concentration.

3.4 Nickel removal

The SBR system reduces nickel concentration ranging from 0.48 to 0.53 mg/L (78.7%) and from 0.53 to 0.55 mg/L (79.2%) for nickel's initial concentration of 2.4 and 2.6 mg/L, respectively. Results of final nickel concentration and its removal efficiency (%) are shown in fig. 4. Nickel removal efficiency dropped after introduction of higher nickel dosage. Studies reported on the same trend as microorganisms are affected with the addition of higher nickel dosage leads to decrease of nickel removal efficiency. However, nickel removal efficiency will start to increase once the microorganisms are adapted with new higher nickel dosage [24–26]. Final nickel concentration was below 1.0 mg/L which meets the DOE Standard B discharge limit.

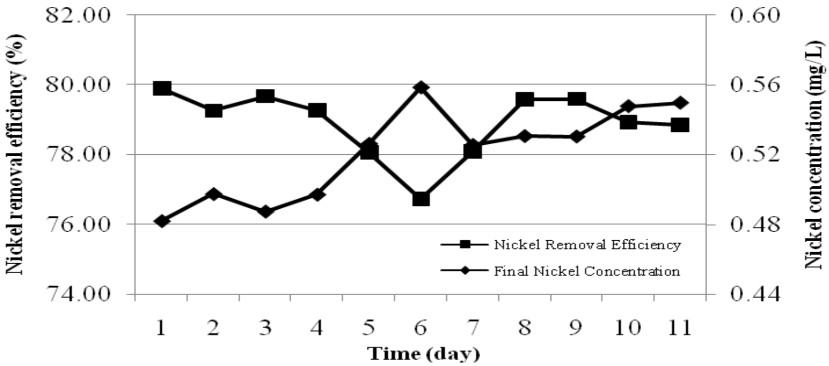

Figure 4: Final concentration of nickel and nickel removal efficiency (%).

4 Conclusions

Physicochemical treatments of wastewater have been used vastly for heavy metals removal such as nickel. However, those treatments involve high cost and production of excessive sludge. Biological systems are suitable choice as they are cheap and have high efficiency of contaminants removal efficiency. SBR systems require small space since no clarifiers are required. SBR has shown successful performance of COD removal efficiency ranging from 70% to 90% and nickel removal efficiency are found to be up to 79.2% in refinery wastewater. This study verifies that SBR is suitable system for heavy metals removal i.e. nickel.

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