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Treatment of the refinery wastewater in a gas–liquid–solid three-phase flow airlift loop bioreactor

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Abstract: Aerobic treatment of refinery wastewater was carried out in a 200 dm^3 gas–liquid–solid three-phase flow airlift loop bioreactor, in which a biological membrane replaced the activated sludge. The influences of temperature, pH, gas–liquid ratio and hydraulic residence time on the reductions in chemical oxygen demand (COD) and NH_4-N were investigated and discussed. The optimum operation conditions were obtained as temperature of 25–35 °C, pH value of 7.0–8.0, gas–liquid ratio of 50 and hydraulic residence time of 4 h. The radial and axial positions had little influence on the local profiles of COD and NH_4-N. Under the optimum operating conditions, the effluent COD and NH_4-N were less than 100 mg dm^{-3} and 15 mg dm^{-3} respectively for more than 40 days, satisfying the national primary discharge standard of China (GB 8978-1996).

Keywords: gas–liquid–solid three-phase flow; airlift loop bioreactor; refinery wastewater; biological membrane

NOTATION

COD	Chemical oxygen demand (mg dm^{-3})
DO	Dissolved oxygen (mg dm^{-3})
H	Axial position from the distributor (m)
HRT	Hydraulic residence time (h)
NH_4-N	Ammonia nitrogen (mg dm^{-3})
r/R	Radial position (dimensionless)
S^{2-}	Sulfide (mg dm^{-3})
SS	Suspended substance (mg dm^{-3})
T	Temperature (°C)
TP	Total phosphor (mg dm^{-3})

INTRODUCTION

The environment is becoming more polluted because of the discharge of various wastes. There are more and more factories and pollutants as a consequence of the modern way of life. Worldwide, the oil industry, vital for modern industry, generates a vast amount of wastewater that is highly contaminating and difficult to treat. Thus, strict discharge standards for refineries have been implemented in many countries.

The regulatory agency in the People's Republic of China has set discharge limits for COD as low as 100–150 mg dm^{-3} and for NH_4-N as low as 15–50 mg dm^{-3}, depending on the needs of the receiving water (GB 8978-1996).[1] To attain these limits, the refinery wastewater treatment plants need additional tanks and equipment, but in many cases the refineries are located in populous areas with little space for expansion. Technologies that can treat large quantities of wastewater with relatively small requirements are, therefore, of particular importance. So, it is necessary to develop some new kinds of reactors for treatment of wastewater. These newly developed bioreactors must have such advantages as better mixing, closer contact between three phases, faster oxygen transfer rate and higher operational flexibility. Gas–liquid–solid three-phase flow airlift loop bioreactors appear to meet these criteria.[2–8] To reduce HRT further, high biomass density is necessary, which can be approached by immobilizing bacteria on carriers.[9–11]

The work presented in this paper focuses on both developing a gas–liquid–solid three-phase flow airlift reactor to treat refinery wastewater and obtaining the optimum operating parameters of this reactor.

MATERIALS AND METHODS

The wastewater

The wastewater used in the experiment was gathered from Luoyang Refinery after oil removal and flotation. Table 1 shows the composition of the wastewater.

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Table 1. Composition of the wastewaters

Constituent	I (mg dm^{-3})	II (mg dm^{-3})
pH	7.80–8.79	8.06
Oil	30–55	34
Volatile phenols	28–80.6	32.3
COD	396–713	442
NH_4-N	40–63	49
SS	128–169	140

I, Concentration range over one year.
II, Concentration in the wastewater used for the determination of the optimum operation conditions.

The ranges of wastewater I were provided by Luoyang Refinery according to the records over one year. The composition of the batch of wastewater II used for the determination of the optimum operating conditions was analyzed according to the national standard of the People's Republic of China when it was sent to the laboratory.

Airlift bioreactor

The schematic diagram of the airlift loop bioreactor is shown in Fig 1. A 1550 mm high Perspex draft tube (6) of 190 mm in diameter was fixed concentrically inside the main 1800 mm high Perspex reactor tube (5) of 300 mm in diameter. Accordingly, the ratio of the diameter of the draft tube to that of the reactor was 0.63. A concentric jet nozzle (13) was designed and located in the bottom of the draft tube. At the end of the reactor was a disengaging cap with 500 mm internal diameter and a height of 400 mm. The wastewater, stored in reservoir (1), was pumped into the bottom of the reactor using a wastewater pump (2). The temperature control system (10) consisted of a coil with cold water and an electric heater coupled with a contact thermometer. The pH was adjusted by a control system (11), consisting of a pH-meter and micropumps supplying alkali or acid as required. The liquid flow rate was measured with a rotameter (4) and controlled by a cutoff valve (3). The role of the baffle plate separator (7) was to separate the carriers or sludge from the liquid in the effluent leaving the reactor and the carriers or sludge was sent back to the reactor. The air was introduced to the draft tube through the jet nozzle with 6 mm diameter holes. The flow rate of air was measured with a rotameter (8) and controlled by a needle valve (9).

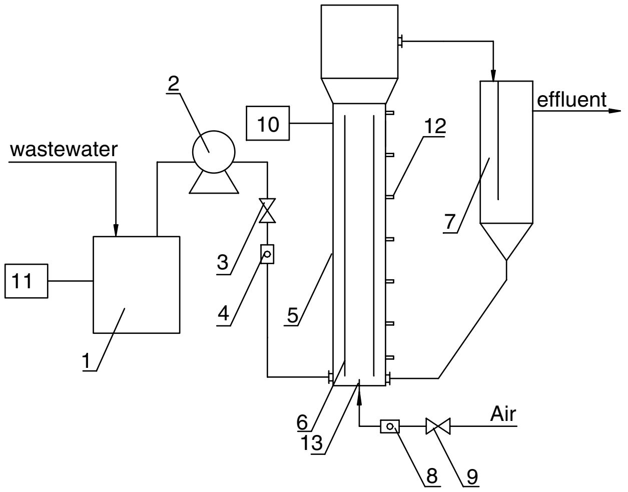

Figure 1. Schematic diagram of the apparatus:1 — reservoir, 2 — pump, 3 — cutoff valve, 4 — liquid rotameter, 5 — airlift loop bioreactor, 6 — draft tube, 7 — baffle plate separator, 8 — air rotameter, 9 — needle valve, 10 — temperature control system, 11 — pH control system, 12 — sample connection, 13 — jet nozzle.

Culture conditions

The strain used in this study was isolated from activated sludge obtained from the wastewater treatment plant of Luoyang Refinery. For the adaptation, 50 dm^3 activated sludge and 150 dm^3 diluted wastewater was introduced into the reactor in the reservoir. The pH of the wastewater had been adjusted to 7.5 by adding alkali. Air was introduced into the bottom of the reactor. The diluted wastewater was batch-fed into the reactor once a day and the concentrations of pollutants in each batch were higher than those in the previous one. After a one-week adaptation, 10 kg activated charcoal with average diameter of 0.2 mm was put into the reactor for culturing of film-forming bacteria and the undiluted wastewater was continuously fed into the reactor. The film-forming was continued until the biomass loading on the activated charcoal had achieved steady state. After 20 days, most free bacteria film was formed on the activated charcoal. This completed the culture process.

Assays

COD was analyzed by the dichromate method according to GB 11 914-89 of the People's Republic of China.[12] Ammonium was analyzed by Nessler's reagent colorimetric method according to GB 7479-87.[12] SS was analyzed by the gravimetric method according to GB 11 901-89.[12] Oil was analyzed by the infrared photometric method according to GB/T 16 488-1996.[12] Volatile phenols were analyzed by a 4-aminoantipyrine spectrophotometric method according to GB7490-87.[12] S^{2-} was analyzed by the submethyl blue spectrophotometric method according to GB/T 16 489-1996.[12] TP was analyzed by the ammonium molybdate spectrophotometric method according to GB 11 893-89.[12] Dissolved oxygen was measured by an RSS-5100 DO meter. Liquor pH was measured using a PHS-2 acidimeter.

Statistics

All experiments were repeated three to five times. The data shown in the corresponding figures are the mean values of the experiments.

RESULTS AND DISCUSSION

Determination of the optimum operating conditions

Influence of temperature on reductions in COD and NH_4-N

Figure 2 illustrates the influence of temperature on the reductions in COD and NH_4-N at solution pH value of 7.5, HRT of 4 h and air influx of $2.5\,m^3\,h^{-1}$, corresponding to an air–liquid ratio of 50. As can be seen from Fig 2, when the temperature was lower than 25 °C, the effluent COD and NH_4-N increased with the increasing in temperature. While it was in the range of 25–35 °C, the effluent COD and NH_4-N varied relatively little, and were less than $100\,mg\,dm^{-3}$ and $15\,mg\,dm^{-3}$, respectively. With further increase in the temperature to higher than 35 °C, the effluent COD and NH_4-N increased, indicating the decrease in the removal efficiency. As a result, the range of 25–35 °C was chosen as the optimum temperature values.

Influence of pH on reductions in COD and NH_4-N

The pH also exerts a remarkable influence on biological removal of COD and NH_4-N. The influence of pH values on reductions in COD and NH_4-N is shown in Fig 3 at the operating temperature of 35 °C, HRT of 4 h, air influx of $2.5\,m^3\,h^{-1}$. It can be seen that the effluent COD and NH_4-N decreased with the increase in pH at values lower than 7.0, and increased with the increase of pH for values higher than 8.0; however, while the pH value varied from 7.0 to 8.0, the effluent COD and NH_4-N achieved relatively low values, with COD $< 100\,mg\,dm^{-3}$ and NH_4-N $< 15\,mg\,dm^{-3}$. As a result, pH was controlled between 7.0 and 8.0 during operating.

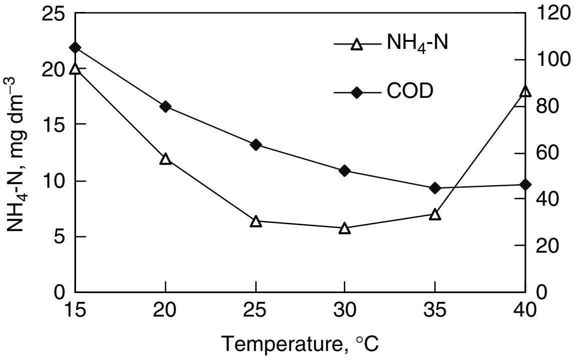

Figure 2. Influence of temperature on reductions in COD and NH_4-N (pH 7.5, HRT 4 h and air influx $2.5\,m^3\,h^{-1}$ with initial concentrations of COD $442\,mg\,dm^{-3}$ and NH_4-N $49\,mg\,dm^{-3}$).

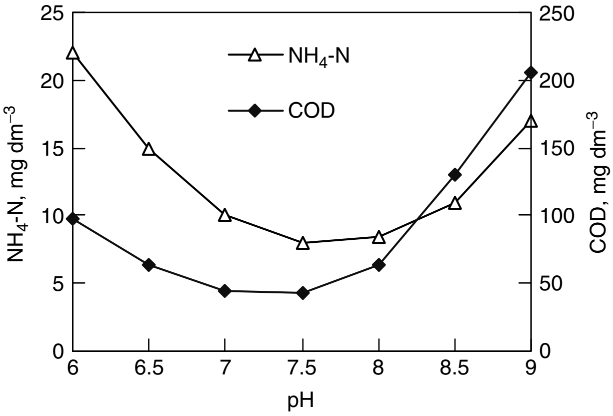

Figure 3. Influence of pH values on reductions in COD and NH_4-N (temperature 35 °C, HRT 4 h, air influx $2.5\,m^3\,h^{-1}$ with initial concentrations of COD $442\,mg\,dm^{-3}$ and NH_4-N $49\,mg\,dm^{-3}$).

Influence of air influx on reductions in COD and NH_4-N

The air influx is an important contributing factor to DO and the removal of COD and NH_4-N. The typical results of DO, COD and NH_4-N as a function of air influx at the given pH value of 7.5, temperature of 35 °C and HRT of 4 h are shown in Fig 4. It is noted that the air influx had great effects on DO, COD and NH_4-N. When the air influx was less than $2.5\,m^3\,h^{-1}$, the carriers inside this bioreactor were fluidized and suspended (called stationary fluidization region). The air–liquid interfacial area and air–liquid mass transfer coefficient increased with the increase in air influx, leading to the increases in DO and the removal efficiencies of COD and NH_4-N. When the air influx reached the value of $2.5\,m^3\,h^{-1}$, the carriers inside the bioreactor were completely fluidized (called complete fluidization region). Here, the profiles of the carriers were completely uniform, and DO achieved the saturated value, resulting in the effluent COD $< 100\,mg\,dm^{-3}$ and NH_4-N $< 15\,mg\,dm^{-3}$. With further increase in the air influx, the DO remained almost the same and the reductions in COD and NH_4-N were insensitive to the air influx. Thus, the optimum air influx was selected as $2.5\,m^3\,h^{-1}$, corresponding to the gas–liquid ratio of 50.

Influence of HRT on reductions in COD and NH_4-N

The HRT is a key operating parameter of wastewater biological treatment. Figure 5 shows the variables of HRT on the reductions in the effluent COD and NH_4-N at the fixed pH value of 7.5, temperature of 35 °C and air influx of $2.5\,m^3\,h^{-1}$. The effluent COD and NH_4-N decreased but the operating charges

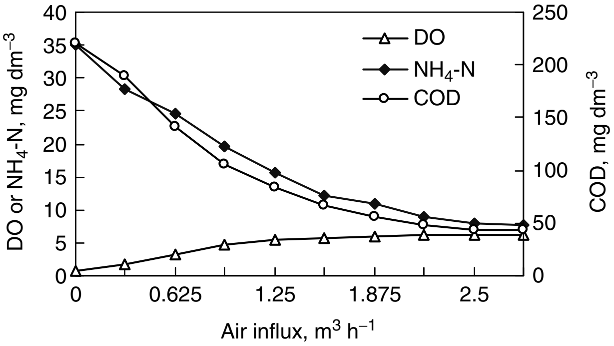

Figure 4. Influence of air influx on reductions in COD and NH_4-N (pH value 7.5, temperature 35 °C and HRT 4 h with initial concentrations of COD $442\,mg\,dm^{-3}$ and NH_4-N $49\,mg\,dm^{-3}$).

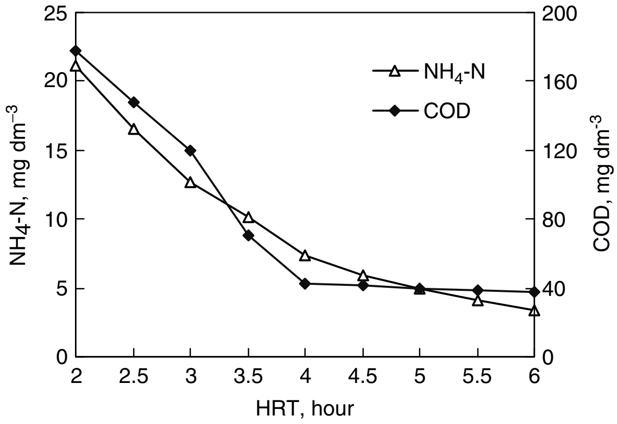

Figure 5. Influence of HRT on reductions in COD and NH_4-N (pH value 7.5, temperature 35 °C and air influx $2.5\,m^3\,h^{-1}$ with initial concentrations of COD $442\,mg\,dm^{-3}$ and NH_4-N $49\,mg\,dm^{-3}$).

would increase with increases in the HRT. At HRT of 4 h, the effluent COD and NH_4-N drop to almost $50\,mg\,dm^{-3}$ and $10\,mg\,dm^{-3}$, respectively. Taking the initial capital investment and operating charges into consideration, 4 h of HRT was selected as the optimum value.

The local profiles of COD and NH_4-N under the optimum operating conditions

The local profiles of COD and NH_4-N were investigated in the different radial and axial positions of this bioreactor under the optimum operating conditions such as the temperature of 25–35 °C, pH value of 7.0–8.0, HRT of 4 h and air influx of $2.5\,m^3\,h^{-1}$; the results are shown in Figs 6 and 7. It was found that the local distributions varied little with the radial and axial positions of this bioreactor, namely the local profiles of COD and NH_4-N were almost uniform. This was mainly attributed to the well-defined flow patterns, better dispersing effects and higher mass transfer coefficients of this airlift loop bioreactor.

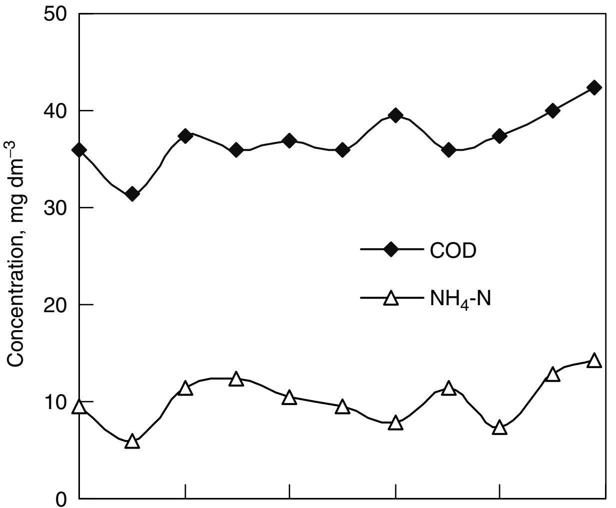

Figure 6. Influence of radial position under the optimum operating conditions (H = 0.7 m).

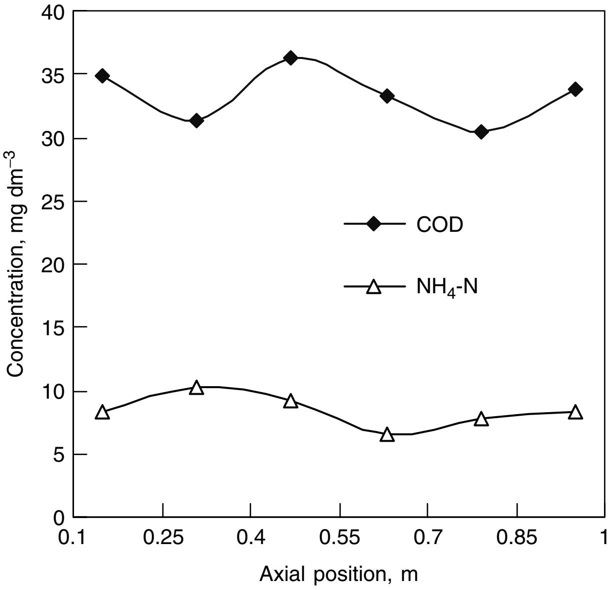

Figure 7. Influence of axial position under the optimum operating conditions ($r/R = 0$).

Continuous bioprocessing of the refinery wastewater under the optimum operating conditions

In order to investigate the flexibility of the gas–liquid–solid three-phase flow airlift loop bioreactor, the continuous bioprocess was used for treating the actual refinery wastewater discharged by Luoyang Refinery, Luoyang City, Henan Province, People's Republic of China. As can be seen from Figs 8 and 9, while the influent COD ranged from 390 to $690\,mg\,dm^{-3}$, and the influent NH_4-N ranged from approximately 50 to $100\,mg\,dm^{-3}$, the effluent COD and NH_4-N were reduced to below $100\,mg\,dm^{-3}$ and $15\,mg\,dm^{-3}$ for more than 40 days using this airlift loop bioreactor under the optimum operating conditions.

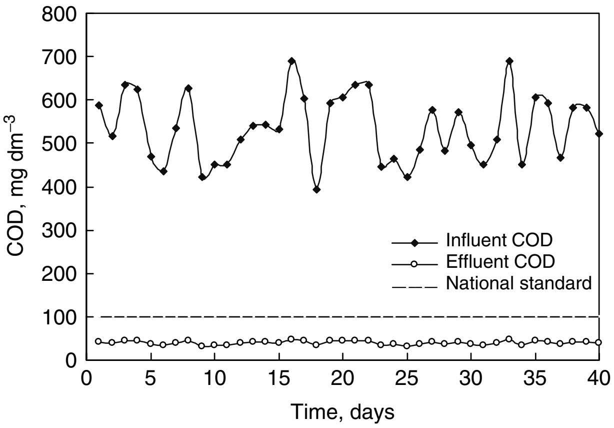

Figure 8. Continuous bioprocess of COD reduction in the wastewater under the optimum conditions (pH value 7.5, temperature 35 °C, HRT 4 h and air influx $2.5\,m^3\,h^{-1}$).

Table 2. Results of continuous bioprocessing of the actual refinery wastewater during the experiment

Waste constituents	SS ($mg\,dm^{-3}$)	Oil ($mg\,dm^{-3}$)	S^{2-} ($mg\,dm^{-3}$)	TP ($mg\,dm^{-3}$)	Volatile phenols ($mg\,dm^{-3}$)
Influent	107–143	37–51	<2.0	<0.5	8–37
Effluent	40–60	4–6	0.5–0.7	0.2–0.3	0.3–0.4
National primary discharge standard of China (GB 8978-1996)	70	10	1.0	0.5	0.5

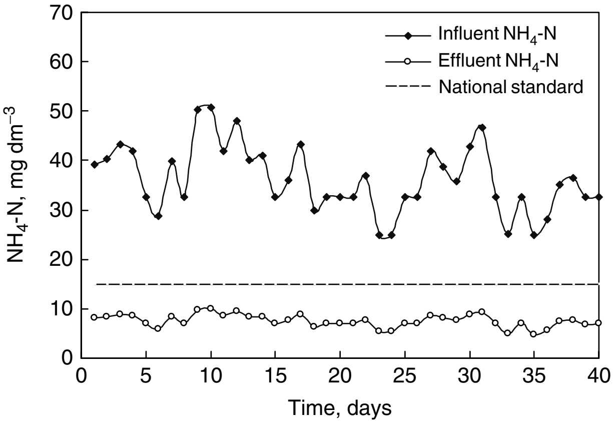

Figure 9. Continuous bioprocess of NH_4-N reduction in the wastewater under the optimum conditions (pH value 7.5, temperature 35 °C, HRT 4 h and air influx 2.5 $m^3\,h^{-1}$).

In addition, the eliminations of other pollutants, such as SS, oil, TP, S^{2-} and volatile phenols, were also studied, and the results are shown in Table 2. It can be seen that the concentrations of all these waste components in the effluent achieved the national primary discharge standards (GB 8978-1996), indicating that this airlift loop bioreactor had a great capacity for treating wastewater from the refinery.

CONCLUSIONS

The feasibility of a gas–liquid–solid three-phase flow airlift loop bioreactor for treating refinery wastewater was verified very well. Under the optimum operating conditions, ie temperature of 25–35 °C, pH value of 7–8, HRT of 4 h and air influx of 2.5 $m^3\,h^{-1}$, the effluent COD and NH_4-N of the gas–liquid–solid three-phase flow airlift loop bioreactor were less than 100 $mg\,dm^{-3}$ and 15 $mg\,dm^{-3}$, respectively.

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