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Investigation of the Removal of 2-Nitrophenol Using Continuous Flow MSBR Reactor and Estimated Expiration

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Abstract

In this research, biological removal of phenol and orthonitrophenol (2NP) pollutants from wastewater by continuous moving bed sequencing batch reactor (MSBR) was studied. The experiments were conducted in various operational conditions to find out the optimum level of the significant parameters. Best performance for removal of Phenols was achieved when parameters were set as follows: pH=7, sludge volume=30%, influent volumetric flow rate=20 $ml.min^{-1}$, number of carriers=150 and aeration flow rate= 12 $ml.min^{-1}$. At this optimum condition, 2NP concentration, Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) indicators reduced 84/7%, 94/8%and94%, respectively. Cost analysis for this treatment method was also assessed and final cost for treatment of 24 L wastewater in each operation was evaluated as 4/46$/L. By increasing treatment sessions, fixed costs would reduce and after treatment of 500 L wastewater, break-even point would achieve, which would turn the final costs down to 2.4 $/L.

Keywords: MSBR, Petrochemical wastewater, 2-Nitrophenol.

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Introduction

Societies are concerned about the extensive organic compounds existing in the ground and underground waters. These pollutants mainly have been made by fossil fuel industries during past several decades [1-3]. Wastewaters produced by oil and petrochemical refineries consist various materials such as oil, fats, light and heavy hydrocarbons, phenols and other dissolved organic materials [4, 5]. Exposure to phenols can be dangerous for organisms. The harmful effects of phenol compounds on human include headache, nausea and dizziness. Phenols available in surface waters and sea can kill the aquatics and also the birds living near the ecosystem [6, 7]. Therefore, phenols should be eliminated from wastewaters.

Removal of phenolic compounds from industrial wastewaters have been reported by various techniques such as aerobic biological treatment [8], chemical treatment by ozonation [9-11], treatment by surface absorbents like activated carbon [12], extraction by solvent [13], and electrochemical techniques [14]. In ozonation method, pollutants in surface and underground waters are treated by hydroxyl radicals. Degradation is relatively slow in this process. Consuming less ozone would make this treatment process faster, but there is probability for incomplete destruction of organic pollutants and production of toxic and unsafe byproducts [11]. Other classical chemical methods have major cons such as high operational costs, long reaction time, and probability of making secondary concentrations and also production of higher volume of sludge [9].Fenton process is an appropriate method for removal of organic materials from wastewater. The main drawback in this method is applying high concentrations of iron, which leads to production of superfluous iron ion. This phenomena makes dewatering of the sludge difficult, therefore another stage will be added to the treatment procedure and operational costs would grow [12]. Electrochemical method is better than traditional coagulating methods in order to remove small colloidal particles, and generally produces lower amounts of sludge. This method does not require much operating space and also does not require storage of chemicals, doing dilution process or pH adjustment procedure [14].

Electrochemical method along with biological methods, have minimal environmental impacts, because no harmful substances are used in these techniques. Biological methods are preferred over physical and chemical methods, because they are capable to break down environmental pollutants, and they are more cost-effective. Chemical oxidation, or physical transfer of pollutants between the stages does not occur in these methods and also they have high flexibility in the removal of organic compounds [17, 19]. The main objective of this research is testing aerobic biological treatment of phenolic compounds by moving sequencing bed reactor (MSBR). MSBR is actually a sequencing bed reactor with carriers added to the system to improve performance and efficiency of the treatments [15-17]. These types of reactors have rotating parts and moving bed and they act based on the biological mass connected to the solid surface of carriers. Sands, gravels, granular carbon and polyethylene are various carriers used in MSBR for wastewater treatment [18, 19]. The advantages of this reactor are better control of biofilm thickness, higher mass transfer properties, being non-pollutant, and having low pressure drop [20].

To realize advantageous of MSBR reactor, several parameters should be regulated. This paper studies removal of 2NP from a synthesized petrochemical wastewater by MSBR in various operational conditions. Parameters investigated include 2NP concentration, volumetric flow rate, pH, SVI (Sludge Volume Index), BOD_5, COD, and finally estimation of the prime cost.

Experimental

Preparation of wastewater

2NP solution with 10 $mg.L^{-1}$ concentration was prepared for doing experiments. Then, to synthesize petrochemical wastewater, 2NP, Toluene, and Benzene solutions were mixed with each other with the ratio of 85%, 7.5%, and 7.5%, respectively.

Activated sludge preparation

The required activated sludge was prepared from recycle line of Gheytarieh wastewater department in Tehran, which its analysis is shown in table 1. Activated sludge (10L), $K_2H_2PO_4$ (5g), NH_4NO_3 (5g) and $C_{12}H_{22}O_{11}$ (5g) were aerated for 24 hours (air flow rate= 10 $L.min^{-1}$).

Table 1. Analysis of the activated sludge prepared from Tehran wastewater department.

Organisms	**Filed count point**	**No. slides count**
Ciliated (Stalked Single)	15	4
Ciliated (Stalked Colonies)	10	4
Ciliated (Free swimming)	17	4
Amoebas	5	4
Large flagellates	4	4
Rotifers	1	4
Nematodes	2	4
Long filaments	1	4

Setup of MSBR

As it can be observed in figure 1, the treatment installations include 3 MSBR (each one with 8 liters functional volume), a wastewater tank (with 30 liters capacity), Aeration pumps (6×6 $L.min^{-1}$ capacity), and other accessories. Polyethylene materials with 1cm diameter have been used as carriers in the reactors.

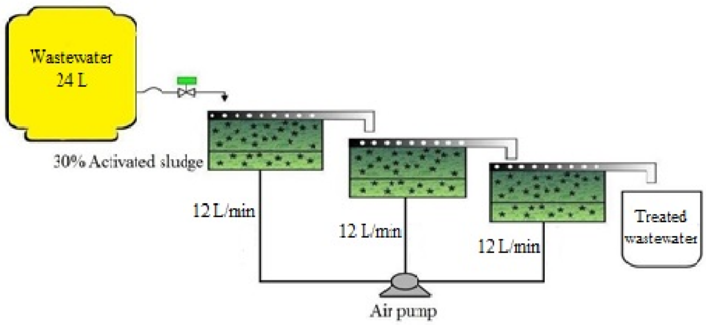

Figure 1.Schematic diagram of MSBR continuous flow reactor.

Measuring 2NP and controlling effective indexes

2NP concentration was checked to measure its removal percentage. The concentration was measured by UV-Visible spectrophotometer. Figure 2 shows the calibration curve (concentration/absorption) for the wastewater, when maximum wavelength is equal to 317 nm (λ_{max} = 317 nm). 2NP removal percentage was calculated based on Equation 1.

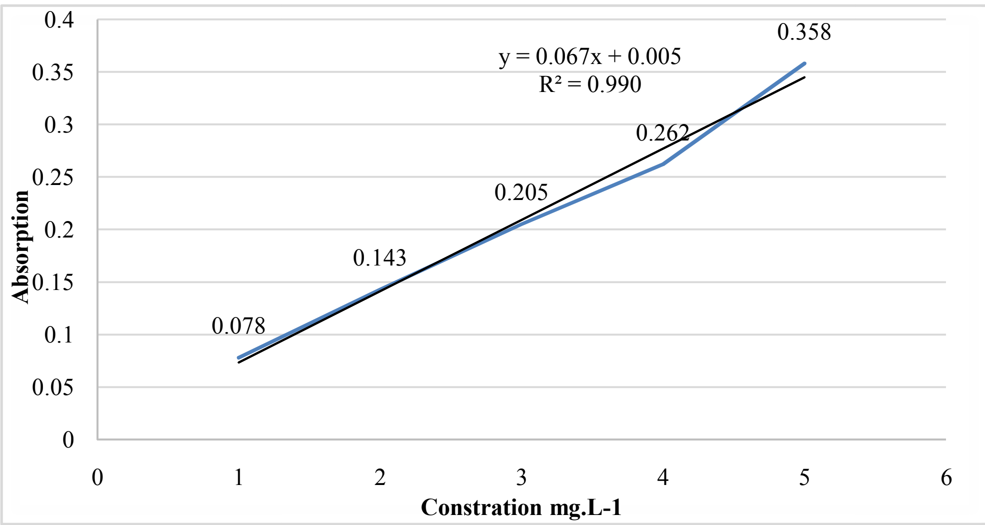

Figure 2. Calibration curve of 2NP.

$$\text{Removal }\% = \frac{C0-C1}{C0} \times 100 \quad \text{Equation (1)}$$

In Equation 1, C_0 and C_1 are initial and final concentrations, respectively.
Other important parameters such as pH, SVI, COD, BOD_5 were also under control and they were measured during the treatment operations.

Optimization of operational treatment parameters and estimation of the prime cost

The operational parameters including sludge volume, aeration flow rate, pH, number of carriers, and volumetric flow rate of wastewater, were optimized individually. Finally, the prime cost of 2NP removal from petrochemical wastewater was calculated.

Results and discussion

Sludge volume

According to Figure 3, when activated sludge volume is 30% (V/V), MSBR has better removal efficiency. For SVI less than 70 $ml.g^{-1}$, formation of needle flocks are observed. From the other hand, when SVI is higher than 150 $mg.L^{-1}$, bulking of sludge occurs. Therefore, SVI in range 80-100 $ml.g^{-1}$ is recommended for a proper utilization of activated sludge [21].

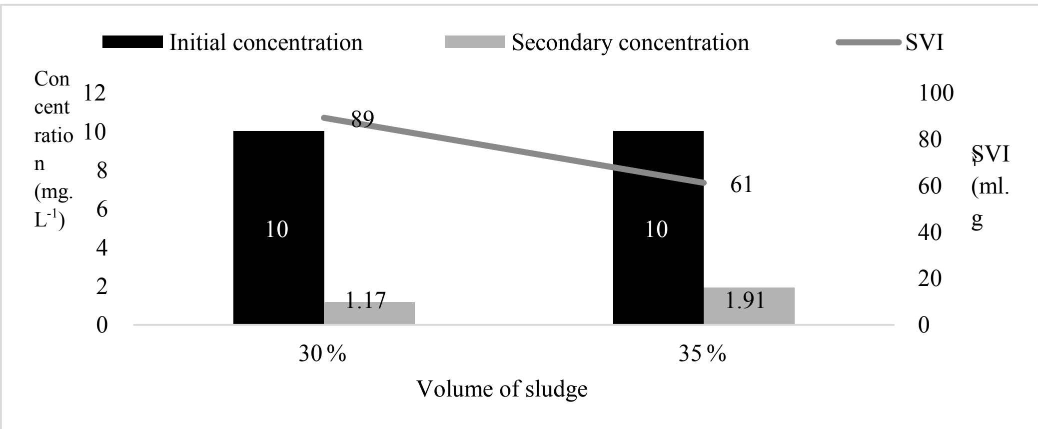

Figure 3. Effect of activated sludge volume on 2NP removal in MSBR reactor.

The effect of aeration flow rate

The results in Figure 4 show when aeration flow rate is 12 $ml.min^{-1}$, SVI is 103.7 and in this condition, 99.8% of phenols would be removed. By increasing the aeration flow rate, SVI would increase and no sedimentation of biological masses in this condition was confirmed.

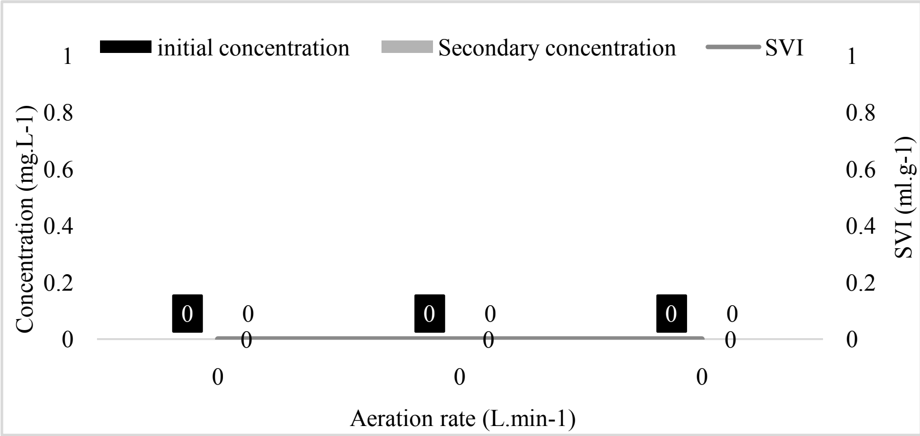

Figure 4. The effect of optimum aeration flow rate on the removal of 2NP in MSBR reactor.

pH

Due to production of basic salts at pH=8 in alkaline conditions, removal rate have increased for the blank sample (without activated sludge). In the original sample (with activated sludge), microorganism will be poisoned in alkaline conditions [22] and as a result, biological performance would decrease. The best removal efficiency is at pH=7 (Figure 5).

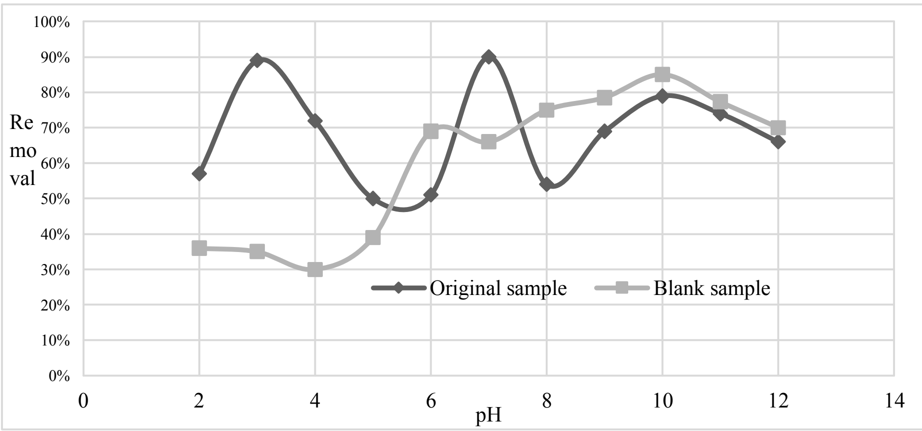

Figure 5. The effect of pH on the removal of 2NP in the MSBR reactor.

Number of carriers

Results for the effect of the number of carriers on 2NP removal are shown in Figure 6. When number of carriers are 150, removal efficiency with 94% is at its' pick. Remained concentration of 2NP is 0.6 $mg.L^{-1}$ in this condition.

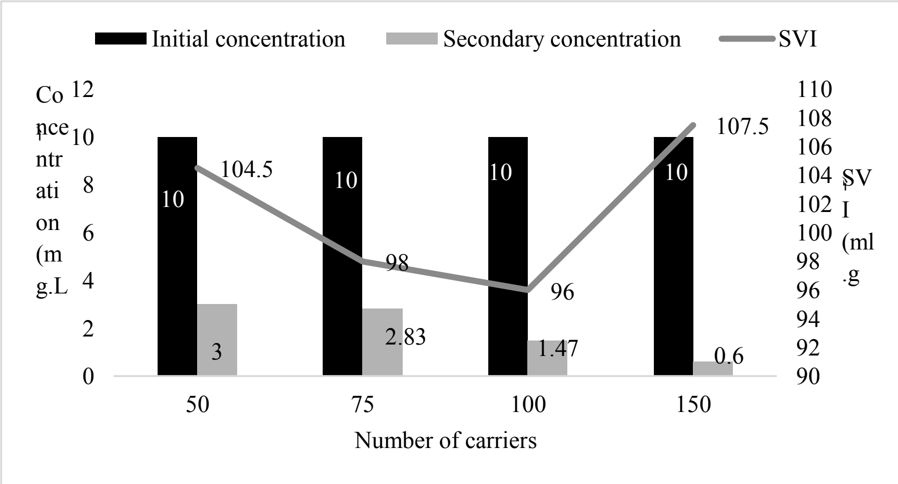

Figure 6. The effect of the number of carriers on the removal of 2NP in MSBR reactor.

Influent flow rate

According to the results in Figure 7, when influent flow rate is 10 ml.min^{-1} and 20 ml.min^{-1}, removal efficiency is at best. But the pollutants (biological mass) released form carriers in these conditions, occurred in 10 hours, which is a long operational time. As we want to consider lower operational time, influent with 20 ml.min^{-1} flow rate was chosen as the best number. SVI is also appropriate at this level of flow rate.

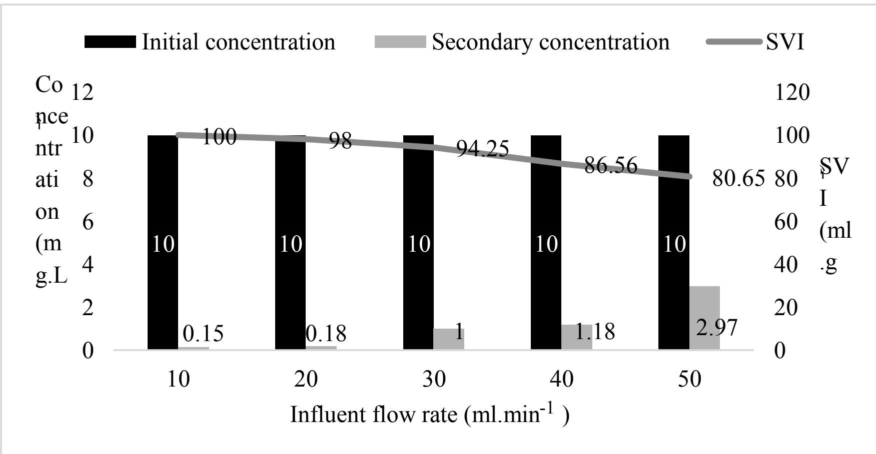

Figure 7. Effect of influent flow rate on the removal of 2NP in MSBR reactor.

Results for the Treatment of synthesized petrochemical wastewater by MSBR at optimum levels

According to optimized operation, removal of 2NP in synthesized wastewater has been investigated in three reactors (MSBR). The results in Figure 8 show that 2NP removal is 84.7%, COD reduction is 94%, and BOD_5 reduction is 94.8%.

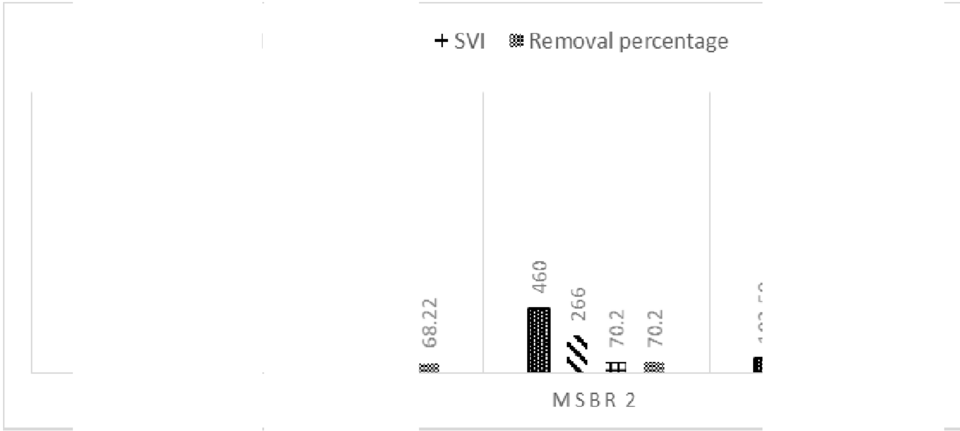

Figure 8. Synthesis effluent treatment with continuous flow MSBR system at optimum levels.

Estimation of the prime cost

Fixed costs

Based on the prices mentioned below, the total price for the equipment evaluated as 52$.

1. Plexiglas reactor 33$
2. Air pump 10$
3. Air nozzles and fittings 5$
4. Wastewater tank and valves 4$

Costs for the chemical materials used in the process

The chemical materials used to prepare activated sludge (10 L) and synthesized wastewaters (24 L) are listed in table 2 with their prices.

Table 2. Costs of chemicals for activated sludge preparation (current costs).

Chemical materials	Unit price ($)	Consumable	Cost price ($) For 24 L wastewater	Price per L of wastewater ($)
Potassium di hydrogen phosphate	40	5 g	8	0.3
Ammonium nitrate	40	5 g	8	0.3
Sucrose	0.8	5 g	0.0004	0.00016
Distilled water	0.21	1 L	0.21	0.008
Activated Sludge	0.266	8 L	2.14	0.88
carrier	10	450 Number	9	0.37
2NP	74.66	1g	0.74	0.03
Benzene	16	5ml	0.08	0.003
Toluene	20	5ml	0.1	0.004
Total			28.27	1.89

Personnel costs for wastewater treatment operations

Personnel salaries (chemistry expert) is about 0.96 $/h. Operation time for treatment of 24 L wastewater is around 28 hours (Table 3).

Table 3. Personnel costs for wastewater treatment.

Personnel performance	Hourly Personnel Wage ($)	Operation time (h)	Total personnel costs ($)
Chemistry expert	0.96	28 (h)	26.88

Electricity costs

4 air pumps for preparation of activated sludge (for 24 h) and 6 pumps for wastewater treatment (for 8 h) have been used (Each pump with 3.5 W power).

Each electricity unit (w) costs around 0.0013 $. Electricity cost for sludge preparation was 0.0004$ and for biological treatment was 0.0007 $, therefore total electricity cost for 24 h of wastewater treatment was 0.001$.

Total cost

According to table 4, total costs were 107.15$ for the treatment of 24 L wastewater.

Table 4. Costs per unit (L).

Wastewater treated (liters)	Fixed cost ($)	Current cost ($)	Total cost($)	Expired expense($/L)	Total sales($)
0	52	0	52	0	0
24	52	55.1	107.1	4.46	57.6
48	52	110.3	162.3	3.38	115.2
72	52	165.4	217.4	3.01	172.8
120	52	275.7	327.7	2.73	288
500	52	1148.9	1200	2.4	1200
600	52	1375.7	1430.7	2.38	1440
700	52	1608.5	1660.5	2.37	1680

* Total cost = fixed cost + current cost

The final cost for treatment of the wastewater is 4.46 $/L for each session and by increasing number of the treatment sessions, cost will be reduced. Considering the sale price for wastewater, which is 2.4$/L, break-even point would be achieved after treatment of 500 liter wastewater. At this point the total cost would be equal to the total sales. The total cost would be reduced to 2.4$/L after this point and treatment process would be economically affordable (Figure 9).

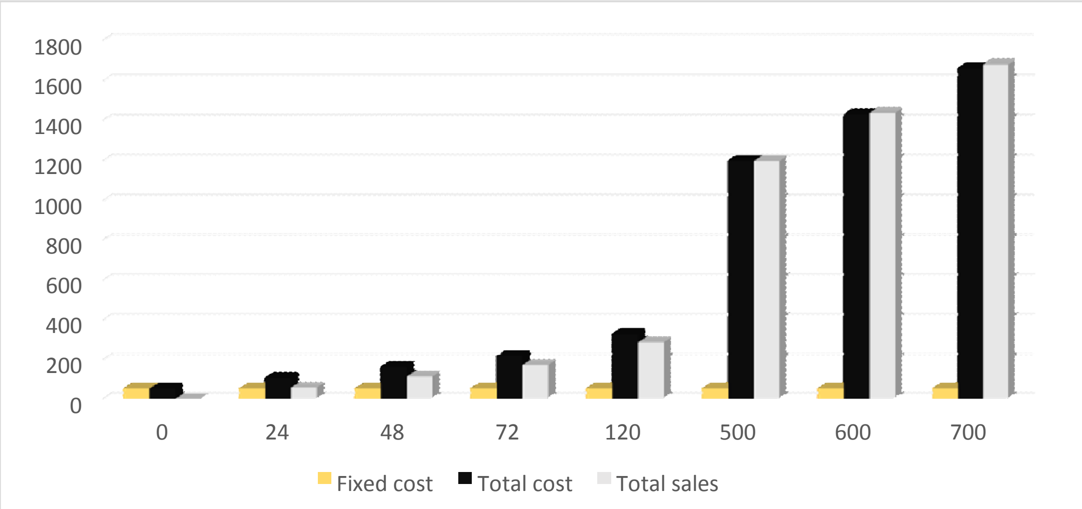

Figure 9. Comparison of expired expense, fixed costs and total cost ($/L).

Price for the activated sludge used in this study is compared with other reported adsorbents in Table 5 [23].

Table 5. Costs of several adsorbents.

Adsorbent	**Cost ($)**
Activated carbon	20
Coal	0.15
Natural zeolite	0.03
Carbonaceous adsorbent	0.1
Activated sludge, MSBR	0.266

The price of the adsorbent used in this research is lower than activated carbon. Price for the other adsorbents are almost in the same range with the activated sludge used here.

Also, the reported costs are highly dependent on local availability, type of the process, equipment and operating conditions. Conditions for operating wastewater treatment with MSBR are easier than ozonation and ion exchange methods, and MSBR is more environmentally friendly.

Conclusion

Removal of 2NP from wastewater in MSBR reactor was studied when activated sludge was presented in the reactor at an aerobic condition. Results for removal of 2NP and reduction of COD at the optimum operational parameters were satisfactory. Cost analysis was done for treatment of 24 L wastewater in each session. By increasing the treatment sessions, final cost would be lowered. In regard to the limitations of the other treatment methods, biological methods are much more cost-effective, accessible and environmental friendly. The treated waste water complies with the standards for discharging effluents and it is safe to be used in agriculture.

References

[1] I. Abdelfattah, A. Ismail, F. Sayed, A. Almedolab, K.M. Aboelghait. *Environmental Nanotechnology. Monitoring & Management,* 6, 176 (2016).

[2] M. A. Al-Obaidi, C. Kara-Zaïtri, I. M. Mujtaba. *Water Process Engineering.* 18, 20 (2017).

[3] N. Roostaei, F. Tezel. *Environmental Management,* 70, 157 (2004).

[4] Y. Zhang, Y. Xu, S. Zhang, Y. Zhang, Z. Xu. *Desalination,* 299, 63 (2012).

[5] Senem UstunHanife Büyükgüngör. *Biotechnology,* 131 (2007).

[6] T. Bekar, M. Bayram, R. Cangi, N. Genc, M. Elmastas. *Scientia Horticulturae,* 225, 343 (2017).

[7] M. Gaytán-Martínez, Á. Cabrera-Ramírez, E. Morales-Sánchez, A. Ramírez-Jiménez, J. Cruz-Ramírez, R. Campos-Vega, G. Velazquez, G. Loarca-Piña, S. Mendoza. *Journal of Cereal Science,* 77, 1 (2017).

[8] A. Brink, C. M. Sheridan, K. G. Harding. *Water Process Engineering,* 19, 35 (2017).

[9] A. Shokri. *International Journal of Nano Dimension,* 7, 160 (2016).

[10] Kadir TurhanSuheyla Uzman. *Desalination,* 229, 257 (2008).

[11] P. Gharbani, M. Khosravi, S. M. Tabatabaii, K. Zare, S. Dastmalchi, A. Mehrizad. *Environmental Science Technology,* 7 (2010).

[12] X. Liu, H. Yin, A. Lin, Z. Guo. *Environmental Chemical Engineering,* 5, 870 (2017).

[13] Ruey-Shin Juang, Wen-Ching Huang, Ya-Han Hsu. *Hazardous Materials,* 164, 46 (2009).

[14] O. Abdelwahab, N. K. Amin, E. S. Z. El-Ashtoukhy. *Hazardous Materials,* 163, 711 (2009).

[15] J. W. Lim, P. E. Lim, C. E. Seng, R. Adnan. *Bioresource Technology,* 129, 485 (2013).

[16] N. Yusoff, S. Ong, L. Ho, Y. Wong, F. Mohd Saad, W. Khalik, S. Lee. *Biochemical Engineering Journal,* 115, 14 (2016).

[17] G. Moussavi, M. Mahmoudi, B. Barikbin. *Water Research,* 43, 1295 (2009).

[18] M. Faridnasr, B. Ghanbari, A. Sassani. *Bioresource Technology,* 208, 149 (2016).

[19] J. W. Lim, C. E. Seng, P. E. Lim, S. L. Ng, A. N. Sujari. *Bioresource Technology,* 102, 76 (2011).

[20] A. P. A. Alves, P. S. Lima, M. Dezotti, J. P. Bassin. *International Bio deterioration & Biodegradation,* 123, 146 (2017).

[21] E. Arnold, L. Greenberg, WEF. Clescori, Standard Methods for the Examination of Water and Wastewater 18th edition (1992).

[22] A. Shokri. *Russian Journal of Applied Chemistry,* 88, 2038 (2016).

[23] Su-Hsia LinRuey-Shin Juang. *Environmental Management,* 90, 1336 (2009).