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APPLICATION OF HYBRID MODIFIED UASB - MBBR TECHNOLOGY FOR WASTEWATER TREATMENT OF SAO THAI DUONG PHARMACEUTICALS AND COSMETICS FACTORY

Trinh Xuan Duc[a,*], Le Anh Tuan[b]

[a] *Science Institute of Infrastructural Engineering & Environment, No 168B Ngoc Khanh street, Ba Dinh district, Hanoi, Vietnam*
[b] *Vietnam Construction & Environment Joint-Stock Company, No 33, 2A, Trung Yen 11 street, Cau Giay district, Hanoi, Vietnam*

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Abstract

Wastewater of Sao Thai Duong Pharmaceuticals & Cosmetics Factory contains high concentration (more than 1000 mg/l) COD and BOD. Besides, some persistent substances are also found such as surfactants, emulsion oil and ammonium. Especially, the quite low BOD/COD ratio of 0.3 makes the treatment process of organic matters more complicated. Furthermore, the troublesome settlement of oil emulsions inhibits the wastewater biological treatment process which results in difficulties for selection of a stable and sustainable technology. For these reasons, it is recommended to use the Upflow Anaerobic Sludge Blanket Filtration (UASB) technique combined with the use of the bio-logical named carriers DHY-01 and DHY-02 (produced by Vinse Company). DHY carriers have a high porosity (92-96%), large surface area (10000-12000 m^2) and apparent specific weight of 33 g/l. The anaerobic treatment tank (Upflow Blanket Filter - UBF) has a retention time of 10-12 hours. Influent COD concentration is about 1000-2000 mg/l, reduced by 65-70% after treatment. Influent BOD concentration is 200-600mg/l, reduced by about 60-65% after treatment. Aerobic tank (moving bed biofilm reactor - MBBR) has a retention time of 4-6 hours. COD and ammonium removal efficiency is about 85-90%.

Keywords: MBBR; UBF; wastewater; DHY

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1. Introduction

The producing and refining of a pharmaceutical product requires a huge amount of water and the wastewater of this process contains toxic pollutants. Wastewater of a pharmaceutical factory has complicated composition which is difficult to treat by traditional technologies. At present, the conventional processes cannot provide a thorough treatment of pollutants, so the wastewater discharged into the environment still contains toxic substances. If it is not treated thoroughly, when these subtances are discharged into the environment in which via the chemical reactions of the different substances in the wastewater, they will be turned into other forms which may be even more toxic and exist longer in the environment. This will cause negative impacts on human as well as the ecological environment.

*Corresponding author. *E-mail address:* ductx.vinse@gmail.com (Duc, T. X.)

Vietnam Construction & Environment Joint Stock Company (VINSE) has conducted the research on the wastewater of Sao Thai Duong Pharmaceuticals & Cosmetics Factory and has found out that it contains many undegradable substances, low BOD/COD ratio (0.3), high TSS concentration of which emulsion oil is very difficult to settle down. The existing treatment system fails to solve these problems. Thus, a research for technological improvement is needed in order to efficiently treat the wastewater of this factory and ensure the quality of the effluent before discharge into the receiving source.

The treatment process of the factory employs conventional technology as shown in the Fig 1. The anaerobic tank has only one chamber (biogas tank), using activated sludge method. Therefore, the anaerobic process is innefficient (the treatment efficiency is only about 40%). There is no stratification of anaerobic micro-orgarnisms, so persistent organic pollutants are not removed thoroughly [1].

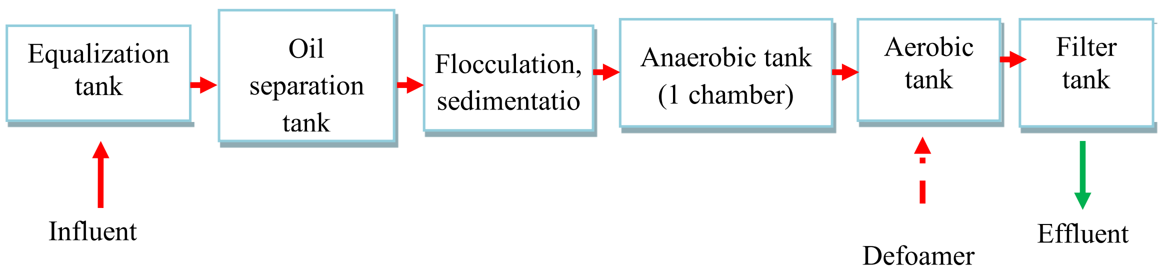

Figure 1. The existing treatment technology system

Aerobic tank uses activated sludge method, so the concentration of COD (400-1000 mg/l) and BOD (120-250mg/l) after treatment is still higher than the required standard and the amonium concentration is also still high (about 20-25mgN/l).

The system is inefficient because of high persistent organic pollutant concentration, low BOD/COD ratio (0.3) and high ammonium concentration. Ammonium concentration is persistently high because of low biomass density and the competition between idiotrophic and heterotrophic aerobic micro-organisms in aerobic tank [2].

In consideration of the actual situation of the factory, the research group of VINSE proposed to use the hybrid UASB-MBBR technology using DHY1 and DHY2 carriers to solve these matters.

UASB-MBBR technology is applied to treat wastewater in many specific industries such as beer and seafood production, etc. In addition, there are some studies on this technology according to the author group A. Tawfik, F. El-Gohary, H. Temmink treatment of domestic wastewater in the text "Treatment of domestic wastewater in an up-flow anaerobic sludge blanket reactor followed by moving bed biofilm reactor". The objective of this study is to assess the performance of the combined UASB-MBBR system for domestic wastewater treatment at different HRT's. This will be carried out by monitoring the removal of the COD fractions ($COD_{suspended}$, $COD_{colloidal}$, $COD_{soluble}$), and faecal coliform removal as well as the nitrification rate. UASB have eight ports for obtaining sludge samples are arranged along the reactor height. The reactor is provided by a conical gas solids separator. MBBR the media is shaped in a cylindrical form and has a length of 1.8 cm and a diameter of 1.85 cm. The results obtained in this study indicated that the combined system consisting of UASB–MBBR system treating domestic wastewater at a total HRT of 13.3 h is very effective for removal of COD fractions, ammonia and faecal coliform. The total system removed over 92% of COD_{total}; 96% of $COD_{suspended}$ 89% of $COD_{colloidal}$ and 80% of $COD_{soluble}$ [3].

Zafarzadeh et al. in 2010 evaluated the nitrogen removal efficiency in wastewater with nitrification and denitrification process by using MBBR using Kadnes K1 media, which has a surface area of 500 m^2/m^3, weight 152 kg/m^3, with a percentage of 40-50% of tank capacity. The circulation rate is 300%. The results showed that the maximum and average specific nitrification rate in the aerobic reactor were 49.4 and 16.6 g NO_x-N/KgVSS.day, respectively and the maximum and average specific denitrification rate as 156.8 and 40.1 g NO_x-N/KgVSS.day in the anoxic reactor, respectively. The results also showed that it is possible to reach a stable partial nitrification with high ratio of NO_2-N/NO_x-N (80% to 85%) during high load ammonium. Under optimal condition of the average treatment efficiency of total N, ammonium and dissolved organic matters, which reached 98.23%; 99.75% and 99.4%, respectively [4].

2. Materials and methods

2.1. Influent wastewater characteristic

Quality of the treated water in the sedimentation tank of Sao Thai Duong Factory in Table 1.

Table 1. Composition of water after sedimentation tank in Sao Thai Duong Factory and effluent requirement

No	Parameter	Unit	Content	QCVN 40:2011/BTNMT Column B
1	pH	-	7.2 ÷ 7.7	5.5 ÷ 9.0
2	Alkalinity	mg$CaCO_3$/L	720 ÷ 790	-
3	Suspended Solids (SS)	mg/L	100	100
4	COD	mgO_2/L	1000 ÷ 2000	150
5	BOD	mgO_2/L	200 ÷ 600	50
6	Ammonia	mgN/L	30 ÷ 40	10

Table 1 shows that the wastewater samples have a stable pH (about 7.2-7.7). Besides, high alkalinity is also an advantage in aerobic reaction (amonium treatment) and anaerobic reaction (pH stabilization in acidation stage). Although the wastewater has passed through the sedimentation tank, COD concentration is still high (COD: 1000–2000 mg/l), meanwhile the BOD concentration is low (200-600 mg/l) and BOD/COD ratio is low (only about 0.3). The ammonium concentration is also high which ranges from 30-40 mg/l.

2.2. Experimental setup

Upflow Anaerobic Sludge Blanket Filtration (UASB) (D × H = 200 × 1200 mm), which is equipped with valves at different levels to serve convenient sampling and tracking of the treatment process of anaerobic micro-organisms in the tank. Water retention time is 10 ÷ 12 hours.

A modified UASB tank with various static filtration beds, bio-carriers was introduced in this study. The bio-carriers provide areas for microbial adhesion on them. The wastewater may flow in the upward direction. The new upflow structure would help to accumulate biomass at a higher density than the downward flow because apart from the microorganisms that adhere to the carriers, there is a microbiological part that exists in suspension state in the empty space between the carriers and below the carriers. The volume of the carriers in the filter column may account for 20% of the volume of water and only about 70% of the height of the filter column. The empty space at the bottom of the column facilitates a uniform distribution of the influent [1, 5].

The MBBR tank had dimension A × B × H = 200 × 200 × 500 mm. This tank was continuously supplied with air diffused by the air distribution system (Fig. 2). Water retention time is 4 ÷ 6 hours.

In the reactor using moving bed biofilm, the substrates, bacteria and dirt substances move chaotically. Initially, organic substances are transported to the biofilm surface by a turbulent flow regime in many types of bioreactors. The adhesion mechanism of large organic matters and particles on the surface of the biofilm may be the impact and filtration-adsorption because of the unsmooth structure of the biofilm [1, 4, 5].

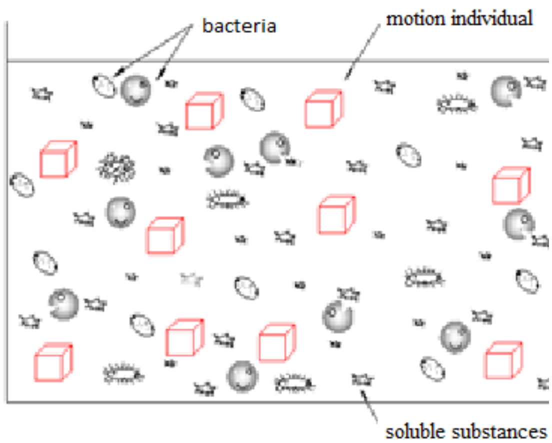

Figure 2. The treatment system using moving bed biofilm

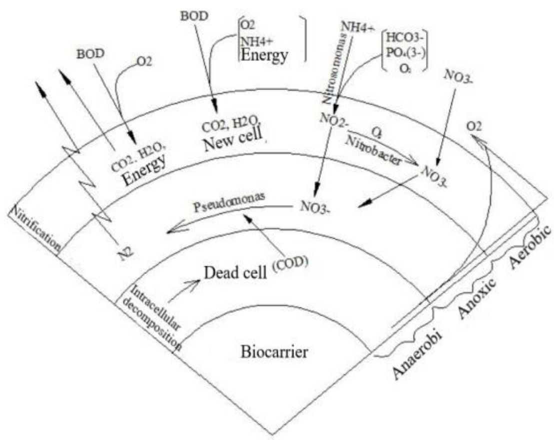

Figure 3. Diagram of the mechanism of biofilm on moving substrates

Fig. 3 illustrates the structure of moving bed biofilms and the formation of biofilm on a moving substrate similar to that on a fixed substrate, however the difference which is a determinant of efficiency of the moving bed biofilm technique is the the contact of substrate, bacteria and dirt substances to be treated in the reactor. The contact area is significantly increased, because it is not limited by the stacking of particles as in the fixed bio-carrier technique, besides the surface area that is created by the porosity of the substrate is also mentioned [6, 7].

DHY carriers are made from Polyurethanes researched and manufactured by Vinse, the surface area of the carriers is calculated based on the geometric size of the substrate and its porous structure. It is the tiny holes inside the substrate that creates surfaces for microbial growth and development; The diffusion and metabolism mechanisms are similar to the fixed biofilms. Therefore, the process of mass transfer in the moving carrier system is higher than the fixed one [1].

Porous-biocarriers DHY-01 (1cm × 1cm × 1cm) and DHY-02 (2cm × 2cm × 2cm): High porosity of 92-96%, surface area of 12,000 m^2/m^3, specific gravity of 33 kg/m^3 depending on the processing method. The structure of polyurethanes looks like being woven from small bundles of fibers, forming meshes. During the film making process, the microorganisms firstly adheres to the fibers and gradually spreads to fill the meshes, developing horizontally, the biofilm covering the mesh accounts for a high proportion of the total microorganism in the film (Fig. 4).

Fig. 5 above is the diagram of the hybrid system using anaerobic biofilter tank and moving bed biofilm reactor technique with large-surface-area carriers. Suspended solids of wastewater were removed to level of less than < 100 mg/l, then pH of the wastewater was adjusted with Na_2CO_3 before the wastewater was pumped into the anaerobic filter. The wastewater, after entering the tank in upward direction, contacted with the anaerobic bio-carriers. The organic pollutants in the wastewater was de-

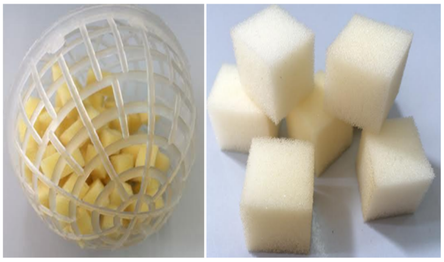

Figure 4. Bio-carrier DHY (produced by VINSE)

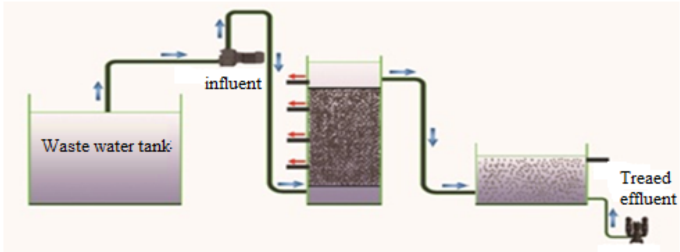

Figure 5. Experimental system using modified UASB combined with MBBR

composed, helping increase BOD/COD ratio. An amount of sediment was retained, settled onto the tank bottom, providing favourable conditions for the development of anaerobic micro-organisms [7]. After that, wastewater was directed into the bio-filter tank using moving bed biofilm reactor method. The aerobic decomposition of organic pollutants took place here. Because the carriers were in cubic form, there were aerobic and anoxic processes taking place simultaneously inside the carriers. Ammonium concentration was reduced significantly. The treated water via this experimental system was analyzed to achieve concentration of fundamental parameters (pH, BOD, COD, alkalinity, N^- NH_4^+).

Experimental system stabilization:

Micro-organisms are taken from the existing treatment systems and provided to anaerobic and aerobic tanks. Water, after passing through sedimentation tank, will enter the intermediate storage tank and pumped continuously into the system. The system will be stable after about 2 ÷ 4 weeks.

System control:

The system was operated at a flow rate of 3 l/h and water retention time were 10 ÷ 12 hours and 4 ÷ 6 hours in anaerobic tank and aerobic tank, respectively.

Sampling:

The samples were analyzed in terms of pH, COD, BOD5, $NH_4^+ - N$ concentration [8]. Samples were taken at the influent points of anaerobic filter tank and at the effluent storage tank of the system. Pollutants will be analyzed following the guidance manual [**?**].

3. Results and discussion

During the experimental process, water samples taken at the influent points will be analyzed to assess COD treatment efficiency in the anaerobic tank. Alkalinity and pH parameters will also be determined to assess the stability of wastewater in the tank.

Figs. 6 and 7 show the treatment efficiency of the anaerobic tank. pH tends to decrease rapidly in the initial stage, but then gradually decrease. The pH stability in this tank thanks to the relatively high alkalinity of the influent (600–800 mg $CaCO_3$/l). Therefore, later acetic acid formation has insignificant impact on pH in the effluent. Fig. 7 shows that the anaerobic tank performs efficiently, with rapid decrease in COD concentration and gradual increase of BOD/COD ratio. So, the treatment of organic pollutants is less complicated.

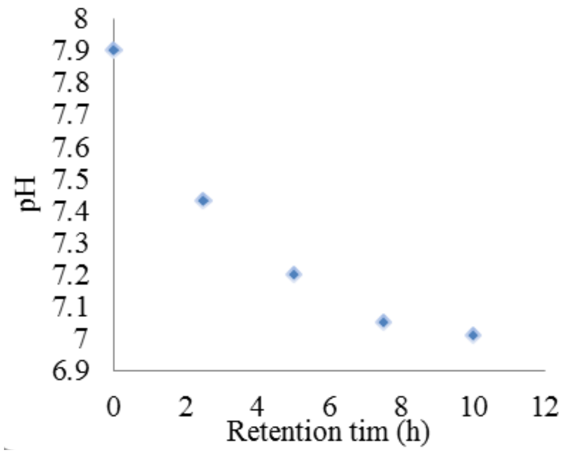

Figure 6. Time-wise pH variation in UABF tank

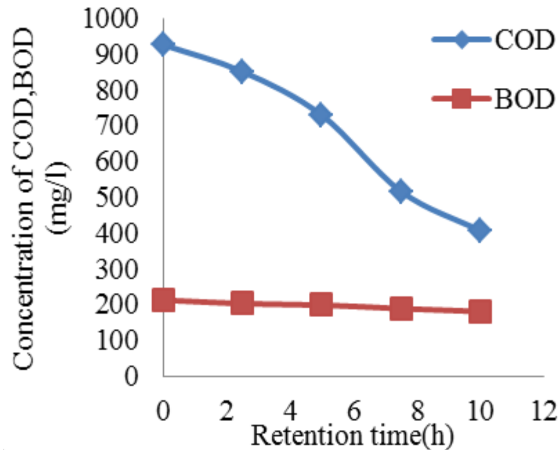

Figure 7. Decrease of BOD, COD concentration in UABF tank

COD concentration in the treated water in anaerobic tank tends to decrease gradually by day, starting from the start-up day. COD removal efficiency of the anaerobic tank increases from 20% to70% (Fig. 8). So, after a period of operation, the COD decomposition efficiency is relatively high, reaching about 70%.

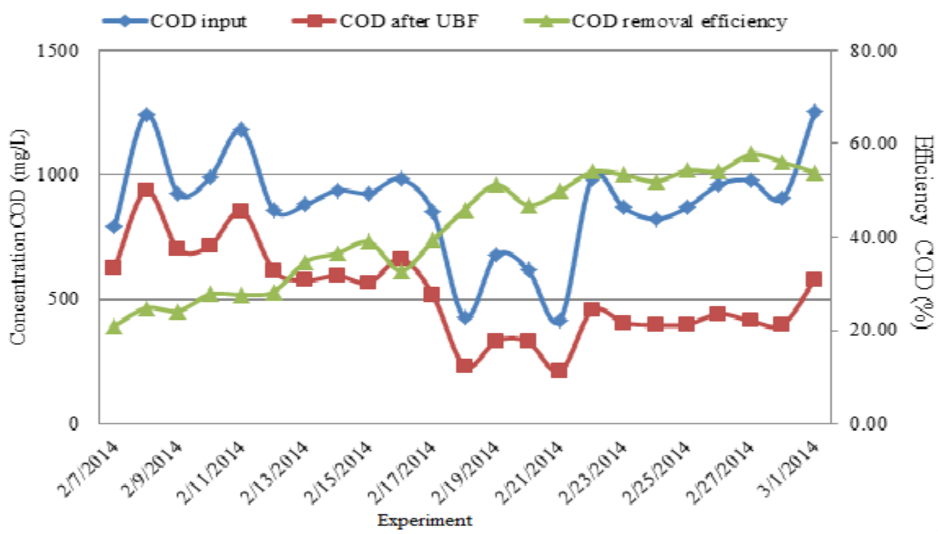

Figure 8. Variation of input/output COD concentration and removal efficiency by experimental days

Compared with the existing anaerobic tank of the factory, the COD removal efficiency increased almost twice, which ranges from 40% to70% and was stable during the experimental period. It also proved that microbial density had increased significantly in DHY-02 carriers.

Under the treatment process of the system, the BOD concentration decreases significantly by days of the experiment (Fig. 9), with removal efficiency possibly reaching 90% and able to reach the standard level (Vietnam National Technical Regulation QCVN 40:2011/BTNMT Column B) [9].

Figs. 8 and 9 show that the COD and BOD concentration after the MBBR tank is 140-160 mg/l

Figure 9. Variation of input/output BOD concentration and removal efficiency

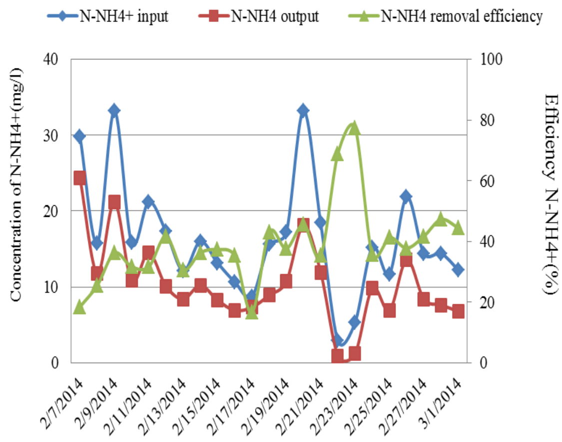

Figure 10. Variation of input/output ammonium concentration and removal efficiency

and 40-60 mg/l fall below the permitted standards of 150 mg/l and 50 mg/l, respectively, meanwhile the existing treatment system of the factory reach 300-340 mg/l and 100-120 mg/l. This suggests that aerobic microorganisms have ensured the sufficient conditions for development according to the ratio of COD:N:P = 250:5:1 and especially the density of microorganisms that stay in the material is high and stable.

After treatment, ammonium reaches the standard < 10 mgN/l according to Vietnam National Technical Regulation QCVN 40:2011/BTNMT [9]. Compared to the existing facility, the ammonium treatment efficiency has increased twice (Fig. 10). Thus, the simultaneous organic and ammonium treatment mechanism under model 3 has been implemented, which means that in the same aerobic environment, there are 3 processes which are aerobic - anoxic - anaerobic.

4. Technological line for wastewater treatment for Sao Thai Duong Pharmaceuticals & Cosmetics Factory

With the above experimental results, a process for wastewater treatment for Sao Thai Duong Pharmaceuticals & Cosmetics Factory was proposed as follows (Fig. 11):

a. Receiving chamber: Wastewater from various areas of the factory is led into the waste water treatment plant through the screening (to remove raw garbage of over 10 mm) to enter the receiving chamber, which is to be pumped to the garbage separator.

b. Garbage separator: Before entering the stabilization tank, the types of over-5 mm garbage are separated and retained in the garbage separator to avoid damage to the pump or obstruction to the works behind. The amount of waste collected is concentrated and disposed properly or burned.

c. Stabilization tank: Wastewater flow is regulated and pollution concentration is neutralized by mechanical mixing system. Chemicals (NaOH, PAC, Polymer) are injected directly on the pipeline connecting to the flotation tank.

d. Flotation tank (DAF): A device used to separate and remove suspended solids from liquids based on changes in solubility of different atmospheric pressure. Air is collected through an air intake device by a high pressure circulating water flow. Water and air is mixed to create micron-sized air bubbles. Tiny air bubbles generate an attractive force that can adhere to suspended particles in the water and lift suspended particles over the surface of the liquid forming a floating sludge layer to be removed by the scraper system. Heavy solids are settled on the bottom, collected and brought back to the sludge tank.

Flotation tank uses the method of attaching sediments in waste water with air bubbles. All bubbles adhering to solids which are very fragile and unstable in floating units must be kept to a minimum level to prevent deterioration in performance.

In this tank, chemical injection is combined with mixing to eliminate the color in the waste water, to create good conditions for anaerobic process in the anaerobic tanks behind.

e. UASB compartment 01: Wastewater from flotation tank CAF self-flows into anaerobic tank 01. With the use of the carrier DHY-02 contained in a 10 cm-diameter ball, wastewater can contact with a large amount of micro-organizations. In this tank, a large amount of organic matters is removed. Periodically, the tank is flushed and drained to flow into the receiving chamber.

f. UASB compartment 02: Wastewater from anaerobic tank 01 self-flows into anaerobic tank 02, in which the carrier DHY-02 is used similar to the anaerobic tank 01. g. UASB compartment 03: Similar to anaerobic tank 02, water from anaerobic tank 02 self-flows, is distributed below the tank, and collected at the top by the distribution and collection system. Water passing through anaerobic tank 03 self-flows into MBBR tank.

The simultaneous use of 3 anaerobic tanks using the carriers creates conditions to adapt and protect micro-organizations against shock.

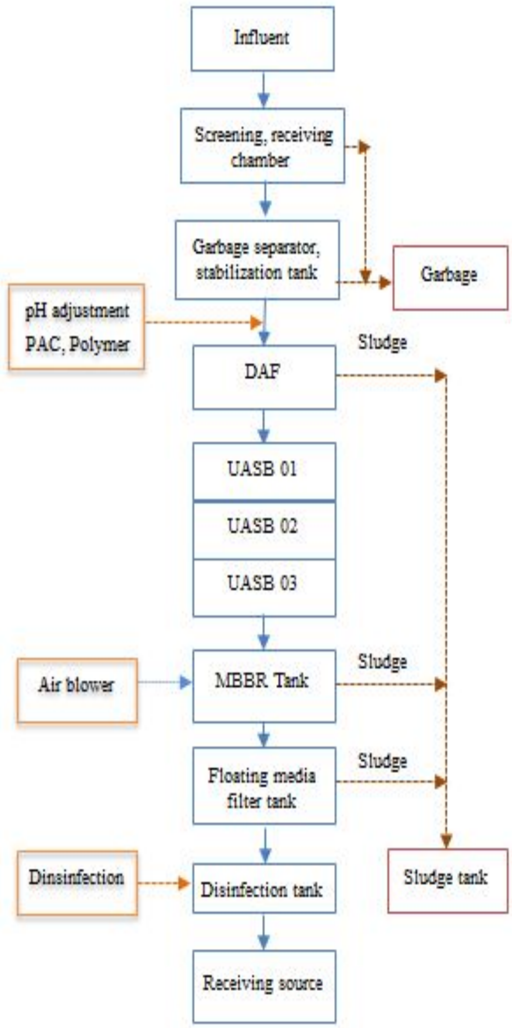

Figure 11. Diagram of treatment process

h. MBBR tank: The water after UASB tank leading into the MBBR (Moving Bed Biofilm Reactor) is a moving bed biofilm technology using carrier DHY-01, which is combined between suspension technique (microorganisms evenly distributed in water environment) and biofilm (microorganisms forming membrane on carriers) with the density of carriers of 10-15% of volume of reaction block to enhance microbial density in a volume unit of the reactor, which increases treatment efficiency. In order to enhance the mass transfer process (treatment tank volume section), the treatment system is designed with the technique of moving biocarriers in the water when the air supply system operates. MBBR technology uses the bio-carriers with high porosity, large contact area to ensure the integration of aerobic, aeration and anaerobic process in a treatment tank thus reducing capacity and treatment duration significantly.

The air distribution system produces fine air bubbles that provides oxygen for mixing and helps bacterial growth as well as keeps suspended matters in the effluent not to be settled down.

Especially, this technology will remove ammonium nitrogen thoroughly through nitrification and denitrification process which has been described elsewhere [5].

i. Filter tank using floating media: The biomasses formed in the waste water after the MBBR tank will be retained in the floating media filter tank.

The floating media with the main component as Polystyrene which is spherical, white and lighter than water has a surface area of 600 m^2/m^3 (3 - 5 mm); 1.150 m^2/m^3 (2-3 mm). When submerged in natural water, the surface of negative electrically grain, similar to the quartz sand used as filter sand, but has an area and adhesion of 3 -10 times larger [10].

Filter tank according to the upward flow filtration principle: wastewater is evenly distributed from the bottom of the filter bed by which the sediments are retained in the bed. The filtered water rises and the surface water is collected and led into the disinfection tank.

Periodically, the sludge is discharged into a sludge tank with the process of washing the filter bed with water of 0.7-1.00 m high above it.

j. Disinfection tank: a certain amount of $Ca(ClO)_2$ solution is injected in wastewater for disinfection before being discharged into the receiving source. The duration for wastewater in the disinfection tank is about 0.5 hours.

k. Sludge tank: Sludge from flotation tank, SBR and floating media filter tank is directed to the sludge tank and periodically drained by specialized vehicles to be treated or buried in accordance with regulations. Excess water of the sludge tank returns to the receiving chamber for treatment.

l. Odor treatment: Odor from anaerobic tank 01, anaerobic tank 02, anaerobic tank 03 and sludge tank will be treated by burning equipment.

The effluent meeting the requirements of column B QCVN 40:2011/BTNMT will be discharged into the environment.

5. Conclusions

The improvement of UASB tank in the form of hybridization with upward flow filtration column using bio-carrier DHY-02 in 10 cm-diameter balls had significantly increased COD removal efficiency (from 20-70%).

MBBR tank system with the bio-carrier DHY-01 has worked effectively in simultaneously treating COD, BOD and ammonium without separating the anoxic treatment system for denitrification.

The used DHY-01 and DHY-02 carriers have a large surface area and high adhesion capacity, which provide favourable conditions for the development of micro-organisms. Besides, with the advantage of porous cubic form of the materials and employment of moving bed biofilm reactor technique in anaerobic tank, there may be nitrification and denitrification processes taking place at the same time, which help reduce partly the volume of tank.

Sao Thai Duong Pharmaceuticals & Cosmetics Factory wastewater is not stable in terms of quality and its composition varies depending on the production materials. Using the bio-filter wastewater treatment method as in the experimental system presented above will help the factory achieve high and stable wastewater treatment efficiency.

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