# CHAPTER IX

## DECOLORIZATION OF MELANOIDINS-CONTAINING WASTEWATER IN MEMBRANE BIOREACTOR

In recent years, membrane technology has emerged as a feasible alternative for convenient treatment of wastewater. Coupled with bacterial treatment processes, membrane technology has gained considerable attention due to its wide range of applicability and the performances of membrane systems that have been established by various investigations during the last decade.

Membrane bioreactors (MBRs), the combination of membrane separation with a suspended growth bioreactor, is a convenient technology for wastewater treatment since it posses advantages such as complete removal of the suspended solids and macro-colloidal material, prolonged microbial retention time (sludge retention time, SRT), reduction in costs, easiness for control of reactor operating conditions. According to these positive aspects, MBR has been applied to various wastewater treatments to achieve higher effluent quality, which is often difficult to be effectively met by conventional activated sludge process. (Judd, 2006; Stephenson et al., 2000; Yun et al., 2006).

In this way, the advantages of MBR are a high mixed liquid suspended solids (MLSS) concentration, a lower excess sludge production. Moreover, the produced treated water can be reused (Meng et al., 2008). High solid retention times (SRTs) enable one to increase the sludge concentration and the applied organic load, thereby increasing the pollutant degradation. This allows the development of microorganisms able to remove highly recalcitrant pollutants contained in wastewater, resulting in improved removal rate.

The main aim of membrane bioreactors is to improve the efficiency of the biological process step for obtaining a high-quality effluent. Because biological treatment and membrane separation are rather distinct processes, the combined MBR process is relatively complex. To optimize the MBR process, many parameters have to be considered. These include the aeration rate and hydraulic retention time (HRT) in the biological step as well as the flux rate, and the membrane materials in the membrane separation performances.

The combination of bacterial decolorization and membrane technology should represent a more promising technology for melanoidins-containing wastewater treatment. Hence, in this chapter, a feasible system may be envisaged by coupling the decolorization capability of bacterial consortium with inherent advantages of membrane bioreactor. The constructed consortium MMP1 was selected as an inoculum for this study. The decolorization performances of the membrane bioreactor are studied to determine the optimum operating conditions, which will be applied to continuous decolorization of a synthetic melanoidins-containing wastewater.

In this study, the effect of operating parameters on melanoidins-containing wastewater decolorization and on the performance of the MBR process for treating the molasses wastewater by bacterial consortium were investigated.

## 9.1 Investigation of decolorization by bacterial consortium using side-stream membrane bioreactor

In side-stream configuration, membrane filtration occurs outside the bioreactor through recirculation. By pumping the mixed liquor from the bioreactor at a high pressure into the membrane unit, the permeate passes through the membrane and the concentrate is returned to the bioreactor. Solid retention time (SRT) in MBR can be controlled completely independently from hydraulic retention time (HRT). Therefore, a very long SRT can be maintained resulting in the complete retention of useful bacteria and this results in greater flexibility of operation. In addition, a side-stream operation is evaluated as a way to provide the increased high surface shear that would enable the operation at high levels of permeate flux.

The membranes used by MBR have pore sizes such that water and most solute species pass through the membrane whilst other larger species, such as solids and microorganisms, are retained. Thus, selection of the membrane materials (polymer or ceramic) and module types (tubular or hollow fiber) plays an important role on the membrane flux achieved. With these aims of investigation, several investigation with polymeric (polysulfone) and mineral (zirconia) membranes have been tested for bacterial decolorization performed in MBR. These experiments were carried out in two runs. The first run was carried out with polysulfone hollow-fiber membrane bioreactor. For the second run, the decolorization was carried out in MBR equipped with the external mineral tubular membrane module.

The objective of this study was to determine the operating parameters that affected the melanoidins decolorization of the constructed bacterial consortium MMP1 in the side-stream laboratory-scale membrane bioreactor, in order to improve the decolorization rate. The experiments presented in this study were carried out in a side-stream cross-flow membrane bioreactor for the aerobic treatment of a synthetic wastewater containing Viandox sauce 2% (v/v) as color substrates.

## 9.2 Decolorization of melanoidins-containing wastewater in polysulfone hollow-fiber membrane bioreactor

In this study, the experiment was performed using a laboratory-scale side-stream membrane bioreactor represented in Figure 9.1. A 2L laboratory scale side-stream MBR with 1.6L of working volume was used to conduct this study. The reactor was connected to an external membrane module, containing a single tubular membrane. In this study, membrane module was a hollow-fiber membrane module (Polymem, Fourquevaux, France), whose main characteristics were listed in Table 9.1. The membrane was made of polysulfone with a pore size of 0.1 μm, and internal/external diameter of 0.4/0.7 mm. The effective membrane filtration area was 0.1 $m^2$.

The aeration was maintained at 0.1 vvm with agitation speed at 150 rpm. The membrane bioreactor was initially inoculated with the constructed bacterial consortium MMP1. Reactor mixed liquor was circulated through the membrane module by mean of a peristaltic pump (Masterflex I/P). A synthetic melanoidins-containing wastewater was then continuously introduced. A water level was used to control the influent pump and to keep the water level in the bioreactor constant. The control of temperature at 30$^{o}$C was obtained using thermostatic recirculation vessel. Samples were taken from the bioreactor and from permeate at regular time and then centrifuged at 10,000 rpm for 10 min. The samples were collected and stored in a refrigerator at 4 $^{o}$C until analyses.

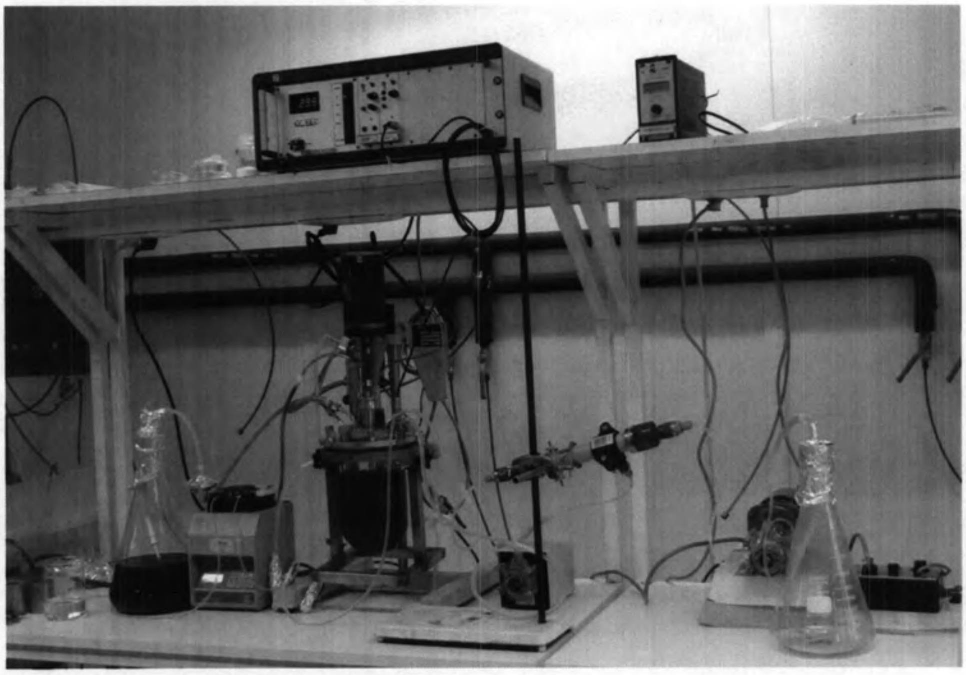

**Figure 9.1** Decolorization experiment using polysulfone hollow-fiber MBR.

**Table 9.1** Characterization of the polysulfone membrane (Polymem, France)

| Classification | Characteristics |
|---|---|
| Membrane material | Polysulfone |
| Module type | Hollow-fiber |
| Internal/external diameter | 0.4 mm /0.7 mm |
| Effective membrane filtration area | 0.1 $m^2$ |
| Mean pore size | 0.1 μm |

**9.2.1 Decolorization experiment using polysulfone hollow-fiber MBR at HRT of 40 hours.**

This experiment was performed in side-stream membrane bioreactor equipped with hollow-fiber membrane module by using HRT of 40 hours. Unfortunately, this experiment was stopped after 72 hours of operation because the membrane bioreactor was contaminated with fungi (Figure 9.2). Indeed, a major limitation of polysulfone hollow-fiber membrane bioreactor was the significant reduction of permeate flux significantly caused by membrane fouling. Membrane fouling can result from the precipitation of less soluble inorganic species, adsorption of organic substances (organic fouling), and adhesion and growth of microbial cells at the membrane surface (bio fouling). In this experiment, studies with polysulfone membrane showed contamination by biomass formed inside the reactor as shown in Figure 9.3. The explanation for the fouling of polysulfone membrane at very short operation time relied on the adhesion and growth of contaminated-microbial cells on the membrane surface, thus causing a major hydraulic resistance. This was a major problem in the polymeric membrane bioreactor because it reduced productivity, shortened membrane life and impaired the fractionation capability of the membrane.

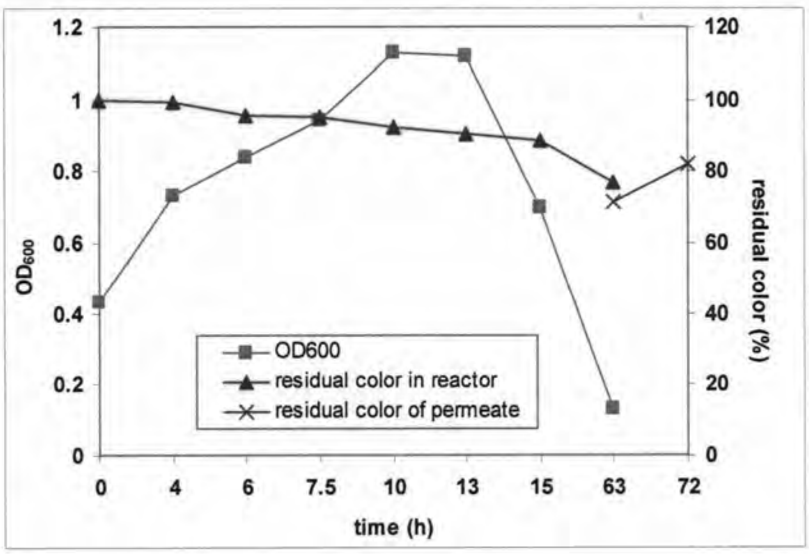


**Figure 9.2** Time course of decolorization of the synthetic melanoidins-containing wastewater medium by the bacterial consortium MMP1 in the polysulfone hollow-fiber membrane bioreactor using a HRT of 40 h.

(a) (b)

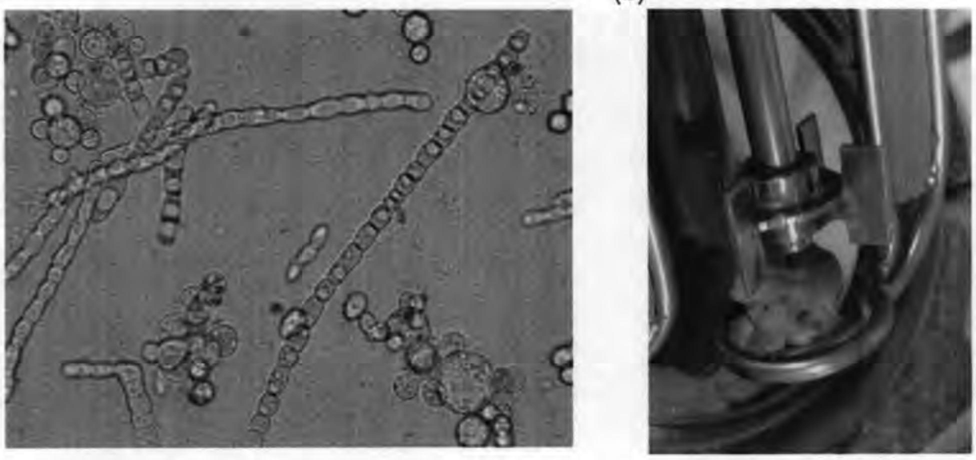

**Figure 9.3** Microscopic photographs of contaminated microorganisms in MBR (a); and cake layer observed on the surface of the mechanical stirrer (b).

## 9.3. Decolorization of melanoidins-containing wastewater in mineral membrane bioreactor

Microfiltration mineral membrane bioreactor seems to be one of the most appropriate reactor to treat distillery wastewaters due to its permeation flux higher than polymeric membrane one. In addition, it is a more biologically compatible membrane material (Doyen et al., 1996). Moreover, it is not affected by solvents and also supports irradiation. These properties allow the easy cleaning of membrane by different processes. Continuous operation of this type of reactor is feasible as long as substrate solutions are supplied to the reactor. The advantages of mineral membrane bioreactors mentioned above make them suitable for operations of continuous processes. The aim of this part of the study is to quantify the performance of a mineral membrane bioreactor for treatment of melanoidins-containing wastewaters.

To investigate the decolorization performance of the bacterial consortium in mineral membrane bioreactor, the experiment was performed in an external membrane bioreactor. The 2L biological reactor contained 1.6L of synthetic melanoidins-containing wastewater was equipped with an aeration system composed of bottom-installed air nozzles. The decolorization experimental system of this study is represented in Figure 9.4 and flow diagram is showed in Figure 9.5. The membrane module was a stainless-steel monochannel (monotubular) microfiltration module, a mineral M14 Carbosep® membrane (Orelis, Miribel, France), whose main characteristics are listed in Table 9.2. The M14 membrane is a composite membrane with a 0.14 µm mean pore diameter of zirconium dioxide ($ZrO_2$) and titanium dioxide ($TiO_2$) filtering layer on a carbon support (6 mm inner diameter, 60 cm long). This carbon-based zirconium membrane is highly resistant to pressure (up to 40 bars), to temperature (up to 350 $^{o}$C), and pH (0-14).

There have been a number of investigations focused on the selection of suitable SRTs for wastewater treatment by MBRs. These reported results suggest that the optimum SRT of MBRs should be controlled at 20-50 days depending on HRT and feed wastewater (Han et al., 2005; Lee et al., 2003; Ng et al., 2006; Zhang et al., 2006). Thus, In this study, SRT at 50 days was selected for this study. The SRT was determined for 50 days by discharging calculated volume of sludge daily, in order to renew the reaction volume in 50 days.

The objective of this study was to determine the effect of different HRT on decolorization performance of the bacterial consortium MMP1. Three independent experiments were carried out at HRT of 40 hours, 20 hours, and 15 hours, respectively

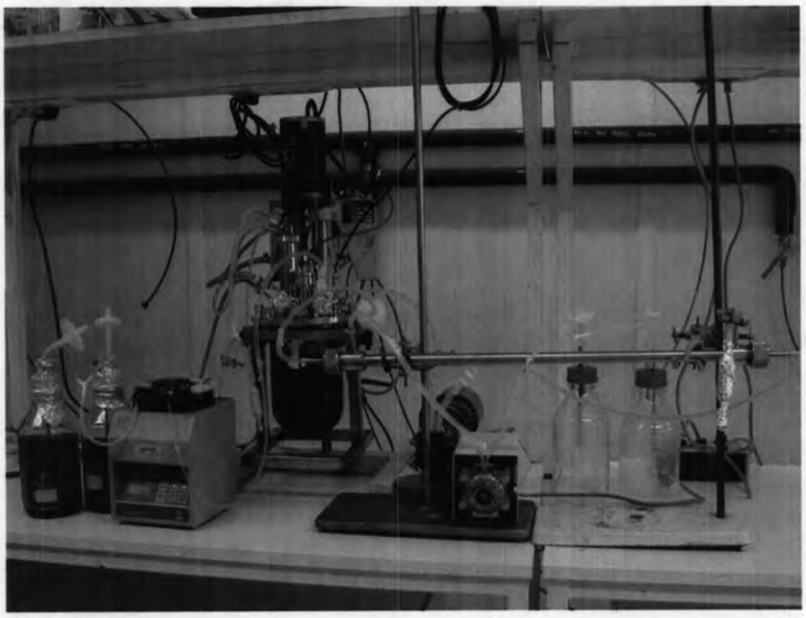

**Figure 9.4** Decolorization experimental device : the external mineral MBR

**Table 9.2** Characterization of the mineral membrane (Carbosep® membrane)

| Classification | Characteristics |
|---|---|
| Mineral support | Carbon |
| Active layer | $ZrO_2$-$TiO_2$ |
| Module type | Tubular |
| Length (m) | 0.6 |
| Internal/external diameter (mm) | 6/10 |
| Mean pore size (µm) | 0.14 |
| Effective membrane filtration area ($m^2$ ) | 0.011 |
| TMP (kPa) | <1,500 |

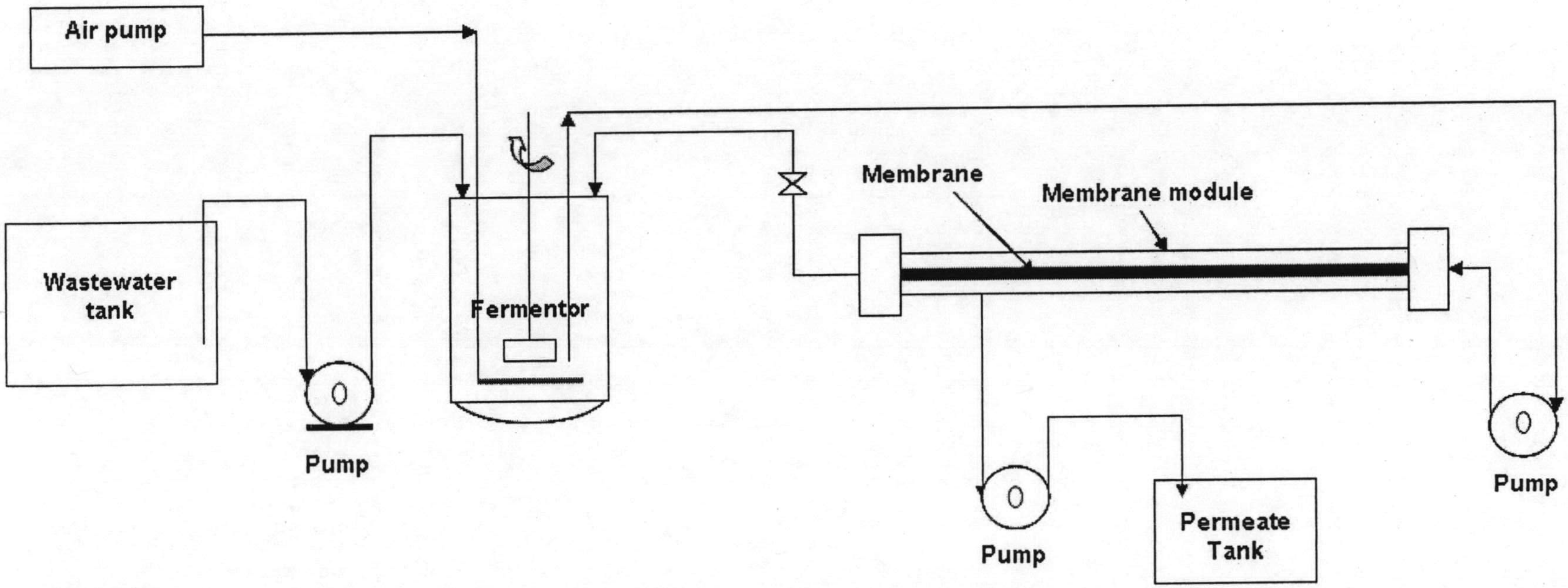


**Figure 9.5** Flow diagram of decolorization of melanoidins system

In this study, all flows were sampled and analyzed weekly with the exception of the MBR effluent, which was sampled and analyzed twice weekly (i.e. every two or three days). Table 9.3 is the matrix that shows the organization of sampling frequencies and analyses for each flow.

**Table 9.3** Testing matrix for laboratory testing

| Material flow | Sampling | Parameters | | | |
|---|---|---|---|---|---|
| | | $OD_{475}$ | $OD_{600}$ | DW | COD |
| Wastewater (Influent) | | x | x | | x |
| Bioreactor sludge | thrice/week | x | x | x | x |
| Permeate (Effluent) | thrice/week | x | | | x |

### 9.3.1 Decolorization experiment using mineral MBR at HRT of 40 hours

**Color variation with time**

The MBR performance was initially investigated with HRT of 40 hours (Figure 9.6- 9.8). Figure 9.6 showed the evolution of biomass and color concentrations during the 50 days of operation. The absorbencies were obtained at 475 nm. The variation of permeate and color in reactor with time are shown in Figure 9.7. The results showed that the residual color of an effluent was consistently lower than the sludge supernatant color inside membrane bioreactor (Figure 9.7 and Figure 9.8). The color in the supernatant is increasing as if some accumulation would happen. Nevertheless, the color of the permeate is slightly lower than the initial one, and rather lower than the supernatant. This observation indicates an ability of the membrane to retain the colorizing molecules. This phenomenon happened after 10 days of operation, probably with an increase of the membrane fouling. Maximum decolorization of 53.53 % was observed in 2 days and the color rather increased until 8 days (185 h). Then, the bacterial consortium in the system could decolorize melanoidins again and later reached steady decolorization but without significant color reduction, because of the accumulation phenomena. After operation for 29 days, the decolorizing activity of bacterial consortium was constant approximately 33% and then the color was slowly increased until 50 days of operation. However, the residual color in bioreactor was dramatically increased from 99.56% after 23 days of operation to 186.14% at the end of experiment (50 days).

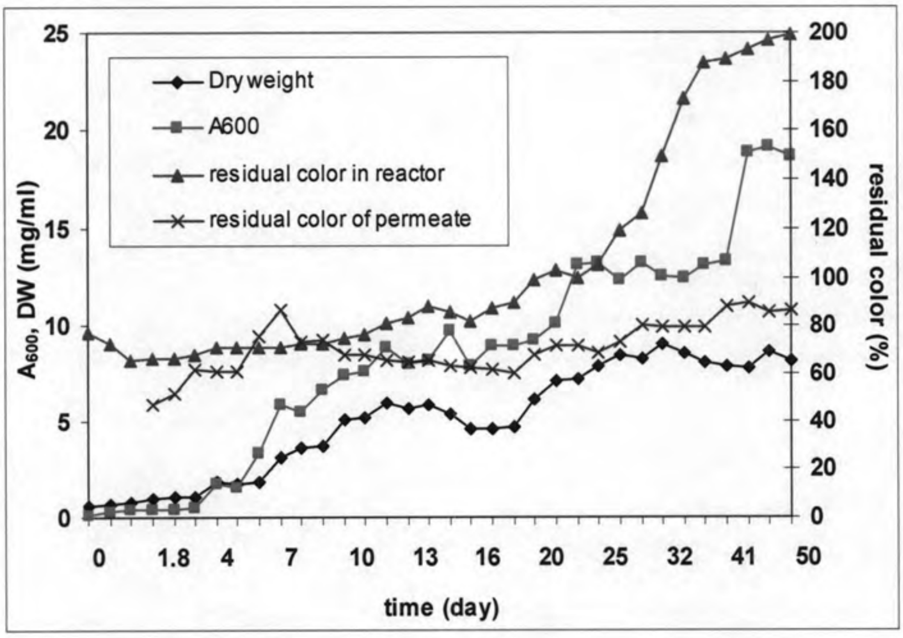


**Figure 9.6** Time course of decolorization of the synthetic melanoidins-containing wastewater medium by the bacterial consortium MMP1 in mineral membrane bioreactor using HRT of 40 hours. The consortium was cultured under the conditions described in the text. Symbols: (▲), residual color of culture medium in bioreactor, (x) residual color of culture medium in permeate, (♦) bacterial dry weight and, (■) optical density at 600 nm.

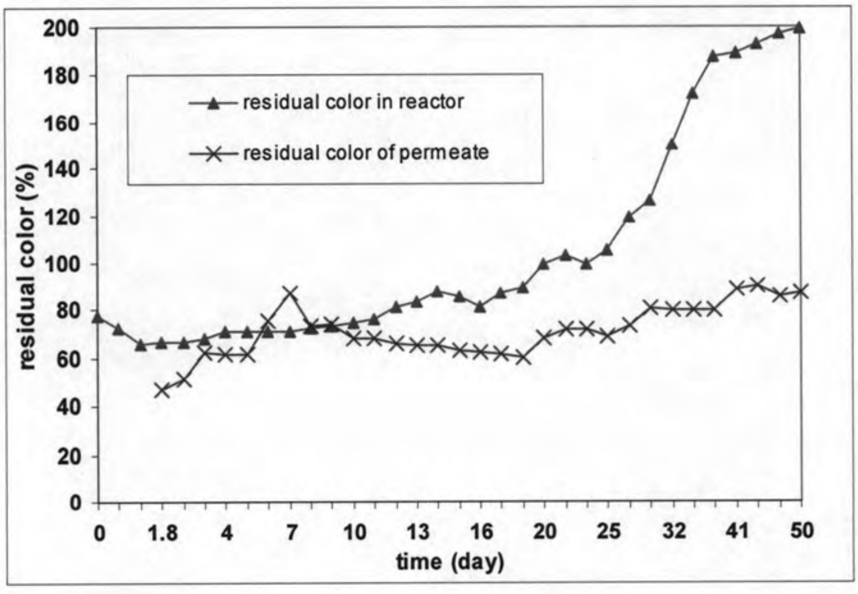


**Figure 9.7** Variations of permeate and feed color with time in mineral membrane bioreactor which using a HRT of 40 hours.

**Figure 9.8** Characteristics of the synthetic melanoidins-containing wastewater before treatment (left-hand) and the permeate of the mineral MBR (right-hand).

An increase in color intensity of wastewater within bioreactor might be due to the accumulation of colored compounds and/or the formation of new colored substances. It is possible that cell debris and some intracellular biomolecules such as proteins, carbohydrates, organic nitrogen, amino acids react with the residual colored compounds resulting in the formation of large molecular weight color compounds (Martins et al., 2000). The low COD removal result as shown in Figure 9.10 also indicates that the recalcitrant compound present in wastewater were not effectively degraded and possibly their concentration increase inside the bioreactors.

Melanoidins, the brown polymers formed through Maillard reaction, are most commonly present in molasses wastewater. The chemical properties of melanoidin are humic substances-like, being acidic, polymeric and highly dispersed colloids, negatively charged due to the dissociation of carboxylic and phenolic groups (Migo et al., 1993). In general, melanoidins are colloidal compounds of molecular weight between 40 and 70 kDa. Increasing degree of polymerization of melanoidins is reported to increase size of the colloids (Pena et al., 2003; Coca et al., 2005). In this study, the formation of colloidal particles had been observed in wastewater within bioreactor after 7 days of operation (Figure 9.9). Based on the above information, thus, another possibility of color increasing in wastewater might be related to the formation of colloidal compounds within bioreactor.

Evidence supporting this idea is the difference of color intensity at 475 nm between wastewater sample in bioreactors and the permeate collected from microfiltration membrane modules with a pore size of 0.14 µm.

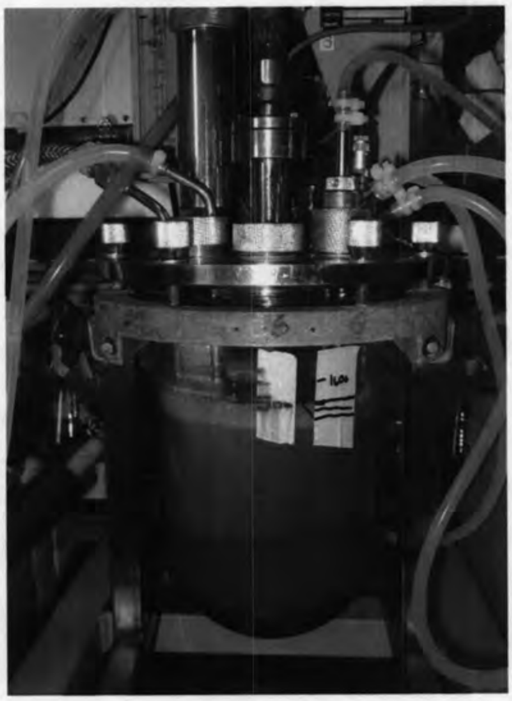

**Figure 9.9** Characteristics of wastewater in bioreactor after 7 days of operation using HRT of 40 hours.

One more possibility in the higher color intensity ($A_{475}$) and turbidity ($A_{600}$) of supernatant in bioreactor after 20-days operation can be related to supernatant colloidal COD (Vogelaar et al., 2002). The increase in colloidal COD in bioreactor might be due to the increasing of free bacterial cells, cell components or extracellular polymeric substances (EPS). In this study, the concentration of COD in the supernatant of wastewater in bioreactor after 20-days operation was slightly higher than in the permeate (Figure 9.10). This indicates that the compounds that are retained in the bioreactor are colloidal COD and it is possible that their concentration increase in the long operating times.

These results showed that the color concentration of treated water required an optimization of the membrane bioreactor to improve the decolorization rate. It must be noticed also that the microorganisms usually required an acclimatizing to the

MBR process, lasting 2 or 3 times the SRT, which has not be respected here for time consuming reasons.

**Sludge production**

The growth of bacterial consortium MMP1 during the experiment is shown in Figure 9.6. Time course of effluent decolorization was studied along with the growth of the consortium MMP1. With the increase of time, there was an increase in cells mass but not decolorization. An increasing trend of bacterial biomass with time resulted mainly from the prolongation of SRT (compared to conventional process) and the retention by the membrane. The large fluctuations of biomass concentrations observed during 50-days operation could be attributed to bacterial acclimation in response to the changes in physico-chemical environments in this MBR (e.g. high shear stress from the recirculating pump). After each decline, the biomass was stabilized; this might be due to the adaptation of microorganisms in membrane reactor.

**COD removal efficiency**

The variation of supernatant inside reactor and effluent COD concentration with time during the experiment is illustrated in Figure 9.10. The COD of permeate and supernatant in reactor after 50 operation days remained at about 16,382 mg/L and 19,007 mg/L, respectively, although the influent COD was around 22,000 mg/L. Thus, the average removal of COD was 25.5%. In this study, though the biomass growth is satisfactory, COD reduction appears to be limited by the presence of recalcitrants (comprising the coloring compounds melanoidins) in the feed, which are known to restrict bacterial growth.

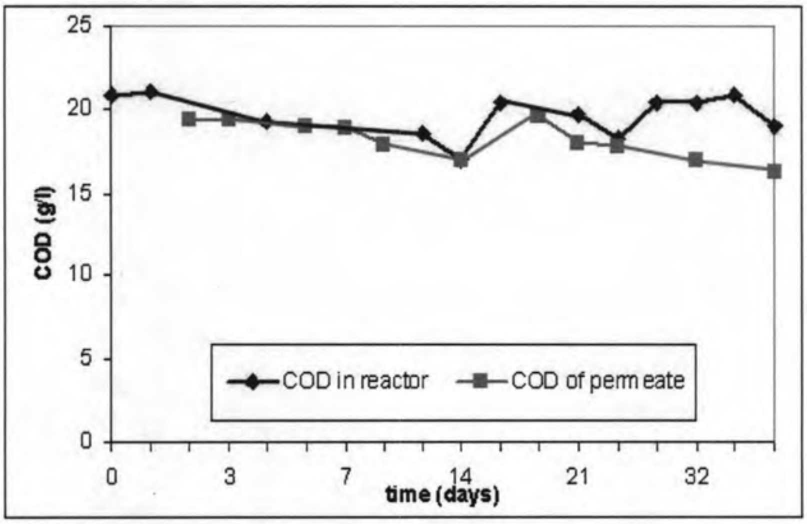


**Figure 9.10** Variations of COD in bioreactor and permeate with time in mineral membrane bioreactor using HRT of 40 hours.

**Membrane permeability**

Permeate flux is influenced by a number of factors including the feed water (composition), the membrane (element geometry/configuration), area and material composition), and operation (hydrodynamics). It is critically determined by the tendency of the membrane to be fouled by feed water components owing to their accumulation on the internal and external structures of the membrane (Stephenson et al., 2000). Figure 9.11 shows the variation of permeability of the mineral membrane before and after operation with HRT of 40 h.

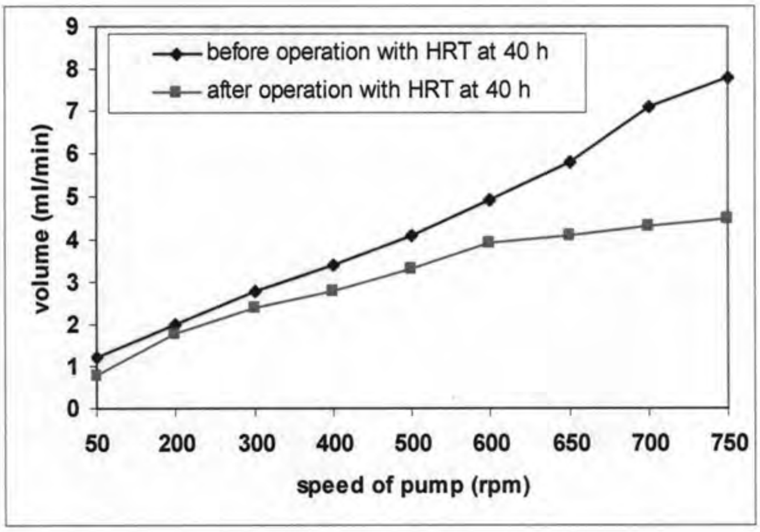


**Figure 9.11** Variation of permeability (at 25°C) of the mineral membrane before and after 50 days of operation with HRT of 40 hours.

The result of the water permeability test in Figure 9.11 shows that the permeability of mineral membrane was slightly decreased after 50 days continuous operation by using HRT of 40 hours. In general, the reduction of membrane permeability could be related to the increase of biomass concentration (Li *et al.*, 1984), the size reduction of mixed liquor biosolids (Bailey *et el.*, 1994), or the size distribution of particles being filtered (Chang *et al.*, 1994).

In this study, the decrease of membrane permeability after operation was probably due to the increase of bacterial biomass within the system and/or the formation of bacterial biofilm on the membrane surface which had been removed easily by washing or increasing fluid velocity.

## 9.3.2 Abiotic control of decolorization experiment using mineral MBR at HRT of 40 hours

Abiotic decolorization study was carried out to check whether the decolorization was obtained from biological activity or non-biological activity. The synthetic melanoidin wastewater was used as a control to analyze the performance of mineral membrane bioreactor.

**Color variation with time**

The variation of permeate and color in reactor with time is shown in Figure 9.12. The results showed that residual color of supernatant inside reactor was consistent. The residual color of effluent at 48 h was around 32 %, then, the color rather increased to 100% until the end of operation. The lower residual color of permeate in first 4 days of operation might result from the water used for washing and sterilization process remained inside the membrane and dilute the color of permeate. The comparison of decolorization of consortium MMP1 from previously study with abiotic control has proved that the color removal for synthetic melanoidins-containing wastewater medium containing 2% (v/v) Viandox was due to biotic activity of bacteria but not adsorption of color substances on the membrane.

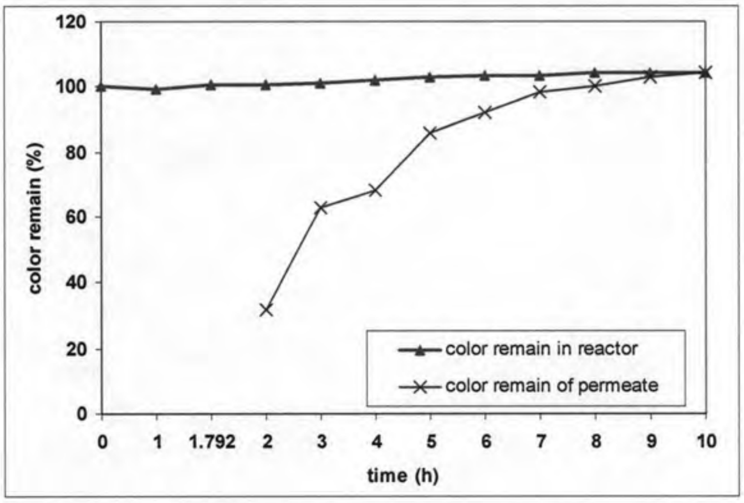


**Figure 9.12** Decolorization of viandox with mineral membrane bioreactor using HRT of 40 hours without bacterial culture.

**COD removal efficiency**

The variation of supernatant inside reactor and effluent COD concentration with time during the experiment is illustrated in Figure 9.13. The COD of supernatant in reactor and permeate after operation for 10 days remained at about 22,000 mg/L and 20,470 mg/L, respectively, although the influent COD was around 22,000 mg/L. Thus, the average removal of COD was 9.09%.

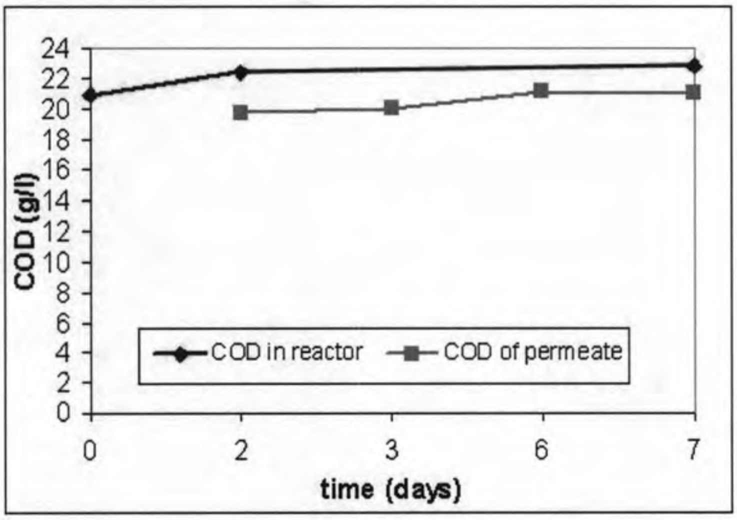


**Figure 9.13** Variation of COD in bioreactor and permeate with time in mineral membrane bioreactor which using a HRT of 40 hours without bacterial culture.

**Membrane permeability**

Figure 9.14 shows the variation of permeability of the mineral membrane before and after operation with HRT of 40 h. The permeability of mineral membrane after 10 days of operation was equal to permeability before being used. It could be concluded that irreversible (adsorption) membrane fouling did not occur under this operating condition.

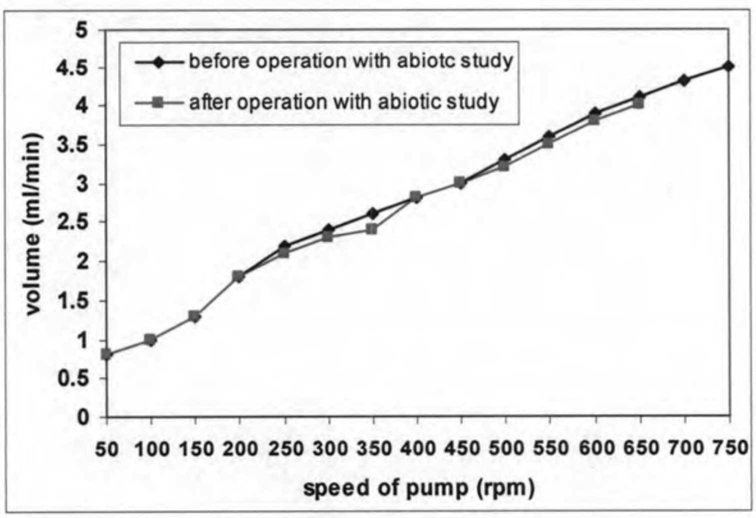


**Figure 9.14** Variation of permeability of the mineral membrane before and after 50 days of operation with HRT of 40 hours without bacterial culture.

### 9.3.3 Decolorization experiment using mineral MBR at HRT of 20 hours.

**Color variation with time**

The MBR performance was initially design with HRT of 20 hours (Figure 9.15-9.16). Figure 9.15 shows the evolution of biomass and color concentrations during 13 days of operation. The variation of permeate and feed color with time is shown in Figure 9.16. The results showed that the residual color of the permeate was consistently lower than the sludge supernatant color inside membrane bioreactor. Maximum decolorization of 51.18 % was observed in 2 days and the color rather increased until 6 days. Then, the bacterial consortium in the system could decolorize melanoidins again and later reached steady decolorization without significant color reduction. After operation for 13 days, the decolorizing activity of bacterial consortium was constant approximately 20 %. These results are quite similar to the previous results at HRT=40 hours, but in lower color removal percentage, due to the lower accumulation effect, itself linked to the reduced HRT.

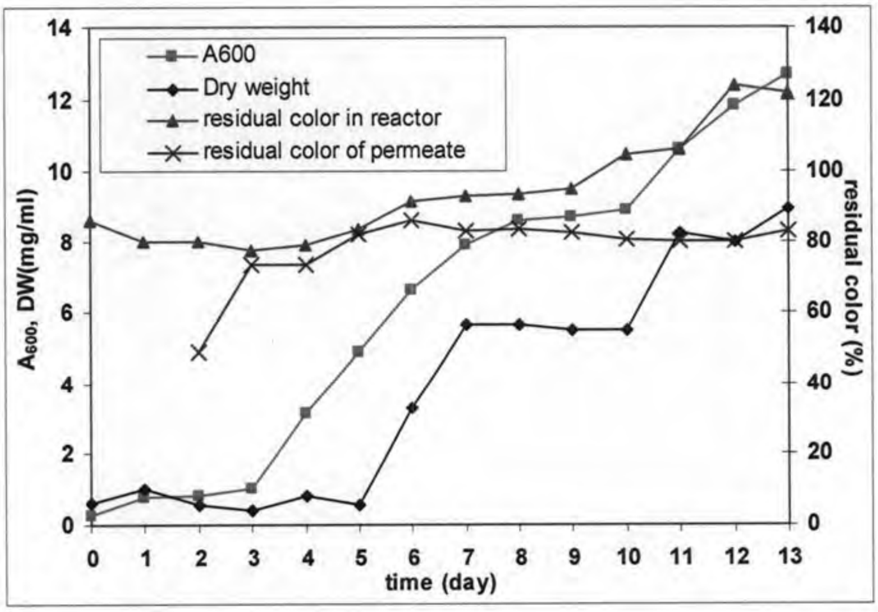


**Figure 9.15** Time course of decolorization of the synthetic melanoidins-containing wastewater medium by the bacterial consortium MMP1 in mineral membrane bioreactor using HRT of 20 hours. The consortium was cultured under the condition described in the text. Symbols: (▲), residual color of culture medium in bioreactor, (x) residual color of culture medium in permeate, (♦) bacterial dry weight and, (■) optical density at 600 nm.

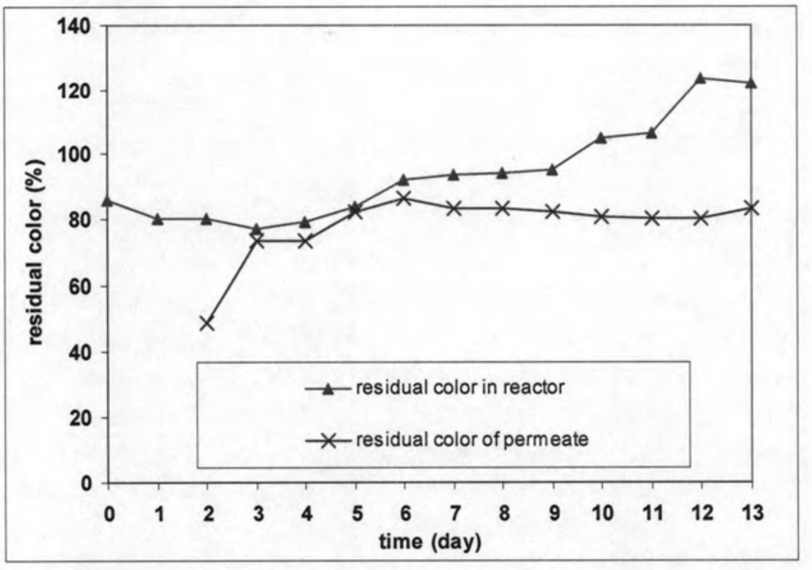


**Figure 9.16** Variation of permeate and feed color with time in mineral membrane bioreactor using HRT of 20 hours.

### Sludge production

The growth of bacterial consortium MMP1 during the experiment is shown in Figure 9.17. Time course of effluent decolorization was studied along with the growth of the consortium MMP1. With the increase of time, there was an increase in cells number. After each decline, the biomass was stabilized; this can be explained by the adaptation of microorganisms in membrane reactor (Badani et al., 2005). The colonies and microscopic photograph of bacterial consortium MMP1 in mineral membrane bioreactor operated with HRT of 20 hours were showed in Figure 9.18.

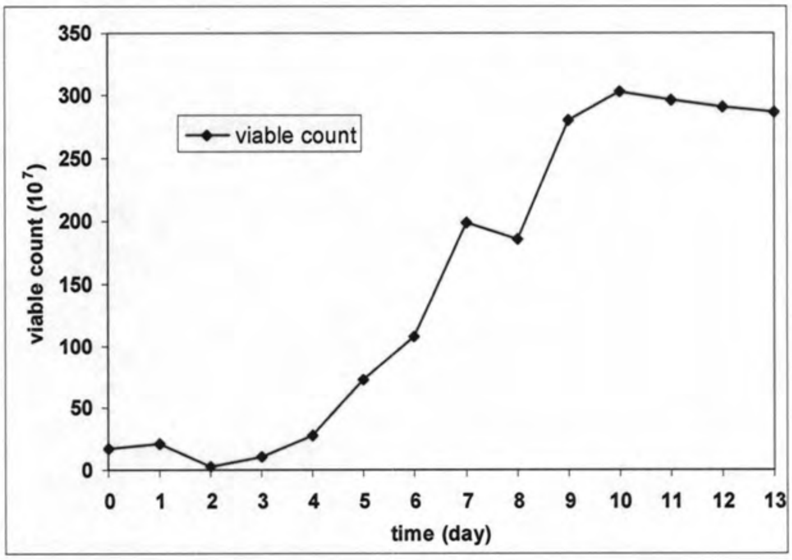


**Figure 9.17** Time course of bacterial growth in the synthetic melanoidins-containing wastewater medium in mineral membrane bioreactor using HRT of 20 hours.

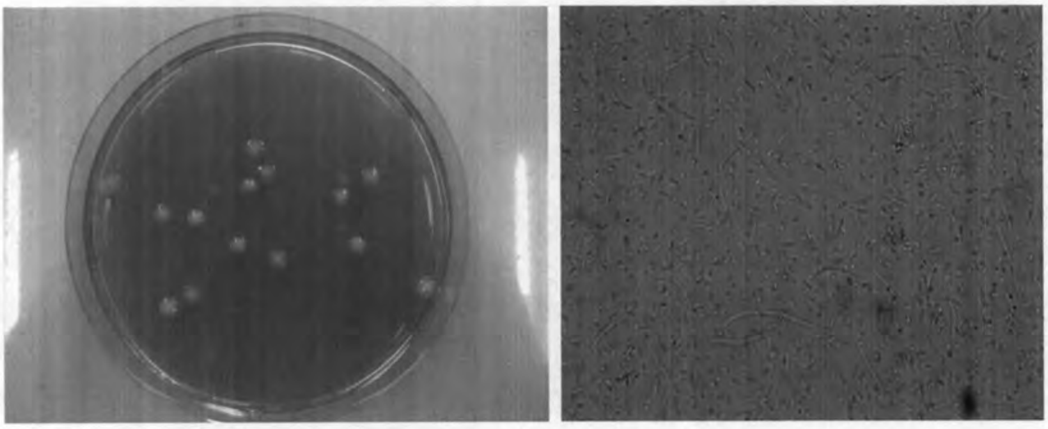

**Figure 9.18** Colonies and microscopic photograph of bacterial consortium MMP1 in mineral membrane bioreactor using HRT of 20 hours.

**COD removal efficiency**

The variation of influent and effluent COD concentration with time during the experiment is illustrated in Figure 9.19. The COD of permeate after 13 operation days remained at about 17,632 mg/L although the influent COD was around 22,000 mg/L. Thus, the average removal of COD was 19.86%.

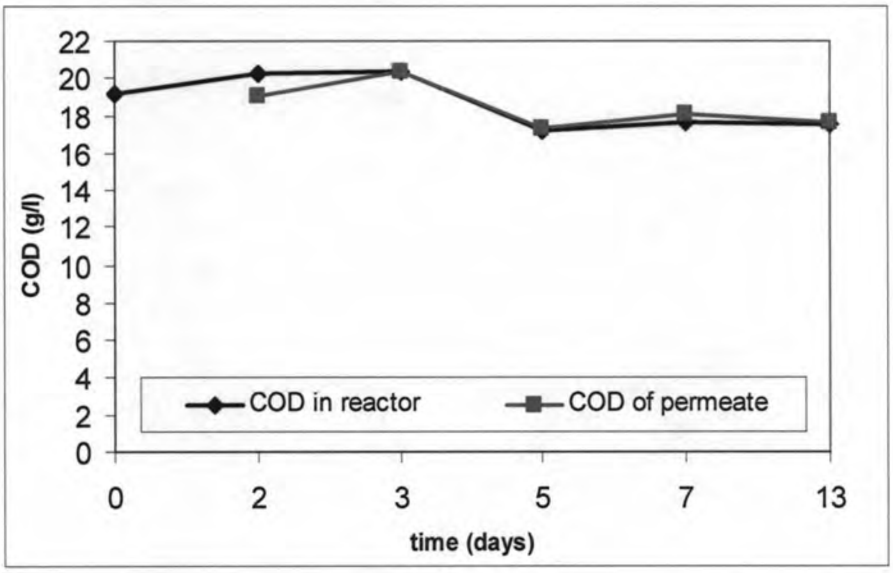


**Figure 9.19** Variation of COD in bioreactor and permeate with time in mineral membrane bioreactor using HRT of 20 hours.

**Membrane permeability**

Figure 9.20 shows the variation of permeability of the mineral membrane before and after operation with HRT of 20 hours. The permeability of mineral membrane was dropped after 13 days of operation. It has been observed in Figure 9.11 for a velocity higher than 500 rpm that the difference in permeabilities before and after experiments is more probably due to some dirty particles present in the water, more than to a real irreversible fouling state of the membrane. Thus, in this study, it could be assumed that there is no fouling due to irreversible phenomena. Then, the problem observed on permeate, leading to stop the experiment is due to a too weak selected cross flow velocity, or more probably to a clogging of the membrane pores by the development of thick biofilm, as previously observed with the hollow fibers membranes.

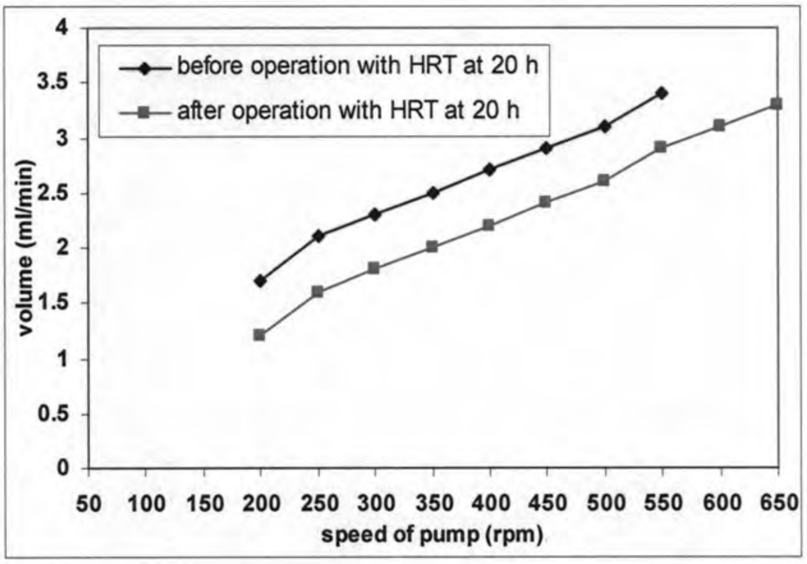


**Figure 9.20** Variation of permeability of the mineral membrane before and after 13 days of operation with HRT of 20 hours.

### 9.3.4 Decolorization experiment using mineral MBR at HRT of 15 hours

**Color variation with time**

In the present study, MBR performance was investigated with a HRT of 15 hours (Figure 9.21- 9.22). The variation of permeate and feed color with time is shown in Figure 9.22. The results showed that the residual color of an effluent was consistently lower than the sludge supernatant inside membrane bioreactor. Maximum decolorization of 50.44 % was observed in first day and then the color rather increased in the second day. After 4 days of operation, the decolorizing activity of bacterial consortium was constant approximately 23.05 %. Unfortunately, the MBR was stopped after operation for 4 days since no more permeate was flowing. Permeate was slowly stopped and the supernatant in the reactor was increased since the membrane was fouling and became clogged.

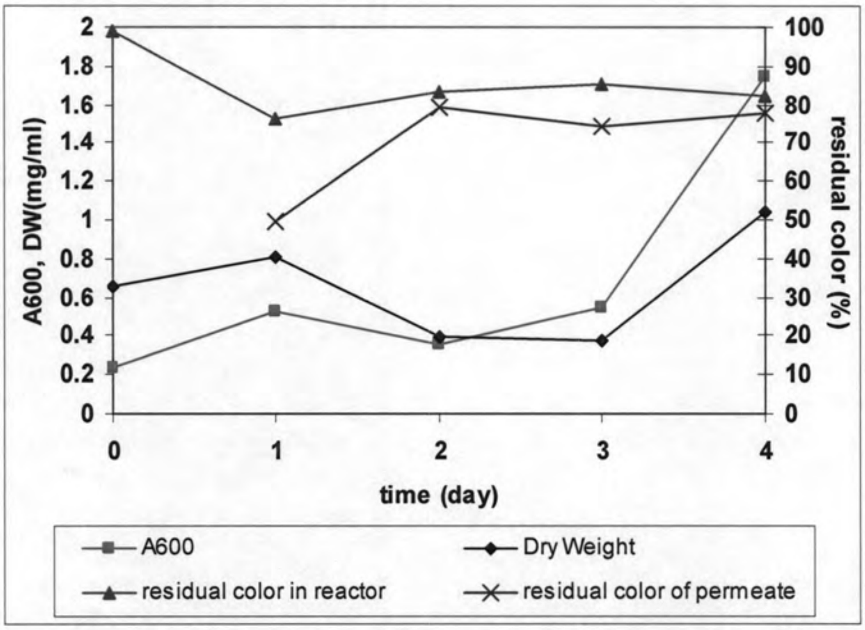


**Figure 9.21** Time course of decolorization of the synthetic melanoidins-containing wastewater medium by the bacterial consortium MMP1 in mineral membrane bioreactor using HRT of 15 hours. The consortium was cultured under the conditions described in the text. Symbols: (▲), residual color of culture medium in bioreactor, (x) residual color of culture medium in permeate, (♦) bacterial dry weight and, (■) optical density at 600 nm.

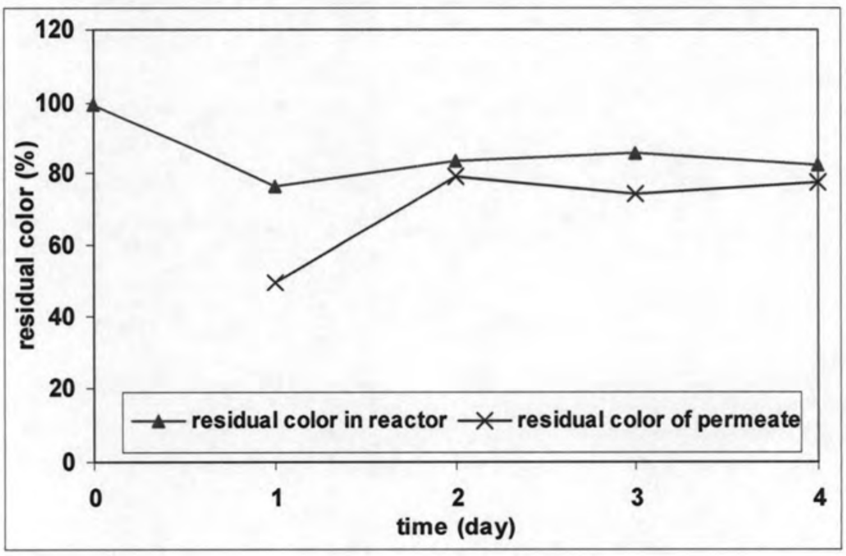


**Figure 9.22** Variation of permeate and feed color with time in mineral membrane bioreactor using HRT of 15 hours.

**Sludge production**

Figure 9.23 showed the evolution of biomass concentration and color concentration during the 4 days of operation. The growth of bacterial consortium MMP1 during the experiment is shown in Figure 9.21. Time course of effluent decolorization was studied along with the growth of the consortium MMP1. The fluctuation of the bacterial number within the first 4 days was assumed that the bacterial consortium MMP1 was acclimatized to the culture condition within MBRs. Unfortunately, system has failed with a membrane fouled and completely clogged. In the present study, as with the others HRT a lag phase of 4 days was observed.

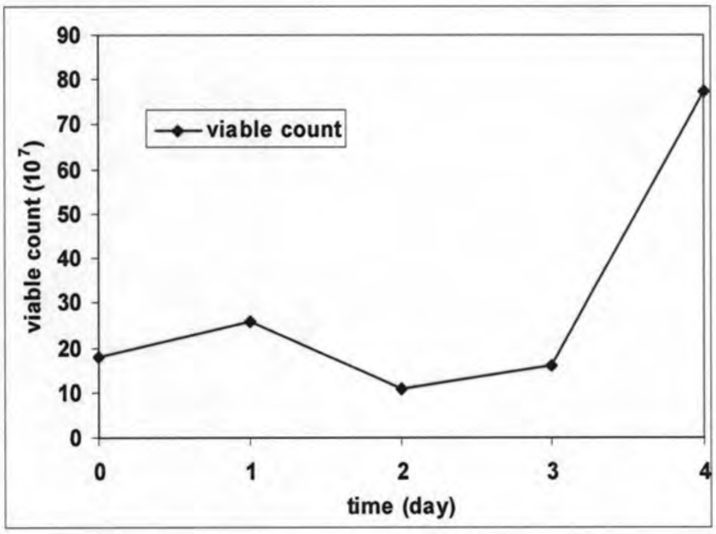


**Figure 9.23** Time course of bacterial growth in the synthetic melanoidins-containing wastewater medium in mineral membrane bioreactor using HRT of 15 hours.

**COD removal efficiency**

The variation of influent and effluent COD concentration with time is illustrated in Figure 9.24. The COD of permeate after 4 operation days remained at about 19,757 mg/L although the influent COD was around 22,000 mg/L. Thus, the average removal of COD was 10.19%. Due to the bacterial cells in bioreactor after 4 days of operation were still in lag-phase thus, the COD removal efficiency in the MBR with 15-hour HRT was lower than the higher HRT.

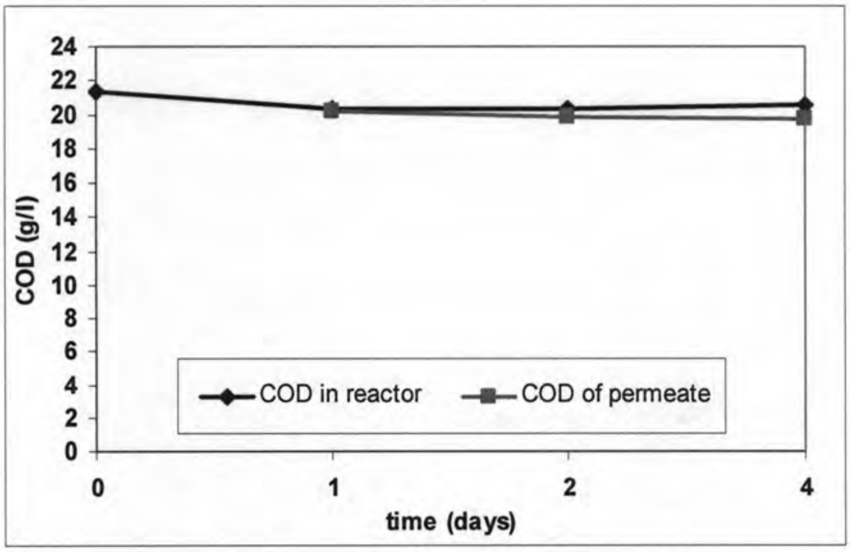


**Figure 9.24** Variation of COD in bioreactor and permeate with time in mineral membrane bioreactor using HRT of 15 hours.

**Membrane permeability**

Figure 9.25 shows the variation of permeability of the mineral membrane before and after operation with the HRT of 15 hours. The permeability of the membrane was dropped down after 4 days of operation then, completely clogged and no more permeate was observed. It could be concluded that membrane fouling occurred under this operating conditions. Also, it can be observed in Figure 9.25 that washing the membrane with cleaning agents (diluted NaOH and $HNO_3$) let increasing the permeability of the used membrane until its original values. Hong et al. (2002) mentioned that permeate flux decline due to irreversible fouling can be recovered by chemical cleaning and mechanical backwashing, that have been done here.

Membrane fouling is often considered to be caused by the deposition of particles on the membrane surfaces. Colloidal particles were identified as a predominant factor controlling membrane permeability, even though they make up a very small fraction of the total particles in MBR systems. In addition, Chang and Kim had found that small colloidal particles might play a critical role in membrane fouling in MBR systems (Chang and Kim, 2005). Because extracellular polymeric substances (EPS) are one of the main components of colloidal particles in MBR wastewater treatment systems, Based on the above information and results in this study, it is possible that the formation of colloidal compounds and dissolved organic compounds in bioreactors might be related to membrane fouling.

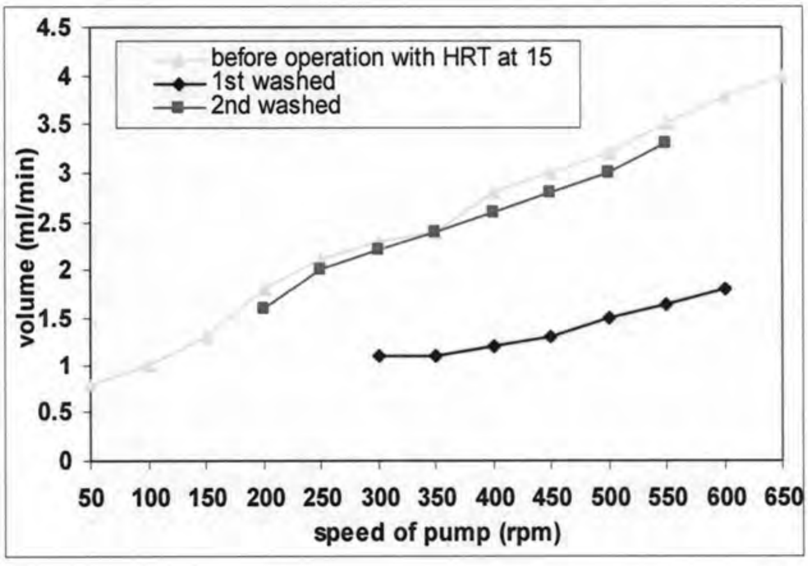


**Figure 9.25** Variation in permeability of the mineral membrane before and after 4 days of operation with the HRT at 15 hours.

The MBR process was found to be useful when a long solid retention time is required and physical retention and subsequent microbial activity in MBR are maximized (Knoblock et al., 1994). This process provides benefits over conventional biological wastewater treatment in terms of high effluent quality, reduced sludge wasting and production and improved biological degradation. Along with biological degradation, the membrane itself physically removes some of the contaminants (Klatt and LaPara, 2003).

In this study, the performance of a laboratory-scale side-stream bioreactor treating the synthetic melanoidins-containing wastewater was investigated. The efficiency of membrane coupled bioreactor systems at different hydraulic retention times of 40, 20 and 15 hours was studied some-days experiments. The study showed that COD, as well as color removal efficiency were dependent on HRT. The operation at longer HRT has shown a slight benefits for treatment of the synthetic melanoidins-containing wastewater. In any case, the HRT must be higher than 20 hours otherwise clogging may occur rapidly.

Unfortunately, because of time spent for each experiment, it had not enough time to try again the same biological conditions with different hydraulic conditions, specially the cross-flow velocity in the tubular membrane. It seems that if some fouling occurred, it is not only irreversible so that tangential velocity should limit it. Moreover it would be convenient to test a device with the ability to measure and increase the transmembrane pressure.

Hydraulic retention time (HRT) plays an important role in the removal of pollutants in conventional bioreactors. In case of MBRs, it is a common observation that with the increase of HRT, some pollutants, the removal efficiency of the system increases (Tay et al., 2003). This retention increases residence time and allows the biomass to degrade these recalcitrant compounds. Unfortunately, these same compounds are thought to lead to membrane fouling. Similarly, the present study shows significant improvement in COD and color removal efficiency were observed with the longer HRT. Moreover, the increase of HRT showed a prolonging of membrane fouling limitation.

Solid retention time (SRT) is one of the most critical parameter for MBRs design as SRT affects the treatment process performance, aeration tank volume, sludge production, and oxygen requirements. The longer retention time of all biomass within the MBR over the conventional biological wastewater treatment allowed for the bacterial consortium MMP1 to acclimatize and sustain its decolorization in the MBR conditions. However, in this study, the color and COD removal efficiency of the synthetic melanoidins-containing wastewater was relatively low due to the presence of recalcitrant organics and growth inhibiting substances, which may be retained by the membrane. Furthermore, COD removal efficiency was not significantly affected by the increase in bacterial concentration. These results showed that for the chosen conditions, the color concentration of treated water requires a post-processing wastewater treatment system in order to eliminate the remaining color, but more probably an optimization of the operating conditions of the MBR will lead to more convenient results, especially a real acclimatization of the biomass in MBR for 2 or 3 times the SRT..

Membrane fouling depends on the characteristics of membrane materials. In this study, fouling of membranes occurred with the experiments of polysulfone hollow-fiber membrane and tubular membrane with HRT of 15 h. Although it is difficult to establish a general rule about membrane fouling in MBRs, fouling are strongly influenced by three factors: membrane characteristics, operating conditions and biomass characteristics (Le-Clech, 2003). However, chemical cleaning of the membrane with the dilute bases and acidic detergents was found to produce an acceptable effect in terms of cleaning time and recovered flux.