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# Removal of Colored Substances from Molasses Waste Water by Biological Treatment Systems Combined with Chemical Treatment

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**Abstract**

In this study, we attempted to combine a biological treatment process which used Bi-Act SCBA system (SCBA) and chemical treatment process to remove chemical impurities such as COD, BOD5 and nutrients as well as colored substances from the molasses waste water (MWW). In the pilot plant experiment, SCBA unit A (SCBA-A) was used for the pre-aeration and uniformity of the MWW before biological treatment. The sludge volume (SV30) was about 50 ml/l in the aeration unit of the SCBA-A. The COD and colored substances could not be removed in this step. However, in both SCBA-B and SCBA-C, $SV_{30}$ increased up to 350-400 ml/l. At the same time, approximately 44.0% and 22.9% of COD of the effluents from SCBA-B and SCBA-C were removed, respectively. On the other hand, the removal of colored substances in SCBA-B and SCBA-C (about 25.0 and 13.3%) was not appreciable. However, the colored substances in the MWW passing through SCBA-B and SCBA-C could be easily precipitated by chemical agents compared with the original MWW. About 93% of the colored substances of the effluent from SCBA-C could be removed in the chemical precipitation step, while the colored substances in the original MWW could not be precipitated.

**Discipline:** Food
**Additional key words:** melanoidin, molasses waste water, Bi-Act SCBA, chemical precipi tation

## Introduction

Many by-products such as molasses, bagasses and fiber cake are produced from cane sugar factories. Among them, molasses is the most important product[4,10] because molasses has a high commercial value due to its use as a carbon source for fermentation industries, biofertilizer and feed for domestic animals[5]. However, the use of molasses as a raw material for fermentation industries is associated with the presence of a large amount of colored substances which remain in the fermentation residue after recovery of the products. The main colored substance, melanoidin, can hardly be decomposed by usual biological treatment processes[1,11] and accounts for the high COD value, which is a major problem for pollution control[5].

In Thailand, all the alcohol-producing factories use molasses as raw materials and discharge molasses waste water (MWW) accounting for about 10 times the amount of alcohol produced. Several processes[7–9] were used for treating the MWW. The use of MWW as feed for aquatic organisms is not suitable economically due to the small volume used. For biofertilizer use, the quality is not as high as that of other biofertilizers or chemical fertilizers (it may be similar to that of soil conditioners). Several alcohol factories have attempted to treat MWW by anaerobic methods such as methane fermentation, anaerobic pond or facultative anaerobic pond, followed by aerobic treatment such as activated sludge, aerated lagoon or oxidation pond[3,6]. However in these treatment processes, the colored substances of MWW still remained and the COD content in the treated waste water was higher than the standard value authorized by the Ministry of Industry, Thailand. Presently, treatment processes such as chemical precipitation, chemical adsorption or carbon adsorption are used for the removal of the colored substances. However, color removal by the above processes still has disadvantages due to the high operation cost, high consumption of chemicals, fluctuation of the color removal efficiency and the high volume of solid waste produced.

Against this background, we applied biological and chemical processes to MWW from the anaerobic pond of the alcohol factory to remove colored substances, COD and $BOD_5$ with high efficiency and at a low cost. The experiments on the biological process were carried out on a pilot plant scale, using the Bi-Act SCBA system[12] which is characterized by low energy consumption and high efficiencies for aeration and mixing in the aeration tank. In this paper, we report the results of the experiments.

## Materials and methods

**Bi-Act SCBA unit:** Three units of Bi-Act SCBA (SCBA)[12] supplied by Uni San Pol. Co. Ltd. were used in these experiments. The scheme of the processes shown in Fig. 1 was as follows: 1 unit of 10 $m^3$ storage tank, 2 units of 10 $m^3$ SCBA (unit A and unit B), 1 unit of 4 $m^3$ SCBA (unit C) and 2-tanks for 1 $m^3$ of nutrient supply. This pilot plant was installed in the waste water treatment plant of Sang Som Distillery Co. Ltd., Nakhon Pathom Province, Thailand.

**MWW:** The MWW used in this experiment was collected from the anaerobic pond of Sang Som Distillery Co. Ltd.

**Supply of nutrients:** Cassava flour was supplied as a nutrient for increasing the $BOD_5$ content in the MWW. Twenty kg of cassava flour was fermented for 1 week in the S1 tank as shown in Fig. 1. The supernatant from S1 tank was transferred to S2 tank before being fed to the SCBA system.

**Start-up procedure and operation of the pilot plant unit:** The concentrated sludge suspension (MLVSS = 10,000 mg/l) from the central waste water treatment plant of BANG-PA-IN Industrial Estate, Ayuthaya, Thailand, was used as the inoculum for starting this pilot plant. The start-up procedure was performed as follows: First, 4, 4 and 2 $m^3$ of concentrated sludge suspensions were put in SCBA-A, SCBA-B and SCBA-C (aeration tank), respectively. Second, water (softened water) was added in all 3 units up to the optimum level and the system was operated without influent feeding overnight. Thereafter, the MWW from the storage tank was fed

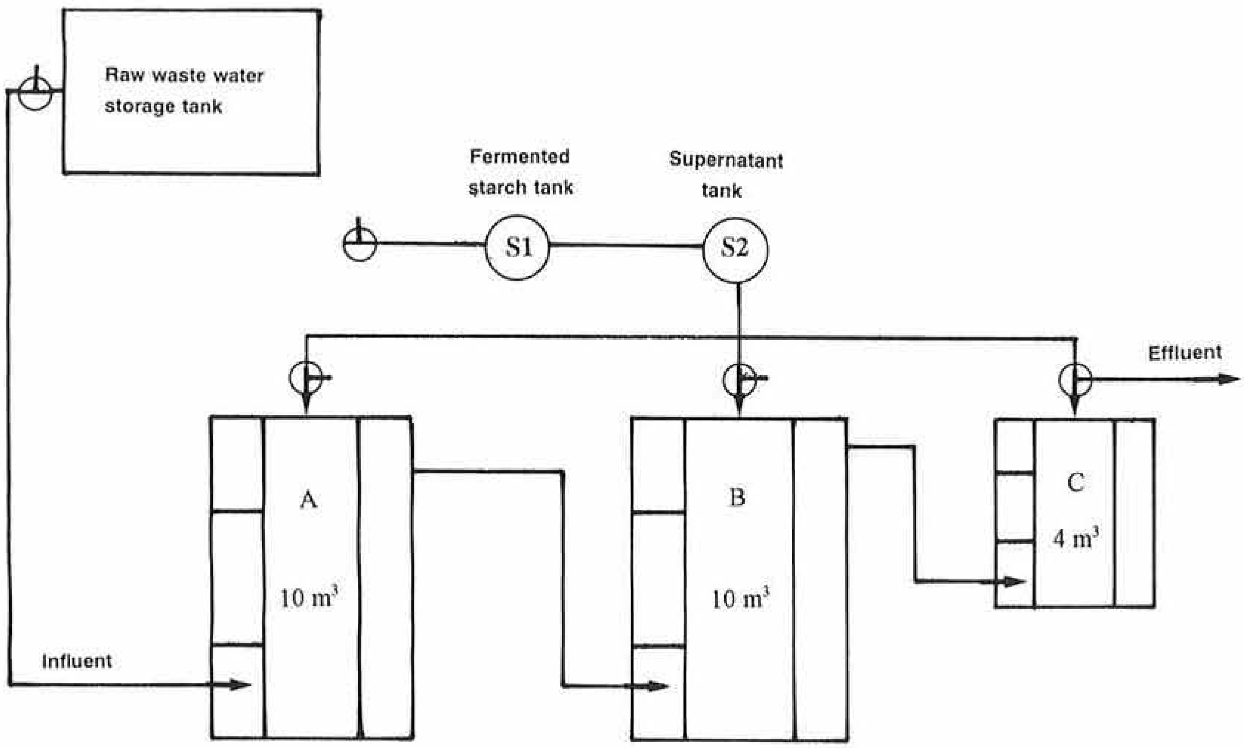


Fig. 1. Scheme of the pilot plant of Bi-Act SCBA system

into the SCBA system at the flow rate of 2 $m^3$/day. At the same time, the nutrients from tank $S_2$ were fed into SCBA-B at the flow rate of 2 $m^3$/day. The system reached the steady state after 2 weeks' operation. The flow rate of the influent from the storage tank slowly increased up to 4 $m^3$/day within 1 week. Also the flow rate of water (underground water or river water) used instead of the nutrient solution increased up to 4 $m^3$/day within 1 week. The MLSS, $SV_{30}$ and pH of the system were monitored until the system became steady. The effluent from the clarifier of each SCBA unit was taken for the analysis of $BOD_5$, COD, SS, TKN, TP, pH and color intensity. Also the mixed liquid from the aeration section of each SCBA unit was collected for measuring the pH and $SV_{30}$ during the period February–December 1996.

**Color removal by chemical precipitation:** The effluent from the clarifier of SCBA-C was collected and used for the determination of optimum concentrations of chemical agents to remove the colored substances. The chemical agents used for precipitation of the colored substances were $FeCl_3$, $Al_2(SO_4)_3$ and sodium hydroxide. The effluents from each SCBA unit were used to determine the optimum color removal efficiency. All the experiments were performed on a laboratory scale. A certain amount of $FeCl_3$ (range of 1 to 8 g) or $Al_2(SO_4)_3$ (range of 4 to 32 g) was added into 1,000 ml of the effluent from SCBA-C. Thereafter, the mixtures were adjusted to pH 7 by the addition of sodium hydroxide solution. The supernatants were collected for the determination of the color intensity, pH and COD.

**Assay of chemical composition of the waste water:** The $BOD_5$, COD, TKN, TP and $SV_{30}$ were determined by a standard method of analysis[2].

**Estimation of color intensity of the waste water and removal yield:** The sample was diluted with 0.1 M acetate buffer solution (pH 6.0) after centrifugation at 6,000 × g for 15 min and the color intensity of the diluted solution was measured at 475 nm with a spectrophotometer (LKB, model Biochrom Ultra-space 2, England). The percentage of color removal was expressed as the color intensity of the waste water treated against that of original waste water. The removal yield was expressed as the degree of decrease in the absorbance at 475 nm against the initial absorbance at the same wavelength.

## Results

**Chemical properties of the MWW:** The MWW collected from the anaerobic pond of the waste water treatment plant of Sang Som Distillery Co. Ltd. for this experiment still contained a high level of chemicals and showed a high color intensity as indicated in Table 1. Chemical properties such as COD, $BOD_5$, contents of total solids and total volatile solids were 33,643, 3,500, 42,250 and 23,180 mg/l, respectively. The color intensity was about 33–35 (optical density at 475 nm).

**Start-up of the SCBA system:** By using the concentrated sludge solution from the central waste water treatment plant of BANG-PA-IN Industrial Estate, the microorganisms in both SCBA-B and SCBA-C could easily grow. The $SV_{30}$ in the aeration tanks of SCBA-B and SCBA-C reached values of 300 and 350 ml/l, respectively within 2–3 weeks, while the level of $SV_{30}$ was low (~50 ml/l) in the aeration tank of SCBA-A. The $SV_{30}$ in the aeration tank of both SCBA-B and SCBA-C remained at the levels of 300 and 350 ml/l during the treatment as shown in Fig. 2.

**Table 1. Chemical properties of MWW from anaerobic pond of Sang Som Distillery Co. Ltd., Thailand**

| Properties | Value (mg/l)[a] |
|---|---|
| pH | 7.91 |
| COD | 33,643 |
| $BOD_5$ | 3,500 |
| Alkalinity as $CaCO_3$ | 11,100 |
| Total solids | 42,250 |
| Suspended solids | 3,575 |
| Settled solids | – |
| VFA | 814 |
| Phosphate | 0.0289 |
| Sulfate | 286 |
| TKN | 1,280 |
| Potassium | 7,875 |
| Calcium | 2,775 |
| Sodium | 115 |
| Total volatile solids (TVS) | 23,180 |
| Color intensity (optical density at 475 nm) | 33–35 |

a): Average value during the period April–December 1996.

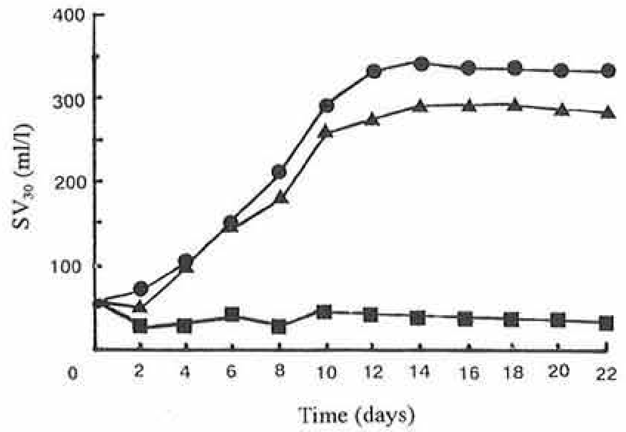


Fig. 2. $SV_{30}$ profiles in the aeration tank of each SCBA unit in the start-up of the system
■ : SCBA-A, ▲ : SCBA-B, ●: SCBA-C.

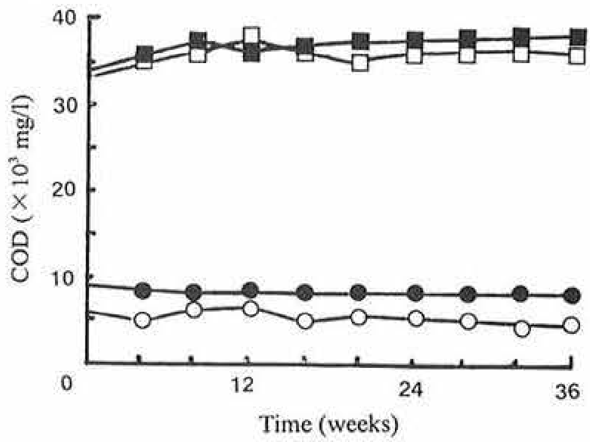


Fig. 3. COD profiles of the influents and effluents of each SCBA unit during the continuous operation
■ : Influent of SCBA-A, □ : Effluent from SCBA-A, ●: Effluent from SCBA-B, ○: Effluent from SCBA-C.

**Continuous treatment by SCBA system:** At 3 weeks after the start-up step, the system reached a steady state with an influent flow rate of 4 $m^3$/day and diluted water was fed into the SCBA-B at the rate of 4 $m^3$/day. The removal percentage of the impurities of the waste water (COD, $BOD_5$, SS and TKN) was high in effluents from SCBA-B and SCBA-C as shown in Table 2, while in the SCBA-A system, the impurities could not be removed effectively. The COD content in the effluent from both SCBA-B and SCBA-C decreased to 44.0 and 22.9%, respectively. Other impurities such as SS, TKN and total phosphate were also removed. For color removal, in SCBA-A the level was only 4.0%, while in the SCBA-B and SCBA-C systems, the removal of the colored substances reached values of 25.0 and 13.3%, respectively, as shown in Table 2. The system could be operated smoothly with a constant COD concentration of the effluents from each SCBA unit up to 36 days, as shown in Fig. 3.

**Color removal by chemicals:** The effluent from the clarifier of SCBA-C was used as the color solution in the chemical precipitation step. Various concentrations of $FeCl_3$ in the range of 0–12% were added to the effluent and the mixed solution was adjusted to pH 7.0. The results are shown in Fig. 4. Addition of $FeCl_3$ at a concentration of 6% in the solution resulted in the highest color removal

**Table 2. Chemical properties of influent and effluent of each SCBA unit**

| Properties[a)] | Influent | | | Effluent | | | Removal (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | A | B | C | A | B | C |
| pH | 8.20 | 8.50 | 8.50 | 8.64 | 8.50 | 8.50 | – | – | – |
| $SV_{30}$[b)] (ml/l) | – | – | – | 50–100 | 300 | 350 | – | – | – |
| Color intensity at 475 nm | 33.5 | 10.0 | 7.5 | 32.15 | 7.5 | 6.5 | 4.0 | 25.0 | 13.3 |
| COD (mg/l) | 33,643 | 10,000–15,000 | 6,000–8,000 | 32,868 | 6,000–8,000 | 5,000–5,800 | 2.3 | 44.0 | 22.9 |
| $BOD_5$ (mg/l) | 3,500 | 1,800 | 200 | 2,500 | 200 | 70 | 28.6 | 88.9 | 65.0 |
| SS (mg/l) | 3,500 | 1,300 | 450 | 3,500 | 450 | 200 | – | 65.4 | 55.6 |
| TKN (mg/l) | 1,280 | 700 | 300 | 1,250 | 300 | 200 | 2.3 | 57.1 | 33.3 |
| Total phosphate (mg/l) | 0.29 | 0.08 | 0.02 | 0.17 | 0.02 | 0.02 | 41.4 | 75.0 | – |

a): Average value during the April–December 1995 experiment.
b): $SV_{30}$ of mixed liquid in the aeration tank of SCBA unit.

efficiency. Various concentrations of $Al_2(SO_4)_3$ solution in the range of 8–30% were also added to the effluent and the mixed solution was adjusted to pH 7.0. The results are shown in Fig. 5. Addition of $Al_2(SO_4)_3$ at a concentration of 20% in the solution was adequate for color removal.

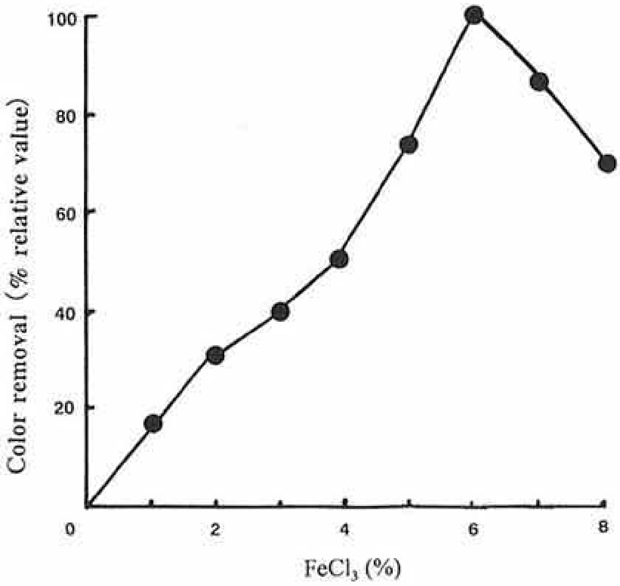


Fig. 4. Removal of colored substances from the effluent of SCBA system by the addition of various concentrations of $FeCl_3$ solutions
The $FeCl_3$ solution was added to 500 ml of effluent from the clarifier of SCBA-C and final concentrations of $FeCl_3$ in the mixture were 1, 2, 3, 4, 5, 6, 7 and 8%. Thereafter, the mixtures were adjusted to pH 7.0.


Fig. 5. Removal of colored substances from the effluent of SCBA system by the addition of various concentrations of $Al_2(SO_4)_3$ solutions
The $Al_2(SO_4)_3$ solution was added to 500 ml of effluent from the clarifier of SCBA-C and final concentrations of aluminum in the mixture were 8, 12, 16, 20, 24, 28 and 32%. Thereafter, the mixtures were adjusted to pH 7.0.

On the other hand, 3 effluents from SCBA-A, SCBA-B and SCBA-C were tested for the removal of color by the addition of $FeCl_3$ (6%) or $Al_2(SO_4)_3$ (20%). After adjustment of the pH to 7.0, the colored substances in the effluents from SCBA-B and SCBA-C were easily removed at the rates of about 28 and 93%, respectively, while those from SCBA-A could not be removed as shown in Table 3. The removal rate by the addition of $FeCl_3$ and $Al_2(SO_4)_3$ was almost the same.

## Discussion

We carried out experiments to remove chemicals such as COD, $BOD_5$, TKN, total phosphorus and colored substances by using the SCBA system combined with the chemical treatment process. The SCBA system, which is a kind of activated sludge system, consisted of a new compact unit for biological treatment used in both domestic and industrial waste water treatment plants in Thailand. The rotary drum in the aeration tank of the system was specially designed, and the mixed liquid in the aeration tank was fully supplied with air and completely mixed.

Actually, each unit of SCBA displayed several characteristics. The chemical properties of the effluent from SCBA-A were not different from those of the influent. Sludge (MLSS) generation in the aeration tank was minimal and there was a high concentration of toxic substances in the waste water[9]. The effluent from SCBA-A was diluted with water and transferred to SCBA-B. In SCBA-B, the $BOD_5$ and COD were removed easily as shown in Table 2. The sludge concentration in the aeration tank ($SV_{30}$) increased up to 400–500 mg/l, reflecting normal conditions of activated sludge process[3,6]. In SCBA-C, the results were the same as in SCBA-B. By the SCBA system, the colored substances in the influents of SCBA-B and SCBA-C could be removed at percentages of 25.0 and 13.3%, respectively.

For color removal by the chemical treatment process, the effluent from SCBA-A was hardly precipitated by $FeCl_3$ and $Al_2(SO_4)_3$ even when a high concentration of chemicals was used. However, the color of effluents from both SCBA-B and SCBA-C could be easily removed and the percentages of color removal were 28 and 93%, respectively, as shown in Table 3.

**Table 3. Comparison of percentage of color removal by chemical precipitation in various kinds of effluents**

| Chemical treatment process | Color intensity at 475 nm | | |
|---|---|---|---|
| | Effluent from SCBA-A | Effluent from SCBA-B | Effluent from SCBA-C |
| Before treatment | 33.0 | 10.0[a)] | 7.2 |
| After treatment | 33.0 | 7.2 | 0.2 |
| Removal (%) | 0 | 28 | 93 |

a): The effluent from SCBA-A (color intensity of 33.0 at 475 nm) was diluted with water (final color intensity of 10.0 at 475 nm) before being sent to the SCBA-B as influent.

Based on the results obtained, the SCBA system was found to be suitable for the treatment of MWW as well as the hitherto known activated sludge system[3,6,8]. Furthermore, the SCBA system enabled to remove colored substances in comparison with the activated sludge system. Namely, the colored substances could be removed at a percentage of about 10% by this system directly and about 90% of the colored substances remaining in the effluent from the system were easily precipitated by treatment with 6% $FeCl_3$ or 20% $Al_2(SO_4)_3$. The reason for easy precipitation could not be determined. It is suggested that the colored substances may have changed or that their structure may have been modified during the passage through the SCBA system.

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