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Granular activated carbon-biofilm configured sequencing batch reactor treatment of C.I. Acid Orange 7

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Abstract

The aim of this study is to investigate the mineralization of C.I. Acid Orange 7 (AO7) by biological process in oxygen limited condition under GAC-biofilm configured sequencing batch reactor (SBCR) operation. The granular activated carbon (GAC) used was immobilized with azo dye-degrading microbes through attachment by immersing the GAC into anaerobic bioreactor treating dye-containing wastewater for more than 200 days. The SBCR system was fed with 2 l of AO7-containing wastewater and was operated in FILL, REACT, DRAW and IDLE periods in a time ratio of 3:20:0.45:0.15 for a cycle time of 24 h. Nearly complete mineralization of AO7 was achieved with the biological system working at initial AO7 concentration of 625 mg/l, dissolved oxygen (DO) below 0.25 mg/l and without the presence of external carbon sources. Reductive environment was well developed in the phases with the addition of external carbon sources, and this had improved the decolorization rate but deteriorated chemical oxygen demand (COD) removal efficiency.

Keywords: Acid Orange 7; Granular activated carbon; Decolorization; Biological process; Biofilm

1. Introduction

Dye stuffs are major constituents of the wastewater produced from many industries related to textile, paint and varnishes, ink, plastics, pulp and paper, cosmetics, tannery etc., and also to the industries that produce dyes. Colored dye effluents pose a major threat to the surrounding ecosystem [1]. Methods for dealing with textile wastewater consist of various biological, physical and chemical treatment methods that can be applied separately or combined [2–5].

Azo dyes are considered to be resistant to attack by aerobic microorganisms and not amenable to aerobic effluent treatment process. The decolorization of azo dye by microorganisms invariably starts by reductive cleavage of azo bond under anaerobic conditions [5,6]. This generates aromatic amines that are not degraded under anaerobic conditions [7] and tend to accumulate to toxic levels [5,8]. However, the aromatic amines are readily further mineralized under aerobic conditions. There are some reports on complete degradation of sulfonated aromatic amines by enriched bacterial communities [9–11]. The only disadvantage of the anaerobic biological techniques, using conventional methods (e.g. stirred tank reactors), is the need for long hydraulic residence times due to the low growth yields of the anaerobic bacteria as a consequence of the low energy yields; usually, less than 10% of the substrate carbon can be incorporated into cell matter, as opposed to around 50% with aerobic bacteria. The above disadvantage can be overcome by the utilization of methods such as immobilization techniques which could retain high densities of specialized microorganisms [12–14].

A very promising method to obtain high concentrations of active biomass is immobilization of microorganisms by colonization on a porous material [15]. There are two types of immobilization technique: attachment and encapsulation.

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Immobilization of microflora on granular activated carbon (GAC) particles as biofilm results in high biomass hold up, which enables the process to be operated significantly at higher liquid throughputs and organic loading rate. GAC as adsorptive medium/carrier materials acts as buffer to reduce the concentration of toxic chemicals during process operation, thereby providing advantage for the treatment of low biodegradable industrial wastewater containing recalcitrant compounds such as dye [16,17]. The objective of this study is to investigate the feasibility of using GAC-biofilm configured sequencing batch reactor (SBCR) in color and organic substrates removals with and without co-substrates. Besides, the color removal by adsorption and biodegradation processes by the use of virgin GAC, living biofilm-GAC and dead biofilm-GAC was compared.

2. Materials and methods

2.1. GAC-biofilm sequencing batch reactor (SBCR)

A SBCR system with dimensions $20 \times 20 \times 20$ cm ($L \times W \times H$) was used to simulate the biological process (Fig. 1). The SBCR system was divided into two compartments, namely GAC compartment and Multipurpose (MP) compartment. The GAC compartment was filled with 2.3 l of granular activated carbon (GAC). The GAC used was immobilized with azo dye-degrading microbes by immersing the GAC into anaerobic sequencing batch reactor (ASBR) for more than a month. The azo dye-degrading microbes were immobilized on GAC through attachment. A mixer was installed in the MP compartment to provide efficient mixing and to control the dissolved oxygen (DO) in the SBCR system, which was recorded by a DO meter. Also, a pH meter and a redox meter were installed in MP and GAC compartments, respectively, to monitor the pH and ORP values in the biological system.

The SBCR system was filled with 2 l of C.I. Acid Orange 7 (AO7)-containing wastewater daily and was operated in FILL, REACT, DRAW and IDLE periods in the time ratio of 3:20:0.45:0.15 for a cycle time of 24 h. The temperature of SBCR system was maintained at 25 ± 1 °C. During FILL and REACT periods, the partially treated AO7-containing wastewater, which flows underneath from GAC compartment to MP compartment will be recycled to the GAC compartment with a flow rate of 20 ml/min for further treatment before being discharged after 24 h of treatment time. Sample was collected during DRAW periods and analyzed for AO7, COD and SS concentrations.

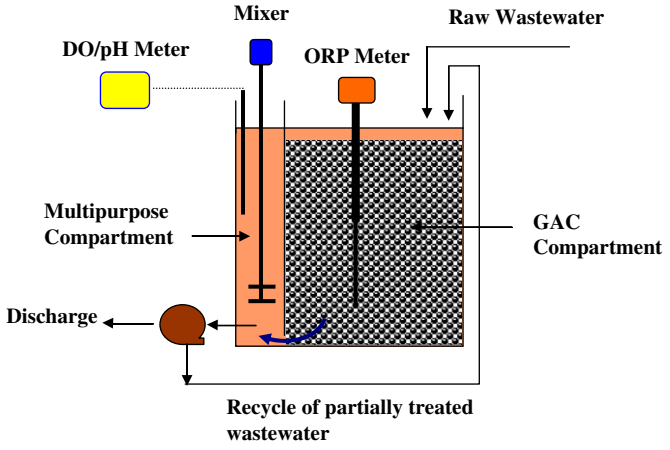

Fig. 1. Schematic diagram of granular activated carbon-biofilm configured sequencing batch carbon reactor (SBCR).

The treatment parameters studied for the present biological system are shown in Table 1. From phase 1 to 5, the SBCR system was operated with increasing AO7 concentration from 125 to 625 mg/l without the presence of external carbon sources. In the following phases, external carbon sources and nutrients were added into the SBCR system. The carbon sources and nutrients (base mixed solution) used consisted of bacto-peptone (188), sucrose (563), NH_4Cl (344), $MgSO_4$ (49), $FeCl_3$ (11.3) and KH_2PO_4 (318) giving a COD of 800–850 mg/l. The DO in SBCR system (MP compartment) was maintained below 0.25 mg/l in phases 1–7, whereas in phase 8, the DO was increased up to 3.5 mg/l to investigate the effects on treatment performance in SBCR system.

2.2. Chemicals and analytical methods

C.I. Acid Orange 7 ($C_{16}H_{11}N_2Na_4S$) and GAC were supplied by Tokyo Kasei Kogyo Co. Ltd. and Wako Pure Chemical Industries Ltd., respectively. All other chemicals were of analytical grade. The AO7 concentration was estimated from the standard curve of dye concentration versus optical density at its maximum absorption wavelength ($\lambda_{max} = 480$ nm) using a UV–vis spectrophotometer (UV-1200, Shimadzu). The chemical oxygen demand (COD) and suspended solids (SS) were determined according to Standard Methods. In the measurements of dissolved COD and color, samples were prepared by filtering through a membrane filter of 0.45 μm.

2.3. Color removal among virgin GAC, living biofilm-GAC and dead biofilm-GAC

This study was conducted to determine the ratio of adsorption and biodegradation in AO7 removal by virgin GAC and GAC from SBCR system. An amount of 15 g virgin GAC was put into a beaker (Beaker A) for AO7 adsorption study.

Table 1
Operating conditions

Phase	Time (day)	Initial COD (mg/l)	Initial AO7 (mg/l)	Base mixed	MP comp. DO (mg/l)
1	0–15	250	125	No	<0.20
2	16–30	450	250	No	<0.20
3	31–45	650	375	No	<0.20
4	46–58	900	500	No	<0.20
5	59–73	1100	625	No	<0.20
6	74–88	1350	625	Yes (10 ml)	<0.20
7	89–103	2500	625	Yes (50 ml)	<0.20
8	104–120	2500	625	Yes (50 ml)	~3.50

To determine the adsorption ratio by dead biofilm-GAC, 15 g of GAC was collected from SBCR system, washed with RO water and then dried in an oven at 105 °C (Beaker B). On the other hand, another 15 g of GAC was collected from SBCR system and put into another beaker (Beaker C) to evaluate the AO7 removal by living biofilm-GAC. Then, 100 ml of AO7 with concentration 150 mg/l was filled into the beakers and samples were collected at certain time intervals to determine the balance AO7 concentration. The samples were filtered with membrane filter of 0.45 μm and then measured with the UV–vis spectrophotometer (UV-1200, Shimadzu) at λ_{max} 480 nm.

3. Results and discussion

3.1. Treatment performance of SBCR system

As shown in Table 1, the AO7 concentration in feed solution was increased from 125 to 625 mg/l during phases 1–5. Since no external carbon source was added into the feed solution, all of the COD (organic matter) was contributed by AO7. As shown in Fig. 2, the average COD removal by SBCR system was about 88%, which indicated the effectiveness of the SBCR system in the mineralization of azo dye AO7-containing wastewater. With regard to color removal, 100% decolorization was achieved in the first 2 phases and this value slightly dropped in the following phases (phases 3–5). Although without the addition of external carbon source, a highly reductive environment, which is required for the reduction of azo bond, has been developed in the bioreactor (Fig. 2(c)). This could be due to the metabolism of aromatic amines by microbes, which generated reducing equivalents for the reduction of azo bond in AO7. Isık and Sponza [18] had reported that the complete decolorization of Congo Red under co-substrate free operation could be attributed to total aromatic amine (TAA) metabolism which may provide the electrons required for the cleavage of azo bond in Congo Red exist in the UASB reactor. Besides, the endogenous substrates from biomass would supply the reducing equivalents needed for the reduction of azo bond. Ong et al. [19] had reported that over 95% of decolorization was achieved with acclimatized microbes in anaerobic sequencing batch reactor with 600 mg/l of AO7 concentration and co-substrate free condition. The MLSS in the anaerobic reactor decreased gradually from about 7200 to 4700 mg/l at the end of the experiments, which indicates that the endogenous lysis of sludge was carried out by anaerobic microbes in order to generate the reducing environment in the bioreactor for decolorization process [19].

The ORP values in SBCR system were in the range of −300 to −400 mV in the first 40 days of operation, whereas it dropped to an average of −120 mV in phases 3–5 (Fig. 2(c)). The slight drop in color removal efficiency corresponding to less reductive environment in the bioreactor showed the importance of sustaining reductive condition in the bioreactor for efficient color removal. As a result, 10 ml of base mixed solutions (equivalent to 250 mg COD/l) was added into the feed solution to try to enhance the reducing

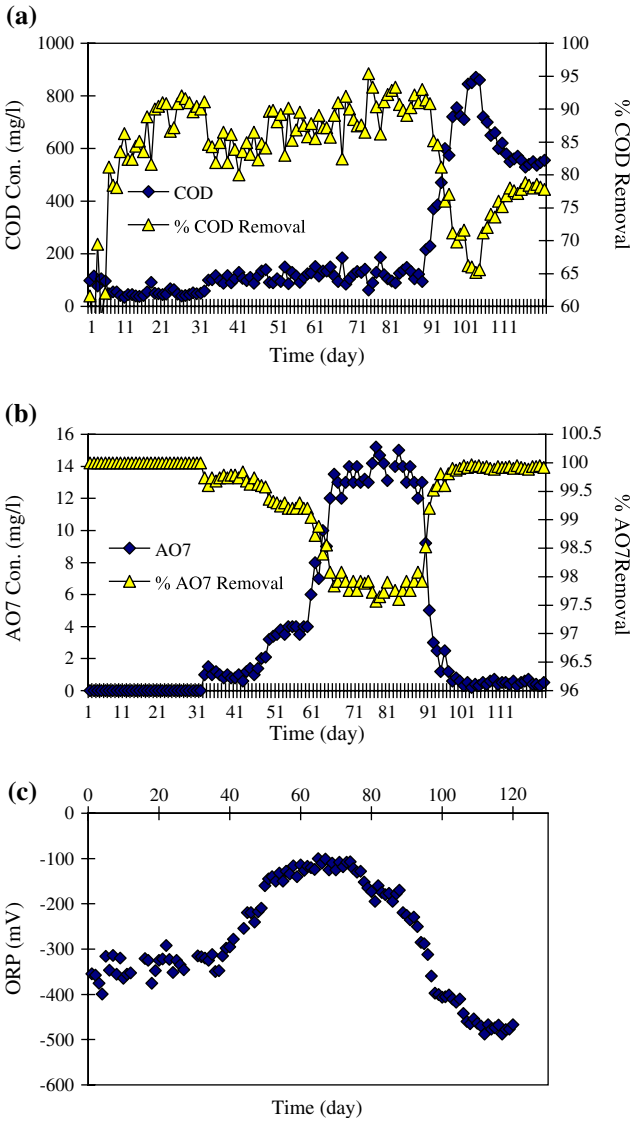

Fig. 2. (a) COD, (b) AO7 and (c) ORP monitoring in SBCR system.

equivalent for azo dye reduction. This action had caused slight improvement in the reductive condition in the bioreactor as shown by the ORP values. However, the color and COD removal efficiencies did not show any improvement but were maintained at 98 and 90%, respectively.

The dosage of base mixed solution was increased in phase 7 (contributed to total initial COD of 2500 mg/l) to investigate the effects of high loading of organic matter in SBCR system. This had improved the reductive condition in the SBCR system as shown by lower OPR value with an average of −480 mV and consequently improved the color removal efficiency to 99.9% or about 0.5 mg/l in treated effluent. The oxidation of external carbon sources (sucrose and bacto-peptone) generated enough reducing equivalents to sustain reductive environment in the SBCR system for azo bond reduction. Georgiouet al. [20] have reported that anaerobic digestion of azo-reactive-dye aqueous solutions in a batch-mode reactor utilizing acetic acid as an external supply of substrate (electron-donor) and acetate-consuming bacteria lead to the complete decolorization of

the dye solutions in 4–5 days of experiment. The presence of external carbon sources (co-substrate) is favorable for the reduction of azo dyes because the oxidation of these compounds produces electrons used for the formation of reduced co-factors (FAD, FMN, and NADH) [5].

On the other hand, the increase of base mixed solution dosage had caused significant deterioration of COD removal, dropping to 65% or about 800 mg COD/l in treated effluent. To enhance COD removal, the DO in MP compartment was increased by aeration to about 3.5 mg/l in phase 8. The increase of COD removal up to 80% indicated that the DO in SBCR system was insufficient to mineralize the organic substrates. The increase of DO did not show any effects on color removal by the biological system. Other researchers have reported that during the dye reduction stage, if the extracellular environment is aerobic, the high-redox-potential electron acceptor, oxygen, may inhibit the dye reduction mechanism. This is because the electrons liberated from the oxidation of electron donors by the cells are preferentially used to reduce oxygen rather than the azo dye, and the reduction product, water, is not a reductant. Also, the postulated intermediates of the dye reduction reaction, which include the hydrazine form of the dye and the azo anion free radical form of the dye, tend to be re-oxidized by molecular oxygen [21–23]. The high removal efficiency with regard to color and COD by SBCR system could be due to the mix of anaerobic and aerobic microbes in the bioreactor. By monitoring the DO in GAC compartment, it was found that the DO values on the surface, medium and bottom were about 1.2, 0.4 and 0.0 mg/l, respectively. In the case of ORP monitoring, the ORP values on the surface, medium and bottom GAC compartment were about −120, −311 and −470 mV, respectively. The high reductive and almost oxygen-free condition at the bottom GAC compartment might be suitable for the growth of anaerobic microbes, which are responsible for azo bond reduction. Meanwhile, low reductive and high DO condition at the top level of GAC compartment might encourage the development of aerobic microbes responsible for organic matter removal. The high treatment performance in terms of color and organic matter removal by oxygen limited condition for SBCR system in one bioreactor definitely would reduce the operation cost in textile wastewater treatment plant. However, further study would be carried out by using real textile wastewater in the near future.

3.2. Comparison of color removal among virgin GAC, living biofilm-GAC and dead biofilm-GAC

The results of this experiment are illustrated as concentration decay curves over 50 h periods (Fig. 3). The virgin GAC demonstrated complete decolorization within 4 h attributing to high adsorption capacity of GAC. The maximum adsorption capacity of virgin GAC was about 120 mg/g according to Langmuir isotherm model. As mentioned earlier, the GAC used in the biological reactor was previously employed in sequential anaerobic–aerobic SBR system [24] and immersed in ASBR for more than a month. As a result, the original adsorption capacity of GAC should be decreased

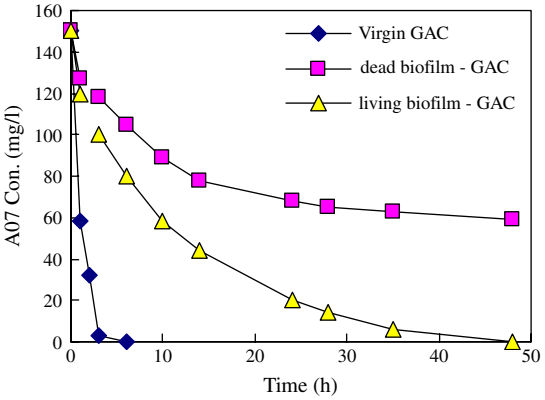

Fig. 3. Comparison of AO7 removal among virgin GAC (Beaker A), dead biofilm-GAC (Beaker B) and living biofilm-GAC (Beaker C).

tremendously or saturated with azo dye and organic materials. The spent GAC exhibited about 4–8 mg/g of maximum adsorption capacity based on Langmuir isotherm model. In the case of biofilm-GAC, it was observed that after an initial period, the living biofilm-GAC reduced color more effectively than the dead biofilm-GAC. The almost similar reaction rate by biofilm-GAC in the initial stages of the experiments (1 h) was probably due to the adsorption process. The subsequent increase in living biofilm-GAC over dead biofilm-GAC was a result of the combination of adsorption and biological degradation of dye. About 100 and 60% color removal was observed in living biofilm-GAC and dead biofilm-GAC, respectively, after 50 h of experiment.

4. Conclusions

In the phases (phases 1–5) without the addition of external carbon sources, 100% color removal was achieved in the first 2 phases and this then slightly dropped in the following phases (phases 3–5). On the other hand, the average COD removal by SBCR system was about 88%, which indicated the effectiveness of the studied system in the mineralization of the azo dye AO7-containing wastewater. The addition of external carbon sources (phase 7) improved the decolorization rate but deteriorated COD removal efficiency. Besides, this had improved the reductive condition in the SBCR system as shown by lower OPR value with average −480 mV, which is important for azo bond reduction. In phase 8, the increase of DO by aeration in the MP compartment had resulted in the enhancement of the efficiency of COD removal up to 80%. The increase of DO did not show any effects on color removal by the biological system. It is believed that the mix of anaerobic and aerobic microbes at different levels in the bioreactor played an important role in the removal of both color and organic matter.

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