

Removal of Organic Matters and Phenol Compounds from the Waste Water by Using Granular Activated Carbon - Sequence Batch Reactor System

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Abstract

The studies were concerned in removal of organic matters together with phenol compounds from the synthetic waste water by using Granular Activated Carbon-Sequencing Batch Reactor System (GAC-SBR). The synthetic waste water used in this experiment contained glucose as COD about 3,400 mg/l and phenol about 1,000 mg/l.

The maximal phenol and COD absorption abilities of GAC in SBR system were 240 and 761 mg/g of GAC, respectively while the maximal phenol and COD absorption abilities of GAC in the normal condition were 213 and 685.1 mg/g of GAC, respectively. The COD and phenol absorption yields of GAC were the highest at the first day of incubation (about 60% and 50% respectively) and were lost after 3 days incubation entirely. The suitable amount of GAC supplemented in the SBR system was 1,000 mg/l. At the condition of 1 day of hydraulic retention time (HRT), the COD and phenol contents in the effluent from GAC-SBR system were 16 and 0.2 mg/l, respectively while the COD and phenol contents in the SBR system were 122 and 3.1 mg/l, respectively. The experiment which concerned in HRT values showed the interested results. In the SBR system, at HRT values as 3, 5 and 10 days, the COD contents of the effluent from SBR system were 48, 32 and 16 mg/l, respectively, and the phenol contents of those were 0.35, 0.18 and 0.018 mg/l, respectively. On the contrary at the same HRT, the COD contents of effluents from GAC-SBR system were 16, 14.5 and 8 mg/l, respectively, and the phenol contents of those were 0.08, 0.023 and 0.018 mg/l, respectively. From all of the results above, GAC gave the advantages for removal of COD and phenol in SBR system

Introduction

The waste water problem became the serious problem in the world. The volume of waste water from domestic and industries were increasing year by year. The pollutants in the industrial waste water were depend on the type of industries. And the suitable treating processes were depend on the type of the pollutants. For example, the biological treatment processes (anaerobic or aerobic systems) were suitable for the waste water from the food processing industries and fermentation industries. The chemical treatment processes were suitable for the waste water contained inorganic matters, heavy metals and toxic substances. But almost of the industrial waste water contained no only organic matters but also toxic substances such as heavy metals or antiseptic substances. Some of toxic substances could repressed the growth of microorganisms in the biological treatment systems. Phenol was the one of the toxic substances and it was discharged from refinery plant, resin industries, plastic industries, dye factories and nylon industries. However, the impurities, especially phenol, should be removed from the waste water. Because, the phenol would effect to the environment. Fish and aquatic life were also affected by phenol at 5-10 mg/l concentration. The phenol could be formed carcinogen with chlorine in the environment (chloro-phenols compounds) at the chlorine concentration of 0.002 mg/l. By using the biological treatment processes for treating the waste water from aboved industries, the microorganisms in the system were killed by phenol.

By the way, it was well-known that activated carbon was a good absorbent for absorption of color, odor suspended solid and organic matters. Actually, activated carbon was wildly used in water, waste water, air and air pollution treatments by the physical absorption mechanisms. Further activated carbon could be used together with the biological treatment processes in the propose of increasing of the removal efficiency and reducing of the HRT of the treatment system. Many experiments (1,2,3) were carried out to compare the BOD₅ removal efficiency by the activated sludge system with

and without supplemented of powder activated carbon (PAC) The results showed that PAC could reduce the HRT of the system^{3,4}) and could adsorb some heavy metals such as Zinc, Copper, Chromium and so on^{4,5,6}). But they got many problem during operation of the activated sludge system such as the effluent of the system was contaminated with PAC, PAC was lost from the system by discharging of the excess sludge the HRT in the sedimentation step had to be increased and the new PAC was added up to the aeration tank during operation. Goeddertz and Weber⁷) carried out the experiment in anaerobic up-flow expanded bed by using granular activated carbon (GAC) as media for treating waste water contained phenol, formaldehyde and methanol. During continuous operation for 2 years, organic removal efficiency was up to 90% and organic loading rates was 0.06g COD/g GAC-d. GAC was also used in the microorganism attached activated carbon fluidized bed process^{8,9}) for treating landfill leachate contained high concentration of ammonia nitrogen and refractory organic matters and the system showed constantly efficiency during more than 700 days continuous operation. The refractory organic matters and ammonia nitrogen compounds could be removed about 60 and 70 %, respectively. There were some information about using of PAC in the activated sludge process for improving the removal efficiency of the system^{11,12}) but not so many information on using of GAC in the biological treatment system.

As we mention above, several problem would be occur during operation of the activated sludge process such as increasing of the hydraulic loading and BOD₅ loading. For solving aboved problems, several researchers tried to used the sequence batch reactor system.

In this study, we tried to use granular activated carbon sequence batch reactor system for treating synthetic waste water which had the chemical composition same as the waste water of the resin industries. The synthetic waste water were contained COD and phenol at the concentration of 3,200 and 1,000 mg/l respectively. The optimum concentration of GAC and the optimum HRT were investigated for observation of the highest removal

efficiency, phenomenal of the removal mechanisms.

Materials and methods

Synthetic industrial waste water: The synthetic waste water (SWW), was prepared based on the waste water from the resin industries as having the final concentration of COD (3,200 mg/l) and phenol(1,000mg/l). The 1,000 ml of SWW contained Bacto-peptone 220 mg, glucose 660mg, MgSO₄ 60 mg, FeCl₃ 13mg, KH₂PO₄ 300 mg, K₂HPO₄ 370 mg/l, NaHCO₃ 400 mg and phenol 1000 mg.

Granular Activated Carbon (GAC): The GAC used in this experiments was CGC-11 with the mesh size of 8x30 mm². It had the total surface area and apparent density of 1050-1150 m²/g and 0.46-0.48 g/ml, respectively.

Sequence Batch Reactor (SBR): The six of ten liters reactors used in this experiment, were made from acrylic plastic (5 mm thick) as shown in fig.1. The dimension of reactor was 18 cm in diameter and 40 cm in height. The working volume was 7.5 liters. The low speed gear motors model P 630A-387 100 V 50/60 Hz 1.7/1.3 A (Japan Servo Co. Ltd., Japan) were used for driving the paddle shape impeller. The speed of impeller was adjusted to 60 rpm. One set of air pump system model EK-8000 6.0 W (President Co. Ltd., Thailand) was used for supplying air for 2 sets of reactor.

Acclimatization of the microorganisms: Sludge from Siam Resin Chemical Co. Ltd., was used for the starter of the SBR system. The sludge was cultivated in the SWW for 1 week before using in the experiments.

Operation of GAC-SBR system: The experiments were done as follows: At first, the acclimatized sludge (the final concentration of the sludge of the system was 2,000 mg/l) and GAC (the final concentration of the GAC of the system was 1000 mg/l) were put in the reactor and the SWW was added to the system up to the maximum capacity (about 7,000 ml) within 1 hr. During feeding the SWW, the system had to be aerated fully and continued aerated for 19

hrs. And then the aeration of the system was shut down for 3 hrs. After fully settle of the sludge, the supernatant had to be removed (7,000 ml) within 0.5 hr and the system must be kept for 0.5 hrs. After that the new SWW (7,000 ml) was filled into the system and repeated operation as the same with above program.

Optimum concentration of GAC in SBR system : The experiments were done in 6 sets of ten liters' reactors with initial sludge concentration (MLSS) of 2000 mg/l, HRT of 1 day and solid retention time (SRT) of 10 days . Each reactor was supplemented with various concentrations of GAC (0, 500, 1000, 2000 and 2500 mg/l, respectively). The program of operation were 20 hrs for aeration and 4 hrs for settle (stop aeration). After sedimentation of sludge, the supernatant was replaced by fresh waste water. The system was operated until the system became steady state. The effluents (supernatants) of the systems were collected for determination of chemical properties.

Determination of HRT of the GAC-SBR system: The experiments were carried out in ten liters' reactor added with GAC as final concentration of 1000 mg/l by using various HRT values such as 3, 5 and 10 days. The conditions for operation were MLSS of 2,000 mg/L and SRT of 10 days. The effluents of the system were collected for determination of the chemical properties.

Chemical Analysis: The COD, phenol, MLSS, pH, dissolved oxygen and SVI of influents and effluents were determined by using standard methods for the examination of water and waste water 13) .

Results

Absorbing capacity of GAC for Phenol and COD : The results were shown in table 1 .The GAC was added in the SBR system showed higher efficiency for adsorption of the phenol and COD in the SBR system than normal. The maximum absorption capacity of GAC for COD and phenol were 686 mg/g GAC and 213 mg/g GAC, respectively. While in the SBR

system were 761mg/g GAC and 240 mg/g GAC, respectively.

Optimum concentration of GAC in SBR system: Various concentrations of GAC such as 0, 500, 1,000, 1,500, 2,000 and 2,500 mg/l were added in SBR system in which 10 liters reactor which working volume 7.5 liters and 2000 mg/l of MLSS were used. The condition of the system were HRT of 1 day and SRT of 10 days. The results were shown in table 2, fig.2. and fig.3. The COD and phenol concentrations of the effluents from SBR system without supplement of GAC (SBR) were higher than standard values of Ministry of Industry of Thailand (Standard value of COD was not more than 60 mg/l) Namely, the COD concentration of effluents were 390 mg/l and 185 mg/l at the first week and second week of treatment, respectively. On the other hand, the SBR system with supplement of GAC(1,000mg/l), the COD contents were rapidly decreased, and its concentration was reduced to 24 mg/l within 2 weeks. For removal of phenol in the SBR system, the phenol concentration were reduced from 1000 mg/l to 125 mg/l within 1 week of treatment and the removal efficiency was 87.5%. After 2nd week of treatment, the phenol concentration of the effluent was reduced to 6.2 mg/l. The phenol removal efficiency in SBR-GAC system was higher than in SBR system in all of the experiments. The phenol concentration of the effluents were reduced to less than 1 mg/l within 2 weeks in SBR-GAC system which contained GAC more than 500 mg/l and gave the removal efficiency of more than 99%.

Effects of HRT for treatment efficiency in GAC-SBR System: The experiments were carried out in 6 sets of 10 liters reactor with working volume 7.5 liters. Among them 3 sets of the reactor were used for GAC-SBR treatment process and other 3 sets were used for SBR treatment process as control. The final concentration of GAC in the reactor was 1000 mg/l.

The removal of the COD in the GAC-SBR and SBR system are shown table 3, 4 and 5 . The COD removal efficiency in the GAC-SBR system was higher than in SBR system in

all experiments (all HRT values). In the GAC-SBR system, the COD could be removed from 3,200 mg/l to 16, 14.5 and 8 mg/l when the HRT were 3, 5 and 10 days, respectively while in SBR system those were 48, 32 and 16 mg/l, respectively.

The removal of phenol in the SBR and GAC-SBR systems were shown in table 3, 4 and 5. The phenol concentration in the GAC-SBR system were reduced from 1000 mg/l to 0.08, 0.023 and 0.014 mg/l at the steady state when the HRT of the system were 3, 5 and 10 days, respectively. But in the case of SBR system (control), the phenol concentration of the system were reduced from 1,000 mg/l to 0.35, 0.18 and 0.018 mg/l at the steady state when the HRT of the system were 3, 5 and 10 days, respectively.

The results of the removal of suspended solids are shown in table 3. In both SBR and GAC-SBR system, the suspended solids concentration in the effluents was almost the same in all of the HRT values (3, 5 and 10 mg/l).

Discussion

Activated carbon is one of the useful materials and is widely used in water purification and waste water treatment (1,2,7,10) . PAC was also added in the biological treatment plant (3,4,5,8,9,10) especially, activated sludge process, for improving and increasing the treatment efficiencies of the system. But some problem would be occur during operation the system such as HRT in the sedimentation tank, return sludge pattern and the lost of the PAC during the discharging of the excess sludge. In our experiment, the GAC could show the good results for absorption of COD and phenol in the waste water. The absorption yields for COD and phenol were 686 mg/g GAC and 213mg/g GAC, respectively in the optimum condition. And also the GAC could show the COD and phenol absorption yields higher than in the SBR system. The COD and phenol absorption efficiencies of GAC in the SBR system were increased as 11.25 and 11.08 %, respectively when compared which the normal condition. It might be effects of the aeration in the SBR system gave the good

conditions for GAC to absorb the COD and phenol^{6,9,10}). The removal efficiencies of the SBR system were highest when more than 1,000 mg/l of GAC was supplied to the system. At one day of HRT, the GAC-SBR system, which was contained optimum concentration of GAC (1,000 mg/l), could reduce the COD and phenol to 16 mg/l and 0.2 mg/l, respectively, while the system without GAC could reduce COD and phenol to 122 mg/l and 3.1 mg/l, respectively. GAC also could reduce the HRT of the treatment system. For example, the COD of the effluents from GAC-SBR system (1000 mg/l of GAC) at HRT of 3, 5 and 10 days contained 16, 14.5 and 8 mg/l, respectively while in those SBR system were 48, 32 and 16 mg/l, respectively. The effect of HRT for the removal of phenol also showed the same trend from the results above, we could say that GAC could be used for improving and increasing the removal efficiency of the SBR system due to the physical mechanisms of GAC. The GAC might be increased the MLSS of the system because the surface area of GAC will be good for microorganisms to attach same as the attached growth treatment system. The GAC could be used as the adsorbent for adsorbing the COD and toxic substances compounds as phenol^{3, 7, 8, 9, 11}). And also the GAC could be used as media for protection of microorganisms from the toxic substance as phenol⁹). For the application, we believed that the GAC-SBR might be more suitable than activated sludge system and activated sludge which supplemented with PAC for treating the waste water from the resin industries, plastic industries or textile industries which the waste water contained both organic substances and some toxic substances such as phenol compound. Comparing with the activated sludge system, the GAC-SBR system might be the best

way for solving some problem which commonly occur in the activated sludge system such as the failing of the system due to the shock loading, or increasing of BOD concentration and volume of waste water. In the case of activated sludge system which added with PAC, it might be the best way for increasing the removal efficiency and reduced the HRT. But the big problem of above system were the effluent was contaminated with some small particles of PAC, some PAC was lost during discharging of the excess sludge from the system. It was very difficult for controlling of the concentration of PAC in the aeration tank. And also it was very difficult to reuse or recycle of the used PAC due to the small size of the PAC. For the conclusion GAC-SBR gave the main advantage that could not find in the activated sludge system and activated sludge system which supplemented with PAC were as followed: First, GAC could be solved above problem in the PAC-activated sludge system, because of the large size of GAC, it was very easy for sedimentation and use for microorganisms to attach same as a media in the attached growth system in the biological treatment process. Second, the SBR system was the best way to solve the problem with occur in the activated sludge system which mention above.

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Table 1 : The comparison of COD and phenol removal efficiencies of GAC in SBR system and normal condition.

The experimental details were described in the text.

Condition of GAC	Removal efficiency of GAC (mg/g of GAC)	
	COD	Phenol
GAC in SBR system	761	240
GAC	686	213

Table2 : Comparison of the COD and phenol concentration of effluent from SBR-GAC system in various concentration of GAC.

The experimental details were described in the text.

G A C in SBR system (mg/l)	Phenol (mg/l)					COD (mg/l)				
	Influent	Effluent		% Removal		Influent	Effluent		% Removal	
		1 st week	2 nd week	1 st week	2 nd week		1 st week	2 nd week	1 st week	2 nd week
0 control	1,000	125	6.2	87.5	99.40	3,000 - 3,200	390	185	87.70	94.20
500	1,000	12.40	1.52	98.8	99.90	3,000 - 3,200	340	64	89.40	98.00
1,000	1,000	6.20	0.24	99.4	99.98	3,000 - 3,200	177	24	94.50	99.30
1,500	1,000	5.40	0.21	99.5	99.98	3,000 - 3,200	150	18	95.30	99.50
2,000	1,000	3.80	0.18	99.6	99.98	3,000 - 3,200	128	30	96.00	99.00
2500	1000	2.64	0.20	99.7	99.97	3,000 - 3,200	112	32	96.70	98.00

Table 3: Comparison of the chemical properties in the effluent at various HRT.
The experimental details were described in the text.

Parameter*	HRT (days)							
	1		3		5		10	
	GAC - SBR	SBR	GAC - SBR	SBR	GAC - SBR	SBR	GAC - SBR	SBR
COD (mg/l)	16	122	16	48	14.5	32	8	16
Phenol (mg/l)	0.20	3.40	0.08	0.38	0.023	0.18	0.014	0.018
MLSS (mg/l)	3705	3355	3550	3960	2420	2525	1555	1560
Effluent SS (mg/l)	24	27	9	12	9	11	7.5	9
SVI (ml/g)	42.5	46	57	78	50	60	56	63
pH	8.28	8.07	7.47	7.23	7.65	7.693	7.89	7.91
DO (ml/l)	6.9	7.1	6.8	6.9	6.7	7	7.1	7

Table 4 : COD and phenol removal efficiency in various HRT.
The experimental details were described in the text.

Removal efficiency (%)	HRT (days)							
	1		3		5		10	
	GAC - SBR	SBR	GAC - SBR	SBR	GAC - SBR	SBR	GAC - SBR	SBR
COD	99.53	96.00	99.50	98.50	99.55	99.01	99.75	99.50
Phenol	99.98	99.66	99.99	99.97	99.99	99.98	99.99	99.99

Table 5 : Comparison of COD and phenol removal efficiency in SBR GAC-SBR and GAC systems.
The experimental details were described in the text.

System	Period of treatment (days)					
	First day		Second day		at steady state (after 15 days)	
	Removal efficiency(%)		Removal efficiency(%)		Removal efficiency(%)	
	COD	Phenol	COD	Phenol	COD	Phenol
GAC	22.91	20.83	0.88	0.00	0.00	0.00
SBR	71.97	82.60	76.60	86.00	96.00	99.66
GAC-SBR	92.71	98.80	96.01	99.17	99.53	99.98

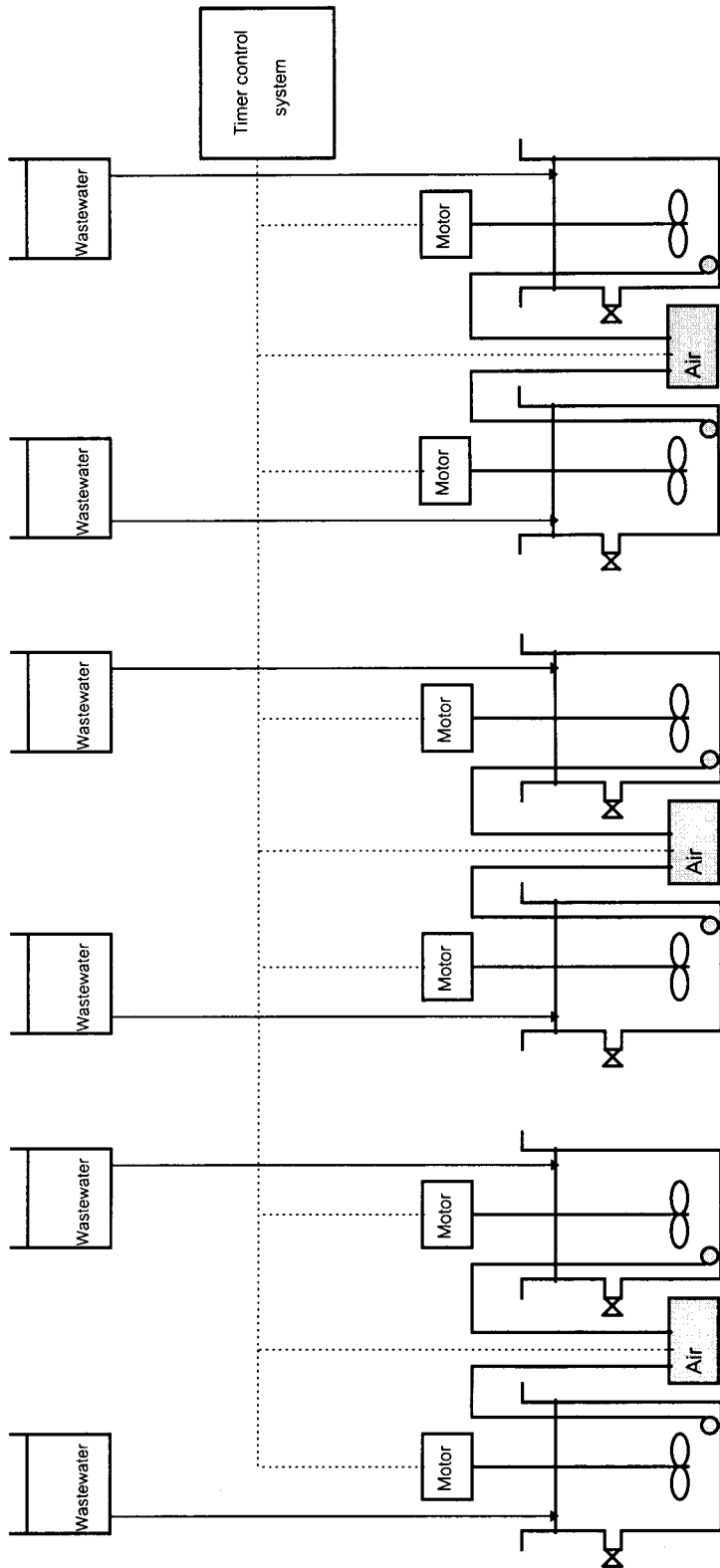


Fig. 1 : Flow diagram of SBR treatment system.

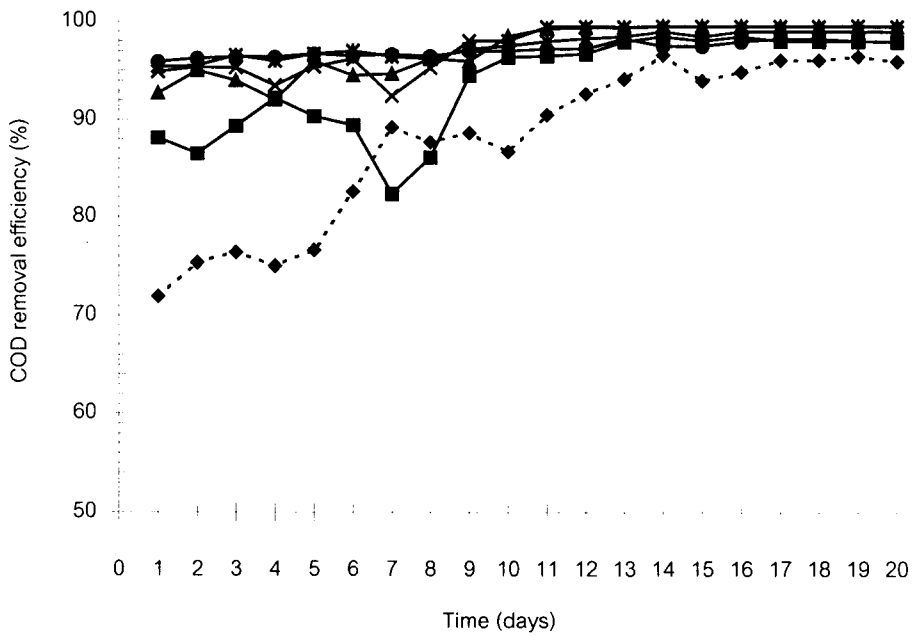


Fig. 2 : The COD removal efficiency of the GAC-SBR system supplied various concentration of GAC

The experimental details were described in the text. Symbols: ◆, control (0 mg GAC); ■, 500 mg GAC; ▲, 1000 mg GAC; ✕, 1500mg GAC; *, 2000 mg GAC; ●, 2500 mg GAC.

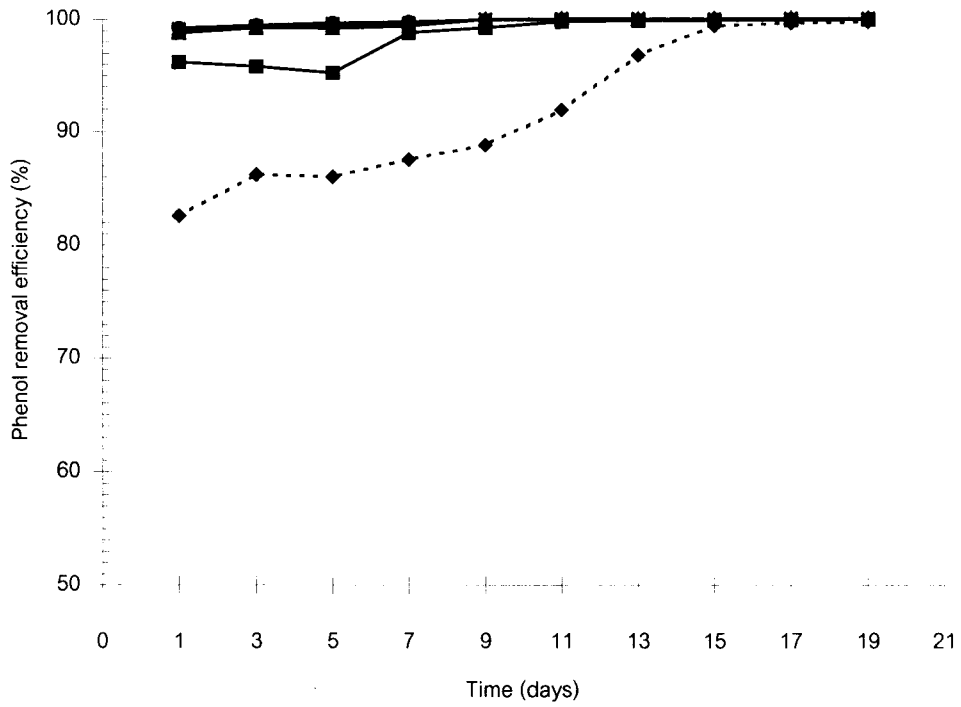


Fig. 3: The Phenol removal efficiency of SBR system supplied various concentration of GAC

The experimental details were described in the text. Symbols: ◆, control (0 mg GAC); ■, 500 mg GAC; ▲, 1000 mg GAC; ✱, 1500 mg GAC; ✱, 2000 mg GAC; ●, 2500 mg GAC.

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