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Mechanisms of granular activated carbon anaerobic fluidized-bed process for treating phenols wastewater

LAO Shan-gen

(Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, China)

Abstract: Granular activated carbon (GAC) anaerobic fluidized-bed reactor was applied to treating phenols wastewater. When influent phenol concentration was 1000 mg/L, volume loadings of phenol and COD_{Cr} were 0.39 kg/(m^3·d) and 0.98 kg/(m^3·d), their removal rates were 99.9% and 96.4% respectively. From analyzing above results, the main mechanisms of the process are that through fluidizing GAC, its adsorption is combined with biodegradation, both activities are brought into full play, and phenol in wastewater is effectively decomposed. Meanwhile problems concerning gas-liquid separation and medium plugging are well solved.

Keywords: granular activated carbon (CAC); anaerobic fluidized-bed; phenol; removal rate

Introduction

Before the 1980s conventional treatment processes of phenols wastewater are solvent extraction, physical adsorption, chemical oxidation and aerobic biological process. Among the biological unit processes activated sludge process is main one. After the 1980s anaerobic biological processes are gradually studied to treat phenols wastewater. Main processes are granular activated carbon anaerobic fluidized-bed and so on. Compared with aerobic treatment anaerobic treatment processes possess some advantages including low energy consume, simple operation, available recovery marsh gas as energy resource and so on. In order to study mechanisms of anaerobic processes treating phenols wastewater, raise removal rate and solve some problems in operation experiments were made to treat phenols wastewater with GAC anaerobic fluidized-bed reactor. Other concerning tests were compared with them. Good results were achieved.

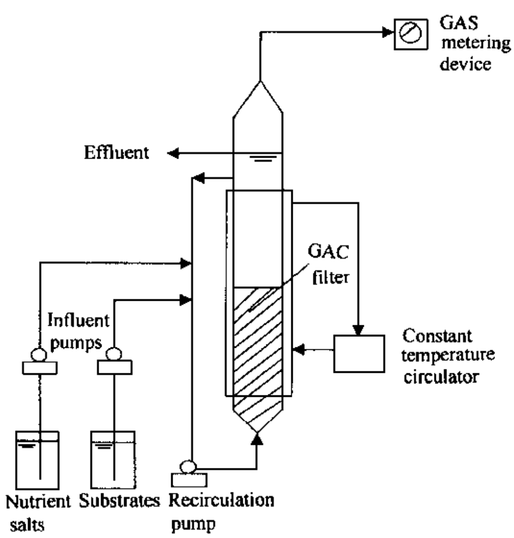

Fig.1 Schematic diagram of experimental apparatus

1 Materials and methods

Fig.1 represents a schematic diagram of the anaerobic fluidized-bed reactor and other experimental apparatus employed in this study. The column bearing warm water jacket was constructed of ethylene chloride, 127 cm long, 10 cm in internal diameter and 10L volume. Average diameter of GAC as carrier was 0.9 mm – 1.1 mm. Recirculated flow was drawn from middle part and was pushed in the bottom of reactor by an electromagnetic pump, formed recirculating circuit for increasing hydraulic loading and made GAC suspended. Expansion rate of GAC reached 25% through regulation of recirculated flow. Artificial wastewater consisted of organic substrates (phenol and natrium acetate) and nutrient salts, filled into two tanks respectively and pushed in the recirculating circuit by two microtube pumps. Concentrations of phenol and natrium acetate were same 1000 mg/L. Nutrient salts were K_2HPO_4, KH_2PO_4, NH_4Cl, $MgCl_2$, $CaCl_2$, NaCl, $FeCl_3$ and vitamin mixture. The warm water in jacket was recirculated by a constant temperature circulator. Therefore water temperature in reactor was kept to 30 ± 1℃. Product gas was collected from the top of reactor and was measured by a wet gas flowmeter. Methane production capacity was calculated by product gas composition.

Before operation reactor was filled with fresh water and 1.5 kg GAC, was added with 100 ml digested sludge of municipal wastewater plant. After that experimental system started.

2 Results and discussion

2.1 Operational condition

Experiment was conducted continuously and was divided into two phases. Phase I was from day 1 – 351. In this phase influent flow was 2 L/d. Phase II continued for 33 days (day 352 – 384). Influent flow of this phase rose from 2 L/d to 4 L/d. During operational time mixed liquor dissolved oxygen concentration in reactor was less than 0.2 mg/L, pH 6.3 – 7.6, ORP-310mv – 210mv and water temperature 30 ± 1℃. Main operational parameters are given in Table 1.

2.2 Organic removal rate

During whole operational time average concentrations of phenol, COD_{Cr}, TOC in influent and effluent and their removal rates are given in Table 2. According to Table 2 removal rates of phenol, COD_{Cr}, TOC reached more than 99%, 96% and 97% respectively.

Table 1 Reactor operational parameters

Time, d	0 — 351	351 — 384
Flow rate, L/d	2	4
HRT, d	5	2.5
Upflow velocity, m/h	0.0106	0.0212
Volume loading phenol, kg/(m^3·d)	0.19	0.39
COD_{Cr}, kg/(m^3·d)	0.58	0.98

Table 2 Substrate concentrations and removal rates

Parameter	Phenol	COD_{Cr}	TOC
Influent, mg/L	952.3	2755.0	1005.7
Effluent, mg/L	0.5	100.5	27.4
Removal rate, %	99.9	96.4	97.3

2.3 Marsh gas production rate

Change of marsh gas production rate with time is given in Table 3. Reactor started to produce gas on day 36. Gas production rate reached 0.54 L/d on day 90. After that it rose sharply and reached maximum of 5.46 L/d on day 210. Then gas production rate came down sharply and tended to a steady level of 2.17 L/d on day 270. From day 352 influent flow rate was increased from 2 L/d to 4 L/d (organic loading was double). After that gas production rate rose rapidly during 1 to 2 days. For about 10 days it tended to a steady level of 4.30 L/d and went to the end.

Table 3 Change of marsh gas production rate with time

Time, d	0 – 36	37 – 90	91 – 209	210	211 – 247	248 – 351	352 – 364	365 – 384
Marsh gas production rate, L/d	0	0.54	↗	5.46	↘	2.17	↗	4.30

2.4 COD_{Cr} material balance relationship

Total COD_{Cr} effluence from reactor was equalled by COD_{Cr} of effluent water plus COD_{Cr} converted from CH_4 produced through anaerobic digestion of organic substrates. Phase I COD_{Cr} material balance relationship is given in Table 4. In the early days of operation (day 28) influent substrates were mainly adsorbed by GAC and stayed in reactor. When microbial domestication was accomplished large substrates (including just influent and remained before) were degradated into CH_4. Therefore effluent COD_{Cr} of this time (day 210) greatly exceeded influent COD_{Cr}. When operation reached a steady state (day 265) influent substrates and effluent substrates basically reached balance. More than 92% effluent substrates were transformed into CH_4. Anaerobic digestion rate was very high. In this case substrates transformed into organism in reactor accounted for only 4% influent substrates. Therefore sludge yield was very low and sludge discharge did not needed actually in continuous operation (384 days).

Table 4 Phase I COD_{Cr} material balance relationship

Time, d	28	210	265
Influent COD_{Cr}, mg/L	3055	2458	3257
Effluent COD_{Cr}, mg/L			
Liquid phase	364	128	133
Gas phase	-	7800	3001
Total	364	7928	3134

3 Treatment mechanisms

3.1 Physical adsorption of activated carbon

Activated carbon is a sort of non-polar adsorption agent. There is weak polar in its surface. Its specific surface area amounts to 800 m^2/g - 2000 m^2/g. Therefore activated carbon possesses strong adsorption activity for non-polar and weak polar organic matters. Monohydric phenols (phenol) and binary phenols (catechol) in industrial wastewater are weak polar organics. They are easily adsorbed by activated carbon.

Firstly domestication of anaerobic bacteria was conducted before starting of apparatus. Phenolic compounds are inhibitory for microbe generally. Especially in high concentration these compounds can destroy cellular protoplasm, thus kill bacteria. But in low concentration through domestication of bacteria they will be gradually adapted to environmental condition and effectively degrade most of phenolic compounds. In the early days (day 1 - 36) of operation though marsh gas was not produced phenol concentration in wastewater came down from 1000 mg/L to less than 1 mg/L. In the early days (day 1 - 140) of similar experiment (Suidan, 1981) without producing gas, but catechol concentration in wastewater declined from 200 mg/L (influent) to less than 5 mg/L (effluent). In the initial stage fresh activated carbon adsorbed a large number of phenolic materials, it was main mechanism for removal of phenols. As a result of this adsorption phenols concentration of mixed liquor in reactor dropped to very low level. It created a favourable environmental condition for growth and reproduction of anaerobic bacteria just inoculated. These microbes were adapted to phenolic substrates for a shorter time and gradually used and transformed these substrates, meanwhile brought degradation activity into play. In this experiment reactor started to produce gas after 36 days of starting and in Suidan's experiment reactor started to produce gas after 140 days of starting. Up to this time domestication of bacteria was basically accomplished.

When reactor was subjected to shock loading activated carbon produced cushioning effect fully. From day 352 of this experiment influent flow was increased by one time without change of substrate concentration. It produced shock loading for reactor. In 1 - 2 days producing gas rate rose. For about 10 days real producing rate of marsh gas approached theoretical level and reached a new balance, whereas phenol concentration of effluent was less than 1 mg/L consistently. In Suidan's experiment catechol concentration of influent was increased from 200 mg/L to 400 mg/L, and then from 400mg/L to 1000 mg/L. Substrate loading had doubled and redoubled. In this case microbes were not subjected to obvious inhibitory action. After serveral days producing gas rate rose rapidly and catechol concentration of effluent still kept low original level. When phenols content of influent was increased suddenly activated carbon rapidly adsorbed a large number of phenols in a short time. Therefore phenols concentration in mixed liquor was not increased very much. Such properly increased phenols substrates stimulated activity of microbes, promoted their growth and reproduction, and raised total degradation capacity. Phenols materials excessively adsorbed to activated carbon formerly were gradually desorbed and were used by microbes. In this process activated carbon brought adjustment into play, effectively relaxed effect of shock loading and kept normal operation of reactor.

3.2 Biodegradation

After starting of production gas production rate of marsh gas gradually rose to a maximum value, then fell and approached to a certain level. In day 210 of this experiment producing gas rate reached maximum (5.46 L/d). In this time total COD_{Cr} of effluent (gas phase plus liquid phase) was 7928 mg/L. Influent COD_{Cr} was 2458 mg/L. Effluent exceeded 222.5% more than influent. In day 167 of Suidan's experiment producing gas rate reached maximum. In this time total COD_{Cr} of effluent (gas phase plus liquid phase) was 650 mg/L. Influent COD_{Cr} was 420 mg/L. Effluent exceeded 54.8% more than influent. The case indicated that after completion of starting period microbes brought metabolic activity into full play, degradated and transformed a large number of phenolic substrates formerly adsorbed to activated carbon into CH_4 and CO_2. Meanwhile activated carbon was regenerated and its activity was restored by means of biodegradation.

When reactor came up to a stable operation phenolic materials in activated carbon and mixed liquor reached dynamic equilibrium. Phenolic substrates passing through reactor were timely degraded and used through metabolism of anaerobic bacteria. COD_{Cr} materials of influent and effluent basically reached balance. In day 365 Suidan's experiment reached balance. About 90% COD_{Cr} of influent flowed off reactor in gas phase and liquid phase. Only about 11% COD_{Cr} of influent was assimilated into organism. In day 265 this experiment reached balance. Influent COD_{Cr} was 3257 mg/L. Effluent COD_{Cr} was 3134 mg/L (gas phase 3001 mg/L and liquid phase 133 mg/L). Substrates assimilated into organism only amounted to about 4% of influent. In this moment GAC was taken out of reactor and adsorption test of phenol was made with this GAC. Test result showed that about more than 22% adsorption capacity was left in the GAC. This case indicated that GAC was regenerated by microbes. According to above results and analyses when this process reached a steady state biodegradation was main mechanism of phenols removal.

3.3 Carrier fluidization

In this experiment GAC carrier was fluidized through push of recirculated flow. Expansion rate of GAC reached 25% – 30%. GAC particles provided a huge surface area for microbe growth. Completely-mixed flow pattern in reactor avoided short pass of flow. Water quality of mixed liquor was basically same every where. Microbes grew and reproduced homogeneously in every part of carbon layer. Microbial content reached very high level. Really measured microbial density was 17.7 g/L. Fluidizing carbon particles continuously collided and rubbed each other. It made surface of carbon particle to preserve a layer of thinner fresh biological membrane. Microbes in this membrane possessed very strong activity and smaller diffusion resistance of substrate. As a result biodegradation rate was greatly increased. Therefore high microbial content and thinner biological membrane possessing strong activity were also efficient mechanisms of this process. Carrier fluidization helped gas release and prevention of possible plugging produced by small medium particles. Thus reactor could be kept normal operation.

4 Conclusions

GAC anaerobic fluidized-bed process was developed on the basis of anaerobic activated sludge method and anaerobic filter and achieved good results in phenols wastewater treatment for more than ten years. The main mechanisms of the process are that through fluidizing GAC, its adsorption is combined with biodegradation. Both activities are brought into full play. Phenols materials are transformed into CH_4 and CO_2 thoroughly and efficiently. Meanwhile gas-liquid separation and medium plugging are solved. Reactor is kept normal operation. Therefore this is an ideal process for treating phenols wastewater. It can be tried to treat other wastewater.

References:

Lao S G, Tong Y Z, Hu H, 1994. Small-scale test on phenol wastewater treatment with anaerobic carbon filter[J]. Technology of Water Treatment, 20(4): 241—244.

Pfeffer J T, Suidan M T, 1989. Continuous processing of toxic organics in a fluidized-bed GAC reactor employing carbon replacement[J]. Biotechnol Bioeng, 33(1):139—148.

Suidan M T, Cross W H, Fong M *et al.*, 1981. Anaerobic carbon filter for degradation of phenols[J]. J Environ Eng Div Proc ASCE, 107 (EE3): 563—579.

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