Kinetics of continuous biodegradation of pesticide organic wastewater by activated carbon-activated sludge*

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Abstract—Organic triazophos wastewater was continuously treated with *Rhodopseudomonas capsulatus* and activated carbon and activated sludge system(PACT-AS) in a plug bioreactor. A kinetic model of PACT-AS wastewater treatment system was established to provide an useful basis for further simulate scale-up treatment of toxic organic wastewater.

Keywords: wastewater treatment, *Rhodopseudomonas capsulatus*, activated carbon-activated sludge, kinetics.

1 Introduction

Novel biological activated carbon and activated sludge system has shown its effective ability to reduce COD in toxic organic wastewater since 80's (Namking, 1987; Dietrich, 1988; Zhou, 1988;1992). Due to its large special surface and strong adsorption capacity, activated carbon facilitate to accumulate organic matter and dissolved oxygen and to form a slime biological layer. As a result, the contact time or retention time between organic matter and microorganisms prolonged, which offers a favorable condition to domesticate microorganisms and makes it possible to degrade some non-degradative organic matter to improve water quality. Meanwhile, because of its high adsorption capacity, activated carbon can reduce the impact load caused by the change of water quality, especially to the toxic wastewater, and enables microorganisms to grow normally under relatively stable conditions. In this paper, authors adopted a plug reactor PACT-AS system to study the kinetic of wastewater treatment, using *Rhodopseudomonas capsulatus* as main strain in activated sludge. The kinetic model of the system provided scientific foundation for pilot organic wastewater treatment.

2 Materials and methods

2.1 Microorganism

Rhodopseudomonas capsulatus was preserved in our laboratory, its culture conditions were according to literature(Zhou, 1988).

2.2 Reaction medium

Organic triazophos wastewater was provided by Xianju Pesticide Co. in Zhejiang Province. Water quality analysis is as follows: COD 16000 mg/L, BOD 6400 mg/L, organic phosphor 2265 mg/L and NH_3-N 125 mg/L.

2.3 Reaction system

Bioactivated carbon and activated sludge was adopted to treat wastewater in experiment, and a four-channel plug reactor with effective volume 1.0 m^3(4 channels $1\times0.8\times0.4$m) was used.

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2.4 Analytical methods

COD was determined by $K_2Cr_2O_7$ oxidation method.

Experiment of adsorption kinetic of methylene blue was conducted as literature(Zeng, 1987).

Cell weight (wet) was measured just after centrifugation under 3500 r/min for 15 min, then the water content of the wet cells was determined to calculate dry base cell weight.

3 Results and discussion

3.1 Effect of dilution rate on degradation of organic matter in PACT-AS system

Treatment experiments with *Rhodopseudomonas capsulatus* in PACT-AS and AS system were carried out both in plug reactor. Input wastewater with different COD value, and the activated carbon added in PACT-AS amounted 0.2% (v/v). Under different dilution rates of continuous treatment and steady-state condition, outlet cell concentration and COD value were determined to calculate biomass per unit time and COD reduce effectively (Table 1, Fig. 1 and Fig. 2).

Table 1 Comparison of effects of different dilution rates in PACT-AS and AS system on microbial concentration, biomass and COD degradation

	AS system									
D, 1/h	0.04	0.10	0.14	0.18	0.24	0.28	0.32	0.34	0.36	
X, g/L	4.96	4.30	4.10	3.55	2.50	2.00	1.18	0.40	0.20	
XD, g/L.h	0.20	0.43	0.57	0.64	0.60	0.56	0.38	0.14	0.07	
ρ, COD, mg/L	700	1100	1450	1820	2340	2820	3730	4310	4510	
r, %	86	78	71	63.6	53.2	43.6	30.6	16.0	3.0	
	PACT-AS system									
D, 1/h	0.04	0.10	0.14	0.18	0.24	0.28	0.32	0.40	0.50	0.60
X, g/L	5.08	4.50	4.25	3.50	2.80	2.30	1.30	0.38	0.25	0.15
XD, g/L.h	0.20	0.45	0.60	0.63	0.67	0.64	0.42	0.15	0.13	0.09
ρ, COD, mg/L	730	1160	1540	1890	2470	3100	4200	4840	5560	6120
r, %	89.6	85.4	80.6	76.8	69.2	62.2	50.6	38.0	16.0	3.0

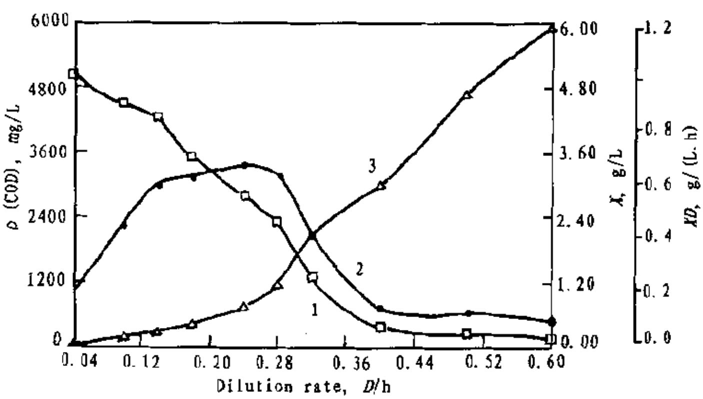

Fig. 1 Curves of kinetic model in PACT-AS system

1. X(microbial concentration in outlet of the reactor, g/L);

2. XD(biomass per unit time in outlet of the reactor, g/(h·L));

3. ρ(COD concentration in outlet of the reactor, mg/L)

Fig. 1 and Fig. 2 indicate that PACT-AS system endured stronger impact load and had higher treatment efficiency than AS system due to that the formed one immobilized *Rhodopseudomonas capsulatus* strain and made the total cell concentration in the reactor higher than the latter though the free cell concentration in both system did not difference so much. Also, PACT-AS system improved the optimum dilution rate from $D_1 = 0.18h^{-1}$ to $D_2 = 0.24h^{-1}$ and the critical dilution rate from $D_{out1} = 0.34h^{-1}$ to $D_{out2} = 0.50h^{-1}$.

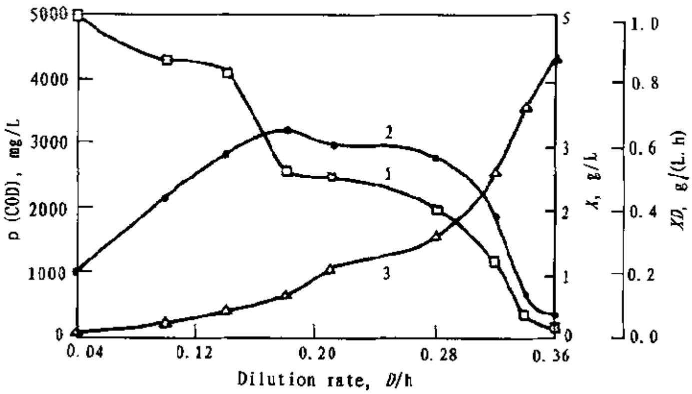

Fig. 2 Curves of kinetic model in AS system
1. X(microbial concentration in outlet of the reactor, g/L);
2. XD(biomass per unit time in outlet of the reactor, g/(h·L));
3. ρ(COD concentration in outlet of the reactor, mg/L)

3.2 Adsorption kinetic features of bioactivated carbon in PACT-AS system

Although some adsorption theories were submitted to bring about some adsorption equilibrium functions such as Langmuir function and Polanyi function(CEMEC, 1985; Yang, 1994), data in our experiment appeared some deviation from these functions. Langmuir function suppose that under isothermal condition, there should be no interaction among the adsorbed solute molecular on uniform surface and such a homogeneous molecular layer was formed. That is, it is misappropriate to the adsorption amount or covering rate of adsorption agent. While, in fact, adsorption rate will logarithmic decrease with the increase of covering rate. So, the Freundich function was used rationally.

According to the Freundich adsorption function, adsorption amount is appropriate to exponential of pressure. But it is hard to measure and less correct. So, under the same concentration of methylene blue, with the relationship of adsorption amount appropriate to adsorption time, a kinetic function of adsorption similar to Freundich function can be written as:

$$\frac{dq}{dt} = \frac{q}{mt}. \quad (1)$$

Integer Equation (1) get:

$$q = kt^{1/m}, \quad (2)$$

or

$$\ln q = \frac{1}{m}\ln t + \ln k, \quad (3)$$

where, q is the adsorption amount, g; t is the adsorption time, min; m and k are the constants.

Based on the Equation (3), plot a figure of $\ln q$ relative to $\ln t$.

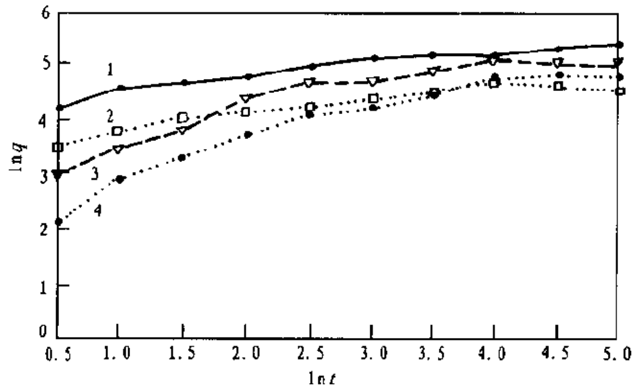

Fig. 3 Isothermal adsorption curves of methylene blue by bioactivated carbon
1. adsorption temperature 30℃, methylene blue concentration 550 mg/L;
2. adsorption temperature 30℃, methylene blue concentration 400 mg/L;
3. adsorption temperature 30℃, methylene blue concentration 325 mg/L;
4. adsorption temperature 30℃, methylene blue concentration 220 mg/L

Fig. 3 shows that the adsorption rater accorded with function (1) when the initial concentration of methylene blue were 220 mg/L to 550 mg/L.

In order to determine the effect of microorganism metabolite on the regeneration of activated carbon during the treatment process, new activated carbon, acid and base regenerated carbon and unregenerated carbon were used to compare their adsorption rate and adsorption amount to methylene blue. The results are shown in Fig.4.

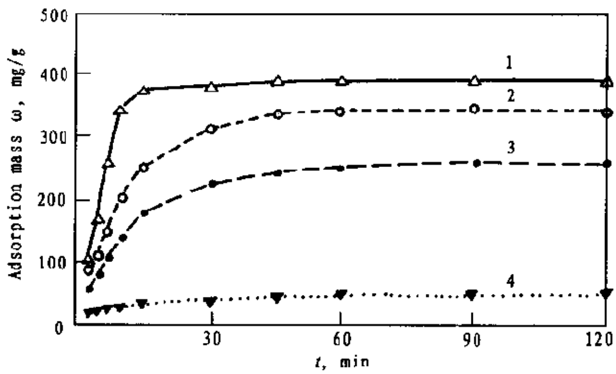

Fig. 4 Adsorption curves of methylene blue by different carbons
1. new activated carbon; 2. regenerated activated carbon;
3. bioactivated carbon; 4. unregenerate activated carbon

Comparing with the new carbon, the adsorption amount of biological activated carbon was about 65% of that of the new carbon while the acid and base regenerated was above 80%. But it shows that the biological activated carbon did have effective regeneration ability and this was of great significance for biological activated carbon to be applied in organic wastewater treatment. Bioregeneration existed in the whole process of PACT-AS wastewater treatment. Activated carbon had very strong adsorption power to adsorb microorganism, organic matter and dissolved oxygen due to its large special surface. As the capacity of adsorption reached the maximum, activated carbon could not adsorb anything more. Where with microorganisms adhering on the surface of activated carbon biodegraded organic matter existing in the millipores of activated carbon and made it possible to regenerate. Thus PACT-AS had synergy of adsorption and degradation. However, the bioregeneration also had a certain limitation. The organic triazophos wastewater was toxic material, it could not be completely degraded by microorganisms. Meanwhile, some could be degraded easily to accumulated in void of carbon and occupied more and more adsorption surface because they irreversibly adhered on the active center of activated carbon. As result, activated carbon would lose its adsorption power. So part of old carbon should be discharged and necessary new carbon could be supplied simultaneously during PACT-AS system treatment process in order to continue the process.

3.3 Kinetic model of PACT-AS system

The functional relationship between the growth of microorganisms and limiting medium had been expressed by many functions, of which Monod equation was the most common one. It was proposed to describe cell growth and reproduction in the ideal state, so it is probably a great oversimplification and has some deviation from the experiment cases.

In the experiment a plug reactor, which in spite of low aeration, had violet backflow, so it could be regarded as continuous reaction system. Assuming: (a) cell mass in the reactor including free cells and immobilized cells, cell mass X_s immobilized by activated carbon was constant and the cell concentration in the inlet was zero; (b) a modified Monod equation was adopted to express the relationship in this case. Under steady-state condition the material balance for cell mass gives

$$\frac{F}{V} \cdot X_t - DX_t - \mu(X + X_s), \tag{4}$$

where, F is the volumetric flow rate of feed and effluent liquid stream, L/h; V is the volume of reactor, L; X_t is the total cell concentration in the reactor, g/L; X is the free cell concentration in the reactor, g/L; X_s is the immobilized cell concentration in the reactor, g/L; D is the dilution rate, 1/h; μ is the special growth rate, 1/h and the steady-state mass balance on substrate consumption is then

$$\frac{F}{V}(S_0 - S) = D(S_0 - S) = \frac{\mu}{Y_{X/S}}(X + X_s), \tag{5}$$

where, S_0 is the feed concentration of substrate, mg/L; S is the effluent concentration of substrate, mg/L; $Y_{x/s}$ is the yield factor,

$$Y_{X/S} = \frac{X}{(S_0 - S)}, \tag{6}$$

so the

$$\mu = \frac{DY_{X/S}(S_0 - S)}{X + X_s}, \tag{7}$$

then the model parameters evaluated as follows: from Table 1 and by regression analysis we get yield factor $Y_{x/s} = 0.933$g cell mass/mmol substrate. By correlation coefficient test (Xiao, 1982; Li, 1981), we can do significant test in Equation (6) and obtain correlation coefficient $r = 0.936$. When considering degree of confidence 0.01, the critical value of the correlation coefficient $r_{0.01} = 0.714$ and $r > r_{0.01}$, it is significant relevance.

Comparing with the normal AS system, PACT-AS system presented large potential, it could increase the optimum dilution rate from 0.18h^{-1} to $0.24\ \text{h}^{-1}$, critical dilution rate from $0.34\ \text{h}^{-1}$

to 0.50h^{-1} and thus increased the efficiency of organic wastewater treatment. This paper emphasis on the kinetic model obtained from the adsorption rate and dilution rate, the model is worthy to guide simulate pilot and itself not very complicated. Wastewater biotreatment is a complex biochemical reaction with a lot of factors interrelated. The kinetic model proposed here needs further studies and improvement as there are still some limitative factors not to be considered.

4 Conclusion

Kinetic of continuous biotreatment of organic triazophos wastewater with *Rhodopseudomonas capsulatus* and activated carbon and activated sludge system(PACT-AS) was studied. Comparing with the normal AS system, under the same dilution rate PACT-AS system could decrease COD value 4%—20%, and under suitable dilution rate could decrease COD value 13%—20%. The optimum dilution rate increased from 0.18h^{-1} to 0.24 h^{-1}, critical dilution rate from 0.34h^{-1} to 0.50 h^{-1}, which presented the PACT-AS system more advantage and impact load resistant capacity.

Adsorption kinetic of methylene blue by bioactivated carbon indicated that microorganisms immobilized in activated carbon showed strong degradation capacity and also made activated carbon regenerated easily, which provide a theory basis for the application of PACT-AS system.

During stable state period of bioreaction, the Monod function in terms of substrate consumption and cell growth was amended. By regression analysis the yield factor $Y_{x/s}=0.933$ g cell mass/mmol substrate, correlation coefficient $r=0.936$ and $r>r_{0.01}$ significant relevance were obtained to show well-consistency between the model and test data.

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