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Influence of inorganic salt on aerobic biodegradability of dyestuffs

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Abstract: In this paper, the influence of inorganic salt on aerobic biodegradability of dyestuffs was studied by means of semi-continuous activated sludge method. It was found that: biodegradability of dyestuffs would decrease with the increase of the concentration of NaCl; however, biodegradability in the condition of NaCl = 30 g/L was better than that in the condition of NaCl = 15 g/L; in the three NaCl conditions, biodegradability of tested dyestuffs followed the following order: NaCl = 0 g/L > NaCl = 30 g/L > NaCl = 15 g/L.

Key words: biodegradability; dyestuffs; inorganic salt; degradation efficiency

Introduction

Industrial wastewater often contains highly-concentrated inorganic salts. Common cations include K^+, Na^+ and Ca^{2+}, and common anions include Cl^-, SO_4^{2-} and NO_3^-. For example, wastewater from the process of dyestuffs, such as cationic blue X-GRRL, basic brown, basic orange, basic violet 5BN and basic green, contains sodium chloride with the concentration of 10 g/L to more than 200 g/L. Because biological treatment process is the prevailing economical and practical process to treat wastewater, it is proper to apply biological process to treat saline wastewater. However, highly-concentrated inorganic salt restricts the application because inorganic salts influence osmotic pressure and decrease the saturation concentration of oxygen in wastewater. Many researchers have focused in biological treatment of saline wastewater (Fikret, 1997; Hamoda, 1995; Shimshon, 1993; An, 1993; Yang, 1995) and many valuable results have been obtained. However, further research on influence of inorganic salt on biodegradability of organic substances has not been reported. Meanwhile, because a large amount of organic substances have entered the sea, which causes serious sea pollution, it is important to study the biodegradability of organic substances in sea water condition with the inorganic concentration from 3.5% to 3.8%. The objective of this research was to study the influence of inorganic salt on biodegradability of dyestuff.

1 Methods and material

1.1 Method to test the biodegradability of organic substances

Some standard methods have been developed to test aerobic biodegradability of organic substances, such as a series of OECD test (OECD, 1981a; 1981b; 1981c, 1981d). In this paper, modified SCAS (semi-continuous activated sludge) method (OECD, 1981c) was employed. The principle of the method is: tested organic substance is one of carbon source in the testing system and the other carbon source is precipitated domestic wastewater. Tested organic substance could contact with the microorganisms completely. The mixture of activated sludge, tested organic substance and domestic wastewater is aerated for 23 hours, and then aeration is stopped and settled for 45 minutes. Then, supernatant is taken and soluble TOC in supernatant is monitored to calculate degradation efficiency that indicates the biodegradability of tested organic substance.

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Then, new tested organic substance and activated sludge are added and mixed with activated sludge and a new period starts. In this experiment, in order to control the concentration of the other carbon source easily, glucose nutrition solution with fixed component took the place of domestic wastewater. It was consisted of: glucose 250 mg/L, NH_4Cl 47.8 mg/L and KH_2PO_4 10.97 mg/L, so that COD : N : P = 100 : 5 : 1. The solution was adjusted to pH = 7.0. Furthermore, the solution contained enough inorganic salt so that the concentration of inorganic salt equaled the required concentration.

1.2 Tested organic substances

As mentioned above, during the production of the five dyestuffs including cationic blue X-GRRL, basic brown, basic orange, basic violet 5BN and basic green, discharged wastewater contains highly-concentrated NaCl. So, the five dyestuffs were selected as tested organic substances.

The storage solutions of the five dyestuffs were prepared as 2 g/L.

1.3 Inorganic salt

The tested inorganic salt was selected as NaCl, because NaCl is the main inorganic salt contained in wastewater and it is the main inorganic salt in seawater. In this paper, the concentrations of NaCl were selected as 15 g/L and 30 g/L.

1.4 Activated sludge

Activated sludge was taken from reactors treating saline domestic wastewater that contained NaCl of required concentration for more than 2 months. It could be thought to be adapted to NaCl. At first, activated sedge was washed with NaCl solution and concentrated into 6 g/L (certainly, the solvent was NaCl solution, too). Then, 50 ml activated sludge was added into five 500 ml flasks, so after 100 ml nutrition solution was added into, the final concentration of activated sludge was 2 g/L.

1.5 Monitoring items

Concentration of dyestuff was calculated from absorbancy at the characteristic absorption peak. Firstly, a linear relationship between concentration and absorbancy was obtained. Then, concentration was calculated once absorbancy at the characteristic absorption peak was given.

Color of dyestuff was measured based on ADMI method (Mary, 1985).

Because of high Cl^-, it is difficult to analyze COD or TOC (Mary, 1985). Degradation efficiency of concentration and colour of dyestuff was applied to show degradability. However, the two indicators are not perfect because the concentration shows the first stage of biodegradation and the colour shows the composition having chromophoric group.

2 Experimental procedures

The following procedure was for cationic blue X-GRRL, and it was also for the other four dyestuffs.

Adding 2 ml storage solution into 100 ml nutrition solution, so that the tested concentration of dyestuff was 40 mg/L. Then the mixture was added into a 500 ml flask. The activated sludge was 2 g/L. The flask was shaken on a thermostatic shaker at 100 r/min and room temperature. After 23 hours, the shaker was turned off and mixture was settled for 45 min. One period includes 23 hours, for aeration and 45 minutes for sedimentation and 15 minutes for sampling. After sedimentation, 102 ml supernatant was taken and analyzed for concentration colour. Then, adding 102 ml nutrition solution with 40 mg/L dye into the flask again. The test lasted 2 weeks, namely 14 periods. For NaCl = 30 g/L, testing period doubled, namely the test lasted 28 periods.

It was noted that if the tested NaCl concentration was x g/L, activated sludge must be adapted to x g/L and the nutrition solution contained x g/L NaCl. In this test, $x = 0$, 15 and 30 mg/L.

3 Results and discussion

Fig.1—5 show degradation efficiency of the five dyestuffs in 14 periods in the three different concentrations of inorganic salt conditions.

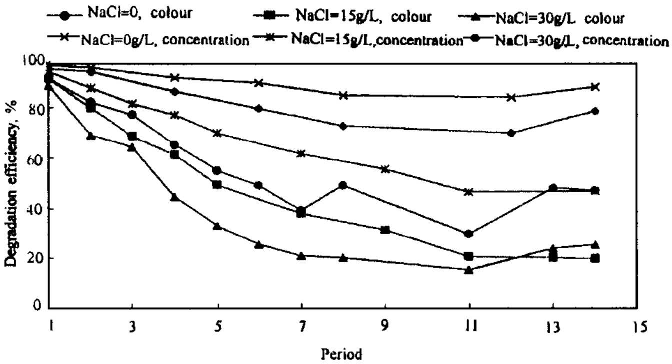

Fig.1 Biodegradation of cationic blue X-GRRL in 14 periods
1. NaCl = 0, colour; 2. NaCl = 15 g/L, colour; 3. NaCl = 30 g/L, colour; 4. NaCl = 0 g/L, concentration; 5. NaCl = 15 g/L, concentration; 6. NaCl = 30 g/L, concentration

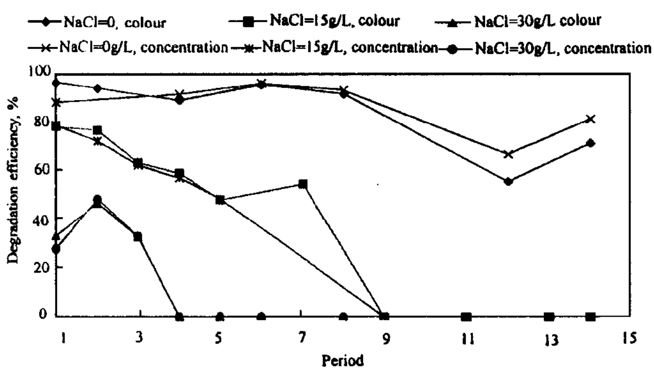

Fig.2 Biodegradation of basic brown in 14 periods
1. NaCl = 0, Color; 2. NaCl = 15 g/L, Color; 3. NaCl = 30 g/L, colour; 4. NaCl = 0, concentration; 5. NaCl = 15 g/L, concentration; 6. NaCl = 30 g/L, concentration

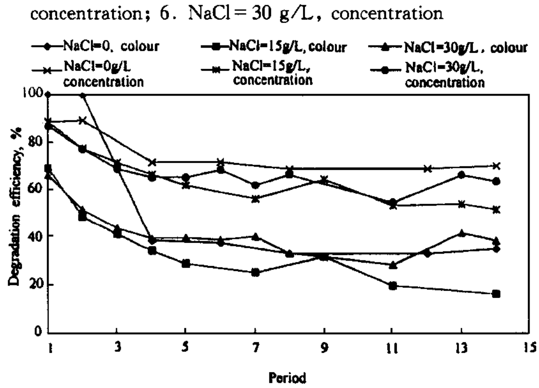

Fig.3 Biodegradation of basic orange in 14 periods
1. NaCl = 0, colour; 2. NaCl = 15 g/L, colour; 3. NaCl = 30 g/L, colour; 4. NaCl = 0, concentration; 5. NaCl = 15 g/L, concentration; 6. NaCl = 30 g/L, concentration

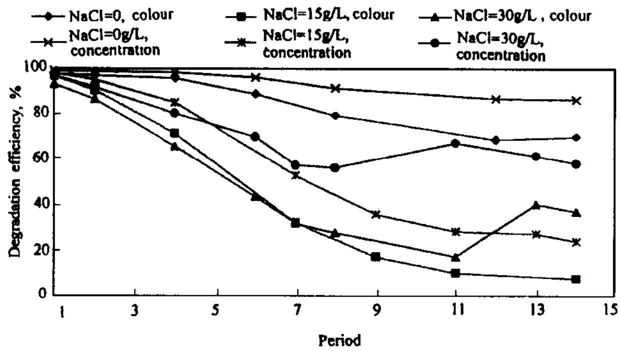

Fig.4 Biodegradation of basic violet in 14 periods
1. NaCl = 0, colour; 2. NaCl = 15 g/L, colour; 3. NaCl = 30 g/L, colour; 4. NaCl = 0, concentration; 5. NaCl = 15 g/L, concentration; 6. NaCl = 30 g/L, concentration

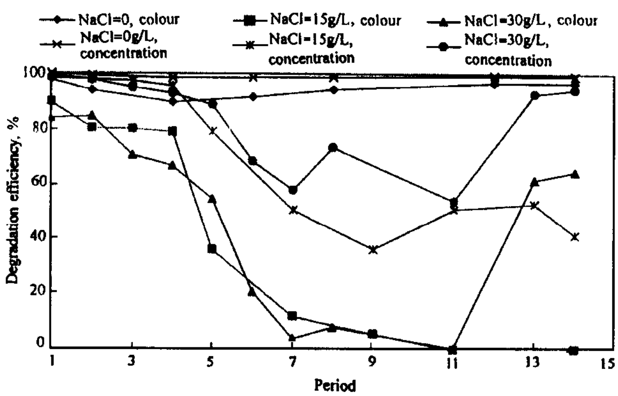

Fig.5 Biodegradation of basic green in 14 periods
1. NaCl = 0, colour; 2. NaCl = 15 g/L, colour; 3. NaCl = 30 g/L, colour; 4. NaCl = 0, concentration; 5. NaCl = 15 g/L, concentration; 6. NaCl = 30 g/L, concentration

From Fig.1—Fig.5, it could be found that:

(1) Because of biological absorption of organic substances on activated sludge, in the first several periods, "degradation efficiency" was high (Pagga, 1986). After certain periods, because of the saturation of absorption, "degradation efficiency" (showed in efficiency axis) lowered. At last, it kept stable or a little higher because of biodegradation after acclimation.

(2) According to "degradation efficiency" on the first period, inorganic salt influenced the first-stage biological adsorption of dyes on activated sludge slightly.

(3) Ultimate degradation efficiency of colour was lower than that of concentration. For example, to basic orange, degradation efficiency of colour was only 35.4%, which was much lower than that of concentration of 70.1%, as was resulted from some new chromophobic products produced in biodegradation of dyestuffs.

(4) Inorganic salt influenced biodegradability of dyestuffs notably: ultimate degradation efficiency of the five dyestuffs in salt-free condition was higher than that in salt condition. Table 1 summarized the degradation efficiency of the five dyestuffs in the three salt conditions.

Table 1 Degradation efficiency of the five dyestuffs in the three salt condition, %

	Cationic blue		Basic orange		Basic brown		Basic violet		Basic green	
	Color	Con.	Color	Con.	Color	Con.	Color	Con.	Color	Con.
NaCl = 0	70.0	86.0	33.3	68.8	71.8	81.8	70.1	86.4	96.7	99.3
NaCl = 15 g/L	20.5	47.8	16.8	51.7	0	0	7.8	27.5	0.6	42.1
NaCl = 30 g/L	24.7	49.5	41.9	66.1	0	0	40.5	61.6	62.3	92.8

Based on degradation efficiency of concentration, biodegradability of dyestuffs could be divided into four categories: if degradation efficiency > 70% , easily biodegradable; if degradation efficiency is 40%—70%, biodegradable; if degradation efficiency is 20%—40%, poorly biodegradable; if degradation efficiency <20% , nonbiodegradable.

According to this classification standard, biodegradability of the five dyestuffs in the three salt conditions is listed in Table 2.

Table 2 Biodegradability of the five dyestuffs in the three salt conditions

	NaCl, 0 g/L	NaCl, 15 g/L	NaCl, 30 g/L
Cationic blue X-GRRL	Very biodegradable	Biodegradable	Biodegradable
Basic orange	Biodegradable	Biodegradable	Biodegradable
Basic brown	Very biodegradable	Non-biodegradable	Non-biodegradable
Basic violet 5 BN	Very biodegradable	Poorly biodegradable	Biodegradable
Basic green	Very biodegradable	Biodegradable	Very biodegradable

(5) When NaCl = 15 g/L and 30 g/L, degradation efficiency of basic brown was zero, as showed that basic grown was not biodegraded. The reason may be that in high inorganic condition the toxicity of basic grown on activated sludge arose. This conclusion could be found in the study on effect of environmental factors on the toxicities of surfactants to marine life (Michael, 1992): salinity increased the toxicity of a granular detergent containing 30% ABS to juvenile eels and mummichogs and anionic surfactant was more toxic to a marine copepod at higher salinities.

(6) From the above two tables, except for basic grown, it was obvious that biodegradability in the condition of NaCl = 15 g/L was lower than that in the condition of NaCl = 30 g/L. The reason may be that in high salt condition the activity of halophilic microorganisms could be performed better than in middle salt condition, while in middle or lower salt condition, such as NaCl = 15g/L, the activity of halophilic microorganism and normal non-halophilic microorganism would be hindered.

(7) From Table 1, the influence of inorganic salt on degradation efficiency of colour was more remarkable than that on degradation efficiency of concentration. The reason was that further biodegradation of chomophoric products was hindered by inorganic salt.

(8) From Table 1, the influence of inorganic salt on biodegradation of dyestuffs varied with the kind of dyestuffs.

In the condition of NaCl = 30 g/L, testing time were doubled to 28 periods. The result is shown in Fig.6 and Fig.7 (because degradation of basic brown is zero, its degradation efficiency was not involved in the two figures).

From Fig. 6 and Fig.7, it could be concluded that in 14 periods, degradation efficiency of concentration and colour of cationic blue X-GRRL, basic orange, basic violet 5BN was stable, so

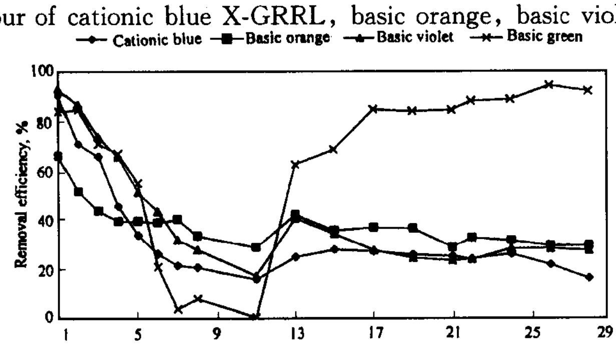

Fig.6 Biodegradation of dyestuffs in 28 periods based on colour, NaCl = 30 g/L
1. cationic blue; 2. basic orange; 3. basic violet; 4. basic green

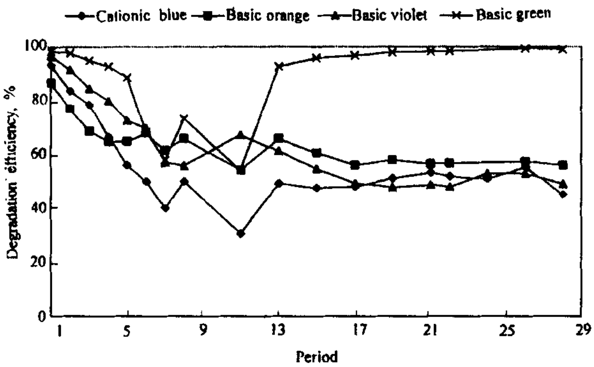

Fig. 7 Biodegradation of dyestuffs in 28 periods based on concentration, NaCl = 30 g/L
1. cationic blue; 2. basic orange; 3. basic violet; 4. basic green

14 periods was proper. However, with respect to basic green, after 14 periods, degradation efficiency still rose steeply, which showed that the complete biodegradation of basic green needs longer time. Therefore, in some cases, 14 periods was short to test biodegradability of organic substances. However, appropriate testing time is difficult to be determined (Grady, 1985).

4 Conclusion

From the experiment, it could be concluded that the effect of NaCl concentration on the biodegradability of dyes followed the order: NaCl = 0 g/L > NaCl = 30 g/L > $CaCl_2$ = 15 g/L. So, the influence of inorganic salt on biodegradability varies with the concentration of inorganic salt. It should be noted that in common opinion, biodegradability of organics would be reduced in high concentration of inorganic salt. However, from the above analysis, the opinion was wrong to some organics. Inorganic salt should be considered as one important factor in biodegradability test while it has been omitted in some methods for testing aerobic and anaerobic biodegradability.

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