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A Study On Surfactant Industrial Wastewater Treatment With Ferric-Carbon Electrical Fenton Method

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ABSTRACT

A study on surfactant industrial (Nekal BX) wastewater treatment by Ferric-Carbon electrical Fenton method was conducted. The technical parameters and treatment effect were presented in this paper. The treatment scheme was coagulating sedimentation-acidified aeration Fe-C electrical Fenton-neutralized sedimentation. When t=40min, pH=4 and Fe:C=1:1 the total removal rate of nekal BX and COD were 87.7% and 83.4% respectively.   © 2006 Trade Science Inc. - INDIA

INTRODUCTION

Nekal BX (1, 2-butylnaphthalene-6-sulfonic sodium) is a kind of toxic biorefractory surfactant with branch chain structure and more chemical stable than LAS for produce special rubber.The effective and cheaper treatment method was not reported at present. This paper studied the Nekal BX wastewater with Ferric-Carbon electrical Fenton method to improve it biodegradability.

The major mechanism of removal pollutant is "Electrical Fenton reaction (pH=3~5)". The cardinal reactions list below:

anode: $Fe-2e \rightarrow Fe^{2+}$ $E_0(Fe^{2+}/Fe) = -0.44v$

cathode:

1) $2H^+ + 2e \rightarrow 2[H] \rightarrow H_2\uparrow E_0(H^+/H_2)=0.00v$ (acidic)

2) $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ $E_0(O_2/H_2O)=1.23v$ (acidic and abounded oxygen)

3) $O_2 + 2H_2O + 4e \rightarrow 4OH^- \rightarrow 2OH^- + H_2O_2$ $E_0(O_2/OH^-)=0.4v$ (neutral and abounded oxygen)

If some Fe^{2+} in the solution, then the "Electrical Fenton reaction" occurs:

$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HO_2$
$Fe^{2+} + HO_2 + H^+ \rightarrow Fe^{3+} + H_2O_2$
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ (the following reactions are "Fenton reactions")

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OH and H_2O_2 produced in the reactions have very strong activation and oxidizability[1-4]. The pollutant molecule could be oxidized by OH and H_2O_2 through electron transfer, addition and dehydrogenation etc[5-8].

MATERIALS AND METHODS

Wastewater quality

The wastewater was collected from a butylnitrile rubber workshop. The quality was Nekal BX 600~800mg/L,CODcr3000~5000mg/L,BOD$_5$ 200~400 mg/L, SS400~700mg/L, pH6~7.

The analytical methods used refer to "Analytical Method of Water and Wastewater"[9].

Methods

Waste paring of low-carbon steel (bulk 10mm ×15mm) was selected for Ferric filling, and the pillar shape activated carbon (bulk 3mm × L12mm) for carbon filling. Dip carbon filling into initial wastewater till saturated adsorption before use. Ferric filling was activated in 1mol/L sulphuric acid 30min, and then scoured off the residual acid. Ferric and carbon filling were put into the triangle bottle (500ml). The wastewater was passed through coagulation sedimentation firstly for reducing a lot of colloid suspensions and adjusted the pH value before put into the reactor (triangle bottle). Air was put into the reactor that laid on the rocking bed (100r/min) for reaction. The pH value of effluent adjusted with $Ca(OH)_2$ at last. The supernatant was the last outflow. Technical process list below:
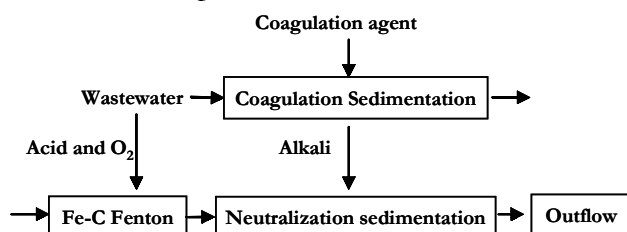
RESULTS AND DISCUSSION

Coagulation sedimentation uniform design

The uniform design[10] is an efficient fractional factorial design. It was proposed by Prof. Fang Kai-

TABLE 1 : Uniform experiment of coagulating sedimentation
(Initial wastewater pH=6.7; CODcr3007mg/L; BX692.3 mg/L)

Initial pH	FeCl$_3$ concentration mg/L	PAM concentration mg/L	CODcr removal rate%	BX removal rate%
5	150	1.5	32.9	2.33
6	250	1.2	38.1	4.65
7	100	1.0	32.9	0.00
8	200	0.5	26.5	4.65
9	300	2.0	35.5	2.33

Tai and Professor Wang Yuan in 1980. It has been successfully used in various fields. The space-filling design has played an important role in large system engineering.

The data of TABLE 1 was regression analyzed by the uniform design. The result shows lower pH, higher concentration of FeCl$_3$ and PAM caused better removal rate of CODcr through the regression analysis of the results in TABLE 1. The sequence of the factors according to the treatment effect was pH< Concentration of FeCl$_3$< Concentration of PAM. The average removal rate of nekal BX and COD was 5~10% and 30~40% respectively when remaining the initial pH value and adding FeCl$_3$ 200mg/L+PAM 1.0mg/L. SS removed entirely at that condition.

Ferric-carbon electrical fenton uniform design

Initial pH, reaction time, Fe:C were investigated and the data in TABLE 2 showed the results of uniform experiment $U_5(5^3)$.

The results in Table 2 showed the removal rate of BX was highest at the second scheme. After regression analysis the best range of initial pH, reaction time and Fe:C were 3-5, 30-50 minute and

TABLE 2: Fe-C electrical fenton uniform experiment
(Initial wastewater CODcr2440mg/L, BX 712.8mg/L)

Initial pH	Effluent pH	T min	Fe:C	COD removal rate%	BX removal rate%
3	4.5	30	1:02	36.6	81.0
4	5.0	60	1:01	35.8	82.1
5	5.8	20	2:01	22.5	71.0
6	7.0	40	3:01	16.3	59.8
7	7.4	80	1:03	8.5	43.2

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1:2,1:1,2:1 respectively.

Effect of initial pH value

The initial pH was optimized and the results were showed in TABLE 3. From TABLE 3, the removal rate of COD and BX decreases with increasing pH value in Fe-C electrical Fenton outflow. It was seen that the decreases of H^+ concentration was not in favor of the electrical Fenton reaction. But compared between the removal rate of BX and the dosage of acid suggested in TABLE 3, the optimal pH value was 4.

TABLE 3: Treatment effect influenced by PH
(Fe:C=1:1, t=40min; inflow CODcr2445mg/L, BX708.4mg/L)

Initial pH	Effluent COD mg/L	COD removal rate%	Effluent BX mg/L	BX removal rate%
3	1537	37.1	134.7	81.0
4	1672	31.6	148.1	79.1
5	1850	24.3	212.0	70.1

Effect of Fe:C

Fe:C value was studied and the results in TABLE 4 make it clear that BX removal effect was best at Fe:C=1:1. But the removal rate of COD was highest when Fe:C=1:2. So Fe:C=1:1was selected for BX was the major pollutant.

TABLE 4: Treatment effect influenced by Fe:C
(pH=4, t=40min; inflow CODcr2445mg/L, BX 708.4mg/L)

Fe:C	Effluent COD mg/L	COD removal rate%	Effluent BX mg/L	BX removal rate %
1:02	1571	35.7	170.7	75.9
1:01	1672	31.6	148.1	79.1
2:01	1770	27.6	186.8	73.6

Reaction time and kinetic analysis

The effect of reaction time was discussed in figure 1. The results of figure 1 showed that the removal of 30% COD and 80% BX take place within the first 40 min, and an additional 40 min yields a further 5% COD and 4% BX removal respectively. So the selected reaction time was 40min because of a little change after 60min.

About 80% BX removed by Fe-C electrical Fenton reaction, but only 35% CODcr removed were
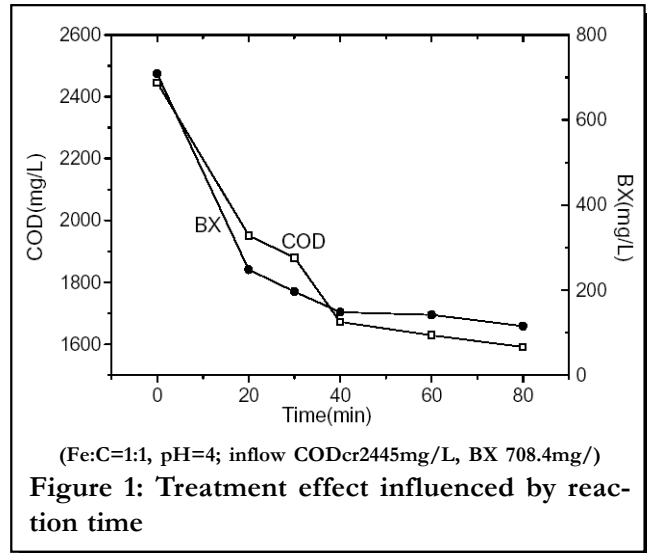

(Fe:C=1:1, pH=4; inflow CODcr2445mg/L, BX 708.4mg/)
Figure 1: Treatment effect influenced by reaction time

C—concentration of COD or BX, mg/L;
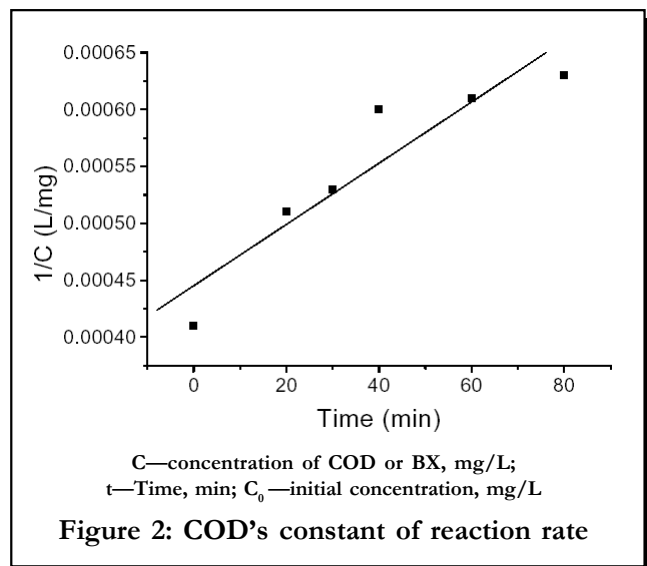t—Time, min; C_0—initial concentration, mg/L
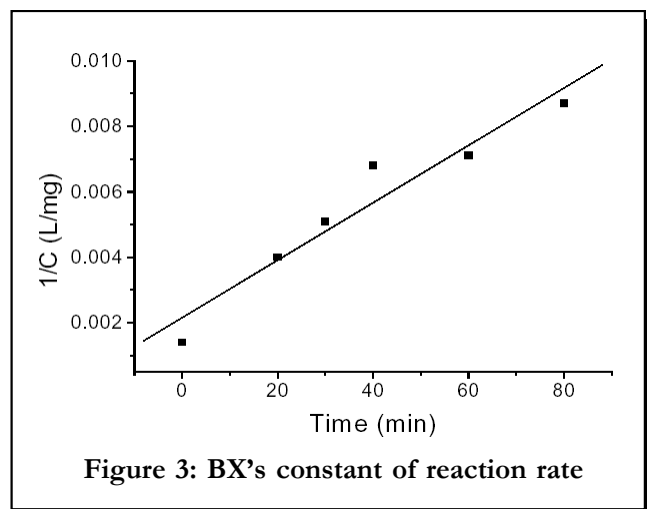**Figure 2: COD's constant of reaction rate**

Figure 3: BX's constant of reaction rate

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present in figure 1. It must be emphasized that about 60% COD come from BX in initial wastewater. Therefore, it was reasonable to postulate that this method oxidize BX into small molecule organic pollutant but not carbon.

Figure 2 and 3 showed 1/C increases linearly with time. The removal rates of COD and BX were in accordance with secondary reaction dynamics.

COD : $r = 0.93101 > r_{min(0.01)} = 0.917$;

BX : $r = 0.9654 > r_{min(0.01)} = 0.959$.

Formula: $\dfrac{1}{C} = \dfrac{1}{C_0} + Kt$

COD: $\dfrac{1}{C} = 4.452 \times 10^{-4} + 2.69 \times 10^{-6}\, t$

BX: $\dfrac{1}{C} = 0.00215 + 8.77 \times 10^{-5}\, t$

Neutralization sedimentation

Initial wastewater was treated with the optimal technical parameters selected from above paragraphs (t=40min, pH=4, Fe:C=1:1). The pH value of the

Figure 4: Effect influenced by neutralization sedimentation

Fe-C electrical Fenton reaction effluent was adjusted to 8-9. Then it was agitated and deposited about 30min. The remain concentration of COD and BX was determined in this process. The quality of inflow was COD1500~2000mg/L, BX 135~200mg/L. And the quality of effluent was COD1100~1700 mg/L, BX130~200 mg/L in neutralization sedimentation process.

As the results in figure 4 demonstrated, COD and BX removed rates could be removed 10~20% and 2~4% respectively in addition.

Proving experiment

Whole technical process was run for proving the optimal technical parameter. From TABLE 5, it was clear BX and COD total removal effect were evident, and that selected parameters were appropriate.

Removal rates mean the treatment effect taken place in every one of the processes list in TABLE 5. Fe:C value was 1:1.

CONCLUSIONS

The results obtained in this work allow the conclusion that pollutant removal effect was evident by the suggested Fe-C techniques. When t=40min, pH=4 and Fe:C=1:1 the total removal rate of nekal BX and COD were 87.7% and 83.4% respectively. The high removal rate of boirefractory BX was benefit for biodegradation later.

In conclusion, the method neither needs the more power supply nor the complicated processing unit. The cost is cheap as well as the effect is notable.

ACKNOWLEDGEMENTS

TABLE 5:Proving trial result
(**1-**Initial wastewater**; 2-**Coagulating sedimentation**; 3-**Fe-C Electrical Fenton**; 4-** Neutralized sedimentation)

Processes	Initial pH	Effluent pH	T (min)	COD removal rate%	BX removal rate%
1	6.8	-	-	-	-
2	6.8	5.9	42	46.3	2.1
3	4.1	5.4	40	50.9	85.6
4	7.9	6.0	20	37.1	12.1
Total removal rate%				83.4	87.7

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