Journal of Environmental Sciences Vol.14, No.3, pp.345—350, 2002

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2002)03-0345-06 **CLC number**: X13 **Document code**: A

Preparation of PFS coagulant by sectionalized reactor

CHANG Qing*, WANG Hong-yu

(Department of Environmental Engineering, Lanzhou Railway College, Lanzhou 730070, China. E-mail: changq@lzri.edu.cn)

Abstract: The oxidation rate of ferrous sulfate is investigated for the preparation of polyferric sulfate (PFS) coagulant. It is proved that this reaction is zero order with respect to Fe^{2+}, first order with respect to $NO_2(g)$, and first order with respect to the interface area between gas phase and liquid phase. According to this mechanism, sectionalized reactor (SR) is used in place of traditional reactor (TR), and the liquid of reaction mixture is recycled by pump. As a result, not only the flow path of reaction liquid is prolonged, but also gas-liquid contact area enlarged, and the reaction distinctly accelerated, compared with traditional reactor. The effects of parameters including temperature, acidity and others on the reaction rate are also discussed.

Keywords: coagulant; flocculant; polyferric sulfate; PFS; oxidation rate; water treatment

Introduction

Polyferric sulfate (PFS) is a sort of inorganic coagulant with high molecular weight. The general formula is $[Fe_2(OH)_n(SO_4)_{3-0.5n}]_m$ ($n < 2$, $m > 10$) (Chang, 1993). It contains polynuclear complex ions such as $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$ formed by OH bridge and a large quantity of inorganic macromolecular compounds. The molecular weight can be as high as 10^5 (Spiro, 1966). These constituents can be adsorbed by colloidal particles so that the surface charge of colloids and suspended substances is neutralized, so the colloidal particles and suspended substances change from repelling each other to attracting each other, then collide and precipitate as large aggregates. Because these large aggregates have very large surface area with excellent adsorption capacity, PFS is more effective than any other inorganic coagulants for removing COD, BOD, color and dissolved organic matter from natural water or waste water. In addition, PFS is very efficient within wider ranges of temperature and pH value because of its strong hydrolysis. So it can be used under low-temperature conditions.

A preparation method of PFS coagulant from $FeSO_4$ was reported by Japanese scientists in the 1970's (Shigeo, 1978; Mikami, 1980). Today, it is still a practicable method because the materials used in this method are very cheap. In this method, iron in a ferrous state is oxidized to ferric state when using O_2 as the oxidant and $NaNO_2$ as the catalyst. After this oxidation, the partial hydrolysis and polymerization of ferric iron are followed. Since the 1980's, the preparation and application of PFS have been widely investigated in China (Yang, 1986; Chen, 1995; Li, 1995; 1998; Bai, 1996; Chang, 2001) and other countries (Tang, 1987a; 1987b; Jiang, 1993; 1998) because of its high coagulation performance in water treatment. But so far the mechanism of the preparation has not been properly understood, as a result, now the time needed to complete the preparation is still too long. In order to shorten the preparation time and consider the scientific relevance, the reaction kinetics and the technological process are investigated.

1 Mechanism of preparation

1.1 The equations of reaction

$$NO_2^-(aq) + H^+(aq) = HNO_2(aq), \quad (1)$$

$$2HNO_2(aq) = N_2O_3(aq) + H_2O, \quad (2)$$

$$N_2O_3(aq) = NO(aq) + NO_2(aq), \quad (3)$$

$$NO(aq) = NO(g), \quad (4)$$

$$2NO(g) = N_2O_2(g), \quad (5)$$

* Corresponding author

$$N_2O_2(g) + O_2(g) = 2NO_2(g)\ , \tag{6}$$

$$NO_2(g) = NO_2(aq)\ , \tag{7}$$

$$Fe^{2+}(aq) + NO_2(aq) = Fe^{3+}(aq) + NO_2^-(aq)\ , \tag{8}$$

$$2mFe^{3+} + 2mSO_4^{2-} + (1 - 0.5n)mH_2SO_4 + mnH_2O = [Fe_2(OH)_n(SO_4)_{3-0.5n}]_m + mnH^+\ . \tag{9}$$

Where $NaNO_2$ acts as the catalyst in these reactions. Eqs. (1)—(3) show that $NaNO_2$ reacts with H^+ producing NO_2 and NO when it is added to the solution. The produced NO in the solution enters gas phase and is oxidized by O_2 becoming NO_2, as shown in Eqs. (4)—(6). The produced NO_2 in the gas phase again enters liquid phase and oxidizes Fe^{2+} to Fe^{3+}, as shown in Eqs. (7)—(8). The NO_2^- produced in Eq. (8) repeats reactions (1)—(8), continuing the oxidation of Fe^{2+} to Fe^{3+}. Eq. (9) shows that the produced Fe^{3+} partially hydrolyzes and polymerizes becoming product PFS at last because the added sulfuric acid is not enough for ferric sulfate to form.

1.2 The transfer rate of NO_2

The rate equation of the transfer can be deduced by a "double membrane model" which is shown in Fig.1. From this figure it can be seen that C is the concentration of NO_2 in the main body of the gas phase or the liquid phase; C' is the concentration of NO_2 in the boundary layers. Because of turbulence in the gas phase and stir in the liquid phase, the concentration of NO_2 is uniform everywhere in the main bodies, but it decreases along the transfer direction in the boundary layers. When the transfer takes place, $NO_2(g)$ first enters the gas boundary layer, then passes through the liquid boundary layer, finally comes into the liquid main body. Because NO_2 transfers by means of diffusion in the boundary layers, the first Fick's law of diffusion is followed:

$$J_g = -D_g A\,[dC_{NO_2(g)}/dX_g] = D_g A[C_{NO_2(g)} - C'_{NO_2(g)})]/X_g\ , \tag{10}$$

$$J_l = -D_l A[dC_{NO_2(aq)}/dX_l] = D_l A[C'_{NO_2(aq)} - C_{NO_2(aq)}/X_l\ , \tag{11}$$

where J_g and J_l are the transfer rate of NO_2, D_g and D_l are the diffusion coefficients of NO_2, X_g and X_l are the thickness of the boundary layers, respectively in the gas boundary layer and the liquid boundary layer, A is the interface area. If Henry's law is followed, we will have $C'_{NO_2(g)} = HC'_{NO_2(aq)}$ and $C_{NO_2(g)} = HC^*_{NO_2(aq)}$, here H is Henry constant, $C^*_{NO_2(aq)}$ is the concentration of $NO_2(aq)$ in the liquid main body when it is in equilibrium with $NO_2(g)$ in the gas main body, and if the transfer reaches a stable state, $J = J_g = J_l$, so Equations (10) and (11) become:

$$J = D_g A[HC^*_{NO_2(aq)} - HC'_{NO_2(aq)}]/X_g\ , \tag{12}$$

$$J = D_l A[C'_{NO_2(aq)} - C_{NO_2(aq)}]/X_l\ . \tag{13}$$

Or

$$JX_g/D_gAH = C^*_{NO_2(aq)} - C'_{NO_2(aq)}\ , \tag{14}$$

$$JX_l/D_lA = C'_{NO_2(aq)} - C_{NO_2(aq)}\ . \tag{15}$$

By summation of (14) and (15), and by substituting $C'_{NO_2(g)}/H$ for $C^*_{NO_2(aq)}$ we have:

$$J = D_gD_lA[C_{NO_2(g)} - C_{NO_2(aq)}]/[X_gD_l + X_lD_gH]\ . \tag{16}$$

Since the solution was strongly stirred, X_l is very small and X_lD_gH can be neglected, Equation (16) becomes:

$$J = D_gA[C_{NO_2(g)} - HC_{NO_2(aq)}]/X_g\ . \tag{17}$$

It can be seen that the larger interface area is, the more quickly NO_2 transfers across the interface,

the higher partial pressure of $NO_2(g)$ is and the more quickly NO_2 transfers across the interface.

1.3 The concentration of NO_2 in the solution

As soon as $NO_2(g)$ enters the solution, it quickly reacts with Fe^{2+}. The concentration of $NO_2(aq)$ in the solution can be obtained by stable state treatment:

$$dC_{NO_2(aq)}/dt = J - VK_8 C_{Fe^{2+}} C_{NO_2(aq)} = D_gA[C_{NO_2(g)} - HC_{NO_2(aq)}]/X_g - VK_8 C_{Fe^{2+}} C_{NO_2(aq)} = 0, \quad (18)$$

where V is the volume of the solution, K_8 is the reaction rate constant of Eq. (8). From Eq. (18), following equation is obtained:

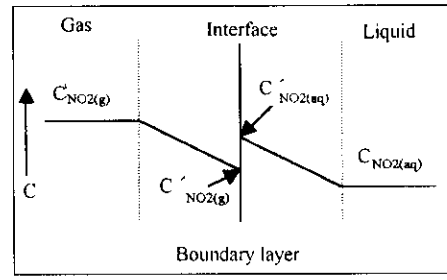

Fig.1 Double membrane model

$$C_{NO_2(aq)} = D_gAC_{NO_2(g)}/[X_g(D_gAH/X_g + VK_8 C_{Fe^{2+}})].$$

Because the gas phase was not stirred, X_g is relatively large. So D_gAH/X_g can be neglected, therefore we have

$$C_{NO_2(aq)} = D_gAC_{NO_2(g)}/X_gVK_8 C_{Fe^{2+}}. \quad (19)$$

1.4 The rate equations of the reaction

According to Eq. (8), the oxidation rate of Fe^{2+} is expressed as following:

$$-dC_{Fe^{2+}}/dt = K_8 C_{Fe^{2+}} C_{NO_2(aq)}. \quad (20)$$

By substituting Equation (19) for $C_{NO_2(aq)}$ in Equation (20), we have

$$-dC_{Fe^{2+}}/dt = D_gAC_{NO_2(g)}/(X_gV) = KAC_{NO_2(g)}, \quad (21)$$

where $K = D_g/(X_gV)$. It is clear that this reaction is zero order with respect to Fe^{2+}, first order with respect to $NO_2(g)$, and first order with respect to interface area A. So in order to reduce the time needed to complete the reaction, the pressure of $NO_2(g)$ can be increased (it was experimentally proved in Fig. 6), but this will make the corrosion of devices more serious, and the pressure resisting devices are to be adopted. Also the interface area between gas phase and liquid phase can be increased to reduce the reaction time.

If the $C_{NO_2(g)}$ and the interface area A are kept constant, Equation (21) becomes:

$$-dC_{Fe^{2+}}/dt = K, \quad (22)$$

the integral equation will be:

$$C_{Fe^{2+}} = -Kt + B, \quad (23)$$

where B is the integral constant. It shows Fe^{2+} decrease linearly with time. This is also proved by our experiment (Fig.4).

From above discussions and Equition (21), it is concluded that the transfer of NO_2 from gas phase to liquid phase is the key procedure and the gas-liquid interface area is an important factor which controls the rate of the whole process.

2 Experiment

2.1 Devices and process flow diagram for preparation of PFS

PFS was prepared by using the devices of traditional reactor (TR) and sectionalized reactor (SR) respectively, as shown in Fig.2 and Fig.3. The reactor volume is 1.5 dm^3 both for TR and for SR. When TR is used, the liquid of reaction mixture is strongly stirred by a stirrer; but when SR is used, the liquid of reaction mixture is recycled at a flow rate of 5 L/h by a wriggle pump during the whole process to prolong

the flow path of reaction liquid and enlarge the gas-liquid contact area.

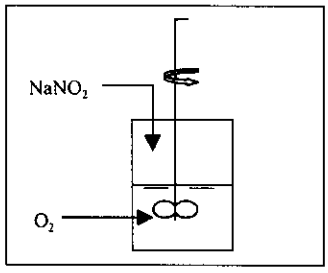

Fig.2 Traditional reactor

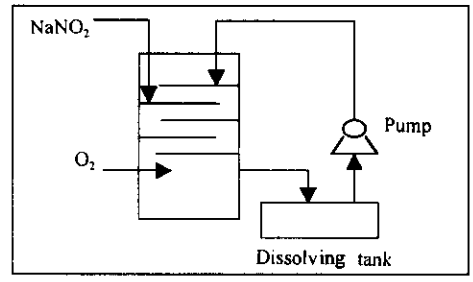

Fig.3 Sectionalized reactor

2.2 Experimental methods and procedures

The total amount of 324g $FeSO_4 \cdot 7H_2O$ was added to the reactor (TR or SR), but first only 162g $FeSO_4 \cdot 7H_2O$ along with 170 ml H_2O and 22 ml H_2SO_4 (95%—98%) were added because the solubility of $FeSO_4 \cdot 7H_2O$ is limited. Then the solution of $NaNO_2$ was slowly added to the reactor from the top of the reactor by a dropping funnel while pure oxygen was being conducted to the reactor from the bottom of the reactor, as shown in Fig.2 and Fig 3. In the following process, the remaining $FeSO_4 \cdot 7H_2O$ (162g) was added in batches, once every 5—10 minutes, until the addition of total amount of $FeSO_4 \cdot 7H_2O$ was finished. During the whole reaction process, temperature was maintained at 50—60℃, and pressure was controlled at 101325 ± 666.6 Pa by a gas receiver and a pressure gauge, and the reaction was carried out under hermetic condition. The solution in the reactors was sampled at intervals, and the total iron (III + II) was determined by potassium dichromate method, and the ferric iron by iodimetric method, and the ferrous iron by potassium permanganate method respectively. When all Fe^{2+} was oxidized to Fe^{3+}, the solution turned red brown. The reaction was ended. The viscosity of the product was measured by ubbelohde viscometer; and the hydrolysity of the product was measured by neutralization method; and the density of the product was measured by densimeter; and the pH value of the product was measured by acidimeter respectively.

3 Results and discussions

3.1 The properties of the product

The properties of the product are shown in the following table.

Table 1 The properties of the product

pH	Density, g/ml	Fe^{2+}, g/L	Fe^{3+}, g/L	Hydrolysity, [OH]/3[Fe]	Viscosity, cp
0.5	1.44	0.16	162	16%	11

It can be seen that the product fulfills the China National Standard Class A.

3.2 Comparison between SR and TR

Ferrous iron linearly decreases with time no matter what kind of reactor is used as shown in Fig.4. This result accords with the Eq.(23), which proves the above oxidation rate theory and the rate equations of reaction proposed by us.

The comparison of reaction rate between SR and TR is also shown in Fig.4. When TR is used, the renewal of liquid surface is made by stirring. Because of limiting stirring rate and small gas-liquid contact area, the reaction is very slow that the time needed to complete the reaction is more than ten hours. But when SR is used, the gas-liquid contact area is enlarged, and the transfer of NO_2 between gas-liquid interface is accelerated, so that the time needed to complete the reaction is cut down to 2-3 hours, again, this proves the theory and rate equation proposed by us.

3.3 Effect of temperature on reaction rate

As from Fig.5, the time needed to complete reaction decreases when temperature is raised within the range from 25℃ to 50℃. But temperature make little difference to reaction rate when it is above 50℃. When temperature is above 80℃, hydrolysis of the polymer is rather serious, so the yellow precipitant of $Fe(OH)SO_4$ forms readily. Therefore the optimum temperature should be controlled at 50℃.

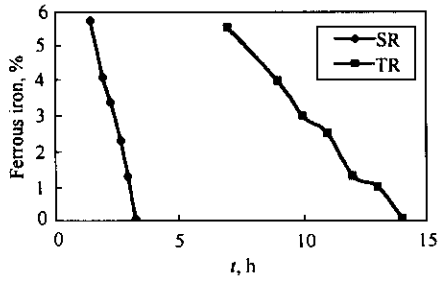

Fig.4 Comparison of reaction rate

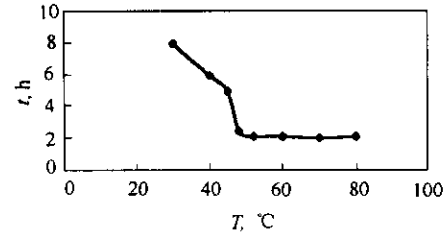

Fig.5 Relation between temperature and reaction time

3.4 Effect of $NaNO_2$ addition rate on reaction rate

The solution of $NaNO_2$ was dropped at intervals into SR during the entire reaction process. When the addition rate of $NaNO_2$ solution is higher, the partial pressure of $NO_2(g)$ is higher, and the ferrous iron more quickly changes to ferric iron, so the concentration of Fe^{2+} more quickly decreases as seen from Fig. 6. This result accords with the Eq.(21), which proves the theory and rate equation proposed above. It can be found that not only the change is slow, but also the total consumption of $NaNO_2$ is higher when the solution of $NaNO_2$ is dropped slowly. So the addition rate of $NaNO_2$ solution should not be too low.

3.5 Effect of acidity on reaction rate

The electrode potential for Fe^{3+}/Fe^{2+} is strongly depending on the acidity (or basicity) of the solution, which can be shown as follows:

in acid solution: $\phi^{\theta}(Fe^{3+}/Fe^{2+}) = 0.771V$;

in basic solution: $\phi^{\theta}(Fe^{3+}/Fe^{2+}) = -0.56V$.

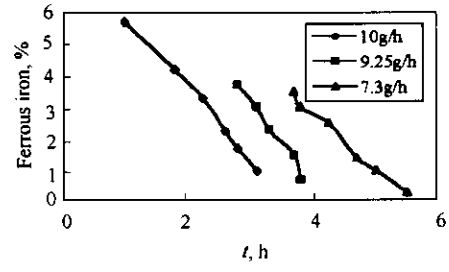

Fig.6 Effect of $NaNO_2$ addition rate on reaction rate

Therefore, when pH value of the solution is lower, Fe^{2+} is more stable than Fe^{3+}, and the former can not be easily oxidized; when pH value of the solution is higher, Fe^{3+} is more stable than Fe^{2+}, and the latter can be readily oxidized. So pH value should be as high as possible for changing Fe^{2+} into Fe^{3+}. But there is a limit because excessively high pH value can cause intense hydrolysis of Fe^{3+} and result in the formation of $Fe(OH)SO_4$ precipitant. Usually pH value should be lower than 1.6. To cope with this problem, both $FeSO_4 \cdot 7H_2O$ and concentrated sulfuric acid should be added in batches to decrease the concentration of Fe^{2+} and concentrated sulfuric acid in the solution.

3.6 Effect of the ratio of total SO_4^{2-} to total Fe on product viscosity

It was noticed that the ratio of total SO_4^{2-} to total Fe affects the viscosity of the product. Viscosity increases as the ratio is raised, as seen from Table 2. Yellow precipitant readily forms when the viscosity is too high, therefore, the ratio of total SO_4^{2-} to total Fe should be controlled carefully.

Table 2 The effect of SO_4^{2-} on the viscosity

No	ΣSO_4^{2-} (mol)/ΣFe(mol)	Viscosity, cp
1	1.20	11.8
2	1.25	13.4
3	1.30	14.8
4	1.35	15.3

4 Conclusions

The oxidation of ferrous sulfate is zero order with respect to Fe^{2+}, first order with respect to $NO_2(g)$, and first order with respect to the interface area between gas phase and liquid phase.

The transfer of $NO_2(g)$ across the interface between gas phase and liquid phase is the key procedure in the oxidation reaction of Fe^{2+} by oxygen. So sectionalized reactor was employed in place of traditional reactor and liquid of reaction mixture was recycled by pump to enlarge the gas-liquid contact area. As a result, the reaction was accelerated distinctly.

The reaction is accelerated when the temperature is raised, but too high temperature not only makes little difference to reaction rate, but also hastens the formation of precipitant. So the temperature should be controlled at 50 ± 2℃.

The reaction is accelerated when the pH value is raised, but too high pH value makes precipitant form readily. So the pH value should be controlled lower than 1.6.

Not only the reaction rate is lower but also the total consumption of $NaNO_2$ is higher when the solution of $NaNO_2$ is dropped more slowly. So the addition rate of $NaNO_2$ solution should not be too low.

References:

Bai Y X, Liu J, Li Y, 1996. Study on the catalyst for the preparation of PFS[J]. Water Treatment for Industry, 2:9—11.

Chang Q, 1993. The principle of flocculation[M]. Lanzhou University Press. 172—175.

Chang Q, 2001. Oxidation rate in the preparation of polyferric sulfate coagulant[J]. J Environ Sci, 13(1): 104—107.

Chen F J, Li F T, Du X R, 1995. Study on the new technology for the preparation of PFS[J]. China Water Supply and Drainage, 11(1): 42—44.

Jiang J Q, Graham N J D, Harward C, 1993. Comparison of polyferric sulfate with other coagulant for the removal of algae and algal-derived organic matter[J]. Wat Sci and Tech, 27(11): 221—229.

Jiang J Q, Graham N J D, 1998. Preparation and characterization of optimal polyferric sulfate(PFS) as a coagulant for water treatment[J]. J Chem Technol Biotecnol, 73:351—358.

Li F T, 1998. The new technology for preparation of PFS by oxidation with catalyst in foreign countries[J]. Water Treatment for Industry, 9: 9—10.

Li X J, 1995. The new technology for production of PFS[J]. Water Treatment for Industry, 1:5—6.

Mikami Hassuka *et al*., 1980. The polyferric coagulant[J]. PPM, 11(5): 24.

Spiro T G, Allerton S E, Renner J *et al*., 1966. The hydrolytic polymerization of iron(III)[J]. J Am Chem Soc, 88:2721—2726.

Shigeo Ban, 1978. Inorganic high MW coagulant[J]. Water Supply for Industry, (232):53.

Tang H X, Stuum W, 1987. The coagulating behaviors of Fe(III) polymeric species-I[J]. Water Res, 21(1): 115—121.

Tang H X, Stuum W, 1987. The coagulating behaviors of Fe(III) polymeric species-II[J]. Water Res, 21(1): 123—128.

Yang B L, Qiu Zh T, Li M J, 1986. Study on the preparation of new coagulant PFS using by-product $FeSO_4$ and waste H_2SO_4[J]. The Technology for Purification of Water, 3: 15—18.

(Received for review April 23, 2001. Accepted July 2, 2001)