

Study on UV Ferrous Activated Persulfate Degradation Conditions of Thiacloprid Pesticide Residues in Environmental Water

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Abstract: In order to degrade thiacloprid pesticide residues in environmental water, a UV ferrous activated persulfate system was constructed. The effects of Fe²⁺ concentration, persulfate concentration, pH value and UV power on the degradation rate of thiacloprid were investigated through a single factor experiment. On this basis, a mathematical model between the influencing factors and the response value was established using response surface experiment. The model fitting results showed that predicted highest thiacloprid degradation rate of the model was 100% when the Fe²⁺ concentration was 0.340mmol/L, the persulfate concentration was 0.610mmol/L and the UV power was 45.81W. The validation test result (99.2%) was basically consistent with the predicted value, indicating that the response surface methodology was feasible for optimizing the degradation of thiacloprid in the UV ferrous activated persulfate system.

Keywords: Pesticide residues; Thiacloprid; Persulfate; UV activation; Ferrous activation

1. Introduction

Thiacloprid is a commonly used neonicotinoid insecticide, which has the characteristics of high efficiency, low toxicity and wide application and has been widely used in recent years. At present, there are more than 2100 kinds of neonicotinoid insecticide products in China [1-4]. The residues of these pesticides seriously affect food safety and damage the ecological environment. For example, thiacloprid that enters the environmental water through surface runoff or wet and dry deposition has the half-life as long as 46-314 days, so it is easy to accumulate in the water environment and has great ecological toxicity [5-6]. Currently, the methods for removal of pesticide pollutants mainly include adsorption method, membrane separation process, advanced oxidation process (AOP) and microbial method. It is difficult to completely remove pesticide residues by adsorption method. The microbial method is applicable under quite rigorous environmental conditions and easy to produce resistance genes. The membrane separation process cannot directly degrade or eliminate pollutants and has high cost. The AOP can degrade macromolecular pollutants with high toxicity to small molecular products with low toxicity or non-toxicity, but its degradation efficiency needs to be improved. The AOP oxidizes macromolecular refractory organic substances into low-toxic or non-toxic small molecular substances through electrical, acoustic, light and other conditions. Among various kinds of AOPs, persulfate oxidation technology is a research hotspot in recent years.

Persulfate can generate sulfate radical anions (SO₄^{•-}) with high redox potential and strong activity [7]. In addition, persulfate is more stable than hydrogen peroxide, which makes it easier to store and transport. At the same time, due to the good stability of SO₄^{•-} in water [8], it has a good prospect in the field of environmental protection. Transition metals can activate persulfates [9]. Transition metals can be divided into homogeneous and heterogeneous types according to their morphology in solution. The advantages of homogeneous system are low mass transfer resistance and high reaction rate [10]. With the advantages of low toxicity and low cost [11], iron has attracted more attention than other transition metals (Co, Cu, Ni, Zn and V). Usually, 254nm is taken as the radiation wavelength of persulfate [12]. UV-persulfate technology has many advantages, such as low oxidant cost, stable properties, high free radical generation efficiency, high reaction rate, high removal efficiency of organic micro-pollutants, low requirements for environmental conditions, and not easy to cause secondary pollution [13-14]. The combination of UV and ferrous iron based on their activation characteristics is expected to contribute to higher degradation efficiency of thiacloprid with lower energy consumption. Based on this, in this study, the UV ferrous activated persulfate system was used to degrade thiacloprid, the influencing factors in the process were optimized by single factor experiment and response surface design, and the actual optimization effect was verified, in order to

provide data basis and scientific basis for the actual operation of thiacloprid degradation process.

2. Materials and methods

2.1 Materials, reagents and instruments

The thiacloprid came from SINOPHARM Medicine Holding Co., Ltd.; the methanol (chromatographically pure) came from Thermo Fisher Scientific; the acetonitrile (chromatographically pure) came from Shanghai Macklin Biochemical Co., Ltd.; and the sodium persulfate, concentrated sulfuric acid, sodium hydroxide, ferrous sulfate heptahydrate, etc. are all ARs that came from SINOPHARM Medicine Holding Co., Ltd.

The 1260Infinity HPLC came from Agilent; the ST2100pH meter came from Shenzhen DYP Technology Co., Ltd.; the STX12022H balance came from Sartorius (Shanghai) Trading Co., Ltd.; the UV-1500 UV spectrophotometer came from Macylab Instruments Inc; the 85-2A magnetic stirrer came from Xinrui Instrument Co., Ltd.; the GPH287T5VH/14W UV lamp came from Guangzhou Zhongxiang Environmental Protection Materials Co., Ltd.; and the 0.22 μ m organic filter membrane came from Tianjin Jinteng Experiment Equipment Co., Ltd.

2.2 Experimental method

Firstly, an appropriate amount of thiacloprid stock solution (100 mg/L) was prepared and then added with a certain amount of pure water and sodium persulfate solution ($\text{Na}_2\text{S}_2\text{O}_8$ concentration is 100mmol/L) to dilute it to 10mg/L. After its pH was adjusted with 0.1mol/L sodium hydroxide and 0.1mol/L dilute sulfuric acid, the solution was transferred to a 250mL conical flask (with reaction volume of 100mL). The conical flask was placed on the magnetic stirrer whose rotation speed was set to 120r/min, and added with a certain amount of ferrous sulfate solution. When the UV lamp is turned on, the total UV power is controlled by the number of UV lamps turned on (the power of each lamp is 15W). Then 1mL were sampled at different times and poured in a centrifuge tube filled with 1mL methanol in advance. After the reaction was terminated, the solution was filtered with a 0.22 μ m membrane, diluted 40 times and placed in a sample injection vial, and the concentration was detected by a high-performance liquid chromatograph (HPLC).

2.3 Analysis method

The concentration of thiacloprid before and after the reaction was quantitatively analyzed by HPLC, in which the ratio of water and acetonitrile in mobile phase was 45:55 (V/V), the injection volume was 10 μ L and the flow rate was 0.6mL/min.

The thiacloprid solution at an initial concentration of 40 μ M (10 mg/L) was tested by HPLC with Agilent 1260Infinity, in which the detection limit of thiacloprid was 0.8 μ M (approximately 0.2 mg/L). In terms of the chromatographic conditions, the detector wavelength was

242nm; the chromatographic column was ZORBAX SB-C18 4-Pack; and the column temperature was 30°C.

2.4 Single factor experiment

The effects of Fe^{2+} concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5mmol/L on the degradation rate were investigated respectively when the persulfate concentration was set at 0.6mmol/L, the UV power was set at 45W and the pH was set at 3.

The effects of sulfate concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0mmol/L on the degradation rate were investigated respectively when the Fe^{2+} concentration was set at 0.300mmol/L, the UV power was set at 45W and the pH was set at 3.

The effects of UV power of 15, 30, 45, 60 and 75W on the degradation rate were investigated respectively when the Fe^{2+} concentration was set at 0.300mmol/L, the sulfate concentration was set at 0.6mmol/L and the pH was set at 3.

The effects of pH of 1, 2, 3, 4 and 5 on the degradation rate were investigated respectively when the Fe^{2+} concentration was set at 0.300mmol/L, the sulfate concentration was set at 0.6mmol/L and the UV power was set at 45W.

2.5 Response surface experiment

According to the single factor experiment results as well as the combined design principle of Box Behnken Design Center, the extraction conditions were optimized by response surface experiment with Fe^{2+} concentration, persulfate concentration and UV power as independent variables, and thiacloprid degradation rate as the response value. Table 1 shows the coding of factors and levels.

Table 1 Coding of factors and levels

Factors	Levels		
	-1	0	1
A. Fe^{2+} concentration/mmol/L	0.200	0.300	0.400
B. Persulfate concentration/mmol/L	0.400	0.600	0.800
C. UV power/W	30	45	60

3. Results and discussion

3.1 Single factor experiment

3.1.1 Effect of Fe^{2+} concentration on degradation rate

The effect of different Fe^{2+} concentrations on the degradation rate is shown in Fig. 1. It can be seen from Fig. 1 that the degradation rate increases significantly with the increase of Fe^{2+} concentration, reaches the maximum when the Fe^{2+} concentration is 0.3mmol/L and then shows a downward trend with the increase of Fe^{2+} concentration. The reason is that transition metals and

their oxides can activate sulfate to degrade organic pollutants [9], and an appropriate amount of Fe^{2+} can effectively activate sulfate to degrade thiacloprid. When the Fe^{2+} concentration is low, the persulfate in the solution cannot be fully activated and a small amount of $SO_4^{\bullet-}$ is produced [15]. At this time, the degradation rate is not high. After the Fe^{2+} concentration is increased, the sulfate in the solution is greatly activated in a short period of time to produce a large amount of $SO_4^{\bullet-}$. However, when $SO_4^{\bullet-}$ is excessive, in addition to degrading the target pollutant thiacloprid, it will have a redox reaction with Fe^{2+} [16], resulting in a decrease in Fe^{2+} concentration, which affects the improvement of the degradation rate of thiacloprid. Therefore, it can be preliminarily determined that the optimal Fe^{2+} concentration is 0.3mmol/L.

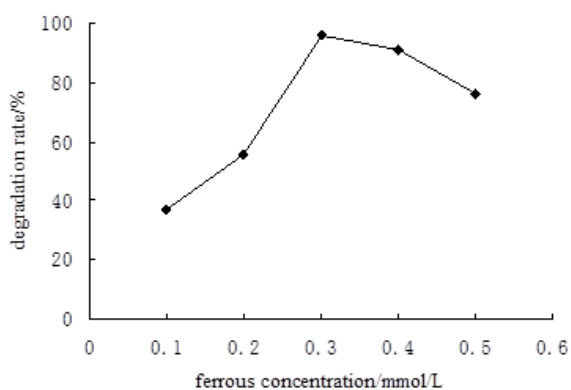


Fig. 1 Effect of ferrous concentration on degradation rate

3.1.2 Effect of persulfate concentration on degradation rate

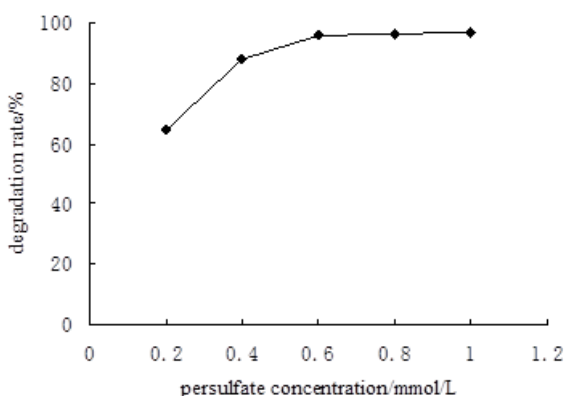


Fig. 2 Effect of persulfate concentration on degradation rate

The effect of different persulfate concentrations on the degradation rate is shown in Fig. 2. It can be seen from Fig. 2 that the degradation rate increases significantly with the increase of persulfate concentration, reaches the maximum when the persulfate concentration is 0.6mmol/L and then changes little with the increase of persulfate concentration. This indicates that higher persulfate concentrations are associated with higher degradation rate of thiacloprid because higher persulfate concentrations favor the degradation of thiacloprid,

whereas excessive persulfate concentration inhibits thiacloprid degradation due to consumption of oxidant. Overall, the optimal persulfate concentration is 0.6mmol/L.

3.1.3 Effect of UV power on degradation rate

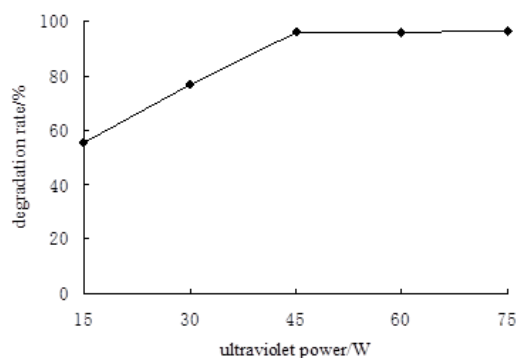


Fig. 3 Effect of UV power on degradation rate

The effect of different UV power on the degradation rate is shown in Fig. 3. It can be seen from Fig. 3 that the degradation rate increases significantly with the increase of UV power, reaches the maximum when the UV power is 45W and then is basically unchanged with the increase of UV power. This is because increasing the UV power can increase the input activation energy, which is conducive to the rate of persulfate activation to $SO_4^{\bullet-}$ [16]. At the same time, more abundant oxidants can be provided by increasing the concentration of persulfate. After the persulfate is activated, more $SO_4^{\bullet-}$ and HO^{\bullet} will be generated, which can ultimately improve the degradation rate of thiacloprid. In addition, UV light can also directly photolyze pollutants, so thiacloprid can degrade by directly absorbing ultraviolet radiation [17]. Since the degradation rate is basically unchanged when the UV power is greater than 45W, the optimal UV power is 45W from the perspective of energy saving.

3.1.4 Effect of pH on degradation rate

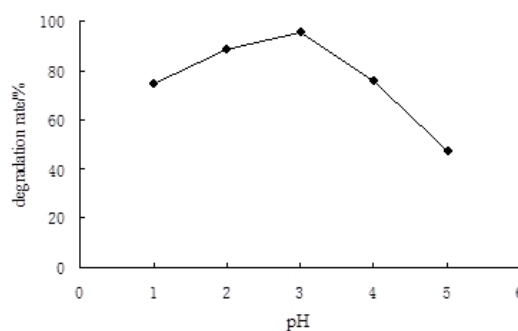


Fig. 4 Effect of pH on degradation rate

The effect of different pH on the degradation rate is shown in Fig. 4. It can be seen from Fig. 4 that the degradation rate increases significantly with the increase of pH,

reaches the maximum when the pH is 0.3mmol/L and then shows a downward trend with the increase of pH. The reason is that different pH will cause the mutual conversion of HO• and SO4•-. SO4•- is the main free radical under acidic condition, and HO• is the main free radical under alkaline condition [18]. Since the oxidation potential of SO4•- is higher than that of HO•, different pH values have different effects on the degradation rate of thiocloprid. Therefore, it can be preliminarily determined that the optimal pH is 3.

3.2 Model building and analysis of variance

The results of response surface experiment are shown in Table 2. Table 3 shows the analysis of variance.

The regression equation obtained by software analysis is as follows:

$$Y=96.10+15.63A+3.35B+2.73C-2.33AB-2.42AC+2.57BC-10.34A^2-7.25B^2-8.48C^2$$

Table 2 Results of response surface experiment

No.	A	B	C	Y: Degradation rate %
1	-1.00	-1.00	0.00	58.14
2	1.00	-1.00	0.00	94.05
3	-1.00	1.00	0.00	67.64
4	1.00	1.00	0.00	94.24
5	-1.00	0.00	-1.00	56.62
6	1.00	0.00	-1.00	92.72
7	-1.00	0.00	1.00	66.69
8	1.00	0.00	1.00	93.1
9	0.00	-1.00	-1.00	75.81
10	0.00	1.00	-1.00	79.23
11	0.00	-1.00	1.00	76.38
12	0.00	1.00	1.00	90.06
13	0.00	0.00	0.00	96.33
14	0.00	0.00	0.00	97.28
15	0.00	0.00	0.00	95.95
16	0.00	0.00	0.00	96.71
17	0.00	0.00	0.00	94.24

Table 3 Analysis of variance for the fitted regression model

Source of variance	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Model	3259.87	9	362.21	206.54	< 0.0001
A	1953.75	1	1953.75	1114.08	< 0.0001
B	89.71	1	89.71	51.16	0.0002
C	59.68	1	59.68	34.03	0.0006
AB	21.67	1	21.67	12.36	0.0098
AC	23.47	1	23.47	13.39	0.0081
BC	26.32	1	26.32	15.01	0.0061
A ²	449.82	1	449.82	256.50	< 0.0001
B ²	221.22	1	221.22	126.15	< 0.0001
C ²	303.03	1	303.03	172.80	< 0.0001
Remaining	12.28	7	1.75		
Lack of fit	6.98	3	2.33	1.76	0.2942
Pure error	5.30	4	1.32		
Total error	3272.14	16			
R ²			0.9962		

It can be seen from Table 3 that the model is extremely significant (P<0.001), the linear relationship between the dependent variable and the investigated independent variable is significant (R2=0.9962), the degree of fit is good, and the lack of fit is not significant (P>0.05).

It can be seen from the significance test in Table 3 that the first-order term of the model is extremely significant; the squared terms A2, B2 and C2 are extremely significant; and the interaction terms AB, AC and BC of the two factors are significant.

3.3 Response surface analysis of thiocloprid removal rate

The 3D response surfaces for the effect of the interaction among the Fe2+ concentration, persulfate concentration and UV power on the degradation rate are shown in Fig. 5, Fig. 6 and Fig. 7.

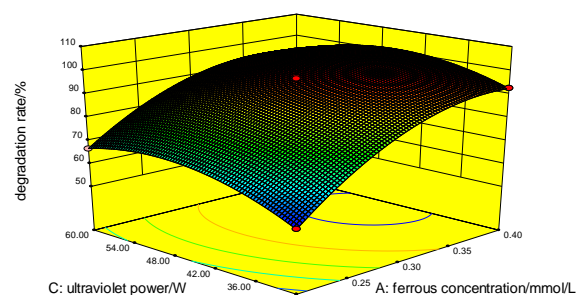


Fig. 5 Response surface for the effect of interaction between Fe2+ concentration and persulfate concentration on degradation rate

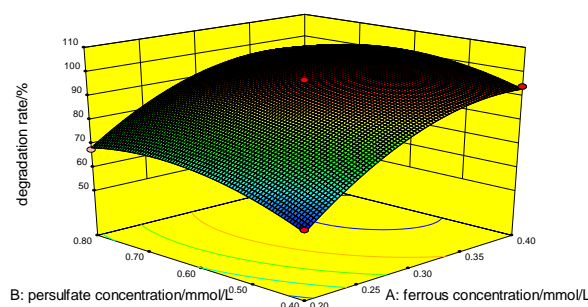


Fig. 6 Response surface for the effect of interaction between Fe2+ concentration and UV power on degradation rate

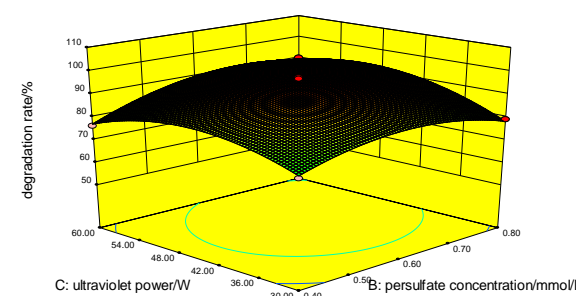


Fig. 7 Response surface for the effect of interaction between persulfate concentration and UV power on degradation rate

Fig. 5 shows the effect of the interaction between Fe²⁺ concentration and persulfate concentration on the degradation rate when the UV power is 45W. The contours tend to be perfectly circular, indicating that the interaction between Fe²⁺ concentration and persulfate is not significant. Fig. 6 shows the effect of the interaction between Fe²⁺ concentration and UV power on the degradation rate when the persulfate concentration is 0.6mmol/L. The 3D graph has a steep curve and a large contour ellipse radian, indicating that the interaction between Fe²⁺ concentration and UV power is significant. Fig. 7 shows the effect of the interaction between persulfate concentration and UV power on the degradation rate when the Fe²⁺ concentration is 0.340mmol/L. The 3D graph has the steepest curve and the largest contour ellipse radian, indicating that the interaction between persulfate concentration and UV power is the most significant.

3.4 Analysis of optimal test results and model validation

When the Design-expert 10 software was adopted to optimize the combination of experimental factors, the predicted optimal experimental conditions for thiacloprid degradation were obtained as follows: The Fe²⁺ concentration was 0.340mmol/L, the persulfate concentration was 0.610mmol/L and the UV power was 45.81W (where the total UV power is controlled by the number of UV lamps turned on as each lamp is 15W). In this study, four 15W UV lamps were used for the actual experimental operation. The verification test was carried out under these conditions. The degradation rate of thiacloprid reached 99.2%, which was close to the predicted value (100%), indicating that the model could accurately simulate the effects of various factors on the removal rate of thiacloprid and had certain practical value.

4. Conclusions

The effects of Fe²⁺ concentration, persulfate concentration, pH value and UV power on the degradation rate of thiacloprid were analyzed by single factor experiment. On this basis, the optimal degradation process parameters of thiacloprid were obtained by response surface experiment as follows: The Fe²⁺ concentration was 0.340mmol/L, the persulfate concentration was 0.610mmol/L and the UV power was 45.81W. Under these conditions, the predicted removal rate of thiacloprid was 100%, while the verification test result was 98.4%, which was very close to the predicted value. This study provides basic data for optimizing the persulfate oxidation system for the treatment of pesticide wastewater.

References

1. Piao X, Ji L, Lin R, et al. Analysis of the registration and management status of neonicotinoid pesticides [J]. *China Plant Protection*, 2015, 35(3): 70-74.

2. Qiu S, Zhang Y. Development and trend of neonicotinoid pesticides [J]. *World Pesticides*, 2014, 36(5): 5-6, 36.
3. Wei L, Ye F. Research progress on the mechanism of action, application and structural modification of neonicotinoid insecticides [J]. *Pesticide Science and Administration*, 2013, 34(5): 27-34.
4. Fent K, Schmid M, Hettich T, et al. The neonicotinoid thiacloprid causes transcriptional alteration of genes associated with mitochondria at environmental concentrations in honey bees[J]. *Environ. Pollut.*, 2020, 266(Pt 1): 115297.
5. Schulz R. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: A review[J]. *Journal of Environmental Quality*, 2004, 33(2): 419-448.
6. Carter A. How pesticides get into water - and proposed reduction measures[J]. *Pesticide Outlook*, 2000, 11(4): 149-156.
7. Huang G X, Wang C Y, Yang C W, et al. Degradation of bisphenol A by peroxymonosulfate catalytically activated with Mn_{1.8}Fe_{1.2}O₄ Nanospheres: Synergism between Mn and Fe[J]. *Environ. Sci. Technol.*, 2017, 51(21): 12611-12618.
8. Lin H, Wu J, Zhang H. Degradation of bisphenol A in aqueous solution by a novel electro/Fe³⁺/peroxydisulfate process[J]. *Separation and Purification Technology*, 2013, 117: 18-23.
9. Rastogi A, Al-Abed S R, Dionysiou D D. Sulfate radical-based ferrous-peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems[J]. *Applied Catalysis B: Environmental*, 2009, 85(3/4): 171-179.
10. Song Q, Feng Y, Liu G, et al. Degradation of the flame retardant triphenyl phosphate by ferrous ion-activated hydrogen peroxide and persulfate: Kinetics, pathways, and mechanisms [J]. *Chemical Engineering Journal*, 2019, 361: 929-936.
11. Kavitha V, Palanivelu K. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol [J]. *Chemosphere*, 2004, 55(9): 1235-1243.
12. [12] Liu X, Liu Y, Lu S, et al. Degradation difference of ofloxacin and levofloxacin by UV/H₂O₂ and UV/PS (persulfate): Efficiency, factors and mechanism[J]. *Chemical Engineering Journal*, 2020, 385: 123987.
13. Huang L, Li Z, Wang G, et al. UV-catalyzed persulfate advanced treatment of leachate from waste incineration plants [J]. *China Environmental Science*, 2021, 41(1): 8.
14. Zhang Y, Xiang Y, Lu X, et al. Characteristics of zerovalent iron activated persulfate degradation of chromium black T in water [J]. *China Environmental Science*, 2020, 40(2): 191-198.
15. Gao J, Han D, Xu Y, et al. Persulfate activation by sulfide-modified nanoscale iron supported by biochar (S-nZVI/BC) for degradation of ciprofloxacin[J].

- Separation and Purification Technology, 2020, 235: 116202.
16. Wen D, Li W, Lv J, et al. Methylene blue degradation by the VUV/UV/persulfate process: Effect of pH on the roles of photolysis and oxidation [J]. *J Hazard Mater*, 2020, 391: 121855.
 17. Acero J L, Real F J, Javier Benitez F, et al. Degradation of neonicotinoids by UV irradiation: Kinetics and effect of real water constituents[J]. *Separation and Purification Technology*, 2019, 211: 218-226.
 18. Yang L, Xue J, He L, et al. Review on ultrasound assisted persulfate degradation of organic contaminants in wastewater: Influences, mechanisms and prospective[J]. *Chemical Engineering Journal*, 2019, 378: 122146.