

Adsorption Performance of Glyphosate on Modified Shell Powder/Ce-N-TiO₂

Wei Zhang^{1,3}, Zhe Liang^{2,*}, Hai Lin⁴, Jinkai Shu^{1,3}, and Aihe Wang^{1,3}

¹Hunan City University, College of Municipal and Geomatics Engineering, 413000 Yiyang, China

²Shenyang Jianzhu University, College of Municipal and Environmental Engineering, 110168 Shenyang, China

³Hunan City University, Hunan Rural Drinking Water Quality Safety Engineering Technology Research Center, 413000 Yiyang, China

⁴Yiyang Commodity Quality Supervision and Inspection Institute, 413000 Yiyang, China

Abstract. Glyphosate is a typical dissolved organic phosphorus that can cause adverse effects on plants, animals, and humans. Modified shell powder/Ce-N-TiO₂ was synthesized by high-temperature doping, and the prepared modified shell powder/Ce-N-TiO₂ was characterized and used response surface methodology to find out the optimum condition for adsorption removal rate. The zeta characterization indicates that the doping of Ce shifts the isotropic potential of the material to the right. The FT-IR and XPS characterization indicated that glyphosate was successfully adsorbed, and the two-two interactions of pH, contact time and dosing amount had a more obvious effect on adsorption by response surface analysis. The process of glyphosate adsorption by modified shell powder/Ce-N-TiO₂ was consistent with the quasi-secondary kinetic model and Langmuir model, and the maximum adsorption amount was 66.98 mg/g. The above results may be useful for the study of other systems of glyphosate wastewater treatment.

1 Introduction

Glyphosate is a broad spectrum, post emergency and non-selective herbicide, widely used for post-emergence weed control [1-3]. Considering that come into contact with glyphosate is toxicologically harmful and can cause to serious health problems, such as cancer, liver and tissue rupture, endoderm destruction, lymphoma, etc [4-5]. So it is essential to choose a reliable application for removing glyphosate.

Many of the available treatment technologies share several drawbacks in respect of their applicability, mainly in view of the expansion of the scale [6-10]. So on, adsorption exist as an operative correction strategy to remove glyphosate pollutants from the aqueous phase, in existence some advantages, such as low cost and simple operation [11-13].

In this study, TiO₂ was modified by heat treatment and doping, and glyphosate was used as the target pollutant. The surface structure, functional groups and bonding energy changes were investigated before and after adsorption by means of scanning electron microscopy, infrared spectroscopy and XPS characterization, and its adsorption properties on glyphosate were explored by adsorption kinetics and thermodynamics.

2 Materials and methods

2.1 Instruments and materials

Experimental instrument: UV-4802S ultraviolet visible spectrophotometer; KSY-14-16 muffle furnace; GJ-2 sealed sample pulverizer; XSB-88 top impact vibrating screen machine; LLS-20-L ultrapure water machine; YC-S30 constant temperature water bath shaker; SJ-6 pH meter for laboratory; 0.22 μM water syringe filter.

Experimental materials: Waste oyster shell; Glyphosate (≥95%) was purchased from Shanghai Shifeng Biotechnology Co,Ltd; Cerium nitrate hexahydrate, purchased from Beijing mairuida Technology Co,Ltd; Urea is analytical pure and purchased from Sinopharm Chemical Reagent Co,Ltd; Tetrabutyl titanate (98.0%) purchased in Shanghai Aladdin Biochemical Technology Co,Ltd; Isopropanol, purchased from Shanghai Aladdin Biochemical Technology Co,Ltd; Sodium hydroxide is analytical pure and purchased from Tianjin Hengxing chemical reagent manufacturing Co,Ltd; Potassium bromide is analytical pure and purchased in Sinopharm Chemical Reagent Co,Ltd; Sodium nitrite is analytical pure and purchased at Shanghai Aladdin Biochemical Technology Co,Ltd; Nitric acid is analytical pure and bought in Hengyang Kaixin Chemical Reagent Co,Ltd. The experimental water is ultrapure water.

2.2 Experimental method

Preparation of modified shell powder/Ce-N-TiO₂ Taken a 100ml beaker and added 60ml isopropanol into it, then

* Corresponding author: 249713349@qq.com

added 0.173g prepared shell powder (calcination temperature 900 °C, sieving particle size 120 mesh, starch dosage 15%, calcination time 2.5h and alkali treatment) was optimized by single factor orthogonal experiment. Shaken with ultrasonic for 10min, then dropped 15ml tetrabutyl titanate under magnetic stirring, and stirred uniformly for 20min to formed solution A. Measured 20ml isopropanol and 2.4ml deionized water, then mixed with 1.313g cerium nitrate hexahydrate and 0.655g urea, and the pH was adjusted to 3 with nitric acid to formed solution B. Slowly dropped solution B into solution a, stirred at a uniform speed for 2h to form sol. Aged at room temperature for 12h, dried and ground in a 65 °C blast drying oven, and calcine in a 450 °C muffle furnace for 4h to obtain modified shell powder/Ce-N-TiO₂.

Adsorption kinetics experiment. The glyphosate solution with 100ml initial concentration of 1000mg/L was poured into the 250ml cone bottle, adjusted the initial pH to 4.0±0.2. Added 0.5g modified shell powder/Ce-N-TiO₂ mixed, shaken for 7h at 25°C and 160r/min. Sampled every 0.5h and measured the absorbance, calculated the adsorption amount. Each experiment was conducted in parallel three times. In addition, the quasi first-order kinetic model is shown in equation (1) and the quasi second-order kinetic model is shown in equation (2) to fit the data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (2)$$

in which q_e and q_t are the equilibrium adsorption capacity of glyphosate and the adsorption at time t (mg/g), k_1 is the equilibrium constant of the quasi-first-order kinetic model (min⁻¹), k_2 is the equilibrium constant of the quasi-second-order kinetic model [g/(mg·min)].

Adsorption thermodynamics experiment. Added separately 100ml glyphosate solution with initial concentration of 1000, 900, 800, 700, 600 and 500mg/L into several 250ml conical flasks. Adjusted the initial pH to 4.0±0.2. Added 0.5g modified shell powder/Ce-N-TiO₂ into it, oscillated for 6h at 15, 25 and 35°C and 160r/min. Measured the change of glyphosate concentration in the solution and calculated the adsorption capacity. Each temperature gradient was parallel three times. Langmuir equation (3) and Freundlich equation (4) are used for linear fitting.

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{1}{q_{max}} C_e \quad (3)$$

$$\ln q_e = \ln K + \frac{1}{n} \cdot \ln C_e \quad (4)$$

in which b is Langmuir adsorption equilibrium constant (L/mg), q_{max} is the maximum adsorption amount (mg/g), C_e is the adsorption equilibrium concentration (mg/L), K is Freundlich adsorption equilibrium constant.

2.3 Determination method of glyphosate concentration and calculation method of adsorption capacity

The concentration of glyphosate was determined by nitrite ultraviolet spectrophotometry.

Formula (5) is used as the evaluation index of glyphosate adsorption effect of modified shell powder/Ce-N-TiO₂.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (5)$$

3 Results and discussion

3.1 Characterization analysis

3.1.1 Surface morphology analysis

The surface morphology of modified shell powder/Ce-N-TiO₂ before and after adsorption was analyzed by scanning electron microscope. The results are shown in Figure 1 and Figure 2.

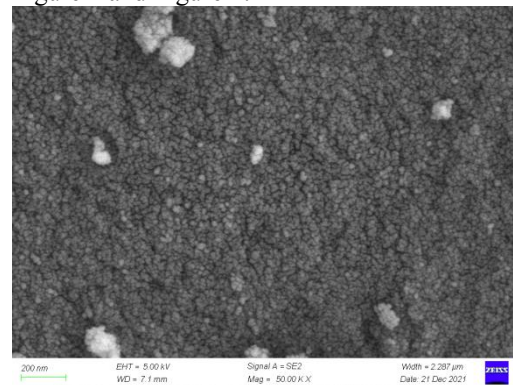


Fig. 1. SEM image before adsorption.

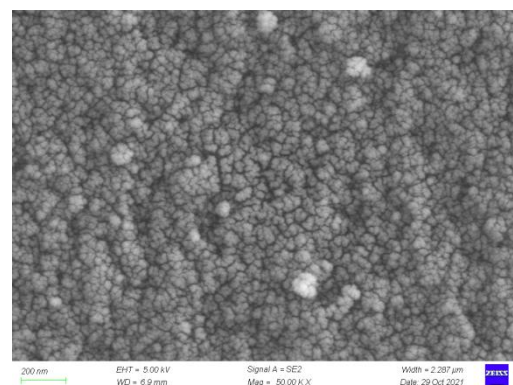


Fig. 2. SEM image after adsorption.

It can be seen from SEM Figure 1 and Figure 2 before and after adsorption. Before adsorption, the surface of the material is blocky, and after adsorption, there is obvious aggregation on the surface, and the surface is dense honeycomb.

3.1.2 Zeta potential analysis

The zeta potential change curves before and after

glyphosate adsorption by modified shell powder/Ce-N-TiO₂ are shown in Figure 3.

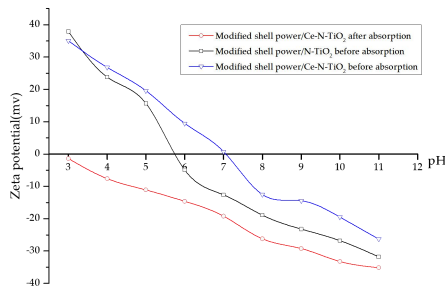


Fig. 3. Zeta potential at different pH conditions.

As shown in Figure 3, the isoelectric point of modified shell powder/N-TiO₂ is 5.7, and that of modified shell powder/Ce-N-TiO₂ is 7. The isoelectric point of modified shell powder/Ce-N-TiO₂ shifts left after glyphosate adsorption. The isoelectric point of metal oxides is determined by the deprotonation and protonation of hydroxyl groups on their surfaces. The leftward shift of modified shell powder/Ce-N-TiO₂ isoelectric point after glyphosate adsorption indicates that glyphosate forms negatively charged inner layer complexes with the surface of modified shell powder/Ce-N-TiO₂.

3.1.3 Surface functional group analysis

The functional group changes of the modified shell/Ce-N-TiO₂ before and after adsorption were analyzed by infrared spectroscopy. The results show that in Figure 4.

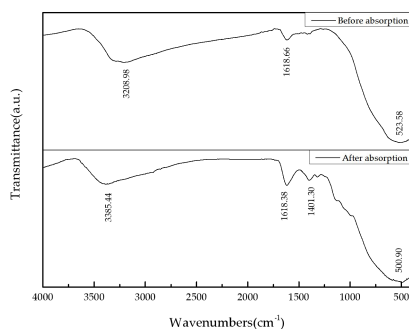


Fig. 4. FT-IR spectra before and after adsorption.

As shown in Figure 4, a symmetric stretching vibration of the carboxylate was observed at 1401.30 cm⁻¹ after the adsorption of glyphosate, indicating the adsorption of glyphosate by it [14].

3.1.4 XPS analysis

The modified shell powder/Ce-N-TiO₂ before and after adsorption were analyzed by XPS. The results show that in Figure 5.

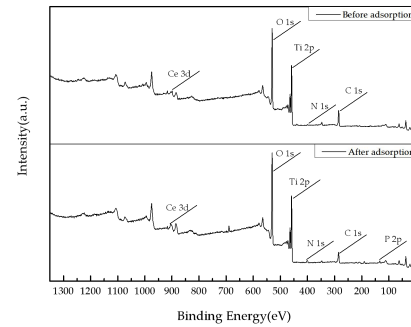


Fig. 5. XPS graphs before and after adsorption.

As shown in Figure 5 after the adsorption of glyphosate, element P appeared, indicating that glyphosate was successfully adsorbed by modified shell powder/Ce-N-TiO₂.

3.2 Response surface analysis

In this experiment, three factors were selected for investigation: pH, contact time and dosing amount, and response value: removal rate of glyphosate. The response surface analysis of three factors and three levels was carried out by using BOX-Behnken design principle, and 17 experimental groups were obtained to analyze the interaction between the influencing factors and obtain the optimization equation in the reaction process. The experimental design factor levels are shown in the Table 1, and the results of experimental runs are shown in the Table 2.

Table 1. Experimental design factor level table.

Level	Factor		
	A pH	B Contact time (h)	C Dosing amount (g/L)
-1	3	4	2
0	4	5	5
1	5	6	8

Table 2. Experimental design and results.

Number	pH	Contact time (h)	Dosing amount (g/L)	Experimental value removal rate
4	5	6	5	61.46
11	4	4	8	62.67
8	5	5	8	63.25
13	4	5	5	61.33

12	4	6	8	65.59
14	4	5	5	61.33
17	4	5	5	61.33
15	4	5	5	61.33
16	4	5	5	61.33
1	3	4	5	57.45
5	3	5	2	55.57
3	3	6	5	64.17
2	5	4	5	56.18
6	5	5	2	55.11
9	4	4	2	56.92
7	3	5	8	63.03
10	4	6	2	61.39

The data in Table 2 were analyzed using Design Expert 10 to obtain a quadratic polynomial regression equation between the response values and each influencing factor. $Y=16.09167+16.65917*A+0.072083*B+1.62958*C-0.36000*A*B+0.056667*A*C-0.12917*B*C-1.95875*A^2+0.44375*B^2-0.014583*C^2$

The actual and predicted values of this polynomial model are compared in Figure 6 and Figure 7.

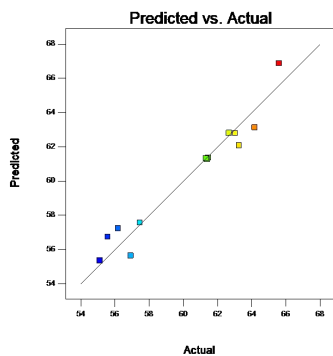


Fig. 6. Distribution of true and predicted values of glyphosate removal rate.

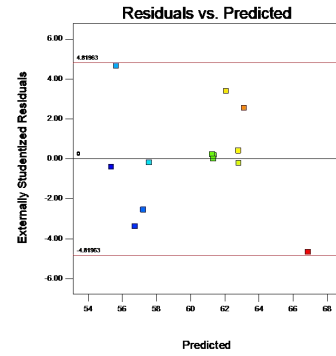


Fig. 7. Distribution of true and predicted values of glyphosate removal rate.

Table 3. Variance analysis results of response surface regression model.

Source	Sum of Squares	df	Mean Square	F Value	P-value	
Model	148.90	9	16.54	13.79	0.0011	Significant
pH	1.45	1	1.45	1.21	0.3077	
Time	34.46	1	34.46	28.73	0.0011	
Amount	41.85	1	41.85	34.89	0.0006	
AB	0.52	1	0.52	0.43	0.5319	
AC	0.12	1	0.12	0.096	0.7652	
BC	0.60	1	0.60	0.50	0.5020	
A ²	16.15	1	16.15	13.47	0.0080	
B ²	0.83	1	0.83	0.69	0.4332	
C ²	0.073	1	0.073	0.060	0.8128	
Residual	8.40	7	1.20			
Lack of Fit	8.40	3	2.80			
Pure Error	0.000	4	0.000			
Cor	157.29	1				

Total 6

As can be seen from Table 3, the P-value of this model is less than 0.0500, which is a good fit and significant. The fitted correlation coefficient $R^2=0.9466$ and adjusted coefficient of determination $R_{adj}^2=0.8780$, this regression equation has credibility and can respond to the true value.

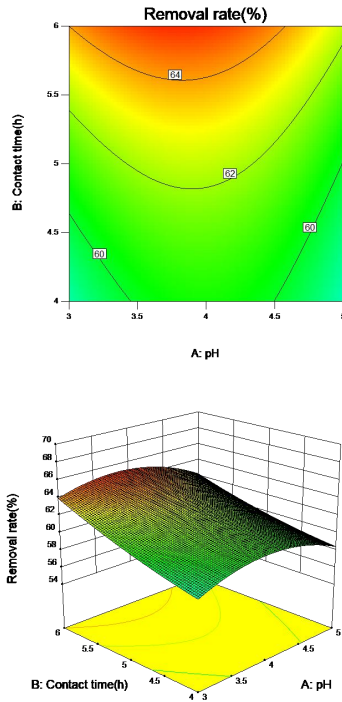


Fig. 8. Interaction of pH and contact time.

Figure 8 shows that the surfaces are relatively flat, indicating that the interaction between these two influencing factors does not have a significant effect on the removal rate. Figure 9 shows the effect of the interaction between pH and dosing amount, and it can be seen that the interaction between the two is significant.

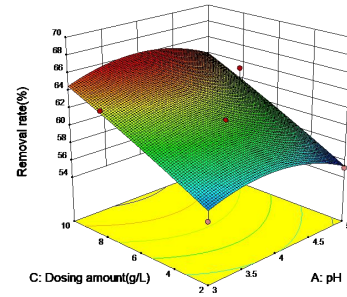
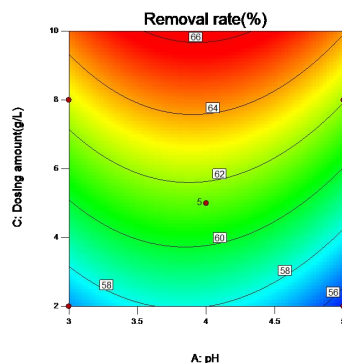


Fig. 9. Interaction of pH and dosing amount.

Figure 10 shows the effect of the interaction between contact time and dosing amount, and it can be seen that the interaction is significant.

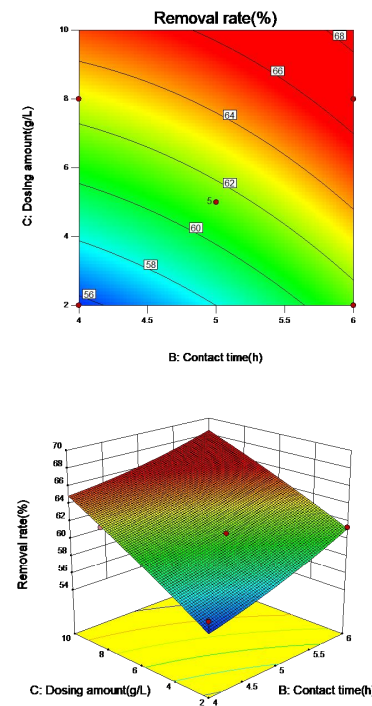


Fig. 10. Interaction of contact time and dosing amount.

According to the response surface analysis above, the effect of three factors on the removal rate of modified shell powder/Ce-N-TiO₂ on glyphosate containing wastewater, and the interaction between two factors were the same as the regression data analysis. This response surface model is reliable for optimization analysis and prediction.

3.3 Adsorption of glyphosate on modified shell powder/Ce-N-TiO₂

3.3.1 Adsorption kinetics

Under the conditions of initial concentration of 1000 mg/L, pH = 4.0±0.2, temperature of 25°C and rotating speed of 160 r/min, the effects of different contact time on the removal of glyphosate from modified shell

powder/Ce-N-TiO₂ were investigated. The results are found in the Figure 11.

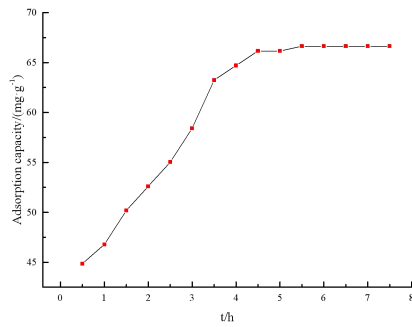


Fig. 11. Effect of adsorption time on the removal of glyphosate by modified shell powder/Ce-N-TiO₂.

As seen in Figure 11 that the adsorption capacity gradually increased in the first 4.5h and reached the highest value of 66.15 mg/g at 5h. The quasi-first-order and quasi-second-order kinetic models are used to fit the data in the Figure 12 and Figure 13.

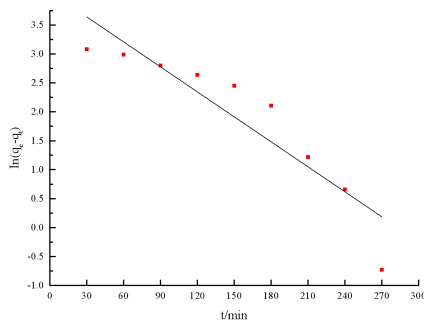


Fig. 12. Quasi-level kinetic model fitting curve.

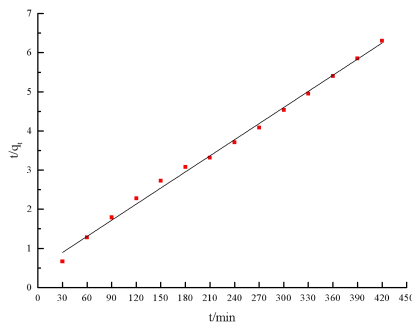


Fig. 13. Quasi-secondary kinetic model fitting curve.

Table 4. Kinetic fitting parameters for the adsorption of glyphosate by modified shell powder/Ce-N-TiO₂.

q _e	Quasi-level kinetic model			Quasi-secondary kinetic model		
	q _{cal}	k ₁	R ²	q _{cal}	k ₂	R ²
66.63	58.67	0.0144	0.827	72.94	0.0004	0.995

It can be seen from the Figure 10 , Figure 13 and Table 4 that the adsorption process of modified shell powder/Ce-N-TiO₂ is better matched with the quasi-second-order kinetic model, and the adsorption process is mainly chemical adsorption.

3.3.2 Adsorption thermodynamics

Under the conditions of pH = 4.0±0.2, rotating speed of 160r/min and contact time of 6h, the adsorption isotherms of glyphosate at 15, 25 and 35°C were carried out respectively. Results are presented in the Figure 14.

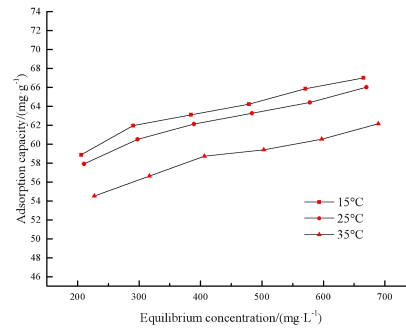


Fig. 14. Isotherm of glyphosate adsorption by modified shell powder/Ce-N-TiO₂.

As can be seen in Figure 14 with the increase of temperature, the adsorption counts of glyphosate by modified shell powder/Ce-N-TiO₂ decreases slightly, indicating that low temperature is conducive to adsorption, which is an exothermic reaction process. The maximum adsorption capacity was 66.98 mg/g at 15°C. Langmuir and Freundlich adsorption isotherms were used for fitting, and the results are shown in the Figure 15 and Figure 16.

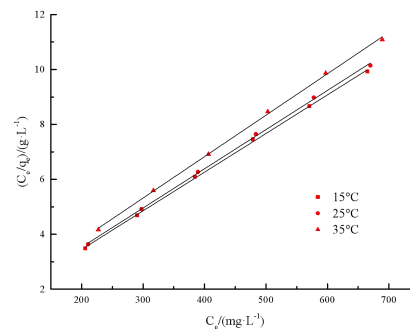
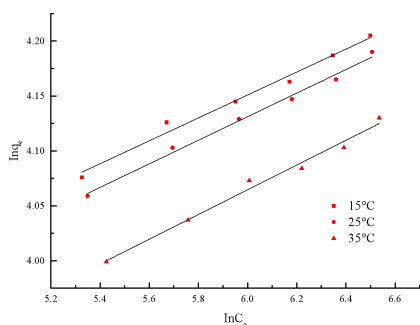


Fig. 15. Langmuir adsorption isotherm



fitting.

Fig. 16. Freundlich adsorption isotherm fitting.

Table 5. Adsorption isotherm fitting parameters for glyphosate adsorption by modified shell powder/Ce-N-TiO₂.

T(°C)	Langmuir parameters			Freundlich parameters		
	q _{cal}	b	R ²	1/n	lnK	R ²
15	71.07	0.0222	0.999	0.1043	3.525	0.983
25	70.13	0.0209	0.999	0.1072	3.488	0.990
35	66.31	0.0189	0.999	0.1125	3.390	0.983

It can be seen from the Figure 15, Figure 16 and Table 5 that the Langmuir model has a higher degree of fitting and is more suitable to describe the adsorption of glyphosate on modified shell powder/Ce-N-TiO₂. It shows that the adsorption process can be explained by single-layer coverage and uniform distribution.

4 Conclusion

(1) The successful adsorption of glyphosate by modified shell powder/Ce-N-TiO₂ and the formation of negatively charged inner layer complexes on the surface of modified shell powder/Ce-N-TiO₂ were demonstrated by SEM, zeta potential, FT-IR and XPS characterization.

(2) The effects of pH, contact time and dosing amount on the removal rate were analyzed by response surface analysis, which indicated that the interaction of two-two factors had significant effects on the adsorption and removal of glyphosate.

(3) Modified shell powder/Ce-N-TiO₂ adsorption of glyphosate was in accordance with the quasi-secondary kinetic model and Langmuir model, and the maximum adsorption amount was 66.98 mg/g.

This paper is one of the phase results of the National Natural Science Foundation of China (No: 42071122), Hunan University Student Innovation and Entrepreneurship Training Program (S202111527011, S202011527003).

References

1. D. Feng, A. Soric, O. Boutin, Treatment technologies and degradation pathways of

glyphosate: A critical review. *Sci Total Environ*: 140559 (2020)

2. Peillex C, Pelletier M. The impact and toxicity of glyphosate and glyphosate-based herbicides on health and immunity. *J Immunotoxicol*, **17**:163-174 (2020).

3. J. Joensson, R. Camm, T. Hall Removal and degradation of glyphosate in water treatment: a review. *Journal of Water Supply: Research and Technology—AQUA*, **62**:395-408 (2013).

4. Ingaramo P, Alarcón R, Muñoz-De-Toro M, Luque E.H. Are glyphosate and glyphosate-based herbicides endocrine disruptors that alter female fertility? *Mol Cell Endocrinol*, **518**:110934 (2020).

5. J.O. Ighalo, O.J. Ajala, A.G. Adeniyi, E.O. Babatunde, M.A. Ajala Ecotoxicology of glyphosate and recent advances in its mitigation by adsorption. *Environ Sci Pollut R*, **28**:1-14 (2020).

6. L. Cao, D. Ma, Z. Zhou, C. Xu, C. Cao, P. Zhao, Q. Huang Efficient photocatalytic degradation of herbicide glyphosate in water by magnetically separable and recyclable BiOBr/Fe₃O₄ nanocomposites under visible light irradiation. *Chem Eng J*, **368**:212-222 (2019).

7. R. Danial, S. Sobri, L.C. Abdullah, M. N. Mobarekeh FTIR, CHNS and XRD analyses define mechanism of glyphosate herbicide removal by electrocoagulation. *Chemosphere*, **233**:559-569 (2019).

8. S. Firdous, S. Iqbal, S. Anwar Optimization and modeling of glyphosate biodegradation by a novel *Comamonas odontotermitis* P2 through response surface methodology. *Pedosphere*, **30**:618-627 (2020).

9. H. Rubí-Juárez, S. Cotillas, C. Sáez, P. Ca Izares, Barrera-Díaz C, Rodrigo M.A. (2016) Removal of herbicide glyphosate by conductive-diamond electrochemical oxidation. *Applied Catalysis B Environmental*, **188**:305-312.

10. M. Xie, Z. Liu, Y. Xu Removal of glyphosate in neutralization liquor from the glycine-dimethylphosphit process by nanofiltration. *Journal of Hazardous Materials*, **181**:975-980 (2010).

11. J.C. Diel, D.S.P. Franco, I.D.S. Nunes, H.A. Pereira, Moreira K.S, de L. Burgo T.A, et al. Carbon nanotubes impregnated with metallic nanoparticles and their application as an adsorbent for the glyphosate removal in an aqueous matrix. *Journal of Environmental Chemical Engineering*, **9**:105178 (2021).

12. J.M. Salman, F.M. Abid Preparation of mesoporous activated carbon from palm-date pits: optimization study on removal of bentazon, carbofuran, and 2, 4-D using response surface methodology. *Water Sci Technol*, **68**:1503-1511 (2013).

13. G.L. Dotto, G. McKay Current scenario and challenges in adsorption for water treatment. *Journal*

- of Environmental Chemical Engineering, **8**:103988 (2020).
14. Y. Huang, Z. Li, K. Yao, C Chen, C. Deng, Y Fang, et al. Suppressing toxic intermediates during photocatalytic degradation of glyphosate by controlling adsorption modes. Applied Catalysis B: Environmental, **299**:120671 (2021).