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Evaluation of adsorption and degradation performance of lanthanum modified mesoporous carbon nitride composite materials for tetracycline wastewater

Wu Zhiqiang*[1,2], Li Yueyi[1], Jiang Pengxi[3], Ma Sisi[1], Dong Wenfei[1], Zhao Hongjian[1], Feng Enke*[,1] and Wang Xuming*[,4]

[1] School of Chemistry and Chemical Engineering, Ningxia Normal University, Guyuan, 756000, P. R. China.

[2] School of Civil and Hydraulic Engineering, Ningxia University, Yinchuan, 750021, P. R. China.

[3] Inner Mongolia Bairun Technology Co., Ltd., Alxa League, Inner Mongolia, 750300, P. R. China.

[4] School of Physics and Electronic and Electrical Engineering, Ningxia University, Yinchuan, 750021, P. R. China.

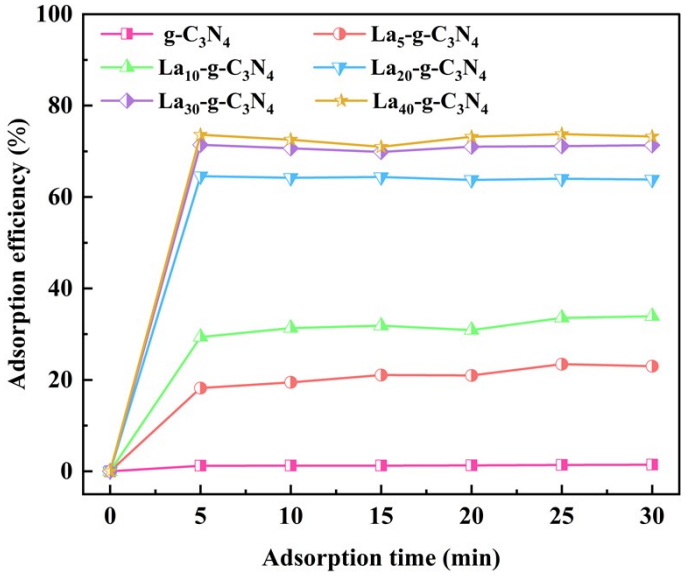

Fig. S1 Adsorption efficiency of g-C_3N_4 and g-C_3N_4 materials with different La doping amounts. (Add 20mg adsorbent to 50mL 20mg/L tetracycline solution; pH=7; T=25℃; 1400r/min)

During the adsorption of tetracycline (TC), both pure g-C_3N_4 and g-C_3N_4 adsorbents with different La doping amounts quickly reached the adsorption-desorption equilibrium, and the bottom-up adsorption efficiency was 1.44%, respectively. 21.05%; 31.83%; 64.38%; 71.32%; 73.28%. Obviously, compared with pure g-C_3N_4, La-doped g-C_3N_4 material has a stronger adsorption capacity for tetracycline, among which the adsorption properties of La_{30}-g-C_3N_4 and La_{40}-g-C_3N_4 are not much different, so the La_{30}-g-C_3N_4 adsorbent with lower production cost is selected for follow-up exploration.

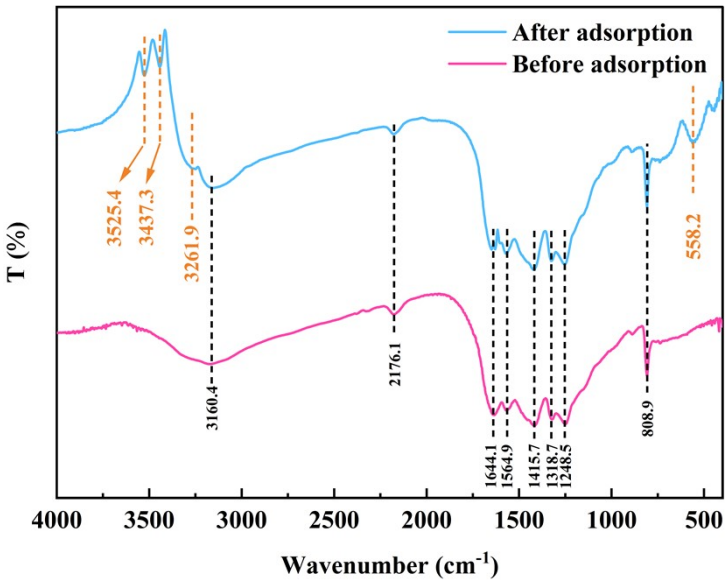

Fig. S2 Comparison of FT-IR before and after adsorption of tetracycline by La_{30}-g-C_3N_4 adsorbent.

It is worth noting that according to the FT-IR comparison diagram before and after adsorption (Fig. S2), three new characteristic peaks appeared in the range of 3200-3600 cm^{-1} for adsorbent after adsorption of TC. This indicates that the hydroxyl group in TC molecules interacts with the nitrogen-containing components of La_{30}-g-C_3N_4 to form hydrogen bonds during the adsorption process. In addition, the new peak at 558.2 cm^{-1} May be caused by the functional group of tetracycline entering the adsorbant.

Fig. S3 Comparison of pH before and after adsorption of tetracycline by La_{30}-g-C_3N_4 adsorbent.

Fig. S3 described the pH comparison before and after tetracycline adsorption with La_{30}-g-C_3N_4 adsorbent. Among them, Fig. S3(a) is the pH before the adsorption of tetracycline by La_{30}-g-C_3N_4, the value is 7.10, and S3(b) is the pH after the adsorption of tetracycline by La_{30}-g-C_3N_4, the value is 5.96. According to the value change of pH, we further proved that the process of La adsorption of tetracycline is chemisorption, and some acidic small molecules may be produced in the process of adsorption degradation, so that the solution is weakly acidic. This result plays a key role in the subsequent analysis of adsorption mechanism.

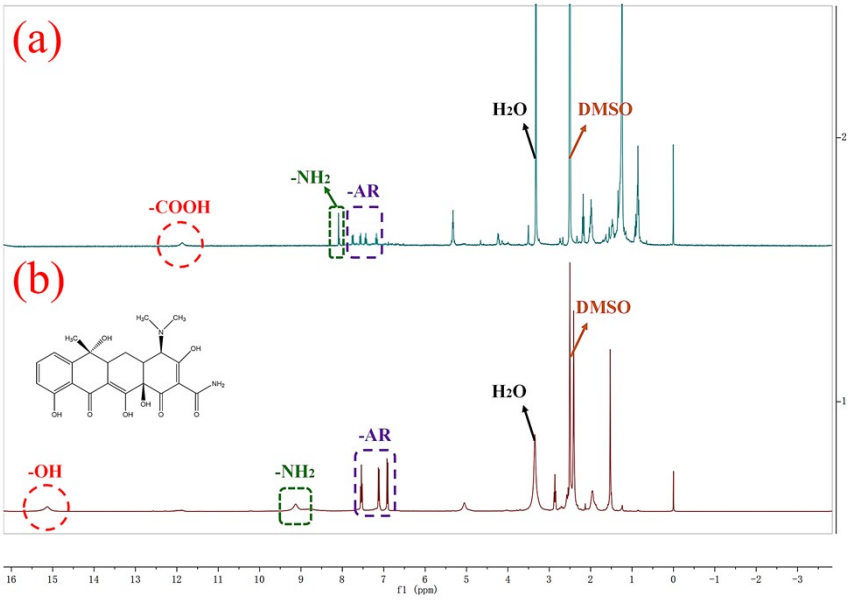

Fig. S4 NMR hydrogen spectroscopy of (a) the TC after adsorption and (b) Pure TC

In addition, in order to further prove the degradation mechanism of wastewater, we performed Nuclear magnetic resonance (NMR) hydrogen spectroscopy characterization of pure tetracycline and degraded tetracycline, and the characterization results were shown in the figure above. Fig. S4(a) shows the hydrogen NMR spectra of degraded tetracycline, and Fig. S4(b) shows the hydrogen NMR spectra of pure tetracycline. Notably, the chemical shift of the hydroxyl peak in panel (b) is 15.2 ppm, while in panel (a) this peak disappears. The reappeared peak with a chemical shift of 11.9 ppm, probably belonging to carboxyl groups. This is consistent with our results that the pH of TC (Fig. S3) solution after degradation is weakly acidic. It was further proved that our prediction in LC-MS (Fig. 14) that there might be small molecules containing carboxyl groups in tetracycline degradation products had certain accuracy. In addition, the chemical shift of the amino group in Figure (a) is 9.1 ppm, while it is shifted to 8.3 ppm in Figure (b). This shift may be attributed to the tetracycline is broken down into small molecules. Finally, the peaks occur at chemical shifts of 7-8 ppm belong to the aromatic ring group. However, the aromatic ring peak in Figure (a) is significantly shifted and weakened compared with that in Figure (b). This is further evidence that tetracycline is adsorbed and degraded into small molecules.