

Supplementary Material

Synergistic advanced oxidation process for enhanced degradation of organic pollutants in spent sulfuric acid over recoverable apricot shell-derived biochar catalyst

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Analytical and characterization methods

The electron spin resonance (ESR) experiments of the radicals trapped by DMPO were performed on an electron paramagnetic resonance spectroscopy (Bruker Ems plus, Germany). The instrument settings were as follows: microwave frequency = 9.84 GHz, microwave power = 20 mW, modulation amplitude = 2 G, sweep width = 100 G, modulation frequency = 100 kHz.

The chemical compositions of OBC were analyzed with an X-ray fluorescence (XRF) spectrometer (Axios, Netherlands).

The surface chemistry of OBC was analyzed by the Boehm titration method and the zero-point charge pH (pH_{PZC}) (Boehm, 1994). The amounts of various acidic oxygen surface groups on OBC were determined by the titration with a series of different strength bases in aqueous solution. 0.3 g of OBC was placed into 25 ml of a 0.05M NaOH, Na_2CO_3 , NaHCO_3 , and NaOC_2H_5 solution, respectively, oscillated for 24h at room temperature, and filtered with a 0.45 μm syringe filter. Next, 10 ml of the filtrate was added into a 20ml 0.05 M HCl solution and back titrated with a 0.05 M NaOH solution until the pH value was neutral. According to the amount of alkaline liquor consumed through titration, the amount of different acid functional groups was calculated: The amount of carboxyl groups was calculated by NaHCO_3 consumption, the amount of lactone groups was calculated by the difference between Na_2CO_3 and NaHCO_3 consumption, the amount of phenol groups was calculated by the difference between NaOH and Na_2CO_3 consumption, and the amount of carbonyl groups was calculated by the difference between NaOC_2H_5 and NaOH consumption. The pH_{PZC} value of OBC was determined by the potentiometric titration. A fixed number of samples (1.0 g) was mixed with 50 mL of 0.1 M NaNO_3 solution, and 0.1-1.0 M HNO_3 or NaOH solution was used to adjust the initial pH (pH_0) of the solution to 2, 4, 6, 8, 10, and 12, respectively. The suspensions were evenly mixed by intermittent oscillation and allowed to stand for 48 hours until the equilibrium was reached. The final pH (pH_f) was determined for the calculation of ΔpH ($\Delta\text{pH} = \text{pH}_f - \text{pH}_0$). The value of pH_{PZC} were determined by plotting the curves of ΔpH versus pH_0 .

The porous structures of OBC were investigated from N_2 adsorption-desorption

isotherms at -196°C by an ASAP 2020 apparatus (Micromeritics Instrument Corp.). OBC was previously outgassed at 250°C under a vacuum pressure of 10^{-4}Pa for 5h, and the data of N_2 isotherms were used to determine: (1) The specific surface area (S_{BET}) of OBC was obtained from N_2 isotherms according to the Brunauer-Emmett-Teller (BET) equation (Brunauer et al., 1938); (2) The micropore surface areas (S_{mic}) of samples were calculated by t-plot method; (3) The total pore volume (V_{total}) of OBC was calculated from a single N_2 adsorption point at p/p_0 0.99; (4) The micropore volume (V_{mic}) of OBC was obtained through t-plot method (Lippens & Boer, 1967); (5) The average pore width D of OBC was obtained from the BJH desorption average pore diameter ($4V/A$) (Seaton et al., 1989).

The surface morphology of OBC was analyzed with a scanning electron microscopy (Hitachi S-4800, Japan).

The surface functional groups of OBC were characterized by a Fourier transform infrared spectrometer (Nicolet iS5, USA), with a scanning range from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} .

The X-ray photoelectron spectroscopy (XPS) experiment of OBC was performed with a ESCALAB Xi+ spectrometer (Thermo Fischer, America), and the data of XPS were calibrated to the $\text{C}1\text{s}$ peak at 284.6 eV .

References

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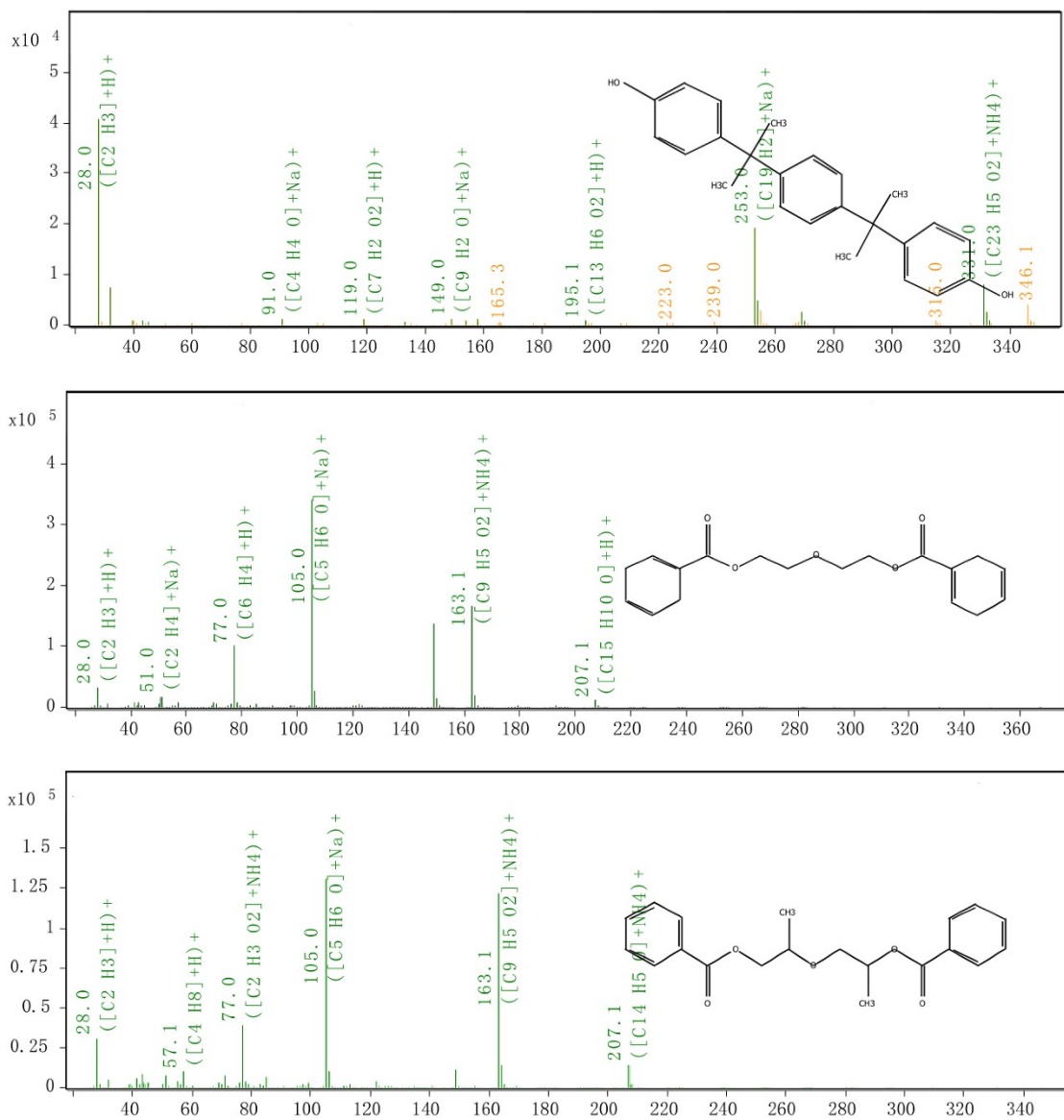


Fig. S1. The MS spectra of the three detected organic pollutants in spent sulfuric acid.

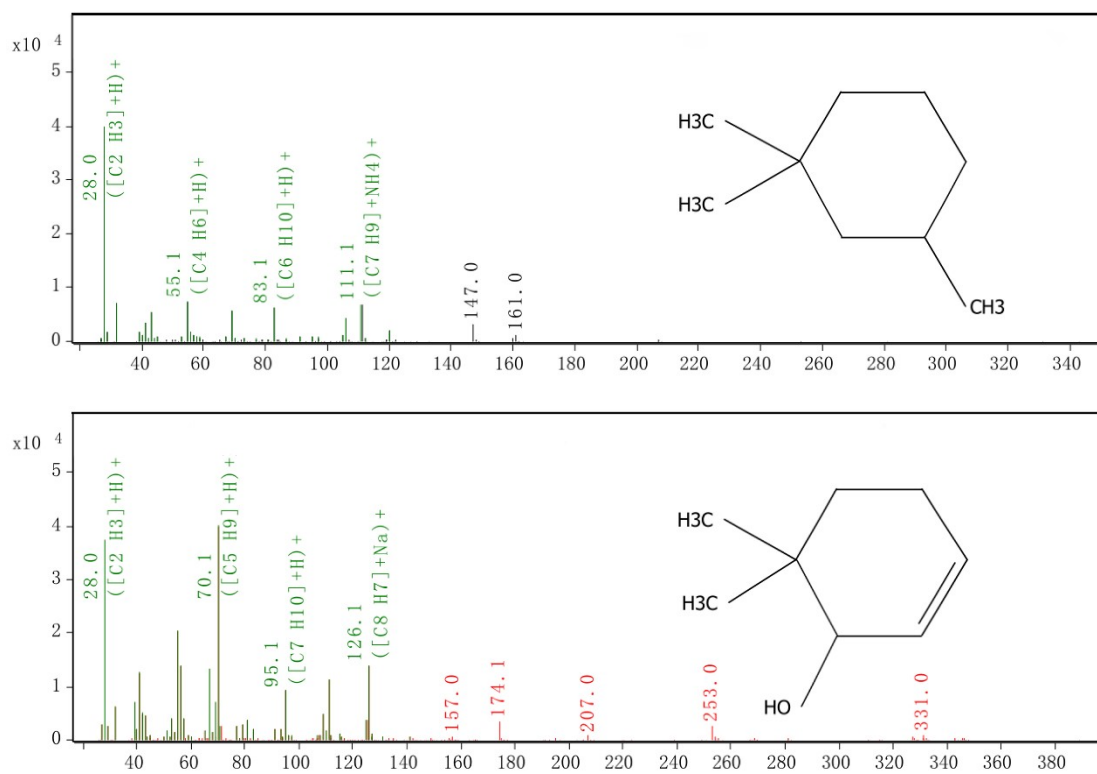


Fig. S2. The MS spectra of the two detected organic pollutants in treated sulfuric acid.