Supporting Information

For

Effective Removal of Aromatic pollutants via Adsorption and Photocatalysis of Porous Organic Frameworks

Congcong Wang#, Wei Wang#, Jian Wang, Peiping Zhang, Shiding Miao, Bo Jin, Lina Li*

Key Laboratory of Automobile Materials of Ministry of Education, State Key laboratory of Inorganic Synthesis & Preparative Chemistry, Solid Waste Recycling Engineering Research Center of Jilin, Jilin University, Changchun, 130022, Jilin Prov., China;

Congcong Wang and Wei Wang contribute equally in this article.

Key Laboratory of Automobile Materials of Ministry of Education, Solid Waste Recycling Engineering Research Center of Jilin, School of Materials Science and Engineering, Jilin University, Changchun, 130022, Jilin Prov, China.

Table of contents

Materials and Methods

All chemical reagents were purchased from commercial suppliers and used without further purification unless otherwise noted.

preparation of PAF-45: PAF-45 was synthesized according to previous method [20]. Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. After pumped to vacuum, the system was trice inflated with inert gas (N_2) and injected 40 mL dried chloroform. After the system had been stirred at 60 ℃ for 1 h, 10 mL chloroform dissolving biphenyl (1.5 mmol, 480 mg) was added into the flask slowly. Then the whole system was heated to reflux for 24 h.

After cooling down to room temperature, the crude product was obtained by filtration. Then, the product was washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification was carried out by Soxhlet extraction with ethanol, THF, and $CHCl_2$ in turn for 48 h. The product was dried in vacuum for 8 h at 80 ℃ to give PAF-45 (469 mg, 98.6 % yield).

Characterization

Fourier transform infrared spectroscopy (FTIR) was was collected on a Bruker IFS 66 v/s spectrometer which was registered between 4000 and 500 cm^{-1} with 128 scans per spectrum. UV−vis absorption spectra were recorded with a spectrophotometer (HITACHI, U-3900H,). The NMR data was performed using a Varian instrument 300MHz Liquid nuclear magnetic resonance analyzer. The UV spectra were measured using a UV-2450 UV-Vis ultraviolet-visible absorption spectrometry, the scope of the test is 800-200 cm^{-1}. The contact angle measurement was using a OCA25DataPhysics contact angle meter.

Experiments for adsorption and photocatalytic degradation reaction:

Static adsorption of benzene series under room temperature and pressure

Two exact same glass bottles and a desiccator were prepared in advance. The first pre-weighed glass bottle was added with a certain amount of PAF-45 (recorded as M_0). The other one was kept as blank. These two glass bottles were deposited in a closed and dark 150 ml desiccator with 20 ml benzene at the bottom. With different time of exposure to benzene vapor, the weights of adsorped benzene were recorded (M) after correction with the blank. Then, the real adsorption capacity of PAF-45 with time can be calculated:

$$\eta=(M-M_0)/M_0*100\%$$

$$\text{Absorbed amount} = M-M_0$$

Measured absorption capacity of toluene, chlorobenzene, bromobenzene, aniline and nitrobenzene were conducted in the similar way above.

Photocatalytic aromatic organic compounds degradation measurements at room temperature and pressure

The photocatalytic degradation of aniline was carried out in a 30 ml glass bottle under white light illumination (350 nm~infrared radiation). The distance between the lamp and bottle was 19.5 cm. 5 mg of the photocatalyst and 10 ml aniline were added into the bottle. After the reactor stirring in the dark for one hour, the lamp was turned on to start the photocatalytic reaction. At different time points, the remaining aniline

solutions concentration were tested with a ultraviolet–visible spectrophotometer by following the signal at wavelength 280 nm that corresponds to the maximal absorption. Then, the photocatalytic degradation rate of aniline was calculated:

$$C/C_0=(C_t-C_0)/C_0*100\%$$

To further determine photocatalytic ability of PAF-45, the photocatalytic degradation of phenol solution(1 mg/L) test was also carried out under similar reaction conditions as described above.

Adsorption of benzene simulation wastewater

Certain amount of PAF-45 (50, 100, 250, or 500 mg) were added in 100 ml 500 mg/L benzene simulated wastewater, respectively. After certain time, the concentration of benzene left in the water was measured with UV spectrophotometry. With that, the benzene adsorption percent of PAF-45 was calculated under different time.

The PAF-45 was collected with laboratory slow paper filter and vacuum filter device after absorption, Then, the recycled PAF-45 on paper filter can be well collected with ethanol wash with recycle rate of around 99 %. Then, it was regenerated by treating it with a mixture of ethanol and acetone, and dried it in a vacuum drying oven, then was added in benzene simulated wastewater in the same condition above. The benzene concentrations in water was measured, with which the repeatability and recyclability of PAF-45 was tested for 8 times.

Table S1 The comparison of AC and PAF-45

	S_{BET}(m^2/g)	V_{total}(cm^3/g)	V_{micro}(cm^3/g)	$V_{meso}+V_{macro}$(cm^3/g)	V_{micro}/V_{total}(%)
activated carbon	1270	0.8	0.506	0.294	63.5
PAF-45	777	0.43	0.236	0.189	55.5

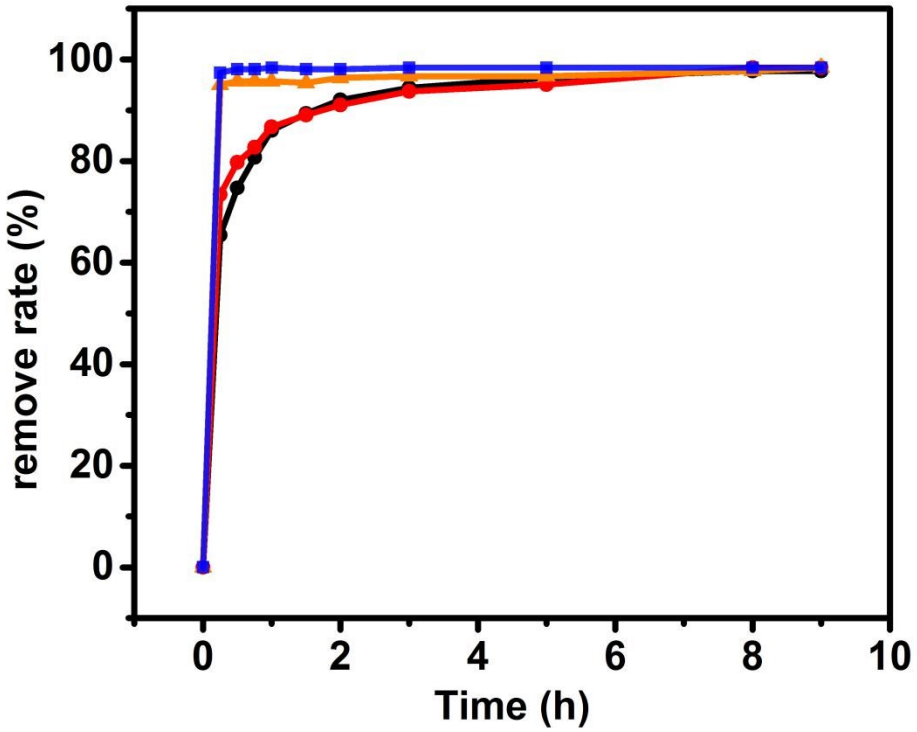

Figure S1. Adsorption of benzene simulation wastewater by PAF-45-50 mg (black) PAF-45-100 mg (red) PAF-45-250 mg (orange) and PAF-45-500 mg (blue).

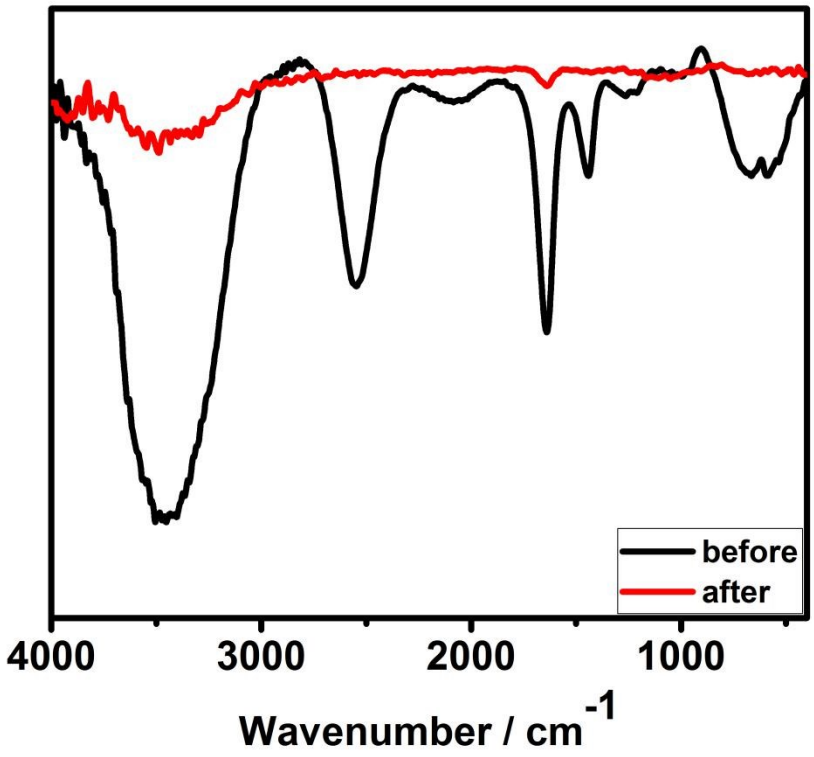

Figure S2. The FTIR spectra of simulation wastewater before (black) and after (red) adsorption by PAF-45.

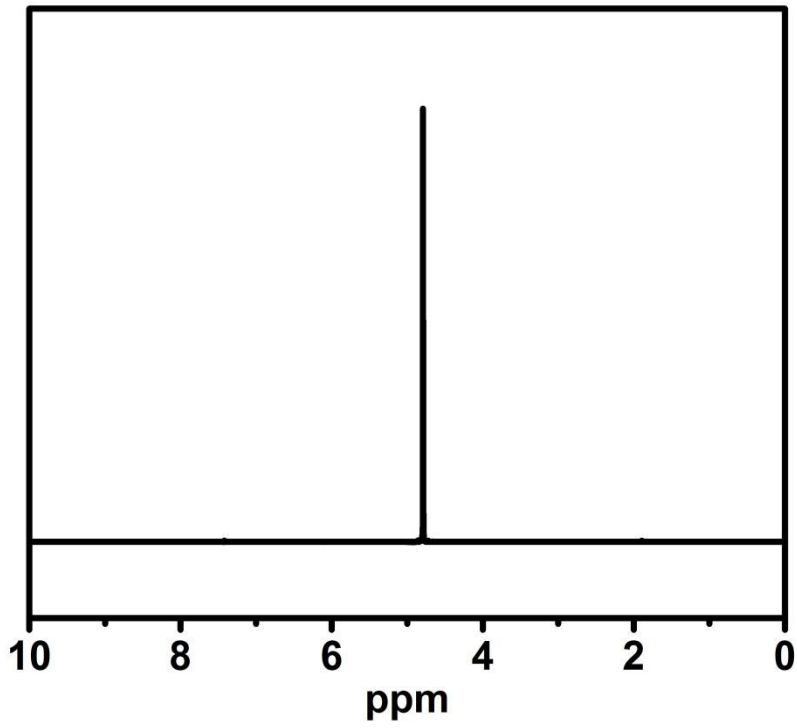

Figure S3. The NMR data of simulation wastewater after adsorption by PAF-45.

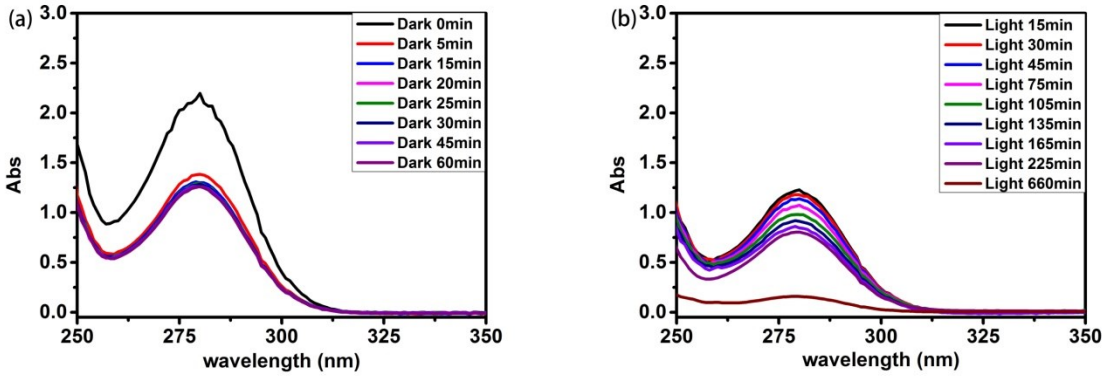

Figure S4. The temporal evolution of the spectral changes of photocatalytic aniline in presence of PAF-45.

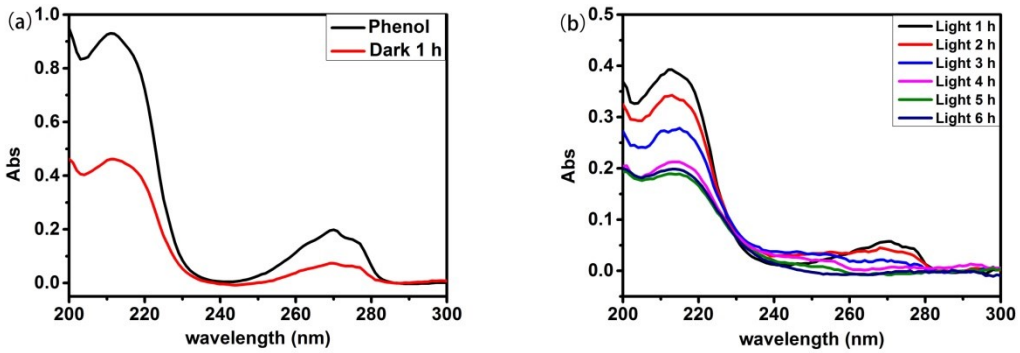

Figure S5. The temporal evolution of the spectral changes of photocatalytic phenol in presence of PAF-45.

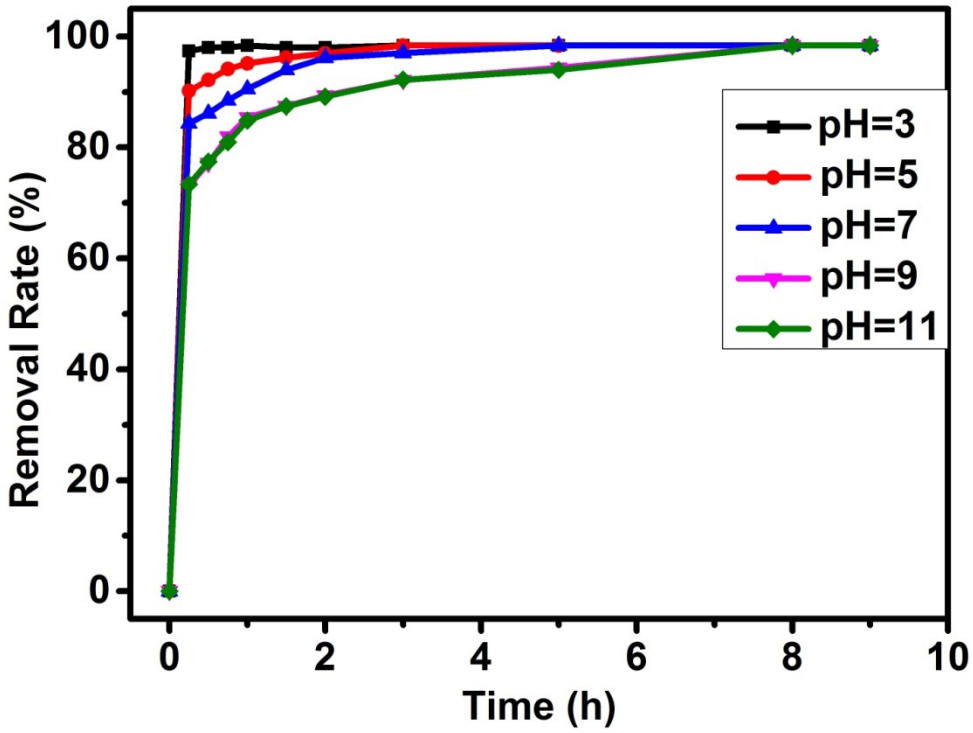

Figure S6. Effects of pH on PAF-45-500mg treating benzene in wastewater.