Supporting Information

for

4-(2-pyridylazo)-resorcinol functionalized polyacrylonitrile fiber through microwave irradiation method for the simultaneous optical detection and removal of heavy metals from water

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Experimental Section:

1. The preparation of PAR immobilized fiber under microwave irradiation.

Step 1: Amination of polyacrylonitrile (PAN) fiber. The PAN fiber was first going through an amination process by reacting with ethylenediamine (EDA).More specifically, 1 g PAN fibers, 40 mL EDA, and 20 mL deionized (DI) water were added into a 250 mL three neck-flask and the solution was stirred for 5 min until homogenously mixed. The MW parameters in the reactor were set up with temperature at 110°C and time at 30 min, and the reaction was refluxed under continuous mechanical stirring. After reaction, the solution was cooled to room temperature, and then suction filtered and washed with hot water until neutral. The obtained fiber (PAN_{MW}-EDA) was placed on a glass plate and dried in a vacuum oven at 60°C overnight.

Step 2: The preparation of PAR modified fibers. The PAR was attached through a Mannich reaction. Initially, PAR (0.5 g) was dissolved and sonicated in the mixture of ethylene glycol (40 mL) and DI water (10 mL). Then, the above mixture, PAN_{MW}-EDA fibers (1.0 g), HCHO (10 mL) were added into the reaction flask successively and nitrogen was bubbled into the system to eliminate the oxygen. The reaction was carried out in the MW reactor with the output power at 300 W and reaction time for 20 min. The mixture was continuously mechanical stirred and then cooled to room temperature. The PAR-immobilized fiber was filtered and rinsed repeatedly with hot water. Subsequently, the fiber was extracted with water/methanol (*V:V*=1:1) solution in a Soxhelt's apparatus for 12 h to remove the residue reagent. Finally, the fiber was vacuum dried overnight at 60°C and the obtained product was named PAN_{MW}-PAR.

2. The preparation of PAR immobilized fiber under conventional heating.

Step 1: Amination of PAN fiber. 1 g PANF, 40 mL EDA, and 20 mL deionized (DI) water were added into a 250 mL three neck-flask and the solution was stirred for 5 min until homogenously mixed. The mixture was refluxed at 100°Cunder continuous mechanical stirring for 7 h. After reaction, the solution was cooled to room temperature, and then suction filtered and washed with hot water until neutral. The obtained fiber (PAN_{CV}-EDA) was placed on a glass plate and dried in a vacuum oven at 60°C overnight.

Step 2: The preparation of PAR modified fibers. 1 gPAR was ultrasonic dissolved in 40 mL DI water and subsequently 1.0 g PAN_{CV}-EDA fibers,10 mL HCHO were added into the reaction flask successively and nitrogen was bubbled into the system to eliminate the oxygen. The mixture was refluxedfor 12 h with continuously mechanical stirring and then cooled to room temperature. The rest procedures were just the same like previous described routes and the obtained product was named PAN_{CV}-PAR.

Fig. S1 Schematic diagram for the synthesis of PAN_{MW}-fibers through MW irradiation method.

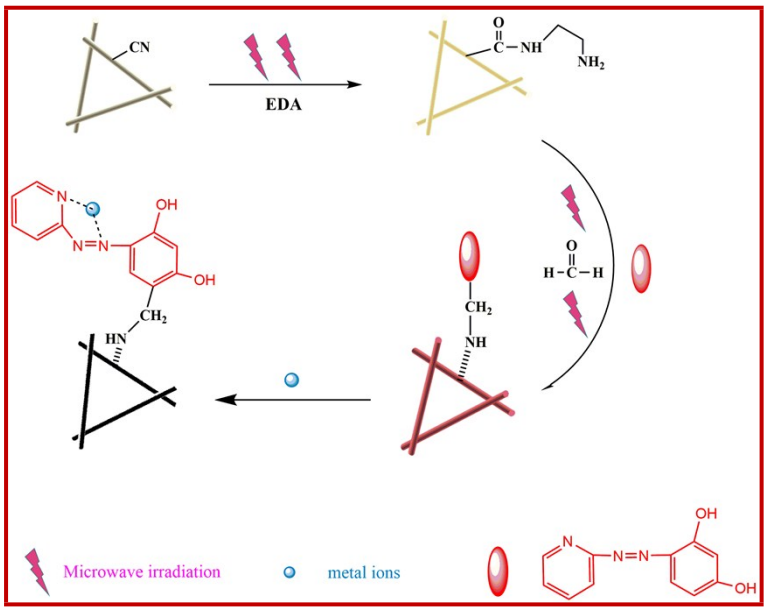


Fig. S2 shows the components of the microwave reactor which purchase from PreeKem Scientific Instruments Co., Ltd. The maximum output of the reactor is 1200 W and the temperature was controlled precisely by inserting fiber optic sensor into the solution. In addition, both mechanical and magnetic stirring are available for application.

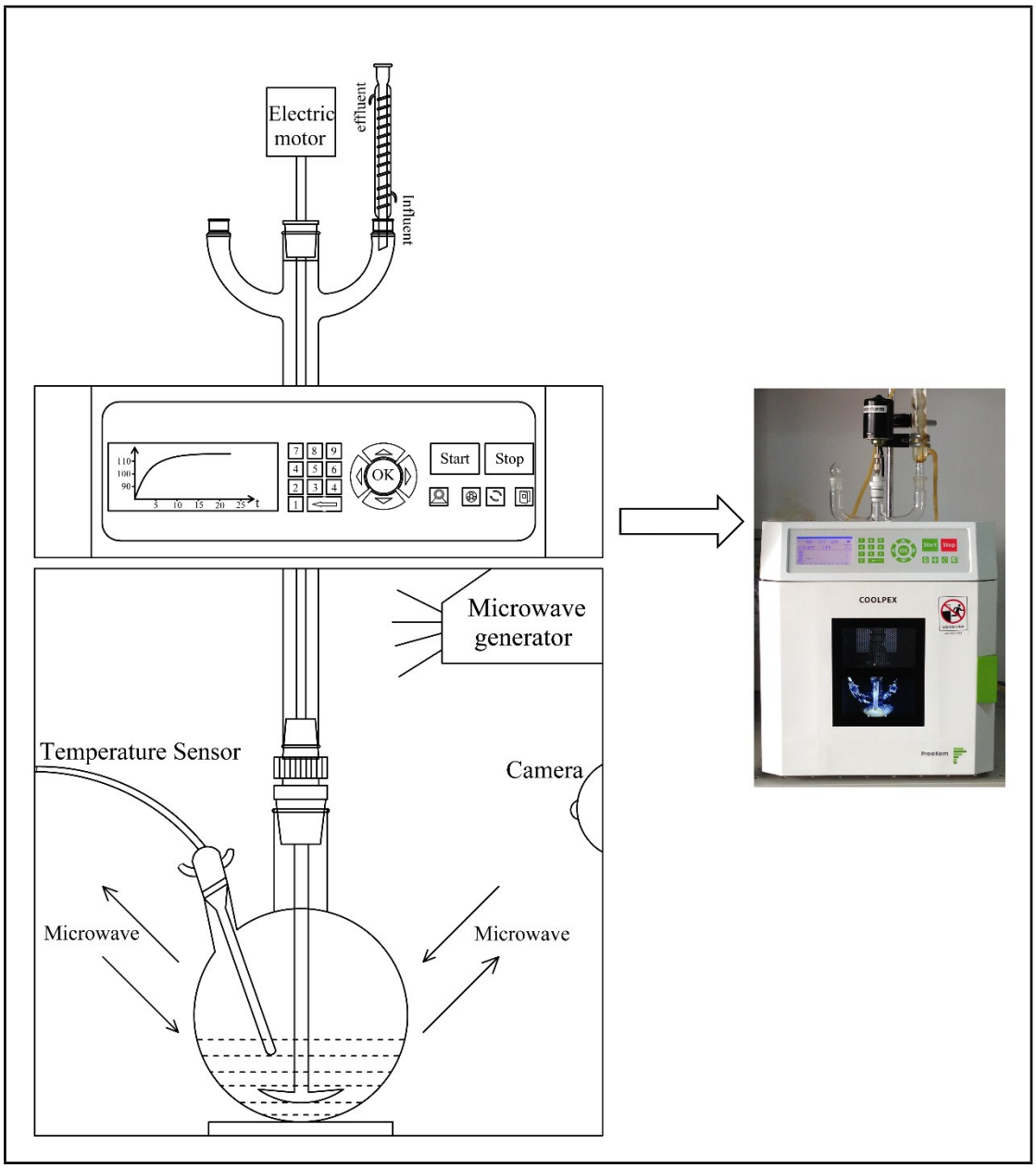


Fig. S2 The feature of the MW reactor (PreeKem Scientific Instruments Co., Ltd.).

Fig. S3 UV-vis adsorption spectra of PAN_{MW}-PAR fibers after interacting with various concentration of Hg^{2+}.

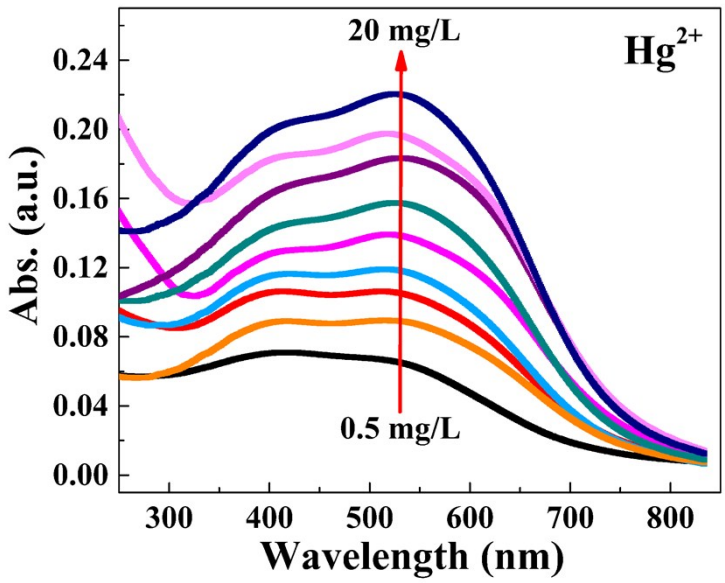
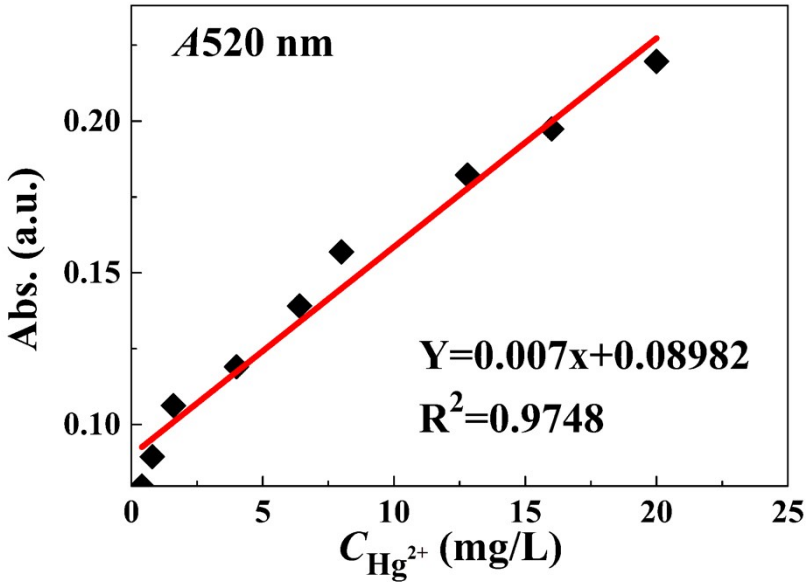


Fig. S4 The adsorption intensity at 520 nm of PAN_{MW}-PAR fibers for Hg^{2+} from 0.5-20 mg/L.



The spectrometer detection limit (D_L) of Hg^{2+} using the optical fibers is calculated from the date in the linear range of the calibration plot, according to the following eq.1[1]:

$$D_L = \frac{S_b \times k}{m} \quad (1)$$

where k is a factor with the value of 3, $S_b$is the standard deviation of the blank and m is the slope of the calibration graph in the linear range. The calculated S_b is 0.0082% after five successive measurements to assure the accuracy and precision of the detection method.

The effect of different solution for regeneration of PAN_{MW}-PAR fibers

In order to be successfully applied in practical treatment, the colorimetric sensor should be rapidly and fully reversible. Three metal ions complexing reagents, EDTA, thiourea and H_2SO_4, were investigated for regeneration. As illustrated in Fig. S5, 0.1 M EDTA exhibits more effective desorption efficiencies for metal ions than 0.1 M thiourea and 0.01M H_2SO_4, and the desorption efficiencies of EDTA are higher than 90%, consistently. This can be attributed to the high affinity feature of EDTA with metal ions. The higher desorption efficiency of thiourea for Hg^{2+} than that of Cu^{2+}, Pb^{2+} and Ni^{2+} ions might due to the stronger interaction of S atom with Hg^{2+}. Hg^{2+} is considered as a soft Lewis acid and S is a soft Lewis base, and soft acid coordinate more strongly with ligands that have soft donor atoms, according to the theory of hard and soft acids and bases. Additionally, all the metal ions can be desorbed by 0.01 M H_2SO_4, which is on account of the comparatively high affinity feature of H^+ and the metal ions were replaced from the fibers subsequently. Based on the above results, EDTA was chosen as the regeneration solution.

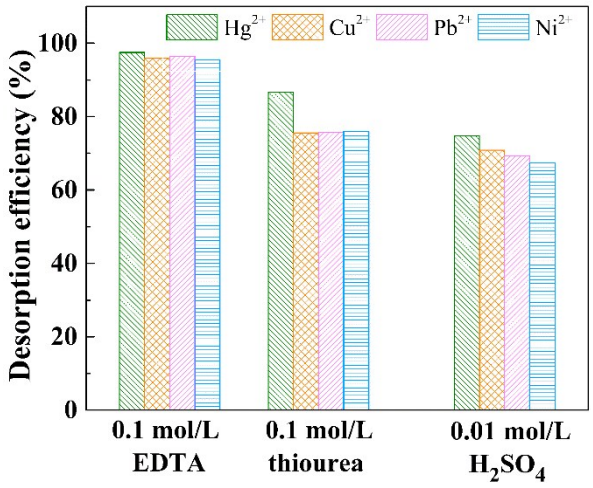


Fig. S5 The effect of different solution for regeneration of PAN_{MW}-PAR fibers.

Langmuir, Freundlichand Temkinadsorption isotherm models were widely used to describe the adsorption progress. The Langmuir isotherm model is based on the assumption that the adsorbate forms a saturated molecular layer on the adsorbent surface, and the surface sites shares the same energy with no solute-solute or solute-solvent interaction in either phase and transmigration of adsorbate on the plane of the surface. The Langmuir isotherm model can be expressed as[2]:

$$q_e = \frac{q_m K_d C_e}{1 + K_d C_e} \tag{2}$$

where $q_e$is the amount of metal ion adsorbed at equilibrium by the adsorbent (mg/g), $C_e$is the equilibrium concentration (mg/L), q_{m} is theoretical saturation adsorption capacity (mg/g), K_{d} (L/mg) is the equilibrium Langmuir constant.

The Freundlich isotherms model, which assumes a heterogeneous surface and a multilayer adsorption with an energetic non-uniform distribution, can be expressed as[3]:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

whereK_{f}(mg/g) and n are constants representing the adsorption capacity and intensity of adsorption.

The Temkin isotherm model considers that due to adsorbent-adsorbate interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. Therefore, the adsorbent surface is a uniform distribution of binding energies. The Temkin adsorption isotherm expression is shown as[4]:

$$q_e = \frac{RT}{B_T} ln(K_T C_e) \tag{4}$$

where K_{T} (L/g) is the equilibrium binding constant corresponding to the maximum

binding energy, B_T (kJ/mol) is the Temkin constants relates to the heat of adsorption, R(8.314 J·mol^{-1}·K^{-1}) is the universal gas constant and T (K) is the absolute temperature.

Table S1.

Isotherm parameters for heavy metal ions uptake onto PAN_{MW}-PAR fibers at room temperature.

Metal ions	Langmuir model			Freundlich model			Temkin model		
	q_m (mg/g)	K_d (L/mg)	R^2	n	K_f (mg/g)	R^2	K_T (L/g)	R^2	B_T (kJ/mol)
Hg^{2+}	181.2	0.03678	0.9918	3.534	73.21	0.8679	1.182	0.9261	82.22
Cu^{2+}	116.9	0.03044	0.9947	2.892	52.75	0.8817	1.418	0.8952	138.4
Pb^{2+}	77.07	0.06195	0.9905	2.378	31.48	0.8754	2.782	0.9387	206.3
Ni^{2+}	70.33	0.06832	0.9907	2.075	30.26	0.8667	2.889	0.9471	224.1

References

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