Supplemental information for

Enhanced removal of roxarsone by Fe₃O₄@3D graphene nanocomposite:

synergistic adsorption and mechanism

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S1. Supplemental Materials and Methods

Preparation of 3D Fe₃O₄@RGO nanocomoposite

GO was prepared with the oxidation of graphite, using the modified Hummers method. ¹ In a typical synthesis, 1 mmol FeSO₄ was mixed with 10 mL of GO suspension with concentration of 2 mg/mL. After sonicating treatment for 5 min, the pH value of the mixture was adjusted to 10 with ammonia. Then the mixed solution was heated to 90 °C for 6 h without stirring to facilitate the formation of graphene hydrogel. The obtained hydrogel was washed with DI water for several times to remove residual impurities. After freeze-dried under -45 °C for 24 h, the 3D Fe₃O₄@RGO nanocomoposite was obtained.

Adsorbents characterization.

The microstructures of Fe₃O₄@RGO, GO-90, RGO and *p*-Fe₃O₄ nanoparticles (NPs) were characterized by a high-resolution field emission gun scanning electron microscope (FESEM, Nova, NanoSEM 430, FEI Company) operating at an acceleration voltage of 15 kV, and transmission electron microscope (TEM, H-7650, Hitachi, Japan) at an acceleration voltage of 80 kV. The crystal structures of the nanocomposites were determined by X-ray diffraction (XRD) analysis, which were collected on a D8-Advance X-ray diffractometer (Bruker, German) with a high-intensity monochromatic nickel-filtered Cu K α radiation generating at 40 kV and 40 mA. Diffraction patterns were collected with a 2 θ range from 5 to 80°. The scan step size was 0.02° at a rate of 1°/min. The Crystal lattices of Fe₃O₄ NPs in Fe₃O₄@RGO and *p*-Fe₃O₄ were determined using High resolution transmission electron microscopy

(HRTEM, Tecnai G2 F20 S-TWIN) at an acceleration voltage of 200 kV. Raman spectra were acquired on a LabRAM Aramis Microscopy system (H. J. Y., France) as the excitation source in the range of 600-1800 cm⁻¹. XPS spectra were analyzed using an Axis Ultra DLD instrument (Kratos Analytical, U.K.) with an A1 K α X-ray source. Spectra were recorded at a pass energy of 160 eV for survey scans and 40 eV for high-resolution scans. The specific surface area (SSA) of the samples was determined using an accelerated surface area and porosimetry analyzer (Micromeritics, ASAP 2020). All samples were degassed at 200 °C for 27 h before the analysis. Zeta potential of the materials was determined using an Omni zeta potential analyzer (Brookhaven, U.S.A.). The tested pH range was from 2 to 9.

Analyses of the adsorption data

Nonlinear Dubinin-Ashtakhov (DA, eq 1), Langmuir (eq 2) and Freundlich models (eq 3) were employed to fit the isotherms on ROX adsorption by $Fe_3O_4@RGO$, GO-90, RGO and *p*-Fe₃O₄ after adsorption for 72 h. The adsorption isotherms under various conditions were plotted to follow the equations: ^{2, 3}

$$q_e = \frac{Q_m}{10^{(\varepsilon/E)^b}} \tag{1}$$

where,

 q_e : the equilibrium adsorbed concentration of solute (mg/g);

 Q_m : maximum adsorption capacity (mg/g);

 ε : the effective adsorption potential (kJ/mol). $\varepsilon = -RT \ln(C_e/C_s)$, where C_e (mg/L) is equilibrium concentration of adsorbate (mg/L), C_s (mg/L) is the water solubility of solute, which is 1000 mg/L for ROX, R [8.314 × 10⁻³ kJ/(mol K)] and T (K) are universal gas constant and absolute temperature, respectively;

E: the correlating divisor (kJ/mol);

b: the fitting parameter.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{2}$$

where,

C_e: equilibrium concentration of adsorbate (mg/L);

- q_e : amount adsorbed at equilibrium (mg/g);
- Q_m : maximum adsorption capacity (mg/g);
- K_L : Langmuir constant (L/mg).

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

where,

- C_e : equilibrium concentration of adsorbate (mg/L);
- q_e : amount adsorbed at equilibrium (mg/g);
- K_{f} : the Freundlich affinity coefficient (mg/g);
- *n*: the Freundlich exponential coefficient.

The kinetics of the ROX adsorption was interpreted using a pseudo-second-order non-linear kinetic model expressed by the following equation: ⁴

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where,

 q_e (mg/g): amount adsorbed at equilibrium;

 q_t (mg/g): amount adsorbed at time t;

t (min): adsorption time;

 k_2 (g/mg·min): the pseudo-second-order rate constant.

Detection of ROX degradation during adsorbed by Fe₃O₄@RGO

The degradation of ROX during adsorption was determined by detecting ROX, As(V) and As(III) species on an Elan DRC-e inductively coupled plasma mass spectrometer (ICP-MS) hyphenated with a PerkinElmer high performance liquid chromatograph (HPLC) . ⁵ Briefly, separation of As(V) and As(III) was achieved on a Hamilton PRP-X100 anion exchange chromatographic column (5 μ m, 4.6 × 150 mm) with 40 mM (NH₄)₂HPO₄ solution (pH adjusted to 5.4 with HNO₃) as the mobile phase.

ROX adsorption by Fe₃O₄@RGO in practical application

Humic acid (90%, Aladdin Bio-chem Technology, China) was employed as model DOM in this study. To prepare stock solution of humic acid, 50 mg of humic acid was dissolved in 5 mL of 0.1 mol/L NaOH and then mixed with distilled water to reach an apparent concentration of 50 mg/L. The solution of humic acid was adjusted to pH 6.0 with 0.1 mol/L HCl and filtered through a 0.45 μ m membrane. The obtained solution of humic acid was diluted to reach apparent concentrations of 5, 10, 20, 30, and 40 mg/L and then was used to prepare the experimental background solution containing

0.02 mol/L NaCl. The DOM concentration was represented by the total organic carbon (TOC) (vario TOC, Elementar, Germany).

The influence of DOM on ROX adsorption was analyzed by the distribution coefficient (K_d) for Fe₃O₄@RGO towards ROX with the DOM concentration of 0, 1.5, 3.5, 8.0, and 12.0, and mg of C/L (prepared using the humic acids in this study). The initial concentration of ROX was 1 mg/L, while the Fe₃O₄@RGO dosage was 0.15 g/L.

For examination of ROX removal by Fe₃O₄@RGO in practical application, adsorption experiments were conducted on a natural swine manure lixivium (obtained from a pig farm in the city of Heyuan, Guangdong province in China) with ROX added standard of 1 mg/L. The swine manure lixivium was prepared by dipping 100 g of fresh swine manure in water for 12 h. The lixivium was then filtered through a 0.45 μ m membrane and diluted 100 times. DOM in the lixivium was determined to be 9.0 mg C/L. Two dosages of Fe₃O₄@RGO (0.15 g/L and 0.30 g/L) were used in this experiment. The solution was shaken at pH 5 ± 0.1 and 25 °C with a speed of 200 rpm for 90 min.

Synchrotron-radiation-based X-ray absorption spectroscopy (XAS) data collection and analysis

The As K-edge (11,867 eV) XAS spectra, including the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were collected at the wiggler beamline of BL17C1 in BSRF. All XAS data were collected in the fluorescence mode at room temperature, using a Lytle detector equipped with Soller slits and Ge filter for screening scattering and fluorescence background. The maximum

absorption edge of sodium arsenate reference was set to 11875 eV. No beam damage was observed during XAS data collection by comparing individual scans of each sample.

The XAS data analysis was performed using the ATHENA and ARTEMIS interfaces to the IFEFFIT version 1.2.11 program package, following the procedures suggested in Liu et al. ⁶ The raw XAS data were processed using ATHENA with data conversion, energy calibration, data alignment and merge, background subtraction, normalization, and Fourier transformation. E_0 was set at the first inflection point in the spectra for all samples. The energy calibrated, aligned, and merged XAS spectra were normalized and background subtracted using a linear pre-edge function between -200 and -20 eV and a quadratic post-edge function between 50 and 1000 eV.

The processed XAS spectra were further transformed from electron energy to photon-electron wave vector unit (k, Å⁻¹) and weighted by k^3 to generate $k^3x(k)$ spectra. The data were then transferred to ARTEMIS through Fourier transformation for EXAFS analysis. The radial distribution function (RDF) within selected k range was 2.0 – 14.0 Å⁻¹ for ROX-adsorbed Fe₃O₄@RGO and p-Fe₃O₄. The EXAFS analysis was then performed by fitting the experimental spectra to the theoretical calculations. Theoretical As–O and As–Fe scattering paths were calculated with FEFF823 extracting from the structural model of scorodite. All spectra were fitted for interatomic distance shift (Δ R), degeneracy of a path (N), Debye–Waller factor (σ^2), and energy shift (Δ E) across the R range from 0 to 5.0 Å. One fixed amplitude reduction factor of 0.95 was applied to all scattering paths. The goodness of fitting was evaluated by R-factor, for which less than 0.05 is considered to be a reasonable fit.⁷

XPS Data Analysis.

The C 1s, O 1s, Fe 3p, As 3d region of XPS spectra were further deconvolution analyzed using XPS peak 4.1 software. For peak curve fitting, Shirley function was applied to subtract background for all spectra. The Fe 3p peak was fitted by fixing BE of 56.7 eV for Fe(III), BE of 54.9 eV for Fe(II), Gaussian/Lorentzian ratio of 40/60, and asymmetry factor of 0.4 for both peaks. ⁸ The C 1s deconvoluted spectra were fitted to four peaks of C–C/C=C (~284.6 eV), C–O (~286.5 eV), C=O (~287.7 eV), and O=C-O (~289.0 eV), with Gaussian/Lorentzian ratio of 100. ⁹ The O 1s spectra were also fitted to four peaks, including Fe-O/As-O (~529.9 eV), Fe-O-C/-OH (~531.5 eV), C=O/H₂O (~532.4 eV), and C-O-C (~533.3 eV) ¹⁰.

S2. Supplemental results and discussion



Figure S1 Molecular formula and pK_a of ROX. The blue imaginary line circles the arsenic group and the red imaginary line circles benzene ring group.



Figure S2. The spectra deconvolution of C 1s XPS for (a) $Fe_3O_4@RGO$, (b) GO, (c) GO-90 and (d) RGO.

Table S1. Surface carbon atoms proportions obtained from the deconvolution of the

	C-C/C=C (%)	С-О (%)	C=O (%)	O-C=O (%)	
Bonding	284 7	286.6	200 2	280.0	
Energy (eV)	204.7	280.0	200.2	289.0	
GO	41.96	45.33	7.58	5.13	
GO-90	55.89	37.45	6.66	0	
RGO	76.41	23.59	0	0	
Fe ₃ O ₄ @RGO	74.61	22.03	0	0.36	

C1s peak from XPS analysis (Figure S2).

XPS analysis of C 1s deconvolution of XPS spectra of GO, GO-90, RGO and Fe₃O₄@RGO (Figure S2) consisted four main components which could attribute to C–C, C–O, C=O, and O=C-O groups. The C-C peak proportions of the carbon-contained materials were ranked as Fe₃O₄@RGO \approx RGO > GO-90 > GO. Simultaneously, proportions of the oxygen-contained carbon peaks were assigned to be GO > GO-90 > Fe₃O₄@RGO > RGO. This result suggested the partial reduction of GO under 90 °C without any reductant, while the addition of Fe²⁺ promoted the reduction of GO to RGO.



Figure S3. XRD patterns Fe₃O₄@RGO, GO-90, RGO, and *p*-Fe₃O₄.



Figure S4. The XPS spectra deconvolution of Fe 3p peaks of XPS for Fe₃O₄@RGO.

The Fe²⁺:Fe³⁺ ratio in Fe₃O₄@RGO calculated from the Fe 3p spectrum was 1:2.09, which was approximate to the stoichiometric ratio of Fe₃O₄ (1:2) and confirmed the structure of Fe₃O₄ iron oxide existing in the nanocomposite ⁸.

Sample	Crystal size	Fe ₃ O ₄ content	Graphene content	^a Specific surface
	(nm)	(%)	(%)	area (m ² /g)
Fe ₃ O ₄ @RGO	25.6	80.2	19.8	61.9
<i>p</i> -Fe ₃ O ₄	34.8	100	-	103.1
GO-90	-	-	100	28.1
RGO	-	-	100	200.3

Table S2 Structural characteristics of Fe₃O₄@RGO, *p*-Fe₃O₄, GO-90, and RGO.

a: The lower specific surface area of Fe₃O₄@RGO than *p*-Fe₃O₄ is due to the nonporous GO substrate with low surface area in the nanocomposite. However, it can be seen from the SEM images (Figure 1) that the Fe₃O₄ NPs in the nanocomposite is much smaller than *p*-Fe₃O₄. Moreover, Fe₃O₄ NPs in the nanocomposite showed fewer aggregations and higher dispersibility than *p*-Fe₃O₄. Therefore, it can be concluded that although the surface area of Fe₃O₄@RGO is lower than *p*-Fe₃O₄, the surface area of Fe₃O₄ NPs in the nanocomposite is higher than that of *p*-Fe₃O₄.



Figure S5. The spectra deconvolution of O 1s peaks of XPS for $Fe_3O_4@RGO$ (a), *p*-Fe₃O₄ (b), and Raman spectra of $Fe_3O_4@RGO$ and GO (c).

Characteristic peaks of C=O and C-O were observed, which were also present in the C 1s peaks of Fe₃O₄@RGO. Moreover, the peak at 531.5 eV could be attributed to Fe-O-C bonds between Fe₃O₄ and graphene and/or adsorbed hydroxyl groups ^{11, 12}. The area ratio of this peak was determined to be 46.06%, which was much higher than that of p-Fe₃O₄ (20.16%, Table S5). Combining with the analysis results of adsorbed hydroxyl groups (see in the analysis of the active adsorption site below and Table S5), it can be concluded that abundant Fe-O-C bonds exist on Fe₃O₄@RGO. Besides, Raman spectra showed an obvious red shift of the G band in graphene from 1581 to 1589 cm⁻¹ after compositing (Figure S5c), suggesting the charge transfer from graphene to Fe₃O₄ NPs.

Table S3. The ROX adsorption capacity and affinity calculated from Langmuir fit of various adsorbents. The amount of ROX adsorption (q_e) at $C_e = 2 \text{ mg/L}$ and $C_e = 20 \text{ mg/L}$ represents for the adsorption capacity of the adsorbents at lower and higher concentration, respectively.

Adaarbanta	Q_m	K_L	$q_e ({ m mg/g})$	$q_e (\mathrm{mg/g})$	Ref.
Ausorbents	(mg/g)	(L/mg)	$(C_e = 2 \text{ mg/L})$	$(C_e = 20 \text{ mg/L})$	
Fe ₃ O ₄ @RGO	454	0.78	204	393	This work
Porous magnetic carbon composites	417	0.21	105	205	13
MOFs (UiO-66 with defects)	730	0.11	195	400	4
Magnetite composites with activated carbon	254	-	27	158	14
Hydrochar-derived magnetic carbon	588	0.063	130	270	15
MOFs (MIL-100-Fe)	387	-	48	225	2
Chitosan-based copolymers	259	0.090	51	166	16
Ferric and manganese binary oxide	142	-	139	-	17
Multi-walled carbon nanotubes	13	0.122	2	9	18

For example, although defective MOFs (UiO-66) has a huge adsorption capacity (up to 730 mg/g), its affinity towards ROX is relatively low (0.11 L/mg) ⁴. Therefore, the evaluated amount (q_e) of adsorbed ROX on Fe₃O₄@RGO is higher than that on UiO-66 at the equilibrium concentrations (C_e) of 2 mg/L, while the q_e value is very close to UiO-66 at the C_e of 20 mg/L. Considering the milder synthesis method and the higher chemical stability of Fe₃O₄@RGO than MOFs, the as-prepared nanocomposite is more potential for the ROX adsorption than MOFs.

For the ferric and manganese binary oxide, ROX was degraded to As(V) and As(III) to manganese oxide and then adsorbed by ferric oxide, which was a more complicated and higher cost process.



Figure S6. HPLC-ICP-MS chromatograms of As(V) and As(III) in different solutions.

Complete	Pseudo-second order kinetic				
Samples	$q_e ({ m mg/g})$	k_2 (g/mg·min)	\mathbb{R}^2		
Fe ₃ O ₄ @RGO	294.11	2.38×10 ⁻⁴	0.9999		
<i>p</i> -Fe ₃ O ₄	121.95	2.30×10 ⁻⁴	0.9998		
GO-90	44.84	1.44×10 ⁻⁴	0.9985		
RGO	69.44	2.07×10-4	0.9999		

Table S4. Parameters of pseudo-second order kinetic for ROX adsorption on $Fe_3O_4@RGO, p-Fe_3O_4$ and GO-90.



Figure S7. Reusability of $Fe_3O_4@RGO$ for the adsorption of ROX. The initial concentration of ROX was 50 mg/L. The desorption agent was 0.05 mol/L NaOH solution.



Figure S8. FTIR (a) and XRD (b) patterns of $Fe_3O_4@RGO$ before and after 4 cycles adsorption.



Figure S9. Equilibrium ROX adsorption as a function of solution pH and the zeta potential of Fe₃O₄@RGO, *p*-Fe₃O₄, RGO, and GO-90 (inset figure).



Figure S10. (a): Arsenic XAFS data of Fe₃O₄@RGO and *p*-Fe₃O₄ after adsorbing ROX. (b): XPS spectrum of As 3d in Fe₃O₄@RGO after adsorption.

The XANES spectra of As (V) in ROX adsorbed by Fe_3O_4 @RGO and *p*-Fe₃O₄ showed that the arsenic remains in the form of As (V) in ROX after adsorption by the two materials (Figure S10a).

As presented in Figure S10b, the fitted As 3d spectrum showed that the binding energy of As in adsorbed ROX was 45.1 eV, which was consistent with the common energy of As 3d peak for phenylarsonic acid. ¹⁹ Meanwhile, no peak at 44.8 eV or 43.5 eV for inorganic As(V) or As(III) was observed ⁶. This result was sufficient to prove that there is no ROX degradation to inorganic arsenic during the adsorption process.



Figure S11. FTIR spectra of $Fe_3O_4@RGO$ and $p-Fe_3O_4$ before and after ROX adsorption



Figure S12. Configurations of As-Fe bidentate binuclear complex.²⁰

Table S5. Proportions of -OH contained peaks participating in As-Fe complex and

	O 1s peak at 531.5 eV (-OH/Fe-O-C)			
	Total content	As-Fe complex	Hydrogen bond	
	(%)	(%)	(%)	
Fe ₃ O ₄ @RGO	46.06	26.30	19.76	
<i>p</i> -Fe ₃ O ₄	20.16	15.96	4.20	

hydrogen bond in O 1s spectra of Fe₃O₄@RGO and *p*-Fe₃O₄.

The O 1s spectra of Fe₃O₄@RGO before and after adsorption can be deconvoluted into four peaks at 530.5, 531.6, 532.2, and 533.3 eV, which refers to Fe-O/As-O from Fe₃O₄ and ROX, Fe-O-C bonds and/or Fe-OH, H₂O, and C-O-C bands, respectively (Figure 6a). ^{21, 22} After adsorption, the increase of Fe-O/As-O peak content from 20.20% to 37.08% could be assigned to As-O bands in adsorbed ROX. Meanwhile, the Fe-O-C/Fe-OH peak content in Fe₃O₄@RGO decreased from 46.06% to 32.91% after adsorption, which was mainly ascribed to the formation of As-Fe inner-sphere complex. ²³ Since the Fe-O-C content maintained the same before and after adsorption, the 13.15% decrease of the peak at 532.6 eV represented the surface Fe-OH content that replaced by As-O groups during the ROX adsorption. According to the As-Fe bidentate binuclear complex (Figure S12), the stoichiometric ratio of the Fe-OH groups before adsorption and replaced by As-O groups during adsorption should be 2:1 the ${}^{2}C$ complexes. 20 Therefore, the surface Fe-OH content in Fe₃O₄@RGO involving in the As-Fe complex could be calculated as 2 times higher of the decreasing content of 13.15%, which was 26.30% in the Fe₃O₄@RGO (Table S5). This value accounted for half of the Fe-O-C/Fe-OH peak content in Fe₃O₄@RGO. Similarly, the Fe-OH groups in *p*-Fe₃O₄ that participated in the formation of As-Fe complex was calculated to be 17.96% (Table S5), which was close to the Fe-OH content in *p*-Fe₃O₄, indicating that As-Fe coordination was the dominating force in the adsorption of ROX by *p*-Fe₃O₄.

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