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Supporting information

Porous graphene oxide based inverse spinel nickel ferrite nanocomposites for the enhanced adsorption removal of arsenic

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2. Materials and methods

2.1 Materials

All chemicals were of analytical grade and used as supplied in the present investigations. Graphite flakes procured from Sigma-Aldrich (USA) were used as a source for graphene oxide preparation in the present study. The stock solution (1000 mg/L) of both As(III) and As(V) was prepared from $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$, respectively. The reagents, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_3 \cdot 9H_2O$, HCl (40%), NH_4OH (56.6%), and H_2SO_4 (98%) were obtained from the Samchun Pure Chemicals Co. Ltd. (Korea); $KMnO_4$ and NaOH (98%) were purchased from Kanto Chemical Co. Inc. (Japan). $NaNO_3$ (98%), which was purchased from Duksan Pure Chemicals (Korea) and H_2O_2 (30%), which was supplied by Junsei Chemicals Co. Ltd. (Japan) were used in the preparation of GO, GONF and rGONF. The reducing agent, hydrazine hydrate supplied by Sigma-Aldrich (USA) was used for the reduction of GONF. 0.1 M $NaNO_3$, NaCl, Na_2SO_4, NaF, Na_2CO_3 and $Na_3PO_4 \cdot 12H_2O$ (Purchased from Samchun Pure Chemicals Co. Ltd. (Korea)) in deionized water, respectively. These solutions were further diluted to suitable concentrations on the day of use.

2.2 Characterization of GONF and rGONF nanocomposites

The crystalline nature and size of the prepared GONF and rGONF nanocomposites were confirmed by X-ray powderdiffraction (XRD) analysis using Rigaku D/Max–2500 X-ray diffract meter (Japan). Spectrum GX & Auto image Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin-Elmer, USA) was used for analyzing the functional groups of GONF and rGONF. ESCALAB–210 (Spain) X-ray photoelectron spectroscopy (XPS) was used for elemental composition analysisof the prepared GONF and rGONF samples. S–4300 & EDX–350 (Hitachi, Japan) was used for the measuring surface morphology and composition of samples. Autosorb-1, Quanta chrome instrument (USA) was used to measure the Brunauer, Emmett and Teller (BET) surface area and pore sizes of GONF and rGONF. Veeco Inc., (New York) atomic force microscopy (AFM) imaging was used to capture AFM-images of GONF and rGONF. Sonics Vibracell (CV 334, USA) was used for the ultrasonification of GO, GONF, and rGONF. Magnetic measurements of GONF and rGONF were performed using a SQUID magnetometer (MPMS–7, Quantum Design, USA). All pH measurements were taken using a 340i pH meter (WTW, Germany). The solution pH was adjusted using HCl and NaOH (0.1 mol/L) solutions. The arsenic concentration in aqueous solution was determined using Optima 2100 DV inductive coupled plasma-optical emission spectroscopy (ICP–OES) (Perkin-Elmer, USA) equipped with auto sampler.

Results and discussion

3.2 Adsorption studies of As(III) and As(V) onto GONF and rGONF

Kinetic models

Pseudo-first and pseudo-second model

The linear form of pseudo first-order rate equation is

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}\, q_e - k_1 t \quad (1)$$

A linear form of pseudo second-order kinetic model is express by eq. (2)

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (2)$$

where q_e and q_t are the amounts of arsenic adsorbed (mg/g) at equilibrium and time t(min), respectively; k_1(min^{-1}) *and* k_2(g·mg^{-1}·min^{-1}) *are* the rate constant of the pseudo first-order and pseudo second-order kinetic models, respectively, for adsorption process.

Weber-Morris kinetics model

Intra-particle mass transfer diffusion model proposed by Weber and Morris can be written as follows:

$$q = k_i t^{1/2} + C \quad (3)$$

where C (mg/g) is the intercept and ki is the intra-particle diffusion rate constant($g \cdot mg^{-1} \cdot min^{-0.5}$) for adsorption.

Boyd model

Boyd model has the following form:

$$Bt = -\ln(1-q_t/q_e) - 0.4977 \quad (4)$$

where q_t and q_e are the amounts of dyes adsorbed on the adsorbent ($mg \cdot g^{-1}$) at time t(min) and at equilibrium time (minute), respectively; $B = \pi^2 D_i / r^2$ (Di is the effective diffusion coefficient of the adsorbate and r is the radius of adsorbent particlesassumed to be spherical).

Table S1 Physical and chemical compositions of real ground water collected from Hagye-dong, Nowon-gu, Seoul, RO Korea (N=3, mean values reported here, the standard deviation is less than 5%)

Physical or chemical compositions	Value or concentration
pH	6.58
ORP	161.3 mv
DO	5.98 mg/L
EC	0.701 ms/cm
Ca^{2+}	28.96 mg/L
Na^{+}	13.31 mg/L
K^{+}	1.72 mg/L
Mg^{2+}	3.62 mg/L
Cl^{-}	29.29 mg/L
NO_3^{-}	36.05 mg/L
SO_4^{2-}	26.13 mg/L
F^{-}	Not detected
As^{3+} or As^{5+}	Not detected

Table S2 BET adsorption surface analysis results for GO, rGO, GONF and rGONF nanocomposites (N=4, number of measurements)

Characteristics	Nanocomposites materials			
	GO	rGO	GONF	rGONF
Surface area, m^2/g	2.59	21.02	122.74	167.26
BET surface area, m^2/g	2.81	21.13	135.99	174.14
Langmuir surface area, m^2/g	3.97	26.59	198.79	240.35
Pore volume, cm^3/g	0.01	0.07	0.12	0.24
Pore size, nm	14.34	12.62	3.42	5.59
Particle size, nm	1000	284.00	44.12	34.46

Figure captions

Fig. S1 XRD and FT-IR pattern for GO, GONF and rGONF nanocomposites prepared in the present study.

Fig. S2 Scanning electron microscopy (SEM) images for GO and its nanocomposites, GONF and rGONF.

Fig. S3 N_2 adsorption desorption isotherms of GONF and rGONF measured by BET analysis.

Fig. S4 Photo image of water dispersed nanocomposites, GONF and rGONF and their separation by external magnetic field.

Fig. S5 Studies of ionic strength effect on adsorption of As(III) and As(V) with GONF and rGONF by using NaCl, KCl, $NaNO_3$, $CaCl_2$ and $MgCl_2$ (0.005 to 0.5 mol/L).

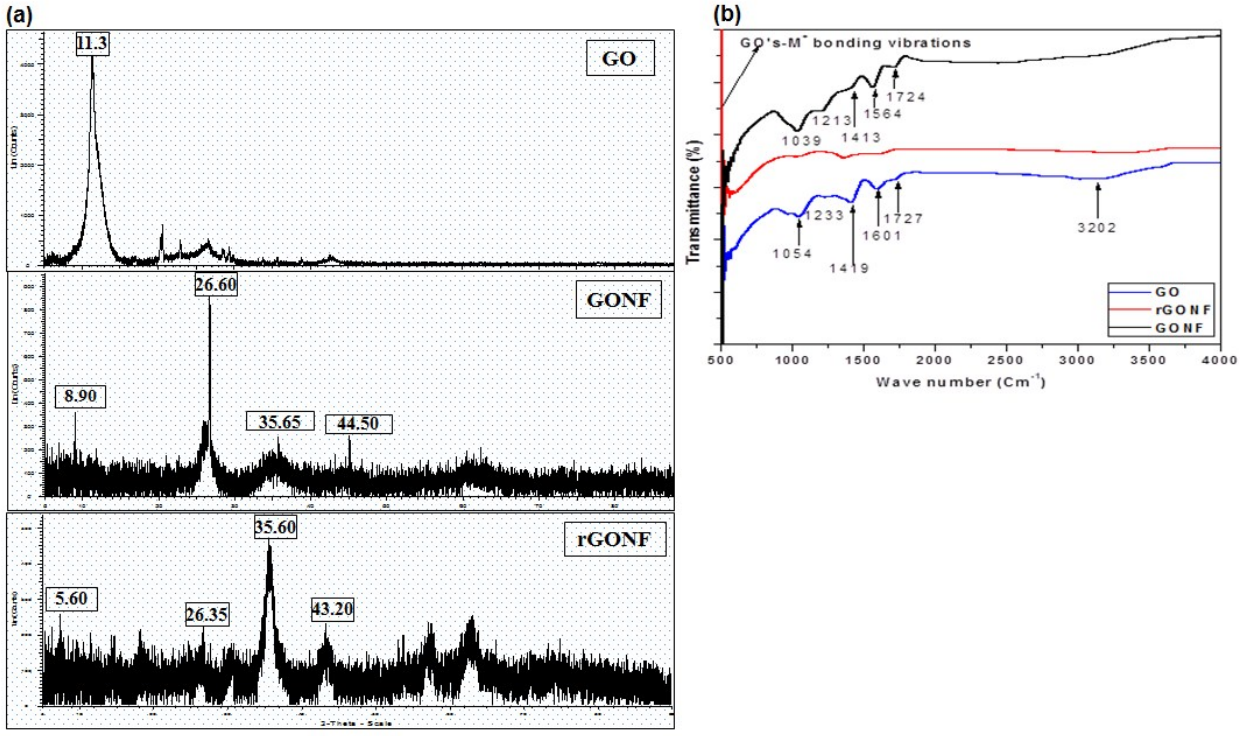

(a)
11.3
GO
26.60
GONF
8.90
35.65
44.50
35.60
rGONF
5.60
26.35
43.20
(b)
GO's-M bonding vibrations
1724
1564
1213
1039
1413
1727
1601
1233
1054
1419
3202
GO
rGONF
GONF
Transmittance (%)
Wave number (Cm-1)
500
1000
1500
2000
2500
3000
3500
4000

Fig. S1

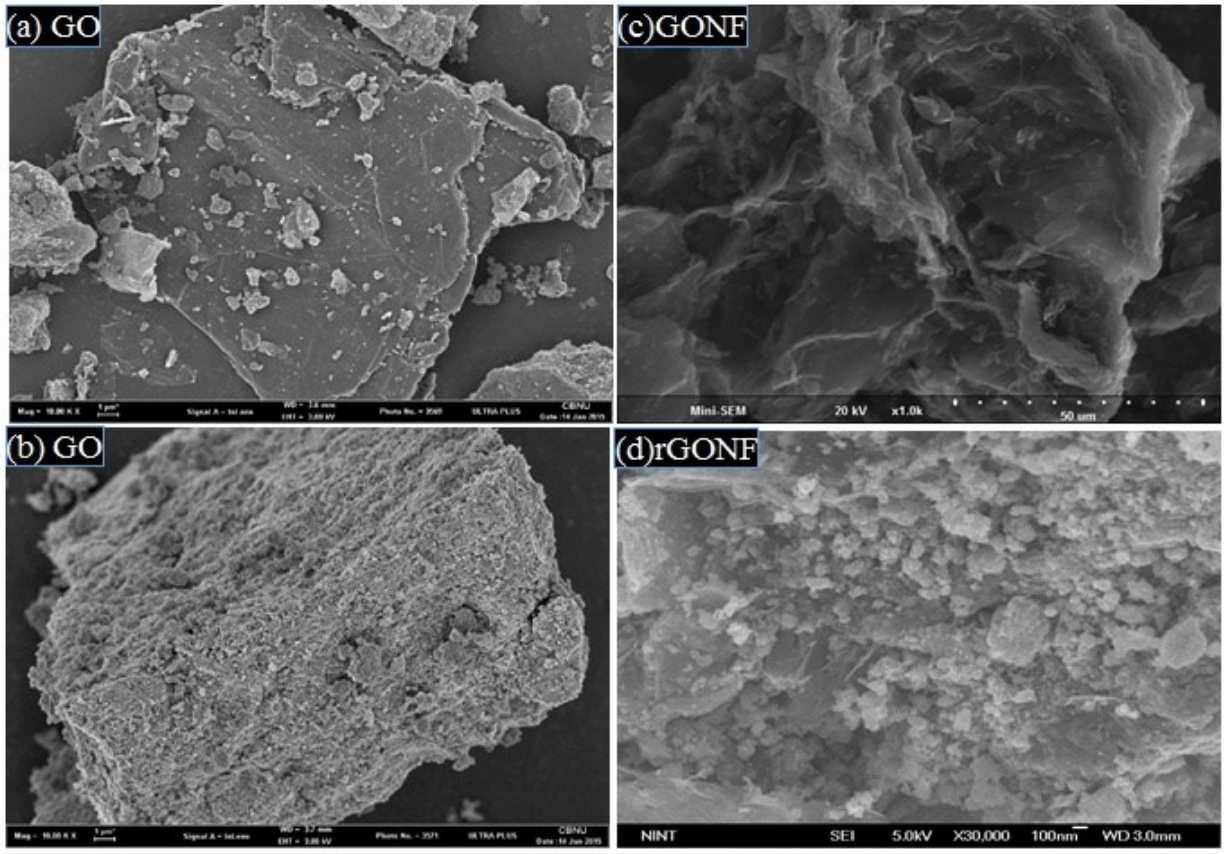

(a) GO
(c)GONF
Mini-SEM 20 kV x1.0k 50 um
(b) GO
(d)rGONF
NINT SEI 5.0kV X30,000 100nm WD 3.0mm

Fig. S2

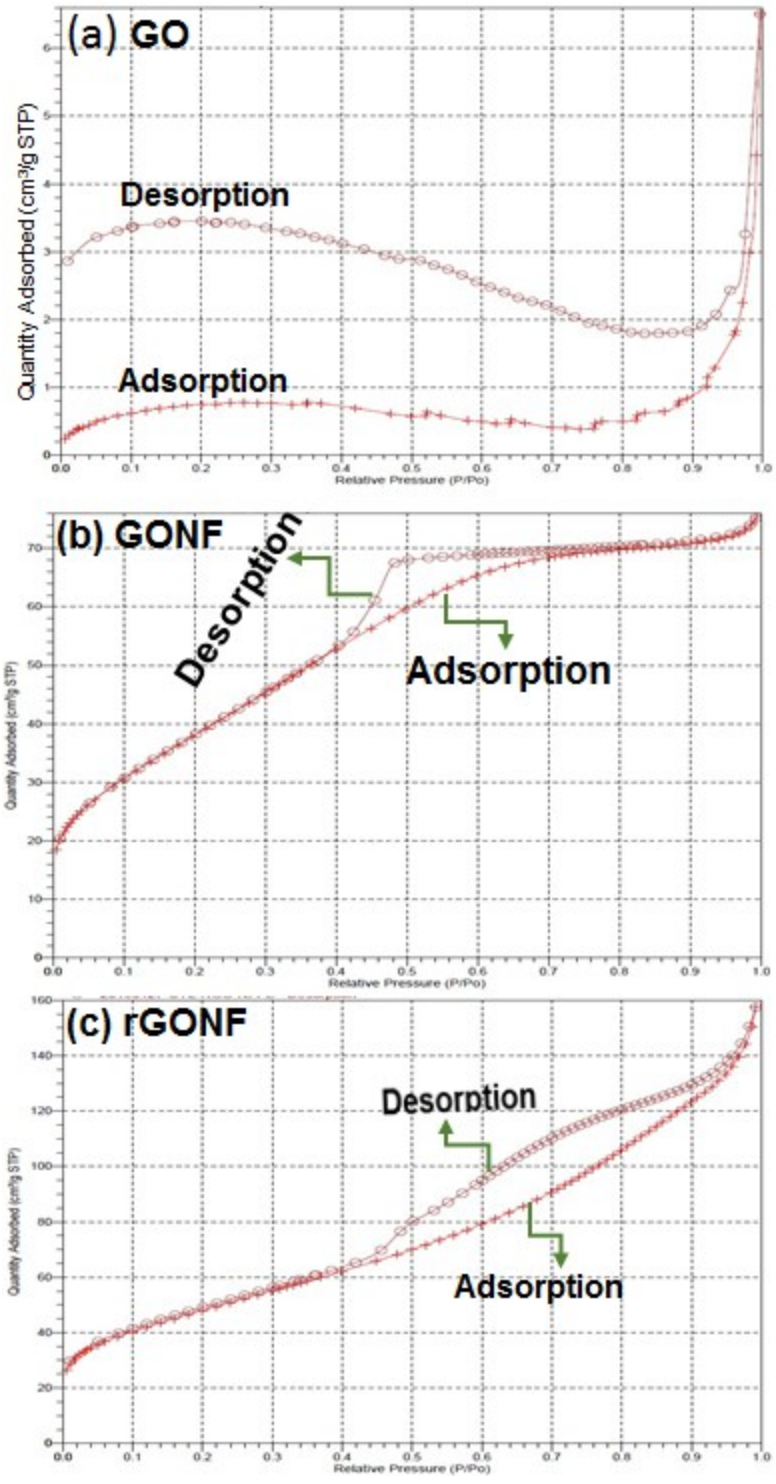
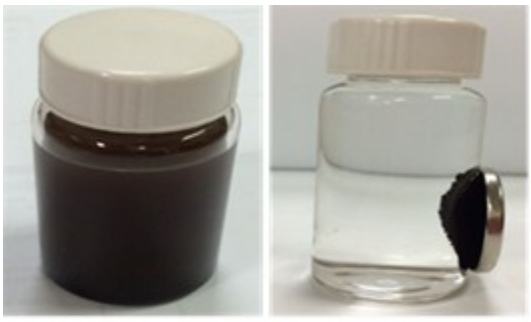

(a) GO
Desorption
Adsorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (P/Po)
(b) GONF
Desorption
Adsorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (P/Po)
(c) rGONF
Desorption
Adsorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (P/Po)

Fig. S3



Before applied external magnetic field

After applied external magnetic field

Fig. S4

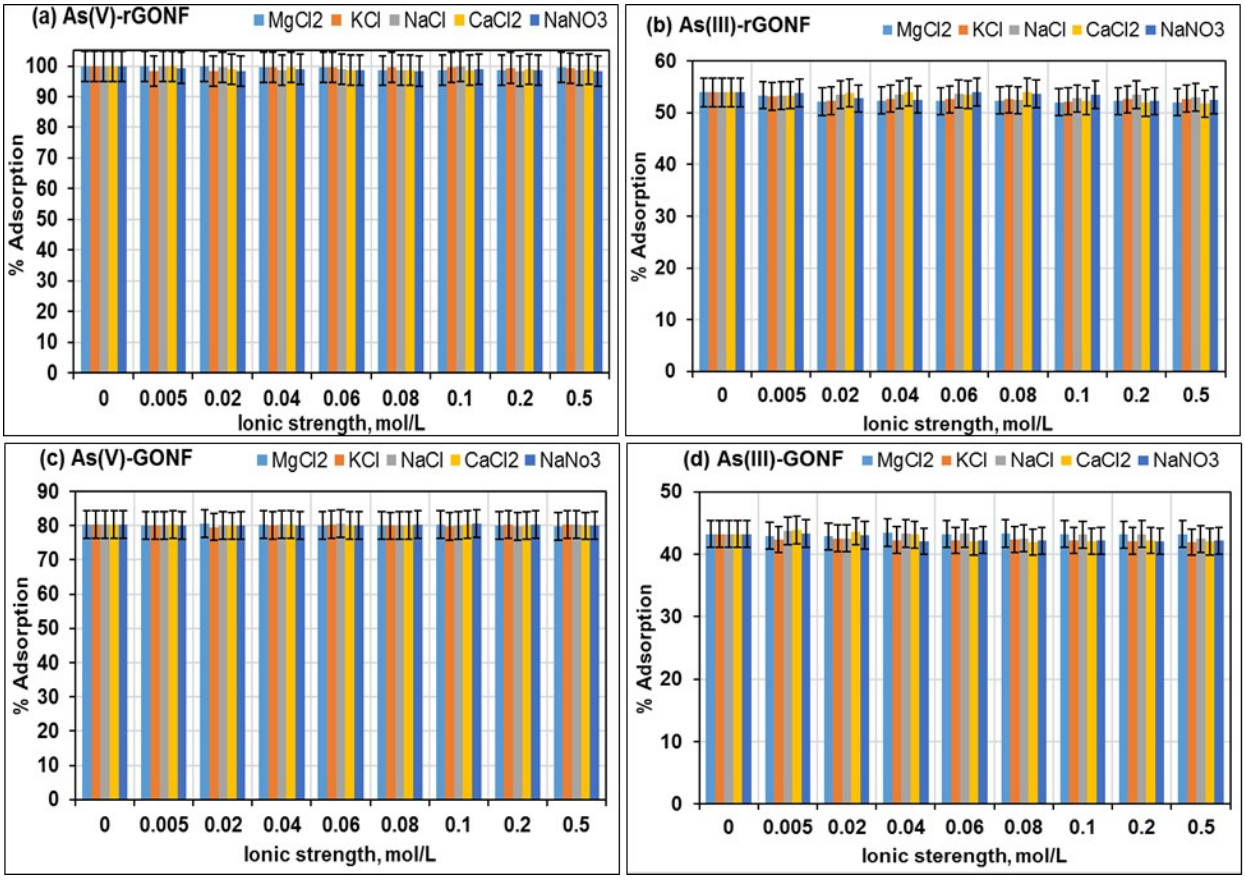


Fig. S5