Magnetically recoverable carbon-coated iron carbide with arsenic adsorptive removal properties

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Abstract

Magnetic particles, generally nanostructured and magnetite-based, have been studied extensively to remove drinking water contaminants. Compositions beyond Fe_3O_4 could address long-standing issues of magnetic recoverability and materials integrity in drinking waters. Herein carbon-coated iron carbide ($\text{Fe}_3\text{C}@\text{C}$) were studied for the first time for their stability, magnetic characteristics, magnetic separability, and arsenic adsorptive properties. Experimental results show that (i) $\text{Fe}_3\text{C}@\text{C}$ with a 9-nm thick graphitic shell is chemically stable in simulated drinking water; (ii) is ferromagnetic with small magnetic remanence and a magnetic saturation that is $\sim 2 \times$ greater than Fe_3O_4 ; (iii) can be separated from water magnetically under continuous-flow conditions with greater than 99% recovery; and (iv) has a surface area-normalized adsorption capacity for arsenic ($6.75 \mu\text{g}/\text{m}^2$) of the same order of magnitude as that of Fe_3O_4 ($9.62 \mu\text{g}/\text{m}^2$). $\text{Fe}_3\text{C}@\text{C}$ can be a viable alternative to Fe_3O_4 with further development, for the magnetic removal of arsenic and other contaminants from drinking water sources.

Graphic abstract A comparative look at the chemical stability, adsorptive prowess, and magnetic capturability of nano-structured carbon-coated iron carbide for arsenic removal from simulated drinking water.

Keywords Environmental nanotechnology · Adsorption · Nano-magnetism · Arsenic

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1 Introduction

Nanocrystalline magnetite is one of the most commonly studied magnetic engineered nanomaterial (ENM) for water treatment [1] due to: (1) its ability to be easily removed from the reaction medium via magnet capture [2], (2) its ability to remove a host of contaminants ranging from heavy metals to organic compounds [2–7], and (3) the relatively low toxicity concern of iron [1, 8]. Nanocrystalline Fe_3O_4 is commercially available, easy to synthesize, and has size dependent magnetic properties such as superparamagnetism which emerges for single crystalline particle sizes < 50 nm, enabling its recovery and reuse. Such advantages have led to pilot-scale testing, for example, layered double hydroxides (LDH)/silica/magnetite and lanthanum-based magnetite ENMs for phosphorous removal from wastewater streams [9, 10] and uncoated magnetite ENMs for treating arsenic contaminated ground water wells in Mexico [11]. Even more so, literature is replete with studies that catalog the use of iron-based nanoparticles for the removal of organic contaminants, heavy metals (i.e., Zn(II), Cu(II), Pb(II), Cr(III)), and anions (i.e., nitrates, arsenates, etc.) [12, 13]. However, there are still barriers (i.e., selectivity, regeneration, capturability, and stability) that prevent magnetic ENM treatment from being implemented in large-scale water treatment applications [9, 14]. Most studies surrounding magnetic ENMs for wastewater applications do not address leaching and lower performance issues that could occur when testing in drinking waters [1, 8, 15, 16].

A major hurdle to using iron oxides in drinking water treatment schemes is that iron-based nanoparticles have limited chemical stability in water [7, 17]. Specifically, for Fe_3O_4 , the surface Fe^{2+} sites of Fe_3O_4 slowly oxidize, which lowers their magnetic saturation [3, 18]. Under acidic conditions, the Fe^{3+} readily leaches into solution [19–22]. To combat these issues, protective coatings are used to increase material stability, but the resulting core–shell structure has lower magnetic strength [23]. A greater magnetic field strength or gradient would be needed for complete recovery, as the attractive magnetic force is dependent in part on the material's magnetization [24–28].

It is notable that most reported nanocrystalline Fe_3O_4 -based adsorbents have non-zero magnetic remanence and coercivity values, and are therefore not technically superparamagnetic [29–31]. However, their magnetic remanence and coercivity values are sufficiently small to allow for aggregation/disaggregation in the presence/absence of a magnetic field. Such materials may be suitable for water treatment scenarios in which partially magnetized particle aggregates can be tolerated.

Alternative iron compositions could improve the magnetic recovery and stability issues of iron oxide-based magnetic ENMs in water treatment. One such material is carbon-coated iron carbide (" $\text{Fe}_3\text{C}@C$ "). Containing 6.7 wt% carbon and 93.3 wt% iron [32], Fe_3C has been studied as a nonprecious metal catalyst for oxygen reduction reactions in neutral and alkaline solutions; it dissolves under acidic conditions though [33, 34]. Fe_3C has a higher magnetic strength than bulk Fe_3O_4 (e.g., ~ 140 emu/g [35] vs. 92 emu/g [30]) and retains its magnetic strength when crystal domain sizes are reduced to the nanoscale [11, 33, 34, 36]. Synthesized through gas-phase pyrolysis or flame spray techniques, nano-sized $\text{Fe}_3\text{C}@C$ carries a graphitic coating that protects the Fe_3C surface from oxidizing. $\text{Fe}_3\text{C}@C$ has magnetic remanence and coercivity values somewhat similar with those of "superparamagnetic" Fe_3O_4 nanoparticles found in literature [29, 31]. A variety of magnetic carbon-based adsorbents such as graphene oxide nickel ferrite, multiwalled carbon nanotubes/iron-oxide composites, magnetic biochar, and carbon encapsulated maghemite/magnetite, etc., are used for arsenic and heavy metal adsorption due to their facile magnetic recovery and the adsorptive prowess of carbon [13, 37–49]. However, none—to the authors knowledge—have studied $\text{Fe}_3\text{C}@C$ for arsenic removal in simulated drinking water.

There are no studies that assess the arsenic removal properties of $\text{Fe}_3\text{C}@C$. Arsenic removal from drinking water sources remains to be an issue of concern [15, 16, 50, 51]. Large rural populations around the world that use private wells as their main source of drinking water, continue to be exposed to arsenic levels above the WHO provisional guideline for arsenic (i.e., 10 $\mu\text{g/L}$) with arsenic levels ranging between 10–50 $\mu\text{g/L}$ [52, 53]. In this work, we evaluate the arsenic adsorptive properties and chemical stability of $\text{Fe}_3\text{C}@C$ in deionized water and simulated drinking water along with its magnetic recovery under flowing conditions. We subjected a commercially sourced $\text{Fe}_3\text{C}@C$ to stability batch tests under mild and aggressive conditions (i.e., 60 °C and pH 3), monitoring for dissolved iron. We quantified its adsorption isotherms for arsenic and studied its magnetic separation from water using an in-house permanent-magnet capture device. We used four common iron-based nanopowders (nanocrystalline materials in powdered form) for comparison: commercially available Fe_3O_4 , commercially available Fe_3O_4 with a SiO_2 coating, as-synthesized Fe_3O_4 , and as-synthesized $\alpha\text{-Fe}_2\text{O}_3$ nanopowder. Our analyses show that $\text{Fe}_3\text{C}@C$ (i) is chemically and magnetically stable in simulated drinking water; (ii) has surface-area-normalized adsorption capacity for arsenic comparable to commercially used iron oxide hydroxide adsorbent Bayoxide E33; and (iii) can be effectively removed from flowing water using a permanent magnet.

2 Materials and methods

2.1 Materials

All iron-based materials studied were nanopowders, *i.e.*, in powdered form and containing XRD-detectible nanocrystalline domains. Carbon coated iron carbide nanopowder ("Fe₃C@C"; prepared through a high-temperature plasma chemical vapor deposition process) from Nanostructured & Amorphous Materials Inc. and commercial Fe₃O₄ nanopowder ("c-Fe₃O₄") from Sigma Aldrich were used for the stability, magnetic recovery, and adsorption experiments (Table S1). As-received iron oxide hydroxide goethite granules (Bayoxide E33; CAS #51274-00-1; from Lanxess) were crushed and used for the adsorption studies. The silica coating for "c-Fe₃O₄@SiO₂" was performed using HCl (35 vol%), and tetraethyl orthosilicate (TEOS) obtained from Sigma Aldrich and used as-received. For the synthesis of s-Fe₃O₄ and α-Fe₂O₃, ACS grade FeCl₂·4H₂O, FeCl₃·6H₂O, Fe(NO₃)₃ and FeCl₃ purchased from Sigma Aldrich were used.

Simulated drinking water was prepared with the following ACS-grade chemicals (Sigma Aldrich): NaHCO₃, CaCl₂, MgSO₄·7H₂O, Na₂SiO₂·9H₂O, NaNO₃, NaH₂PO₄·H₂O, and NaF (fluoride standard solution from Ricca Chemical). A single sodium arsenate standard (Na₃AsO₄ in the form of an Atomic Adsorption Spectroscopy Arsenic Standard from Sigma Aldrich; 1000 mg/L As in 2% nitric acid prepared with high purity As₂O₃, HNO₃, NaOH, and H₂O) was used.

For the NEMI 3500 Fe-B iron detection method, HCl (35 vol%), hydroxylamine, ammonium acetate, acetic acid, and 1,10-phenanthroline monohydrate were obtained from Sigma Aldrich and used as-received.

2.2 Synthesis of c-Fe₃O₄@SiO₂ nanopowders

The c-Fe₃O₄@SiO₂ nanopowder was prepared as follows: 1 g of c-Fe₃O₄ nanopowder was placed in 0.1 M HCl aqueous solution (50 mL) and ultrasonicated for 10 min, magnetically separated and washed three times with DI water, and then dispersed in a solution of ethanol (80 mL), DI water (20 mL) and concentrated ammonia (1.0 mL, 28 wt% aqueous solution). The 0.1 M HCl is to clean off the surface of the c-Fe₃O₄ nanoparticles from any pre-existing impurities from the manufacture in order to prepare them for functionalization [54]. TEOS (0.9 g, 4.32 mmol) was added immediately afterwards. The resulting mixture was stirred at room temperature for 12 h, and the resulting solid product was magnetically collected, washed with ethanol and water three times, and dispersed in ethanol.

2.3 Synthesis of s-Fe₃O₄ and α-Fe₂O₃ nanopowders

Fe₃O₄ nanopowder was synthesized by dissolving 1.4 g of FeCl₂·4H₂O and 2.7 g of FeCl₃·6H₂O in 100 mL of DI water. The resulting solution was heated to 80 °C. Ammonium hydroxide (25 wt%) was added dropwise until the nanopowder precipitated out of solution. After being separated from the solution with a neodymium magnet, the nanopowder was washed with DI water and ethanol and dried overnight under vacuum at 80 °C (synthesized Fe₃O₄ or "s-Fe₃O₄"). The α-Fe₂O₃ nanopowder was synthesized from Fe(NO₃)₃ and FeCl₃ through forced hydrolysis, as described in an earlier report [55].

2.4 X-ray diffraction

Each nanopowder was analyzed by powder x-ray diffraction (XRD) using a Rigaku diffractometer with Cu Kα radiation (1.5418 Å). The data was collected from 3° to 90°. The average crystallite size of each nanopowder was calculated using Scherrer's formula [56].

2.5 X-ray photoelectron spectroscopy

The atomic ratio of the Fe₃C@C nanopowder was obtained from x-ray photoelectron spectroscopy (XPS) performed using a PHI Quantera SXM with an Al source (focused beam of 1.5 kV, 25 W). The pass energy of the survey spectra was 140 eV with step size of 0.5 eV, while the one of atomic spectra was 26 eV with step size of 0.1 eV. Each sample was dried and loaded to Al foil. XPS spectra was analyzed with MultiPak software. All peak positions were corrected based on C 1s at 284.8 eV.

2.6 Nitrogen physisorption analysis

The specific surface area of the nanopowders and the Bayoxide E33 powder was determined by first degassing each sample at 250 °C under vacuum overnight. Once degassed, nitrogen adsorption–desorption isotherms were collected at 77 K using a QuantaChrome (Model #AS3B) instrument. The specific surface area for each nanopowder was calculated with a standard five-point BET analysis method ($P/P_0 = 0.10, 0.15, 0.20, 0.25, \text{ and } 0.30$). The pore size distribution and pore volume of the Fe₃C@C nanopowder were determined from the adsorption branch of the nitrogen isotherms using the non-localized density functional theory (NLDFT) model [57].

2.7 Magnetic measurements

Magnetic characterization was conducted with the Superconducting Quantum Interference Device (SQUID) fitted

with a MPMS XL (Quantum Design Inc.). For each hysteresis curve generated, the nanopowder was weighed, wrapped in Teflon tape, and analyzed at 27 °C from – 10 to 10 kOe.

Magnetic stability measurements were performed using 15 mg of c-Fe₃O₄ and 15 mg of Fe₃C@C placed into 15 mL of a solution of simulated drinking water. The resulting dispersions were then sonicated for 10 min and placed on a shake table for 4 weeks at 25 °C. Periodically, liquid aliquots were taken from the suspension and dried on Teflon tape under vacuum at 40 °C. The resulting dried nanopowders were weighed, wrapped in Teflon, and measured from – 10 to 10 kOe at 27 °C.

2.8 Simulated drinking water preparation

Simulated drinking water was prepared in accordance with the NSF 53 [58] challenge water by using the following salt concentrations: NaHCO₃ (252 mg/L), CaCl₂ (147 mg/L), MgSO₄·7H₂O (124 mg/L), Na₂SiO₃·9H₂O (95 mg/L), NaNO₃ (12 mg/L), NaF (2.2 mg/L), and NaH₂PO₄·H₂O (0.18 mg/L). The solution was adjusted to pH 7.5 using HCl (1.0 M). The resulting ionic strength and total dissolved solids (TDS) values were 8.5 mM and 478 mg/L, respectively.

2.9 Stability batch tests

The stability of the magnetic materials was assessed in simulated drinking water at 25 °C and neutral pH (~ 7.5), and also at an elevated temperature (60 °C) and neutral and low pH values (~ 7.5 and ~ 3) to accelerate any potential iron leaching. We chose the elevated temperature of 60 °C, which was the temperature used by Sidhu et al. in their study of dissolution of iron oxides at low pH values [59]. The amount of dissolved iron for the stability tests was quantified with a Perkins Elmer Optima 8300 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) and, separately, a colorimetric procedure adapted from the National Environmental Methods Index (NEMI). For ease of sample preparation and UV-vis photometric measurements, we primarily used the NEMI 3500 Fe-B (phenanthroline) method [52]. The pH of the bulk solution was adjusted to a desired pH (~ 7.5 or ~ 3) with dropwise additions of HCl solution (1.0 M), and the resulting solution was used immediately. An appropriate amount of water was combined with the desired nanopowder such that the final weight concentration of each nanopowder suspension was 500 mg/L.

After sonication for 10 min, 2-mL aliquots were taken from each sample, filtered with a 0.2-μm PTFE syringe filter, and stored in 2-mL microcentrifuge tubes. The sonicated solutions were then placed inside a temperature-controlled shake table (60 °C, shaking speed of 150 rpm)

for 24 h. The suspension pH did not change during the 24-h period.

Liquid aliquots (2 mL) were extracted from each sample and filtered with a 0.2-μm PTFE syringe filter. All samples were then analyzed for dissolved iron concentrations by using adapted procedures from the National Environmental Methods Index (NEMI). Specifically, the NEMI 3500 Fe-B (phenanthroline) method, which is well suited for field tests, was used [60]. For each sample, 1 mL was removed and combined with a solution containing HCl (40 μL; 38 wt% conc. aqueous solution), hydroxylamine (20 μL, 22.14 mM), ammonium acetate buffer (200 μL, 587 mM), and phenanthroline solution (80 μL, 0.31 mM). The resulting solution (final pH of ~ 3.3) was vigorously agitated and then allowed to sit for 30 min before being analyzed with UV-vis spectroscopy at 510 nm (Shimadzu UV-2450 UV-Spectrophotometer).

2.9.1 Arsenic adsorption experiments

Batch arsenic equilibrium adsorption experiments were conducted in simulated drinking water at 25 °C. The initial pH value of the solution was set to ~ 7.5 and the initial concentration of arsenate was set to ~ 50 μg-As(V)/L. Fe₃C@C, c-Fe₃O₄, and Bayoxide E33 were used as the adsorbent media. The adsorbent dosages ranged from 4 to 400 mg/L. Experiments were conducted in LDPE wide-mouth bottles, and the samples were continuously agitated for ~ 3 days to ensure equilibrium. When collecting samples (2 mL) for analysis, the adsorbent was removed from the suspension via a 0.2-μm Nylon syringe filter. The equilibrium water-phase concentration of arsenic was quantified using a tuned Thermo Scientific X-Series II Inductively Coupled Plasma Mass Spectrometer (ICP-MS) [52].

Adsorption data was fitted to linearized forms of the Freundlich (Eq. 1) and Langmuir (Eq. 2) isotherm models using the following equations:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (1)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \quad (2)$$

where q_e is the adsorption capacity (units of μg-adsorbate/g-adsorbent), K_f is the Freundlich adsorption capacity parameter (units of μg-adsorbate/g-adsorbent)(mg-adsorbate/L)^{1/n}, C_e is the equilibrium concentration of the contaminant (units of μg-adsorbate/L), n is the Freundlich affinity of adsorption parameter, b is the adsorption equilibrium constant (units of L/μg-adsorbate), and q_m is the maximum adsorption capacity (units of μg-adsorbate/g-adsorbent) as determined by the Langmuir isotherm

fitting [61]. The “Freundlich derived” maximum adsorption capacity, q_{e-max} , was determined using the largest measured adsorption capacity value taken from the Freundlich isotherm fitting.

2.9.2 Magnetic column separation experiments

Our benchtop magnetic capture unit was set up like a conventional high gradient magnetic separator (HGMS), permanent magnets were used instead of electromagnets [26, 62, 63]. A column packed with magnetically susceptible wires (e.g., stainless steel wool, SSW) causes an applied magnetic field to dehomogenize, producing large field gradients (regions where the magnetic field is no longer uniform) around the wires to attract magnetic particles to their surface. The strong magnetic forces produced by the large field gradients at the SSW wire surface are extremely effective at capturing fine particles (< 100 microns) of weakly magnetic substances [64].

Our bench-top magnetic capture unit consisted of a cylindrical quartz column with an internal radius of 0.330 cm and a length of 12 cm (a total volume of 4.11 cm³) (Fig. 1). The 5-cm bed length was filled with SSW (wire diameter of 50 μ m, 550 mg, grade 434 stainless steel), such that the bed density was 321.6 mg-SSW/cm³ (void fraction = 0.96). The column was placed in a 2-cm gap between two permanent magnets housed within a rectangular steel frame. The total magnetic field strength produced was estimated to be within the range of 1.5–2.0 T (15–20 kOe).

A nanopowder suspension (50 mL) was pumped through the column at a desired flow rate (1, 3, 5, or 7 mL/

min) using a KD Scientific Syringe Pump System (Model number: 100, Series number: 4377). The empty bed contact time ($\text{volume}_{\text{EmptyBed}} \div \text{flow rate}$) for each flow rate was 1.71 min, 0.57 min, 0.34 min, and 0.24 min, respectively. The respective residence times ($\text{volume}_{\text{EmptyBed}} \times (\text{void fraction}) \div \text{flow rate}$) were 1.64 min, 0.55 min, 0.33 min, and 0.23 min. A high inlet suspension concentration of 500 mg/L (362, 467, and 350 mg/L-Fe for c-Fe₃O₄, Fe₃C@C, and α -Fe₂O₃, respectively) was chosen to test the robustness of the magnetic capture unit. Collected periodically, the dissolved iron concentration in the effluent samples were analyzed with the NEMI Fe 3500-B method (Fig. S1).

3 Results and discussion

3.1 Nanopowder characterization

Figure 2 shows the x-ray diffraction (XRD) patterns for the nanopowders. The c-Fe₃O₄, c-Fe₃O₄@SiO₂, and s-Fe₃O₄ materials were verified to have the magnetite Fe₃O₄ crystalline phase [65], with the s-Fe₃O₄ having a smaller grain size (Table 1). The silica content of c-Fe₃O₄@SiO₂ estimated to be ~21 wt%, based on molar ratios, indicating a thickness of ~2 nm as detected through TEM (Fig. S2). The α -Fe₂O₃ sample was verified to be the α phase of Fe₂O₃ (hematite) [66].

The Fe₃C@C nanopowder has the cementite crystalline phase [34]. From x-ray photoelectron spectroscopy (XPS) analysis, the C:Fe atomic ratio of Fe₃C@C is 2.08:1, which is higher than the C:Fe atomic ratio for Fe₃C (1:3) due to the carbon coating. The coating accounts for ~14 wt% of the Fe₃C@C material, suggesting ~26 monolayers of graphene (a single sheet is 0.34 nm thick) [57]. This closely matches the carbon coating thickness (~9 nm) as detected through TEM (Fig. S3). As measured, Fe₃C@C has a specific surface area (SSA) of 24.9 m²/g and (Table 2). In comparison, c-Fe₃O₄ displayed superparamagnetic-like behavior, with its low magnetic remanence (M_r) and coercivity (H_c) values (Fig. 3, Table 1) [67, 68]. The magnetic saturation (M_s) of c-Fe₃O₄ and c-Fe₃O₄@SiO₂ were 77.1 emu/g and 54.4 emu/g, respectively.

Even after normalizing to only the Fe₃O₄ content (77.1 emu/g-Fe₃O₄ and 68.9 emu/g-Fe₃O₄), the magnetic saturation was lower after coating, which is possibly due to surface spin disorder caused by the silica shell and the interactions between the non-magnetic SiO₂ atoms and the magnetic c-Fe₃O₄ atoms [65, 69, 70]. In addition, the c-Fe₃O₄@SiO₂ had greater magnetic remanence and coercivity values than c-Fe₃O₄, due to the presence of its SiO₂ shell [71]. The s-Fe₃O₄ had a similar magnetic saturation to that of the c-Fe₃O₄, but had lower magnetic remanence and coercivity values. Fe₃C@C had the

Fig. 1 The bench top magnetic capture unit with the quartz column (containing the stainless-steel wool, SSW) shown above and outside the two magnetic faces. Inset: Close-up of the SSW packing

Fig. 2 XRD patterns for $\text{Fe}_3\text{C}@C$ (green), $c\text{-Fe}_3\text{O}_4$ (blue), $c\text{-Fe}_3\text{O}_4@\text{SiO}_2$ (orange), $s\text{-Fe}_3\text{O}_4$ (red), and $\alpha\text{-Fe}_2\text{O}_3$ (gray) nanopowders

Table 1 Structural and magnetic properties of tested nanopowders

Nanopowders	d_{XRD} (nm)	SSA (m^2/g)	M_s (emu/g)	M_r (emu/g)	M_r/M_s	H_c (Oe)
$\text{Fe}_3\text{C}@C^a$	11	24.9	138.2	20.6	0.161	200
$c\text{-Fe}_3\text{O}_4^b$	22	44.2	77.1	8.06	0.105	80
$c\text{-Fe}_3\text{O}_4@\text{SiO}_2^b$	22	15.5	54.4	9.00	0.165	160
$s\text{-Fe}_3\text{O}_4^b$	11	54.5	70.0	1.08	0.015	4
$\alpha\text{-Fe}_2\text{O}_3^c$	32	55.4	n/d	0.196	n/d	2.75

^aFerromagnetic [30]

^bFerrimagnetic [30]

^cAntiferromagnetic [30]

Table 2 Leaching experiments in simulated drinking water

Nanopowders	25 °C (or 60 °C) and pH 7.5		60 °C and pH 3	
	[Fe] (mg/L) Time = 0 day	[Fe] (mg/L) Time = 1 day	[Fe] (mg/L) Time = 0 days	[Fe] (mg/L) Time = 1 day
$\text{Fe}_3\text{C}@C$	BD	BD	7.89 ± 1.4	9.34 ± 0.04
$c\text{-Fe}_3\text{O}_4$	BD	BD	BD	0.69 ± 0.09
$c\text{-Fe}_3\text{O}_4@\text{SiO}_2$	BD	BD	BD	BD
$s\text{-Fe}_3\text{O}_4$	BD	BD	0.24 ± 0.03	0.82 ± 0.06
$\alpha\text{-Fe}_2\text{O}_3$	BD	BD	BD	BD

BD denotes below the detection level of the calibration curve from the NEMI 3500 Fe-B method (i.e. 0.1 mg/L)

highest magnetic saturation of all the iron-based nanopowders analyzed, with a measured magnetic saturation value of 138.2 emu/g, slightly lower than the value for bulk

Fe_3C ($M_s \sim 140$ emu/g) [35] and 80% higher than that for $c\text{-Fe}_3\text{O}_4$. $\text{Fe}_3\text{C}@C$ has a higher M_s than $c\text{-Fe}_3\text{O}_4$ because it has more iron and less oxygen; a materials magnetic

Fig. 3 Magnetization curves for $\text{Fe}_3\text{C}@\text{C}$ (green), $\text{c-Fe}_3\text{O}_4$ (blue), $\text{c-Fe}_3\text{O}_4@\text{SiO}_2$ (orange), $\text{s-Fe}_3\text{O}_4$ (red), and $\alpha\text{-Fe}_2\text{O}_3$ (gray) nanopowders, at 27°C from -10 kOe to 10 kOe. Inset top left: zoomed-in view of the magnetization curve for the $\text{Fe}_3\text{C}@\text{C}$ nanopowders with the

magnetic remanence (M_r) and coercivity (H_c) labeled. Inset bottom right: Magnetization curve for $\alpha\text{-Fe}_2\text{O}_3$ at 27°C from -50 kOe to 50 kOe

saturation capacity is dependent upon the individual atoms that comprise the material and the arrangement of those atoms. Fe_3C contains mostly iron (93.3 wt% iron) whereas ~ 72 wt% of Fe_3O_4 is iron. Oxygen has a lower magnetic moment (i.e., a single oxygen molecule has a magnetic moment of 2.85 bohr magnetons) than iron (i.e., 5.92 bohr magnetons).

The ratio of magnetic remanence to magnetic saturation (M_r/M_s) indicates the extent of ferromagnetism. $\text{s-Fe}_3\text{O}_4$ can be considered less ferromagnetic (or more superparamagnetic, $M_r/M_s = 0.015$) than $\text{c-Fe}_3\text{O}_4$ ($M_r/M_s = 0.105$), consistent with its smaller grain size [29]. To contrast, $\alpha\text{-Fe}_2\text{O}_3$ is antiferromagnetic [30] and did not reach magnetic saturation within the magnetic field range of -50 kOe to 50 kOe (Fig. 3, inset). Being technically a ferromagnetic material, $\text{Fe}_3\text{C}@\text{C}$ can be considered to have superparamagnetic-like property ($M_r/M_s = 0.161$) as $\text{c-Fe}_3\text{O}_4@\text{SiO}_2$ ($M_r/M_s = 0.165$).

Within error (± 9.59 emu/g), the $\text{c-Fe}_3\text{O}_4$ and the $\text{Fe}_3\text{C}@\text{C}$ nanopowders were magnetically unchanged after one month of being immersed in simulated drinking water (pH ~ 8.5) and DI water (pH ~ 6.5) at room temperature, indicating structural stability and a lack of iron leaching (Tables S1–S2).

3.2 Iron leaching behavior in simulated drinking water

For all nanopowders tested at room temperature in simulated drinking water, the amount of dissolved iron found after the 24-h testing window was below the ICP-OES detection limit (< 0.1 mg/L) (Table 2). Dissolved iron was also not detected when the samples were subjected to testing at 60°C (Table 2).

Under the more aggressive acidic water condition for accelerated testing, $\text{c-Fe}_3\text{O}_4$ and $\text{s-Fe}_3\text{O}_4$ both leached significantly due to low-pH dissolution ($\text{FeOOH} + 3\text{HCl} \rightarrow \text{FeCl}_2^{2+} + 2\text{Cl}^- + 2\text{H}_2\text{O}$). Dissolved iron levels reached 0.69 mg/L and 0.82 mg/L, respectively (Table 2) [72]. $\alpha\text{-Fe}_2\text{O}_3$ also leached, but the extent of iron leaching was considerably less; of all iron oxides, hematite is the most stable [59]. Dissolved iron concentrations were monitored at the beginning of the leaching experiments (i.e., immediately after the nanopowders were added to the room temperature solution) also. Roughly 30% of the total amount of leached iron from $\text{s-Fe}_3\text{O}_4$ was released initially. Coating $\text{c-Fe}_3\text{O}_4$ with SiO_2 is well noted in literature to reduce and even prevent leaching

[73]. Over the 24-h period, no leaching was detected for $c\text{-Fe}_3\text{O}_4\text{@SiO}_2$ (Table 2).

It was hypothesized that $\text{Fe}_3\text{C@C}$ would behave similarly to $c\text{-Fe}_3\text{O}_4\text{@SiO}_2$ since both have a protective coating. However, $\text{Fe}_3\text{C@C}$ leached significantly at pH 3 after 24 h (Table 2). It leached significantly at the beginning of the leaching experiment also, releasing > 80% of the total dissolved iron. While the protective carbon coating of the $\text{Fe}_3\text{C@C}$ fully covers the Fe_3C core, the leaching might be attributable to its detected porosity (PSD of ~ 40 nm and $\text{PV} \sim 0.04 \text{ cm}^3/\text{g}$ from N_2 adsorption measurements), which would allow the acid to reach the Fe_3C core.

3.3 Arsenic adsorption experiments

Arsenic equilibrium adsorption data for $\text{Fe}_3\text{C@C}$ and $c\text{-Fe}_3\text{O}_4$ were fit to the Freundlich isotherm model (Fig. 4, Table 3) and the Langmuir isotherm model (Fig. S5, Table S3). In literature, activated carbon and graphene-based materials have been shown to remove arsenic, although the process and optimal conditions for arsenic

adsorption remain unclear [74–76]. In our studies, $\text{Fe}_3\text{C@C}$ shows slight adsorption aversion for the negatively charged arsenate species (i.e., H_2AsO_4^- and HAsO_4^{2-}) common in groundwaters – as indicated by its Freundlich adsorption affinity parameter ($1/n = 1.13$) being greater than 1. Surface chemistry is critical in arsenic removal by metal oxide species with electrostatic attraction between the anionic arsenic species being favored on positive surfaces. The pH of zero point of charge or the isoelectric point can be an indicator of the removal of anionic arsenic species [52]. Given the negatively charged carbon surface of $\text{Fe}_3\text{C@C}$ at $\text{pH} \sim 7.5$, the anionic arsenate species would be averse to adsorbing onto its surface (Fig. S4; isoelectric point (IEP) of $\text{Fe}_3\text{C@C} \sim 4.2$). Despite this aversion between the negatively charged carbon surface and the anionic arsenate species, an appreciable arsenic adsorption capacity emerges for $\text{Fe}_3\text{C@C}$. Much like in other porous materials (i.e., iron, aluminum, titanium, zirconia, etc.), the anionic arsenate species diffuses through the porous carbon coating of $\text{Fe}_3\text{C@C}$ (porosity: PSD of ~ 40 nm and $\text{PV} \sim 0.04 \text{ cm}^3/\text{g}$) and adsorbs onto the positively charged (i.e., IEP ~ 10) iron-carbide core [77].

$\text{Fe}_3\text{C@C}$ was benchmarked against $c\text{-Fe}_3\text{O}_4$. $c\text{-Fe}_3\text{O}_4$ adsorbed $1.4 \times$ more arsenic by mass than $\text{Fe}_3\text{C@C}$ at an equilibrium concentration C_e of 20 $\mu\text{g}/\text{L}$, and $\sim 2 \times$ more arsenic at $C_e \sim 40 \mu\text{g}/\text{L}$. When normalized to surface area, the maximum arsenic adsorption capacity of $\text{Fe}_3\text{C@C}$ was $\sim 70\%$ of $c\text{-Fe}_3\text{O}_4$ [11] ($q_{e\text{-max-SSA}} = 9.62$ vs. $6.75 \mu\text{g}/\text{m}^2$, respectively), which was less due to differences in arsenic affinity. As a nonmagnetic comparison material and as a commonly used As adsorbent, Bayoxide E33 adsorbed $\sim 9 \times$ more arsenic on a mass basis than $\text{Fe}_3\text{C@C}$ at an equilibrium arsenic concentration C_e of 20 $\mu\text{g}/\text{L}$ and $\sim 5 \times$ more arsenic at $C_e \sim 40 \mu\text{g}/\text{L}$, due to greater arsenic affinity and a $4.8 \times$ higher surface area. When normalized to surface area, the arsenic adsorption capacity of $\text{Fe}_3\text{C@C}$ was closer (88%) to that of Bayoxide E33 ($q_{e\text{-max-SSA}} = 6.75$ vs. $7.67 \text{ mg}/\text{m}^2$, respectively).

We gained limited insights by fitting the equilibrium adsorption data to a Langmuir model. Fitted values for the Langmuir constant and the maximum sorption capacity were negative for $\text{Fe}_3\text{C@C}$, indicating that the

Fig. 4 Freundlich isotherm fittings for arsenic equilibrium adsorption within simulated drinking water after a contact time of 3 days for Bayoxide E33 (purple), $\text{Fe}_3\text{C@C}$ (green), and $c\text{-Fe}_3\text{O}_4$ (blue) at a pH of ~ 7.5. Initial As concentration ($C_{0\text{-As}}$) ~ 50 $\mu\text{g}/\text{L}$. Adsorbent dosage range for Bayoxide E33, $\text{Fe}_3\text{C@C}$, and $c\text{-Fe}_3\text{O}_4$: 4 mg/L to 400 mg/L. Note: no iron leaching was detected for any of the adsorbents via ICP-MS

Table 3 Freundlich parameters for arsenic adsorption

Adsorbent	K_f : Freundlich Adsorption Capacity Parameter ($\mu\text{g}/\text{g}$) ($\mu\text{g}/\text{L}$) ^{-1/n}	Specific Surface Area (m^2/g)	1/n: Freundlich Affinity of Adsorption Parameter	$q_{e\text{-max}}$: As Adsorption Capacity ($\mu\text{g}/\text{g}$ of adsorbent)	$q_{e\text{-max-SSA}}$: Normalized As Adsorption ($\mu\text{g}/\text{m}^2$)
E33	32.75	120.0	0.906	920	7.67
$\text{Fe}_3\text{C@C}$	2.095	24.9	1.13	168	6.75
$c\text{-Fe}_3\text{O}_4$	0.491	44.2	1.73	425	9.62

Maximum adsorption capacity ($q_{e\text{-max}}$) measured at $C_e = 50 \mu\text{g}/\text{L}$

Table 4 % Magnetic recovery for Fe₃C@C and c-Fe₃O₄ nanopowders (500 mg/L, 50 mL total volume) in simulated drinking water at pH ~ 7.5. Influent c-Fe₃O₄ and Fe₃C@C nanopowder suspensions were 362 mg/L and 467 mg/L, respectively

Flow rate (mL/min)	Residence time (min)	Total dissolved iron in effluent (Fe ₃ C@C) (mg/L)	Total dissolved iron in effluent (c-Fe ₃ O ₄) (mg/L)
1	1.64	BD	BD
3	0.55	BD	BD
5	0.33	0.13 ± 0.02	BD
7	0.23	BD	BD

BD denotes below the detection level of the calibration curve from the NEMI 3500 Fe-B method (0.1 mg/L)

monolayer adsorption assumption of the model did not apply for arsenic adsorbing onto this nanopowder (Table S3). Multilayer adsorption of arsenic seems to play more of a role in arsenic adsorption onto the surface of Fe₃C@C because of its porous nature [78]. The fitted values for the Langmuir constant and the maximum sorption capacity for c-Fe₃O₄ were negative also. On the other hand, the Langmuir model applied to Bayoxide E33 material; its maximum As adsorption capacity was 5 mg/g (= 41.7 µg/m²) (Table S3, Table 3).

3.4 Magnetic separation flow results

The removability of the Fe₃C@C nanopowder suspended in simulated drinking water was tested at different flow conditions in the bench-top magnetic capture unit. Effluent samples were collected and acidified, and any non-captured nanopowder was quantified using the NEMI 3500-B method. For the Fe₃C@C nanopowder, the total dissolved iron levels in the effluent were below the US EPA secondary maximum contaminant level (SMCL ≤ 0.3 mg/L) at all flow rates tested, and below or near the lower limit of detection (0.1 mg/L) (Table 4, Table S4). The low Fe₃C@C concentrations in the effluent should not raise much toxicity concerns, as the Fe₃C@C composition is being studied for biomedical applications [79]. For the comparison material, c-Fe₃O₄ nanopowder, the total dissolved iron levels were below the SMCL and below detection limit (< 0.1 mg/L). Both magnetic nanopowders were successfully magnetically captured from simulated drinking water regardless of contact time for the tested flow rates below. To explore the applicability of Fe₃C@C for larger water treatment schemes, a magnetic capturing unit that can accommodate larger volumes and higher flow rates of water is being developed.

4 Conclusion

The aim of this work was to quantify the stability, magnetic separation, and arsenic adsorptive properties of nanostructured carbon-coated iron carbide ("Fe₃C@C") in simulated drinking water for the first time to address long-standing issues of magnetic recoverability and material integrity of iron-based adsorbents in drinking water sources. Fe₃C@C is highly magnetic, with a magnetic saturation value that is at least 80% higher than that of Fe₃O₄ nanopowders. It retains its chemical integrity and superparamagnetic-like property in simulated drinking water, and it is completely removable using a permanent magnet flow device (*i.e.*, we were able to achieve a percent removal of > 99% using an in-house magnetic separation column). While it adsorbs arsenic with a surface-area-normalized capacity that is modestly lower compared to Bayoxide E33 goethite (by ~ 12%) and Fe₃O₄ (by ~ 30%), Fe₃C@C is magnetically recoverable (whereas Bayoxide E33 is not). This paper demonstrates the ability of Fe₃C@C to provide a functionalizable carbon surface (that Fe₃O₄ does not have), to remove arsenic and plausibly other contaminants from drinking water sources.

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Author contributions CDP and MSW conceived of the experimental plan. CDP and LMG conducted the methylene blue and arsenic adsorption experiments. CDP conducted the materials characterization and magnetic column separation experiments. CAC analyzed and conducted N₂ adsorption measurements of the Fe₃C@C nanopowder. KV, AWL, and SG synthesized the s-Fe₃O₄ nanopowder, α-Fe₂O₃ nanopowder, and the c-Fe₃O₄@SiO₂ nanopowder respectively. PW developed arsenic adsorption methodology. AJA conducted ICP-MS for the arsenic adsorption experiments. All authors (CDP, SG, LMG, KV, AWL, CAC, AJA, DV, JBZ, PW, MSW) contributed to data analysis and manuscript preparation.

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Compliance with ethical standards

Conflict of interest There are no conflicts to declare.

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