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Superparamagnetic Nalidixic acid grafted Magnetite (Fe₃O₄/NA) for Rapid and Efficient Mercury Removal from Water

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A new nanomaterial, Nalidixic acid grafted magnetite (Fe₃O₄/NA), was synthesized *via* chemical reaction with nano sized magnetite particles. The Fe₃O₄/NA was superparamagnetic at room temperature and could be separated by an external magnetic field. The presence of mercury in groundwater in wide scale industrial areas of the world has been a huge problem and the prepared Fe₃O₄/NA nanoparticles showed high adsorption capacity towards Hg(II) as compared to bare magnetite particles. The high adsorption capacity of NA grafted Fe₃O₄ (9.52 mg g⁻¹) was due to the increased adsorption sites in the magnetite-nalidixic acid (Fe₃O₄/NA). The sorption equilibrium data obeyed the Langmuir model while kinetic studies demonstrated that the sorption process of Hg(II) followed well the pseudo second order model. Since the Fe₃O₄/NA showed (over 99.8%) removal of the initial 1000 ppb Hg(II) within 60 min, it should be practically usable for Hg(II) contaminated water. The desorption of Hg(II) loaded on Fe₃O₄/NA could be successfully achieved with 0.001 M HCl containing 0.3 M thiourea, and the sorbent exhibited excellent reusability.

Introduction

The toxic, heavy metal contamination in water has remained the matter of great environmental concern for the last few years. In the context of toxic metals, mercury is considered to be one of the most poisonous metals, widely found in surface and groundwater.¹ Owing to its high bioaccumulation and biomagnification potential, the presence of minute concentration in water causes severe problems to both aquatic organisms and human beings.³ Exposure of mercury may provoke variety of detrimental health effects of central nervous system, gastrointestinal tract, liver, impairment of pulmonary, kidney function and chest pain.^{4, 5} Many cases of Minamata disease were diagnosed among the general population due to consumption of fish and shellfish in different countries around the world.⁶ Major contamination sources through which mercury enters the water bodies are through wastes from industrial processes such as chloralkali, paper and pulp, nuclear fuel production, mining, electroplating, oil refinery, paint and battery manufacturing, and etc.^{3, 7} As a result of its toxic nature, the US Environmental Protection Agency (US EPA) has prescribed the maximum level of mercury contamination in drinking water at 2 ppb.⁸

The removal of aqueous mercury can be achieved by variety of conventional techniques including coagulation⁷, precipitation⁹, ion

exchange¹⁰, membrane separation¹¹, reduction¹², amalgamation¹³, and adsorption¹⁴. Among these, adsorption is considered to be the most effective and simplest approach due to its low cost, ease of operational setup, and availability of wide range of adsorbents.^{15, 16}

In the recent years, magnetic nanoparticles (MNPs) have been extensively used in water treatment because of their cost-effectiveness, extremely small size, high surface to volume ratio and convenient magnetic field assisted separation¹⁷. However, it has been observed that bare magnetic nanoparticles are highly susceptible to auto oxidation, easily agglomerated and not target selective in various environmental conditions^{18, 19}. These factors can be compensated with help of surface coating using inorganic materials^{20, 21}, polymers^{22, 23}, carbon^{24, 25}, and biomolecules^{26, 27} to show high stability and enhanced sorption capacity.

Active Pharmaceutical Ingredients (APIs), one of major classes of organic compounds, have been investigated as metal extracting agents for radioactive, transition and rare earth metals.²⁸ Among them, Nalidixic acid (NA shown in Fig. 1) was used in fluorometric determination of some lanthanides²⁹, spectrophotometric determination of Fe(III)³⁰, online pre-concentration of Uranium and Scandium on XAD-4 resin^{31, 32}, and liquid-liquid extraction of Eu(III) and Nd(III) in dichloromethane.³³ Remediation of heavy metals *via* NA or magnetite based composites has motivated us to synthesize magnetite-nalidixic acid (Fe₃O₄/NA) nanoparticles for Hg(II) removal.

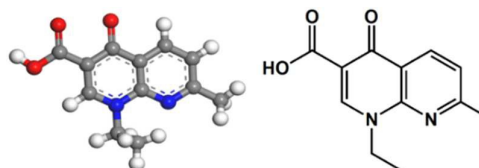


Fig. 1 Chemical structure of nalidixic acid

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Here, we report a synthesis of novel kind of magnetite grafted with NA in situ at low temperature (80 °C). The prepared Fe₃O₄/NA showed nearly complete removal (99.8%) of Hg(II) below 2 ppb in water, as a practical approach for Hg(II) removal from water due to their increased sorption sites in the presence of NA.

Experimental

Materials

The chemicals used in these experiments were of analytical grade and used as received. Nalidixic acid was procured from Sigma Aldrich (98% purity). Stock solutions were prepared by dissolving salts in Milli-Q water.

Preparation of Fe₃O₄/NA

Fe₃O₄/NA was synthesized by chemical co-precipitation method. The procedure is shown schematically in Fig. 2. First 2.85 g of FeCl₃·6H₂O and 1.35 g of FeSO₄·7H₂O were dissolved in 50 ml of Milli-Q water and heated to 80 °C on the hot plate. Afterward, 43 mg of NA solid and 6 mL of ammonium hydroxide (25%) solution were rapidly and sequentially added into the vessel. The mixture was continually stirred at 80 °C for 40 min and then cooled to room temperature. The black Fe₃O₄/NA precipitates were collected by using an external magnet, rinsed several times with Milli-Q water, and dried in a vacuum oven. The control sample of bare Fe₃O₄ MNPs was also prepared in a similar way without NA addition.

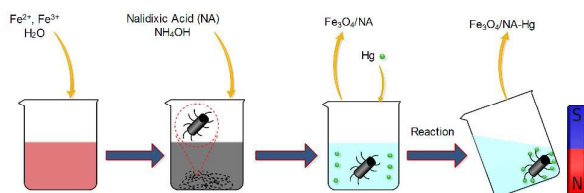


Fig. 2 Schematic preparation of Fe₃O₄/NA and its application for mercury adsorption

Characterization methods

Inductively coupled plasma atomic emission spectrometry (ICP-AES-6300-Thermo Scientific) was used to determine Hg(II) concentration in aqueous samples. Attenuated Total Reflection FTIR spectra of bare Fe₃O₄ and Fe₃O₄/NA were recorded with a Nicolet iS50 FTIR spectrometer (Thermo Scientific, USA) in the range of 4000–800 cm⁻¹, equipped with ZnSe crystal. The spectral resolution was set to 4 cm⁻¹, and 64 scans were collected for each spectrum. The size and morphology of the prepared Fe₃O₄/NA was studied by field-emission scanning electron microscopy (FESEM, JEOL-7401F) and transmission electron microscopy (TEM, JEM-2200FS). The X-ray diffraction patterns of the products were recorded on a PANalytical X'Pert diffractometer using Cu K α radiation with scanning step length of 0.016°. The surface chemical composition of the samples was determined by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 250 spectrometer using monochromatic Al K α X-ray source (1486.8 eV). The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution were determined by N₂ adsorption method using an ASAP 2010 system (Micromeritics Corp., USA) at 77 K. The zeta potential (ξ) and hydrodynamic size

distributions were measured with Zetasizer ELSZ-1000. Magnetic behaviour was characterized by Quantum Design PPMS Value Stream Mapping (VSM) system. A 3-Star Orion bench top pH meter (Thermo Scientific) was used for pH measurement during the experiment.

Procedure of Hg adsorption

All the adsorption experiments were carried out in duplicate at pH 6 \pm 0.1 and 298 K. Briefly, 0.04 g of Fe₃O₄/NA was added to 30 mL of a 5 mg L⁻¹ Hg(II) solution. The solution was sonicated for a one minute and placed on the rolling mixer (33 rpm) for 1 h. The pH of solution was adjusted by 0.1 M HCl or 0.1 M NaOH and all pH measurements were maintained during the course of experiment. Effect of solution pH and ionic strength was interpreted in the range of (3–9) and (1–100) mM NaCl solutions, respectively. Adsorption kinetics was investigated by varying the equilibration time from 1 to 60 minutes. Adsorption isotherms and thermodynamics were evaluated by varying initial mercury concentration (5–50 mg L⁻¹) and temperature in the range of 298–323K, respectively.

The efficiency of Fe₃O₄/NA towards combine Hg(II), Cd(II) and As(V) removal was also assessed by spiking 1000 μ g L⁻¹ of each Hg(II) Cd(II) and As(V) in groundwater sampled from Yeoncheon, South Korea. This sample contained Ca²⁺, Na⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻, NO₃⁻, and pH was found to be 7.8. After adsorption, the particles were separated in few seconds by applying an external magnetic field and equilibrium concentration of Hg(II) was determined. The interaction between the sorbent (Fe₃O₄/NA) and Hg(II) is illustrated in Fig. 2.

The adsorption capacity q_e (mg g⁻¹), the quantity of Hg(II) adsorbed at equilibrium, was calculated according to following equation:

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad (1)$$

where C_0 is the initial Hg(II) concentration in solution (mg L⁻¹), C_e is the equilibrium Hg(II) concentration (mg L⁻¹) after adsorption, V is solution volume (L), and m is mass of adsorbent (g).

Desorption and regeneration experiments

The desorption experiments were performed with 0.001 M HCl containing 0.3 M thiourea because a thiourea acted as a source of sulphide in reactions with soft metals ions. Briefly, 0.04 g of Hg(II) loaded Fe₃O₄/NA was washed twice with distilled water to remove the any loosely attached Hg(II) to PET bottle. Then 10 mL of desorbent was added to PET bottle and placed on the rolling mixer (33 rpm) for one hour. Magnet was used to separate Fe₃O₄/NA in desorbent and Hg(II) in solution was quantified with ICP-AES.

Results and discussion

Characterization of Fe₃O₄/NA

FTIR spectroscopy was utilized for qualitative determination of NA, grafted on the Fe₃O₄ surface (Fig. S1 (ESI[†])). Infrared spectrum describes the symmetrical stretching vibrations of C=N and C=C bands of naphthyridine ring at 1490 and 1450 cm⁻¹, respectively as shown in Fig. 3a. The band at 1253 cm⁻¹ is ascribed to CH deformation³⁴. Strong band at 1630 cm⁻¹ shows C=O stretches of Fe₃O₄/NA, indicating the carboxylate anion interacting with iron oxide surface as the C=O stretches in free carboxylic acid is above 1700 cm⁻¹.³⁵

Fig. 3b represents the wide scan XPS spectra, that reveals the surface composition (w/w), i.e. 17.7 % O, 8.7 % N and 73.6 % C for the NA raw material, whereas 55.03 % O, 1.49 % N, 29.09 % C, and 14.39 % Fe for $\text{Fe}_3\text{O}_4/\text{NA}$. On the basis of Fe content, it was examined that $\text{Fe}_3\text{O}_4/\text{NA}$ surface contained 80.11 % NA, and the NA in $\text{Fe}_3\text{O}_4/\text{NA}$ consisted of 68.7 % O, 1.85 % N, and 36.31 % C. The O content in NA coated Fe_3O_4 was significantly higher as compared to the NA raw material, suggesting that the NA fractions abundant with O based functional groups were selectively coated on the surface of Fe_3O_4 during the synthesis of $\text{Fe}_3\text{O}_4/\text{NA}$. Moreover, by taking into account of high synthesis temperature (80°C) it was also possible that some fractions of NA degraded to form products with higher contents of O-based functional group which adsorbed preferentially on the surface of Fe_3O_4 .³⁶

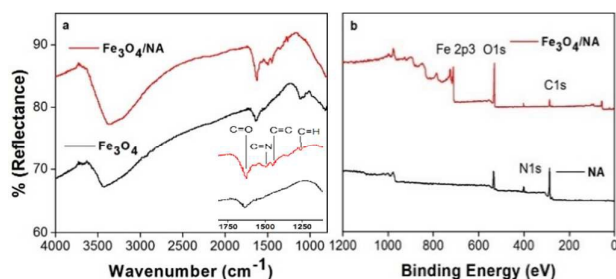


Fig. 3 IR Spectra (a) and X-ray photoelectron spectroscopy (XPS) (b) of the synthesized $\text{Fe}_3\text{O}_4/\text{NA}$

The typical SEM and TEM images of $\text{Fe}_3\text{O}_4/\text{NA}$ are shown in Fig. 4a and 4b, respectively. The SEM image reveals that the product is composed of irregular shaped rods which are interconnected each other. The TEM image represents the core of Fe_3O_4 magnetic nanoparticles, having a typical size of ~ 10 nm, but the entire $\text{Fe}_3\text{O}_4/\text{NA}$ particles contain aggregates with no uniform size and fractal feature. The average particle size as determined in suspension by DLS was 1776 nm which was larger than the size measured by TEM. The difference in size was due to both aggregation and water solvation around the particles.

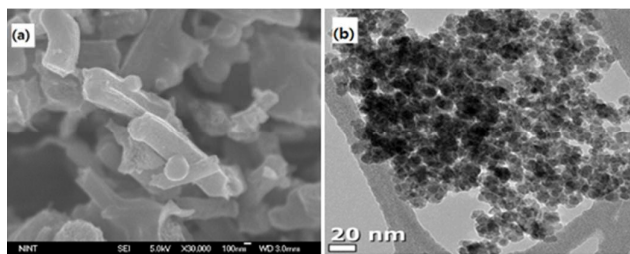


Fig. 4 SEM (a) and TEM (b) images of the prepared $\text{Fe}_3\text{O}_4/\text{NA}$

According to TOC analysis, the actual NA content was found to be ~ 0.62 wt. % of $\text{Fe}_3\text{O}_4/\text{NA}$. The XRD spectrum of bare Fe_3O_4 was compared with $\text{Fe}_3\text{O}_4/\text{NA}$ as shown in Fig. 5a. The XRD pattern of the magnetite nanoparticles exactly matched the JCPDS reference no. 19-629. These two patterns were quite similar, and all of the diffraction peaks were indexed as face centered cubic faces of Fe_3O_4 . These results corroborated that NA did not result in phase change in the structure of Fe_3O_4 .

The respective zeta potential of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{NA}$ under varying pH was measured to investigate the point of zero charge

(PZC) as shown in Fig. 5b. The PZC for $\text{Fe}_3\text{O}_4/\text{NA}$ was found to be around pH 3.9 which was much lower than that of Fe_3O_4 (pH 6.1). The low PZC value of $\text{Fe}_3\text{O}_4/\text{NA}$ indicated that the NA cover the surface of Fe_3O_4 which facilitated more adsorption of positively charged $\text{Hg}(\text{II})$ over a wide range of pH values.

To determine the magnetic properties of the sorbent, a VSM was used. The $\text{Fe}_3\text{O}_4/\text{NA}$ particles were found to be superparamagnetic with a magnetization (M) value of 45 emu g^{-1} at room temperature (Fig. 5c). The hysteresis loop demonstrated that the coercivity and remanence were almost negligible (Fig. S2 (ESI[†])), which is desirable for many practical applications.

The N_2 adsorption-desorption isotherms and the pore size distribution of $\text{Fe}_3\text{O}_4/\text{NA}$ are shown in Fig. 5d. The BET analysis revealed that the specific surface area of $\text{Fe}_3\text{O}_4/\text{NA}$ were to be $126 \text{ m}^2 \text{ g}^{-1}$ which was almost four times higher than pure Fe_3O_4 ($32 \text{ m}^2 \text{ g}^{-1}$). The BET surface area, the large total pore volume ($0.035 \text{ cm}^3 \text{ g}^{-1}$) and the pore size (10.84 nm) strongly indicate that the $\text{Fe}_3\text{O}_4/\text{NA}$ have a mesoporous structure which is desirable for enhanced adsorption performance.

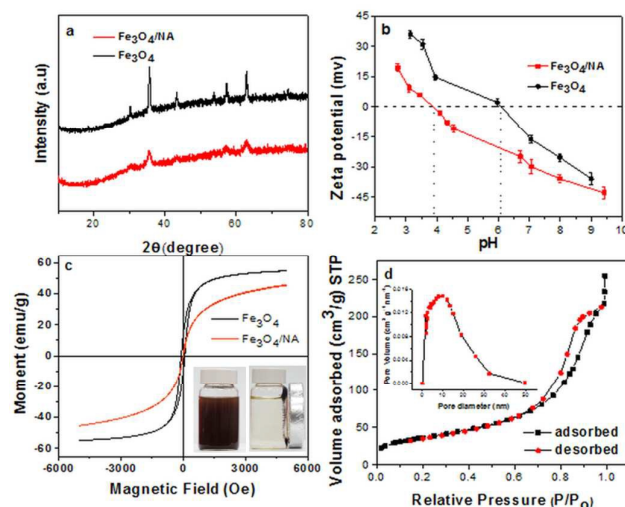


Fig. 5 (a) XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{NA}$. (b) Zeta potentials of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{NA}$ as function of pH in 1mM NaNO_3 . (c) Hysteresis loop of $\text{Fe}_3\text{O}_4/\text{NA}$ at 300 K and (inset) dispersed water solution and magnetic separation (d) Nitrogen adsorption-desorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution plot (inset) of the prepared $\text{Fe}_3\text{O}_4/\text{NA}$

Adsorption Kinetics

The adsorption kinetics of $\text{Hg}(\text{II})$ to $\text{Fe}_3\text{O}_4/\text{NA}$ and bare Fe_3O_4 is presented in Fig. 6a. It could be seen that the adsorption of $\text{Hg}(\text{II})$ in two systems increased rapidly in first 10 min of contact time and then maintained the level with subsequent increase in time. $\text{Fe}_3\text{O}_4/\text{NA}$ achieved the better adsorption efficiencies as compared to bare Fe_3O_4 . Such a fast adsorption could be due to the absence of internal diffusion resistance²⁰ and is favorable for the practical application of $\text{Fe}_3\text{O}_4/\text{NA}$ as sorbent for removal of toxic metals. The relatively high removal capacity of $\text{Fe}_3\text{O}_4/\text{NA}$ is expected from their greater surface area which contributes to the increase in the number of binding sites for metal ions. On the basis of adsorption kinetic data, 60 min shaking time was employed in the following experiments to ensure complete equilibrium. In order to investigate the adsorption mechanism the experimental kinetic data of $\text{Hg}(\text{II})$ adsorption on bare Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{NA}$ were evaluated by the pseudo-first-order and pseudo-second-order kinetic models.^{37, 38}

The pseudo first order kinetic model is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption, while q_e and q_t are the adsorption capacities of Hg(II) (mg g^{-1}) at equilibrium and at time t (min), respectively.

The pseudo second order kinetic model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) t \quad (3)$$

where k_2 is the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The q_e and k_2 values of the pseudo-second-order model was determined from the linear plot of t/q_t vs t as shown in Fig. 6b.

The calculated kinetic parameters from both model fittings are listed in Table S1 ESI†. The validity of both models was estimated by comparing the correlation coefficient (R^2) values. Here the R^2 value for the pseudo-second-order model was higher than that for the pseudo-first-order model. Moreover, the experimentally determined $q_{e,exp}$ (3.63 mg g^{-1}) from the pseudo-second-order model fitting was much closer to the theoretically obtained pseudo-second-order model $q_{e,cal}$ (3.60 mg g^{-1}) as compared to the pseudo first order model $q_{e,exp}$ (0.80 mg g^{-1}). These results predicated that the adsorption system obeyed the pseudo-second-order kinetic model and therefore, supported the assumption that sorption was due to chemisorption instead of mass transport.^{39,40}

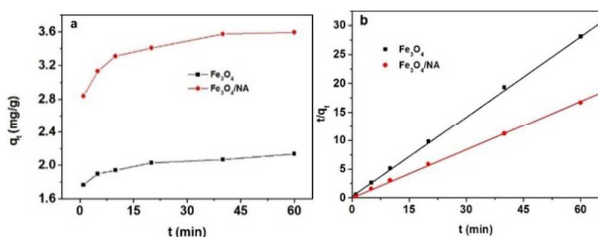


Fig. 6 (a) Effect of time on Hg sorption on bare Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{NA}$. (b) Pseudo-second order model fitting of sorption kinetic data.

Effects of pH and salinity

The effect of pH on the adsorption of Hg(II) onto $\text{Fe}_3\text{O}_4/\text{NA}$ is shown in Fig. 7a. It was observed that removal capacity was highly dependent on pH. The removal capacity increased with the increasing of pH value and reached a plateau after pH 5. This result suggests that $\text{Fe}_3\text{O}_4/\text{NA}$ would be useful in contaminated natural waters with broad range of pH values. It is expected that the change in pH of the solution results in forming different Hg aqueous species⁴¹ such as Hg^{2+} , HgOH^+ , and $\text{Hg}(\text{OH})_2$ and different surface charges of $\text{Fe}_3\text{O}_4/\text{NA}$. When the pH was lowered than the Point of Zero Charge (PZC) of $\text{Fe}_3\text{O}_4/\text{NA}$ (~ 3.9), the surface of $\text{Fe}_3\text{O}_4/\text{NA}$ was positively charged and had very weak interaction with mercury cations due to protonation of the surface functional groups accompanied with the competition between mercuric ions and H^+ or H_3O^+ ions present in the solution. On the other hand, when pH was higher than the PZC of $\text{Fe}_3\text{O}_4/\text{NA}$, the surface of $\text{Fe}_3\text{O}_4/\text{NA}$ was negatively charged and more functional groups are available for metal cation binding due to deprotonation, resulting in electrostatic attraction between Hg(II) and $\text{Fe}_3\text{O}_4/\text{NA}$.

Since interaction of various chemical compounds and electrolytes may change the surface properties of sorbent materials, removal capacity was investigated using various

concentrations of NaCl solutions (Fig. 7b). It was noted that removal of Hg(II) onto $\text{Fe}_3\text{O}_4/\text{NA}$ gradually decreased as the ionic strength of NaCl solution increased from 1 to 100 mM. The adverse effect of ionic strength is described by two factors: (i) the electrolyte ions (Na^+) compete with positively charged mercury ions for the same binding sites and (ii) the ionic strength influences the interfacial potential of mercury metal ions, which would in turn limit their transfer to the $\text{Fe}_3\text{O}_4/\text{NA}$ surface.⁴²

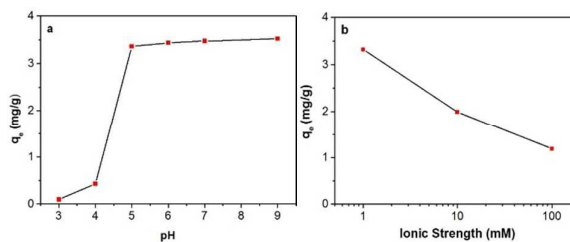


Fig. 7 Influence of pH (a) and ionic strength (b) on Hg(II) sorption on $\text{Fe}_3\text{O}_4/\text{NA}$

Effects of initial concentration and adsorption isotherm

The concentration dependence of Hg(II) adsorption onto $\text{Fe}_3\text{O}_4/\text{NA}$ was studied under the optimized conditions of equilibration time and pH and the results are depicted in Fig. S3a (ESI†). It was observed that the adsorbed amount of Hg(II) on $\text{Fe}_3\text{O}_4/\text{NA}$ (q_e) almost linearly increased with the increasing the initial concentration of Hg(II) and reached a plateau at higher concentrations which might be resulted from saturation of the limited number of binding sites in a fixed amount of adsorbent^{39,43}. The experimental data relating to the adsorption of Hg(II) onto $\text{Fe}_3\text{O}_4/\text{NA}$ was interpreted by Langmuir and Freundlich sorption isotherms using equations given below:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where q_e and C_e are the equilibrium concentrations of Hg(II) in the adsorbed and liquid phases in mg g^{-1} and mg L^{-1} , respectively. Q_{\max} and b are the Langmuir constants which are related to adsorption capacity and energy of adsorption, respectively, and can be obtained from the intercept and slope of the linear plot (Fig. S3b, ESI†), C_e/q_e vs C_e . n and K_F are the Freundlich constants related to sorption intensity and capacity, respectively. Their values can be calculated from the intercept and slope of the linear plot (Fig S3c, ESI†) for $\log q_e$ vs $\log C_e$. The corresponding parameters related to the Langmuir and Freundlich adsorption models are given in Table 1. The correlation coefficients (R^2) for Langmuir and Freundlich models were 0.98 and 0.94, respectively. The good agreement between the adsorption data and the Langmuir model confirms surface homogeneity, monolayer surface coverage, and no lateral interaction between sorbed molecules.

Table 1 Equilibrium parameters for Hg(II) adsorption on $\text{Fe}_3\text{O}_4/\text{NA}$

Q_{\max} (mg g^{-1})	Langmuir		K_F	Freundlich	
	b (L mg^{-1})	R^2		N	R^2
9.52	0.50	0.98	1.90	4.97	0.94

Adsorption thermodynamics

Thermodynamic behavior of the adsorption of Hg(II) onto Fe₃O₄/NA was evaluated with help of thermodynamic parameters including standard free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). These parameters were estimated from the following equations:

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

where K_D (q_e/C_e) is distribution coefficient, R is universal gas constant (8.314 J mol⁻¹K), and T is temperature (K). The values of ΔH° and ΔS° were calculated from the slope and intercept of linear van't Hoff plot, as shown in Fig. S4 ESI†, using the following expression.

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

The thermodynamic parameters were given in Table S3 ESI†. The negative values of ΔG° indicate that the adsorption of Hg(II) onto Fe₃O₄/NA is thermodynamically feasible and spontaneous in nature. The decrease in numerical value of $-\Delta G^\circ$ with rise in temperature exhibits that Hg(II) sorption process on Fe₃O₄/NA is exothermic and less favorable at higher temperatures⁴⁴. These results correspond to Jeon and coworkers⁴⁵ who suggested that mercury escape from the surface site increased with rise in temperature and the amount adsorbed decreased, resulting in reduction in boundary layer thickness. The ΔH° parameter was found to be -9.63 kJ mol⁻¹. The negative ΔH° indicates the exothermic nature of the adsorption process of Hg(II) at 25–50°C. The ΔS° parameter was found to be -15.73 J mol⁻¹ K⁻¹. The negative ΔS° value indicates a decrease in the randomness at the solid/solution interface during the adsorption process of Hg(II) onto Fe₃O₄/NA.

Material stability and environmental significance

Escape of sorbent fractions into treated water is undesirable. Therefore, in order to ensure the permanent incorporation of NA in Fe₃O₄/NA matrix, a leakage test was performed under the stated experimental conditions and the contact time was prolonged to 56 hours as shown in Fig. 8a. No leakage of NA was observed, which confirmed the stability of Fe₃O₄/NA and supporting its use in real environments.

The presence of competitive ions in the adsorptive medium may change the environment and solution chemistry of the target metal ions, which affects the adsorption efficiency of conventional adsorbent. Table S4 (ESI†) describes the presence of different ions in groundwater collected from Yeoncheon, South Korea. The performance of the Fe₃O₄/NA in the real groundwater spiked with mixed heavy metal ions, containing 1000 µg L⁻¹ of each Hg(II), Cd(II) and As(V), was investigated as shown in the Fig. 8b. It was observed that despite the presence of high concentration of various cations and anions in groundwater, not only the Hg(II) but also higher percentage of Cd(II) and As(V) was removed in similar conditions. This suggested that Fe₃O₄/NA could be used to mitigate other toxic heavy metals in real groundwater systems.

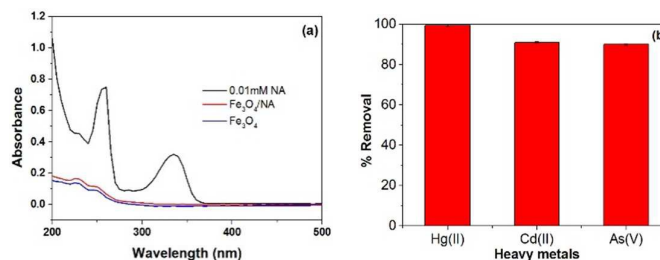


Fig. 8 Leakage test of Fe₃O₄/NA (a), The removal efficiency of heavy metals in groundwater (b), (the water contained mixed Hg, Cd and As with initial concentration of 1000 µg L⁻¹ for each metal ion).

Mechanism of Hg(II) removal

The removal of metal at the adsorbent surface can be attributed to different plausible mechanisms including adsorption, ion exchange, absorption, surface precipitation, coprecipitation, diffusion and etc.^{46, 47} The XPS analysis of Fe₃O₄/NA-Hg revealed vital information which was valuable in order to investigate the removal mechanism of Hg(II) by using Fe₃O₄/NA. Figure 9a shows narrow XPS scan of Hg in 4f region and the peak at 101.5 eV corresponds to binding energy of 4f_{7/2} of Hg(II)⁴⁷, indicating Hg(II) is adsorbed onto the Fe₃O₄/NA. The narrow scan of the binding energy (BE) of oxygen (O1s) of Fe₃O₄/NA-Hg (Fig. 9b) indicates the relatively stronger intense peak at 530.9 eV in which O atom is present in low binding energy region corresponding to more reduced state.

This may be due to the formation HgO in which Hg shared electrons with oxygen, which consequently decreases the electronic cloud density of oxygen atom of iron oxide.⁴⁸ Moreover, the supplemented affinity towards Hg(II) by NA grafted magnetite Fe₃O₄/NA can also be predicted on the basis of the Hard Soft Acid Base, (HSAB) theory, which classify the Hg(II) as a soft acid due to the large ionic size, high polarizability and low electronegativity, capable to form strong bonds with soft bases containing N and S atoms.⁴⁹ Therefore, our study on the adsorption of Hg(II) by Fe₃O₄/NA-Hg showed the participation of oxygen in complexation with heavy metal through XPS analysis with synergistic interaction between N and Hg(II).

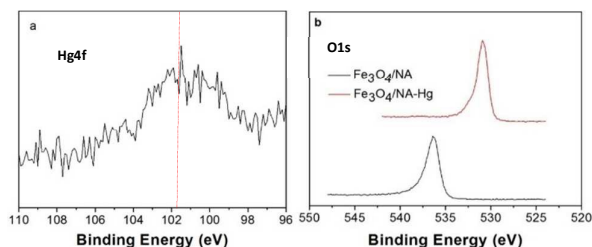


Fig. 9 Hg4f narrow scan of Fe₃O₄/NA-Hg (a), O1s narrow scan before and after adsorption of Hg(II) (b).

Regeneration and reusability

The recycling and reusability is a basic economic necessity for the practical and industrial application of sorbents. In this context,

the regeneration and reusability of $\text{Fe}_3\text{O}_4/\text{NA}$ was verified to assess its application potential in the decontamination of $\text{Hg}(\text{II})$ bearing water. Taking into consideration, the negligible adsorption capacity exhibited by $\text{Fe}_3\text{O}_4/\text{NA}$ at low pH, acid treatment was found to be a feasible approach for regeneration. Therefore, 0.001 M HCl containing 0.3 M thiourea was used as a complexing agent to recover $\text{Hg}(\text{II})$ for consecutive five cycles and the desorption efficiency was found to be still above 90%. As shown in Fig. 10a, after first adsorption cycle there was a decrease of $\sim 6\%$ in removal efficiency, but for the remaining cycles it was remained to $\sim 93\%$, representing the excellent regeneration and reusability. The slight reduction in adsorption capacity might be expected due to incomplete desorption of $\text{Hg}(\text{II})$ from the surface of $\text{Fe}_3\text{O}_4/\text{NA}$. The SEM images of freshly prepared and regenerated samples after fifth cycle are shown in Fig. 10b. After five cycles, the surface of $\text{Fe}_3\text{O}_4/\text{NA}$ appeared to be little bit rougher with some broken spheres but it still kept rod-like morphology. Overall, $\text{Fe}_3\text{O}_4/\text{NA}$ can be easily regenerated, collected in short time and reused several times, which ensures its long-term use for $\text{Hg}(\text{II})$ removal from wastewater.

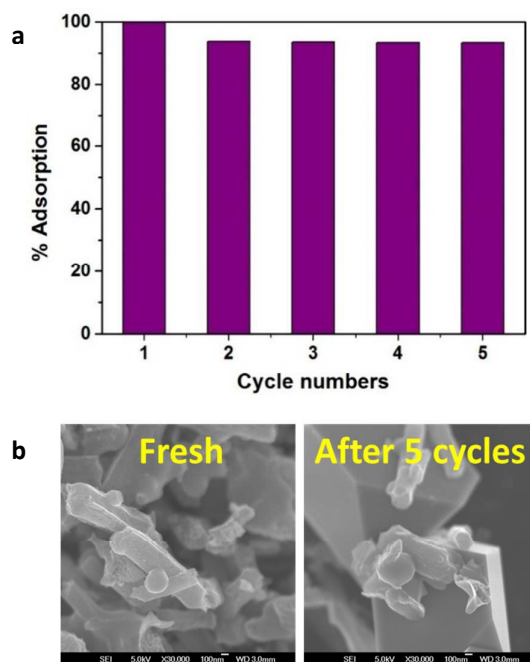


Fig. 10 Recycling of $\text{Fe}_3\text{O}_4/\text{NA}$ in the removal of $\text{Hg}(\text{II})$ with initial concentration of $1000 \mu\text{g L}^{-1}$ (a), SEM images of fresh and recycled $\text{Fe}_3\text{O}_4/\text{NA}$ (b)

Comparison with other sorbents

In order to verify the effectiveness of $\text{Fe}_3\text{O}_4/\text{NA}$ as a potential sorbent for $\text{Hg}(\text{II})$ Q_{max} was compared carefully with those of other sorbents reported in previous literatures as listed in Table S2 ESI†. It can be seen that the maximum adsorption capacity of $\text{Fe}_3\text{O}_4/\text{NA}$ is higher than that of clay, fly ash, rice husk ash, activated carbon, magnetic nanoparticles modified with 2-mercaptobenzothiazole, naphthalimide-functionalized magnetic nanosensor and comparable with silica grafted methyl amino ethyl methacrylate while lower than dithiocarbamate grafted magnetite particles and thiol-modified magnetite beads-porous materials. Despite some good benefits of dithiocarbamate and thiol-modified materials, the

complex, tedious synthetic procedure and expensive raw materials cost limit their wide scale application.

In comparison to others, $\text{Fe}_3\text{O}_4/\text{NA}$ can be synthesized by the facile and controllable method with economical nalidixic acid and iron precursors at low temperature. In addition, $\text{Fe}_3\text{O}_4/\text{NA}$ is magnetically retrievable, stable, attain the equilibrium within one hour and can be reused for several times. It is important to mention here that the $\text{Fe}_3\text{O}_4/\text{NA}$ is capable to reduce the initial $\text{Hg}(\text{II})$ ($1000 \mu\text{g/L}$) concentration to values lower than $2 \mu\text{g/L}$ in real groundwater. This fact is attributed not only to their adsorption capacity but also because the number of previous studies consider initial mercury concentrations very high which does not reflect exact degree of contamination observed in the actual environment.

Conclusions

For mercury removal from water, we have synthesized nalidixic acid grafted magnetite nanoparticles ($\text{Fe}_3\text{O}_4/\text{NA}$) with high surface area by a facile, low cost and time saving route. $\text{Fe}_3\text{O}_4/\text{NA}$ can be easily separated by an external magnetic field in less than 20 seconds. The $\text{Fe}_3\text{O}_4/\text{NA}$ nanoparticles showed near complete removal of 1000 ppb of initial $\text{Hg}(\text{II})$ and the enhanced rate constants at near neutral pH was due to the increased sorption sites in the presence of nalidixic acid. The adsorption process was found to be exothermic and spontaneous with decreased randomness at the solid–solution interface. The strong affinity towards $\text{Hg}(\text{II})$ was attributed to the synergistic effect of the soft interaction (Hg-N) and the formation of HgO . The adsorbed $\text{Hg}(\text{II})$ could be effectively desorbed by 0.001 M HCl containing 0.3 M thiourea without the destruction of particles and subsequently be reused for consecutive adsorption–desorption experiments. The $\text{Fe}_3\text{O}_4/\text{NA}$ can also be used to remediate other heavy metals such as cadmium and arsenic in groundwater. The proposed method has opened a new class of organic reagent based magnetite that can be utilized as a selective complexing agent for various metal ions.

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Notes and references

1. P. Holmes, K. A. F. James and L. S. Levy, *Sci. Total Environ.*, 2009, **408**, 171–182.
2. G. K. Darbha, A. K. Singh, U. S. Rai, E. Yu, H. Yu and P. C. Ray, *J. Am. Chem. Soc.*, 2008, **130**, 8038–8043.
3. F. Zahir, S. J. Rizwi, S. K. Haq and R. H. Khan, *Environ. Toxicol. Pharm.*, 2005, **20**, 351–360.
4. G. Bayramoğlu and M. Y. Arica, *J. Hazard. Mater.*, 2007, **144**, 449–457.

5. L. I. Sweet and J. T. Zelikoff, *J. Toxicol. Env. Heal., B*, 2001, **4**, 161-205.
6. E. Hodgson, *A Textbook of Modern Toxicology*, Wiley & Sons, 2004.
7. I. Wagner-Döbler, H. Von Canstein, Y. Li, K. N. Timmis and W. D. Deckwer, *Environ. Sci. Technol.*, 2000, **34**, 4628-4634.
8. USEPA. National primary drinking water regulations. <http://www.epa.gov/safewater/contaminants/index.html#inorganic> (accessed June 2015)
9. M. M. Matlock, B. S. Howerton and D. A. Atwood, *J. Hazard. Mater.*, 2001, **84**, 73-82.
10. M. Huebra, M. P. Elizalde and A. Almela, *Hydrometallurgy*, 2003, **68**, 33-42.
11. H. Bessbousse, T. Rhlalou, J.-F. Verchère and L. Lebrun, *Chem. Eng. J.*, 2010, **164**, 37-48.
12. K. Chakrabarty, P. Saha and A. K. Ghoshal, *J. Membrane Sci.*, 2010, **346**, 37-44.
13. S. Chiarle, M. Ratto and M. Rovatti, *Water Res.*, 2000, **34**, 2971-2978.
14. P. N. Diagboya, B. I. Olu-Owolabi and K. O. Adebowale, *RSC Advances*, 2015, **5**, 2536-2542.
15. J. Goel, K. Kadirvelu and C. Rajagopal, *Environ. Technol.*, 2004, **25**, 141-153.
16. I. Ali, *Chem.Rev.*, 2012, **112**, 5073-5091.
17. Y. Wang, J. Ma and K. Chen, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19415-19421.
18. S. C. N. Tang and I. M. C. Lo, *Water Res.*, 2013, **47**, 2613-2632.
19. D. Maity and D. C. Agrawal, *J. Magn. Magn. Mate.*, 2007, **308**, 46-55.
20. E. J. Kim, C. S. Lee, Y. Y. Chang and Y. S. Chang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9628-9634.
21. K. Mandel, F. Hutter, C. Gellermann and G. Sextl, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5633-5642.
22. A. Farrukh, A. Akram, A. Ghaffar, S. Hanif, A. Hamid, H. Duran and B. Yameen, *ACS Appl. Mater. Interfaces*, 2013, **5**, 3784-3793.
23. S. Shin and J. Jang, *Chem. Commun.*, 2007, 4230-4232.
24. S. Shi, Y. Fan and Y. Huang, *Ind. Eng. Chem. Res.*, 2013, **52**, 2604-2612.
25. J. Zhu, S. Wei, H. Gu, S. B. Rapole, Q. Wang, Z. Luo, N. Haldolaarachchige, D. P. Young and Z. Guo, *Environ. Sci. Technol.*, 2012, **46**, 977-985.
26. X. Liu, Q. Hu, Z. Fang, X. Zhang and B. Zhang, *Langmuir*, 2009, **25**, 3-8.
27. L. Zhou, T. L. Thanh, J. Gong, J.-H. Kim, E.-J. Kim and Y.-S. Chang, *Chemosphere*, 2014, **104**, 155-161.
28. S. Sadeghi and E. Sheikhzadeh, *Microchim. Acta*, 2008, **163**, 313-320.
29. X. Jia, L. Li and H. Huang, *Fenxi Huaxue*, 1996, **24**, 1218.
30. P. B. Issopoulos, *Acta Pharm. Jugosl.*, 1989, **39**, 267-274.
31. S. Shahida, A. Ali, M. H. Khan and M. M. Saeed, *Environ. Monit. Assess.*, 2013, **185**, 1613-1626.
32. S. Shahida, A. Ali and M. H. Khan, *J. Iran. Chem. Soc.*, 2013, **10**, 461-470.
33. A. Ali, Y. Arafat Abbasi, M. Haleem Khan and M. Mufazzal Saeed, *Radiochim. Acta*, 2010, **98**, 513-517.
34. S. Gunasekaran, R. K. Natarajan, R. Rathikha and D. Syamala, *Indian J. Pure and Appl. Phys.*, 2005, **43**, 503-508.
35. W. Yantasee, C. L. Warner, T. Sangvanich, R. S. Addleman, T. G. Carter, R. J. Wiacek, G. E. Fryxell, C. Timchalk and M. G. Warner, *Environ. Sci. Technol.*, 2007, **41**, 5114.
36. E. Illés and E. Tombácz, *Colloids Surface., A*, 2003, **230**, 99-109.
37. Y. S. Ho and G. McKay, *Water Res.*, 1999, **33**, 578-584.
38. Y. S. Ho and G. McKay, *Process Biochem.*, 1999, **34**, 451-465.
39. S. Pan, H. Shen, Q. Xu, J. Luo and M. Hu, *J. Colloid Interf. Sci.*, 2012, **365**, 204-212.
40. Y. S. Ho, *J. Hazard. Mater.*, 2006, **136**, 681-689.
41. F. F. S. Zhang, J. O. Nriagu and H. Itoh, *Water Res.*, 2005, **39**, 389-395.
42. Z. Reddad, C. Gerente, Y. Andres and P. Le Cloirec, *Environ. Sci. Technol.*, 2002, **36**, 2067-2073.
43. B. S. Inbaraj and N. Sulochana, *J. Hazard. Mater.*, 2006, **133**, 283-290.
44. A. Sari and M. Tuzen, *J. Hazard. Mater.*, 2009, **171**, 500-507.
45. C. Jeon and H. P. Kwang, *Water Res.*, 2005, **39**, 3938-3944.
46. C. S. Kim, J. J. Rytuba and G. E. Brown Jr, *Colloid Interf. Sci.*, 2004, **271**, 1-15.
47. Y. Kim and Y. J. Lee, *J. Colloid Interf. Sci.*, 2014, 48.
48. C. R. Collins, D. M. Sherman and K. V. Ragnarsdottir, *J. Colloid Interf. Sci.*, 1999, **219**, 345-350.
49. P. Miretzky and A. F. Cirelli, *J. Hazard. Mater.*, 2009, **167**, 10-23.
50. W. U. Senevirathna, H. Zhang and B. Gu, *Water Air Soil Poll.*, 2011, **215**, 573-584.
50. A. K. Sen and A. K. De, *Water Res.*, 1987, **21**, 885-888.
51. Q. Feng, Q. Lin, F. Gong, S. Sugita and M. Shoya, *J. Colloid Interf. Sci.*, 2004, **278**, 1-8.
53. X. Lu, J. Jiang, K. Sun, J. Wang and Y. Zhang, *Mar. Pollut. Bull.*, 2014, **78**, 69-76.
54. H. Parham, B. Zargar and R. Shiralipour, *J. Hazard. Mater.*, 2012, **205-206**, 94-100.
55. J. Dong, Z. Xu and F. Wang, *Appl. Surf. Sci.*, 2008, **254**, 3522-3530.
56. L. Zhao, J. Sun, Y. Zhao, L. Xu and M. Zhai, *Chem. Eng. J.*, 2011, **170**, 162-169.
57. J. Zhao, B. Zhu, H. Yu, L. Yan, Q. Wei and B. Du, *J. Colloid Interf. Sci.*, 2013, **389**, 46-52.
58. Figueira, P., Lopes, C. B., Daniel-da-Silva, A. L., Pereira, E., Duarte, A. C., & Trindade, T. *Water Res*, 2011, **45**, 5773-5784.

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