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Pollution magnet: nano-magnetite for arsenic removal from drinking water

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Abstract Arsenic contamination in groundwater is a severe global problem, most notably in Southeast Asia where millions suffer from acute and chronic arsenic poisoning. Removing arsenic from groundwater in impoverished rural or urban areas without electricity and with no manufacturing infrastructure remains a significant challenge. Magnetite nanocrystals have proven to be useful in arsenic remediation and could feasibly be synthesized by a thermal decomposition method that employs refluxing of FeOOH and oleic acid in 1-octadecene in a laboratory setup. To reduce the initial cost of production, $US 2600/kg, and make this nanomaterial widely available, we suggest that inexpensive and accessible "everyday" chemicals be used. Here we show that it is possible to create functional and high-quality nanocrystals using methods appropriate for manufacturing in diverse and minimal infrastructure, even those without electricity. We suggest that the transfer of this knowledge is best achieved using an open source concept.

Key words Arsenic remediation ·
Drinking water · Kitchen synthesis ·
Magnetite nanocrystals · Open source software ·
Underdeveloped countries

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Introduction

Arsenic (As) in drinking water is an epidemic affecting millions of people living in Southeast Asia (Hossain et al. 2005). Since the current limit of maximum permissible concentration is fivefold lower than that previously established (10 μg/l), many countries in this region and across the world are trying to implement new standards (Mohan and Pittman 2007). Some, like Bangladesh, face hard times since their average arsenic levels already vastly exceed the limit (Acharyya et al. 1999).

Arsenic is naturally present in groundwater in the forms of arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}). These anions resemble phosphite (HPO_3^{2-}) and

phosphate (PO_4^{3-}) ions, and it is this similarity that is the dominant source of their toxicity: arsenite and arsenate block ATP $\rightarrow$ ADP conversions by permanently replacing phosphate groups (Jain and Ali 2000).

In underdeveloped countries, such as Bangladesh, poor villagers collect their potable water from ponds, rain water, dug (shallow) wells, and deep wells (Harvey et al. 2002). These sources are associated with a number of health risks, ranging from microbial infections (at those sources close to the ground) to diseases such as arsenicosis (from the deeper aquifers that have high arsenic levels). Since the 1980s, both governments and the public have preferred deeper wells as the water therein appeared to contain no visible contaminants (arsenic species are colorless and odorless) and was no longer contaminated with waterborne microbial diseases, such as diarrhea. The appearance of the first reports containing evidence that many of these drinking water sources had high arsenic levels (Chakraborty and Saha 1987; Nickson et al. 1998) resulted in only 29% of the affected population switching to safer wells (Ahmed et al. 2006).

The failure of arsenic removal practices in these wells was mainly due to maintenance difficulties, which were both costly and labor-intensive. Several measures suggested by the National Policy for Arsenic Mitigation (NPAM; 2004), such as a piped water system, rainwater collectors, pond sand filters, dug wells, and arsenic removal units, have had only a minor effect (2–4%) (Ahmed et al. 2006). Consequently, Ahmed and co-workers have insisted on regular monitoring of water quality regardless of the mitigation technique, broader public awareness campaigns, and the wise use of the water sources that are low in arsenic (Ahmed et al. 2006). However, the issue currently remains unresolved (Ball 2005; Bhattacharjee 2007).

Open source concept for arsenic remediation

Open source software benefits from the contributions of individuals that are not the original authors of that software, thereby leading to a dynamic optimization that is well-suited to the specific application for which they are intended. If freely licensed, free and open source software (FOSS) puts underdeveloped countries on an equal footing with the developed

world in terms of innovating new technologies (Weber 2004; Kelty 2008). This concept could also be employed to disseminate life-saving technologies, such as diagnostic tools, sustainable energy sources, and in our case, arsenic remediation (Lounsbury et al. 2009). Here, we demonstrate a pathway to the development of an open source nanotechnology method that has the potential to be used in the rural villages of Bangladesh where no electricity or pumps are available. Properly denoted as "kitchen synthesis", this method employs everyday materials, such as edible oils, rust, and vinegar, that are commonly found in an ordinary kitchen.

Materials and methods

Materials

Edible oils [Bertolli Extra Light Tasting olive oil, Market Pantry vegetable oil (soybean oil), Market Pantry all natural corn oil], Market Pantry white distilled vinegar (5% acidity), and Johnson's Drano Max gel were obtained from Target (USA). Roebic brand crystal drain opener was purchased from Lowe's hardware store. Additional vinegar (Hill Country Fare extra strength distilled white vinegar with 9% acidity) was obtained from HEB. Water was used from municipal tap water without further purification. Rust was obtained from different sources of rusted steel, such as the iron stand that was found in a laboratory hood, high school fences, and rods found in the playground on the university campus.

Soapmaking process

Crystal drain opener (15 g) is dissolved in 30 ml of tap water and, while warm, poured into a glass bowl containing 100 g of an edible oil type. The mixture is stirred first with a spoon and then with a magnetic stir bar until tracing and texture are observed. The resulting slurry is left in a ventilated area to dry and cure, with stirring with a spoon each day until a thick, hard soap is obtained.

Production of fatty acid mixture

The cured soap (60 g) is finely grated on a cheese grater and mixed with 650 ml of vinegar (9% acidity). The

resulting solution is boiled for 15–30 min, with stirring, until all soap chunks disappear. Upon cooling, two distinctive layers are formed. The top organic layer is removed using a syringe and placed in a pan. This cloudy yellow mixture is heated to a boil until the remaining water and acetic acid evaporates.

Magnetite nanocrystal synthesis

Rust is obtained from rusted steel sources by shaving. Rust powder (1 g) is mixed with 20 g fatty acid mixture (FAM) and placed into the pan. Covered by a lid, the solution is boiled for 2 h, producing a thick smoke. This thick smoke diminishes in time, and the end product is a black gelatinous magnetic material.

Transferring magnetite nanocrystals into water

The soap (10 g) is ground into 100 ml of tap water and boiled until dissolved. Excess soap is filtered away by decanting. The black slurry (3–5 g) from the pan is then combined with the soapy water and boiled for 30 min. Any unreacted solid is removed by filtering. Water-soluble magnetite nanocrystals are then magnetically collected from the brownish solution. The deposits on the magnet are then washed with water and redispersed in water or ethanol.

Results and discussion

In terms of technology, the current leading choices for removing arsenic from a water source include coprecipitation, adsorption in fixed-bed filters, membrane filtration, anion exchange, electrocoagulation, and reverse osmosis (Twidwell et al. 1999; Mohan and Pittman 2007). Most of these techniques, however, are not as effective as nano-magnetite, require large initial and maintenance costs, and are intensive labor since the affected area is very large (Hossain et al. 2005).

In a previous study carried out in collaboration with the Mason Tomson group, we showed that fine sizes of nano-magnetite (Fe_3O_4, 12 nm) can remove 200-fold more arsenic than existing commercial sorbents (Yean et al. 2005; Yavuz et al. 2006; Mayo et al. 2007). Table 1 shows the concentrations of arsenic remaining in a stock solution containing 500 μg As/l and the associated percentage removal

Table 1 Arsenic removal efficiency test in which 2 l of an As-containing solution (500 μg/l) is treated with 1 g Fe_3O_4 (adapted from Yavuz et al. 2006)

Particle size (nm)	As(V) or As(III)	Residual As concentration (μg/l)	Percentage removal
12	As(III)	3.9	99.2
20	As(III)	45.3	90.9
300	As(III)	375.7	24.9
12	As(V)	7.8	98.4
20	As(V)	17.3	96.5
300	As(V)	354.1	29.2

efficiency after treatment with 1 g of 12-nm nano-magnetite (developed in our laboratory), 20-nm magnetite (commercially produced), or 300-nm magnetite (commercially produced). The results prove the potential of nano-magnetite to make a sizable cut in material costs: 15 g of nano-magnetite is equal to 1.4 kg of bulk iron oxide in terms of removing the same amount of arsenic (500 μg/l) from 50 l of water. Nano-magnetite can be synthesized from alternative, sustainable sources, as discussed in subsequent sections of this article. Our goal is to develop a procedure that can be performed using the most basic of tools and chemicals that are present in every household or kitchen.

Magnetite (Fe_3O_4) nanocrystals

In its nanoscale form, the most magnetic of all natural minerals, magnetite (Fe_3O_4), is effective in remediating arsenic (Yean et al. 2005; Yavuz et al. 2006, 2007; Mohan and Pittman 2007; Shannon et al. 2008). Equally important is the development of manufacturing methods that are scalable as well as cost effective since arsenic remediation requires both cheap and plentiful materials (Hossain et al. 2005). The synthesis of fine sizes of magnetite usually require highly pure chemicals and laboratory tools, such as temperature-controlled heaters, stirrers, and inert atmosphere. Non-aqueous mediums are also preferred for high monodispersity and uniformity (Roca et al. 2006).

In a typical *laboratory synthesis*, an iron salt or oxide is mixed with a surfactant and boiled in a high boiling point solvent under air-free reflux conditions. The most notable examples of this type of synthesis

are refluxing iron acetylacetonate, oleic acid, oleyl-amine and 1,2-hexadecanediol in diphenyl ether (Sun and Zeng 2002; Sun et al. 2004), heating iron oxo-hydrate (FeOOH) with oleic acid in 1-octadecene (ODE) (Yu 2004), precipitating FeCl₃ with oleic acid and further heating to a boiling in 1-octadecene (ODE) (Jana et al. 2004), and mixing FeCl₃ and sodium oleate before refluxing the precipitate in a mixture of oleic acid and ODE (Park et al. 2004). All of these methods, however, require high purity grade chemicals, thereby limiting their use in very low cost operations, such as water filtrations.

A very probable mechanism of laboratory grade non-aqueous synthesis of magnetite nanocrystals has been reported in the literature (Jana et al. 2004; Park et al. 2004; Sun et al. 2004; Yu 2004). In these syntheses, a major intermediate is shown to be iron(III) oleate, which is a direct salt of iron(III) with the oleate anion (Fig. 1).

Kitchen synthesis

An alternative approach to reducing costs without sacrificing too much quality would be to replace the expensive reagents with affordable, accessible, and relatively less pure ingredients, such as those found in a kitchen. Existing green and cost-effective synthetic methods are unfortunately limited in the field of nanotechnology. To date, only olive oil (Sapra et al. 2006) and Therminol 66 (Asokan et al. 2005) have
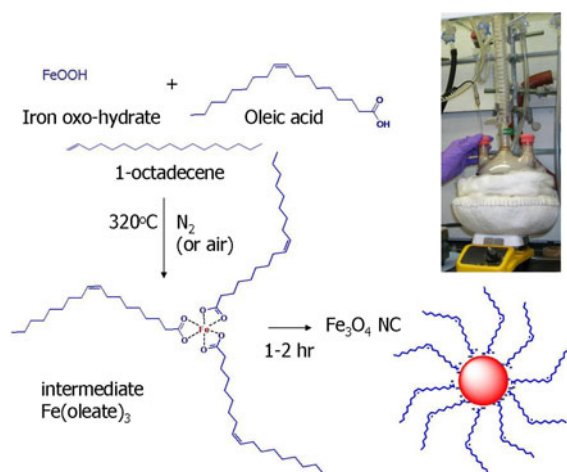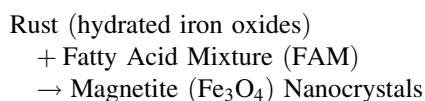
been shown to be directly usable as solvents. Our research on rust (hydrated iron oxides) collected from refuse and a fatty acid mixture obtained from edible oils has revealed that the costs of the starting materials can be reduced by more than two orders of magnitude (from \$US 2600/kg to \$US 22/kg). In this greener, alternative synthetic route, the key ingredients of the synthesis, iron precursor and the oleic acid, can be substituted with everyday chemicals. Edible oils show a potential for replacing oleic acid with a mixture of fatty acids that are formed via saponification that is followed by acidification. Rust from an iron- or steel-based tool is an affordable replacement of FeOOH, the iron precursor. The new chemical reaction then becomes:

Rust (hydrated iron oxides)
   + Fatty Acid Mixture (FAM)
   → Magnetite (Fe_3O_4) Nanocrystals

A saponification reaction of edible oils produces soap, which is a mixture of fatty acid salts. The FAM, which is a mixture of long-chain organic acids, forms once this soap is acidified with vinegar. There are a number of different fatty acids that constitute FAMs, but four of these are almost always dominant: oleic acid [(9Z)-octadec-9-enoic acid], linoleic acid [(9Z, 12Z)-octadeca-9, 12-dienoic acid], stearic acid (octadecanoic acid), and palmitic acid (hexadecanoic acid) (see Fig. 2 for their chemical formula; Gan et al. 2005). To investigate whether or not these fatty acids would produce nanocrystals, we performed control experiments with dilute oleic acid (Fig. 3a), concentrated oleic acid (Fig. 3b), stearic acid (Fig. 3c), and

Fig. 1 Accepted mechanism of the solvothermal decomposition of iron oleate for magnetite nanocrystals. *Inset* Digital picture from a batch setup
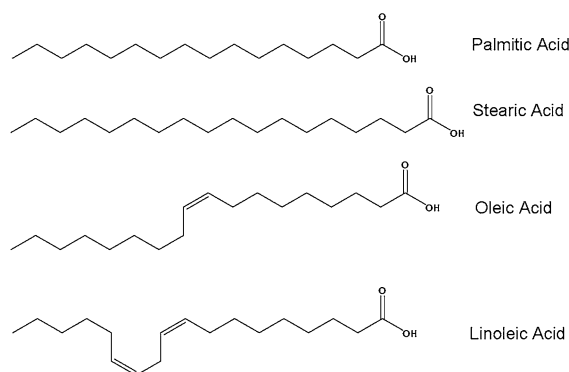

Fig. 2 The chemical formula of the four fatty acids that are the dominant constituents of the oils. Most oil types contain these at a concentration of ≥90% (w/w) (Gan et al. 2005)
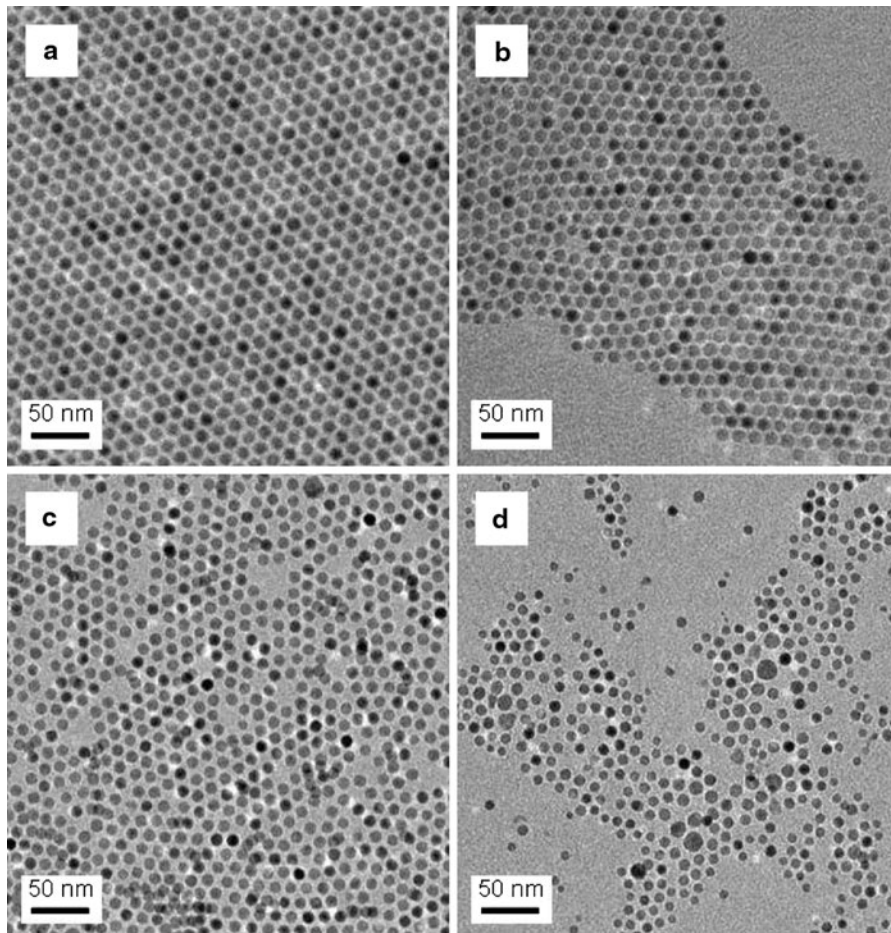
Fig. 3 Transmission electron micrographs (TEM) of magnetite nanocrystals that are synthesized from FeOOH and **a** oleic acid (10.84 ± 0.55-nm nanocrystals), **b** concentrated oleic acid (9.41 ± 0.92-nm nanocrystals), **c** stearic acid (8.90 ± 0.60-nm nanocrystals), **d** linoleic acid and 1-octadecene (ODE) (7.68 ± 1.47-nm nanocrystals)

linoleic acid (Fig. 3d). Evaluation of the particle sizes of the nanocrystals did not indicate any correlation between the size of the crystals and the structure of the fatty acid since the use of mono-unsaturated 18-carbon-long oleic acid resulted in 10.84 ± 0.55-nm nanocrystals, saturated 18-carbon-long stearic acid produced 8.90 ± 0.60-nm nanocrystals, and doubly unsaturated 18-carbon-long linoleic acid formed 7.68 ± 1.47-nm nanocrystals.

The solvent, ODE, is a common nanocrystal synthesis solvent that has many more applications (Al-Salim et al. 2007). In an environment without electricity, however, a proposed reaction should be as simple as possible. For this reason, we tested the nano-magnetite synthesis procedure with and without

the solvent (Fig. 4) and found that even in the absence of the solvent, we were able to produce nanocrystals, although the crystallite size was larger.

The third parameter would be the composition of the iron source. For this investigation, we used rust collected from refuse in our controlled experiments. Although rust is predominantly FeOOH (Misawa et al. 1974), it may contain unoxidized, zero valent iron (Fe) since rusting usually stops when the surface of the iron-containing tool is fully covered. Figure 5 shows X-ray diffraction data on different trials with two different rust sources. Note that both spectra fit the standard magnetite peaks perfectly. The trial shown in Fig. 5c also contains some zero valent iron (Fe).
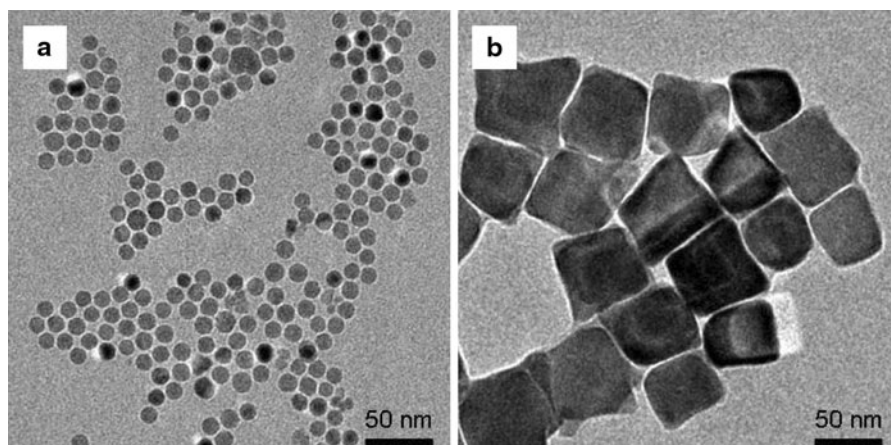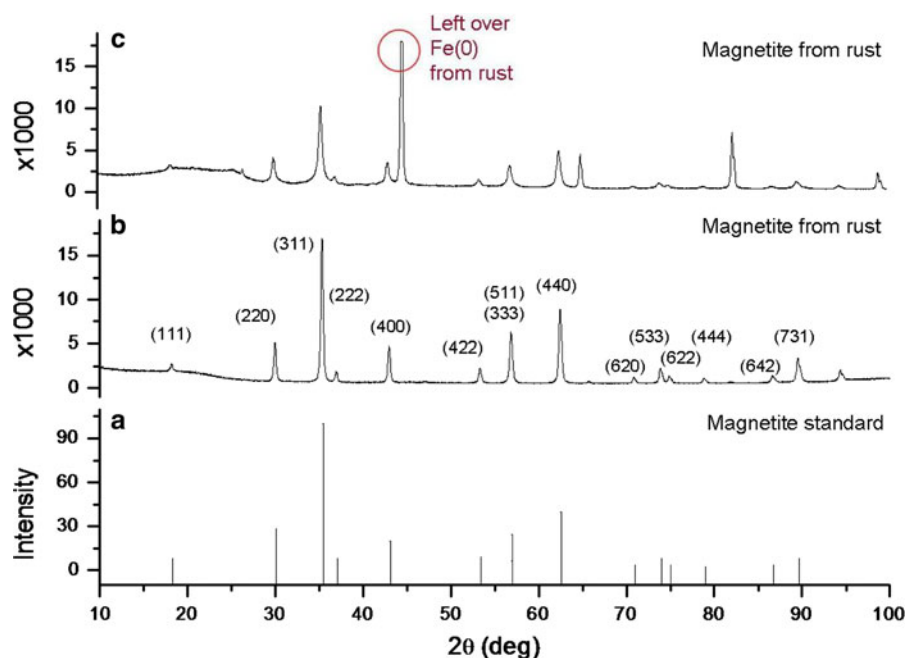
Fig. 4 Magnetite nanocrystal synthesis with FeOOH and oleic acid in ODE (**a**; 12.04 ± 1.23-nm nanocrystals) and in the absence of ODE (**b**; 66.80 ± 13.56-nm nanocrystals)

Fig. 5 Effect of rust composition on the synthesis of the nanocrystals. **a** Magnetite standard taken from the JADE diffraction database, **b** magnetite from rust source 1, **c** magnetite from rust source 2 where zero valent iron [Fe(0)] is also present

The last parameter is the control over the reaction setup and procedure. Temperature changes are of primary concern since laboratory synthesis uses a calibrated temperature controller. It would be hard to maintain a constant temperature with tools that are available in a rural household, which is the reason for monitoring the visible cues of the reaction; for example, when it stops smoking, the reaction is deemed stopped. Figure 6 shows the steps of a kitchen synthesis. A comparison of the results of the kitchen synthesis with the controlled laboratory process is shown in Table 2.

Conclusions

When approached as open source nanotechnology, the kitchen synthesis of magnetite nanocrystals can become a new way to advance and foster technology transfer to the underdeveloped world. Open source

Fig. 6 Scheme of the kitchen synthesis. **a** Ingredients for a typical nanocrystal synthesis include: oil, vinegar, pan, crystal drain opener, and rust. **b, c** Synthesis begins with soapmaking, the first step of which is mixing the oil with the crystal drain opener and water. **d** After curing for 1 day, the soap solidifies. **e–h** For efficient dissolution in subsequent steps, the soap is ground to a fine powder (**e**), then mixed with vinegar (**f**) while heating on a stove (**g**, **h**). I, **j** Once all of the soap is dissolved, the solution forms two layers: a *yellow top* layer and a *cloudy white/yellow bottom* layer. **k** The *top* layer is the fatty acid mixture (FAM). This needs to be heated at 110°C to remove excess water and vinegar by-products. **l** Clear *yellow* FAM is collected. **m,n** Rust is scraped off of rusted metals and is ground to a fine powder. **o** FAM and rust are mixed. **p**, **q** Mixture is heated for 2 h at below and near boiling temperatures. The temperature is measured using a standard mercury thermometer. **r**, **s** Magnetite (*black*) begins to form. **t** TEM micrograph is obtained after magnetic separation in chloroform. *Scale bar*: 50 nm

Table 2 Comparison of laboratory (Lab) versus kitchen (FAM) synthesis products

Laboratory vs. kitchen synthesis	Average diameter (nm)	Standard deviation (nm)	Diffraction check
Lab 1	10.84	0.55	Magnetite
Lab 2	66.80	13.56	Magnetite
FAM 1	12.04	1.23	Magnetite
FAM 2	52.69	12.56	Magnetite

FAM Fatty acid mixture

principles can be applied to provide and improve accessibility to the technique, especially in water treatment applications. Through an interactive website (http://www.opensourcenano.net) potential partic-ipants can give feedback for the whole process after their own trials and help build a free-licensed tech-nology which will address their immediate problems, i.e., arsenic poisoning.

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