



Selective formation of copper nanoparticles from acid mine drainage using nanoscale zerovalent iron particles

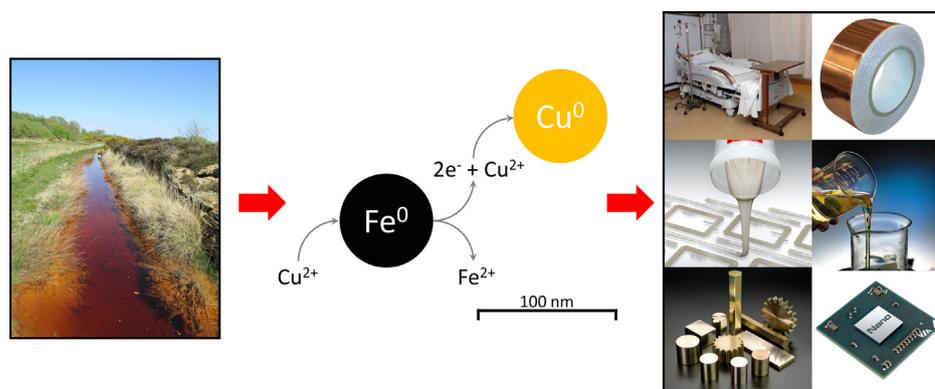
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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 May 2017

Received in revised form 4 December 2017

Accepted 5 December 2017

Available online 18 December 2017

Keywords:

Nanoscale zerovalent iron particles

Copper

Cementation

Acid mine drainage

Aluminium

ABSTRACT

Nanoscale zerovalent iron (nZVI) has been investigated for the selective formation of Cu nanoparticles from acid mine drainage (AMD) taken from a legacy mine site in the UK. Batch experiments were conducted containing unbuffered (pH 2.67 at t = 0) and pH buffered (pH < 3.1) AMD which were exposed to nZVI at 0.1–2.0 g/L. Results demonstrate that nZVI is selective for Cu, Cd and Al removal (>99.9% removal of all metals within 1 h when nZVI ≥ 1.0 g/L) from unbuffered AMD despite the coexistent of numerous other metals in the AMD, namely: Na, Ca, Mg, K, Mn and Zn. An acidic pH buffer enabled similarly high Cu removal but maximum removal of only <1.5% and <0.5% Cd and Al respectively. HRTEM-EDS confirmed the formation of discrete spherical nanoparticles comprised of up to 68% wt. Cu, with a relatively narrow size distribution (typically 20–100 nm diameter). XPS confirmed such nanoparticles as containing Cu⁰, with the Cu removal mechanism therefore likely *via* cementation with Fe⁰. Overall the results demonstrate nZVI as effective for the one-pot and selective formation of Cu⁰-bearing nanoparticles from acidic wastewater, with the technique therefore potentially highly useful for the selective upcycling of dissolved Cu in wastewater into high value nanomaterials.

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1. Introduction

Acid mine drainage (AMD) is an acidic solution that typically contains elevated concentrations of heavy metals and is caused by the microbial oxidation of pyrite and other sulphidic minerals, as

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a consequence of the mining and processing of metal ores and/or coals [1,2]. Sulphidic minerals are extremely common and consequently many effluents derived from abandoned mines and mine wastes therefore exhibit a net acidity [1]. If left untreated AMD can contaminate ground and surface water and thereby damage ecosystems and potentially impact human health. As such the generation of AMD is often cited as one of the most prominent environmental issues currently facing the mining industry [1]. For example, in the UK alone it is estimated that as many as six percent of all surface water bodies are currently adversely affected by AMD derived from legacy metalliferous mines [3]. Similarly in the USA it is estimated that as many as 19,300 km of rivers and more than 180,000 acres of lakes and reservoirs have been damaged by AMD [4]. Consequently, the development of cost-effective remediation solutions for AMD has been the subject of intense research for several decades. Despite such interest, conventional AMD remediation technologies remain relatively expensive and/or require significant construction space (e.g. passive treatment), which poses a major challenge [1]. AMD often contains a wide range of metals and metalloids which while being toxic to the environment would also be beneficial to recover (e.g. Cu, Ni, Zn). Whilst it is possible to recover metals from dilute aqueous effluents using existing active treatment technologies e.g. ion exchange [1], the absence of widespread commercial practices for the recovery of metals from AMD indicates that the economic value of the metals rarely offsets the operating costs of recovery. As such a fundamental barrier exists where either the cost of AMD treatment needs to significantly decrease or the economically valuable metals present in such waste needs to be valorised into higher-value products, i.e. products which are worth significantly more than their raw metal value. With regard to the latter, one potential solution is to develop methodologies to *directly synthesise* high-value nanomaterials from AMD. Such nanomaterials could then be directly utilised as high value materials and/or reagents in a range of different processes, and as such provide significantly greater economic return than their equivalent bulk scale metal.

In recent years, nanoscale zero-valent iron (nZVI) has gained much attention for its use in a wide range of water treatment applications due to its unique properties, including high surface area to volume ratio and an ability to be injected into the subsurface as a colloidal suspension [5–8]. To date nZVI has been demonstrated as highly effective for the removal and/or degradation of a wide range of metals and metalloids (e.g. [7,9–17]), inorganic anions (e.g. [18]) and organic contaminants (e.g. [19–21]) from solution. Very little is known, however, with regard to the physicochemical properties of metals and metalloids when sorbed and/or chemically reduced by nZVI, and in particular whether such precipitates/particles could be recovered for economic gain. In particular almost all studies to date have investigated the use of nZVI for the sorption and/or enmeshment (i.e. the immobilisation) of metal and metalloid species. In contrast the use of nZVI for the *in situ* synthesis and recovery of functional (nano)materials from wastewater or contaminated land is a new research arena. Preliminary evidence has already been presented on the formation of iron-bearing nanomaterials from AMD [22], however, to the best of our knowledge no studies have yet investigated the selective formation of heavy metal (e.g. Cu, Zn, Al) nanomaterials from AMD.

It is well known that nZVI is highly efficient for the removal of aqueous Cu under a range of different chemical conditions (e.g. [10,23] and [24]), however, the extent at which nZVI might be selective for the removal of aqueous Cu from wastewater (such as AMD) remains unknown. Furthermore very little is known with regard to the physico-chemical properties of such recovered Cu, such as whether, and if so under what conditions, discrete Cu-bearing nanoparticles might form due to the cementation reaction between aqueous Cu and Fe⁰. This study has been established in order to investigate these phenomena in order to gain an understanding of

the extent at which nZVI could be used for the selective formation of Cu-bearing nanoparticles from AMD which could prove a highly useful mechanism for the valorisation of Cu-bearing AMD, thereby unlocking a new economic incentive for AMD treatment. Such novel approaches are urgently required from addressing AMD which is one of the most prominent environmental issues currently facing the mining industry, and regarded by the European Environment Bureau and the US Environmental Protection Agency and as “second only to global warming and stratospheric ozone depletion in terms of global ecological risk” [25].

2. Methodology

2.1. AMD sampling location

The AMD used in this study was collected from Parys Mountain which is a disused open cast Cu-Pb-Zn mine on Anglesey (Wales, UK) [26]. Samples were collected from the Duffryn Adda adit (GPS location: 53°23′40.96N, 4°21′01.80W) and sealed in high-density polyethylene bottles (without headspace) and stored at 4 °C until required (maximum storage time was 7 days). The AMD initially contains low concentrations of dissolved oxygen (DO), (e.g. <2 mg/L), however, it quickly equilibrates with the atmosphere when in surface waters to reach oxygen concentrations more typical for that of vadose and/or surface waters (e.g. ~7–10 mg/L), changing its redox potential and associated heavy metal transport properties in the process.

2.2. Zero-valent iron nanoparticle synthesis

Pure nZVI were synthesised following the methodology first described by Glavee et al., [27] and then adapted by Wang and Zhang [28]. 7.65 g of FeSO₄·7H₂O was dissolved in 50 mL of Milli-Q water (>18.2 MΩ cm) and the pH was adjusted to 6.8 using 4 M NaOH. NaOH addition was performed slowly, drop-wise, to avoid the formation of hydroxo-carbonyl complexes. The salts were reduced to nZVI by the addition of 3.0 g of NaBH₄. The nanoparticle product was isolated from the aqueous phase via centrifugation (Hamilton Bell v6500 Vanguard centrifuge, 6500 rpm for 120 s), rinsed with absolute ethanol (Fisher Scientific, 12478730; ratio of 50 mL/g of nZVI) and then centrifuged (Hamilton Bell v6500 Vanguard centrifuge, 6500 rpm for 120 s). This step was then repeated three more times. The nanoparticles were dried in a vacuum desiccator (approx. 10⁻² mbar) for 72 h and then stored in an argon filled (BOC, 99.998%) MBraun glovebox until required.

2.3. Exposure of nZVI to the AMD

Prior to conducting any nZVI-AMD exposure experiments the AMD was removed from the refrigerator and allowed to equilibrate in the ambient laboratory (temperature = 20.0 ± 1.0 °C) for 24 h. Unless specified differently all batch systems comprised 200 mL volume of the AMD in 250 mL clear soda lime glass jars. Following nZVI addition the batch systems were immediately sonicated for 120 s using an ultrasonic bath (Grant, XB3). Each system was then sealed (using a screw cap) and placed on the benchtop in the open laboratory. Periodic sampling of dissolved oxygen (DO), oxidation reduction potential (ORP) and pH was conducted by gently agitating each batch system in order to ensure homogeneity. The pH, Eh and DO probes were calibrated prior to each measurement. The measured Eh values were converted to Eh (vs. standard hydrogen electrode) by subtracting the difference between the measured Eh of the reference solution (220 ± 5 mV) with the true Eh of the reference solution (Mettler Toledo 220 mV/pH 7 reference solution). 5 mL aqueous-nZVI suspensions were periodically taken using an auto-pipette. The extracted suspensions were centrifuged

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