

Synthesis, characterization and application of starch stabilized zerovalent iron nanoparticles in the remediation of Pb-acid battery soil



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ARTICLE INFO

Keywords:

Heavy metals
Nanoparticle
Speciation
Remediation

ABSTRACT

Arable and residential soils are being lost in major metropolitan cities and remote areas. The need for innovative and advanced materials that are cost effective and efficient in the environmental remediation of heavy metals continue to remain a major challenge both in developed and developing nations. In this regard, nanoparticles have received considerable attention for its potentials in the remediation of groundwater and sites. This study reports on the effect of starch supported zero-valent iron nanoparticles on Pb-acid battery soil physico-chemical properties. The starch stabilized zero-valent iron nanoparticles (nZVI-Starch) were synthesized using the chemical reduction method. The nZVI-Starch nanoparticles crystallographic, magnetic and particle size distribution properties were investigated using X-ray diffraction (XRD), physical property measurement system (PPMS) and zetasizer techniques. Composite soil samples were collected from a lead acid battery dump-site, characterized and used to evaluate effects of nZVI-Starch on the physico-chemical properties of Pb acid battery polluted soils. XRD pattern of S-ZVFe powder corresponds to that of pure nZVI-Starch nanoparticles, having an average diameter size 9.28 nm as calculated using the Debye Scherer equation. The hydrodynamic size distribution shows that the nanoparticles were mono-dispersed and superparamagnetic in nature with saturation magnetization of 27 emu/g. Speciation results showed that Zn was associated with the mobile fraction of the soil and Pb was fairly distributed in the organic, Fe-Mn, and residual fractions. After treatment of the parent soil with 1000 mg/kg of nZVI-Starch, the fractions of the heavy metals in the mobile fractions became redistributed in the less mobile/bioavailable fractions.

1. Introduction

Soil is a very important component of the ecosystem. However the contamination of the soil as a result of human activities is becoming very prevalent leading to the loss of arable and residential lands (Ugbune and Okuo, 2011). Among these very important contaminants are the heavy metals (Tangahu et al., 2011). Heavy metal pollution is difficult to deal with because they cannot be destroyed and over time and can get bioaccumulated in soils (especially soils with low pH), plants and aquatic animals, inflicting its toxicity on the environment (Ioan et al., 2008). The mere presence of heavy metals is not sufficient to say that the soil is polluted. It has to be present such that it can be taken up by an organism (Semple et al., 2004). This uptake among other parameters such as biological organism is very much dependent on the elemental speciation of the soil (Gil-Díaz et al., 2013) which in turn is governed by pH. Low pH levels of soil increases the solubility

and hence the bioavailability of cationic metals (McBride, 1994). In situ immobilization has proven to be a cheaper alternative for effectively remediating heavy metal contaminated soils and sediments (Chen et al., 2003; Zhao et al., 2009) and may provide a long term remediation solution through the formation of stable minerals or/precipitates (McGowen et al., 2001). This technique is aimed at reducing the heavy metal solubility and bioavailability without removing them from the contaminated soil (Ma and Rao, 1997). It is a technique which employs the addition of chemicals (these chemicals are sometimes referred to as amendments, additives or chemical immobilizing/stabilizing agents) to contaminated soils in order to immobilize/reduce the available fractions of the heavy metals or to change their redox state, thus effectively reducing the mobility, bioavailability and toxicity of the heavy metals in soils/sediments (Wang et al., 2009). Large particle size of the immobilizing agent can slow the reaction kinetics and as such large quantities of the immobilizing agent will be needed to effectively

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remediate a polluted site. This can lead to secondary pollution as in the case of eutrophication associated with phosphates. In regards to slow reaction kinetics mentioned earlier, nanotechnology is being developed as an extremely versatile and innovative tool in the transformation of a wide variety of contaminants (Agarwal and Joshi 2005; Gueye et al., 2015; Li et al., 2006; Yuvakkumar et al., 2011 and Zou et al., 2016).

The use of stabilized zerovalent iron nanoparticles that have been dispersed in a liquid medium can help to eliminate the limited reaction kinetics. Low concentrations of the nanoparticles are effectively able to immobilize these toxic metals because the relative small sizes (within 1–100 nm) of the nanoparticles create a larger surface area for sorption reactions. Furthermore their extremely reducing property can reduce a wide range of redox amenable contaminants to their immobile forms relatively. Their high reactivity and ability to diffuse and disperse in water, soil, sediments thus enable the nanoparticles to get to the target contaminant for effective immobilization, thereby eliminating the excessive input of the immobilizing agent and consequently reducing cost (Zhao et al., 2009). The automobile battery industry is known to be responsible for extremely large concentrations of Pb (Adie and Osibanjo, 2009). Since bioavailability is majorly determined by the soil physico-chemical properties, the primary aim of this work is thus to synthesize and evaluate the effects of starch stabilized zerovalent iron nanoparticles on the physico-chemical properties of Pb acid battery soils. The objectives of this study are: (1) Determination of the total concentration of Pb, Cr, Ni and Cd in soils samples (2) Preparation of zerovalent iron nanoparticles for the in situ immobilization of Pb, Cr, Ni and Cd. (3) Evaluation of the effectiveness of the synthetic immobilizing agents in the remediation of the contaminated soils.

2. Materials and method

2.1. Soil sampling

Soil samples were collected within the premises of Union batteries, Umunzu quarters of Otolu- Newwi, Nigeria. An area of land measuring 100 m × 100 m was partitioned into square grids measuring 10 m × 10 m. Five soil samples from the top (0–15 cm) were randomly collected from each square grid to make a composite sample. The soils were air dried, sieved through 2 mm stainless steel sieve and thoroughly mixed to ensure uniformity and then stored in polythene bags at room temperature and then tagged as the parent soil.

2.2. Characterization of soil

The parent and treated soils were characterized using standard methods. pH was measured in a 1:10 w/v mixture of soil and distilled water using a standardized pH meter. Cation exchange capacity was determined using the ammonium acetate method described by Rhoades (1982). Organic carbon and organic matter were done using Walkley–Black wet oxidation method as described by Nelson and Sommers (1982) while total heavy metals of the soil were determined by Atomic Absorption Spectrophotometer (Buck Scientific, 210 VGP) after acid digestion using the method of Chen and Ma (1999). Particle size was done using the hydrometer method (Bouyoucos, 1962). All analyses were done in triplicates and all reagents were of analytical grade

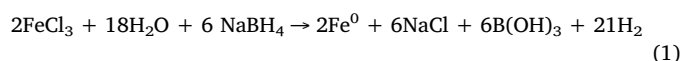
2.3. Sequential extraction of soil – sorbed heavy metals

The procedure of Ma and Rao (1997) which is a modification of Tessier et al. (1979) method as described by Iwegbue (2007), was used to obtain six operational fractions.

2.4. Preparation of nZVI-Starch

Zerovalent iron nanoparticles was prepared by modifying the methods of Rashmi et al. (2013), Selvarani and Prema (2012), Wang

et al. (2015). All aqueous solution was purged with nitrogen gas prior to synthesis and all the reactions were done in a 250 mL conical flask under nitrogen purge. 1.62 g of iron (III) chloride hexahydrate was dissolved in 24 mL deionized water; the ferric solution was then added dropwise through a syringe to a 6 mL solution of starch under simultaneous stirring to yield a 0.2% w/v of starch concentration. 0.80 g of sodium borohydride was dissolved in 50 mL nitrogen purged deionized water and was thereafter added dropwise through a syringe to the iron (III) chloride/starch complex under vigorous stirring. Slowly the solution turned black and was stirred for five minutes after all the sodium borohydride had been added. The black particles were collected using a magnet, washed via centrifugation with 50 mL of nitrogen saturated deionized water followed with washing in three portions of 25 mL absolute ethanol and then oven dried at a temperature of 60 °C for 12 h. The reaction was carried out at ambient temperature. Fe³⁺ was reduced according to Eq. (1)



2.5. Characterization of starch stabilized zerovalent iron nanoparticles

2.5.1. X-ray diffraction analysis

Powder X-ray diffraction studies were performed to determine the crystal structure of synthesized nZVI-Starch in an angle range of 25–70° on an X-ray diffractometer (Philip's X'pert Pro) with Cu K α radiation ($\lambda = 0.154$) employing an X'celerator detector and a monochromator at the diffraction beam side. Powder samples were used by employing a standard sample holder. The sizes of the nanoparticles were evaluated from XRD data using Debye-Scherrer equation (Huang and Tang, 2005), which gives a relationship between particle size and peak broadening.

$$d = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

Where d is the particle size of the crystal, k is the Scherrer constant (0.9), λ is the X-ray wavelength (0.15406 nm), β is the line broadening in radian obtained from width at half maximum, and θ is the Bragg diffraction angle of the XRD diffraction patterns.

2.6. Particle size analysis (PSA)

nZVI-Starch size was determined using dynamic light scattering (DLS) via ZETA Sizer Nanoseries (Malvern instruments Nano ZS). An aliquot (20 μL) of the synthesized starch stabilized zerovalent iron nanoparticles suspended in water (2 mgmL^{-1}) was vortexed, and sonicated for 10 min for complete dissolution. All size measurements were performed at ca. 25 °C, and all data were recorded at 90°, with an equilibration time of 5 min and individual run times of 30 s (10 runs per measurement). The average diameters described in this work are number-weighted and were collected from 3 independent measurements.

2.7. Magnetic property

The magnetic property of starch stabilized zerovalent iron nanoparticles was determined at 305 K under magnetic field up to 50 kOe using physical property measuring system (PPMS) quantum design, Dyna cool with the vibrating sample magnetometer (VSM) option, calibrated by a DyO standard. The superconducting magnets were zeroed before each non-field cooled measurement and the VSM frequency was held at 40 Hz.

2.8. Treatment of soil with starch stabilized zerovalent iron nanoparticles

0.001 g of starch stabilized zerovalent iron nanoparticles was added

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