Synthesis and characterization of magnetic nanoparticles and study their removal capacity of metals from acid mine drainage

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HIGHLIGHTS

- Increased temperature and pH resulted in well crystallised MNPs.
- Usage of NH_4OH and $NaOH$ limited incorporation of calcium and magnesium into ferrite.
- Higher degree of crystallinity of MNPs synthesised when NH_4OH was used than $NaOH$.
- Treating AMD with MNPs accelerated ferrite formation and increased magnetic moment.
- Under different conditions mixtures of ferrite MNPs were produced from AMD.

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ABSTRACT

In this study, the possibility of synthesising magnetic nanoparticles (MNPs) with and without heat from pure chemicals and real acid mine drainage (AMD) by co-precipitation method was explored. In addition, the influences of temperature, pH and stirring time on the crystalline size of MNPs were studied. The results revealed that possibility of synthesising Fe_3O_4 and $CoFe_2O_4$ from their corresponding binary salts under these conditions. Further, the method was applied on simulated and real AMD; however, formation of well crystalline MNPs at lower pH and temperature from both samples were hampered due to interfering and combined effect of the metal cations. Increasing pH and temperature increased crystalline size of synthesised MNPs as confirmed by XRD results. Similarly, these observations were further reflected by the formation of Fe_3O_4, γ-Fe_2O_3, Mn_3O_4, MnO_2 and ZnO mixtures as major components from real AMD. Treating AMD in the presence of MNP seeds accelerated formation of ferrite and resulted in increased magnetic moment of ferrite sludge. Under all conditions, higher intensity and better resolution of XRD peaks of synthesised MNPs were obtained when NH_4OH (aq.) was used for neutralization than NaOH (aq.). In general, this study demonstrates that the possibility of converting environmental pollutants into commercially valuable chemicals.

1. Introduction

Magnetic nanoparticles (MNPs) are commonly synthesised by chemical co-precipitation method either from analytical grade chemicals [1–6] or acid mine drainage [7–9]. Synthesis of MNPs is of interest because at nanoscale unique optical, electrical and other properties emerge [10,11]. MNPs have a strong capacity, fast kinetics and high reactivity for contaminant removal. The main reason is that besides their magnetic property, they have extremely small particle size and high surface area to volume ratio which enhances their chemical reactivity [12]. As the result, they can be used for multipurpose such as adsorbent and catalyst [13–19], as additive to ceramics and paint as pigment [20,21], manufacturing of electronic materials [12], drug delivery and cancer gene therapy [22]. Adsorption by MNPs and their composites have been considered as an economic and effective method used in wastewater treatment, and it is the main focus area of research for the removal of metals [10,15–17,23–25], dye removal [19,26,27], and anion reduction [28]. These researches show the wide application of MNPs in different areas. The main reasons of using MNPs for wastewater or particularly acid mine drainage (AMD) treatments are due to their ability to remove most divalent and some other trivalent metal ions. Furthermore, MNPs are highly efficient, easily applied, form stable precipitate, readily recovered by magnetic filtration and commercially important [19,29,30].

Most of them do not change in their magnetic properties upon adsorption and can be reused [17].

Minerals containing iron, copper, gold, lead, silver, mercury and zinc are manly found underground as sulphide ores deposit in enormous quantities [30]. During mining time, these minerals are exposed to atmospheric conditions and then sulphide is oxidized to sulphate and easily forms sulphuric acid of low pH, which is commonly called AMD. Composition of AMD varies widely from site to site [31]. However, high concentration of dissolved iron (II) and sulphate are the most common. Moreover, metals such as arsenic, manganese, aluminium, nickel, zinc, cobalt, and copper are commonly found in AMD [13,32].

Conventionally, AMD are treated by chemical neutralization using lime or limestone which results in huge amount of sludge. The metals in the sludge are easily released to the environment and causes potential environmental pollution. This further requires storage facilities and disposal mechanisms to minimize environmental pollution. However, the storage and disposal of sludge is very expensive because special designs are required to avoid the re-dissolution and subsequent migration of the toxic trace metals [33,34]. In order to achieve sound environmental protection and sustainable remedy, means of recovery of the valuable minerals and reuse of the resource should be developed. Thus, the main aim of this work was to investigate optimum conditions under which MNPs could be produced from analytical grade chemicals at low temperature and pH and apply optimized conditions to real AMD so as to produce commercial valuable chemicals.

2. Materials and methods

2.1. Chemicals and standards

Analytical grade chemicals of purity $\geqslant 98\%$ of $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany) were used for synthesise of Fe_3O_4 and $CoFe_2O_4$ MNPs by co-precipitation method. Inductively coupled plasma (ICP) multi-element standard containing $100\ mg\ L^{-1}$ of each metal (Ca, Mg, Ba, Al, Mn, Fe, Co, Ni, Cu, Cr, Pb, Ti and Zn) in 2–5% N nitric acid (VWR International LTD, England) was used for calibration. To adjust the pH of the solution, either 5 N NaOH (aq.) prepared from pure sodium hydroxide pellets and standardized by hydrochloric acid or 25% ammonium hydroxide solution (NH_4OH (aq.)) was used.

2.2. Synthesis of Fe_3O_4 and $CoFe_2O_4$ MNPs

For each experimental set up, required amount of salts (Fe^{3+}/Fe^{2+} or Fe^{3+}/Co^{2+} at a mole ratio of 2:1) were weighed accurately using analytical balance, dissolved by deionized water in 1.5 L volumetric flask and the pH of the solution was recorded. For each sets, six replicates of 200 mL of the solution was measured separately and added to 250 mL beaker. For comparison purpose, pHs of paired samples were adjusted to 8.5 and 11.5 by using 5 N NaOH (aq.); and in between 8.5 and 9 by using 25% NH_4OH (aq.). After which each set of pair of samples, one with heat at 60 °C and another without heat were carried out under continues stirring for 2 h. Thereafter, samples were filtered through Whatman No 1 filter paper, precipitate was repeatedly washed using deionized water until the pH of the filtrate was about 7 and dried at 105 °C in the oven for 6 h to remove water and other volatile substances adhered to synthesised MNPs. Among dried samples, four samples were selected and small part was taken and further heated at 500 °C in muffle furnace for 3 h to observe the effect of high temperature. Finally, these synthesised MNPs were stored at room temperature for further characterization and investigation of their removal capacity of metals from AMD.

2.3. Simulated AMD

Simulated AMD was prepared from $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $CrCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany). It has been observed that the concentration of metals vary from site to site, however, in this study approximate average metal concentration detected in gold mine of South Africa were used. In addition, despite the presence of high and medium concentration of calcium and magnesium in AMD of South Africa, respectively; these ions were not included into mole ratio calculation. These cations are not easily incorporate into spinal structure of ferrite. Salts were weighed to achieve a desired 2:1 mol ratio of trivalent to bivalent ions present in the spinal structure of ferrite. Accordingly, salts containing 2.90, 5.79, 0.79, 0.12, 0.16, 0.19, 0.05, and 0.05 mmol (millimole) of Fe^{2+}, Fe^{+3}, Al^{+3}, Cr^{3+}, Co^{+2}, Mn^{+2}, Ni^{+2} and Zn^{+2}, respectively were dissolved in 100 mL of ultra-pure Milli-Q water of conductivity 0.055 $\mu S\ cm^{-1}$ in 500 mL beaker and made up to a volume of 300 mL. The sample was shared into two equal portions, pH adjusted to 9 by NaOH (aq.) and NH_4OH (aq.) for the first and second samples, respectively. Each sample was heated at an average temperature of 60 °C for 2 h with continuous stirring.

2.4. Real AMD

Samples of AMD were collected from Emalahleni coal and Randfontein gold mining sites in September 2014, South Africa. The corresponding concentration of metals, pH and conductivity of each sample was initially determined using ICP-OES, digital pH and conductivity meter, respectively. In order to determine fraction of AMD possibly to be oxidized and mixed with fresh AMD, to attain 2:1 ratio of trivalent:divalent metals in the ferrite, types and concentrations of metals present in the AMD was determined. For oxidation of Fe^{2+} to Fe^{3+} 1 L of fresh AMD was taken and added into 2.5 L plastic container; its pH was adjusted in between pH 5–6 using either NaOH (aq.) or NH_4OH (aq.) and then aerated for 2 h using compressed air. At the same time, the change of pH of the solution during aeration was monitored in an interval of 10 min and adjusted by drop wise addition of the corresponding alkaline solution initially used for pH adjustment. It is worth mentioning that due to low concentration of other trace metals (trivalent or divalent) in both AMD, only $Fe^{3+}:Fe^{2+}$ ratio was considered. Further, to observe the impact of high temperature, separate experiment was conducted at a boiling point of water and stirred for 2 h after a pH was adjusted to 9 using NH_4OH (aq.).

2.5. Effect of Fe_3O_4 and $CoFe_2O_4$

Removal capacity of metals from AMD was tested by addition of 125 mg of each synthesised MNPs to 60 mL (20 mL fresh + 40 mL aerated AMD) sample and its pH was adjusted to 8.5. Duplicate set of samples, with and without heat was tested through continuous stirring for 1 h. At the same time, similar experiment was also conducted using 60 mL of fresh AMD in the presence of the same amount of MNPs. After 1 h, the reaction was stopped and sample filtered, residue dried and subjected to XRD analysis while the filtrate was analysed using ICP-OES.

2.6. Chemical analysis and characterization

Metal ions present in the filtrate were determined using ICP-OES. Magnetic moment measurement was done using Auto Magnetic Susceptibility Balance (Auto MSB) Sherwood. Powder X-ray diffraction (XRD) was used to investigate formation of MNPs. The XRD was recorded on a Rigaku Ultima IV