



Effects of cetyltrimethylammonium bromide on the morphology of green synthesized Fe₃O₄ nanoparticles used to remove phosphate

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ABSTRACT

In this paper, iron oxide nanoparticles (IONPs) are successfully synthesized using *Eucalyptus* leaf extract in the presence of cetyltrimethylammonium bromide (CTAB) to enhance the dispersion and reduce aggregation of IONPs. CTAB was used as a stabilizing and capping agent in biosynthesis of IONP was observed. The particle size decreased from 183.9 ± 30.1 nm to 89.8 ± 17.1 nm as the concentration of CTAB increased from 0 to 0.4 mM CTAB, indicating that CTAB reduce the aggregation of IONPs and enhance the reactivity. In addition, the removal efficiency of phosphate declined from 95.13% to 89.58% when the CTAB concentration increased from 0.4 to 10 mM, indicating that a CTAB impacted on micelles and lipophilic biomolecules in *Eucalyptus* leaf extract, and hence affected the formation of IONPs. Furthermore, SEM image showed that the smaller spherical with some irregularly shaped CTAB-IONPs having a diameter of 80–90 nm in the presence of 0.4 mM CTAB were observed. The data from EDS, FTIR and TGA suggested that the CTAB capped on the surface of CTAB-IONPs, while XRD showed that zero-valent iron and iron oxide were formed. Finally, the formation mechanism of IONPs was proposed.

1. Introduction

Phosphate is an essential macronutrient [1] in aquatic environments but excess phosphate can cause eutrophication and algal blooms, thereby distorting aquatic biology [2]. For some decades now, phosphate removal from wastewater has been regarded as a vital environmental sustainability problem. Various techniques, such as chemical precipitation, adsorption, biological removal, reverse osmosis, membrane, ion exchange, and constructed wetlands, have been tested for their ability to remove phosphate from wastewater [3]. Among them, phosphate adsorption is one satisfactory solution from an economic perspective of water treatment. This is due to the fact that adsorption process has stable phosphate removal outcomes and produces little sludge under simple operating conditions [3]. To date, various adsorbents have been used to remove phosphate including fly ash [4], active red mud [5], natural wollastonite [6], iron humate [7], biogenic iron oxides [8] and other waste materials [9]. In the past few decades, the synthesis of inorganic nanomaterials has made great progress and applied to various fields, particularly in medicine and biology [10]. For example, inorganic nanoparticles, due to their excellent properties, can be used as medicine in treating antibiotic resistant bacteria [11], as

versatile drug carriers [12,13], as electrochemical sensing of biomolecules [14–16]. Additionally, they have shown great potential in bioimaging and photodynamic therapy [10]. Recent times have witnessed the increasing use of engineered magnetic nanoparticles for remediation and water treatment [17,18] because of their simplicity to operation and separation [19].

Iron oxide nanoparticles, as biocompatible and recyclable magnetic adsorbents, have received much attention [20]. Currently, various chemical and physical routes are available for the synthesis of IONPs such as co-precipitation, micro-emulsion, thermal decomposition, hydrothermal and sonochemical techniques [21]. However, these methods are limited due to low production rates, high energy consumption and high cost, as well as toxicity of the used chemicals and by-products [22,23]. A suggested alternative with much potential is the green synthesis using plant leaf extract since it is generally cost-effective, biocompatible, non-toxic, and eco-friendly [22,23]. This method can convert plant waste into high-value products and realize sustainable development. In our previous study, *Eucalyptus* leaf extract containing polyphenols and flavonoids has been shown to act as a reducing and capping agent in the plant-mediated synthesis of iron-based nanoparticles (Fe NPs), including zero-valent iron and iron oxide

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nanoparticles [24]. Yet the easy agglomeration and oxidation of IONPs (especially magnetite) generally resulted in loss of reactivity. Therefore, the surfaces of IONPs are often modified to keep their stability by coating or grafting, such as silica, metal oxides, polymers and surfactants [21].

A typical cationic surfactant, namely cetyltrimethylammonium bromide (CTAB), is chosen to improve the properties of a nanomaterial. CTAB with a hydrophilic head and hydrophobic tail can serve as a capping or protecting agent for nanoparticles against external forces [24,25]. Previous studies have shown that CTAB as a capping agent can greatly inhibit particle aggregation in the synthesis of metallic nanoparticles [25,26]. Furthermore, the capping of nanoparticles with CTAB enhances the adsorption capacity owing to the interactions between surface CTAB molecules and contaminants [27]. To date, there is no report on using CTAB as a stabilizing and capping agent in the biosynthesis of IONPs to: firstly, improve their dispersion; and secondly, form the multifunctional IONPs. Therefore, we hypothesized that the size and dispersion of IONPs could be tuned by CTAB in plant-mediated synthesis, and consequently, their capacity to remove phosphate could be enhanced.

To understand the potentially useful applications of CTAB in green synthesis of IONPs, this study investigates CTAB in terms of a stabilizing and capping agent. We evaluated the reactivity between CTAB-modified IONPs and uncapped IONPs in removing phosphate from aqueous solutions. The effects of various CTAB concentrations on the ability to remove phosphate were investigated. Characterizations including SEM, EDS, XRD, FTIR and TGA were employed to demonstrate the role of CTAB in the formation of IONPs. Finally, a possible mechanism is proposed.

2. Experiment

2.1. Preparation of *Eucalyptus* leaf extract

Eucalyptus leaves (EL) were collected from a local farm in Fuzhou, China. After being thoroughly washed with de-ionized water and sundried, 15 g of EL was added to 250 mL aqueous solution and the mixture was heated at 80 °C. Then it was vacuum-filtered to obtain the extract. In making it ready for further experiments, the extract was stored at 4 °C.

2.2. Synthesis of CTAB-IONPs and uncapped IONPs

4.32 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 13.12 g of sodium acetate were dissolved in 80 mL of *Eucalyptus* leaf extract. Following this a specified amount of CTAB was added to the solution, and subsequently the mixture was stirred vigorously at 70 °C for 2 h. The color of the solution turned homogenous black, indicating the formation of IONPs colloid. After being filtered the obtained IONPs were washed with de-ionized water and ethanol, and vacuum dried at 45 °C overnight. The obtained IONPs, mainly containing magnetite and capped with CTAB were described as CTAB-IONPs. For comparison purposes, uncapped IONPs were synthesized employing the same procedure without CTAB. The formation of IONPs can be described by two steps. Firstly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ hydrolyzes to form $\text{Fe}(\text{OH})_3$ precipitate and releases H^+ ions in the proper pH at 70 °C. Secondly, $\text{Fe}(\text{OH})_3$ was partially reduced by polyphenols and flavonoids of *Eucalyptus* leaf extract to form IONPs and oxydates [28]. All chemicals used in this investigation were of analytical grade and utilized without further purification.

2.3. Phosphate removal experiment

To evaluate the removal capacity of CTAB-IONPs and uncapped IONPs, phosphate removal experiments were conducted under identical conditions. The desired phosphate solutions were prepared by diluting the KH_2PO_4 stock solution (50 mgP/L). The experiments were carried

out at an initial phosphate concentration of 20 mg/L with a sample dose of 2 g/L in 25 mL aqueous solution. Then the solutions were agitated on a rotary shaker at 25 °C and 250 rpm without any pH adjustment. Following different reaction times, they were filtered through a 0.45 μm filter paper. The concentration of phosphate was determined using a UV-Spectrophotometer (752 N, Shanghai, China) at 700 nm, which was done according to the ascorbic acid method. In addition, the amount of CTAB in the biosynthesis of IONPs was considered and a series of phosphate removal experiments in the presence of CTAB with different concentrations were executed. All the experiments were repeated in duplicate and the mean values were reported.

2.4. Characterization

The morphology, size distribution and chemical composition of CTAB-IONPs and IONPs were examined using a scanning electron microscope (SEM) (JSM 7500F, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) (Inca, Oxford Instruments, UK).

Fourier transform infrared (FTIR) spectra were collected using a FTIR spectrophotometer (Nicolet 5700, Thermo Corp., USA) with KBr as background with a range of 4000–400 cm^{-1} .

Thermogravimetric analysis (TGA) was done using a TGA analyzer (TGA-SDTA851, Mettler Toledo, Switzerland) from 30 °C to 700 °C in a N_2 flow of 80 mL/min at a heating rate of 10 °C/min.

The phase and purity of the product were determined using a X-ray powder diffractometer (XRD) (X'Pert Pro MPD, Philips, Netherlands) with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 40 mA.

3. Results and discussion

3.1. Phosphate removal experiment

As shown in Fig. 1, phosphate was removed from an aqueous solution containing an initial concentration of 20 mg/L using CTAB, IONPs and CTAB-IONPs after 60 min. In fact, 95.0% of phosphate was removed from the solution within the hour using CTAB-IONPs, while only 81.0% and 23.0% were removed using IONPs and CTAB, respectively. When pure CTAB was added, electrostatic interactions between CTA^+ and negatively charged phosphate groups induced phosphate-surfactant complex formation and phosphate removal. For uncapped IONPs, the phosphate groups were adsorbed onto the surface oxide layers just by ligand exchange, where phosphates displaced water or hydroxyls from the surface of hydrous iron oxides [20].

Meanwhile, CTAB-modified IONPs shows a higher removal

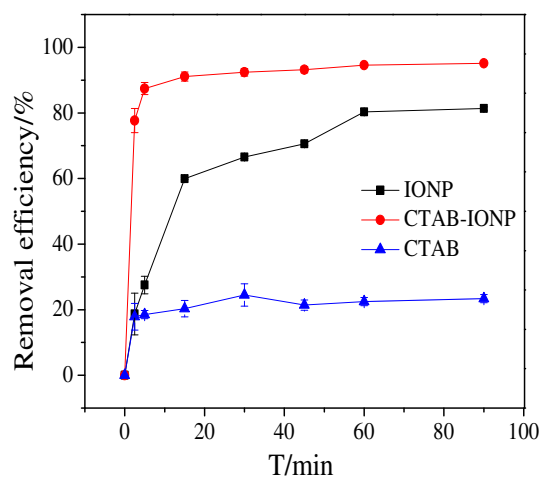


Fig. 1. Comparison of efficiency in removing phosphate using various materials. Conditions: $\text{C}(\text{PO}_4^{3-}) = 20 \text{ mg}\cdot\text{L}^{-1}$; initial pH; temperature: 298 K; CTAB = 0.4 mM; rotative speed: 250 rpm; sample dose: $2 \text{ g}\cdot\text{L}^{-1}$.

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