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Short communication

Microemulsion prepared magnetic nanoparticles for phosphate removal: Time efficient studies

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ABSTRACT

The present study investigates the effective removal of phosphate in sewage wastewater using magnetic iron oxide nanoparticles (MION). The microemulsion-prepared magnetic iron oxide nanoparticles (ME-MION) of around 7–10 nm was synthesized using *water-in-oil* microemulsion method. The interaction of ME-MION and phosphate was studied using *In situ* FT-IR technique. Batch experiments were carried out with wastewater to determine the conc. and time efficiency using ME-MION for removal of phosphate. The vibration peak at 1004 cm^{-1} and the presence of hydroxyl group (OH^-) at 3673 cm^{-1} confirms the binding of phosphate to ME-MION. ME-MION with 0.44 g L^{-1} exhibited more than 95% phosphate reduction in 5 min and close to 100% in 20 min. Conversely the experimental data obtained has been fitted with Langmuir isotherm model and also exhibited high correlation coefficients. The ME-MION was regenerated and can be reused for minimum 5 consecutive times. Efficient and fast reduction of phosphate was attained while the recovery of nanoparticles was achieved by an external magnetic field. To the author's knowledge, this is the first report that underscores around 100% phosphate removal from wastewater using ME-MION in 20 min. The approach utilized in this study offers a potential technique in the reduction of phosphate in wastewater whilst, reducing the time and reuse of nanoparticles.

Introduction

Eutrophication occurs due to excess nutrients in particular nitrogen and phosphorous into the ecosystem and it promotes immense growth of algae. Phosphorous is one of the nutrients present in sewage wastewater obtained from detergents, fertilizers, *etc.*, and thus it is important to remove phosphorus from wastewater. In general, phosphate (P) removal has been carried out by chemical precipitation or by biological process in the wastewater treatment process (WWTP) [1]. However, there are still problems in neutralization of the effluent in meeting the quality standards. Recently, physical methods such as reverse osmosis, electro dialysis, contact filtration and adsorption has also been suggested [2]. Adsorption methods could overcome these problems by offering superior means of nutrient removal in aqueous solutions. Lately, the application of low cost and easily available materials like fly ash, slag, dolomite, iron oxide, calcite, peat, mesoporous materials have been investigated for wastewater treatment [3,4]. Nevertheless, the capacity of adsorption and efficiency of the adsorbents were dependent on the materials used. For example, zirconium oxide was a suitable material for phosphate adsorption and desorption for recycling [5], whilst it is difficult for separation and calls for new methods. The unique superparamagnetic behaviour of magnetic iron oxide nanoparticles (MION) can offer a better method for the ease of separation during the treatment process with an external magnet.

The unique physical and chemical properties of the nanometer sized magnetic nanoparticles have received much attention due to their small size and large specific surface area [6–8]. The behaviour of magnetic nanoparticles strongly depends on size, surface chemistry, state of aggregation and preparation methods. Among several methods studied, microemulsion based methods seem to be powerful tool for the preparation of magnetic nanoparticles [9–11]. It can exhibit superparamagnetic behaviour and/or less susceptible to change when prepared in a controlled environment [12,13], and tailor-made desired size and surface specificity enhances their efficiency [14]. These properties make microemulsion systems unique and the most studied materials for different applications such as protein purification, water treatment, drug delivery, and as catalysts [9,15]. It has been reported that the protein-functionalized nanoparticles for the removal of suspended particles in low turbid water do not affect the ionic strength in lake

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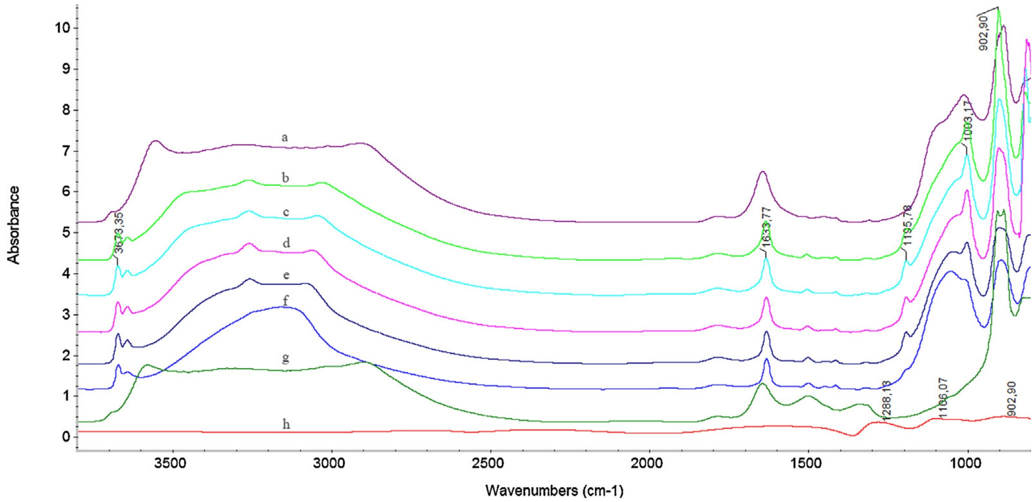

Fig. 1. FT-IR spectra of the ME-MION and phosphate interaction, (a) ME-MION+ phosphate (P) in air at room temperature (RT); (b) ME-MION+ P under primary vacuum at RT; (c) ME-MION+ P under secondary vacuum at RT; (d) ME-MION+ P at 50 °C; (e) ME-MION+ P at 100 °C; (f) ME-MION+ P at 150 °C; (g) ME-MION alone and (h) phosphate (P) alone.

water thus could be a potential water treatment agent [17]. The use of magnetic nanoparticles prepared from microemulsion based systems for the removal of P is not yet explored.

The aim of the present study is to investigate the removal of phosphate from sewage wastewater using microemulsion prepared magnetic nanoparticles (ME-MION). ME-MION was tested for optimal time required for maximum removal of P, concentration and reuse of ME-MION on phosphate removal efficiency were reported. The interaction of phosphate on to ME-MION was studied using FT-IR technique.

Materials and methods

Synthesis of magnetic nanoparticles

A detailed protocol for synthesis of ME-MION was followed as described earlier [15]. The prepared nanoparticles has the size of around 7–10 nm with surface area of 142 $m^2\,g^{-1}$ [16]. Briefly ME-MION was prepared from *w/o* microemulsion system using the single-step mode. The precursor solution containing 2:1 mole ratio of iron salts ($FeCl_3$ and $FeCl_2$) were dissolved in Milli-Q water and added to the mixture of CTAB/1-butanol/*n*-octane, resulted in the formation of a microemulsion. Formation of magnetic nanoparticles was achieved by adding the precipitating agent (aqueous NH_3) to the microemulsion upon vigorous stirring. The resultant ME-MION was washed and suspended in Milli-Q water until further use.

In situ *FT-IR study of magnetic nanoparticles with phosphate*

Fourier transform infrared spectroscopy (FT-IR; Nicolet 5700 spectrometer) was used to investigate the phosphate interaction with ME-MION. For FT-IR analysis, 100 mg of ME-MION were mixed with 1 L phosphate solution (10 mg L^{-1} of KH_2PO_4). The samples such as ME-MION alone, potassium phosphate (KH_2PO_4) alone and ME-MION with potassium phosphate (KH_2PO_4) were dissolved in de-ionized water. *In situ* FT-IR analysis was performed using a disc method with an area of 2 cm^2 by temperature measurements under the atmospheric air and vacuum conditions. All samples were recorded in the range of 4000–400 cm^{-1}.

Removal of phosphate using magnetic nanoparticles

The prepared ME-MION was tested for phosphate removal from sewage wastewater (inflow) from Hammarby Sjöstadsverk, Sweden. Initially, concentrations ranging from 0 to 0.88 g L^{-1} of ME-MION in 50 mL wastewater were tested with a mixing speed of 15 rpm for 30 min. Later 0.44 g L^{-1} of ME-MION was used to determine the time efficacy of P removal (0, 5, 10, 15, 20, 30, 40, 50 and 60 min). ME-MION was separated from the treated samples with an external magnet within 2–3 min. The phosphate content was analyzed in the samples before and after treatment using PhosVer 3 phosphate reagent pillow from HACH Company.

Recovery and reuse of magnetic nanoparticles

In order to reuse ME-MION after phosphate adsorption from sewage wastewater (0.44 g L^{-1}, 20 min mixing), the collected ME-MION+ P nanoparticles complex was dispersed in 1 mL of 0.01 M hydrochloric acid (HCl) and kept under shaking conditions for 10 min [18]. The samples were placed in to the magnet and collected the liquid and nanoparticles separately. The collected ME-MION was washed several times in de-ionised water to neutralize the acidic conditions. After washing step, ME-MION was used again with new batch of sewage wastewater for phosphate removal. The washing and reuse of ME-MION steps was repeated for five times. Removal percentage of phosphate was calculated according to Eq. (1). The experiment was performed in triplicates and reported in mg L^{-1}.

$$Reduction\,\% = \left(\frac{Initial - Final}{Initial}\right) \times 100 \qquad (1)$$

Results and discussion

In situ *FT-IR study of magnetic nanoparticles with phosphate*

The interaction study of ME-MION with phosphate was investigated using simulated water since it is difficult to analyze the interaction of ME-MION and phosphate in complex sample such as wastewater. The spectra of ME-MION alone, phosphate alone and ME-MION+ P were collected as (i) spectra in air, (ii) spectra in primary vacuum, (iii) spectra in secondary vacuum, (iv) spectra in vacuum at 50 °C (v) spectra in vacuum at 100 °C (vi) spectra in vacuum at 150 °C. The IR spectra of ME-MION alone were extracted from Okoli et al. [15]. The vibration peak at 900 and 800 cm^{-1} corresponds to the iron oxide structure and peaks at 3673, 3660 and 3625 cm^{-1} correspond to OH group (Fig. 1).