Magnetic Relaxation-Based Sensing of Phosphate Ion

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ABSTRACT

We report a novel magnetic relaxation-based sensing method for sensitive and selective detection of phosphate ions in aqueous media using paramagnetic nanoparticles. The method can detect phosphate ions at physiological pH quantitatively with high selectivity, even in a commercial fertilizer without separation.

KEYWORDS

Phosphate ion; magnetic relaxation; paramagnetic nanoparticles

1. Introduction

Phosphate anion is one of the most abundance species on the earth surface, and plays vital roles in living systems [1]. It is crucial for many biological processes. Yet high amounts of phosphate can disrupt the balance of the ecosystem [2,3]. Uses of phosphate-containing fertilizers and detergents are the main sources of the increase of phosphate concentration in the environment [4-6]. Pollution from phosphate and phosphorylated compounds is one of the main reasons for the eutrophication of natural water sources, which is leading to a dangerous increase in the toxic algal blooms [7]. According to US EPA, accelerated eutrophication is one of the major problems facing the Nation's lakes and reservoirs [8]. Depletion of dissolved oxygen as a result of eutrophication due to the overabundance of phosphate in water can subsequently cause a variety of problems, including low water quality and death of aquatic life [9-11].

Therefore, there is an ongoing need for sensors that can determine phosphate concentrations accurately and preferably in real-time. The need of phosphate ion sensors in the field of environmental, industrial, and medicinal analysis is driving researchers to develop new methods for the fast, accurate, reproducible, and selective detection of phosphate over a wide range of concentrations in various samples with sufficient sensitivity [12-15]. Thus far, there have been many kinds of methods for the determination of phosphate, including electrochemistry [16], UV-vis spectroscopy [17], chromatography [18], fluorescence spectroscopy [19], and enzymatic biosensors [20]. However, most of these methods use organic solvents as the detection media. The detection of phosphate in aqueous solutions, hence, remains a challenge [21].

Nuclear magnetic relaxation (MR) based sensing has been one of the emerging methods that promise fast and reliable results for detection of targets in aqueous solutions using nuclear magnetic resonance (NMR) relaxometer [22-25]. These methods are based on the use of surface-functionalized magnetic nanoparticles (MNPs), typically superparamagnetic iron oxide nanoparticles, to detect specific

targets in a variety of mixture without any separation or washing steps [26]. Interaction of targets with MNPs leads to a significant change in the transverse relaxation time (T_2) of water protons in the solution [27-30].

Paramagnetic metal ions, such as Gd^{3+} , Fe^{3+} , Mn^{2+} , Mn^{3+} and Cu^{2+} , in aqueous solutions can affect the longitudinal (T_1) and transverse (T_2) relaxation times of the surrounding water protons. Their chelates can serve as contrast agents in magnetic resonance imaging (MRI) [31-33]. In our previous study, we showed that nanoparticles with chelated paramagnetic metal ions could also be used for MR-based sensing [34]. Compared to the more commonly used superparamagnetic iron oxide nanoparticles, such nanoparticles are less likely to become aggregated, which would affect the detection.

Herein we report a nuclear magnetic relaxation based method that can detect phosphate ions in aqueous solution without separation. Unlike our previous study, where Fe^{3+} ions served as the paramagnetic agents, Gd^{3+} ions are used in this work, taking advantage of their high magnetic moment and good stability at physiological pH [35,36].

2. Materials and methods

2.1. Chemicals and materials

(Trimethoxysilylpropyl)ethyldiaminetriacetic acid trisodium salt (TMS-EDTA) (35 wt% solution in water) was purchased from Gelest. Tetraethylorthosilicate (TEOS), Triton X-100 (TX-100), n-hexanol, cyclohexane, ammonium hydroxide (30 wt%), gadolinium (III) chloride hexahydrate, KH_2PO_4 and glacial acetic acid were from Sigma-Aldrich. Fertilizer (Schultz Expert Gardener) was purchased from a local store. All chemicals were used without further purification. Deionized (DI) water (18 M Ω -cm) was used for the preparation of all solutions.

2.2. Synthesis of Gd^{3+} -chelated SiO_2 nanoparticles ($SiO_2@TMS-EDTA@Gd^{3+}$)

Paramagnetic $\text{SiO}_2\text{@TMS-EDTA@Gd}^{3+}$ nanoparticles were prepared in two steps following a modified version of the previously published protocol [34]. First, $\text{SiO}_2\text{@TMS-EDTA}$ nanoparticles with EDTA groups on surface were synthesized by mixing 1.77 g Triton X-100, 7.5 mL cyclohexane, 1.6 mL n-hexanol, and 480 μL DI water in a glass vial and stirring for 5 min to form a microemulsion system. Next, 60 μL of NH_4OH was added to the microemulsion and stirred for 20 min, followed by the addition of 50 μL TEOS. The mixture was stirred at room temperature for 24 h. Then, 50 μL of TEOS was added to the microemulsion and stirred for 30 min, and finally 25 μL of TMS-EDTA was added, followed by another 24 h stirring. Subsequently, approximately 20 mL of acetone was added to disrupt the microemulsion system. $\text{SiO}_2\text{@TMS-EDTA}$ nanoparticles were recovered by centrifuging the mixture at 14000 rpm for 20 min, and then washed three times with acetone, ethanol and DI water, respectively. The resulting $\text{SiO}_2\text{@TMS-EDTA}$ nanoparticles were dispersed in DI water. The $\text{SiO}_2\text{@TMS-EDTA}$ nanoparticles were mixed with excess amount of 0.1 M GdCl_3 solution and stirred overnight at 40 $^\circ\text{C}$. The resulting $\text{SiO}_2\text{@TMS-EDTA@Gd}^{3+}$ nanoparticles were washed three times with DI water and then dispersed in 20 mM of tris buffer (pH 7.5) for storage.

2.3. Characterizations of nanoparticles

TEM measurements were done on a Biotwin 12 transmission electron microscope. The amount of Gd^{3+} ions in $\text{SiO}_2\text{@TMS-EDTA@Gd}^{3+}$ nanoparticle solution was determined by ICP-MS. The quantification was carried out by external five-point-calibration between 10 and 10,000 $\mu\text{g/L}$ GdCl_3 in HNO_3 (3% v/v). GdCl_3 stock solutions were diluted with 3% HNO_3 solution to relevant concentration levels. Separately, 0.1 mL of $\text{SiO}_2\text{@TMS-EDTA@Gd}^{3+}$ nanoparticle sample was mixed with 0.9 mL of 1M HCl:NaF (1:1) solution, and heated at 80 $^\circ\text{C}$ overnight to fully digest the silica nanostructures and release Gd^{3+} ions. The resulting sample was further diluted using 3% HNO_3 solution for measurements, which were carried out on an Agilent 7700 CE inductively coupled plasma mass spectrometer.

2.4. Nuclear magnetic relaxation measurements

Transverse relaxation times (T_2) were measured at 1.41 T on a Bruker Minispec mq60 relaxometer operating at 40 °C. For the nuclear magnetic relaxation measurements, Carr-Purcell-Meiboom-Gill (CPMG) spin-echo pulse sequences were used to limit the effect of magnetic inhomogeneity of instrument [31].

2.5. Detection of phosphate ions

KH_2PO_4 stock solution was first prepared, and serially diluted. In a typical run, T_2 measurements of the $\text{SiO}_2@\text{TMS-EDTA}@Gd^{3+}$ nanoparticles in tris buffer (pH 7.5) were first taken at 40 °C. Then, KH_2PO_4 samples were added to the $\text{SiO}_2@\text{TMS-EDTA}@Gd^{3+}$ nanoparticle solution and incubated for 6 h at 40 °C before the T_2 measurements were taken again. To test the specificity of the sensing method, several $\text{SiO}_2@\text{TMS-EDTA}@Gd^{3+}$ nanoparticle solutions were prepared in tris buffer. Then 1 mL solutions containing 0.1 M of CO_3^{2-} , acetate, Cl^- , F^- , NO_3^- , H_2PO_4^- and SO_4^{2-} , respectively, were prepared and added to each of the $\text{SiO}_2@\text{TMS-EDTA}@Gd^{3+}$ nanoparticle solutions to reach an anion concentration of 4 mM in each sample. T_2 measurements were taken after 6 hr of incubation.

In the case of determining phosphate ions in fertilizer, one gram of fertilizer was dissolved in DI water and then serially diluted. Fertilizer samples were introduced to the $\text{SiO}_2@\text{TMS-EDTA}@Gd^{3+}$ NPs in tris buffer. After incubation for 6 hr, T_2 measurements were taken.

3. Results and discussion

The principle of the sensing scheme is shown in Figure 1. Gd^{3+} chelates are the most commonly used contrast agents in magnetic resonance imaging (MRI) thanks to their high magnetic moment. In our design, Gd^{3+} ions are chelated and stabilized by the EDTA groups grafted on the surface of silica nanoparticles (SiO_2 NPs). The chelated Gd^{3+} ions are stable around physiological pH without forming

the insoluble Gd^{3+} oxides. These Gd^{3+} ions would affect the relaxation rate of the surrounding water protons due to their access to water protons. Phosphate ions have strong affinity to Gd^{3+} ions [37-39] due to the thermodynamic stability of hard acid-hard base interaction. The presence of phosphate ions would bind to the Gd^{3+} ions, disturbing their access to water protons and subsequently resulting to the change in the T_2 relaxation time of water protons in the solution. By monitoring the change of T_2 of water protons we can quantitatively detect phosphate ions.

[Figure 1]

The synthesized $\text{SiO}_2@\text{TMS-EDTA}@\text{Gd}^{3+}$ nanoparticles were characterized by a number of techniques. The average diameters of the $\text{SiO}_2@\text{TMS-EDTA}$ nanoparticles are ~60 nm according to transmission electron microscopy (TEM) as shown in **Figure 2**. The amount of Gd^{3+} ions in the $\text{SiO}_2@\text{TMS-EDTA}@\text{Gd}^{3+}$ nanoparticle stock solution was quantified using ICP-MS and determined to be 0.52 mg/mL.

[Figure 2]

The transverse relaxivity (R_2) of the $\text{SiO}_2@\text{TMS-EDTA}@\text{Gd}^{3+}$ nanoparticles is determined by measuring the transverse relaxation times (T_2) of water protons of solutions containing different concentrations of $\text{SiO}_2@\text{TMS-EDTA}@\text{Gd}^{3+}$ nanoparticles. As shown in Figure 3, R_2 of the $\text{SiO}_2@\text{TMS-EDTA}@\text{Gd}^{3+}$ nanoparticles is calculated to be $203.2 \text{ mM}^{-1}\text{s}^{-1}$, which is much higher than the clinically used Gd-DTPA complex ($4.6 \text{ mM}^{-1}\text{s}^{-1}$) [40]. This is likely attributed to that the chelation with the pentadentate TMS-EDTA [41] leaves Gd^{3+} ion, which tends to form complexes with a

coordination number of nine [42], with more available coordination sites to interact with water protons [43], as compared to the chelation of Gd^{3+} ion with DTPA.

[Figure 3]

The percentage change of T_2 relaxation time ($\Delta T_2\%$) upon the binding of phosphate ions to $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles is calculated using the following equation [42,44]:

$$\Delta T_2\% = (T_{2,target} - T_{2,blank}) \times 100 / T_{2,blank}$$

where $T_{2,blank}$ and $T_{2,target}$ is the average T_2 relaxation time of three replicates of nanoparticle solution before and after the addition of phosphate ions, respectively.

We first test the working principle of this sensing method using pure KH_2PO_4 as the phosphate source. As shown in Figure 4, a significant increase in $\Delta T_2\%$ occurs as a result of phosphate addition to the nanoparticle solution in tris buffer. A linear relationship between $\Delta T_2\%$ and phosphate concentration is observed in the μM range with a correlation coefficient (R^2) of 0.9999 and a detection limit of 0.1 μM .

[Figure 4]

To examine the specificity of this sensing method, the change in T_2 relaxation time of water protons, as a result of interaction of $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles with various common anions, including CO_3^{2-} , acetate, Cl^- , F^- , NO_3^- , $H_2PO_4^-$ and SO_4^{2-} , was measured under the same conditions. The final concentration of all anions was set at 4 mM. Results are shown in Figure 5. Notice

that only phosphate ions cause a significant increase in $\Delta T_2\%$, while F^- ions can slightly affect the $\Delta T_2\%$. All other anions have negligible effect.

[Figure 5]

To test the utility of this sensing method in a complex matrix for actual applications, commercial phosphate-containing fertilizer was used in this study. The fertilizer contains the following ingredients as labeled: total nitrogen 20%, available phosphate 30%, soluble Potash 20%, chelated iron 0.1%, chelated Mn 0.05%, and chelated Zn 0.05%. Results shown in Figure 6 demonstrate that $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles can detect phosphate content in the fertilizer quantitatively. A linear relationship between the concentration of phosphate in the fertilizer and $\Delta T_2\%$ is observed in the μM range with a correlation coefficient (R^2) of 0.995 and a detection limit of 0.5 μM . We note that the phosphate in the fertilizer was directly measured in the complex matrix without separation.

[Figure 6]

4. Conclusions

In summary, we report a sensitive and specific sensing method to detect phosphate ions in aqueous media using the $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles. The $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles have excellent water dispersibility and colloidal stability at physiological pH, which allows their use in biological systems. The Gd^{3+} ions in the $SiO_2@TMS-EDTA@Gd^{3+}$ nanoparticles serve as both the contrast agent for nuclear magnetic relaxation and the phosphate recognition element.

The method has high selectivity towards phosphate ions over many other common anions. We also demonstrate that it can detect phosphate in fertilizer quantitatively with a detection limit of 0.5 μM without separation. The results pave way for further development and usage of similar types of paramagnetic nanoparticles for nuclear magnetic relaxation based sensing.

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Figure caption

Figure 1. Schematic representation of the detection mechanism. Phosphate binding to SiO₂@TMS-EDTA@Gd³⁺ nanoparticles leads to the increase of T₂ relaxation time of water protons.

Figure 2. TEM images of the SiO₂@TMS-EDTA@Gd³⁺ nanoparticles. Scale bar is 100 nm.

Figure 3. R₂ relaxivity measurement of SiO₂@TMS-EDTA@Gd³⁺ nanoparticles.

Figure 4. ΔT₂% as a function of phosphate concentration in tris buffer.

Figure 5. Specificity test of the phosphate sensing. ΔT₂% after adding various anions to the SiO₂@TMS-EDTA@Gd³⁺ nanoparticle solution at pH 7.5.

Figure 6. ΔT₂% as a function phosphate concentration of fertilizer in tris buffer.

Novelty statement:

We report a novel nuclear magnetic relaxation-based sensing method for sensitive and selective detection of phosphate ions in aqueous media, which can quickly detect phosphate ions at physiological pH quantitatively, even in a commercial fertilizer without separation.

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