Title: \( p \)-Phosphonated calix\([n]\)arene stabilized superparamagnetic nanoparticles for nitrate and phosphate uptake

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**Abstract:** Highly faceted superparamagnetic magnetite nanoparticles ~11 nm in diameter are readily accessible in the presence of p-phosphonated calix[n]arenes of different ring sizes (n = 4, 5, and 6), using a simple co-precipitation technique. In contrast, the larger calixarene, n = 8, affords spherical particles, of comparable size. The maximum magnetization is 70-60 emu g⁻¹ which decreases with increasing size of calixarene macrocycle, and the evidence supports the calixarenes binding to the surface of the nanoparticles via the phosphonate head groups rather than the phenolic oxygen centers. The stabilized nano-particles show dual functionality, in removing up to 62% of nitrate-nitrogen and 48% of phosphate from an aqueous effluent after 24 hours at only 1 g L⁻¹ concentrations of calixarene-coated nanoparticles.

**Introduction**

Nitrates and phosphates are common contaminants in effluent outflows and run off into water bodies, and their presence are critical factors in the phenomenon of eutrophication, which leads to toxic algal blooms, hypoxia and deterioration of natural waterways. Excessive amounts of nitrates in drinking water obtained from ground water can lead to health problems, particularly in infants and are potential carcinogens. The United States Environmental Protection Agency (EPA) sets the maximum level of nitrate-nitrogen [NO₃⁻]⁻ content below 10 mg L⁻¹.

Removal of highly soluble nitrate ions from liquid effluents is inherently difficult, with several methods established. These can be generally categorised into five types: ion exchange, reverse osmosis, adsorption, chemical destruction and biological processing. Ion exchange and biological processing are favoured by the World Health Organisation (WHO), while reverse osmosis and ion exchange are part of the best practices of the US EPA.

Each method has limitations in costs and waste. Ion exchange and reverse osmosis both produce highly saline by-products. While ion exchange has 8 times lower operational costs than reverse osmosis methods, the resin used in the process requires regular regeneration. In addition, ion exchange is less effective with waters containing organic compounds and solid particulates. Biological methods require careful control of waste water environments, removal of micro-organisms and biomass waste disposal/recycling, requiring much more complex treatment plants and monitoring.

Adsorption methods, where contaminants are adsorbed onto substrates, are usually simple, convenient and inexpensive. Adsorption techniques are similar to ion exchange and they typically use clays, zeolites and plant matter rather than specialist resins. Wastes are dependent on the adsorbent used. Many adsorption technologies can be regenerated and reused or recycled for other purposes.

Recently we established that graphite exfoliated by p-phosphonated calix[8]arenes (PCalix[8]) is effective in removing nitrate from waste water which involves nitrate binding to PCalix[8]. p-Phosphonated calix[n]arenes, n = 4, 5, 6 and 8 (PCalix[n]), Figure 1, are non-toxic and water soluble, depending on pH. They are versatile, being used as surfactants, agents for drug delivery, 2D material exfoliation and nanoparticle stabilisation.

**Figure 1:** Structure of p-phosphonated calix[n]arene.

In general, the high surface area of nanoparticles or nanosheets is advantageous in creating a large surface area for small amounts of material. However, small particles aggregate readily as they are more strongly affected by small electric and magnetic forces. Superparamagnetic magnetite nanoparticles have been used in a variety of applications, with superparamagnetism typically observed in magnetite for nanoparticles < 20 nm in diameter. Superparamagnetism is caused by the ferromagnetic magnetite domains becoming so small that they can no longer hold their magnetic alignments. However, once placed into a magnetic field, the particles align perfectly. Superparamagnetic particles are more stable and less likely to form clusters under applied magnetic fields than larger particles. This is particularly important with repeated use in ion adsorption technology as aggregation reduces the active surface area of the particles.
Change in properties with size is a defining characteristic of nanoparticles and it requires that the particle size distribution is carefully controlled. High temperature decomposition methods can produce very small monodispersed particles of magnetite. However, these methods often require further processing to make the nanoparticles water soluble and non-toxic for the ensuing applications.\textsuperscript{[19]} Aqueous co-precipitation methods can be simple, low cost and environmentally friendly.

Control over the size distribution of the nanoparticles requires careful choice of precursor salts, namely the ratios of iron(II) and iron(III), and the pH.\textsuperscript{[20]} However, aqueous co-precipitation methods are limited by difficulties in reproducibility, and indeed the mechanism of formation is only now beginning to be understood.\textsuperscript{[21]} The lack of control over the size arises from the tendency of the particles to aggregate. This can be overcome by using surfactants and polymer stabilisers such as $p$-sulfonated calixarenes,\textsuperscript{[22]} thereby improving their potential use in a variety of applications.

Magnetite alone has been studied as a potential adsorbent material. It is effective for the removal of heavy metals\textsuperscript{[23]} and heavy metal oxides. Iron oxide particles have also been used to adsorb orthophosphates\textsuperscript{[23c, 24]} which, like nitrates, are linked to eutrophication. Binding of such ions in an aqueous environment is a surface process, being more favoured for smaller sized nanoparticles with large surface areas and associated improved adsorbance and rates of reaction.\textsuperscript{[25]}

Importantly the magnetic properties of magnetite nanoparticles allow for collecting them via a magnetic field for reuse, for both nitrate and phosphate uptake. The focus of this research is on the synthesis and characterisation of superparamagnetic nanoparticles including a simple co-precipitation method involving $p$-phosphonated calix\textsuperscript{n}arenes. In addition, the efficacy of this material has been tested for the removal of nitrate and phosphates from aqueous solutions.

**Results and Discussion**

All the PCalix\textsuperscript{n} ring systems studied herein, $n = 4, 5, 6$ or 8, produced stable solutions at 0.025 mM, 0.0025 mM and 0.00025 mM calixarene concentrations. In the following sections the PCalix\textsuperscript{n} coated magnetite nanoparticles are characterised and their nitrate and phosphate adsorption capabilities tested.

X-ray powder diffraction confirmed that magnetite was produced when PCalix\textsuperscript{n} was used as a surfactant (Figure 2). This was demonstrated by the strong characteristic peaks shown in Figure 2 at 30.3$^\circ$, 35.7$^\circ$, 43.2$^\circ$, 54$^\circ$, and 57.1$^\circ$. These peaks have been previously assigned to the (220), (311), (400), (422) and (511) crystal planes, respectively.\textsuperscript{[26]} The very broad peak between 20 2$\theta$ and 30 2$\theta$ in Figure 2 does not align with literature spectra of magnetite and is ascribed to the presence of amorphous material.\textsuperscript{[27]}

![Figure 2: XRD powder pattern for magnetite nanoparticles synthesised in the presence of 2.5 mM PCalix\textsuperscript{4} compared with a standard spectrum](image)

As shown in Figure 2, the characteristic XRD peaks are broad which is related to small particle sizes according to the Scherer equation.\textsuperscript{[28]} The particle size as estimated by the Scherer equation using the intense (311) peak gave an average nanoparticle diameter of 10.9 nm.\textsuperscript{[29]} This suggests that the particles produced via this process are well within the size regime necessary for superparamagnetism.\textsuperscript{[29]}

As shown in Figure 3, the FTIR of the generated materials show additional characteristic bands corresponding to the expected bands for PCalix\textsuperscript{n}, confirming their presence in the bulk samples. The spectra of pure PCalix\textsuperscript{n} and surface bound PCalix\textsuperscript{n} are similar, except for two notable differences. First, the strong C-O absorption band at 1280 cm$^{-1}$ for free PCalix\textsuperscript{n}\textsuperscript{[29] is not present in the spectra.
observed for surface bound PCalix[n]. Second, the broad P-O absorption band at 980-880 cm⁻¹ in the unbound calixarene shifts to higher wave numbers and was split into two peaks at 1040 and 980 cm⁻¹. This is consistent with the PCalix[n] being attached to the surface.[30]

FTIR can also determine how the calixarene binds to magnetite. For instance, it has been shown that p-sulfonated calixarenes (SCalix[n]) bind to the surface of magnetite through the phenolic oxygen centres.[20] However, in comparison to sulfonate the binding of phosphate to iron oxides is much stronger[31] and hence it is unlikely that the PCalix[n] binds in the same way as the SCalix[n]. This is further implied by the three bands at 1116, 1040, and 980 cm⁻¹ which align with literature for hydrogen orthophosphate binding to an iron oxide surfaces.[30, 32] In contrast SCalix[n] has a strong 1460 cm⁻¹ which shifts to 1400 cm⁻¹, and strengthen, when exposed to iron oxide. This was not evident for PCalix[n].[32] Thus, the shifts in the P-O band are consistent with binding via the phosphate head group of the calixarene rather than the lower rim phenolic tail.

Transition Electron Microscopy (TEM) was used to establish the shape and size of the magnetite particles. Figure 4 shows that three basic morphologies are present, namely amorphous material, faceted particles and spherical particles. As depicted in Table 1 and shown in Figure 4a, amorphous material was produced at a PCalix[4] concentration of 0.25 mM. Hence, this concentration was not tested for the other PCalix[n]. The amorphous material is probably a complex of iron (II/III) with PCalix[4]. Complex formation has been previously observed for PCalix[4] in the presence of calcium ions.[33] Furthermore, it has been previously been reported that PCalix[4] prevents the precipitation of barium sulphate even when it is at low concentrations.[34] Hence, at 0.25 mM in the present study (PCalix[n] to Fe(II)/Fe(III) ratio of 1 to 100) complex formation appears to prevail over particle production.

A PCalix[n] concentrations of 0.025 mM and 0.0025 mM for PCalix[4], [5] and [6] produced faceted particles (Figure 4 b-c and Figure 5 b-c). However, as shown in Figure 5b, there was a mixture of faceted and non-faceted particles for PCalix[5]. A high resolution TEM image for particles produced with 0.0025 mM PCalix[4] is shown in the supplementary information (Figure S1). At the lowest concentration of 0.00025 mM, all PCalix[n]s produced spherical particles (Figure 4d), although, PCalix[4] still produced some faceted particles. As shown in Figure 5a, in the absence of PCalix[n] only spherical particles were formed.

Strongly faceted particles of magnetite are uncommon due to a greater surface energy in comparison to spherical particles.[35] The mechanism of the shape direction in this case likely occurs through the partial oxidation of the surface by the phosphate functional groups.[30] The surface oxidation then causes a surface rearrangement to a more densely packed surface and the formation of facets.[36]

Thus, the lowest concentration tested was presumed to be too low to oxidise the magnetite surface sufficiently for the onset of the rearrangement into faceted particles.

Unlike the smaller PCalix[n], the largest macrocycle studied, PCalix[8], did not appear to exert shape control over the crystal growth with the concentrations studied. This result was unanticipated given the ability of PCalix[8] to preferential order on the surface of graphene[12] and direct the growth of ultra-small faceted nanoparticles of platinum.[134] The conformational flexibility of the large ring presumably promotes its interactions with the flat surfaces of carbon materials[96-97] However, PCalix[8] has greater conformational flexibility compared to that of the smaller PCalix[n]s, and this possibly relates to the difference in the morphology of the magnetite. Such conformational flexibility of PCalix[8] may result in less specific binding stabilising a less dense magnetite surface, thereby preventing surface rearrangement that results in faceted particles.[30]

Figure 4: TEM images of nanoparticles synthesised in the presence of PCalix[4] at (a) 0.25 mM, (b) 0.025 mM, (c) 0.0025 mM, and (d) 0.00025 mM.

Table 1: Particle shapes for different concentrations of each PCalix[n] tested where ■ represents faceted particles and ● represents spherical particles (determined using TEM).

<table>
<thead>
<tr>
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<tr>
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<td>N/A</td>
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<tr>
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<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
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<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>0.00025</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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</table>
Table 2: Particle size measurements from TEM images, showing the number of particles measured, mean, standard deviation, median size and maximum size in nanometres.

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<tr>
<th>Coating</th>
<th>Number</th>
<th>Median (nm)</th>
<th>Mean (nm)</th>
<th>Standard deviation (nm)</th>
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</thead>
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<td>10.39</td>
<td>10.63</td>
<td>2.5</td>
</tr>
<tr>
<td>PCalix[5]</td>
<td>1365</td>
<td>10.65</td>
<td>11.02</td>
<td>2.46</td>
</tr>
<tr>
<td>PCalix[8]</td>
<td>1385</td>
<td>10.83</td>
<td>11.04</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Figure 5: TEM images of magnetite nanoparticles synthesised in the absence of PCalix[r] (control), (a) and in the presence of 0.0025 mM PCalix[5], (b), 0.0025 mM PCalix[6], (c) and 0.0025 mM PCalix[8], (d).

Particle size measurements were taken from TEM images produced in the presence of 0.0025 mM PCalix[r] (Table 2). As shown in Table 2, all of the particle diameters were well below the 20 nm threshold for induction of superparamagnetism in magnetite. Table 2 also shows that there does not appear to be a significant difference in particle size produced by the different PCalix[r] used in the magnetite synthesis. Thus, it appears that the PCalix[r] mainly exerted shape control and not size control over the synthesis.

Magnetic properties of the synthesised particles are important for the efficiency of magnetic collection. The magnetic properties of the samples were measured using two techniques: the results of which are shown in Figure 6. First is a hysteresis loop, Figure 6 (a), which shows the magnetic response of particles to a changing applied magnetic field. The magnetic field is measured first in the direction negative to positive then reversed from positive to negative. Figure 6 (a) shows a characteristic S shaped hysteresis loop of superparamagnetic nanoparticles, and this was the case for all samples.

The maximum value seen in the hysteresis loop is the magnetic saturation. It signifies the strength of the response to an applied magnetic field and hence is a description of the ease of nanoparticle collection. The magnetisation saturation for PCalix[4] stabilised magnetite particles at room temperature was 73 emu g⁻¹. The magnetic saturation of the magnetite particles increased with a decrease in size or increase in rigidity (less conformational mobility) of the calixarene ring: PCalix[8] 64 emu g⁻¹, PCalix[6] 66 emu g⁻¹ and PCalix[5] 68 emu g⁻¹. Particles prepared in the absence of PCalix[r] had a maximum magnetism of 68 emu g⁻¹ (Supplementary information, Table 1). However, the accuracy of the magnetic saturation measurements for the uncoated control, PCalix[5] and PCalix[8] samples was limited, with the calculated mass of magnetite greater than the measured mass of the sample by 0.5-0.7 mg (supplementary information, Table S2). The method of determining the mass of magnetite in the sample assumes all iron present is in the form of magnetite. However, this is not the case. The additional iron is probably in the form of Fe-PCalix[r] complexes.[33]

The measured magnetic saturation was lower than for bulk magnetite at 92 emu g⁻¹,[216] but is still considered good for small nanoparticles.[38] Small nanoparticles exhibit low magnetic saturation due to broken bonds, substitutions and defects on the surface.[39] As particles get smaller the proportion of surface atoms gets greater and the effect of these surface anisotropies is to increase the magnetic anisotropy of the whole material.[40] The strong binding of the PCalix[r] to the surface helps to order the surface of the nanoparticle reducing vacancies.[30] It also acts as an inhibitor for further oxidation.[41] However, given the errors in mass measurement no improvement in magnetic saturation over uncoated magnetite can be considered significant.

The second measurement performed is the zero field cooled curve (ZFC) magnetic measurement technique seen in Figure 6 (b). It measures the energy required to align the magnetic domains within the materials by measuring the internal magnetism as the temperature is raised from 5K to room temperature. For superparamagnetic nanoparticles the measured response of particles cooled in the presence and absence of a magnetic field should meet at low temperatures. A meeting of the curves indicates a low energy barrier for alignment of internal magnetic fields with an applied field and therefore the absence of multiple domains and magnetically disordered domain walls. Energy barriers reduce the speed of response of a magnetic material to an applied magnetic field.
As can be seen in Figure 6b, the ZFC was still below that of the field cooled (FC) control at room temperature. Typically, this is due to the presence of larger multi domain particles in the sample. However, the TEM images and size measurements did not agree with this result. Also of note is that the measured particle size was within one standard deviation of that measured by XRD. This implies that the particles measured by TEM were representative of the bulk sample. The gap between the maximum of the ZFC and the FC has been reported to be due to particle-particle interactions.[42]

![Figure 6: Magnetic measurements on 0.0025 mM Pcalix[4] coated magnetite (Top) Hysteresis loop at 300K, and (Bottom) 9K ZFC curve compared to a FC curve.](image)

The ability to instantly retrieve the superparamagnetic magnetite nanoparticles stabilized by the different calixarenes using a magnet (neodymium magnet 1.33 Tesla) is highlighted in Figure 7. This is before and after the adsorption of nitrates and phosphates for potential reuse. However, a centrifugal technique, detailed in the experimental section, was used to remove magnetite nanoparticles before analysis.

As shown by Figure 8 all of the magnetite samples tested successfully removed nitrate from the effluent. Furthermore, according to the nitrate adsorption tests PCalix[8] coated magnetite removed significantly more nitrate-nitrogen compared to the uncoated magnetite (Figure 8). Although the uncoated magnetite sample initially adsorbed the nitrate at a similar rate to the coated samples it began to release the nitrate back into the effluent after only 6 hours, removing a total of 8% of the nitrate-nitrogen after 24 hours which is in agreement with literature.[43] The PCalix[8] performed significantly better than the uncoated material and slightly better than the other Calix[n] removing 62% (25 to 10 mg/L) of the nitrate-nitrogen from the effluent, followed by PCalix[5] at 51%, PCalix[6] at 47% and finally PCalix[4] at 46%. The PCalix[8] also effectively adsorbed enough nitrate-nitrogen for the effluents nitrate nitrogen concentration to drop below the 10 mg/L EPA limit for drinkable water after less than 24 hours.

PCalix[n] coated magnetite was also tested on its ability to remove orthophosphates from water (Figure 8). The tests revealed that uncoated magnetite has similar phosphate removal capabilities to the PCalix[n] coated magnetite. These results indicate that the phosphate removal is primarily associated with the presence of iron-magnetite rather than the presence of PCalix[n] coatings. The average removal of phosphate was around 43%, which agrees with the literature value for phosphate removal of uncoated magnetite at pH 7.[44] Although, this test does not show differentiation between materials tested, it demonstrates that the Calix[n] can effectively remove both nitrate and phosphate from the same effluent. The best performing sample, PCalix[8], adsorbed 62% of the nitrate-nitrogen as well as 48% of the phosphate in the combined nitrate and phosphate effluent.

An understanding of the affinity of PCalix[8] towards nitrate ions has been investigated in earlier work using molecular modelling with graphene.[12] This indicated that the bonding between PCalix[8] and nitrate ions occurs through the hydroxyl groups on the lower rim. FTIR shown in Figure 3 is consistent with the binding of the calixarenes to magnetite through the phosphates, leaving the hydroxyl...
groups free to interact with the nitrate. Thus, a similar regime for binding nitrates is probably occurring in the present work. The modelling work on graphene also suggested that the reason for the superior nitrate removal and retention is related to the greater conformational flexibility of the PCalix[8], which allows for the formation of pockets where there is favourable hydrogen bonding for adsorption. In the present work, the similar formation of pockets may allow hydrogen bonding between the surface of the magnetite particles, orthophosphate and the PCalix[8]. This would explain the capability of the calixarene coated magnetite particles to remove both nitrate and phosphate, and also the higher effectiveness of PCalix[8].

**Figure 8:** Mixtures of solutions of magnetite with various PCalix[n] coatings with aqueous MLA media that has an overall nitrate and phosphate concentrations of 26 mg/L, nitrate-nitrogen and 17 mg/L phosphate. (Top) Nitrate-nitrogen removal. (Bottom) Phosphate removal

**Conclusions**

A simple co-precipitation method has been used to prepare magnetite nanoparticles stabilized by p-phosphonated calix[n]arenes (PCalix[n]) of different ring size. PCalix[n] is bonded to the surface of the magnetite particles via the phosphonate head groups. The particles are strongly faceted when PCalix[4],[5] and [6] are used as the stabilizer, and spherical when PCalix[8] is used. The particles are approximately 11 nm in diameter, independent of the choice of PCalix[n] ring size. Approximately 1 gL⁻¹ of PCalix[8] coated magnetite nanoparticles were used to remove 62% of nitrate-nitrogen and 48% of phosphate after 24 hours from waste water, outperforming both the other PCalix[n]s and uncoated magnetite nanoparticles. Overall, the study demonstrates the ability to design and stabilize functional superparamagnetic nanoparticles for targeted anion binding, which can be easily collected using an external magnet.

**Experimental Section**

Magnetite nanoparticles were produced in the presence of the previously synthesized p-phosphonated calix[n]arenes (n= 4, 5, 6 or 8) (PCalix[n]) using stock solutions containing 20 mM iron (III) and 10 mM iron(II) in Milli-Q water previously purged with argon gas. PCalix[n] stock solutions were made at a concentration of 50 mM in Milli-Q water; 0.1 M NaOH was added to adjust the pH of the otherwise sparingly soluble PCalix[4] to 9.92. Each experiment used 4 mL of stock iron solution to which was added an amount of the PCalix[n] stock solution (4 mL, 400 μL, 40 μL, 4 μL) and Milli-Q water to make the total volume to 8 mL, with calixarene concentrations of 0.25 mM, 0.0525 mM, 0.000525 mM and 0.000025 mM. To each solution 100 μL of 28% ammonia solution was quickly injected and the sample shaken. Iron(II) chloride was purchased from Sigma Aldrich and iron(III) chloride was purchased from Alpha Aesar. The ammonia solution (28%) was from Univar and sodium hydroxide from Merck. Water was filtered using a Milli-Q filtration system. PCalix[n] were synthesised in accordance with the literature procedures.

A JEOL 2000FX transmission electron microscope (TEM) instrument operating at 80 kV was used to determine the size and morphology of the magnetite nanoparticles. Samples were prepared by diluting magnetite solutions by 1 in 10 with Milli-Q water then placing a drop on top of carbon-coated 200 mesh copper grids, removing excess liquid and letting them dry. TEM data was processed by Image-J software. The particle size measurements were volume weighted for better comparison with magnetic measurements.

Experiments were scaled up to produce enough material for further characterisation. Iron solutions of 25 mL, 20 mM were made of 22.5 mL Milli-Q water and 2.5 mL of PCalix[n] stock solution to which 500 μL of NH₃ was quickly injected. Samples were centrifuged at 3000 g for 10 min and the supernatant discarded. The pellets were then freeze dried with liquid nitrogen and VirTis freeze mobile 35EL.

Quantum Design 7 T MPMS superconducting quantum interference device (SQUID) magnetometer was used for measuring the magnetic properties of the PCalix[n] coated iron oxide nanoparticles. The typical measurement is to produce a magnetization-magnetizing field (M-H) hysteresis loop which establishes the ferromagnetic properties of the materials. This magnetization data was normalized with respect to the iron content of the samples, which was determined using ICP-AES. A second type of measurement possible on the SQUID is the production of the zero-field-cooled (ZFC) curve which depicts the change of...
magnetism with temperature, and indicates whether the material is superparamagnetic or otherwise.

Powder X-Ray diffraction (XRD) was measured using a Panalytical Empyrean XRD instrument operating with Cu Kα radiation (λ = 0.154060 nm). FT-IR experiments were performed on a Perkin Elmer spectrometer.

To investigate the efficacy of these particles to remove NO₃⁻ and PO₄³⁻ from water the liquid, mixtures (1 mL) containing stabilized magnetic nanoparticles were mixed with aqueous MLA media (4 mL) with a buffered pH of 7.5[48], which has the amount of nitrate and phosphate ions that can simulate a wide range of wastewater effluent from ground-water to the effluents of the sewage treatment plants.[46] The amount of nitrate and phosphate ions remaining in the solution was monitored at various time intervals (0, 2, 4, 6, 12 and 24 hours). Before each analysis, liquid mixtures were centrifuged at 18400 x g for 5 minutes and the suspension-free supernatants were collected for their spectrophotometric analysis.

The cadmium reduction method[49] was used to analyse the nitrate-nitrogen content, using a chemical kit (HACH®, NitraVer® Nitrate Reagent). The nitrate-nitrogen [NO₃⁻-N] assay measures the amount of nitrogen (N) present in aqueous solutions as nitrate ions (NO₃⁻).[50] The colorimetric ascorbic acid method[49] was used to monitor the phosphate concentration of the remaining solution, using another dedicated chemical kit (HACH®, PhosVer® 3 Phosphate Reagent). A colorimeter (HACH® DR/8970) was used for the spectrophotometric analysis of both nitrate-nitrogen and phosphate content.[51]

The dry weight (dw) was obtained by centrifuging sample solutions (2 mL) at 18400 x g for 5 minutes, discarding the excess supernatant, and drying the remaining pellets overnight at 60 °C. Each sample was found to have a similar dry weight concentration of around 1 g L⁻¹, with slight differences resulting from the variations in the PCaix[n] moiety, n = 4, 5, 6 or 8. The control sample without any calixarene present had the lowest dry weight pre-absorption study of 0.95 ± 0.05 g L⁻¹, which is followed by PCaix4: 1.06 ±0.04 g L⁻¹; PCaix5: 1.12 ±0.02 g L⁻¹; PCaix6: 1.14 ±0.04 g L⁻¹; and PCaix8: 1.19 ±0.01 g L⁻¹.

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Keywords: Nanoparticles • Magnetite • Phosphonate Calixarene • Nitrate removal • Phosphate removal


Highly faceted superparamagnetic magnetite nanoparticles ~11 nm in diameter form in the presence of $p$-phosphonated calix[4, 5 or 6]arenes which are effective in remove nitrate-nitrogen and phosphate from aqueous effluent.

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Page No. – Page No.

$p$-Phosphonated calix[n]arene stabilized superparamagnetic nanoparticles for nitrate and phosphate uptake.