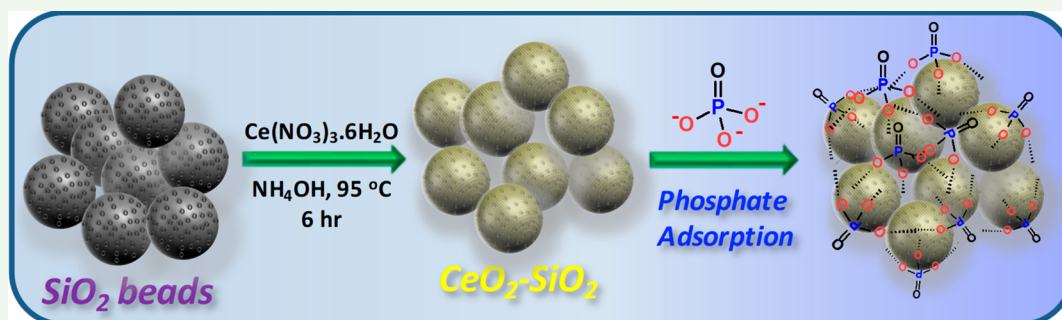


Recyclable Adsorbents Based on Ceria Nanostructures on Mesoporous Silica Beads for the Removal and Recovery of Phosphate from Eutrophic Waters

Ali Othman,¹ Peter Vargo, and Silvana Andreescu^{1*}

Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam, New York 13699-5810, United States

^S Supporting Information



ABSTRACT: While phosphorus (P) is an essential nonrenewable resource and a key nutrient for agricultural production, its excessive accumulation in the environment can cause overgrowth of water plants and algal blooms that produce dangerous toxins and create “dead zones” in the body of water, leading to eutrophication. Main approaches to remove P in its most abundant and stable form, phosphate (PO₄³⁻), involve the use of carbon-based adsorbents that are relatively nonspecific, have limited sorption capacity, and cannot be used to recover this critical resource. Herein, we report a ceria (CeO₂)-based adsorbent that has the capability to rapidly and reversibly capture PO₄³⁻ enabling its further recovery for potential reuse. The adsorbent consists of ceria nanoparticles patterned on mesoporous silica (CeO₂-SiO₂), which can bind PO₄³⁻ through ion exchange and Lewis-acid based interactions. The adsorbent shows excellent sorption/desorption capability of up to 110 mg/g with 99% removal within 60 min. The adsorbent maintained high removal efficiency over a pH ranging from 4 to 8.5 and showed no significant effect to common coexisting anions, indicating high selectivity for PO₄³⁻. A procedure to regenerate the adsorbent by hydrogen peroxide (H₂O₂) treatment was developed which enabled the reuse of the adsorbent for up to six cycles and the recovery of the PO₄³⁻. The designed CeO₂-SiO₂ provides an example of regenerable high-performance adsorbents based on ceria chemistry that can be used to control and manage PO₄³⁻ levels in environmental water systems to address issues related to eutrophication.

KEYWORDS: ceria-based adsorbent, phosphate, regeneration, adsorbent selectivity, redox, eutrophication, environmental remediation, batch adsorption

1. INTRODUCTION

Water management is a challenging problem at local and global levels.¹ The availability of clean and safe water resources is essential for ensuring the water needs for human consumption and natural ecosystems. Industrial activities and agricultural practices can affect water quality and impact the nutrient cycle, affecting a variety of processes in the ecosystem, with one of the most altered involving the phosphorus (PO₄-P) cycle. The use of P-based fertilizers and detergents generate an oversupply of P compounds in inland and coastal waters.² A large amount is entering the water circuit through soil leaching from the use of fertilizers or food waste (1 million tons).³ Excessive P in the environment causes overgrowth of water plants and toxic algal blooms and creates “dead zones” in the body of water, resulting in changes of habitats and raising drinking water treatment costs. It is estimated that about 40% of rivers and

water streams in the US are P rich, leading to poor water quality and an inability to support aquatic life,⁴ making P pollution a serious challenge.⁵

Given the essential role of P in the environment, it is critical to develop solutions to improve the overall management of the P-cycle and ensure an overall nutrient balance, while preserving the beneficial uses of P for agricultural food production. Therefore, effective strategies to remove the excess of P are needed to prevent algal growth and minimize cyanotoxin formation. Removal of P is also needed to create a source of recycled P-compounds. Previous work has demonstrated the use of adsorbent for the removal of P species, particularly the

Received: August 7, 2019

Accepted: October 7, 2019

Published: October 7, 2019

most abundant form as inorganic phosphate (PO_4^{3-}), using materials such as activated carbon,⁶ zirconium hydroxide⁷ and zirconia-functionalized graphite oxide,⁸ zeolites,⁹ amorphous calcium carbonate,¹⁰ and iron(III) oxides.¹¹ While these adsorbents have shown good performance for phosphate removal, they lack selectivity, do not allow for the recovery of PO_4^{3-} and cannot be reused.

Ceria (CeO_2) and CeO_2 -based adsorbents have received great interest as promising adsorbent for water treatment. The high surface charge density, rich functionalities, and the high affinity of surface hydroxyl groups facilitate rapid formation of cerium-ion (e.g., phosphate, arsenic, etc.) complexes to their surface,^{12–14} making them effective adsorbents for environmental remediation. Few recent reports described the potential of CeO_2 in nanoparticles¹⁵ and hydrous forms loaded on porous silica microsphere (Ce-SiO_2)¹⁶ and $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ magnetic nanoparticles¹⁷ as potential candidates for the removal of PO_4^{3-} . While PO_4^{3-} adsorption on CeO_2 has been reported, none of these studies address evident needs to regenerate and recycle the sorbent.

Herein, we describe a recyclable CeO_2 -based adsorbent that has the capability to catch and release PO_4^{3-} , enabling its recovery, and the reuse of the adsorbent. To design the adsorbent, we use the high binding ability of CeO_2 nanostructures for PO_4^{3-} , by forming cerium phosphate complexes at the CeO_2 surface. To fabricate the adsorbent, CeO_2 nanostructures were grafted on mesoporous SiO_2 , which can be conveniently used in the fabrication of membranes and filters or as packing media for separation columns. The high surface area and affinity of CeO_2 for these compounds make them suitable adsorbents for PO_4^{3-} removal and recovery. This is the first study demonstrating the regenerability of CeO_2 -based materials as reusable adsorbents for the selective PO_4^{3-} removal and environmental remediation applications.

2. EXPERIMENTAL SECTION

2.1. Materials. The cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99%) was of analytical grade and was purchased from Sigma-Aldrich. Silica gel (60–200 Mesh) and sodium sulfate were purchased from J.T. Baker. Dipotassium hydrogen phosphate (K_2HPO_4 , >99.9%), sodium chloride, sodium fluoride were purchased from Fisher. Ascorbic acid was purchased from LabChem. Ammonium molybdate (para) tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), antimony potassium tartrate hydrate ($\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot \text{H}_2\text{O}$, 98%), and sodium perchlorate were purchased from Alfa Aesar. Stock solutions were all prepared with ultrapure water.

2.2. Preparation of Adsorbent. The adsorbent material (i.e., $\text{CeO}_2\text{-SiO}_2$) was prepared via coating silica gel beads with CeO_2 nanostructures. Seeding of CeO_2 onto SiO_2 was achieved using a modified synthesis procedure reported in literature.¹⁸ Two hundred milliliters of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.2 M was preheated to 95 °C and then was mixed with 10 g of silica gel into 20 mL of H_2O . Afterward, 300 mL of NH_4OH (0.2 M) was added under vigorous stirring. Then the mixture was kept at this temperature and stirred for 6 h. The product was filtered and washed thoroughly with water to eliminate unbound cerium nitrate or ceria. Finally, the product was dried at 80 °C overnight and placed in a capped container.

2.3. Instrumentation. The spectroscopic analysis was performed using UV–vis spectrophotometer (UV-2401PC, Shimadzu) (1.5 mL methacrylate cuvettes, Fisher Sci.) and Fourier transform infrared (FTIR) equipped with Attenuated total reflectance (ATR-FTIR) (iS10 FT-IR, ATR diamond crystal, Thermo Nicolet). For surface charge measurement, zeta (ζ) potential of the adsorbent solutions using Zeta PALS analyzer (Brookhaven) were measured at 25 °C with $n = 5$. Thermogravimetric analysis (TGA) of the adsorbent was performed using an Exstar TG/Differential Thermal Analyzer (DTA)

6200 analyzer, (Seiko). All tests were performed with a heating rate of 20 °C/min under N_2 atmosphere in the range of 30–600 °C. To study the elemental composition and oxidation state of species at the surface of the adsorbents, X-ray photoelectron microscopy (XPS) (SSX-100, Surface Science (ESCA)) was used equipped with a monochromatic Al $K\alpha$ X-ray source (1486.6 eV) at 1 mm diameter beam size, a 55° emission angle, an operating pressure of $\sim 2 \times 10^{-9}$ Torr, 150 V pass energy for wide/survey scans, and 50 V for high-resolution scans. For charge neutralization of nonconductive samples a flood gun was used. The surface morphology and chemical composition were evaluated using field emission scanning electron microscopy (FE-SEM), (JEOL JSM-7400F) equipped with an energy-dispersive X-ray analysis (EDS) using a. The samples were applied on carbon tape, vacuum-dried, and coated with gold (Au)/palladium (Pd) film (60:40%) for 40 s for conductivity purposes. High-resolution transmission electron microscopy (HRTEM), (JEOL JSM-2010) was further used for morphology analysis. The samples were deposited on a TEM copper grid (obtained from Ted Pella) and dried under vacuum before analysis.

To evaluate the crystallinity of the adsorbents a D-8 X-ray diffractometer (Bruker), using Cu $K\alpha 1$ radiation source was used. To study the surface area, nitrogen (N_2) adsorption/desorption isotherms using Autosorb IQ automated gas sorption analyzer (Quantachrome) were carried out. Results were calculated using the Brunauer–Emmett–Teller (BET) method at 77 K. The pore size distribution were obtained based on the quenched solid density functional theory (QSDFT). Survey samples were degassed at 100 °C for 20 h prior to the measurements.

2.4. Phosphate Isotherm Adsorption Study. The PO_4^{3-} adsorption capacity by the $\text{CeO}_2\text{-SiO}_2$ adsorbent was measured by using a batch adsorption methodology. Working PO_4^{3-} solutions were prepared from a stock solution of PO_4^{3-} (1000 mg/L) prepared in DI water. Briefly, 2 mg/mL of $\text{CeO}_2\text{-SiO}_2$ was added into centrifugation tubes containing PO_4^{3-} at a concentration range of 0.5–100 mg/L. Thereafter, the centrifugation tubes were placed in an automatic shaker (Vari-Mix, Thermolyne) and mixed for 60 min. The sample tubes were further centrifuged and filtered using 0.2 μm filters. Finally, supernatants were taken and analyzed by the molybdenum blue (MB) method for PO_4^{3-} concentration.¹⁹ SiO_2 beads were tested as control using the same procedure. The PO_4^{3-} removal efficiency ($q\%$) and the amount of adsorbed PO_4^{3-} was calculated using

$$q\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{W} \quad (2)$$

where q_e is the adsorbed PO_4^{3-} onto the $\text{CeO}_2\text{-SiO}_2$ surface (mg/g), C_i and C_e are the initial and equilibrium concentrations of PO_4^{3-} (mg/L) in solution, V is the volume of the sample (L), and W is the weight of $\text{CeO}_2\text{-SiO}_2$, (g).

2.5. Kinetic Study of PO_4^{3-} Adsorption. The kinetic of PO_4^{3-} adsorption was studied by batch experiments at different incubation times. In these experiments, $\text{CeO}_2\text{-SiO}_2$ (2 mg/mL) was added to centrifuge tubes containing 17.5 mg/L of PO_4^{3-} placed on a shaker (Vari-Mix, Thermolyne) and mixed for different time periods from 1 to 60 min at room temperature. The concentrations were optimized based on the molybdenum blue method. After incubation, the supernatant was analyzed for residual PO_4^{3-} concentration.

2.6. Adsorbent Dosage and pH Effects. The $\text{CeO}_2\text{-SiO}_2$ dosage was optimized by testing amounts of adsorbent in the range of (0.5, 1, 2.5, 5, and 10 mg/mL). The adsorbent was exposed to PO_4^{3-} (17.5 mg/L) mixed and placed on shaker for 60 min. The samples were then centrifuged and filtered and the amount of PO_4^{3-} was analyzed using the MB method for PO_4^{3-} detection. The pH range investigated was between 4 and 10. Solutions of different pH values were obtained by adjusting the pH of PO_4^{3-} solutions (50 mL of 17.5 mg/L) with 0.1 M NaOH or HCl. Two mg/mL of $\text{CeO}_2\text{-SiO}_2$ adsorbent were added to the PO_4^{3-} solutions of different pH

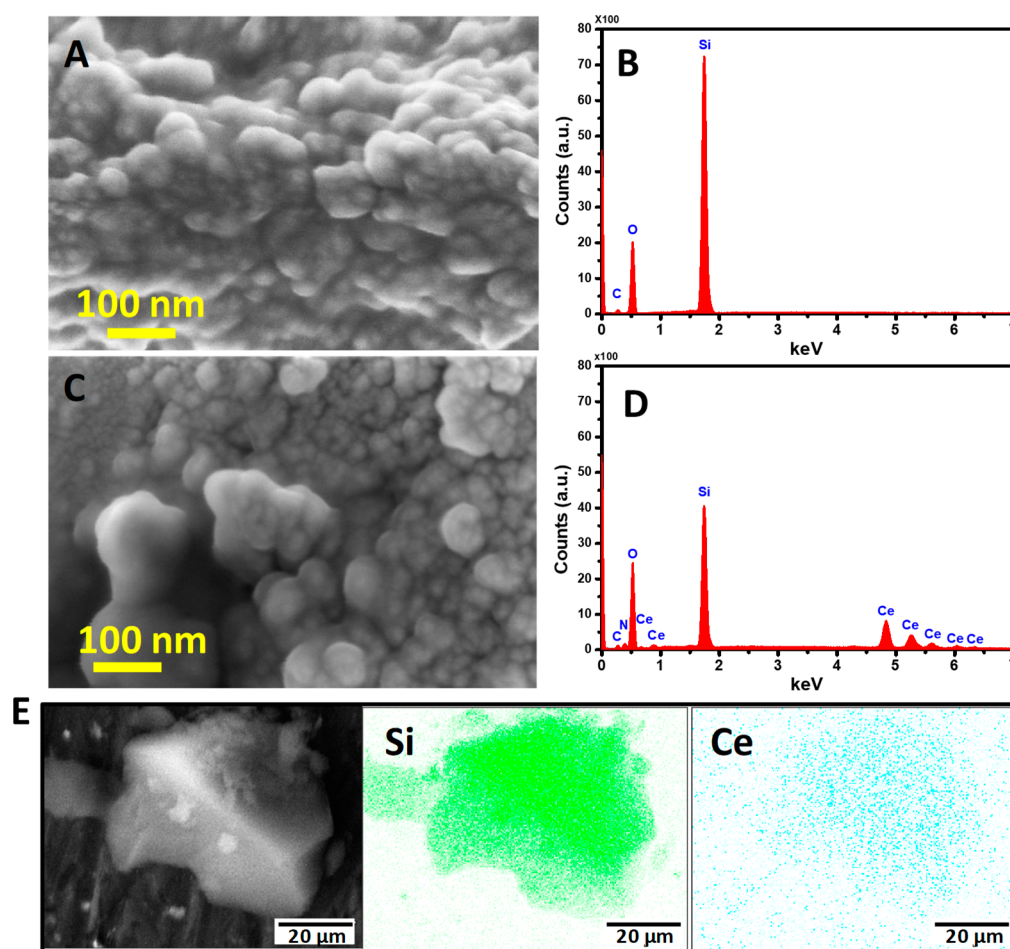
Scheme 1. Schematic Representing the Functionalization of SiO₂ with CeO₂ NPs

Figure 1. SEM images of SiO₂ beads (A) and CeO₂-SiO₂ adsorbent (C) with their corresponding EDS analysis (B and D, respectively). (E) The corresponding elemental mapping of CeO₂-SiO₂ adsorbent.

values, and the adsorbed PO₄³⁻ was determined using the same procedure as in the adsorption study.

2.7. Recyclability and Regeneration. Regeneration of the adsorbent was achieved by washing with H₂O₂, which competitively displaces the adsorbed PO₄³⁻. To regenerate the CeO₂-SiO₂, the spent adsorbents were added to H₂O₂ solution (0.1 M) and then mixed on a shaker for 1 h. The CeO₂-SiO₂ was washed with DI water, and then centrifuged and dried at 100 °C to decompose the adsorbed Ce-peroxide and regenerate the adsorbent. Thereafter, six repetitive experiments of PO₄³⁻ adsorption/desorption cycles for were carried to evaluate the reusability of the adsorbent.

Note: All experiments were carried out with solutions at a pH 7.0 (except for the pH study), at room temperature. The calibration curve for PO₄³⁻ using the MB method was developed based on three replicates (*n* = 3).

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization. Silica beads offer a strongly hydrophobic environment with the ability to entrap and anchor metal oxides in/onto its microstructure producing a highly uniform conjugate.²⁰ In particular, CeO₂ is known to form strong Ce-O-Si bonds with the SiO₂ surface. By

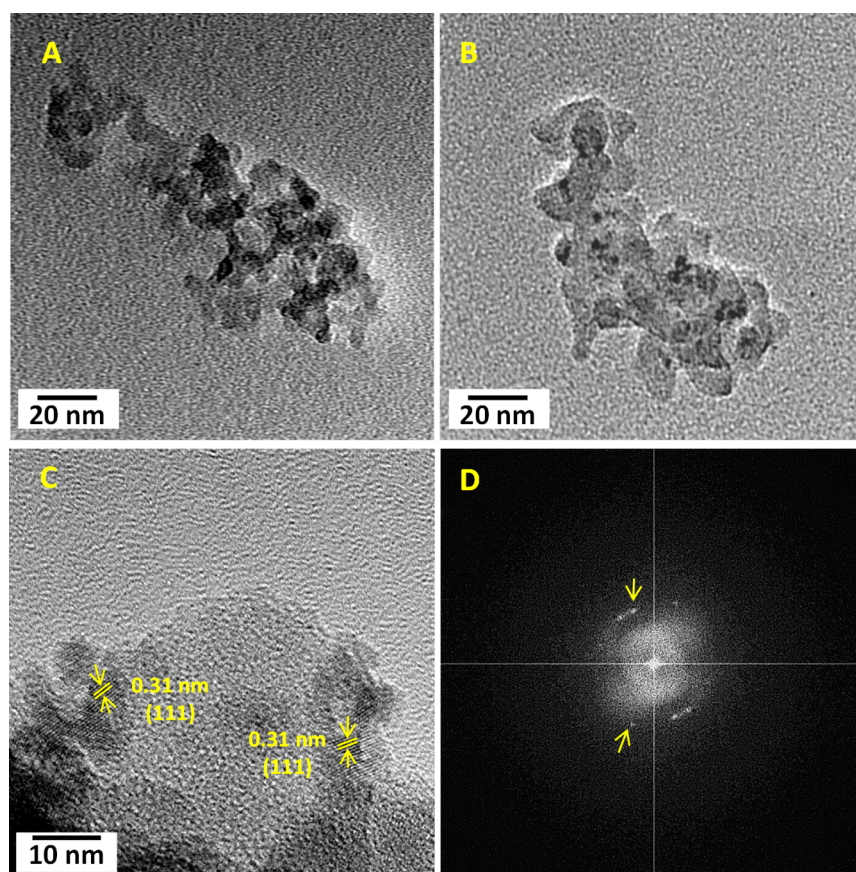


Figure 2. HR-TEM micrographs of (A) SiO₂ and (B) CeO₂-SiO₂ adsorbent. Panels C and D are the HRTEM images of CeO₂-SiO₂ adsorbent at high magnification with the corresponding fast Fourier transformation (FFT) pattern.

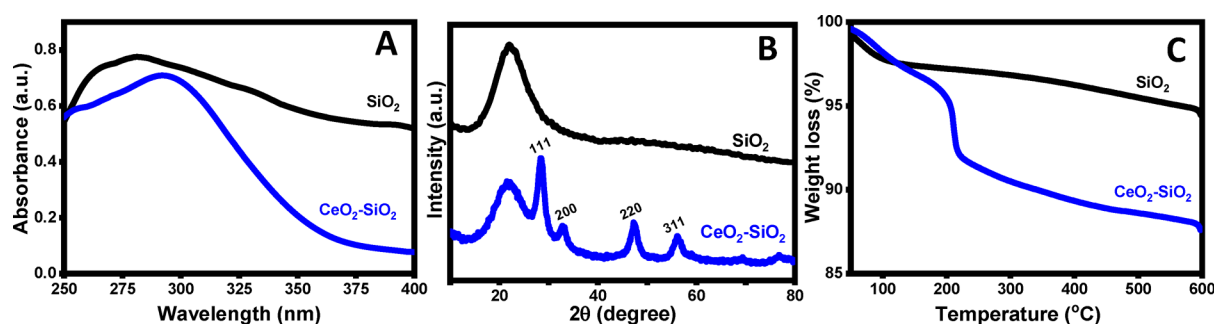


Figure 3. Chemical structure characterization of the CeO₂-SiO₂ adsorbent: (A) UV-vis spectra, (B) XRD patterns, and (C) TGA profiles.

depositing a nanostructured CeO₂ on the SiO₂ beads, we create a high surface area structure with high density capturing sites for PO₄³⁻ species. It is known that PO₄³⁻ can interact strongly with CeO₂ and promote CePO₄ formation.²¹ The procedure for preparing the CeO₂-SiO₂ adsorbent consists in direct CeO₂NPs precipitation onto the SiO₂ surface as illustrated in Scheme 1. The pH value of the as-prepared CeO₂-SiO₂ has a point of zero charge (pzc) at pH 4.1, higher than the pH associated with the pzc of the initial SiO₂ beads (3.6) (Figure S1). The change in ζ/pH evolution is the first confirmation of a successful CeO₂ coating of the silica beads.

The morphology and the chemical composition of the adsorbent were assessed by SEM and EDS analysis. The SEM images of both SiO₂ and CeO₂-SiO₂ (Figure 1A and C) show that the morphology of the material is maintained after functionalization. The chemical composition was confirmed by

EDS analysis (Figure 1B and D). As compared to the EDS spectrum of SiO₂, the CeO₂-SiO₂ shows the presence of Ce indicating the successful modification of SiO₂ with CeO₂. Additionally, the corresponding elemental (Si and Ce) mapping of CeO₂-SiO₂ adsorbent (Figure 1E) illustrates a homogeneous distribution of CeO₂ over the SiO₂ surface.

The surface properties and the porosity analysis of the SiO₂ beads and the CeO₂-SiO₂ adsorbent are shown in (Figure S2) the parameters are displayed in Table S1. The N₂ adsorption/desorption isotherms exhibit a similar type IV curve for both materials: SiO₂ and CeO₂-SiO₂ beads. The specific surface area (*S*_{BET}) value of SiO₂ decreased slightly from 287.5 (SiO₂) to 274.0 m²/g (CeO₂-SiO₂). The values of the pore volume also decreased from 1.033 (SiO₂) to 1.025 cm³/g (CeO₂-SiO₂). These results demonstrate that the CeO₂-SiO₂ maintained a mesoporous structure after functionalization.

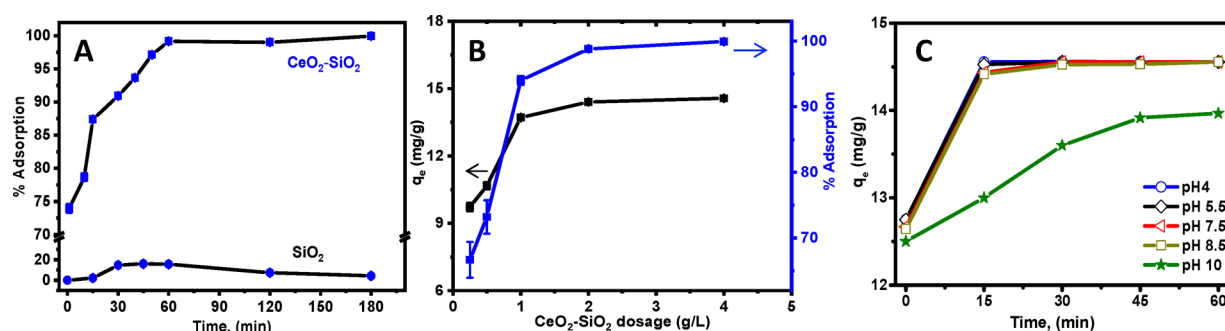


Figure 4. Effect of (A) contact time, (B) adsorbent dosage, and (C) pH on the adsorption capacity of PO_4^{3-} . $[\text{PO}_4^{3-}]_{\text{ini}} = 17.5 \text{ mg/L}$. $n = 3$.

Surface modification of SiO_2 by CeO_2 was further studied by HR-TEM analysis. Figure 2 shows a spherical shape which is maintained after functionalization. The HR-TEM of the CeO_2 - SiO_2 adsorbent at high magnification (Figure 2C) confirms the presence of CeO_2 NPs with a spherical-like shape structure distributed on the SiO_2 . The image also shows fine particles in the range of average size of 5–15 nm uniformly distributed in the sample and possess a lattice fringe characteristics of a d -spacing of 0.31 nm attributed to the (111) facet of fcc of CeO_2 NPs. The fast Fourier transformation (FFT) data (Figure 2D) are consistent with a diffraction pattern of fcc crystals in the (111) planes.

Further characterization was performed by UV-vis, XRD, and TGA (Figure 3) techniques. The UV-vis spectrum of SiO_2 (Figure 3A) shows an absorbance peak at 280 nm. After CeO_2 was precipitated onto the SiO_2 beads, a new absorbance peak with a maximum wavelength at $\sim 300 \text{ nm}$ is present. This peak is a well-known characteristic of CeO_2 , confirming its presence on the SiO_2 surface. The PXRD pattern of the SiO_2 (Figure 3B) shows a broad peak around $2\theta = 22^\circ$ associated with an amorphous structure of this material. After introducing CeO_2 , the intensity of this peak is reduced, which is associated with the appearance of 2θ diffraction peaks at 28.4° , 32.8° , 47.2° , and 56.1° . These peaks are characteristics of the 111, 200, 220, and 311 planes, assigned to the face-centered cubic (fcc) CeO_2 structure.²² The interplanar spacing and the crystallite size of the CeO_2 estimated by considering the (111) plane were 0.31 and 4.4 nm, according to the Scherrer equation. These spectroscopic and structural data confirm the presence and the nanosized feature of the CeO_2 in agreement with the HR-TEM data. The TGA profiles of both SiO_2 and CeO_2 - SiO_2 (Figure 3C) show an initial loss of $\sim 2.5\%$ in the range of 50–150 $^\circ\text{C}$ because of the loss of the adsorbed water. An extra slight weight loss of $\sim 1.5\%$ up to 600 $^\circ\text{C}$ was observed which can be attributed to the condensation of silanol groups.²³ For the CeO_2 - SiO_2 , a $\sim 9\%$ weight loss at 150–250 $^\circ\text{C}$ was observed. Since the synthesized CeO_2 contains hydrated ceria onto the surface, this loss is due to the elimination of water.²⁴

Surface modification was further investigated using ATR-FTIR and XPS techniques. The ATR-FTIR spectra of bare and CeO_2 -coated SiO_2 shown in (Figure S3A) exhibits bands at 960 and 1632 cm^{-1} corresponding to the (Si-O or Ce-O) vibrations in bare SiO_2 and CeO_2 - SiO_2 , respectively.²⁵ The very intense and broad band at $\sim 1110 \text{ cm}^{-1}$ and the band at 805 cm^{-1} both correspond to the Si-O-Si stretching vibration.²⁶ The small shoulder at 960 cm^{-1} is assigned to the stretching of (Si-OH or Ce-OH).²⁷ For CeO_2 - SiO_2 , these peaks shift to lower wavenumbers due to the insertion of

CeO_2 in the silica framework, with formation of Ce-O-Si bonds. In addition, new peaks at 1385 and 1462 cm^{-1} are also seen after functionalization, associated with the Ce-O-Ce and Ce-OH vibrations.²⁸

XPS analysis (Figure S3B and C) in the range of 0–1200 eV shows the Si 2p signal in both SiO_2 and CeO_2 - SiO_2 samples with the signal shifted from 104.7 for SiO_2 to 103.8 eV for CeO_2 - SiO_2 . This 0.9 eV shift toward lower binding energy could be explained by the interaction of Si with Ce ions. As expected, Ce 3d was absent in the SiO_2 sample and observed only in the CeO_2 - SiO_2 sample as can be seen from the (Figure S3B and C), respectively. The Ce 3d spectrum of CeO_2 - SiO_2 (inset of Figure S3C) showed evidence of a mixed oxidation state ($\text{Ce}^{3+}/\text{Ce}^{4+}$). The peaks at 886 and 906 eV are due to Ce in the 3+ state, while the peaks at 882, 900, and 916 eV are attributed to Ce in the 4+ oxidation state.²⁹ These results indicate the presence of CeO_2 onto SiO_2 confirming the successful preparation of the CeO_2 - SiO_2 adsorbent.

3.2. Adsorption of PO_4^{3-} on CeO_2 - SiO_2 . CeO_2 NPs are known for their ability to interact with PO_4^{3-} creating cerium phosphate (Ce-PO_4) at their surface.^{30,31} Therefore, decoration of CeO_2 onto the surface of porous support provides sites for PO_4^{3-} adsorption on and within the mesoporous structure, significantly enhancing the adsorption capacity of this material. It was also reported that binding of phosphate anions induces changes in the redox state of CeO_2 (i.e., $\text{Ce}^{3+}/\text{Ce}^{4+}$) through coordination to cerium cations on Ce^{3+} -rich CeO_2 without affecting the crystal structure of CeO_2 .^{30,31} A recent computational study reports a preferential interaction of PO_4^{3-} with Ce^{3+} and highlights the role of hydroxyl groups in the phosphate ion adsorption, although it was suggested that the interaction between phosphate (PO_4^{3-}) and hydroxyl (OH^-) groups appear to be minimal and independent of the OH concentration.²¹ However, CeO_2 NPs could suffer from agglomeration because of the van der Waals interactions or leaching through filtration or separation. As a result, the sorption capacity, selectivity, and mechanical strength are significantly decreased making them less feasible for use in water systems. To overcome this disadvantage, CeO_2 NPs were decorated on mesoporous SiO_2 beads, which are commonly used as packing or filtration material. The effect of solution pH, contact time, and chemical composition was studied further to understand the effect of these parameters on PO_4^{3-} adsorption by CeO_2 - SiO_2 .

3.2.1. Study of the Contact Time Effect on PO_4^{3-} Adsorption. Incubation times ranging between 1 and 180 min were tested to determine the optimum adsorption of PO_4^{3-} . Batch sorption experiments were used in these studies. For comparison, PO_4^{3-} adsorption on the CeO_2 - SiO_2 was

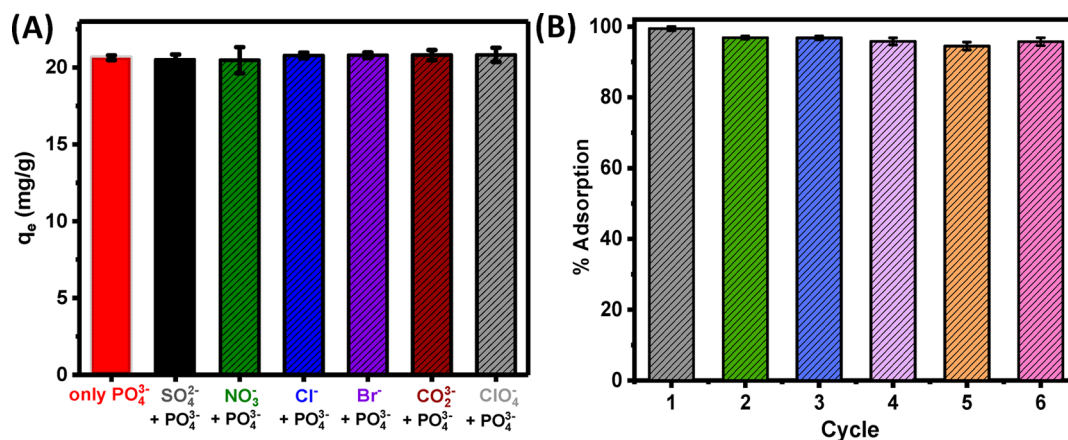


Figure 5. (A) Effect of coexisting anions on PO_4^{3-} adsorption by $\text{CeO}_2\text{-SiO}_2$. $[\text{PO}_4^{3-}]_{\text{ini}} = [\text{Anion}]_{\text{ini}} = 25 \text{ mg/L}$, time = 60 min. (B) Recyclability test on PO_4^{3-} adsorption by $\text{CeO}_2\text{-SiO}_2$. $[\text{PO}_4^{3-}]_{\text{ini}} = 35 \text{ mg/L}$.

compared with that obtained on unmodified SiO_2 as a control. Bare SiO_2 (Figure 4A) showed almost no PO_4^{3-} adsorption, while the $\text{CeO}_2\text{-SiO}_2$ displayed a fast time dependent adsorption process. The % amount of PO_4^{3-} adsorbed by $\text{CeO}_2\text{-SiO}_2$ increased with time from 74% due to increase of the contact between the PO_4^{3-} and the adsorbent until it reached equilibrium at 60 min, with more than 99% adsorption. Extending the contact time above 60 min did not show a significant change in the amount of adsorbed PO_4^{3-} , indicating that the adsorption phase reached equilibrium. This behavior suggests that the kinetics is fast at the earlier stages of the adsorption process due to the accessibility of the active binding sites, followed by slow kinetics due to blocking of binding sites of $\text{CeO}_2\text{-SiO}_2$ by PO_4^{3-} species.³²

3.2.2. Adsorbent Dosage Effect. $\text{CeO}_2\text{-SiO}_2$ concentrations in 0.25–4 g/L range were tested to determine the adsorption capacity of PO_4^{3-} (Figure 4B). According to the results of the batch adsorption experiments, the equilibrium between the surface adsorption and adsorbent concentration was reached at 2 g/L which corresponds to an adsorption capacity of up to 99% with q_e of 14.6 mg/g.

3.2.3. pH Effect. One of the key factors that play a role in the adsorption process is the pH of the solution, since the pH affects the surface charge of both the adsorbent and adsorbate. The effect of pH on the adsorption capacity of PO_4^{3-} by $\text{CeO}_2\text{-SiO}_2$ was studied in the pH range of 4 to 10. Results in Figure 4C show that the removal of PO_4^{3-} by $\text{CeO}_2\text{-SiO}_2$ occurs at a similar rate for pH values between 4 and 8.5, with a slight enhancement at acidic pH. When the pH exceeded 10, the adsorption capacity decreased. This is in agreement with previous reports indicating that higher pH values tend to facilitate PO_4^{3-} desorption.^{33,34} The lack of pH dependency demonstrates that the adsorption process is independent of the hydroxyl concentration in this pH range and the P– CeO_2 are very stable over a wide range of pH.

3.3. Adsorption Study. **3.3.1. Adsorption Isotherm Study.** Adsorption isotherms describing the relationship between the amount of the PO_4^{3-} adsorbed by the $\text{CeO}_2\text{-SiO}_2$ were then assessed. The amount of the adsorbed PO_4^{3-} by the $\text{CeO}_2\text{-SiO}_2$ was calculated using eq 2. The Langmuir and Freundlich isotherm models were used to calculate the adsorption parameters by applying eqs 3 and 4. The Langmuir model is applicable when the surface is energetically homogeneous and the extent of adsorbate coverage is limited

to a monolayer. For accurate representation of the equilibrium data, the nonlinear Langmuir model isotherm form was applied.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (\text{linear form})$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (\text{nonlinear form}) \quad (3)$$

where q_m in (mg/g) is the maximum adsorption capacity and K_L represents the Langmuir adsorption constant, associated with the adsorption bonding energy (or the affinity of the binding sites (L/mg)). The Freundlich model describes an adsorption process when the heterogeneous surface of an adsorbent is available. The adsorbate coverage is limited to a multilayer and adsorption sites are energetically not equal. The Freundlich isotherm model is expressed as

$$\log q_e = \log K_f + \frac{1}{n} \log C \quad (\text{linear form})$$

$$q_e = K_f C_e^{1/n} \quad (\text{nonlinear form}) \quad (4)$$

where K_f is the Freundlich constant associated with the adsorption capacity and $1/n$ indicates the extent of adsorption favorability.

Experimental data and the nonlinear fitted equilibrium curves using the nonlinear forms of Langmuir and Freundlich equilibrium isotherms models are shown in Figure S4. The nonlinear Langmuir isotherm exhibited a good fit with a correlation coefficient of ($R^2 = 0.99$). The maximum adsorption capacity (q_m) of PO_4^{3-} onto $\text{CeO}_2\text{-SiO}_2$ is high with a value of 110 mg/g. The nonlinear fitting of the isotherm data of $\text{CeO}_2\text{-SiO}_2$ using the Freundlich model also exhibited a good fit with a correlation coefficient of ($R^2 = 0.96$). In addition, the values of $1/n$ is <1 , indicating a favorable adsorption of PO_4^{3-} on $\text{CeO}_2\text{-SiO}_2$. The parameters calculated by using the nonlinear forms of Langmuir and Freundlich models are tabulated in Table S2. These results suggest that the Langmuir model more favorably describe the PO_4^{3-} adsorption behavior onto $\text{CeO}_2\text{-SiO}_2$.

3.3.2. Adsorption Kinetics. The adsorption mechanism was further investigated by applying the pseudo-first-order and pseudo-second-order kinetics models to fit the experimental data according to eqs 5 and 6

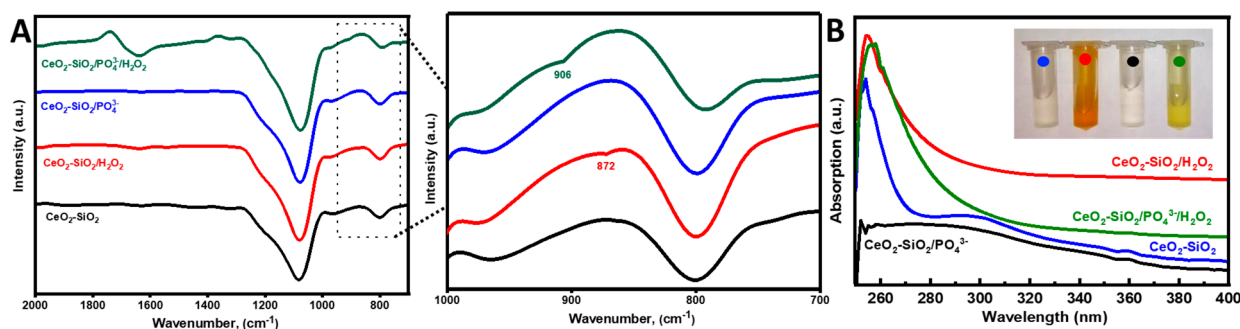


Figure 6. (A) ATR-FTIR with the expanded region (700–1000 cm^{-1}) and (B) UV-vis spectra with the inset of the color response of untreated and treated $\text{CeO}_2\text{-SiO}_2$ and $\text{CeO}_2\text{-SiO}_2/\text{PO}_4^{3-}$ with H_2O_2 .

pseudo-first-order kinetics model

$$\ln(q_e - q_t) = \frac{\ln q_e - K_1 t}{2.303} \quad (\text{linear form})$$

$$q_t = q_e (1 - e^{-K_1 t}) \quad (\text{nonlinear form}) \quad (5)$$

pseudo-second-order kinetics model

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (\text{linear form})$$

$$q_t = \frac{K_1 q_e^2 t}{1 + K_1 q_e t} \quad (\text{nonlinear form}) \quad (6)$$

In the present work, the kinetics study was performed at different PO_4^{3-} adsorption times by employing the nonlinear forms of pseudo-first- and second-order kinetics. According to the regression data presented in Figure S5 and Table S3, the calculated equilibrium adsorption capacity (q_e) values are 14.2 and 15.3 mg/g for the pseudo-first-order and pseudo-second-order models, respectively. In addition, the correlation coefficient (R^2) of the pseudo-first- and pseudo-second-order models are 0.52 and 0.86, respectively. These suggest that the pseudo-second-order model offers a satisfactory adsorption kinetic fitting, indicating that the chemical adsorption mechanism (i.e., chemisorption) is the rate controlling step, and consequently, it may involve chemical valence forces through sharing or exchanging electrons.³⁵

3.4. Interference Study. To study the effect of the coexisting ions on PO_4^{3-} adsorption, several ions that are concurrently present in groundwater and wastewater, such as SO_4^{2-} , NO_3^- , Cl^- , Br^- , CO_3^{2-} , and ClO_4^- in 1:1 ratio were investigated (Figure 5A). The results show no significant interference of these ions, demonstrating selectivity of the $\text{CeO}_2\text{-SiO}_2$ adsorbent for PO_4^{3-} .

3.5. Recyclability and Regeneration. In the next set of experiments, we examined the possibility of recycling the adsorbent for six consecutive adsorption-desorption cycles by using an ion exchange mechanism with peroxide treatment³⁶ (Figure 5B). The reaction of CeO_2 with H_2O_2 is known to form stable cerium-oxo and peroxide bonds onto the CeO_2 surface.³⁷ We used this process to competitively replace the adsorbed PO_4^{3-} by formation of Ce-O_2^{2-} , creating a pathway for PO_4^{3-} recovery. The adsorbed O_2^{2-} can further be decomposed by slightly heating at 100 $^\circ\text{C}$,³⁸ enabling the reuse of the adsorbent.

The effect of H_2O_2 treatment on the $\text{CeO}_2\text{-SiO}_2$ surface was measured by ATR-FTIR and UV-vis after several

consecutive adsorption-desorption cycles. After H_2O_2 treatment, the solid adsorbent was removed by centrifugation, washing with DI water, and drying under vacuum. The ATR-FTIR spectrum (Figure 6A) shows that the $\text{CeO}_2\text{-SiO}_2$ adsorbent treated with H_2O_2 developed a new peak at 872 cm^{-1} that is absent in the spectra of both bare and the PO_4^{3-} -treated adsorbent. A peak in the same 830–950 cm^{-1} region reappears after regeneration of the adsorbent by heating. This peak corresponds to the formation of Ce-O_2^{2-} complexes onto the $\text{CeO}_2\text{-SiO}_2$ surface formed after H_2O_2 addition, proving a ligand exchange mechanism on the surface of the CeO_2 .^{37,39} To evaluate the regenerative capability of $\text{CeO}_2\text{-SiO}_2$ after PO_4^{3-} adsorption by H_2O_2 , untreated and treated adsorbents were also analyzed by UV-vis. When $\text{CeO}_2\text{-SiO}_2$ was exposed to H_2O_2 , a colorimetric change from colorless to dark yellow/orange was developed. The initial peak position associated with Ce in the UV-vis spectrum shifted to a higher wavelength in the H_2O_2 -treated sample due to Ce^{+3} to Ce^{+4} oxidation.^{38,40} When the $\text{CeO}_2\text{-SiO}_2$ with sorbed PO_4^{3-} was treated with H_2O_2 , the color intensity decreased slightly and a red shift was noticed (Figure 6B). These findings can be explained by a partial blocking of the CeO_2 surface by PO_4^{3-} . The zeta potential measurement (Table S4) of the PO_4^{3-} -exposed to $\text{CeO}_2\text{-SiO}_2$ adsorbent shows a decrease in stability from -18 to -13 mV after H_2O_2 treatment. This result agrees with the UV-vis data and the regeneration study (Figure 5B) both of which showed decreased adsorption of PO_4^{3-} after the first regeneration cycle. There was no significant decrease in the adsorption capacity for the next regeneration cycles; the PO_4^{3-} recovery was nearly identical for the remaining five cycles. Overall, these results prove that H_2O_2 is able to exchange the PO_4^{3-} species adsorbed on the adsorbent. On the basis of these results, we can conclude that the adsorbent can be successfully regenerated and reused multiple times. Additionally, the adsorbed PO_4^{3-} can be recovered and further reused.

3.6. Adsorption Mechanism. To further understand the mechanism of PO_4^{3-} adsorption by the $\text{CeO}_2\text{-SiO}_2$ adsorbent, the nature of the chemical species formed at the $\text{CeO}_2\text{-SiO}_2$ surface before and after exposure to PO_4^{3-} was studied by ATR-FTIR and XPS analysis. ATR-FTIR spectra after PO_4^{3-} adsorption (Figure S6) show significant decrease in the main bands at 960, 1385, 1632, and 3405 cm^{-1} , corresponding to the Ce-O and C-O, and O-H stretching and bending vibrations. This indicate that PO_4^{3-} ions were successfully replaced with the surface hydroxyl groups of the CeO_2 .⁴¹ Unfortunately, the characteristic bands of P-OH and P=O stretching overlap with the characteristic bands of Si-O-Si

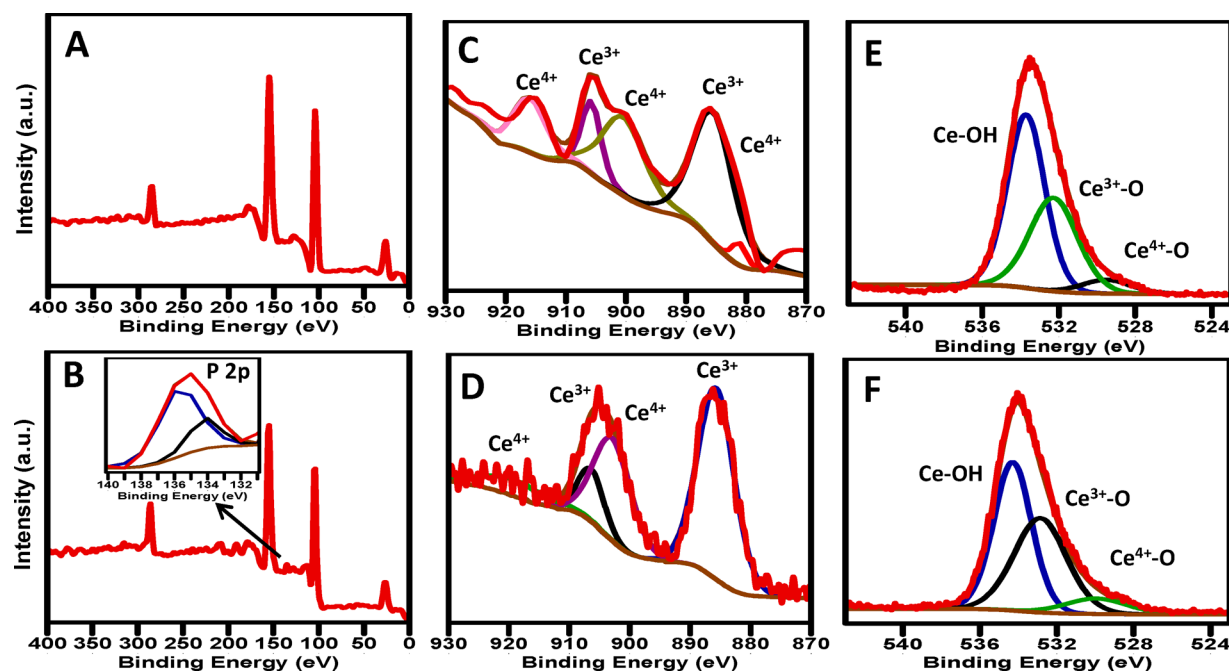


Figure 7. XPS spectra of $\text{CeO}_2\text{-SiO}_2$: (A) Survey, (C) Ce 3d, and (E) O 1s. Panels B, D, and F are the survey, Ce 3d, and O 1s, respectively, of $\text{CeO}_2\text{-SiO}_2/\text{PO}_4^{3-}$ (inset in survey is P 2p spectrum).

(or Ce–O–Si) in the region of $1000\text{--}1250\text{ cm}^{-1}$. These significant changes are in line with previous findings indicating a reaction of the PO_4^{3-} with the hydroxyls of metal oxide surface⁴² and supports a ligand exchange process in which the hydroxyl oxygen on the surface of the metal oxide is replaced by the phosphate oxygen.⁴³

Further insight was gained from the XPS analysis of the $\text{CeO}_2\text{-SiO}_2$ adsorbent before and after incubation with PO_4^{3-} (Figure 7). The P 2p peak at binding energy of 135 eV was only observed in the sample exposed to PO_4^{3-} (Figure 7B). The deconvolution of this peak results into two peaks at 135.6 and 134 eV associated with P(+5) state.⁴⁴ The presence of this peak is clear evidence of phosphate species adsorption (PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^-).⁴⁵ The Ce 3d peaks of $\text{CeO}_2\text{-SiO}_2$ and $\text{CeO}_2\text{-SiO}_2/\text{PO}_4^{3-}$ are presented in (Figure 7C and D). The relative concentration of the different Ce species⁴⁶ can be evaluated from the peaks area integration associated with the Ce(+3) and Ce(+4) states before and after exposure to PO_4^{3-} . The relative content of Ce^{3+} was found to increase from 48.2% for $\text{CeO}_2\text{-SiO}_2$ to 62.3% for $\text{CeO}_2\text{-SiO}_2/\text{PO}_4^{3-}$, supporting the theory that PO_4^{3-} binding alters the redox sites of CeO_2 .³¹ A Ce^{3+} percentage increase as a result of phosphate adsorption was also reported in a recent computational study of PO_4^{3-} -treated CeO_2 nanoparticles.²¹ Next, we analyzed the O 1s XPS spectra (Figure 7E and F). The fitted and deconvoluted O 1s XPS spectrum of $\text{CeO}_2\text{-SiO}_2$ at binding energies of 529.6 and 532.3 eV are assigned to the oxygen bound to Ce^{3+} and Ce^{4+} , respectively, while that at 533.7 eV is assigned to hydroxyl groups (–OH) or absorbed H_2O molecules.^{47–51} In the O 1s XPS spectrum of $\text{CeO}_2\text{-SiO}_2/\text{PO}_4^{3-}$, these three peaks shifted to higher binding energy at 530, 532.8, and 534.4 eV by differences of 0.4, 0.5, and 0.7 eV for the $\text{Ce}^{(3+/4+)}\text{-O}$ and $\text{Ce}(\text{OH}/\text{H}_2\text{O})$, respectively. These changes may be due to surface defects induced by the adsorption of PO_4^{3-} and might involve a ligand exchange with the surface hydroxyl groups (–OH) to form Ce-O-P .

At pH below the pzc (pH = 4.1), the adsorbent possesses a positive charge on its surface. The hydroxyl groups of the CeO_2 surface in the aqueous environment provide a site for ligand exchange. This might take place by formation of inner sphere complexes in which the phosphate anions react with Ce^{3+} on the structure of the hydroxylated CeO_2 surface, leading to complex formation and the release of hydroxyl anions (OH^-) from the CeO_2 surface.³⁴ Furthermore, the pH of the solution containing $\text{CeO}_2\text{-SiO}_2$ increased from 4.9 to 6.9 after PO_4^{3-} adsorption, which suggests the replacement of OH^- by PO_4^{3-} . Considering the successive pK values of H_3PO_4 dissociation (2.13, 7.2 and 12.33), in the pH range of our study (4–9), the main species are HPO_4^{2-} and H_2PO_4^- , as well as PO_4^{3-} . In this case, inner-sphere complexation of phosphate ions with the metal (hydro)oxide can lead to monodentate or bidentate phosphorus compounds.^{43,52} Since the adsorption process is independent in a pH range from 4 to 8.5 (Figure 4C), where the adsorbent surface is negatively charged, the contribution of electrostatic forces is minimal. These results suggest a mechanism involving ion exchange and Lewis acid–base interactions that implies electron donor–acceptor between the hydroxylated CeO_2 sites and phosphate anions.³⁴ Figure 8 provides a schematic illustrating the proposed mechanisms of phosphate adsorption by $\text{CeO}_2\text{-SiO}_2$.

3.7. Comparison with Other Adsorbents. Table 1 summarizes the performance of the $\text{CeO}_2\text{-SiO}_2$ with previously reported PO_4^{3-} adsorbents. The $\text{CeO}_2\text{-SiO}_2$ exhibits higher adsorption capacity (110 mg/g) compared with other adsorbents, including several types of metal oxides and activated carbon. The adsorption obtained with our $\text{CeO}_2\text{-SiO}_2$ is rapid with up to 99% removal and equilibrium being achieved after 1 h. This is an important factor for increasing treatment efficiency. By incorporating a redox-based regeneration process using H_2O_2 , we presented evidence that the adsorbent can be regenerated and reused for 6 multiple cycles without losing adsorption capacity. While other

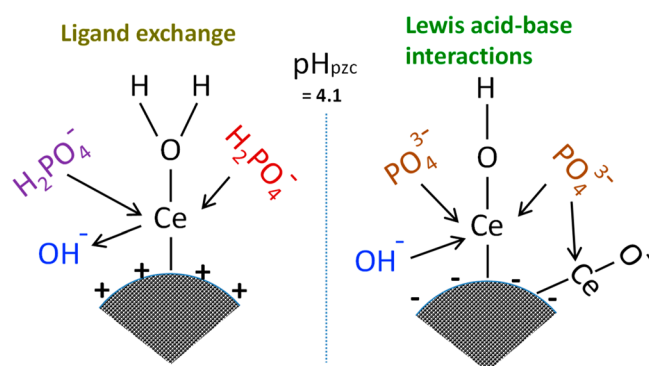


Figure 8. Proposed phosphate adsorption mechanism by the CeO_2 - SiO_2 sorbent.

adsorbents such as activated carbon are available, their adsorption capacity is low due to the minimal and nonspecific binding of PO_4^{3-} on carbon materials. In future developments of this technology, this adsorbent could be grafted or incorporated on different materials, such as polymers or graphene composites, or can be used to construct membranes and separation columns to further increase removal efficiency and develop practical systems based on these materials. These results demonstrate very promising characteristics of the CeO_2 -based adsorbent to reversibly reuse the adsorbent and remove the bound PO_4^{3-} .

4. CONCLUSION

In summary, a CeO_2 - SiO_2 adsorbent was synthesized and characterized for the removal of PO_4^{3-} . The CeO_2 - SiO_2 was obtained by grafting nanostructured CeO_2 onto the surface of mesoporous SiO_2 beads through Si-O-Ce bond formation. The modification of SiO_2 with CeO_2 was found to provide enhanced PO_4^{3-} adsorption of bare SiO_2 , and impart selectivity. The material shows a maximum adsorption capacity of 110 mg/g with 99% removal reached within 1 h. Kinetic models fitted with the experimental batch adsorption data, indicating chemical adsorption as a rate controlling step. Furthermore, the Langmuir model and the analysis of surface properties suggest a monolayer adsorption mechanism involving ion exchange and Lewis acid–base interactions. The process shows high tolerance to changes in pH in the range between pH 4 and 8.5 and the adsorption was selective,

with no interferences from coexisting anions. Results also show that the adsorbent can be regenerated and reused for up to 6 consecutive cycles without a significant decline in performance. The removal efficiency was superior to that of other adsorbents and demonstrates advantages of these materials for use in environmental remediation applications. Our work highlights the potential of CeO_2 -based adsorbents for the removal of PO_4^{3-} . The CeO_2 - SiO_2 developed in this work can be further integrated in separation devices, for example, membranes, filters, and column reactors, to improve treatment and recovery of P-based nutrients from environmental waters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.9b01512.

Description of the zeta potential versus pH measurement; surface area measurement; ATR-FTIR and XPS analysis of the as-prepared adsorbent material; adsorption equilibrium isotherm study of CeO_2 - SiO_2 material with fitted Langmuir and Freundlich isotherm with the corresponding parameters; pseudo-first- and pseudo-second-order kinetics obtained by using the nonlinear fitting with the corresponding parameters; zeta potential measurement of the regeneration process; and ATR-FTIR spectra of CeO_2 - SiO_2 before and after PO_4^{3-} adsorption for mechanism explanation (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: eandrees@clarkson.edu. Fax: +(315) 268 6610. Tel: +(315) 268 2394.

ORCID

Ali Othman: 0000-0002-7960-4995

Silvana Andreescu: 0000-0003-3382-7939

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by NSF Grant 1610281. Also, this work made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (DMR-1719875). Financial support

Table 1. Comparison of PO_4^{3-} Adsorption Capacities of Various Adsorbents

adsorbent	adsorption capacity (q_m , mg/g)	adsorbent dosage (g/L)	pH	equilibrium time	removal (%)	ref
magnetic iron oxide NPs	5.0	0.6	6.0	12 h	97	53
magnetite (Fe_3O_4)	27.2	1.0	7.0	24 h	85	54
coir–pith activated carbon	7.7	4	6.0	3 h		55
Fe–Zr binary oxide	41.8	1	4.0	2 h	86	56
coir–pith–Fe	70.9	2	3.0	12 h		57
CuFe_2O_4	41.3	0.6	2.6	2 h	65	58
amorphous ZrO_2 NPs	99	0.1	6.2	8 h	99	59
hydrous niobium oxide	15	2	12	4 h	>88	60
zirconium oxide	30	1.2	6.7	5 h	54	61
hydrous zirconium oxide	66	2	5	8 h	99	62
$\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{--CeO}_2$	26.5	0.5	6	400 min		63
$\text{Fe}_3\text{O}_4@/\text{SiO}_2@m\text{CeO}_2$	64.1	0.7	6	1 h	91	17
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	112.2	0.1	6.2	1 h	92	30
$\text{CeO}_2\text{--SiO}_2$	110	2	7.0	1 h	99	this work

provided by the New York State Pollution Prevention Institute through a grant from the New York State Department of Environmental Conservation is also acknowledged.

REFERENCES

- (1) Cosgrove, W. J.; Loucks, D. P. Water Management: Current and Future Challenges and Research Directions. *Water Resour. Res.* **2015**, *51* (6), 4823–4839.
- (2) Elser, J.; Bennett, E. Phosphorus Cycle: A Broken Biogeochemical Cycle. *Nature* **2011**, *478* (7367), 29–31.
- (3) Canfield, D. E.; Glazer, A. N.; Falkowski, P. G. The Evolution and Future of Earth's Nitrogen Cycle. *Science* **2010**, *330* (6001), 192–196.
- (4) EPA. *National Rivers and Streams Assessment 2008–2009: A Collaborative Survey (Draft)*; Office of Wetlands, Oceans, and Watersheds, Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC; <https://www.epa.gov/national-aquatic-resource-surveys/nrsa> (accessed on 29 October 2014).
- (5) Sharma, L. K.; Bali, S. K.; Zaeen, A. A. A Case Study of Potential Reasons of Increased Soil Phosphorus Levels in the Northeast United States. *Agronomy* **2017**, *7* (4), 85.
- (6) Zhang, L.; Wan, L.; Chang, N.; Liu, J.; Duan, C.; Zhou, Q.; Li, X.; Wang, X. Removal of Phosphate from Water by Activated Carbon Fiber Loaded with Lanthanum Oxide. *J. Hazard. Mater.* **2011**, *190* (1–3), 848–855.
- (7) Awual, M. R.; Jyo, A.; Ihara, T.; Seko, N.; Tamada, M.; Lim, K. T. Enhanced Trace Phosphate Removal from Water by Zirconium-(IV) Loaded Fibrous Adsorbent. *Water Res.* **2011**, *45* (15), 4592–4600.
- (8) Zong, E.; Wei, D.; Wan, H.; Zheng, S.; Xu, Z.; Zhu, D. Adsorptive Removal of Phosphate Ions from Aqueous Solution using Zirconia-Functionalized Graphite Oxide. *Chem. Eng. J.* **2013**, *221*, 193–203.
- (9) Jiang, C.; Jia, L.; He, Y.; Zhang, B.; Kirumba, G.; Xie, J. Adsorptive Removal of Phosphorus from Aqueous Solution using Sponge Iron and Zeolite. *J. Colloid Interface Sci.* **2013**, *402* (Supplement C), 246–252.
- (10) Yagi, S.; Fukushi, K. Removal of Phosphate from Solution by Adsorption and Precipitation of Calcium Phosphate onto Monohydrocalcite. *J. Colloid Interface Sci.* **2012**, *384* (1), 128–136.
- (11) Geelhoed, J. S.; Hiemstra, T.; Van Riemsdijk, W. H. Phosphate and Sulfate Adsorption on Goethite: Single Anion and Competitive Adsorption. *Geochim. Cosmochim. Acta* **1997**, *61* (12), 2389–2396.
- (12) Lüring, M.; Waajen, G.; van Oosterhout, F. Humic Substances Interfere with Phosphate Removal by Lanthanum Modified Clay in Controlling Eutrophication. *Water Res.* **2014**, *54*, 78–88.
- (13) Othman, A.; Karimi, A.; Andreescu, S. Functional Nanostructures for Enzyme based Biosensors: Properties, Fabrication and Applications. *J. Mater. Chem. B* **2016**, *4* (45), 7178–7203.
- (14) Andreescu, D.; Bulbul, G.; Ozel, R. E.; Hayat, A.; Sardesai, N.; Andreescu, S. Applications and Implications of Nanoceria Reactivity: Measurement Tools and Environmental Impact. *Environ. Sci.: Nano* **2014**, *1* (5), 445–458.
- (15) Recillas, S.; García, A.; González, E.; Casals, E.; Puentes, V.; Sánchez, A.; Font, X. Preliminary Study of Phosphate Adsorption onto Cerium Oxide Nanoparticles for Use in Water Purification; Nanoparticles Synthesis and Characterization. *Water Sci. Technol.* **2012**, *66* (3), 503–509.
- (16) Li, C.-m.; Zhang, Y.-s.; Wang, X.-p.; Yin, X.-b.; Luo, N.-n.; Khayambashi, A.; Wei, Y.-z. The Synthesis and Characterization of Hydrous Cerium Oxide Nanoparticles Loaded on Porous Silica Micro-Sphere as Novel and Efficient Adsorbents to Remove Phosphate Radicals from Water. *Microporous Mesoporous Mater.* **2019**, *279*, 73–81.
- (17) Ding, H.; Zhao, Y.; Duan, Q.; Wang, J.; Zhang, K.; Ding, G.; Xie, X.; Ding, C. Efficient Removal of Phosphate from Aqueous Solution using Novel Magnetic Nanocomposites with Fe₃O₄@SiO₂ Core and Mesoporous CeO₂ Shell. *J. Rare Earths* **2017**, *35* (10), 984–994.
- (18) Lee, S.-H.; Lu, Z.; Babu, S. V.; Matijević, E. Chemical Mechanical Polishing of Thermal Oxide Films using Silica Particles Coated with Ceria. *J. Mater. Res.* **2002**, *17* (10), 2744–2749.
- (19) Fogg, D. N.; Wilkinson, N. T. The Colorimetric Determination of Phosphorus. *Analyst* **1958**, *83* (988), 406–414.
- (20) Sathe, T. R.; Agrawal, A.; Nie, S. Mesoporous Silica Beads Embedded with Semiconductor Quantum Dots and Iron Oxide Nanocrystals: Dual-Function Microcarriers for Optical Encoding and Magnetic Separation. *Anal. Chem.* **2006**, *78* (16), S627–S632.
- (21) Molinari, M.; Symington, A. R.; Sayle, D. C.; Sakthivel, T. S.; Seal, S.; Parker, S. C. Computer-Aided Design of Nanoceria Structures as Enzyme Mimetic Agents: The Role of Bodily Electrolytes on Maximizing Their Activity. *ACS Appl. Bio. Mater.* **2019**, *2* (3), 1098–1106.
- (22) Khalil, K. M. S.; Elkabee, L. A.; Murphy, B. Formation and Characterization of Different Ceria/Silica Composite Materials via Dispersion of Ceria Gel or Soluble Ceria Precursors in Silica Sols. *J. Colloid Interface Sci.* **2005**, *287* (2), 534–541.
- (23) V., M.; Mody, H. M.; Bajaj, H. C.; Jasra, R. V. Adsorption of Cu²⁺ on Amino Functionalized Silica Gel with Different Loading. *Ind. Eng. Chem. Res.* **2009**, *48* (19), 8954–8960.
- (24) Andreescu, D.; Matijević, E.; Goia, D. V. Formation of Uniform Colloidal Ceria in Polyol. *Colloids Surf., A* **2006**, *291* (1), 93–100.
- (25) Pop, O. L.; Diaconeasa, Z.; Mesaroş, A.; Vodnar, D. C.; Cuibus, L.; Ciontea, L.; Socaciu, C. FT-IR Studies of Cerium Oxide Nanoparticles and Natural Zeolite Materials. *Bull. Univ. Agric. Vet. Med. Cluj-Napoca, Food Sci. Technol.* **2015**, *72* (1), 50–55.
- (26) Wang, X.-D.; Shen, Z.-X.; Sang, T.; Cheng, X.-B.; Li, M.-F.; Chen, L.-Y.; Wang, Z.-S. Preparation of Spherical Silica Particles by Stöber Process with High Concentration of Tetra-Ethyl-Orthosilicate. *J. Colloid Interface Sci.* **2010**, *341* (1), 23–29.
- (27) Antony, R.; David Manickam, S. T.; Kollu, P.; Chandrasekar, P. V.; Karuppasamy, K.; Balakumar, S. Highly Dispersed Cu(II), Co(II) and Ni(II) Catalysts Covalently Immobilized on Imine-Modified Silica for Cyclohexane Oxidation with Hydrogen Peroxide. *RSC Adv.* **2014**, *4* (47), 24820–24830.
- (28) Vivek, S.; Arunkumar, P.; Babu, K. S. In situ Generated Nickel on Cerium Oxide Nanoparticle for Efficient Catalytic Reduction of 4-Nitrophenol. *RSC Adv.* **2016**, *6* (51), 45947–45956.
- (29) Reddy, B. M.; Katta, L.; Thirumurthulu, G. Novel Nanocrystalline Ce_{1-x}La_xO_{2-δ} (x = 0.2) Solid Solutions: Structural Characteristics and Catalytic Performance. *Chem. Mater.* **2010**, *22* (2), 467–475.
- (30) Su, Y.; Yang, W.; Sun, W.; Li, Q.; Shang, J. K. Synthesis of Mesoporous Cerium–Zirconium Binary Oxide Nanoadsorbents by ASolvolothermal Process and Their Effective Adsorption of Phosphate from Water. *Chem. Eng. J.* **2015**, *268*, 270–279.
- (31) Singh, S.; Dosani, T.; Karakoti, A. S.; Kumar, A.; Seal, S.; Self, W. T. A Phosphate-Dependent Shift in Redox State of Cerium Oxide Nanoparticles and its Effects on Catalytic Properties. *Biomaterials* **2011**, *32* (28), 6745–6753.
- (32) Wan, J.; Tao, T.; Zhang, Y.; Liang, X.; Zhou, A.; Zhu, C. Phosphate Adsorption on Novel Hydrogel Beads with Interpenetrating Network (IPN) Structure in Aqueous Solutions: Kinetics, Isotherms and Regeneration. *RSC Adv.* **2016**, *6* (28), 23233–23241.
- (33) Almeelbi, T.; Bezbaruah, A. Aqueous Phosphate Removal Using Nanoscale Zero-Valent Iron. *J. Nanopart. Res.* **2012**, *14* (7), 1–14.
- (34) Li, M. X.; Liu, J. Y.; Xu, Y. F.; Qian, G. R. Phosphate Adsorption on Metal Oxides and Metal Hydroxides: A Comparative Review. *Environ. Rev.* **2016**, *24* (3), 319–332.
- (35) Song, J.; Kong, H.; Jang, J. Adsorption of Heavy Metal Ions from Aqueous Solution by Polyrhodanine-Encapsulated Magnetic Nanoparticles. *J. Colloid Interface Sci.* **2011**, *359* (2), S05–S11.
- (36) Do, M. H.; Phan, N. H.; Nguyen, T. D.; Pham, T. T. S.; Nguyen, V. K.; Vu, T. T. T.; Nguyen, T. K. P. Activated Carbon/Fe₃O₄ Nanoparticle Composite: Fabrication, Methyl Orange Removal

and Regeneration by Hydrogen Peroxide. *Chemosphere* **2011**, *85* (8), 1269–1276.

(37) Damatov, D.; Mayer, J. M. (Hydro)peroxide ligands on colloidal cerium oxide nanoparticles. *Chem. Commun.* **2016**, *52* (67), 10281–10284.

(38) Ornatska, M.; Sharpe, E.; Andreescu, D.; Andreescu, S. Paper Bioassay Based on Ceria Nanoparticles as Colorimetric Probes. *Anal. Chem.* **2011**, *83* (11), 4273–4280.

(39) Li, C.; Domen, K.; Maruya, K.-I.; Onishi, T. Oxygen Exchange Reactions over Cerium Oxide: An FT-IR Study. *J. Catal.* **1990**, *123* (2), 436–442.

(40) Perez, J. M.; Asati, A.; Nath, S.; Kaitanis, C. Synthesis of Biocompatible Dextran-Coated Nanoceria with pH-Dependent Antioxidant Properties. *Small* **2008**, *4* (5), 552–556.

(41) Lin, J.; Wu, Y.; Khayambashi, A.; Wang, X.; Wei, Y. Preparation of a Novel CeO₂/SiO₂ Adsorbent and its Adsorption Behavior for Fluoride Ion. *Adsorpt. Sci. Technol.* **2018**, *36* (1–2), 743–761.

(42) Daou, T. J.; Begin-Colin, S.; Grenèche, J. M.; Thomas, F.; Derory, A.; Bernhardt, P.; Legaré, P.; Pourroy, G. Phosphate Adsorption Properties of Magnetite-Based Nanoparticles. *Chem. Mater.* **2007**, *19* (18), 4494–4505.

(43) Othman, A.; Dumitrescu, E.; Andreescu, D.; Andreescu, S. Nanoporous Sorbents for the Removal and Recovery of Phosphorus from Eutrophic Waters: Sustainability Challenges and Solutions. *ACS Sustainable Chem. Eng.* **2018**, *6* (10), 12542–12561.

(44) Kralchevska, R. P.; Pucek, R.; Kolařík, J.; Tuček, J.; Machala, L.; Filip, J.; Sharma, V. K.; Zbořil, R. Remarkable Efficiency of Phosphate Removal: Ferrate(VI)-Induced in Situ Sorption on Core-Shell Nanoparticles. *Water Res.* **2016**, *103* (Supplement C), 83–91.

(45) Xie, F.; Wu, F.; Liu, G.; Mu, Y.; Feng, C.; Wang, H.; Giesy, J. P. Removal of Phosphate from Eutrophic Lakes through Adsorption by in Situ Formation of Magnesium Hydroxide from Diatomite. *Environ. Sci. Technol.* **2014**, *48* (1), 582–590.

(46) Xu, J.; Harmer, J.; Li, G.; Chapman, T.; Collier, P.; Longworth, S.; Tsang, S. C. Size Dependent Oxygen Buffering Capacity of Ceria Nanocrystals. *Chem. Commun.* **2010**, *46* (11), 1887–1889.

(47) Barth, C.; Laffon, C.; Olbrich, R.; Ranguis, A.; Parent, P.; Reichling, M. A Perfectly Stoichiometric and Flat CeO₂(111) Surface on a Bulk-Like Ceria Film. *Sci. Rep.* **2016**, *6*, 21165.

(48) Mullins, D.; Overbury, S.; Huntley, D. Electron Spectroscopy of Single Crystal and Polycrystalline Cerium Oxide Surfaces. *Surf. Sci.* **1998**, *409* (2), 307–319.

(49) Hasegawa, T.; Shahed, S. M. F.; Sainoo, Y.; Beniya, A.; Isomura, N.; Watanabe, Y.; Komeda, T. Epitaxial Growth of CeO₂ (111) Film on Ru (0001): Scanning Tunneling Microscopy (STM) and X-Ray Photoemission Spectroscopy (XPS) study. *J. Chem. Phys.* **2014**, *140* (4), 044711.

(50) Henderson, M. A.; Perkins, C.; Engelhard, M. H.; Thevuthasan, S.; Peden, C. H. Redox Properties of Water on the Oxidized and Reduced Surfaces of CeO₂ (111). *Surf. Sci.* **2003**, *526* (1), 1–18.

(51) Duval, Y.; Mielczarski, J. A.; Pokrovsky, O. S.; Mielczarski, E.; Ehrhardt, J. J. Evidence of the Existence of Three Types of Species at the Quartz-Aqueous Solution Interface at pH 0–10: XPS Surface Group Quantification and Surface Complexation Modeling. *J. Phys. Chem. B* **2002**, *106* (11), 2937–2945.

(52) Xie, J.; Wang, Z.; Lu, S.; Wu, D.; Zhang, Z.; Kong, H. Removal and Recovery of Phosphate from Water by Lanthanum Hydroxide Materials. *Chem. Eng. J.* **2014**, *254*, 163–170.

(53) Yoon, S.-Y.; Lee, C.-G.; Park, J.-A.; Kim, J.-H.; Kim, S.-B.; Lee, S.-H.; Choi, J.-W. Kinetic, Equilibrium and Thermodynamic Studies for Phosphate Adsorption to Magnetic Iron Oxide Nanoparticles. *Chem. Eng. J.* **2014**, *236*, 341–347.

(54) de Vicente, I.; Merino-Martos, A.; Cruz-Pizarro, L.; de Vicente, J. On the Use of Magnetic Nano and Microparticles for Lake Restoration. *J. Hazard. Mater.* **2010**, *181* (1), 375–381.

(55) Kumar, P.; Sudha, S.; Chand, S.; Srivastava, V. C. Phosphate Removal from Aqueous Solution Using Coir-Pith Activated Carbon. *Sep. Sci. Technol.* **2010**, *45* (10), 1463–1470.

(56) Long, F.; Gong, J.-L.; Zeng, G.-M.; Chen, L.; Wang, X.-Y.; Deng, J.-H.; Niu, Q.-Y.; Zhang, H.-Y.; Zhang, X.-R. Removal of Phosphate from Aqueous Solution by Magnetic Fe–Zr Binary Oxide. *Chem. Eng. J.* **2011**, *171* (2), 448–455.

(57) Krishnan, K. A.; Haridas, A. Removal of Phosphate from Aqueous Solutions and Sewage using Natural and Surface Modified Coir Pith. *J. Hazard. Mater.* **2008**, *152* (2), 527–535.

(58) Tu, Y.-J.; You, C.-F. Phosphorus Adsorption onto Green Synthesized Nano-Bimetal Ferrites: Equilibrium, Kinetic and Thermodynamic Investigation. *Chem. Eng. J.* **2014**, *251*, 285–292.

(59) Su, Y.; Cui, H.; Li, Q.; Gao, S.; Shang, J. K. Strong Adsorption of Phosphate by Amorphous Zirconium Oxide Nanoparticles. *Water Res.* **2013**, *47* (14), S018–S026.

(60) Rodrigues, L. A.; da Silva, M. L. C. P. Thermodynamic and Kinetic Investigations of Phosphate Adsorption onto Hydrous Niobium Oxide Prepared by Homogeneous Solution Method. *Desalination* **2010**, *263* (1), 29–35.

(61) Liu, H.; Sun, X.; Yin, C.; Hu, C. Removal of Phosphate by Mesoporous ZrO₂. *J. Hazard. Mater.* **2008**, *151* (2), 616–622.

(62) Rodrigues, L. A.; Maschio, L. J.; Coppio, L. d. S. C.; Thim, G. P.; Pinto da Silva, M. L. C. Adsorption of Phosphate from Aqueous Solution by Hydrous Zirconium Oxide. *Environ. Technol.* **2012**, *33* (12), 1345–1351.

(63) Liu, J.; Cao, J.; Hu, Y.; Han, Y.; Zhou, J. Adsorption of Phosphate Ions from Aqueous Solutions by a CeO₂ Functionalized Fe₃O₄@SiO₂ Core-Shell Magnetic Nanomaterial. *Water Sci. Technol.* **2017**, *76* (11), 2867–2875.