

## Efficient removal of phosphate from aqueous solution using novel magnetic nanocomposites with $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core and mesoporous $\text{CeO}_2$ shell

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**Abstract:**  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  magnetic nanoparticles functionalized with mesoporous cerium oxide ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{CeO}_2$ ) was fabricated as a novel adsorbent to remove phosphate from water. The prepared adsorbent was characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), nitrogen adsorption-desorption and vibrating sample magnetometry (VSM), and its phosphate removal performance was investigated through the batch adsorption studies. Characterization results confirmed that mesoporous cerium oxide was successfully assembled on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles, and the synthesized adsorbent possessed a typical core-shell structure with a BET surface area of 195  $\text{m}^2/\text{g}$ , accessible mesopores of 2.6 nm, and the saturation magnetization of 21.11 emu/g. The newly developed adsorbent had an excellent performance in adsorbing phosphate, and its maximum adsorption capacity calculated from the Langmuir model was 64.07 mg/g. The adsorption was fast, and the kinetic data could be best fitted with the pseudo-second-order kinetic model. The phosphate removal decreased with the increase of solution pH (2 to 10), while the higher ionic strength slightly promoted the phosphate adsorption. The presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  could enhance the adsorption of phosphate whereas  $\text{HCO}_3^-$  had interfering effect on the phosphate adsorption. The adsorption mechanism was studied by analyzing Zeta potential and FTIR spectroscopy, and the results indicated that the replacement of the surface hydroxyl groups by phosphate ions with the formation of inner-sphere complex played a key role in the phosphate adsorption. The spent adsorbent could be quickly separated from aqueous solution with the assistance of the external magnetic field, and the adsorbed phosphate could be effectively desorbed using a 1 mol/L NaOH solution.

**Keywords:** magnetic nanoparticles; mesoporous cerium oxide; phosphate removal; adsorption; mechanism; rare earths

In the past few decades, eutrophication has been recognized as a serious environmental problem in many natural water bodies largely due to the excessive phosphate present in wastewater discharged from municipal or industrial plants<sup>[1]</sup>. Eutrophication can cause the reduction of biodiversity in aquatic environment, deteriorate water quality and negatively affect the recreational function of natural resources<sup>[2,3]</sup>. Thus it is imperative to remove phosphate ions from wastewater before discharge to protect against eutrophication.

For the treatment of wastewater, removal of phosphate through adsorption method proved to be more promising because of its relatively low cost, wide availability and high adsorption capacity, compared with other phosphate removal technologies such as chemical precipitation, biological removal and ion exchange<sup>[4]</sup>. Therefore, various types of adsorbents have been developed and studied for phosphate removal, which include red mud<sup>[5]</sup>, fly ash<sup>[6]</sup>, mesoporous zirconia<sup>[7,8]</sup>, aluminum-based adsorb-

ents<sup>[9,10]</sup>, iron-based composite oxides<sup>[11–13]</sup>, manganese-based adsorbents<sup>[14,15]</sup>, lanthanum-based adsorbents<sup>[16–18]</sup> and layered double hydroxides<sup>[19]</sup>, etc.

In recent years, cerium oxide, which has been widely applied in the field of catalysts, solar energy devices, optical display technology and corrosion prevention due to its excellent physical and chemical properties<sup>[20–22]</sup>, has also exhibited excellent performance for the removal of various anions including bichromate<sup>[20,23]</sup>, fluoride<sup>[24,25]</sup> and arsenate<sup>[26–28]</sup>. Considering that phosphate has an ionic structure similar to that of arsenate, and the adsorption processes of phosphate and arsenate onto metal oxides are both chemisorption involving the ligand exchange between the surface hydroxyl groups on metal oxides and adsorbates<sup>[19,28]</sup>, cerium oxide could serve as an efficient adsorbent for phosphate removal as predicted in the literature reported by Li et al.<sup>[29]</sup> who directly discussed the material criterion for the selection of highly efficient adsorbents. Accordingly, some novel

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CeO<sub>2</sub>-based adsorbents have been developed recently to remove phosphate ions from wastewater<sup>[30,31]</sup>. Su et al.<sup>[30]</sup> successfully synthesized mesoporous cerium–zirconium binary oxide nanoadsorbents through a facile process and found that the phosphate adsorption capacity of Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> nanoparticles could reach ~112.23 mg/g. In addition to good adsorption performance, cerium oxide is a relatively cheap and abundant rare earth oxide which has high resistance against acid and base, and it does not elute during the removal of harmful ions from wastewater<sup>[23]</sup>. These advantages make the application of cerium oxide in phosphate removal more promising.

However, although phosphate might be effectively removed by using cerium oxide as the adsorbent, it is difficult to regenerate and reuse this adsorbent because cerium oxide nanoparticles in fine powder form can not be easily recovered once put into water. To overcome this problem, granulation of powder adsorbents could be a solution but it would reduce the specific surface area and the amounts of surface active sites, eventually leading to the reduction of the phosphate removal capacity<sup>[32]</sup>. Recently, magnetic nanocomposites have attracted increasing attention in many applications such as biomedicine<sup>[33,34]</sup>, catalysis<sup>[35]</sup> and adsorption<sup>[36,37]</sup>, because they can be conveniently separated from liquid phase through an external magnetic field, avoiding many problems encountered in other separation methods including filtration, centrifugation and gravity sedimentation<sup>[8]</sup>. Among these magnetic nanocomposites, a novel material, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CeO<sub>2</sub> microsphere, has been reported for the phosphopeptide capturing and labeling, where the Fe<sub>3</sub>O<sub>4</sub> magnetic core can facilitate the rapid enrichment and isolation<sup>[33]</sup>. Thus, an efficient and easily recyclable adsorbent for phosphate removal could be synthesized through the combination of magnetite and cerium oxide. However, to the best of our knowledge, there is no report on the adsorbent with such combination for the phosphate removal in literature.

In current study, we prepared a novel magnetic adsorbent (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mCeO<sub>2</sub>) with a core-shell structure by loading mesoporous CeO<sub>2</sub> onto the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles, where the silica coatings were used to protect the Fe<sub>3</sub>O<sub>4</sub> magnetic cores and offer an active surface for further modification, and mesoporous CeO<sub>2</sub> with large specific surface area was expected to improve the adsorption capacity for phosphate. The synthesized adsorbent was characterized using different techniques, and its adsorption properties for phosphate were evaluated through the studies of adsorption kinetics and adsorption isotherm. The effects of different parameters such as solution pH, ionic strength and coexisting ions on the phosphate adsorption were investigated in detail, and the desorption of phosphate was also studied. Based on the analyses of Zeta potential and FTIR spectroscopy, the adsorption mechanism of phosphate onto

the newly developed adsorbent was explored and elucidated.

## 1 Materials and methods

### 1.1 Materials

All chemicals were of analytical reagent grade and used as-received without any further purification. Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O), cerous chloride heptahydrate (CeCl<sub>3</sub>·7H<sub>2</sub>O), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), sodium citrate (99%) and cetyltrimethylammonium bromide (CTAB, 99%) were obtained from Aladdin (Shanghai, China). Tetraethyl orthosilicate (TEOS, 99%), ammonia (NH<sub>3</sub>, 28%), hydrazine (80%), ethanol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd.. The water used was purified through a Millipore system.

### 1.2 Adsorbent preparation

#### 1.2.1 Preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by the modified coprecipitation method based on the previous literature<sup>[38]</sup>. In a typical process, 4 g of FeCl<sub>3</sub>·6H<sub>2</sub>O and 1.5 g of FeCl<sub>2</sub>·4H<sub>2</sub>O were dissolved in 30 mL of de-oxygenated water. Then, the freshly prepared solution was dropwise added into 60 mL of 2.0 mol/L ammonia solution under an inert atmosphere and stirred at 90 °C for 30 min. Subsequently, 6 g of sodium citrate dissolved in 10 mL of deionized water was also added into the above solution, followed by stirring at 90 °C for another 1 h. After cooling to room temperature, the resulting Fe<sub>3</sub>O<sub>4</sub> nanoparticles were collected by a permanent magnet, washed several times with deionized water, and then dried at 50 °C in a vacuum oven for 12 h.

#### 1.2.2 Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles

The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanoparticles were prepared using the biphasic method according to the study of Zou et al.<sup>[39]</sup>. Typically, 0.1 g of as-prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles were ultrasonically dispersed in a solution containing 100 mL of deionized water and 2 ml of hydrazine. Subsequently, 0.4 ml of TEOS was added into the above magnetic fluids, and the mixtures were refluxed with stirring at 90 °C for 2 h. Finally, the silica coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles were separated by centrifugation and dispersed in deionized water for the next step.

#### 1.2.3 Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mCeO<sub>2</sub> nanoparticles

The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mCeO<sub>2</sub> nanoparticles were synthesized through a soft templating approach as described in the following procedure. Firstly, the obtained Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were homogeneously dispersed in a mixed solution consisting of 80 mL of water, 60 mL of ethanol, 0.3 g of CTAB and 1.2 mL of concentrated ammonia (28 wt.%) by mechanical stirring for 30 min.

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