



# Phosphate adsorption using modified iron oxide-based sorbents in lake water: Kinetics, equilibrium, and column tests

Jacob Lalley<sup>a,b,1</sup>, Changseok Han<sup>a,1</sup>, Xuan Li<sup>a</sup>, Dionysios D. Dionysiou<sup>b</sup>, Mallikarjuna N. Nadagouda<sup>a,\*</sup>

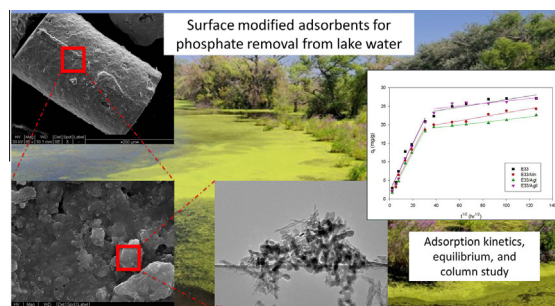
<sup>a</sup>The U.S. Environmental Protection Agency, ORD, NRMRL, WSWRD, WQMB, 26 W. Martin Luther King Jr. Drive, Cincinnati, OH 45268, USA

<sup>b</sup>Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), University of Cincinnati, OH 45221, USA

## HIGHLIGHTS

- The adsorbent E33 was successfully modified with silver and manganese nanoparticles.
- One silver modified sorbent had similar  $\text{PO}_4^{3-}$  adsorption capacity compared to E33.
- Phosphate desorption for its recovery was accomplished by base leaching with NaOH.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 15 June 2015

Received in revised form 24 August 2015

Accepted 26 August 2015

Available online 2 September 2015

### Keywords:

Adsorption

Nutrients

Nutrient removal/recovery

Phosphate

Water treatment

## ABSTRACT

Adsorption behavior of Bayoxide® E33 (E33) and three E33-modified sorbents for the removal of phosphate from lake water was investigated in this study. E33-modified sorbents were synthesized by coating with manganese (E33/Mn) and silver (E33/AgI and E33/AgII) nanoparticles. Adsorbent characterization was done by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), surface area analyzer (BET), transmission electron microscopy (TEM), and high resolution TEM (HR-TEM) analysis. Batch, equilibrium, and column experiments were conducted to determine various adsorption parameters. Equilibrium data were fitted to different adsorption isotherms and the Langmuir isotherm provided the best fit. Based on the Langmuir model, it was found that E33/AgII had a slightly higher maximum monolayer adsorption capacity ( $38.8 \text{ mg g}^{-1}$ ) when compared to unmodified E33 ( $37.7 \text{ mg g}^{-1}$ ). Data for adsorption kinetics were found to best fit with the pseudo-second-order model, suggesting chemisorption is the mechanism of sorption. Intra-particle diffusion studies indicated that the rate-limiting step for phosphate sorption onto E33 and modified E33 was intra-particle diffusion. Although limited improvements were seen, the results of this study suggest that the surface of E33 can be modified with nanoparticles to enhance the adsorption of phosphate from aqueous solutions and may give other advantages such as limiting biofouling over an extended lifetime of numerous recovery/regeneration steps.

Published by Elsevier B.V.

## 1. Introduction

Phosphates ( $\text{PO}_4^{3-}$ ), as essential and often limiting nutrients in most aquatic environments, can result in the acceleration of eutrophication; leading to an increase in costs associated with water treatment [1], decreased recreational value of the waterway

\* Corresponding author. Tel.: +1 (513) 569 7232; fax: +1 (513) 569 7172.

E-mail address: [Nadagouda.mallikarjuna@epa.gov](mailto:Nadagouda.mallikarjuna@epa.gov) (M.N. Nadagouda).

<sup>1</sup> Contributed equally to this work.

[2], and the formation of harmful algal blooms (HABs) that may pose a risk to human health from the production of cyanotoxins [3]. Therefore, the remediation of phosphates from aquatic ecosystems is a growing environmental concern. While phosphates are naturally found in surface and waste water, anthropogenic sources from agriculture [4] (fertilizer/animal feed run-off), industry [5] (detergents), and sewage [6] have increased phosphate loads in surface waters, thus accelerating eutrophication.

While conventional treatment techniques like chemical precipitation and biological phosphorus removal exist, problems remain. Chemical precipitation is a costly process, requiring the purchasing, transportation, and storage of chemical precipitants, and produces vast quantities of sludge which must be properly disposed [7]. Biological processes like enhanced biological phosphorus removal (EBPR) are quite sensitive to water parameters including influent carbon source [8] (e.g., acetate, propionate, etc.) and temperature [9], resulting in decreased stability and reliability. Yet, while phosphates act as pollutants at high concentrations, their demand is growing for industrial purposes including fertilizer production and the manufacturing of detergents. As a non-renewable resource with no known alternatives, the need for phosphate recovery and recycling may become necessary. Though experts disagree on when (between 60 and 700 years) [10,11], it is acknowledged that our phosphate reserves will eventually be depleted. Thus, future studies should focus on  $\text{PO}_4^{3-}$  recovery as well as removal.

One technique that can both remove and recover phosphate is adsorption. Adsorption is a surface-based phenomenon resulting in the adhesion of an adsorbate on the surface of an adsorbent through covalent bonding and electrostatic interactions [12,13]. Unlike chemical precipitation and biological removal processes, adsorption is unique in that it can remove contaminants over a wide pH range and at low concentrations [14]. The iron oxide hydroxide goethite ( $\alpha\text{-FeOOH}$ ) is a highly adsorptive material for phosphate remediation. As the most thermodynamically stable iron oxide in most environmental conditions, goethite is the most frequently encountered iron oxide in nature and occurs in almost every soil type in every climatic region [15].

Iron oxides like goethite typically occur as poorly ordered, minute crystals with large specific surface areas ( $50\text{--}300\text{ m}^2\text{ g}^{-1}$ ) [16] with hydroxide surface functional groups. These properties substantially contribute to the specific adsorption of anions like  $\text{PO}_4^{3-}$  as inner sphere complexes. Phosphate adsorption results from the completion of the ligand shell of surface Fe atoms, where the  $\text{PO}_4^{3-}$  ion reacts with two singly coordinated Fe–OH groups, forming a bridging, binuclear, bidentate complex  $(\text{Fe}-\text{O})_2\text{-PO}_2\text{H}$  [17]. Due to goethite's affinity for ion adsorption and relative availability, LANXESS Deutschland GmbH has produced Bayoxide® E33 Adsorption Media (E33), a goethite-based adsorbent which was originally designed for arsenic remediation [18–20], yet studies have shown the ability of E33 to sorb a wide range of ions, including phosphates [21–23].

Previous research has explored phosphate adsorption equilibrium and adsorption kinetics of E33 and three surface modified E33-based adsorbents using a stock phosphate solution [24]. In this study, however, lake water was used to determine the effects of competing species on phosphate removal. The phosphate adsorption capacity and kinetics of E33 and modified E33 were determined, as well as the desorption of phosphate to explore possible reuse.

## 2. Experimental

### 2.1. Materials

The E33 adsorbent used to investigate phosphate adsorption was acquired from LANXESS Deutschland GmbH. Lake water,

obtained from Winton Lake in Winton Woods (Cincinnati, OH), was spiked with analytical grade sodium phosphate monohydrate ( $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ ), obtained from Fisher Scientific, at a target concentration of  $140\text{ mg L}^{-1}$  and used in all experimentation. The pH of the lake water was maintained constant at pH 7 using propanesulfonic acid (MOPS), obtained from Sigma Aldrich. Modified E33 was synthesized by the deposition of either silver or manganese nanoparticles to the surface of E33. Silver modified E33 was synthesized using reagent grade silver nitrate ( $\text{AgNO}_3$ , obtained from Sigma Aldrich). Either sodium borohydride ( $\text{NaBH}_4$ , Sigma Aldrich) or tea powder (Red Label, India) were used as capping/reducing agents. Manganese modified E33 was synthesized using manganese acetate tetrahydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ) obtained from Sigma Aldrich. The synthesized adsorbents consisted of either manganese or silver coated E33. The procedure for synthesis can be found in our previous study [24].

### 2.2. Sample characterization

The crystal structure of the adsorbents was determined by X-ray diffraction (XRD) analysis using a Panalytical (Expert) 2-theta diffractometer (Panalytical, Almelo, Netherlands) at a wavelength of  $1.54\text{ }\mu\text{m}$  and at 2-theta range  $2\text{--}90^\circ$  under  $\text{CuK}_\alpha$  radiation. The BET surface area, total pore volume, and porosity of the adsorbents were determined using a Tristar 3000 porosimeter analyzer (Micromeritics). Before analysis, the adsorbent samples were purged with nitrogen gas for 2 h and at  $150\text{ }^\circ\text{C}$  using the Micromeritics FlowPrep 060. For the characterization of the surface morphology of the adsorbents, an environmental scanning electron microscope (ESEM, Philips XL 30 ESEM-FEG), at an accelerating voltage of 30 kV was used. Physical properties of the adsorbent were also studied with transmission electron microscopy (TEM), where a FEI CM20 TEM operated at 200 kV was employed. To further characterize the physical properties of the surface-modified adsorbents, high-resolution TEM (HR-TEM, JEM-2010F, obtained from JEOL) was employed with a field emission gun at 200 kV. Prior to characterization, the adsorbents were prepared and dispersed by ultrasonication (2510R-DH, Branson) in 99.8% pure isopropyl alcohol (obtained from Pharmco-AAPER) for 30 min. Then, on a carbon-coated copper grid (LC325-Cu, EMS), a drop of the supernatant was fixed and dried at room temperature. The images obtained from the HR-TEM were analyzed using ImageJ, an image processing software (National Institutes of Health, Maryland, USA). Finally, as adsorption is highly dependent on the adsorbent surface charge, the point of zero charge for the adsorbents was evaluated using a SurPass Surface Electrokinetic Analyzer (Anton Paar, Australia). The zeta potential was measured at different pH values to determine the point of zero charge for the samples. To explore the stability of deposited nanoparticles onto the surface of E33, the concentration of Mn and Ag were determined after adsorption experiments using an Agilent Technologies Inc. (Santa Clara, CA) 7500cs Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The solutions were first filtered through  $0.45\text{ }\mu\text{m}$  Whatman nylon syringe filters and solubilized using nitric acid.

### 2.3. Adsorption studies

Variable dose isotherm experiments were conducted to determine equilibrium adsorption parameters. Varying masses of adsorbent, ranging from 0.1 to 1.5 g, were placed in 125 mL Nalgene polypropylene bottles with 100 mL of the lake water solution. The solution was prepared by dissolving sodium phosphate monohydrate ( $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ ) in Winton Lake lake water (at a target concentration of  $140\text{ mg PO}_4^{3-}\text{ L}^{-1}$ ). To this, 15 mM MOPS buffer was added and pH was adjusted to 7.0 with 1 N NaOH. The bottles were placed on a G10 Gyrotary shaker (New Brunswick

Download English Version:

<https://daneshyari.com/en/article/146042>

Download Persian Version:

<https://daneshyari.com/article/146042>

[Daneshyari.com](https://daneshyari.com)