



## Adsorption–desorption mechanism of phosphate by immobilized nano-sized magnetite layer: Interface and bulk interactions

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### ABSTRACT

Phosphate adsorption mechanism by a homogenous porous layer of nano-sized magnetite particles immobilized onto granular activated carbon (nFe-GAC) was studied for both interface and bulk structures. X-ray Photoelectron Spectroscopy (XPS) analysis revealed phosphate bonding to the nFe-GAC predominantly through bidentate surface complexes. It was established that phosphate was adsorbed to the magnetite surface mainly via ligand exchange mechanism. Initially, phosphate was adsorbed by the active sites on the magnetite surface, after which it diffused into the interior of the nano-magnetite layer, as indicated by intraparticle diffusion model. This diffusion process continues regardless of interface interactions, revealing some of the outer magnetite binding sites for further phosphate uptake. Desorption, using NaOH solution, was found to be predominantly a surface reaction, at which hydroxyl ions replace the adsorbed phosphate ions only at the surface outer binding sites. Five successive fixed-bed adsorption/regeneration cycles were successfully applied, without significant reduction in the nFe-GAC adsorption capacity and at high regeneration efficiency.

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### 1. Introduction

Phosphorus is one of the more understood nonrenewable available nutrients for fertilizers production. It has been established that phosphorus reserves will be depleted within 60–130 years [1]. However, the presence of trace amounts of phosphate (even below 1 µg/L) in treated wastewater from municipalities and industries is often accountable for eutrophication which leads to short- and long-term environmental and esthetic problems in lakes, coastal areas, and other confined water bodies [2]. As a consequence, phosphate removal, and recovery from wastewater has been considered as an important environmental sustainability concern [1].

Adsorption is one of the most attractive approaches in water treatment, with the advantage of having high removal efficiency without yielding harmful by-products [3]. It is well known that phosphates have a strong affinity for mineral surfaces [4]. Its affinity for (hydr)oxide surfaces depends on one hand on the anions' complexing capacity, which allows binding to surface groups by ligand exchange reactions, and on the other hand on electrostatic interactions with the charged (hydr)oxide surfaces [5].

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Phosphate can be adsorb on iron oxides to form a variety of surface species [6], including mononuclear monodentate, mononuclear bidentate, and binuclear bidentate (Fig. 1). However, in most cases, iron oxides present slow adsorption kinetics owing to diffusion resistance and their separation from aqueous solutions after adsorption is difficult [3]. Enhanced adsorption may be accomplished by reducing the iron oxides particles size since nano-particles have a large surface-to-volume ratio compared to other bulk materials. Yet, small-sized particles may not be separated from aqueous solutions by gravitational sedimentation and therefore are difficult to use in continuous flow systems. Hence, immobilization of the nano-adsorbents onto supporting materials enables efficient use of the nano-particles extended surface area [7].

The applicability of an iron-oxide-based adsorbent depends not only on the adsorption capacity but also on its reusability. The equilibrium between phosphate ions in solution and solid surfaces may be altered by changing the concentration of phosphate ions in solution, the pH of the suspension, and other variables of less influence such as ionic strength and temperature [8]. Some previous studies indicated that the regeneration capacity of phosphate from iron oxides is limited by the fact that strong alkaline solution causes an alteration of the solid surface which results in occlusion of part of the adsorbed phosphate ions [8–10]. However, other studies indicated that by applying the desorption procedure toward either ferrihydrite or well-crystallized goethite, full phosphate regeneration was achieved [11,12]. In those cases, full regeneration was achieved after 0.5 h treatment with NaOH and

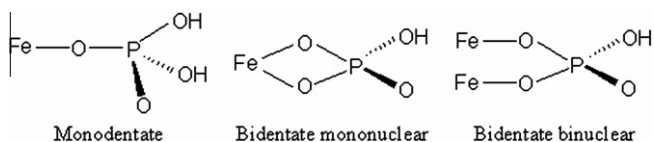


Fig. 1. Possible configuration of the phosphate surface complexes.

was attributed to the physical structure of the oxides' surface. Complete understanding of the uptake and release of phosphate by adsorbents requires knowledge of mechanism at the molecular scale.

The objective of this study was to determine the adsorption–desorption mechanism of phosphate by a homogenous porous layer of nano-sized magnetite particles immobilized onto granular activated carbon (nFe-GAC). Determination of the surface bonding was achieved through analytical experiment (interface mechanism), whereas adsorption–desorption mechanism was comprehensively determined by conducting batch and fixed-bed experiments (bulk mechanism). The reusability of this adsorbent was also evaluated.

## 2. Experimental

### 2.1. Materials

Charcoal activated granulated carbon (pure) particle size: 0.5–1.6 mm was supplied by Riedel de Haën (Germany).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{HPO}_4$  were purchased from Merck (Germany);  $\text{KMnO}_4$  and  $\text{NaOH}$  from Frutarom (Israel). All chemicals were used as received, and all solutions were prepared with de-ionized (DI) water.

### 2.2. Adsorbent preparation

Charcoal granular activated carbon (GAC) was modified using potassium permanganate and impregnated with ferric chloride solution (0.18 M) at a ratio of 20 mL iron solution per 1 g GAC for 2 h at 25 °C. A detailed procedure is described elsewhere [7].

### 2.3. Batch adsorption

A total of 35 mL of phosphate solution at a concentration of 500 mg/L were mixed with 0.7 g nFe-GAC and agitated in a water

bath at 25 °C and 200 rpm. At regular intervals, an aliquot of supernatant was analyzed for phosphate. Adsorption isotherm was obtained by adding various amounts of nFe-GAC (5–40 g/L) to 500 mg/L phosphate solution at pH 6.3 and 25 °C. Equilibrium time was determined at 24 h.

### 2.4. Fixed-bed adsorption

Fig. 2 represents a schematic description of the experimental system (loading and regeneration).

#### 2.4.1. Loading of phosphate

Fixed-bed experiments were performed using a short glass column (25 × 2.5 cm id) packed with 3 g nFe-GAC corresponding to 2.1 cm bed height. Phosphate solution at initial concentration of 10 mg/L (pH 6.7) was loaded onto the bed in a down-flow mode at a rate of 5 mL/min (corresponding to 30 Bed Volume (BV) per h) using Masterflex pump (ColePalmer, USA).

The amount of adsorbed phosphate was calculated by integrating the phosphate adsorbed vs. the throughput volume (Eq. (1)).

$$q_{\text{PO}_4} = \int_0^{V_T} \frac{(C_0 - C_t) dV}{M_{\text{Fe}}} \quad (1)$$

where  $q_{\text{PO}_4}$  is the adsorbed phosphate (mg  $\text{PO}_4/\text{g Fe}$ );  $V_T$  is the volume of effluent collected upon exhaustion of the bed;  $C_0$  and  $C_t$  are the initial and effluent concentrations, respectively (mg/L);  $M_{\text{Fe}}$  is the mass of iron immobilized onto the GAC (g).

The gradual saturation of inner adsorption sites was demonstrated by applying five successive loading cycles, at which once breakthrough was reached the column was drained and left closed overnight prior to the next loading.

The effect of inlet feed pH (2.0, 3.0, 4.0, 6.7, and 9.0) was tested at flow rate of 20 mL/min. The phosphate solution pH was adjusted, prior to the initiation of the experiments, using 0.5 M HCl or NaOH.

#### 2.4.2. Regeneration

Desorption was applied immediately following breakthrough using an alkaline solution (0.05 M NaOH for 30 min) in an up-flow mode and a close-loop configuration, at a rate of 100 mL/min resulting in approximately 50% bed expansion. Following the NaOH re-circulation, the nFe-GAC was neutralized with 0.01 M HCl for 30 min.

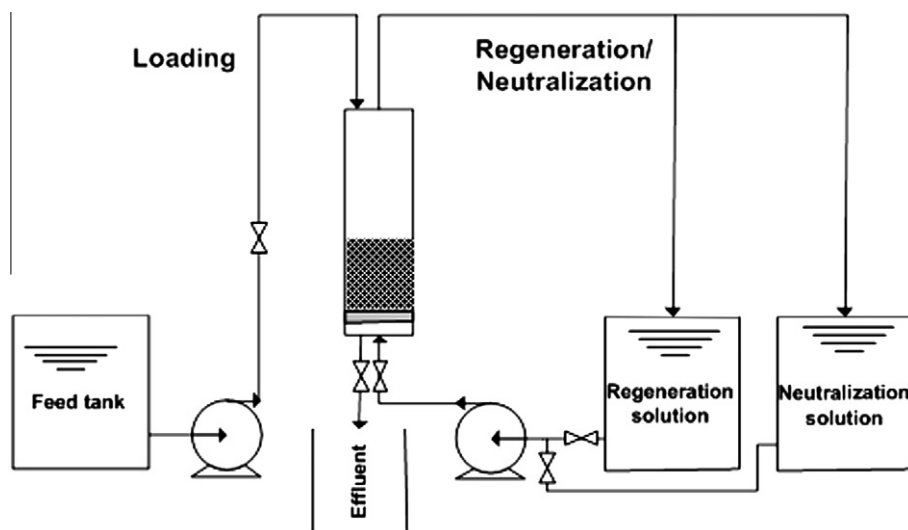


Fig. 2. A schematic description of the experimental system.

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