Phosphate and organic contaminants removal from polluted water and tertiary treated wastewater

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Abstract
An iron (Fe$^{3+}$) oxide/hydroxide nanoparticles-based agglomerates (AggFe) suspension adsorbent was synthesized for efficient, cost-effective phosphate removal. A strong effect of AggFe concentration and pH level of water containing phosphate on removal efficiency was shown. It was found that phosphate adsorption onto the AggFe suspension may be described by pseudo-second-order reaction kinetics and the Langmuir isotherm model. The unique adsorption properties of synthesized AggFe adsorbent are demonstrated. This technique achieved a residual phosphate concentration of less than 0.05 ppm as PO$_4$ (<20 ppb as P), which is acceptable by water quality regulations, and at least 95-99% regeneration efficiency of the phosphate with the proposed adsorbent. The phosphate adsorption capacity on the AggFe at an equilibrium concentration of 0.1 ppm as P in the solution is about 1.5-1.9 times higher than these values for granulated ferric hydroxide (fraction < 63 µm) and more than one order of magnitude higher than other values reported in the literature. This technique enables recovery of the adsorbent while producing a concentrated phosphate solution that may be treated further to obtain phosphate crystals while recovering the cleaning solution.

Keywords: adsorption, agglomerates, iron (Fe$^{3+}$) oxide-hydroxide, phosphate, recovery, suspension, water purification.
INTRODUCTION

Phosphates are often present in drinking water, groundwater and industrial wastewater. Phosphate is an essential nutrient in the aquatic environment, but an excessive phosphate concentration in surface water may lead to eutrophication [1,2]. Sewage and urban wastewater contain 10-30 ppm of phosphate. Treated sewage contains a lower concentration, down to 1-5 ppm. Physicochemical treatment and biological nutrient removal are the two most commonly used methods for the removal of phosphate from municipal and industrial wastewater [1,3-5]. Physicochemical treatment methods essentially transfer phosphate from the liquid to the sludge phase, which must be hauled and disposed of elsewhere. The most widely used activated sludge biological wastewater treatment methods achieve a removal of only 75-85% of total phosphate [6,7].

The presence of phosphate ions causes a severe fouling problem if high recovery reverse osmosis (RO) purification is performed on tertiary treated sewage water, polluted groundwater or industrial wastewater, which limits water recovery. These ions can readily lead to membrane blockage through the precipitation of calcium phosphate salt. Most of the available anti-scalants of calcium phosphate scale inhibition are not very effective in preventing precipitation [8]. As a result, the ineffectiveness of anti-scalants leads to poor efficacy of RO purification of wastewater. Crystallization of calcium-phosphate salts is a frequently used phosphate removal method mainly because of its low cost and ease of handling. Removal is achieved by direct precipitation of calcium phosphate (hydroxyapatite, Ca$_3$(PO$_4$)$_3$(OH) using calcite or calcium silicate hydrate as seeding material [9,10]. The hydroxyl-apatite crystallizes at a pH of 8.0-8.5 without inducing the precipitation of calcium carbonates, which usually adversely affects the process. The calcium-phosphate precipitation method achieves removal efficiencies in this process ranging from 75% to 85% [11].

Recovering phosphorus from wastewater crystallization may be achieved using struvite: (MgNH$_4$PO$_4$·6H$_2$O) precipitation. Struvite is highly soluble at acidic pH and insoluble at alkaline pH. Struvite crystals precipitate by increasing the pH of wastewater liquors to 9.0-9.5 [12-15]). Up to 97% phosphorus removal was achieved using struvite when the magnesium/phosphorus molar ratio was at least 1.05:1. Below this ratio, a 72% phosphorus removal was observed [13]. Phosphate recovery efficiency through struvite formation increased from 40% to 80% by increasing pH values from 8.2 to 9.5, respectively [16].

![Figure 1: Particle size distribution of the AggFe at different pH$_{Fe}$ values. Solid line represents pH$_{Fe}$=4, dashed line represents pH$_{Fe}$=6. Size distributions based on volume (left axis) and area (right axis).](image-url)
phosphate removal [2,17-20, 24-31]. Adsorbents are chosen from materials having a porous structure and large internal surface area, such as granular or powder-activated carbon, activated alumina, mineral clay, zeolite, ion exchangers, or mixtures thereof [17,21-23,31]. The removal of phosphates using Fe$^{+3}$ oxides/hydroxides has been studied intensively and published in recent years [18,20,24-30]. Advanced phosphorus removal by adsorption can be used as a post-treatment step for membrane bioreactors [29,30], for the purification of drinking water and groundwater, and for the cleaning of industrial wastewater after pre-treatment of wastewaters by the above-mentioned methods.

Attempts have been made and reported here to exploit low-cost sorbent to remove phosphate contaminants from water. Using adsorption processes for water treatment requires recovery of the adsorbent material. Application of an adsorbent depends on its cost and on its adsorptive capacity after several adsorption-recovery cycles. Therefore, novel materials and methods are needed for the treatment of water containing phosphate. The objective of this study was to investigate phosphate removal and its recovery using iron (Fe$^{+3}$) oxide/hydroxide nanoparticles-based agglomerates (AggFe) suspension as adsorbent.

2. EXPERIMENTAL

2.1. Materials

Iron-chloride hexa-hydrate, FeCl$_3·$6H$_2$O (analytical grade; Merk KGaA, Germany) and potassium dihydrogen phosphate (analytical grade; Sigma-Aldrich Laborchemikalien GmBH) were used as received.

2.2. Analysis and equipment

A Malvern Nano ZetaSizer model ZEN3600 and Mastersizer 2000 were used to measure size and zeta-potential of the nano-sized particles and nanoparticles-based agglomerate size. pH was determined using a Consort P-931 electrochemical analyzer. Iron and phosphate content analyses were carried out using a data logging Hach DR/2010 spectrophotometer by FerroVer and PhosVer 3 methods. Detection limits for the methods are 0.02 ppm Fe and 0.01 ppm PO$_4$, respectively.

2.3. Preparation and characterization of iron (Fe$^{+3}$) oxide/hydroxide nanoparticles sol and iron (Fe$^{+3}$) oxide nanoparticles-based agglomerates suspension adsorbents

Iron (Fe$^{+3}$) oxide/hydroxide-based nanoparticles sol and iron (Fe$^{+3}$) oxide/hydroxide-based nanoparticles agglomerates suspension were prepared by hydrolysis and pH changes. For the sake of simplicity, the nano iron (Fe$^{+3}$) particles will be referred in this article as NanoFe and the agglomerated nanoparticles as AggFe. The particles were prepared in water and kept until used as suspension. The particles were not separated and dried as reported elsewhere (32-36).

2.3.1. Preparation and characterization of NanoFe sol

NanoFe sol was prepared from iron chloride hexa-hydrate, FeCl$_3·$6H$_2$O (analytical grade; Merck) by hydrolysis to make a 10% iron nanoparticles sol according to:

$$\text{FeCl}_3·6\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{NanoFe} + \text{HCl} + \text{H}_2\text{O} \quad (1)$$

An acidic pH=0.8 in the sol obtained a direct result of the hydrolysis. This formed a mixture of iron oxides and hydroxides where small crystals immediately started to form.

Experiments with NanoFe particles in sol were conducted by diluting the initial solute to the chosen concentration. Particle size distribution was made with a Malvern Nano Zetasizer using the prepared particles solutions. TEM pictures and particle size distribution of these nanoparticles were already presented in our previous articles [37,38].
2.3.2. Preparation of AggFe suspension

The AggFe adsorbent was prepared from the NanoFe solution by agglomeration using a 5 M NaOH solution that was added slowly under vigorous stirring until the required pH values were obtained. The prepared adsorbent suspension was aged for 120 hr. Figure 1 shows the particle volume size distribution (left axis) and area-based size distribution (right axis) of the same AggFe suspension at different pH values. An average AggFe particle size for pH 4 showed particles having volume-weighted mean $D(4,3)=23\mu m$ and surface-weighted mean $D(3,2)=19.4 \mu m$, while by increasing to pH=6, larger sizes were obtained: $D(4,3)=42\mu m$, and $D(3,2)=30.3 \mu m$, respectively.

No drying stage was applied in this method for treating a fluid containing phosphate traces; drying these particles causes a change in structure and leads to changes in surface area. The BET method cannot be used so no measurements of surface area were made. The agglomerates produced are large enough to be separated easily from the solution by precipitation or filtration.

3. RESULTS AND DISCUSSION

In order to treat an aqueous solution containing phosphate traces using the NanoFe sol and AggFe suspension, three stages must be considered:

a) The removal stage where phosphate is adsorbed on particles of adsorbent material.

b) Separation of the loaded adsorbent from the solution by producing a concentrated slurry.

c) Recovery of the adsorbent for reuse by removing the phosphate and producing concentrated phosphate-containing crystals.

3.1. Phosphate removal by NanoFe

3.1.1. Effect of nanoparticles concentration on phosphate removal efficiency

Experiments using NanoFe in solution were carried out at room temperature with initial phosphate solution concentrations of 10, 20, 30 and 40 ppm as $PO_4$. The Nano-Fe concentration ranged from 5 to 60 ppm. Adsorbent loaded with phosphate contaminants were separated from solution by filtration with 0.45 microns of filtration paper.

Figure 2 illustrates how efficient the phosphate was removed by NanoFe. The lines in the figure show a significant influence of nanoparticles concentration on residual phosphate concentration.
Therefore, increasing NanoFe concentration leads to a decrease in residual phosphate concentration and in a weight ratio of removed phosphate to NanoFe adsorbent.

3.1.2. Effect of pH level on phosphate removal

A series of experiments was conducted to investigate the effect of pH value on phosphate removal by NanoFe adsorbent. The results presented in Figure 3 show a marked effect of pH level on phosphate removal and its residual concentration. For pH levels over 9, phosphate adsorption onto nanoparticles was not observed. It is well known that at this pH level, surfaces of metal oxides in solution are covered with hydroxyl groups [28,33,39]. Anion adsorption takes place by positive adsorbent surface charge. Phosphate adsorption on the NanoFe adsorbent makes the surface charge more negative by the acidic nature of the phosphate anions. Direct measurement of the surface charge is very difficult. The zeta potential gives an estimated measure of the surface charge [40]. All of the zeta potential measurements were made at room temperature (25°C) with initial phosphate concentrations of 10 and 40 ppm as PO₄ and a NanoFe concentration of 40 ppm. Figure 4 illustrates the zeta potential changes of NanoFe and phosphate-loaded NanoFe versus pH. An increase in pH value leads to a decrease in adsorbent surface charge and hence to a decrease in adsorbent capacity. The surface charge of the adsorbent is neutral at the point of zero change when pH=pH_{pzc}. An increase in pH value above pH_{pzc} makes the adsorbent surface negatively charged, and leads to a repulsion between negatively charged adsorbent particles and phosphate anions. This stops the adsorption process and also leads to the release of adsorbed phosphate anions at a higher pH.

Figure 3: Phosphate removal at different pH values of the polluted water. Initial phosphate concentration: 40 ppm as PO₄. Concentration of NanoFe, ppm: ▲ - 40, ● - 75.

Figure 4: Zeta-potential at different pH values. Initial phosphate concentration, ppm as PO₄: ● - 0, ▲ -10, ▼ - 40.
3.1.3. **Phosphate adsorption kinetics on NanoFe**

The experimental conditions that were maintained during the investigation of the effect of contact time on phosphate adsorption onto the NanoFe adsorbent were: initial phosphate concentrations of 10, 20, 30 and 40 ppm as PO$_4^-$, pH levels of polluted solution 3.5-6, and NanoFe adsorbent concentrations of 10-60 ppm, respectively.

The experimental results (not shown) demonstrated that the phosphate uptake with NanoFe was completed and equilibrium was achieved within a time shorter than 1 minute. No influence was found in the connection with the initial phosphate concentration in solution or with the pH level.

3.2. **Phosphate removal by AggFe suspension adsorbent**

Operating under a relatively low pH consumes a significant amount of expensive acid. It is important to reuse the adsorbent material in order to reduce costs, as well as to prevent the nano adsorbent existence in the clean solution after the cleaning process. Removal of nanoparticles from solution is possible using ultra-filtration or micro filtration membranes. Increasing the operational pH not only saves on the cost of the acid consumed, it also aggregates the NanoFe into larger sized particles. The question is how much will this affect the adsorption capacity of the NanoFe as AggFe.

3.2.1. **Effect of AggFe concentration on phosphate removal efficiency**

![Figure 5: A. Phosphate removal at different AggFe concentrations. Initial phosphate concentration: 10 ppm as PO$_4^-$, pH values of polluted solution: $\bullet$ – 5; $\blacktriangle$, ○ – 6; and $\times$ – 7, pH level of AggFe suspension, pH$_{Fe}$: $\bullet$, $\blacktriangle$, and $\times$ – 4, ○ – 6, accordingly.](image)

![Figure 5: B. Phosphate removal at different pH values of polluted solution. Initial phosphate concentration 10 ppm as PO$_4^-$, Concentration and pH level of AggFe agglomerates suspension are 100 ppm and pH=6, respectively.](image)

Figure 5 illustrates the efficiency of AggFe suspension concentration on phosphate removal for an initial phosphate concentration of 10 ppm and pH=4 of the added AggFe suspension. Phosphate solution pH values were adjusted to 5, 6 and 7. As shown above for NanoFe solution, the AggFe concentration had a significant effect on residual phosphate concentration and weight ratio of
removed phosphate to AggFe adsorbent due to the increase in total surface area of the adsorbent. Iron agglomerate concentrations needed for the required residual phosphate level at pH are also shown in Figure 5.

3.2.2. Effect of pH level using AggFe suspension

Experiments to investigate the effect of pH level of the solution and AggFe adsorbent on phosphate removal were carried out at an initial phosphate concentration of 10 ppm as PO$_4^{3-}$, while the pH of phosphate solution was changed from 5 to 7. The AggFe suspension concentration varied from 60 to 120 ppm, and the pH of the added adsorbent solution values were 4 and 6.

The effect of pH level on phosphate removal in the phosphate-containing solution is shown in Figures 5A and B. Figure 5B illustrates the effect of pH level of polluted solution on phosphate removal for the AggFe suspension concentration of 100 ppm and an initial pH value of 6. By increasing the pH level of the polluted solution to 7, the residual phosphate concentration increases insignificantly. An increase in pH level leads to a significant increase in residual phosphate concentration.

An increase in the pH level of the AggFe suspension under otherwise constant conditions leads to an increase in residual phosphate concentration. Increasing the pH of the phosphate solution reduces the AggFe adsorbent surface charge, which leads to a reduction in adsorbent capacity (see Fig. 5A and 3.1.2).

As can be seen, the initial pH level of the added suspension of the adsorbent plays a significant role in the final adsorption results. It is assumed that the adsorption process is rapid and depends on the initial size and zeta potential of the particles involved. It is also speculated that the phosphate ions interact with the nanoparticles before they finally aggregate.

3.2.3. Phosphate adsorption kinetics on AggFe suspension adsorbent

Phosphate adsorption kinetics on the AggFe particles in suspension was investigated as a function of time at an initial phosphate concentration of 10 ppm as PO$_4^{3-}$. The pH values of the AggFe suspension were 4 and 6, the pH levels of phosphate-containing solution varied between 5 and 7, and AggFe adsorbent concentration was chosen between 60-120 ppm. The effect of time on phosphate removal at different AggFe suspension concentrations for pH 7 in the phosphate solution is shown in Figure 6A. The results show that the adsorption process can be divided into two stages: a rapid first stage of phosphate adsorption where about 95-99% of the removed phosphate was adsorbed over a short time, about 1 min; and a slower second stage that achieved equilibrium residual phosphate concentration. A decrease in AggFe suspension concentration leads to an increase in the time needed to achieve equilibrium residual phosphate concentration. The rapid phosphate adsorption of the AggFe suspension adsorbent in the first adsorption stage can be attributed to the large external surface adsorption area [34,41]. The adsorbate can easily access the active sites enabling rapid phosphate adsorption. A decrease in adsorption rate in the second stage is attributed to the penetration by diffusion into micro-pores of the adsorbent – a slow process that requires more time [32]. So, the time for phosphate adsorption with AggFe suspension for equilibrium phosphate concentration of 0.15 ppm as PO$_4^{3-}$ (0.05 ppm as P) is about 30 min. This can be compared to the equilibrium time for phosphate adsorption by granulated ferric hydroxide (fraction < 63 µm) of about 96 hr [30].

Phosphate removal using AggFe adsorbent may be simulated by the pseudo-second-order kinetic equation as:
where $Q_t$ is the adsorption capacity at time $t$ (mg/g):

$$Q_t = \frac{C_0 - C_t}{C_{Fe}}$$

where $C_0$ is the initial phosphate concentration, $C_e$ is the phosphate concentration in solution at equilibrium, $C_t$ is the phosphate concentration in solution at time $t$, $C_{Fe}$ is the AggFe adsorbent concentration, $Q_e$ is the equilibrium adsorption capacity, and $k$ is the second-order rate constant.

Figure 6A also shows the $t/Q_t$ ratio from Eq. (2) versus time of reaction $t$ for different AggFe concentrations. The linearity of the curves demonstrates the validity of the adsorption model adapted for phosphate adsorption onto AggFe suspension. From this linear graph, constants $k$ and $Q_e$ may be calculated and were determined.

The residual phosphate concentration $C_t$ in solution may be obtained from Eq. (2) as follows:

$$C_t = C_0 - \frac{C_{Fe}t}{Q_e + \frac{1}{kQ_e^2}}$$

The kinetic experimental data were simulated by the pseudo-second-order reaction kinetics model. The curved lines in Figure 6A represent the simulation of phosphate concentration calculated according to Eq. (4). The calculated values are in good agreement with the experimental values.

This kinetic model cannot identify the diffusion mechanism. The rate-limiting stage of phosphate adsorption onto AggFe suspension may be described by the intra-particle diffusion controlled by the diffusion of ions onto and within the adsorbent [42-44]:

$$Q_t = K_t t^{1/2}$$

where $K_t$ is the intra-particle diffusion rate constant (mg/g/min$^{1/2}$).

Figure 6B shows the amount of adsorbed at time $t$ phosphate versus square root of time for different pH levels of polluted solution and AggFe concentration of 100 ppm. The linearity of the curves in Figure 6B exhibits the validity of the intra-particle diffusion model adapted for phosphate adsorption onto AggFe adsorbent. A plot of $Q_t$ versus $t^{1/2}$ can be divided into two parts with different slopes: the first relates to the film diffusion ($D_1$), and the second with a lesser slope represents the internal micro-porous process of adsorbate diffusion into the adsorbent ($D_2$). By assuming that the diffusion follows Fick’s law, the relationship between adsorbed at time $t$ phosphate and time is given [45,46] at small times:

$$\frac{Q_t}{Q_e} = 6\sqrt{\frac{D_1}{\pi r^2} t}$$

and at moderate and large times:

$$\ln \left(1 - \frac{Q_t}{Q_e}\right) = \ln \frac{6}{\pi} - \left(\frac{D_2 \pi^2}{r^2} t\right)$$

where $r$ is the particle size.
Diffusion coefficients $D_1$ and $D_2$ are determined from the slopes of plots $Q_t/Q_e$ versus $t^{1/2}$ and of $\ln(1-Q_t/Q_e)$ versus $t$ [45]. The values of the film diffusion coefficient $D_1$ for 100 ppm AggFe concentration at pH level 6 for different acidities of phosphate solution are given in Figure 6C. The values of the pore diffusion coefficient $D_2$ are $(0.79-0.81)E-08$ cm$^2$/s. The film diffusion coefficient $D_1$ value is two orders of magnitude higher than the pore diffusion coefficient $D_2$.

3.3. Adsorbed phosphate removal from AggFe suspension adsorbent

After loading the phosphate on the AggFe particles, they are filtered with 0.45 micron filter paper from a wet cake. As shown above, by exposing the cake solution to a solution at a high pH value above of the point of zero charge $\pH > \pH_{PZC}$, the adsorbent surface is negatively charged. This leads to the repulsion between negatively charged adsorbent particles and phosphate anions (See 3.1.2 and Fig. 4). The adsorbed phosphate anions are released to the high pH solution. The pH was adjusted to values between 12 and 13.5. The cake was separated again by filtration, washed, diluted and acidified to the level required for reuse.

The phosphate recovery efficiency $R$ calculated from a mass balance is as follows:

$$R = \frac{m_t}{m_i} \times 100(\%) = \frac{Q_tC_t}{Q_eC_0} \times 100(\%)$$

where $m_i$ is the mass of phosphate in initial solution, $m_t$ is the mass of phosphate in concentrated phosphate solution after adsorbent recovery, $C_0$ is the initial phosphate concentration, $C_t$ is the phosphate concentration in concentrated solution after recovery of the
adsorbent, $Q_0$ is the initial volume of phosphate solution, and $Q_1$ is the volume of concentrated phosphate solution after recovery.

Figure 7 illustrates the effect of pH value on phosphate recovery efficiency from the AggFe adsorbent. An increase in pH value to 12.5-13.5 causes the phosphate recovery efficiency to increase to 90-99%. The AggFe adsorbent that is almost free of phosphate at this stage was removed by filtration from the high pH phosphate-containing solution and washed for secondary usage. It is important to note that the wash solution has a volume that is a few orders of magnitude smaller than the water treated with the AggFe. By choosing a proper volume of high pH solution to treat the loaded AggFe wet cake mass, the concentration of the phosphate accumulated at the high pH solution could easily reach a high level. As an example, a single experiment was conducted when a solution of NaOH at pH 13 containing 20,000 ppm of phosphate was mixed with AggFe adsorbent containing 127 mg P/g Fe. Following separation of the treated AggFe, the filtrated AggFe contained 3.8 mg P/g Fe, which is equivalent to 97% removal of phosphate from the adsorbent. This result needs further investigation and optimization in order to determine the best operational conditions. However, it shows the loading capability of the high pH solution.

The AggFe wet cake washed and separated from the high pH solution was diluted and acidulated to the operational pH solution that may be applied again and reused. Concentrated high pH wash solution can be recovered by precipitating phosphates with concurrent cations such as Ca$^{2+}$ using CaCl$_2$ or Ca(OH)$_2$. This process is based on the low solubility of calcium phosphate salts. The salt particles are removed from wash solution by filtration. This permits reuse of the high pH wash solution.

3.4. Phosphate adsorption isotherm

Equilibrium experiment results of phosphate adsorption on AggFe particles in suspension are shown in Figure 8. Langmuir solute isotherm [28] was used to fit the results as in Eq. (8):

$$\frac{C_0 - C_e}{C_{Fe}} = bQ_m \frac{C_e}{1 + bC_e}$$  (8)

where $C_0$ is the initial phosphate concentration, $C_e$ is the phosphate equilibrium residual concentration, $C_{Fe}$ is the AggFe adsorbent concentration, $Q_m$ is the maximum adsorbate loading capacity per unit adsorbent mass, and $b$ is the Langmuir constant. The values for Langmuir isotherm parameters $Q_m$ and $b$ were calculated from the data presented in Figure 8 and are shown in Table 1.

As can be seen, the solid lines calculated using Eq. (8) are well fitted to the points representing the experimental results. The relatively high weight ratio of phosphate to iron at low phosphate concentration is an important aspect of this adsorbent. The dashed line in
3.5. **Comparisons of adsorption properties of AggFe with other adsorbents**

Direct comparisons of adsorption properties of AggFe suspension with other adsorbents are very difficult due to the different applied experimental conditions. Due to the demand of residual phosphate concentration in purified water of 0.05-0.1 ppm, a capacity of different adsorbents was compared by equilibrium phosphate concentration at \( C_e = 0.1 \text{ ppm} \) as \( P \). The capacity values of different adsorbents under the above conditions were calculated using reported Langmuir equation constants and are summarized in Table 1.

The AggFe suspension adsorbent demonstrated a higher phosphate adsorption efficiency. The phosphate adsorption capacity with AggFe suspension for equilibrium with a phosphate concentration of 0.1 ppm as \( P \) for a pH level of 6 in solution was about 1.8 times higher than values reported for GFH at a pH level of 5.5 (fraction < 63\( \mu \)m) (see Table 1 and Fig. 8) and more than one order of magnitude higher than values reported in the literature (see Table 1). It is important also to emphasize that the equilibrium time for phosphate adsorption with AggFe is about 60-90 min and around two orders of magnitude lower than this value for GFH (96 hr, fraction < 63\( \mu \)m) [29,30]. This followed from the fact that this research leaves out a drying or freeze-drying stage of the produced adsorbent, a procedure that causes a change in agglomerates structure and physical properties, and consequently surface area, pore volume and pore size distribution, which subsequently leads to a change in sorption properties. In addition, the current technique demonstrated a lower cost of adsorbent preparation since the cost of preparing dry granulated iron oxide is higher than the cost of producing wet AggFe.

It is also important to emphasize that the NanoFe and its agglomerate adsorbents demonstrate an extremely high phosphate removal activity also for close to neutral pH solutions. The results show that the AggFe suspension adsorbent is a cost-effective promising route for phosphate removal from aqueous solution.
Table 1: Phosphate adsorption/removal capacities of different adsorbents.

<table>
<thead>
<tr>
<th>Material</th>
<th>Size, mm</th>
<th>Surf. area, m²/g</th>
<th>pH</th>
<th>Langmuir Constants</th>
<th>Adsorbance capacity, Cs mg P/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)/Cr(III) hydroxide</td>
<td>0.075-0.15</td>
<td>4</td>
<td>6.5</td>
<td>0.027</td>
<td>0.017# [47]</td>
</tr>
<tr>
<td>Dry iron oxide tailings</td>
<td>0.068</td>
<td>49.7</td>
<td>6.8</td>
<td>0.027</td>
<td>0.35# [18]</td>
</tr>
<tr>
<td>CP (Coir Pith)-Fe</td>
<td>155.2</td>
<td>3</td>
<td>70.9</td>
<td>0.1</td>
<td>0.70# [48]</td>
</tr>
<tr>
<td>RM (Red Mud)</td>
<td>0.14</td>
<td>14.1</td>
<td>113.9</td>
<td>0.0027</td>
<td>0.031# [49]</td>
</tr>
<tr>
<td>RM 700</td>
<td>9.7</td>
<td>161.6</td>
<td>345.5</td>
<td>0.000888</td>
<td>0.036# [49]</td>
</tr>
<tr>
<td>RM 0.25</td>
<td>19.3</td>
<td>95.9</td>
<td>202.9</td>
<td>0.0021</td>
<td>0.042# [50]</td>
</tr>
<tr>
<td>Activated RM</td>
<td>0.14</td>
<td>14.1</td>
<td>63.2</td>
<td>0.00046</td>
<td>0.003# [49]</td>
</tr>
<tr>
<td>RM700</td>
<td>15.7</td>
<td>58.9</td>
<td>202.9</td>
<td>0.0021</td>
<td>0.042# [50]</td>
</tr>
<tr>
<td>RMAH</td>
<td>21.8</td>
<td>78.4</td>
<td>202.9</td>
<td>0.0021</td>
<td>0.042# [50]</td>
</tr>
<tr>
<td>FA( Fly Ash)</td>
<td>0.14</td>
<td>14.5</td>
<td>90.1</td>
<td>0.040</td>
<td>0.36# [51]</td>
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<tr>
<td>FA 700</td>
<td>12.2</td>
<td>1.5</td>
<td>90.9</td>
<td>0.078</td>
<td>0.70# [51]</td>
</tr>
<tr>
<td>FA 0.25</td>
<td>18.7</td>
<td>0.2</td>
<td>107.5</td>
<td>0.21</td>
<td>2.18# [52]</td>
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<tr>
<td>SCS (synthetic coated sand)</td>
<td>0.8-2</td>
<td>2.61</td>
<td>1.5</td>
<td>0.2</td>
<td>0.029# [52]</td>
</tr>
<tr>
<td>CB (coated crushed brick)</td>
<td>3.325</td>
<td>1.75</td>
<td>1.75</td>
<td>0.23</td>
<td>0.039# [52]</td>
</tr>
<tr>
<td>Granulated ferric hydroxide</td>
<td>&lt;0.063</td>
<td>208-230</td>
<td>23.3</td>
<td>20.4</td>
<td>15.6# [30]</td>
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<tr>
<td>Activated aluminum oxide</td>
<td>230-300</td>
<td>5.5</td>
<td>16.9</td>
<td>8.8</td>
<td>7.9# [30]</td>
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<tr>
<td>Synthetic goethite and akaganeite</td>
<td>2</td>
<td>13.8</td>
<td>13.2</td>
<td>7.8# [30]</td>
<td></td>
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<tr>
<td>Hydrous ferric oxide</td>
<td>0.15-0.3</td>
<td>4</td>
<td>12.0</td>
<td>6.3</td>
<td>4.6# [25]</td>
</tr>
<tr>
<td>Blast furnace slag</td>
<td>0.02-0.03</td>
<td>8.5</td>
<td>24*</td>
<td>28*</td>
<td>7.7** [53]</td>
</tr>
<tr>
<td>Fe₂O₃-GAC</td>
<td>0.5-1.6</td>
<td>1024</td>
<td>37.51</td>
<td>0.16</td>
<td>0.6# [54]</td>
</tr>
<tr>
<td>AggFe</td>
<td>See Fig. 1</td>
<td>5</td>
<td>30.7</td>
<td>263.4</td>
<td>29.6</td>
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<tr>
<td></td>
<td>pHᵢₛ=4</td>
<td>6</td>
<td>28.9</td>
<td>241.3</td>
<td>27.8</td>
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<tr>
<td></td>
<td>pHᵢₛ=6</td>
<td>7</td>
<td>23.4</td>
<td>131.9</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>26.5</td>
<td>71.3</td>
<td>23.2</td>
</tr>
</tbody>
</table>

# Calculation according to Langmuir isotherm at equilibrium phosphate concentration of Ce=0.1 ppm as P
* Maximum phosphate uptakes
^ Maximum blast furnace slag capacity to remove 500 ppm phosphate
** From phosphate adsorption isotherm

This study
4. CONCLUSIONS

This study presents information about phosphate removal from water and its recovery for reuse by using NanoFe sol and AggFe suspension adsorbents. The main conclusions are as follows:

- A strong influence of AggFe concentration and pH level on phosphate removal efficiency was demonstrated, also at neutral pH levels.
- Phosphate adsorption onto the AggFe suspension adsorbent may be described by pseudo-second-order reaction kinetics and the Langmuir isotherm model.
- Phosphate adsorption kinetics onto AggFe may be defined by two stages: the first relates to the external surface adsorption, and the second represents the internal micro-porous process of adsorbate diffusion within the AggFe adsorbent.
- The phosphate adsorption capacity using AggFe adsorbent in equilibrium with a phosphate concentration of 0.1 ppm as P in solution is about in 1.5-1.9 times higher than these values for GFH (fraction < 63 µm) and more than one order of magnitude higher than other values reported in the literature.
- It was shown that 95-99% phosphate recovery efficiency is gained by using AggFe adsorbent. The recovered iron particles and high pH wash solution can be easily reused.

NOTATION

AggFe  Iron (Fe$^{3+}$) oxide/hydroxide nanoparticles-based agglomerates

$b$  Langmuir isotherm constant, L/mg

$C_0$  Initial phosphate concentration, ppm, mol

$C_e$  Phosphate equilibrium residual concentration, ppm, mol

$C_{Fe}$  NanoFe or AggFe concentration, ppm, mol

$C_t$  Phosphate concentration in solution at time t, ppm, mol

$C_1$  Phosphate concentration in concentrated phosphate solution after recovery from iron oxide adsorbent, ppm, mol

NanoFe  Iron (Fe$^{3+}$) oxide/hydroxide-based nanoparticles

$Q_m$  Maximum sorption capacity, mg/g

$m_0$  Mass of phosphates in initial solution, mg

$m_1$  Mass of phosphates in concentrated phosphate solution after regeneration, mg

$pH_{Fe}$  pH value of AggFe suspension adsorbent

$R$  Phosphate recovery efficiency

REFERENCES


