Role of iron oxidation byproducts in the removal of phosphate from aqueous solution†

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Zero Valent Iron (ZVI) is widely investigated in water treatment processes; the removal of contaminants may take place at the surface of ZVI or at the surface of its oxidation byproducts that have flaked off into the bulk solution. In this work, iron byproducts were synthesized under different aeration conditions (4 or 8 mg O2 per L) and aging times (40 h or 6 days). The prepared iron oxidation byproducts were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman spectroscopy, zeta potential, BET surface area, and particle size analyses. XRD analysis showed that the prepared iron oxidation byproducts were composed mostly of lepidocrocite, maghemite, and magnetite. These flaked off iron oxidation byproducts were used alone (without ZVI) to remove phosphate. Equilibrium and kinetic studies were conducted to determine the sorption capacities and the rate of phosphate ion uptake at various pH values by the prepared byproducts. The experimental data showed that phosphate sorption adhered to a pseudo second order kinetic model and the maximum sorption capacity was determined at 2.5 mg P per g. Phosphate removal capacities of synthetic pure iron oxides and oxy-hydroxides were also determined. Raman and FTIR spectroscopy showed that phosphate was retained by inner sphere complexation.

1. Introduction

Phosphorus (P) is an essential element needed for plant and biota growth, but excessive amounts of released phosphorus can lead to ecological unbalance manifested by eutrophication, one of the main threats of environmental, sanitary and aesthetic problems in water bodies such as reservoirs and lakes. Phosphorus is released to water bodies from agricultural practices and from the uncontrolled discharge of domestic and industrial wastewater. According to the USEPA, to prevent the development of biological nuisances and to control eutrophication, total phosphorus should not exceed 50 µg L⁻¹ in any stream at the point where it enters any lake or reservoir, or 25 µg L⁻¹ within the lake or reservoir. A desired goal for the prevention of plant nuisances in streams or other flowing waters not discharging directly to lakes or impoundments is 100 µg L⁻¹ total P. Moreover, phosphorus concentration in treated wastewater was set by the European Union at 1–2 mg L⁻¹ according to the directive 91/271/EE.

Various biotic and abiotic factors (pH, ionic strength, water composition, temperature, nature of the adsorbent, ...) may affect the speciation, mobility, reactivity and bioavailability of P. However, phosphate can be removed by chemical precipitation, co-precipitation and adsorption by divalent or trivalent metal salts (e.g., aluminum sulfate and ferric chloride). Phosphorus can also be removed by biological treatment using microorganisms called phosphorus accumulating organisms (PAO) which requires alternating between aerobic and anaerobic conditions. Biological treatment can remove over 85% of phosphorus in wastewater. Recently, the removal of phosphate using adsorption has attracted much attention. Several low cost and waste materials were used for phosphate removal from aqueous solutions using ferric sludge, Al-bentonite, Fe-bentonite and Al-Fe-bentonite, fly ash, alum sludge, iron hydroxide-eggshell waste, magnetic nanoocomposites, and Fe(m) modified montmorillonite. Iron oxides and hydroxides are among the low cost materials used for phosphate removal such as goethite (α-FeOOH), akaganeite (β-FeOOH), green rust, and lepidocrocite. Researchers have also investigated the use of iron from iron mine tailing for the sequestration of phosphorus in lake sediments as well as the effects of hypolimnetic aeration on phosphate uptake by iron in lakes.

Most recently there has been an increased interest in ZVI for the removal of phosphate from water and wastewater because of
its low cost, nontoxic characteristics, good reactivity and potential longevity. Phosphate removal by ZVI may take place at the surface of ZVI or at the surface of its byproducts synthesized and flaked off into the bulk solution. The existing data of ZVI efficiency to remove contaminants do not consider separately the reactivity at the surface of ZVI and on the byproducts flaked off from the ZVI surface. In aqueous solutions and under oxic conditions, Fe(0) can be oxidized to Fe(II) which can form ferrous precipitates (Fe(OH)2) at the interface, resulting from the reaction between Fe(II) and OH− or can be transported away from the surface to form iron byproducts precipitates. The formed ferrous hydroxide will be oxidized to a Fe(II)/Fe(III) mixed phase such as magnetite over time. Maghemite can also be formed on the surface of ZVI. Water molecules are the primary oxidant of the Fe(0) surface and Fe(II) is the initial oxidation product. Under anaerobic conditions oxidation of ZVI will be limited due to the lack of oxygen. Furthermore the efficiency of the oxides to remove various species may be affected by aging as reported by Mao et al. (2012) and Smith et al. (2008) who showed that phosphate adsorption onto Hydrous Ferric Oxides (HFO) decreased with the oxide age. Oxygen and aging conditions are therefore two main parameters that may highly affect iron byproducts reactivity. Iron fillings are used to remove phosphate but the effects of these two parameters are rarely considered.

In this study only synthesized iron oxidation byproducts (without ZVI) will be used in order to study their efficiencies. The objectives of this study are (i) to determine the composition and nature of the iron oxidation byproducts prepared under different oxygen and aging conditions, and; (ii) to study the efficiency of the iron oxidation byproducts for phosphate removal at environmental pH.

2. Materials and methods

2.1 Materials

All the chemicals used in this study were of analytical grade. NaCl (99.5%) was supplied by Fluka, whereas KH2PO4 and ZVI (99%) (average size about 250 μm) were obtained from Sigma-Aldrich and Jeulin, respectively. Stock solution of 1000 mg P L−1 was prepared by dissolving an appropriate amount of KH2PO4 in ultra-pure water. Adjustment of pH was made with 0.1 mol L−1 NaOH and 0.1 mol L−1 HCl.

2.2 Preparation of iron oxidation byproducts

To highlight the role of oxygen in the formation and efficiency of the iron oxidation byproducts, two iron corrosion materials were prepared. The first set was prepared by fixing the aging time at 40 hours and varying the dissolved oxygen concentration between 4 mg O2 per L (4 mg L−1 to 40 h) and 8 mg O2 per L (8 mg L−1 to 40 h). Similarly, to highlight the role of aging time on the iron oxidation byproducts, two sets of iron oxidation byproducts were prepared, the first set was aged for 40 h (4 mg L−1 to 40 h) whereas the second set was aged for 6 days (6 d to 4 mg L−1).

Oxidation of ZVI was conducted in a 1000 mL beaker at 20 ± 3 °C by mixing 10 g of ZVI in 1 L of 0.01 mol L−1 NaCl. For this purpose, a jar test was used at 200 rpm to mix the iron fillings. Oxygen concentration was set at 4 or 8 mg L−1 in the different reactors. To achieve these oxygen concentrations, systems were either pumped with oxygen (using aquarium air pump) or just sealed with parafilm. The concentration of dissolved oxygen in the oxygen saturated systems was kept stable at 8 mg L−1 for the duration of the experiment; as for the oxygen limited systems, oxygen concentration dropped from 8 to 4 mg L−1 during the first hour of the experiment and remained stable at 4 mg L−1 thereafter.

The pH variation was measured as a function of time using a Mettler Toledo pH-meter whereas dissolved oxygen concentration was measured using an HQ30d flexi oximeter. Once the iron byproducts were prepared under these different conditions, elemental iron (ZVI) was removed from the suspensions as follow. When the reaction time (40 h or 6 d) was reached, the beakers were allowed to stand for 30 s in order to let the ZVI settle down. The iron oxidation byproducts along with the suspensions, excluding elemental iron (ZVI) which settled to the bottom, were then gently transferred to a new beaker. During this transfer, a magnet was fixed outside, at the bottom of the beaker in order to hinder ZVI transfer. After that, a magnet was dipped in the beaker containing the suspension in order to ensure that no ZVI remained with the suspension. A minor portion of the magnetic iron oxidation byproducts may have been removed by the magnet along with ZVI. In order to compare quantitatively the formation of oxides in the systems with different oxygen concentrations, we defined two fractions namely “particulate” and “filterable”. The differentiation between dissolved and particulate iron was based on physical separation by filtration using 0.45 μm syringe filter. Filterable fraction contains both soluble and colloidal iron; however the particulate fraction was obtained by subtracting the filterable fraction from the total iron. Total iron was obtained by acidifying samples for 3 hours at 90 °C by adding 2 mL of HNO3 65% and 1 mL HCl 37% for 10 mL of each sample. After acidification, samples were filtered using 0.45 μm syringe filter. Samples were then analyzed by flame atomic absorption spectroscopy (AAS) using Varian SpectraAA220; quantification limit was 0.1 mg L−1.

The synthesized suspensions (without ZVI) were dried at 40 °C for 24 hours, then stored in a closed container for later characterization and used for phosphate adsorption.

2.3 Characterization methods

Three samples were characterized to capture the effects of oxygen conditions and aging time on the formation of the iron oxidation byproducts. The set of selected samples included (4 mg L−1 to 40 h), (8 mg L−1 to 40 h) and (4 mg L−1 to 6 d).

These byproducts were identified using XRD, Raman spectroscopy and Fourier Transform – Infrared spectroscopy (FT-IR). In addition, the iron oxidation byproduct samples were characterized before and after phosphate adsorption in order to understand the mechanism of phosphate removal.
XRD patterns for the prepared samples were obtained using a Bruker D8 focus diffractometer using Cu/Kα radiation ($\lambda = 0.154$ nm). The patterns were then analyzed using XPert High Score Plus version 2.0 (by PANalytical B.V.) for peak identification and semi-quantification. The samples were dried and powdered before they were analyzed. Raman Spectroscopy analyses were performed for structural information using a Horiba Jobin Yvon T64000. The excitation source was an Ar$^+$ laser operating at 514.5 nm. The incident power was limited to 2 to 5 mW using density filter to avoid potential deterioration and transformation of the compounds. Typical spectral resolution for the Raman system with an 1800 mm$^{-1}$ grating monochromator was about 2.5 cm$^{-1}$ at the exciting line and the diameter of the laser spot focused on the sample was about 1 μm. FTIR was also used to characterize the functional groups on the surface of the synthesized samples using an FT/IR - 6300 JASCO.

The specific surface area of the iron oxidation byproducts was measured using an ASAP 2020 by Micromeritics whereas the surface morphology was analyzed using a Scanning Electron Microscope (SEM – Philips XL 30, 20 kV). The particle size distribution was obtained by Laser Scattering Particle Size Distribution Analyzer LA950V2 (HORIBA).

Zeta potential was determined by measuring the mobility in an electric field using a Zeta photometer IV Model Z4000. The pH values of the samples were adjusted by using HCl or NaOH to cover the range of pH from 3 to 11. Samples were placed in an electrophoresis chamber and the voltage applied was 95 ± 5 mV. The zeta potential was then calculated automatically by using the Helmholtz–Smoluchowski equation.

The point of zero charge (PZC) was determined by acid base titration of 5 mg L$^{-1}$ suspension. Titration was conducted by adding 0.1 mol L$^{-1}$ NaOH and HCl every 5 minutes (0.2 mL added every time). Surface charge was calculated according to the equation below:

$$Q = (C_a - C_h + [OH^-] - [H^+])/m$$

(1)

$Q$ is the surface charge in mol g$^{-1}$, $C_a$ and $C_h$ (mol L$^{-1}$) are the concentration of added acid and base respectively and $m$ (g L$^{-1}$) is the solid concentration.

2.4 Synthesis of pure iron oxides and oxy-hydroxides

Lepidocrocite, goethite, maghemite and magnetite were synthesized in the laboratory using the methods of Schwertmann (2000) with minor modifications.$^{27}$ Lepidocrocite (Lp) was synthesized by dissolving 11.93 g of FeCl$_2$·4H$_2$O (60 mmol Fe) in 300 mL of ultra-pure water with stirring, simultaneously adjusting the pH to 6.7–6.9 with 1 mol L$^{-1}$ NaOH (120 mL). The suspension was maintained under air flow and stirring for one night. Goethite (Gt) was synthesized by mixing 100 mL of Fe(NO$_3$)$_3$·9H$_2$O 1 mol L$^{-1}$ with 180 mL of NaOH 5 mol L$^{-1}$. Red brown precipitate was formed; the suspension was then diluted to 2 L water and heated at 70 °C for 60 hours. Maghemite (Mgt) was synthesized by dissolving 80 g of FeSO$_4$·7H$_2$O in 560 mL deionized water at 90 °C and by adding 240 mL of free oxygen solution containing 6.46 g of KNO$_3$ and 44.9 g KOH; the reaction was carried out under N$_2$ purging. Maghemite (Mgh) was synthesized by heating fresh magnetite in a furnace at 250 °C for 2 hours. X-ray diffraction data (given in the ESI, Fig. S1†) revealed that the synthesized solids were a well-crystallized pure oxides (maghemite and magnetite) and oxy-hydroxides (lepidocrocite and goethite).

2.5 Phosphate sorption experiments

Batch experiments were conducted in 1000 mL closed polyethylene bottles at ambient temperature where the solution volume was set at 200 mL. All experiments were carried out using an orbital agitator (HS 501 Digital IKA-WERKE) at 133 rpm. For the kinetics experiments, adsorbent dose was fixed at 1.5 g L$^{-1}$ of iron oxidation byproducts whereas the concentration of phosphate was set at 10 mg L$^{-1}$ as P (ratio Fe/P = 97). The initial pH was set at 7.2 (representative of environmental pH) and remained stable throughout the experiments (pH 7.2 ± 0.1). Samples were collected at several time intervals (0, 10, 20’, 30’, 45’, 60’, 80’, 100’, 120’, 3 h, 5 h, 8 h, 24 h and 48 h). At each sampling time, 1 mL of the homogenized suspension was filtered using 0.45 μm syringe filters and then analyzed for phosphate concentration using a colorimetric method. An antimonyl/phosphomolybdate complex was reduced with ascorbic acid, giving blue specie whose absorbance was measured at 880 nm in 1 cm cells with an Agilent 8453 UV-visible spectrometer; the limit of quantification was 100 μg L$^{-1}$.

For the isotherm experiments, the adsorbent dose was fixed at 1.5 g L$^{-1}$ of iron byproducts and 1 g L$^{-1}$ for iron oxides and oxy-hydroxides; the concentration of phosphate varied from 2 to 20 mg L$^{-1}$ as P for the iron byproducts and from 2 to 100 mg P L$^{-1}$ for the synthetic oxides and oxy-hydroxides. The pH value and mixing time were respectively fixed to 7.2 and 24 h. This time period of 24 h was determined from kinetics experiments as sufficient for reaching equilibrium conditions. Phosphate uptake by the sorbent was calculated as follows:

$$q_t = ([P]_0 - [P]_t)/V/m$$

(2)

where $q_t$ is the adsorption rate (mg P per g adsorbent); $[P]_0$ is the initial concentration of P (mg L$^{-1}$); $[P]_t$ is the concentration of P at time $t$; $V$ is the volume of the solution (L) and $m$ is the mass of the adsorbent (g).

Pseudo first and second order models were used to simulate the kinetic experiments data whereas Langmuir and Freundlich models were used for the isotherm data results. Equilibrium models can be expressed as follows:

$$q_e = (q_mK_LC_e)/(1 + K_LC_e) \text{ Langmuir equation,}$$

(3)

$$q_e = K_FC_e^{1/n} \text{ Freundlich equation,}$$

(4)

where $q_e$ is the amount of phosphate adsorbed onto the solid phase (mg P per g) at equilibrium, $q_m$ is the maximum adsorption capacity (mg P per g), $C_e$ is the equilibrium phosphate concentration (mg P L$^{-1}$), $K_L$ is the Langmuir constant (L mg$^{-1}$), $K_F$ (mg$^{(1-1/n)}$ L$^{1/n}$ g$^{-1}$) and $n$ are Freundlich constants.
constant \( n \) refers to the interaction between surface sites in the adsorbent and phosphate ions in aqueous solution.\(^{19}\) Non-linear regression analysis was performed using STATISTICA 6.1 for kinetic and isotherm data.

To study the influence of pH on the adsorption of phosphate by the iron byproducts, three different pH values were fixed over time at 4.2, 7.2 and 9.2 for 24 h. The pH was kept stable using an automatic titrator, Titrino 720 with an automatic burette containing HCl or NaOH 0.1 mol L\(^{-1}\). Samples were collected as a function of time and filtered at 0.45 \( \mu \)m to be analyzed for phosphate concentration as cited above. The (8 mg L\(^{-1}\) to 40 h) sample was selected to study the effects of pH on phosphate uptake by iron oxidation byproducts.

### 3. Results and discussion

#### 3.1 ZVI oxidation monitoring

The variation of pH and the concentration of iron in the dissolved/colloidal fraction (filtrated 0.45 \( \mu \)m) and particulate fraction (total – dissolved/colloidal) were monitored as a function of time. An increase of 1.8 pH unit was observed after about 80 h in the continuous aerated reactor (8 mg L\(^{-1}\) dissolved O\(_2\)) where pH remained constant thereafter (Fig. 1). In the presence of oxygen, oxidation of Fe(0) results in an increase in OH\(^{-}\) concentration which may be responsible for the pH increase (eqn (5) and (6)). Fe(n) could then be oxidized into Fe(m) releasing more OH\(^{-}\). As pH increased beyond the onset of precipitation of Fe(n) and Fe(m), both cations fall out of solution as hydroxide precipitates consuming OH\(^{-}\) and thus capping any further increase in pH. When the concentration of dissolved oxygen was limited (4 mg L\(^{-1}\)), the production of dissolved/colloidal iron and particulate iron was delayed and was lower as compared to the oxygen saturated condition (8 mg L\(^{-1}\)). The higher pH and particulate Fe concentration in the 8 mg O\(_2\) per L system, in comparison with the 4 mg O\(_2\) per L system illustrate the role of oxygen concentration in the rates of formation and oxidation of ZVI. Oxygen promoted the corrosion of iron as well as the transformation of Fe(ii) to Fe(III) in solutions.\(^{22,28}\)

The concentration of particulate iron byproducts became significant after 24 hours of reaction and increased over time to attain 3.3 g L\(^{-1}\) under saturated oxygen conditions after 6 days (results not shown). Equilibrium took place between Fe(n) and OH\(^{-}\) once their rate of production was equal to their rate of consumption through precipitation.\(^{22,29}\) Iron oxidation byproducts consisted firstly of a mixture of amorphous and poorly crystallized Fe oxides and the crystallization will increase over time (eqn (7) and (8)).\(^{30}\)

\[
\text{Fe}(0) + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}(\text{ii}) + 2\text{HO}^- \tag{5}
\]

\[
\text{Fe}(\text{ii}) + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}(\text{iii}) + \text{HO}^- \tag{6}
\]

\[
\text{Fe}(\text{iii}) + 3\text{H}_2\text{O} \rightarrow \text{Fe(HO)}_3 + 3\text{H}^+ \tag{7}
\]

\[
\text{Fe}(\text{iii}) + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ \tag{8}
\]

It is worth noting that the initial colorless solution turned to yellowish in the first minutes for the two oxygen conditions (limited with 4 mg L\(^{-1}\) and saturated with 8 mg L\(^{-1}\)). After that, the formed precipitates turned orange then brownish in the 8 mg O\(_2\) per L system and black in the limited oxygen condition. Triszcz et al. (2009) suggested that this color change was the result of a shift from particles containing mostly Fe(ii) to particles containing Fe(ii) and Fe(III) when dissolved oxygen concentration decreased.\(^{22}\)

#### 3.2 Iron byproducts characterization

XRD patterns (Fig. 2) showed that the prepared iron oxidation byproducts included mostly lepidocrocite and some peaks assigned to maghemite and/or magnetite. Patterns for the different analyzed samples showed peaks at the positions of 14.16°, 27.09°, 36.39°, 38.18°, 46.9°, 52.9° and 60.7° 2θ, which were assigned to lepidocrocite. Lepidocrocite was cited by Huang and Zhang (2005) as the major product of corrosion of ZVI at the initial stages (after 1 h) whereas lepidocrocite and magnetite became predominant at later stages.\(^{23}\) Two peaks observed at 57.4° and 62.6° 2θ were attributed to maghemite and magnetite respectively. Two other peaks observed in all patterns at the positions of 35.5° and 43.3° 2θ may be attributed to maghemite and/or magnetite. All peaks were compared with the XRD database cited by Pecharroman et al. (1995) and Cornell (2003).\(^{22,23}\) Lepidocrocite, maghemite and/or magnetite were present in the three samples. FTIR spectra (Fig. 3) confirmed the results obtained by XRD. Two strong peaks for lepidocrocite at 742 and 1020 cm\(^{-1}\) and a broad shoulder at 1160 cm\(^{-1}\) were found in the three different iron byproducts.\(^{33}\)

Oxygenation between limited and saturated conditions did not seem to have an important effect on the composition of the iron byproducts; the diffractogram of the different samples are very similar indicating the presence of lepidocrocite, maghemite and magnetite (Fig. 2). Likewise, no significant influence of aging was found on the composition of iron byproducts. The semi-quantitative XRD simulations (given in the ESI, Fig. S2†)
showed the repartition of the different crystallized oxides and oxy-hydroxides in the iron oxidation byproducts samples.

SEM images (Fig. 4) showed a homogeneous morphology for the different samples (4 mg to 40 h, 8 mg to 40 h, 4 mg to 6 d) where some crystals characteristic of lepidocrocite with short lath like shape were observed with a size approximately about 3 to 6 µm in length.

Table 1 shows the average surface area and particle size for the three samples. Particle size was similar for the different conditions, about 6 µm. After 40 h in the two oxygen conditions, the specific surface areas were very close between 63 and 69 m² g⁻¹. However upon further aging from 40 h to 6 days, the samples exhibited lower surface area measured at 46 m² g⁻¹. Surface areas were found not correlated with the diameter of the particles and thus indicated differences in the structure of aggregates.

One of the most important parameters in adsorption studies is the surface charge of the adsorbent because it serves as an indicator of reactivity and stability of the material. It influences the affinity between anions and cations, stability and particle interactions. For this purpose, Point of Zero Charge (PZC) and IsoElectric Point (IEP) measurements were conducted for the three different iron byproducts (Table 2). Table 2 shows no significant variation in IEP and PZC with the age of oxy-hydroxides (40 h and 6 days). However, oxygen concentration showed limited influence on the surface charge; IEP and PZC increased when oxygen concentration increased for the 40 h samples. In theory, when there is no specific adsorption, IEP and PZC should be equal. In our case there was a small offset.

Table 1  Average diameter (µm) and surface area (m² g⁻¹) of the oxy-hydroxides synthesized in three different conditions

<table>
<thead>
<tr>
<th>Samples</th>
<th>4 mg L⁻¹ to 40 h</th>
<th>8 mg L⁻¹ to 40 h</th>
<th>4 mg L⁻¹ to 6 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (µm)</td>
<td>5.9 ± 0.8</td>
<td>6 ± 2</td>
<td>6.1 ± 0.3</td>
</tr>
<tr>
<td>Surface area (m² g⁻¹)</td>
<td>63 ± 1</td>
<td>69 ± 1</td>
<td>46 ± 1</td>
</tr>
</tbody>
</table>
between PZC and IEP which could be due to the fixation of impurities on the surface of the material.

In order to understand the mechanism of phosphate removal using these byproducts, a comparison of the spectra before and after phosphate adsorption was conducted. As the samples did not show significant differences in their composition and reactivity, only one sample was analyzed. FTIR and Raman spectroscopy analysis were compared for the sample 8 mg L\(^{-1}\) to 40 h before and after phosphate adsorption. A comparison of the FTIR and Raman spectra was also conducted for the unloaded and phosphate loaded byproducts in order to determine any new peaks, intensity variation or wavelength shifts (Fig. 3 and 5). The FTIR spectra showed a strong and broad band between 3000 and 3600 cm\(^{-1}\) which was associated with the O–H stretching vibrations of the hydroxyl groups in the layers and interlayers water molecules (Fig. 3).\(^{55}\) Another absorption band corresponding to water with O–H bending vibrations was recorded around 1634 cm\(^{-1}\) indicating physically adsorbed water molecule on the surface of the adsorbent. Strong peaks at 742 and 1020 cm\(^{-1}\) confirmed the presence of surface hydroxyls of lepidocrocite.\(^{33}\) After phosphate adsorption, a new peak appeared at 890 cm\(^{-1}\) and 1077 cm\(^{-1}\) which were broad; these peaks could be assigned to the vibration of P–OH and the asymmetry vibration of P–O bond, respectively, indicating that the surface hydroxyl groups could be replaced by the adsorbed phosphate (Fig. 3). It may be deduced that the surface hydroxyl groups (M–OH) could be exchanged with phosphate (M–O–P) which possibly indicates the formation of inner-surface sphere complex between phosphate and these iron byproducts.\(^{36,37}\)

Raman spectra of the synthesized byproduct in 8 mg L\(^{-1}\) to 40 h before and after phosphate adsorption are displayed in Fig. 5. Before adsorption, two sharp peaks at 250 and 373 cm\(^{-1}\) and three broad peaks at 520, 651, and 1295 cm\(^{-1}\) were ascribed to lepidocrocite according to the Raman spectrum of synthetic lepidocrocite.\(^{33,38,39}\) After adsorption of phosphate (10 mg P L\(^{-1}\)), new peaks were identified in the Raman spectrum. Strong peaks were identified at 215 and 300 cm\(^{-1}\) and can be attributed respectively to lepidocrocite and goethite. The vibration bands of the anions intercalated in the interlayers of the iron oxides were very weak. Two new broad peaks appeared after phosphate adsorption at 1050 and 1135 cm\(^{-1}\) and could be assigned to the stretching vibration band of P–O.\(^{40,41}\) Raman and FTIR results indicated the replacement of the hydroxyl groups by phosphate which confirmed the formation of inner sphere complex.

### Table 2  PZC and IEP measurements for the different oxy-hydroxides

<table>
<thead>
<tr>
<th>Samples</th>
<th>4 mg L(^{-1}) to 40 h</th>
<th>8 mg L(^{-1}) to 40 h</th>
<th>4 mg L(^{-1}) to 6 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZC</td>
<td>6.0 ± 0.2</td>
<td>7.0 ± 0.2</td>
<td>6.3 ± 0.1</td>
</tr>
<tr>
<td>IEP</td>
<td>6.9 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td>6.8 ± 0.1</td>
</tr>
</tbody>
</table>

3.3 Phosphate removal

3.3.1 Kinetics and isotherms experiments. Several factors can influence phosphorus retention capacities and adsorption kinetics such as surface area, crystallinity and morphology of the iron oxides. Experiments were conducted to investigate the kinetics of phosphate removal from water using the different iron byproducts.

The adsorption constant values for the pseudo second order model, the correlation coefficients \(R^2\), and the predicted \(q_e\) values are given in Table 3. Based on values of the correlation coefficient \(R^2\) of the iron oxidation byproducts, pseudo second order model \((R^2 \geq 0.96)\) was found to better fit than the pseudo first order one \((R^2 \leq 0.92)\), thus the data of the pseudo first order will not be shown here. Pseudo second order model indicates that adsorbent interacts with two surface sites.\(^{46}\) The samples aged for 40 h (both 4 mg L\(^{-1}\) H\(_2\)O and 8 mg L\(^{-1}\) H\(_2\)O), showed the

![Graph](Fig. 5 Raman spectra of the iron oxidation byproducts (8 mg L\(^{-1}\) to 40 h) before (a) and after phosphate adsorption (b and c) \((P = 10 mg L^{-1})\) on different locations at the surface of the sample.)
same uptake capacity near 2.4 mg g⁻¹ iron oxidation byproducts where no influence of oxygen was found for these different conditions. Phosphate removal percentages were 23, 37 and 39% for the samples 4 mg L⁻¹ to 6 d, 8 mg L⁻¹ to 40 h and 4 mg L⁻¹ to 40 h, respectively.

Fig. 6 represents the isotherms (experimental data, Langmuir and Freundlich models). Isotherm results for the iron oxidation byproducts indicated that Freundlich model was a better fit for the experimental data, in accordance with the observations of Chitrakar et al. (2006) (Table 4 and Fig. 6). It appears that there is a progressive saturation during adsorption with modification of the surface properties. The adsorption capacities of the adsorbents synthesized after 40 h in two different oxygen conditions were similar, \( q_m = 2.5 \pm 0.1 \text{ mg P per g iron oxidation byproduct} \) (3.8 mg P per g Fe) and 2.42 \( \pm 0.09 \text{ mg P per g iron oxidation byproduct} \) (3.7 mg P per g Fe) for 4 mg L⁻¹ to 40 h and 8 mg L⁻¹ to 40 h respectively. The sample prepared using 6 days under oxygen limited conditions showed the lowest adsorption capacity \( q_m = 1.5 \pm 0.1 \text{ mg P per g iron oxidation byproduct} \) (2.3 mg P per g Fe). The difference in the phosphate uptake between samples aged for 40 h and 6 days can be attributed to aging effect; as aging time increased, the efficiency decreased. An increase in the crystallinity over time can take place and amorphous iron oxides can be transformed to crystalline phases. This mineral transformation could explain the decrease of the surface area and the subsequent decrease of phosphate sorption. These results are in agreement with previous aging effect work published in the literature.

Mao et al. (2012) showed that the more the hydrous ferric oxides are aged, the lower the phosphate removal is, without

Table 3  Pseudo second order kinetic parameters for the sorption of phosphate onto the synthesized iron byproducts (40 h to 4 mg L⁻¹, 40 h to 8 mg L⁻¹, 6 d to 4 mg L⁻¹) and the synthetic goethite, lepidocrocite, maghemite and magnetite. Adsorbent concentration = 1.5 g L⁻¹ iron byproducts and 1 g L⁻¹ iron oxides; [P] = 10 mg L⁻¹, \( T = 20 ^\circ \text{C}, \text{NaCl} = 0.01 \text{ mol L}^{-1} \)

<table>
<thead>
<tr>
<th>Samples</th>
<th>( K ) (g mg⁻¹ min⁻¹)</th>
<th>( q_e ) (mg g⁻¹)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mg L⁻¹ to 40 h</td>
<td>2.3 ( \pm 0.6 )</td>
<td>2.20 ( \pm 0.07 )</td>
<td>0.97</td>
</tr>
<tr>
<td>8 mg L⁻¹ to 40 h</td>
<td>2.5 ( \pm 0.6 )</td>
<td>2.00 ( \pm 0.07 )</td>
<td>0.96</td>
</tr>
<tr>
<td>4 mg L⁻¹ to 6 d</td>
<td>4 ( \pm 2 )</td>
<td>1.40 ( \pm 0.05 )</td>
<td>0.96</td>
</tr>
<tr>
<td>Goethite</td>
<td>2.8 ( \pm 0.6 )</td>
<td>1.40 ( \pm 0.04 )</td>
<td>0.98</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>9 ( \pm 2 )</td>
<td>2.03 ( \pm 0.05 )</td>
<td>0.98</td>
</tr>
<tr>
<td>Maghemite</td>
<td>6 ( \pm 2 )</td>
<td>0.56 ( \pm 0.02 )</td>
<td>0.97</td>
</tr>
<tr>
<td>Magnetite</td>
<td>8 ( \pm 6 )</td>
<td>0.40 ( \pm 0.03 )</td>
<td>0.90</td>
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Fig. 6  Adsorption isotherms of phosphate on the different iron byproducts. Experimental data (dots), model fits (curves) Langmuir: full curve, Freundlich: dashed curve. Adsorbent concentration = 1.5 g L⁻¹; [P] = 2–20 mg L⁻¹, \( T = 20 ^\circ \text{C}, \text{NaCl} = 0.01 \text{ mol L}^{-1} \).
any information given about the physico-chemical characteristics of the samples. The apparent capacity of phosphate removal determined by Berkowitz et al. (2006) using aluminum hydroxides (Al(OH)₃) decreased also with aging of the hydroxides (from 4 to 180 days of aging); as floe age increased, the crystallinity increased too, which was responsible for the decreased adsorption capacities over time.

Table 4  Freundlich and Langmuir models regression constants for phosphate removal by the three different iron byproducts and synthesized iron oxides. Adsorbent concentration = 1.5 g L⁻¹; [P] = 2–20 mg L⁻¹ (iron byproducts) and 2–100 mg L⁻¹ (1 g L⁻¹ iron oxides and oxy-hydroxides), T = 20 °C, NaCl = 0.01 mol L⁻¹

<table>
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<tr>
<th>Sorbent</th>
<th>pH</th>
<th>Capacity mg P per g</th>
<th>[Adsorbent] g L⁻¹</th>
<th>[P] mg L⁻¹</th>
<th>Ref.</th>
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<tr>
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<td>1.0</td>
<td>1</td>
<td>2–100</td>
<td>This study</td>
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<tr>
<td>Iron byproducts (4 mg L⁻¹ to 40 h)</td>
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<td>2.5</td>
<td>1.5</td>
<td>2–20</td>
<td>This study</td>
</tr>
</tbody>
</table>
reported in the literature, it appears that the capacities of the iron byproducts obtained in this work were mostly lower (Table 5). However, in same experimental conditions, the highest sorption capacities reported in the literature were for experiments conducted with low pH conditions (3 or 5), which favor anionic species sorption and are not representative of environmental conditions.

3.3.2 Effect of pH. Fig. 7 shows that the adsorption capacity decreases from 3.77 to 1.44 mg g\(^{-1}\) with pH increasing from 4.2 to 9.2 respectively, with 8 mg L\(^{-1}\) to 40 h. When pH increased, the surface charge of synthesized iron byproducts varied from positive to negative, according to the point of zero charge (between 6.0 and 7.0) due to deprotonation of surface hydroxyls. At the same time, the phosphate species exist in solution in different forms (H\(_2\)PO\(_4^-\) and HPO\(_4^{2-}\)) and at different ratios depending on pH. The three pK\(_a\) of phosphate species are pK\(_a\) (H\(_2\)PO\(_4^-\)/HPO\(_4^{2-}\)) = 2.2, pK\(_a\) (HPO\(_4^{2-}\)/H\(_2\)PO\(_4^-\)) = 7.2 and pK\(_a\) (HPO\(_4^{2-}\)/PO\(_4^{3-}\)) = 12.2. Phosphate anions change from monovalent to dibasic, then an electrostatic repulsion with the oxides takes place.\(^{41}\) The phosphate uptakes by common oxides are summarized in Table 5. It can be observed that the highest adsorption capacities for the various adsorbents in the same experimental conditions are found to pH close to 4, which is in agreement with our results. Thus it indicates that iron oxides have more affinity for the monovalent form of phosphate (H\(_2\)PO\(_4^-\)). As pH increases, adsorption decreases due to the competition between OH\(^-\) and phosphate anions.\(^{14,16}\) Beyond the IEP value, a negatively charged oxides lead to lower phosphate adsorption.\(^8\) In our study we fixed the pH at 7.2 during the kinetics and isotherms experiments to represent water treatment conditions; however this pH is not the optimal one for the highest phosphate adsorption efficiency. To further investigate the uptake of phosphate at neutral pH it is worthwhile looking at the speciation of phosphate as a function of pH and at the PZC values of the iron byproducts.\(^{46}\) The PZC of the iron byproducts were found to range between 6.0 and 7.0 (Table 2). Phosphate adsorption onto iron oxides has been widely investigated and the main mechanisms are reported based on specific and nonspecific adsorption: ligand exchange and electrostatic interaction. The electrostatic bonding is based on the charge of the surface and the charge of the sorbed ions. Electrostatic based removal predominates when the oxide surface has positive global charge and phosphate species is negatively charged. In our case, as the surface charge of the byproducts is zero or negative, there will be no adsorption of anions through electrostatic adsorption. In contrast where specific adsorption is involved, an overall positive surface charge is not required, which explains why adsorption can occur at pH above the PZC.\(^9\)

4. Conclusion

Synthesized iron oxidation byproducts in the three different conditions (4 or 8 mg O\(_2\) per L, aging time 40 h or 6 days) were mainly formed by lepidocrocite with presence of some peaks of maghemite and magnetite. The kinetic data were better described by a pseudo second order adsorption kinetic model. The maximum sorption capacity was determined at 2.5 mg g\(^{-1}\) for the 4 mg L\(^{-1}\) to 40 h sample. This result was in the same range as phosphate sorption capacities obtained with pure maghemite, maghemite and magnetite. FTIR and Raman results indicated an exchange of the hydroxyl group by phosphate via the formation of inner sphere complex was the main mechanism responsible for phosphate adsorption on the surface of the iron byproducts. The operating conditions (pH, dissolved oxygen concentrations and aging) strongly affect the nature of the oxidation of iron fillings and therefore the sorption properties of the byproducts. These operating conditions need to be framed in a very precise model in order to implement applicable reaction pathways using this support material.\(^{16}\)

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References