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Finland

RETENTION OF ORTHOPHOSPHATE, ARSENATE AND ARSENITE
ONTO THE SURFACE OF ALUMINUM OR IRON OXIDE-COATED
LIGHT EXPANDED CLAY AGGREGATES (LECAs): A STUDY OF
SORPTION MECHANISMS AND ANION COMPETITION

DOCTORAL THESIS IN SOIL AND ENVIRONMENTAL CHEMISTRY

NADER YAGHI

ACADEMIC DISSERTATION
To be publicly discussed, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, in Walter Hall, EE-Building, Agnes Sjöbergin katu 2, Helsinki, on June 17th, 2015 at 12 o'clock

Helsinki 2015
“To my beloved parents who continue to love, learn and grow and who have been a source of encouragement and inspiration to me throughout my life. Your prayers for me were what sustained me thus far.”
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Helsinki, May 2015

Nader Yaghi
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<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Al-LECAs</td>
<td>Aluminum oxide coated LECAs</td>
</tr>
<tr>
<td>Al_{ox}</td>
<td>The poorly crystalline aluminum oxide</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>As^{V}</td>
<td>Arsenate</td>
</tr>
<tr>
<td>As^{III}</td>
<td>Arsenite</td>
</tr>
<tr>
<td>ATP</td>
<td>Adenosine triphosphate</td>
</tr>
<tr>
<td>CWs</td>
<td>Constructed wetlands</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DPS</td>
<td>Degree of Phosphorus Saturation</td>
</tr>
<tr>
<td>EAsC</td>
<td>Equilibrium arsenic concentration (µg L⁻¹)</td>
</tr>
<tr>
<td>EPC</td>
<td>Equilibrium phosphorus concentration (µg L⁻¹)</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe-LECAs</td>
<td>Iron oxide coated LECAs</td>
</tr>
<tr>
<td>Fe_{ox}</td>
<td>The poorly crystalline iron oxide</td>
</tr>
<tr>
<td>HG-ICP-OES</td>
<td>Hydride Generation - Inductively Coupled Plasma Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>KL</td>
<td>Coefficient related to bonding energy (L mg⁻¹)</td>
</tr>
<tr>
<td>LECAs</td>
<td>Light Expanded Clay Aggregates</td>
</tr>
<tr>
<td>NADP</td>
<td>Nicotinamide Adenine Dinucleotide Phosphate</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
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<tr>
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ABSTRACT

In terms of chemistry, phosphate (P\textsuperscript{V}) and arsenate (As\textsuperscript{V}) are similar, but their biochemical roles are completely different. Phosphorus (P) is an important nutrient for all forms of life but when entering to watercourses it increases the eutrophication risk. Arsenic (As) is a metalloid, the inorganic species of which are toxic, with As\textsuperscript{III} classified as a first group carcinogen. This work was undertaken to investigate the potential of Light Expanded Clay Aggregates (LECAs) to act as sorbents to remove P and As species from the aqueous phase. Detailed studies were undertaken to determine if the efficiency of LECAs can be improved by coating them with aluminum (Al) or iron (Fe) oxide.

The ability of various LECA materials to remove P from water was compared at different pH values, and the reversibility and kinetics of the reactions were investigated. The results revealed that the oxide-coated LECAs were superior to LECAs as P sorbents. Furthermore, Al-LECAs was superior to Fe-LECAs, which is redox-sensitive and therefore may lose its sorption properties in temporarily prevailing anoxic conditions, e.g., in constructed wetlands (CWs) used for wastewater purification. Studies of the reaction kinetics, impact of the degree of P saturation (DPS) and P desorption revealed that the oxide-coated materials retained P more strongly than LECAs.

The experiments with As were designed to simulate the conditions in groundwater where As exists as As\textsuperscript{V} or As\textsuperscript{III}, depending on the redox potential. The optimal pH for the sorption of both As species, the effect of oxidizing agents on the sorption of As\textsuperscript{III} and the effect of competing phosphate anions on As sorption were investigated in systematic studies, which revealed that the oxide coatings decisively increased the sorption of both As species. For As\textsuperscript{V} at a pH of 4, Al-LECAs appeared to be a better sorbent than Fe-LECAs. However, Fe-LECAs were superior to Al-LECAs at a pH of 6. The sorption of As\textsuperscript{III} increased with elevated pH. At a pH of 9, sorption was greater onto Al-LECAs than Fe-LECAs. However, the opposite trend was obtained at a pH of 10. The oxidation of As\textsuperscript{III} to As\textsuperscript{V} enhanced sorption by LECAs. Moreover, the oxidation-reduction reaction created new sorption sites for As\textsuperscript{V} on the manganese dioxide (MnO\textsubscript{2}) surface.

The competition with P for sorption sites relatively diminished the retention of As onto LECAs compared to the oxide-coated LECAs. In the Al-LECAs, the P-induced decrease in the As\textsuperscript{V} sorption was larger than that in the Fe-LECAs. The competition between P and As\textsuperscript{III}
lowered the sorption by oxide-coated LECAs most markedly in acidic media. Thus, LECAs seem to be the best option for removing As$^{\text{III}}$ and As$^{\text{V}}$ from groundwater with high P.

The sorption properties of LECA materials were assessed by means of sorption isotherms describing the sorption as a function of the sorbate concentration in the solution after equilibration. The actual P sorption capacity was assessed as the P retained at a P concentration of 20 µg L$^{-1}$ in the equilibrium solution ($X_{20}$), which is close to the upper limit (25 µg L$^{-1}$) allowed in surface water to avoid eutrophication. The corresponding actual sorption capacity for the As species was determined at an equilibrium concentration of 10 µg As L$^{-1}$ ($X_{10}$), which is the highest allowable level in drinking water.
Fosfaatti ($P^{V}$) ja arseenaatti ($As^{V}$) ovat kemiillisesti samankaltaisia, mutta niiden biokemialliset roolit ovat täysin erilaisia. Fosfori (P) on kaikelle elämälle tärkeä ravinne, mutta voi vesistöihin kulkeutuessaan aiheuttaa rehevöitymistä. Arseeni (As) puolestaan on puolimetalli, jonka epäorgaaniset muodot ovat toksisia. $As^{III}$ luokitellaan ensimmäisen ryhmän karsinogeeniksi. Tässä työssä selvitettiin luonnonsavesta valmistettujen LECA-rakeiden (Light Expanded Clay Aggregates) kykyä sitoa ja poistaa P:a ja As:n eri spesieksää liuosfaasista. Yksityiskohtaisissa tutkimuksissa selvitettiin, voidaanko rakeiden tehokkuutta paran-taa päällystämällä ne alumiinin (Al) ja raudan (Fe) oksidilla.


oloissa. Näin ollen LECA näyttää olevan paras vaihtoehto As\textsuperscript{III}:n ja As\textsuperscript{V}:n poistamiseen pohjavedestä, jossa on korkea P-pitoisuus.

LECA-materiaaleille tehtiin sorptioisotermit, joi-den avulla selvitettiin niiden todellinen P:n pidätyskyky. Niistä määritettiin pidättyneen P:n määrä tilanteessa, jossa tasapainoliuoksen P-pitoisuus oli 20 µg L\textsuperscript{-1} (X\textsubscript{20}) eli lähellä pinta-vesille rehevöitymisen kannalta annettua enimmäispitoisuutta (25 µg L\textsuperscript{-1}). Vastaavanlainen todellinen sorptiokapasiteetti määritettiin As spesieksille tasapainoliuoksen pitoisuutasolla 10 µg As L\textsuperscript{-1} (X\textsubscript{10}), joka on korkein sallittu pitoisuus juomavedessä.
LIST OF ORIGINAL PUBLICATIONS


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Author’s contribution

The experiments were built on the ideas of Nader Yaghi; the final designs were planned by Nader Yaghi together with Professor Helinä Hartikainen. Nader Yaghi conducted the laboratory work. The manuscripts were written under the guidance of Professor Helinä Hartikainen. Both authors participated in the interpretation of the results.
1.0 INTRODUCTION

Water covers more than 70% of Earth’s surface, but more than 97% is salty and not suitable as drinking water or for other domestic purposes. Globally, fresh water is a scarce and, thus, very valuable natural resource. Approximately 2% of fresh water is locked up in polar ice caps and glaciers. Only 1% of fresh surface water is in rivers, lakes, and streams, which can be used for the production of drinking water, irrigation, recreation, industries and other human activities. Access to water is a basic human need and a fundamental human right. Currently, more than 1.1 billion people, especially in developing countries, suffer from a lack of clean water, and 2.6 billion people live without adequate sanitation. Consequently, more than 1.8 million children die every year because of diarrhea and other diseases caused by unclean water and poor sanitation.

Water quality affects human and animal health and food production and security; the fresh surface water used by humans for drinking, washing, cooking, food industries or watering animals should pass through a purification treatment prior to use. Fresh surface water can be used for irrigation without any purification treatment. However, irrigation with water containing detrimental impurities results in the gradual contamination of surface soils. Soils in watersheds, in turn, affect the quality of recipient water and groundwater. A portion of the rainwater that falls onto soil ends up in surface water with drainage water or surface runoff or in groundwater with percolating water. In the latter case, chemical and microbiological processes remove impurities from the passing water. Thus, environmental loading threatens the quality of fresh surface water more than that of groundwater, which is protected by soil layers acting as filters. Actually, one of the goals of environmentally sound soil management practices is to protect water quality and prevent the transport of nutrients and detrimental substances to groundwater.

Since the Industrial Revolution that started in England between the 18th and 19th century, living standards have improved and infant mortality has declined. Consequently, the rapidly increasing population has increased the demand for food, water, various raw materials, and energy. The intensification of agricultural production was achieved by introducing chemical fertilizers and pesticides to control plant diseases. Phosphorus (P) is one of the main nutrients added to soil in fertilizers. It is usually the main nutrient limiting the growth of phytoplankton in fresh surface water; thus, any P entering watercourses enhances primary production. This process gradually causes eutrophication and may result in toxic algal blooms that threaten human and animal health and eco-diversity. According to the
United States Environmental Protection Agency (US EPA) (1976), P concentrations exceeding 25 µg L\(^{-1}\) in surface water may cause eutrophication. Currently, the eutrophication of watercourses have been reported worldwide, e.g., in Sweden, Norway, the United Kingdom, Ireland (Ulén et al., 2007), the United States, Canada (Borggaard et al., 2004), Bangladesh (Jahan et al., 2010) and India (Martin et al., 2011). For example, in the United States alone, eutrophication accounts for almost one-half of the impaired lake area and 60% of the impaired river reaches (Smith, 2003).

However, the most efficient pesticides that have been used contain arsenic (As). Thus, the long-term use of fertilizers and pesticides has resulted in the accumulation of large amounts of P and As in soils. Moreover, As is also released into the environment from the use of coal in power plants. Compared to the release of P and As from bedrock in weathering processes, human activity has drastically enhanced the transport of these elements into the environment. Bhattacharya et al. (2007) indicated that the Industrial Revolution left behind extensive As-contaminated sites in England.

The rising demand for drinking water cannot be met by eutrophic surface water, leading to increased dependence on groundwater in many parts of the world. In Bangladesh, for example, surface water has been the main source of drinking water. However, the increasing population density and lack of adequate sanitation has led to severe microbial contamination in addition to eutrophication. Therefore, the use of groundwater has increased to overcome this problem (Welker et al., 2005). Unfortunately, this is not always a feasible solution. Along the coastal area of West Bengal in Bangladesh and India (Das et al., 1996; Bhattacharya et al., 1997), the groundwater has elevated As concentrations mainly due to geological reasons. A similar problem has been reported in several regions worldwide, including Argentina (Bundschuh et al., 2004), Chile, China, the USA (Bhattacharya et al., 1997), Ghana (Smedley, 1996) and Mexico (Rodriguez et al., 2004).

Arsenic is an extremely toxic metalloid classified to belong to the first group of carcinogens based on human epidemiology. In the most well-known problem areas in Bangladesh, high As levels occur in 52 out of 64 districts (Karim, 2000). Here, approximately 80 million people are exposed to groundwater with As concentrations far above the highest allowable value (10 µg L\(^{-1}\)) (Ratnaike, 2003). In Bangladesh, the groundwater chemistry (i.e., redox potential, pH and presence of phosphates) (see Mukherjee and Bhattacharya, 2001) may aggravate these problems.
1.1 Phosphorus and arsenic in the environment

Phosphorus (P) is an important nutrient for all forms of life, rivalling carbon and nitrogen in the maintenance of life. One of its main roles in living organisms is as a component in energy transfer (ATP, NADP), nucleic acids (RNA, DNA) and membranes (phospholipids). Phosphorus cycling as orthophosphates in soil and water ecosystems is naturally present in the solution phase in low concentrations. In mass terms, Phosphorus does not rank among the first 10 elements. In the lithosphere, it is the eleventh most abundant element (at 1180 ppm on average), behind Al, and the thirteenth most abundant in seawater (average concentration of 70 ppb), which places it between nitrogen and iodine (Smil, 2000).

Phosphorus originates in P-containing minerals such as hydroxyapatite or fluorapatite \([\text{Ca}_5\text{(PO}_4\text{)}_3\text{OH, F]}\). The weathering of apatite in soil is a very slow reaction but can be enhanced by organic acids released from plant roots and the microbial decomposition of organic materials. In addition, \(\text{CO}_2\) produced from respiration along plant roots and soil microbes in soil is assumed, to some extent, to contribute to the dissociation of P-containing minerals by producing carbonic acid (Kelly et al., 1998):

\[
\text{Ca}_5(\text{PO}_4)_3\text{OH} + 4\text{H}_2\text{CO}_3 \rightarrow 5\text{Ca}^{2+} + 3\text{HPO}_4^{2-} + 4\text{HCO}_3^- + \text{H}_2\text{O}
\]

However, owing to the weak stability of \(\text{H}_2\text{CO}_3\), this reaction pattern can be extremely slow. Inorganic P in soil is also produced during the mineralization of organic P compounds such as inositol phosphates by the phytase enzyme (Turner et al., 2002). Phosphorus is also added to soils from anthropogenic sources, such as fertilizers used in agriculture and wastewaters discharged into soil (Penn and Sims, 2002).

Arsenic (As) is a ubiquitous element in the environment, being the twentieth most abundant element in Earth’s crust with an average concentration of 3 mg kg\(^{-1}\) (Zhao et al., 2010), twelfth in the human body and fourteenth in seawater (Mandal and Suzuki, 2002). This element occurs naturally in over 200 different minerals, most often as arsenate (60%) sulfides and sulfosalts (20%) and the rest including arsenides, arsenites, and oxidic, silicatic or elemental arsenic (Onishi, 1969). The most widespread As-containing minerals are arsenopyrite (AsFeS), realgar (AsS) and orpiment (As\(_2\)S\(_3\)). In igneous and sedimentary rocks, the average As concentration is 2 mg kg\(^{-1}\), while in some reduced marine sediments the concentration might be as high as 3000 mg kg\(^{-1}\). Arsenic may have co-precipitated with iron hydroxides and sulfides in sedimentary rocks (Mandal and Suzuki, 2002). It is present in higher concentrations in soil than in rocks, and its average concentration in uncontaminated
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

soils ranges between 1 and 40 mg kg$^{-1}$, the highest concentrations usually recorded in alluvial and organic soils and the lowest in sandy soils (Mandal and Suzuki, 2002).

Arsenic ends up in the environment from natural (geogenic) and anthropogenic processes. Natural sources include volcanic emissions and the natural weathering of As containing minerals. According to Mukherjee and Bhattacharya (2001), the high As concentration in the groundwater in the Bengal Delta Plain is attributed to sediments deposited by meandering river channels during the Late Quaternary or the Holocene Age. In these sediments, the As originated from As-rich parent rocks from both the Himalayas and the highlands in neighboring areas.

There are three main natural processes that release As into the environment: 1) the oxidation of pyrite in alluvial sediments by atmospheric oxygen, 2) the desorption of As anions from minerals in sediment to the solution phase by the competitive exchange of P anions, and 3) the reduction of As-rich minerals (iron and manganese (oxy)hydroxides) in anoxic groundwater (Nickson et al., 1998; McArthur et al., 2001; Mukherjee and Bhattacharya, 2001; Goldberg and Johnston, 2001; Polizzotto et al., 2008). Furthermore, a mechanism proposed by Bhattacharya et al. (1997) is the oxidation of organic matter by microbial activity during sediment burial, which can develop anoxic conditions and lead to the reduction of As-rich minerals and, consequently, the release of As.

Arsenic is also released into the environment as a result of human activities such as mining and the smelting of metals, the landfilling of industrial wastes, the combustion of fossil fuels (Mohan and Pittman Jr., 2007), wood treatment with CCA compounds containing 34% As$_2$O$_5$ (Cooper, 1994), and agricultural chemicals containing As. The most common compounds used in insecticides are lead arsenate [Pb$_3$(AsO$_4$)$_2$] and zinc arsenite [Zn(AsO$_2$)$_2$]. Germicides use calcium arsenate [Ca$_3$(AsO$_4$)$_2$], which is found in rodenticides. The insecticide Paris-Green features copper (II) acetoarsenite [Cu(CH$_3$COO)$_2$·3Cu(AsO$_2$)$_2$]. Herbicides and fungicides include MSMA (monosodium methanearsonate), DSMA (disodium methanearsonate) and agent Blue [(CH$_3$)$_2$AsO$_2$H)] (Mandal and Suzuki, 2002).

1.2 Chemical similarities and differences between phosphorus and arsenic

In terms of chemistry, P and As are relatives and belong to the group V(A) in the periodic table and form species with similar chemical properties. For example, these elements are present as oxyanions of three analogous acids in aqueous systems but show clear chemical differences, as shown in Table 1. Depending on the pH, P is present exclusively as
orthophosphate species, as shown in Figure 1. Undissociated phosphoric acid (H$_3$PO$_4$) exists only in extremely acidic solutions (pH < 2.14), while orthophosphate exists as H$_2$PO$_4^-$ in solutions of pH > 2.14 and pH < 7.2 and HPO$_4^{2-}$ is the predominating species in alkaline conditions (pH > 7.2 and pH < 13). In extremely alkaline conditions (pH > 12.7), which are not found in natural systems, the predominating species is PO$_4^{3-}$.

Table 1 – Acid dissociation constants for arsenic and phosphoric acid species at 25 °C and ionic strength 0 M (Lin and Puls, 2000; Haynes, 2012).

<table>
<thead>
<tr>
<th>Dissociation constant</th>
<th>Phosphoric acid (H$_3$PO$_4$)</th>
<th>Arsenic acid (H$_3$AsO$_4$)</th>
<th>Arsenous acid (H$_3$AsO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK$_{a1}$</td>
<td>2.1 (H$_2$PO$_4^-$)</td>
<td>2.2 (H$_2$AsO$_4^-$)</td>
<td>9.2 (H$_2$AsO$_3^-$)</td>
</tr>
<tr>
<td>pK$_{a2}$</td>
<td>7.2 (HPO$_4^{2-}$)</td>
<td>7.0 (HAsO$_4^{2-}$)</td>
<td>12.1 (HAsO$_3^{2-}$)</td>
</tr>
<tr>
<td>pK$_{a3}$</td>
<td>12.6 (PO$_4^{3-}$)</td>
<td>11.5 (AsO$_4^{3-}$)</td>
<td>13.4 (AsO$_3^{3-}$)</td>
</tr>
</tbody>
</table>

In soil, P occurs in organic and inorganic forms. Organic P is present in plant and animal residues or synthesized by soil microorganisms. The main part of the identifiable organic P exists as orthophosphate monoesters, e.g., inositol orthophosphates (Turner et al., 2002). The phosphate groups in these compounds are known to have the same sorption mechanisms as inorganic phosphate species.

Figure 1 – The pH distribution of phosphate series (reprint from Kurosaki and Seo (2003) with permission from Elsevier).
In contrast to P, As occurs in the environment in several oxidation stages: -III, 0, +III and +V, but the oxidation state 0 is very rare. In soil and aquatic environments, As speciation is dictated not only by pH but also by redox potential (Fig. 2). Arsenic acid (H$_3$AsO$_4$) and arsenous acid (H$_3$AsO$_3$) decisively differ in their dissociation and distribution of hydrolysis species (Fig. 3). In well-oxidized environments, the predominating species is arsenate (As$^V$), whereas in reduced environments the predominating species is arsenite (As$^{III}$) (Fendorf et al., 1997; La Force et al., 2000). The oxidation state -III is possible only in extremely reduced environments (Wang and Mulligan, 2006).

![Figure 2](image-url) – The Eh-pH diagrams for arsenic at 25 °C and 101.3 kPa (reprinted from Mohan and Pittman Jr (2007) with permission from Elsevier).

The dissociation constants given in Table 1 reveal that As$^V$ is present as a neutral molecule (H$_3$AsO$_4$) in extremely acidic environments (pH < 2.3) not found in natural systems. This state exists predominately as H$_2$AsO$_4^-$ in the pH range 2.3 – 6.9 and as HAsO$_4^{2-}$ in the pH range 7 – 11.5 (Fig. 2). At pH levels normally present in natural conditions, As$^{III}$ exists as the undissociated acid H$_3$AsO$_3$; in alkaline conditions (pH > 9), as H$_2$AsO$_3^-$; and at pH higher than 12, as HAsO$_5^{2-}$. In extremely alkaline conditions (pH > 13.4) not found in nature, the predominating species is AsO$_3^{2-}$ (Table 1 and Fig. 3).
Figure 3 – Dissociation of arsenate (a) and arsenite (b) as a function of pH (reprinted from Smedley and Kinniburgh (2002) with permission from Elsevier).

Organic As species such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO) may be formed through the methylation of inorganic As species by microorganisms including bacteria (such as *Escherichia coli*, *Flavobacterium* sp and *Methanobacterium* sp) and fungi (such as *Aspergillus glaucus* and *Candida humicola*) (Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002). Chemical structures with names and abbreviations for most common arsenic species in nature are presented in Appendix I.

1.3 Environmental problems caused by phosphorus and arsenic

In aquatic environments, P is usually the growth-limiting nutrient for algal growth, whereas any P that enters watercourses increases the eutrophication risk. The results are the excessive production of autotrophs, especially algae and cyanobacteria. High primary production easily leads to high bacterial oxidative decomposition and, consequently, the depletion of oxygen. Hypoxia or even anoxia in hypolimnion in thermally stratified water triggers a chain of reduction reactions. The Al- and Fe-bound P fractions differ in their binding strength and responses to chemical changes in the aquatic phase, such as pH and redox conditions. When bound to Fe\textsuperscript{III} (hydr)oxide surfaces, P is prone to be released by lowered redox potential, rendering Fe\textsuperscript{III} to soluble Fe\textsuperscript{II}. The soluble P, in turn, can be resorbed by Al (hydr)oxides that are not redox-sensitive or cycled back to productive layers during water turnover (Hartikainen, 1979). The latter process enhances the eutrophication of surface water.
Phosphorus transported to watercourses in dissolved forms or with particulate material originates either in non-point sources, such as agricultural runoff, or in point sources, such as wastewater discharge. In runoff water, P is transported in soluble forms and bound to particulate material. Fine particles are higher in Al and Fe (hydr)oxides and more easily transported with runoff water than coarse ones. However, in Europe, more than 50% of the P that enters watercourses is estimated to come from wastewater discharge (Cucarella and Renman, 2009), where P is in inorganic soluble forms or potentially bioavailable organic forms. Soluble inorganic P is immediately bioavailable and, thus, enhances primary production in recipient water. The reactivity of apatitic P in eroded soil material depends on the pH, whereas the fraction sorbed into hydrated Al and Fe oxides is in dynamic equilibrium with the P in the surrounding solution (Beckett and White, 1964; Hartikainen et al., 2010).

If P is transported with seepage water to deeper soil horizons, it will be efficiently sorbed onto oxide surfaces. In deeper soil horizons, the degree of P saturation (DPS) of oxides is rather low; therefore, retention by oxides is efficient. As a result, groundwater is normally low in P. The same reaction patterns function when As\textsuperscript{V} ends up in surface soil. The vertical transport of dissolved As through soil layers purifies leaching water prior to reaching the groundwater. Thus, most of the As in groundwater is natural by origin. In contrast to P, As in aquatic environments is a toxic metalloid. Currently, many countries worldwide, especially developing countries, face the problem of As contamination in groundwater.

The toxicity and mobility of As depends on its species; the toxicity of organic As species is several hundred times lower than that of inorganic As (Silva et al., 2010). Inorganic As has been classified as a group 1 carcinogen based on human epidemiology; As\textsuperscript{III} is 25-60 times more toxic than As\textsuperscript{V} (Raven et al., 1998). Humans can be exposed to As mainly through the intake of food and water. Although food is usually the major source of As exposure for people, the most adverse effects are caused by As in drinking water (Abernathy et al., 2003). Long-term exposure to inorganic As may cause lung, bladder, liver, renal, prostate gland and skin cancer (Ng et al., 2003). Even at low concentrations, As leads to acute and chronic poisoning involving the respiratory system, gastro-intestinal diseases (Bissen and Frimmel, 2003), diabetes mellitus, ischemic heart disease, childhood leukemia and vascular disease (Tsai et al., 1999). Therefore, the World Health Organization (WHO) adopted a new standard of 10 µg L\textsuperscript{-1} for As in drinking water in 1993, replacing the previous standard of 50 µg L\textsuperscript{-1} (World Health Organization, 2011). However, Bangladesh and other countries still operate with the 50 µg L\textsuperscript{-1} standard (Karim, 2000).
The detoxification process in the human body involves the methylation of inorganic As species, which reduces the affinity of the compound for tissue (Jain and Ali, 2000). Most mammals methylate inorganic arsenic to MMA and DMA, which are rapidly excreted in urine. For example, Aposhian et al. (2000) detected MMA$_{\text{III}}$ and DMA$_{\text{III}}$ in the urine of humans chronically exposed to inorganic As in their drinking water. Organic As species are mostly found in marine animals, i.e., fish and shellfish, and marine plants, such as edible seaweed. The predominant As species in marine animals and plants is arsenobetaine. However, arsenosugars can also occur at significant concentrations in marine animals that feed on algae, such as scallops. The toxicology of arsenosugars has not been fully assessed but is likely to be more complicated than that of arsenobetaine (Francesconi et al., 2002).
2.0 REMEDIATION METHODS OF WATER LOADED WITH PHOSPHORUS AND ARSENIC

Much effort has been exerted to prevent the environmental loading of P and As and to purify polluted waters. Treatment methods developed to remove P from wastewater include ion exchange (Zhao and Sengupta, 1998), precipitation and co-precipitation (Clark et al., 1997), microfiltration (Akay et al., 1998) and nanofiltration (Ballet et al., 2007). Moreover, constructed wetlands (CWs) have been introduced to prevent P loading from agricultural fields (Juwarkar et al., 1995; Drizo et al., 1999; Prochaska and Zouboulis, 2006; Vohla et al., 2011). Constructed wetlands, i.e., areas saturated by surface water and covered with vegetation adapted to grow under these conditions, were initially developed approximately 40 years ago in Europe and North America (Shutes, 2001). They are a natural option to remove P from agricultural runoff water or wastewater discharged directly to fields. Actually, CWs have gained increasing attention as an option for wastewater treatment. They are considered not only to offer a purification technique but also to benefit the ecosystem, e.g., by increasing biodiversity (Thiere et al., 2009). Constructed wetlands are reported to be efficient in decreasing biological oxygen demand (BOD) and removing total suspended solids (TSS) from wastewater. However, Brix et al. (2001) reported that the removal of P by means of CWs brings about paramount problems.

The high primary production in CWs tends to elevate the pH in the water body as a result of HCO$_3^-$ uptake by aquatic plants and phytoplankton and the subsequent release of OH$^-$ ions. This reaction pattern may lower the P sorption tendency of oxides by rendering their surface charge more negative. Furthermore, the decomposition of biomass by aquatic organisms will deplete the free oxygen and turn the conditions to anaerobic, which further enhances the desorption of P from the sediment (Prem et al., 2014). Therefore, efforts have been made to develop new materials to remove P from water. A prerequisite is that these materials have a high sorption capacity and stability under changing environments to maintain the efficient removal of P. However, constructed wetlands cannot be used for the removal of As because this element is toxic. Thus, several chemical and physical methods have been used to remove As from wastewater and groundwater, including ion exchange (Kim and Benjamin, 2004), precipitation and co-precipitation (Meng et al., 2001), coagulation (Wickramasinghe et al., 2004), ultrafiltration (Brandhuber and Amy, 2001), nanofiltration (Košutić et al., 2005; Harisha et al., 2010) and reverse osmosis (Ning, 2002). In general, all of the above-mentioned methods used in the removal of P or As have disadvantages, such as high cost, high reagent and energy requirements, incomplete removal and the generation of toxic sludge or other
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

waste products (Ahalya et al., 2003; Lafferty et al., 2011). Until now, sorption has received the most attention as an option to purify water and wastewaters from oxyanions because of its high efficiency and low costs (Oguz et al., 2003; Chen et al., 2007; Jiménez-Cedillo et al., 2011).

2.1 Sorption reactions of anions

Sorption is a general term referring to the removal of a soluble compound from a solution phase to a solid phase. Depending on the driving forces between the sorbent and sorbate, sorption can be either chemical or physical by nature. As defined, e.g., by Karge and Weitkamp (2008), chemical sorption implies the transfer of electrons and formation of a covalent chemical bond between the sorbate and a specific sorption site on the sorbent as an inner-sphere complex, which results in a monolayer. This type of sorption may be an irreversible reaction. However, in physical sorption, weak chemical interactions such as hydrogen and van der Walls bonds occur between the sorbent and sorbate over a long range, resulting in mono- and multi-layers. Thus, the force between the sorbent and sorbate is often weaker than the force in chemical sorption; therefore, physical sorption is considered a reversible reaction. The outer-sphere complex is an example of physical sorption.

2.2 Sorbent materials used to remove oxyanions from water

Since the end of the 1990s several types of sorbents have been used to remove P and As species through sorption processes. The sorbents used can be classified into categories ranging from natural materials to man-made products and industrial by-products (see Appendix II). Currently, efforts have been made to develop or find cheap, easily available, non-toxic, and selective sorbents to purify various types of waters from P and As. Many researchers have reported that materials containing or coated by Al or Fe oxides efficiently retain P (e.g., Borggaard et al., 1990; Persson et al., 1996; Ayoub et al., 2001; Borggaard, 2001; Penn et al., 2005; Borggaard et al., 2005; Arias et al., 2006) and As (e.g., Thirunavukkarasu et al., 2001; Lenoble et al., 2002; Gupta et al., 2005; Borggaard et al., 2005; Haque et al., 2008; Amiri et al., 2011).

2.2.1 Light expanded clay aggregates

LECA is an abbreviation of the term Light Expanded Clay Aggregates, and the corresponding abbreviation LWA refers to the term Lightweight Aggregate. This aggregate was first produced by Lemvigh – Muller & Munck A/S Copenhagen, Denmark, in 1939. Its raw material is plastic clay, which was burnt at extremely high temperature (approximately
1200 °C) in a rotary kiln. This temperature burns any organic compounds that are present, and the expanding clay forms pellets with a honeycomb structure. The outside surface of each granule melts and becomes sintered. The final lightweight products are brown ceramic pellets consisting of thousands of pores. LECAs, which are produced from clay, contain Fe and Al oxides produced in the weathering of primary minerals. These materials are environmentally friendly, non-biodegradable, non-combustible and chemically neutral. Because of their high crushing resistance, LECAs will not break down in water. Moreover, they have excellent sound and thermal insulation properties, fire resistance and freezing and melting resistance (Arioz et al., 2008; Malakootian et al., 2009). Owing to these favorable properties, LECAs are traditionally used as constructions and hydroponic materials (Kourti and Cheeseman, 2010).

Currently, LECAs have been widely used to clean up the environment from several types of pollutants, including metalloids such as As (Haque et al., 2008; Amiri et al., 2011), heavy metals such as lead and cadmium (Malakootian et al., 2009), non-metals such as fluoride (Sepehr et al., 2014) and phosphate (Drizo et al., 1999; Lyngsie et al., 2014), gases such as ammonia (Liu et al., 2014) and volatile sulfur compounds (Tabase et al., 2013). These materials are also used to remove carcinogenic organic pollutants from water, e.g., MCPA (4-chloro-2-methylphenoxyacetic acid) (Dordio et al., 2007).

2.2.2 Aluminum and iron oxides

Aluminum (Al) oxide and iron (Fe) oxide are universal terms used to refer to the hydroxides, oxides, and oxy-hydroxides of these metals. Aluminum is a ubiquitous metal in Earth’s crust and is the most abundant metal (8.1% by mass), and iron is the second most abundant metal (5.1% by mass). They are produced naturally in the weathering processes of common primary minerals such as micas and feldspars. As a result of prolonged desiccation, which removes silica and alkali and earth alkaline cations from soils, these metals form identifiable secondary minerals (examples given in Table 2).

Theoretically, the oxidation state of Fe ranges between 0 – VI, but the species in soils and water are Fe^{II} and Fe^{III}. The Fe speciation is dictated by the oxygen conditions, whereas Al exists only in the oxidation state +III and does not undergo oxidation-reduction reactions in natural conditions.
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECA s): a study of sorption mechanisms and anion competition

Table 2 – The major Fe and Al oxides in nature.

<table>
<thead>
<tr>
<th>Fe- oxides</th>
<th>Structure</th>
<th>Al- oxides</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>α-FeOOH</td>
<td>Diaspore</td>
<td>α-AlOOH</td>
</tr>
<tr>
<td>Akaganeite</td>
<td>β-FeOOH</td>
<td>Boehmite</td>
<td>γ-AlOOH</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
<td>Gibbsite</td>
<td>γ-Al(OH)₃</td>
</tr>
<tr>
<td>Ferricyanide</td>
<td>Fe₃O₄. 9H₂O</td>
<td>Bayerite</td>
<td>α-Al(OH)₃</td>
</tr>
</tbody>
</table>

The basic structural unit of all Fe³⁺ and Al³⁺ oxides is an octahedron, with the Fe or Al cations coordinated by O²⁻, OH⁻ or H₂O groups (e.g., Goldberg et al., 1996; Schwertmann and Cornell, 2008). Furthermore, the speciation of hydrated Al³⁺ and Fe³⁺ as (oxy)hydroxides is a highly pH-dependent process. Because the pKₐ value of Fe³⁺ is much lower than that of Al³⁺ (Table 3), acidic conditions favor the formation of (oxy)hydroxy species of Fe³⁺ over those of Al³⁺ (Fig. 4). These reaction patterns also explain the pH-dependent charge properties of Fe and Al (oxy)hydroxides and the proportion of H₂O and OH⁻ ligands on their hydration sphere.

Table 3 – Hydrolysis constants for Al and Fe³⁺ at 25 °C and zero ionic strength (modified from Gregory and Duan (2003) with permission from Elsevier).

<table>
<thead>
<tr>
<th>Al species</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Al(H₂O)₆]³⁺ + H₂O = [Al(H₂O)₅(OH)]²⁺ + H⁺</td>
<td>4.9</td>
</tr>
<tr>
<td>[Al(H₂O)₆]³⁺ + 2H₂O = [Al(H₂O)₄(OH)₂]¹⁺ + 2H⁺</td>
<td>5.6</td>
</tr>
<tr>
<td>[Al(H₂O)₆]³⁺ + 3H₂O = [Al(H₂O)₃(OH)₃]⁰ + 3H⁺</td>
<td>6.7</td>
</tr>
<tr>
<td>[Al(H₂O)₆]³⁺ + 4H₂O = [Al(H₂O)₂(OH)₄]⁻¹ + 4H⁺</td>
<td>5.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fe species</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(H₂O)₆]³⁺ + H₂O = [Fe(H₂O)₅(OH)]²⁺ + H⁺</td>
<td>2.2</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺ + 2H₂O = [Fe(H₂O)₄(OH)₂]¹⁺ + 2H⁺</td>
<td>3.5</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺ + 3H₂O = [Fe(H₂O)₃(OH)₃]⁰ + 3H⁺</td>
<td>6.0</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺ + 4H₂O = [Fe(H₂O)₂(OH)₄]⁻¹ + 4H⁺</td>
<td>10.0</td>
</tr>
</tbody>
</table>
The surface chemistry of Al and Fe oxides varies with pH. At a certain pH, called the point of zero charge (PZC), the net surface charge of Al and Fe oxides is neutral. Each mineral and even mineral crystal structure has a given PZC. For Al oxides, the PZC ranges between 4.8 and 9.8 (Parks, 1965; Goldberg et al., 1996) and that for Fe oxides ranges between 6 and 10 (Parks, 1965; Cornell and Schwertmann, 2003). However, these values are obtained by using different methods depending on the investigator. Because the sorption of P and As onto Al and Fe (hydr)oxides is known to be highly pH-dependent, knowing the PZCs of these oxides makes it possible to predict the efficiency of the sorption process. In solutions with a pH higher than the PZC of the oxide, the surface will have a net negative charge. Correspondingly, when the solution’s pH is lower than the PZC, the oxide’s surface will have
a net positive charge. In solutions with a pH equaling the PZC, the surface will be electrically neutral.

Aluminum and Fe oxides have properties suitable for use in environmental protection. Because they have a relatively high affinity to sorb several toxic inorganic anions and oxyanions, they are able to regulate the mobility of these species in soils and water (Gu et al., 1995; McBride and Martínez, 2000; Babel and Kurniawan, 2003; Hua et al., 2012). The sorption process is controlled by the net surface charge of the Al and Fe oxides, the protonation of the sorbents, or both factors in some cases. The sorption of P and As\textsuperscript{V} is mainly controlled by the net surface charge of Al and Fe oxides. For example, at a pH of 2 – 5, the dominant species of P and As\textsuperscript{V} are H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-} and H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{-}, respectively (Table 1). In this pH range, the surface of the Al and Fe oxides can be assumed to be positively charged because their PZCs are reported to be above this range (~ 5 – 10) (Parks, 1965; Goldberg et al., 1996; Cornell and Schwertmann, 2003). Contrary to P and As\textsuperscript{V}, the sorption of As\textsuperscript{III} onto Fe and Al oxides is controlled by the dissociation of its corresponding acid. H\textsubscript{2}AsO\textsubscript{3}\textsuperscript{-} and HAsO\textsubscript{2}\textsuperscript{2-} species dominate in the solution at a pH of 9 – 12, which is higher than the PZC. Thus, the surfaces of the Al and Fe oxides obviously have a negative surface charge.

2.3 Mechanism of ligand exchange onto surfaces of (oxy)hydroxides

The oxyanions of P and As are mainly bound to Al and Fe hydr(oxides) by a ligand exchange mechanism, first described by Hingston et al. (1967). In this reaction, a basic oxyanion replaces an aqua group (H\textsubscript{2}O) or hydroxyl group (OH\textsuperscript{-}) on the oxide’s surface and is bound through the formation of an inner sphere complex with the metal. This reaction can take place on a neutral or positively or negatively charged oxide surface. In acidic conditions, the OH\textsuperscript{-} groups on the oxide’s surface will be protonated, leading to the formation of aqua groups that are more easily replaced by oxyanions than OH\textsuperscript{-} groups. Alkaline conditions are less favorable to ligand exchange because the oxide’s surface becomes more negatively charged and the oxyanion has to replace the more reluctant OH\textsuperscript{-} ion. Depending on the charge of the group replaced and the anion species sorbed, the surface charge of the oxide becomes more negative or remains unchanged.

At low pH, phosphate is sorbed onto Al and Fe oxides as an inner-sphere complex at low pH and as an inner sphere complex and outer-sphere complex at high pH (Manning and Goldberg, 1996; Johnson et al., 2002; Khare et al., 2005; Van Emmerik et al., 2007). At a pH of 4, phosphate is sorbed onto Al oxides, forming a mono-protonated (H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}) bidentate
binuclear complex or di-protonated (\(\text{HPO}_4^{2-}\)) monodentate complex. At a pH of 9, a non-protonated (\(\text{H}_2\text{PO}_4\)) species forms a bidentate binuclear or a mono-protonated monodentate complex (Zheng et al., 2012). According to Kwon and Kubicki (2004), phosphate, when sorbed onto Fe oxides, forms a di-protonated bidentate complex at a pH of 4 – 6 and a mono-protonated monodentate complex at a pH of 7.9, whereas a non-protonated bidentate complex is formed at a pH of 7.5. However, a mono-protonated monodentate complex would be more stable at a pH of 7.5 – 7.9, and a non-protonated monodentate complex is formed at a pH of 12.8.

Arsenate is usually sorbed on the surfaces of amorphous Al and Fe oxides by forming an inner-sphere complex and is attached predominantly by bidentate or monodentate linkage (Goldberg and Johnston, 2001). Waychunas et al. (1993) concluded that \(\text{As}^{\text{V}}\) mainly forms bidentate complexes, but some monodentate complexes may be formed at very low coverages. However, \(\text{As}^{\text{III}}\) is sorbed on amorphous Fe oxide surfaces as inner- and outer-sphere complexes and forms bidentate binuclear complexes (Manning et al., 1998; Guo and Chen, 2005). At a pH lower than 5.5, \(\text{As}^{\text{III}}\) is sorbed onto Al oxides as an inner-sphere and forms bidentate binuclear complexes. However, Al oxides form mixtures of inner- and outer-sphere complexes at a pH higher than 5.5 (Arai et al., 2001).
3.0 OBJECTIVES OF THIS STUDY

This study was undertaken to investigate the chemical reactions of P and As with Al and Fe oxides in manufactured materials. Light Expanded Clay Aggregates (LECAs) were coated by Al or Fe oxides to investigate their potential to act as sorbents for P and As from problematic water. The chemical composition of the LECAs and oxide-coated LECAs was investigated in Article I. The main aim of this study was to compare their potential to act as sorbents in CWs and enhance the removal of P transported with agriculture runoff and effluents. The sorption kinetics of P onto LECAs and oxide-coated LECAs were determined, and the impact of the degree of P saturation and pH on the desorption of sorbed P from LECAs were investigated. Furthermore, the removal of As species by LECAs and oxide-coated LECAs were compared at various pH levels (Article IV). The sorption envelopes of As$^{\text{V}}$ and As$^{\text{III}}$ on various sorbents were determined to understand the sorption mechanisms of these species.

In groundwater, several anions always coexist; thus, there is always a competition between anions for the same sorption sites. For example, due to the chemical similarities between phosphate and As$^{\text{V}}$, the sorption of As$^{\text{V}}$ or As$^{\text{III}}$ is affected by competition with phosphate. This competition was investigated in Articles III and IV. Moreover, the redox potential in groundwater is low, so As is present mainly as As$^{\text{III}}$, which has a decisively lower sorption tendency than As$^{\text{V}}$. Furthermore, Fe is present in ferrous form (Fe$^{2+}$), which cannot retain any anions. Therefore, the use of manganese dioxide (MnO$_2$) as an oxidant to transform As$^{\text{III}}$ to As$^{\text{V}}$ and keep Fe in ferric form (Fe$^{3+}$) was also investigated (Article II). For all of the anion species, their maximum sorption (at various pH levels) onto LECA materials was determined by means of sorption isotherms. Furthermore, the actual sorption maximum of each anion species was also determined. This parameter refers to the concentration on the solid material that results in the highest acceptable P or As concentration left in the ambient equilibrium solution, i.e., in the purified water (Articles I, III and IV).
4.0 MATERIALS AND METHODS

4.1 Preparation and chemical characterization of the LECA materials

The LECAs used in this study were purchased from BioLan Oy (Article I-IV). The procedures used to prepare the sorbent materials were described in Article I and are depicted in Figure 5. For the chemical analyses, the LECA materials were digested by microwave digestion (MarsX press, CEM) with a matrix of strong acid including hydrofluoric acid (HF) to analyze the total Al and Fe contents (Article I). A 0.25-g sample of each sorbent was put in a Teflon vessel containing 2 mL of 67% HNO₃, 6 mL of 37% HCl and 2 mL of 40% HF. Then, the sorbent-acid mixture was digested for 10 min at 160°C (1600 W, 8.3 bar). Thereafter, the digested solution was transferred to a plastic flask, diluted to 100 mL by ultrapure Milli-Q water and filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate).

In addition, the poorly crystalline Al (Al₉ox) and Fe (Fe₉ox) oxides were determined according to the method of Niskanen (1989) as follows: 1.0 g of each sorbent was shaken with 50.0 mL of ammonium oxalate (pH 3.3) at 280 rpm for 2 h in the dark. Subsequently, the mixture was centrifuged for 10 min at 2500 rpm (Hermile Z513K, Hermle Labortechnik). Then, the solution was filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate) and 10 mL of the filtrate was diluted to 100 mL with 0.1 M HCl (Article I). The tests in these experiments were carried out with three replicates.

Finally, the solutions obtained in the microwave digestion and oxalate extracts were analyzed for Al and Fe by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer 5100, sampler Perkin Elmer AS 90 Controller) at wavelengths of 309.3 nm and 259.9 nm, respectively (Article I).
Figure 5 – Procedure to produce LECA materials (note that LECA is also a product).
4.2 Kinetics for phosphorus reaction

A kinetics experiment was undertaken to compare the contact time required by various LECA materials to reach an equilibrium (Article 1). To study the sorption, 1.0 L of KH$_2$PO$_4$ solution containing 20 µg P L$^{-1}$ was prepared and its pH was adjusted to 4 by adding 0.1 M HNO$_3$ dropwise (Table 4). Subsequently, 100 mL of KH$_2$PO$_4$ solution was introduced into acid-washed plastic bottles containing approximately 0.1 g of sorbent (weight was recorded). The mixtures were stirred at 110 rpm at room temperature. The supernatant LECA samples were taken after equilibration times of 0, 1, 2, 3, 4, 5, 6, 10, 15 or 20 h. For Al-LECA and Fe-LECA, the solution was allowed to settle for 2 min after equilibration times of 0, 20, 40, 60, 80, 100, 120, 140, or 240 min, and 3.0 mL of solution was collected from the top of the supernatant. Subsequently, the mixture was centrifuged for 10 min at 2500 rpm. Then, the solution was filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate), diluted to a volume of 10 mL with ultrapure Milli-Q water and analyzed for P. The kinetic test was carried out with three replicates.

4.2.1 First- and second-order Lagergren kinetic models

The pseudo first- and second-order Lagergren kinetic models used in this study are based on the Ritchie Equation (Eq. 1) (Cheung et al., 2001).

\[
\frac{dq}{dt} = k_n (q_e - q)^n 
\]  

where \( \frac{dq}{dt} \) is the sorption rate (mg P kg$^{-1}$ (sorbent) min$^{-1}$), \( k_n \) is the sorption constant of n order (kg$^{n-1}$ (sorbent) mg$^{-(n-1)}$ P min$^{-1}$), and \( q \) is the concentration of anions in the solid phase (mg P kg$^{-1}$ (sorbent)). In this study, we hypothesized that \( n \) is related to the number of surface sites occupied by each phosphate anion. Integrating Eq. 1 for \( n=1 \),

\[
\int_{q_0}^{q_t} \frac{dq}{(q_e-q)^n} = k_n \int_{t_0}^{t} dt 
\]  

results in the following Equation:

\[
q_t = q_e [1 - \beta_1 \exp(-k_1 (t - t_0))] 
\]  

where \( q_e \) and \( q_t \) are the sorption capacity (mg P kg$^{-1}$ (sorbent)) at the equilibration time (24 hours) and time \( t \), respectively; \( k_1 \) is the sorbent constant of the pseudo first-order Lagergren model (min$^{-1}$); and \( \beta_1 = 1 - \frac{q_0}{q_e} \) is the initial surface coverage of the sorbent by the phosphate. Because the sorbent initially has an empty surface, \( q_0 \) will be equal to zero, so \( \beta_1 = 1 \) and \( t_0 = 0 \), and Eq. 3 becomes the pseudo first-order kinetic model proposed by Lagergren (Vilar et al., 2006):

\[
q_t = q_e [1 - \exp(-k_1 t)] 
\]
The linear form of the pseudo first-order Equation of Lagergren is generally expressed as follows:

\[
\ln\left(\frac{1}{q_e - q_t}\right) = k_1 t - \ln q_e
\]  

(5)

A plot of \(\ln\left(\frac{1}{q_e - q_t}\right)\) against \(t\) has a slope \(k_1\) and an intercept \(-\ln q_e\).

For the second-order model where \(n = 2\), Eq. 1 was derived as follows:

\[
\frac{1}{q_e - q_t} - \frac{1}{q_e - q_0} = \beta_2 + k_2 (t - t_0)
\]  

(6)

\[
q_e = q_e \left[1 - \left(\frac{1}{\beta_n + q_e k_2(t - t_0)}\right)\right]
\]  

(7)

where \(q_e\) and \(q_t\) are the sorption capacity (mg P kg\(^{-1}\) (sorbent)) at the equilibration time (24 hours) and time \(t\), respectively; \(k_2\) is the sorbent constant of the pseudo second-order Lagergren model (kg (sorbent) mg\(^{-1}\)(P) min\(^{-1}\)); and \(\beta_2 = \frac{q_e}{q_e - q_0}\). When presupposed that the sorbent initially has an empty surface, \(q_0\) will be equal to zero, so \(\beta_2 = 1 \) and \(t_0 = 0\); thus, Eq. 7 results in the pseudo second-order kinetic model proposed by Lagergren (Vilar et al., 2006):

\[
q_e = q_e \left[1 - \left(\frac{1}{1 + q_e k_2 t}\right)\right]
\]  

(8)

The linear form of the pseudo second-order Equation of Lagergren is generally expressed as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(9)

A plot of \(\frac{t}{q_t}\) versus \(t\) has a slope \(\frac{1}{q_e}\) and an intercept \(\frac{1}{k_2 q_e}\). The regression coefficient (\(R^2\)) was used to judge between the two models.

### 4.3 Determination of the sorption envelopes for arsenic species

The optimal pH for the sorption of As\(^{V}\) and As\(^{III}\) by LECA materials was estimated by means of sorption tests carried out at broad pH ranges (Article IV). The pH range for As\(^{V}\) was 2 – 9, and for As\(^{III}\) 5 – 11 (Table 4). The experiment was carried out as follows: eight 1.0-L solutions containing 100 µg As\(^{V}\) L\(^{-1}\) (Na\(_2\)HAsO\(_4\).7\(\text{H}_2\)O) and seven 1.0-L solutions containing 100 µg As\(^{III}\) L\(^{-1}\) (NaAsO\(_2\)) were prepared; the pH of each solution was adjusted to the target level by adding 0.1 M HCl or 0.1 M NaOH dropwise. Afterwards, a 100-mL portion was transferred into 250-mL acid-washed plastic bottles containing 0.1 g of sorbent (weight was recorded). The solution–sorbent mixtures were stirred at 130 rpm (KS501 digital, IKA®-Werke GmbH & Co) at room temperature for 24 h. Then, the mixture was centrifuged for 10 min at 2500 rpm. Then, the solution was filtered through a 0.2-µm membrane filter.
(Nuclepore® polycarbonate). The sorption envelopes experiments were carried out with three replicates.

4.4 Phosphorus and arsenic sorption isotherms

The sorption behaviors of P and As\textsuperscript{V} at a pH of 3 – 8 and that of As\textsuperscript{III} at a pH of 3 – 10 were investigated by means of sorption isotherms (\textit{Articles I – IV}). Stock solutions containing 100 mg L\textsuperscript{-1} of P or As were used to prepare sets of addition solutions of 10 – 200 µg L\textsuperscript{-1}. Ultrapure Milli-Q water served as the zero addition solution. For P, the pH was adjusted to the target levels by adding drops of 0.1 M NaOH or 0.1 M HNO\textsubscript{3}, and in the case of As by adding drops of 0.1 M NaOH or 0.1 M HCl. The chemicals used, the volume of each stock solution, and the concentrations of P and As and the pH levels in the addition solutions are summarized in Table 4.

For the sorption isotherms, a 50-mL portion of the P or 100-mL portion of As\textsuperscript{V} or As\textsuperscript{III} solutions with different pH levels were introduced into 100-mL or 250-mL acid-washed plastic bottles, and 0.1 g of LECAs, Al-LECAs or Fe-LECAs sorbent was added (weight was recorded). The solution–sorbent mixtures were stirred at 130 rpm at room temperature for 24 h. Thereafter, the mixture was centrifuged for 10 min at 2500 rpm. Then, the solution was filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate) and preserved at 4°C before the analyses. The sorption tests were carried out with three replicates.
**Table 4** – **Summary of the P and As species and the concentrations and pH levels of the solutions used in the experiments.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical formula</th>
<th>Portion mL&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Initial conc. µg L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>pH</th>
<th>Article</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kinetics experiment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>KH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1000 (1)</td>
<td>20</td>
<td>4</td>
<td>I</td>
</tr>
<tr>
<td>2. Sorption envelopes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As&lt;sup&gt;V&lt;/sup&gt;</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;HAsO&lt;sub&gt;4&lt;/sub&gt;·7H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1000 (8)</td>
<td>100</td>
<td>2, 3, 4, 5, 6, 7, 8 or 9</td>
<td>IV</td>
</tr>
<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 (7)</td>
<td>100</td>
<td>5, 6, 7, 8, 9, 10 or 11</td>
<td>IV</td>
</tr>
<tr>
<td>3. Sorption isotherms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>KH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>500 (6)</td>
<td>0, 10, 20, 50, 100, or 200</td>
<td>3, 4, 5, 6, 7 or 8</td>
<td>I</td>
</tr>
<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>500 (5)</td>
<td>0, 10, 25, 50, 100</td>
<td>7</td>
<td>II</td>
</tr>
<tr>
<td>As&lt;sup&gt;V&lt;/sup&gt;</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;HAsO&lt;sub&gt;4&lt;/sub&gt;·7H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1000 (3)</td>
<td>0, 10, 20, 50, 100, or 200</td>
<td>3, 4 or 6</td>
<td>IV</td>
</tr>
<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 (2)</td>
<td>0, 10, 20, 50, 100, or 200</td>
<td>9 or 10</td>
<td>IV</td>
</tr>
<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 (4)</td>
<td>0, 10, 20, 50, 100, or 200</td>
<td>3, 5, 7 or 10</td>
<td>III, IV</td>
</tr>
<tr>
<td>4. Oxidizing agent (MnO&lt;sub&gt;2&lt;/sub&gt;) experiment</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 (5)</td>
<td>0, 10, 25, 50, 100</td>
<td>6</td>
<td>II</td>
</tr>
<tr>
<td>5. Competition experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>KH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>--------</td>
<td>0, 10, 20, 50 or 100</td>
<td>--------</td>
<td>IV</td>
</tr>
<tr>
<td>As&lt;sup&gt;V&lt;/sup&gt;</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;HAsO&lt;sub&gt;4&lt;/sub&gt;·7H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>500 (1)</td>
<td>50</td>
<td>6&lt;sup&gt;e&lt;/sup&gt;</td>
<td>IV</td>
</tr>
<tr>
<td>As&lt;sup&gt;III&lt;/sup&gt;</td>
<td>NaAsO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>500 (4)</td>
<td>50</td>
<td>3, 5, 7, or 10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>III</td>
</tr>
</tbody>
</table>

<sup>a</sup> Number in brackets refers to number of bottles divided for each pH level.

<sup>b</sup> Manganese dioxide (MnO<sub>2</sub>) acted as a sorbent in this experiment.

<sup>c</sup> pH adjusted for P and As<sup>V</sup> mixtures.

<sup>d</sup> pH adjusted for P and As<sup>III</sup> mixtures.
4.4.1 Analytical methods of phosphorus and arsenic

The phosphorus in the equilibrium solutions in Article I was analyzed colorimetrically (Lachat, QuikChem® 8000 Method 10-115-01-1-B (1.00 – 200 µg P L⁻¹)) by the ammonium molybdate - ascorbic acid method at a wavelength of 880 nm. The arsenic in Article II-IV was analyzed by using a hydride generation inductively coupled plasma optical emission spectrometer (HG-ICP-OES) (Perkin Elmer 5100, sampler Perkin Elmer AS 90 Controller). The principle of this method is based on the conversion of soluble As to volatile arsine (H₃As). To improve the sensitivity of the analysis, the samples containing As⁵⁺ were pre-reduced to As³⁺ prior to the analysis by adding 2.0 mL of concentrated hydrochloric acid (37% HCl) and 1.0 mL of reducing solution containing 10% (w/v) potassium iodide and 5% (w/v) ascorbic acid to a 1.0-mL sample. The solution was left to stand for 45 min to allow the conversion of As⁵⁺ to As³⁺ to occur. Following this procedure, a four-channel sample pump (iCAP 6500 instruments, Thermo scientific™) was used as a chamber to generate the gas phase hydride. The reaction was started by acidifying the sample in the cap with 5% HCl; then, the acidified sample was reacted with 0.5% sodium borohydride (NaBH₄) prepared in 0.05% sodium hydroxide solution (NaOH). After that, the vapor was introduced to the ICP-OES for As analysis at a wavelength 189 nm.

4.4.2 Sorption isotherms and calculation of sorption parameters

The amount of sorbate retained onto a specific sorbent depends on the affinity of the sorbate for the sorbent, the sorbent concentration in the solution and other factors, such as the pH, temperature and, presence of any other sorbates. The amount of sorbate sorbed by the sorbent was described mathematically by means of sorption isotherms, describing the amount of sorbate bound to the sorbent as a function of the sorbate concentration left in the solution after equilibration.

Data derived from sorption isotherms will typically fit one of five different isotherm curves (see Appendix III). The type I isotherm is the well-known Langmuir sorption isotherm (Brunauer et al., 1940). Langmuir is considered to describe chemical sorption. This corresponds to the formation of a monolayer covering the surface of the sorbent, where no multilayers are formed. The type II isotherm indicates an indefinite multi-layer formation after the completion of the monolayer. Type III shows a steady increase in the sorption capacity with increasing sorbate concentration, corresponding to the formation of a multilayer without prior monolayer formation (Ross, 2012). In this type, the sorbate has a low attractive force for the sorbent (Balbuena and Gubbins, 1993). The type IV isotherm indicates the
formation of a monolayer, followed by diffusion into pour space and finally the formation of a multilayer, while the type V isotherm indicates diffusion into pour space and then a multilayer without prior monolayer formation (Ross, 2012). The type IV and V curves can exhibit hysteresis, a condition where the desorption (backward isotherm) does not follow the sorption isotherm (Thomas and Crittenden, 1998).

The isotherms for each anion species were produced by expressing its sorption at each addition level as a function of the concentration in the equilibrium solution. The sorption parameters for each sorbent were calculated from the Langmuir Equation rearranged to a linear form (Barrow, 1978):

\[
\frac{C}{Q} = \frac{1}{K_L X_m} + \frac{1}{X_m} C
\]

where \( C \) is the concentration of sorbate (P or As) in the equilibrium solution (mg sorbate L\(^{-1}\)), \( Q \) is the amount of sorbed anions (mg sorbate kg\(^{-1}\) sorbent), \( X_m \) is the sorption maximum (mg sorbate kg\(^{-1}\) sorbent) and \( K_L \) is a coefficient related to the bonding energy (L mg\(^{-1}\) sorbate). Moreover, the actual sorption capacity for P, As\(^V\) or As\(^III\) was calculated (Articles I, III and IV). This refers to the sorption of a given element at the equilibrium solution concentration corresponding to its highest allowable level in water.

4.5 Degree of phosphorus saturation (DPS)

To assess the impact of pH on the P sorption capacity of the LECA materials, the degree of P saturation (DPS) was determined at a pH of 3 – 8 (Article I). The DPS value was calculated as the molar ratio of P bound at the addition level 200 µg L\(^{-1}\) (P\(_{Q200}\)) to the molar sum of oxalate-soluble Al\(_{ox}\) and Fe\(_{ox}\) considered to represent the active sites (Pautler and Sims, 2000) on the LECA sorbents:

\[
DPS = \frac{P_{Q200}}{Al_{ox}+Fe_{ox}} \times 100\%
\]

4.6 Desorption of sorbed phosphorus

To study the reversibility of P sorption reactions, P desorption was studied using P-loaded LECA materials collected from the isotherm experiment after equilibration for 24 h with a P solution of 20 µg L\(^{-1}\) at a pH of 4 and 8 (Article I). The LECA materials were rinsed with 50 mL of 1.0 M KCl solution to remove free P in the interstitial water. It was assumed that the high ionic strength of the rinsing solution counteracts the desorption tendency of P to form the oxide surfaces. The P concentration in the rinsing water was less than 1.0 µg L\(^{-1}\) (Article I). Thereafter, the materials were rinsed with 50 mL Milli-Q water and allowed to dry
for 3 days at room temperature. Afterwards, each sorbent material was divided into ten portions, which were delivered to acid-washed plastic bottles containing Milli–Q water adjusted to a pH of 4 using 0.1 M HNO₃ or a pH of 8 using 0.1 M NaOH. The ratios between the sorbent (g) and Milli-Q water (mL) in the desorption test were 1:10, 50, 100, 150 or 200. The mixtures were stirred at 110 rpm at room temperature overnight, and then the solutions were filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate). The desorption test was carried out with three replicates.

4.7 Effect of oxidizing agents on the sorption of arsenite

The effect of oxidizing agents on the removal of As³⁺ from solution by LECA materials was assessed by means of sorption isotherms with and without MnO₂ (*Article II*). The experiment was carried out by transferring 50 mL of As³⁺ solution containing 0, 10, 25, 50, or 100 µg As³⁺ L⁻¹ into acid-washed plastic bottles containing approximately 10 mg MnO₂ and 100 mg of LECA materials (weights were recorded). A parallel set of samples was prepared without added MnO₂. The pH levels of the mixtures were fixed to a pH of 6 by adding drops of 0.1 M NaOH or 0.1 M HCl. The control treatment with MnO₂ was carried out at a pH of 6 without LECA materials as follows: 100 mg of MnO₂ was put in acid-washed plastic bottles containing 50 mL of 0, 10, 25, 50, or 100 µg As³⁺ or As⁵⁺ L⁻¹ solutions. The mixtures were stirred at 130 rpm at room temperature for 24 hours, centrifuged for 10 min at 3500 rpm, and filtrated through a 0.2-µm membrane filter (Nuclepore® polycarbonate). The experiment was carried out with three replicates.

4.8 Competition between phosphorus and arsenic species

To study the competitive impact of P on the sorption of As⁵⁺ and As³⁺ onto LECAs (*Article III and IV*), a set of KH₂PO₄ solutions containing 0, 10, 20, 50 or 100 µg P L⁻¹ was prepared (*Table 4*). A volume of 50 mL of each solution was poured into a 250-mL acid-washed plastic bottle containing approximately 0.1 g of LECAs, Al-LECAs or Fe-LECAs (weight was recorded) and 50 mL of solutions containing 50 µg As⁵⁺ L⁻¹ or 50 µg As³⁺ L⁻¹. The pH of the As⁵⁺ mixture was adjusted to 6 and that of the As³⁺ mixture to 3, 5, 7 or 10 by adding either 0.1 M NaOH or 0.1 M HCl dropwise (*Table 4*). Thereafter, the solution-sorbent mixtures in both sample sets were stirred at 130 rpm at room temperature for 24 hours. Thereafter, the mixture was centrifuged for 10 min at 2500 rpm. Then, the solutions were filtrated through a 0.2-µm membrane filter (Nuclepore® polycarbonate) and preserved at 4°C before the As analyses. This experiment was carried out with three replicates.
5.0 QUALITY CONTROL OF THE ANALYSES AND STATISTICAL ANALYSIS

5.1 Quality control of the analyses

The water used in the P experiment (Article I) was de-ionized (Cillit-Clear-filter 77SN, Cillit, Wassertechnik GmbH, Germany), and its quality was controlled by measuring its electric conductivity (Electric conductivity CDM 210, MeterLab™) and pH (Consert C860). The water used in the As experiments (Article II-IV) was ultrapure Milli-Q water (Milli-Q® Integral, Q-POD, Millipak® 40 Express Final Filter, resistivity is 18.2 μΩ.cm and TOC is 2 ppm at 25°C). The chemicals used in this study were of analytical grade (for more details, see Appendix IV). The ICP standard solution with a concentration of 1000 µg As L⁻¹ was obtained from AccuStandard®, and the Al and Fe standard solutions with a concentration of 1000 mg L⁻¹ for the ICP measurements were obtained from Merck KGaA (ICP multi-element standard). Phosphate, arsenate and arsenite stock solutions with a concentration of 100 mg L⁻¹ were prepared from potassium phosphate monobasic (KH₂PO₄), sodium arsenate dibasic heptahydrate (Na₂H₂AsO₄·7H₂O) and sodium arsenite (NaAsO₂), respectively. Blank samples were included in all of the sample series. The exact amounts of the chemicals and sorbents were obtained by using high sensitivity balance (100A – 300M, Precisa) scales.

All of the experiments were carried out by using polypropylene bottles. The P and As solutions were prepared in borosilicate volumetric flasks. All of the bottles, volumetric flasks and other laboratory equipment used in the experiments were washed by soaking in acid solution (2% HNO₃ + 2% HCl) for 24 hours, followed by rinsing eight times in running ultrapure Milli-Q water. All of the devices used in the measurements were calibrated according to the manufacturer’s instructions before use. The operation of the ICP-OES was confirmed by running external standards of known concentrations every 20 samples. To avoid damaging the sample introduction system in the ICP-OES (nebulizer, spay chamber, etc.) due to the use of HF, the sample introduction system in the ICP-OES was replaced with a Duo HF sample introduction kit (iCap™ 6000 series ICP-consumable kit, Thermo scientific™).

5.2 Statistical analyses

The Statistical Package for the Social Sciences for Windows (SPSS /PASW version 18) was used for the data analysis of the experiments. All of the experiments in this study were carried out with three replicates. The fitting of the model was assessed by calculating the standard error (SD), relative standard deviation (RSD) and regression coefficient (R²).
Equation used for the standard error was $SD = \frac{S}{\sqrt{N}}$, and that used to calculate the relative standard deviation was $RSD = \frac{S}{\bar{x}} \times 100\%$, where $S$ is the standard deviation ($S = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2}$), $N$ is the number of replicates, and $x_i$ and $\bar{x}$ are the observed value and the mean value of the sample, respectively.
6.0 RESULTS AND DISCUSSION

6.1 Chemical compositions of the LECA materials

The chemical compositions of LECA materials depend on the mineralogy of their raw material. When clay minerals originate in muscovite, they are rich in Al\(^{3+}\), which is the central cation of octahedral sheets and can replace some Si\(^{4+}\) cations in tetrahedral sheets via isomorphous substitution. Because the central cations for biotite in the octahedral sheet are Mg\(^{2+}\) and Fe\(^{2+}\), the clay minerals produced from it are lower in total Al\(^{3+}\) than those produced from muscovite.

The LECA pellets used in our studies were much richer in total Al than total Fe on a molar basis. However, the relative portion of poorly crystalline Al was lower than that of Fe (Table 5). It is likely that Fe\(^{2+}\) released from the mineral lattice in clay materials is subjected to oxidation – reduction cycles, retarding the crystallization process. The high temperature used to produce LECA materials augments the crystallization of Al and Fe components and, consequently, lowers their chemical reactivity by decreasing the specific surface area (Sørensen et al., 2000).

Table 5 – Total and poorly crystalline (oxalate-soluble) Al and Fe and their portion (%) in LECA, Al-LECA, and Fe-LECA materials (±SD = standard deviation) (n = 3).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Total</th>
<th>Poorly crystalline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aluminum</td>
<td>Iron</td>
</tr>
<tr>
<td>LECAs</td>
<td>2.2 ± 0.03</td>
<td>0.8 ± 0.04</td>
</tr>
<tr>
<td>Al-LECAs</td>
<td>3.2 ± 0.1</td>
<td>0.6 ± 0.04</td>
</tr>
<tr>
<td>Fe-LECAs</td>
<td>2.2 ± 0.12</td>
<td>4.7 ± 0.42</td>
</tr>
</tbody>
</table>

Coating LECA materials with Al and Fe oxides increased not only the proportion of the oxides but also the proportion of their poorly crystalline forms. The Fe coating elevated the total Fe approximately 6 times but increased the poorly crystalline fraction 7 times. Interestingly, this process also increased the proportion of poorly crystalline Al 4 times without any effect on the total Al. On the contrary, the Al oxide coating increased the total Al only 1.5 times but increased the poorly crystalline fraction 15 times. Moreover, the Al coating diminished the total Fe by 1.3 times and the proportion of poorly crystalline Fe by as much as 3 times (Table 5). Based on the concept that \(pe + pH = constant\), it can be concluded that the drastic elevation in the pH caused some reduction of Fe\(^{3+}\) to more soluble Fe\(^{2+}\).
The contrasting features of poorly crystalline Al and Fe in the coating procedure could also be partially attributable to the different temperatures used to dry the Al-LECAs and Fe-LECAs (Article I). Schwertmann and Cornell (2008) concluded that the crystallization of hydroxide is enhanced by elevated temperatures. Moreover, the NaOH step in the coating procedure will convert some of the structural Al in the LECAs into a more amorphous form; according to the solubility diagrams for $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ presented by Lindsay (1979), this alkali addition will dissolve oxidic $\text{Fe}^{3+}$ more easily than oxidic $\text{Al}^{3+}$ from the LECAs structure.

6.2 Kinetics of phosphorus sorption onto LECA materials

The results of the kinetic studies demonstrated that P sorption increased with longer reaction time. As for the oxide-coated LECAs, the sorption onto Fe-LECAs was faster than that onto Al-LECAs. Equilibrium was achieved in the Fe-LECAs at 100 min, when more than 98% of P was removed. In the Al-LECAs, equilibrium was achieved in 140 min, when 82% of P was removed. However, in uncoated LECAs, the reaction was very slow, with equilibrium reached after 24 h and only 6% of the added P retained (Fig. 2 in Article I).

The experimental sorption data were plotted with pseudo first- and second-order Lagergren Equation models (Eq. 5 and Eq. 9, respectively). The calculated parameters revealed that the sorption of P onto uncoated LECAs occurred through the pseudo first-order model ($R^2 = 0.9581$) and the sorption rate constant calculated from the slope was 0.37 min$^{-1}$. However, the correlation between the sorption capacity of LECAs and the equilibration times in the pseudo second-order model was weak ($R^2 = 0.6361$). When applied to the oxide-coated LECAs, the models produced matching outcomes. The correlation between the sorption capacity of oxide-coated LECAs and the equilibration time in the pseudo second-order model was stronger than that obtained with the pseudo first-order model. The kinetic rate constant ($k_2$) for the Al-LECAs and Fe-LECAs calculated from the intercept and slope of the lines of the second-order reaction was 2.4 and 3.2 kg (sorbet) mg$^{-1}$ (P) min$^{-1}$, respectively.

According to Vilar et al. (2006), the essential assumption of the pseudo second-order model is that one phosphate ion is sorbed onto two sites on the surface. Therefore, it can be concluded that each phosphate ion occupied two surface sites on the Al-LECAs and Fe-LECAs through the formation of a stable bidentate binuclear complex (see Fig. 6 C, F, I, L and O). However, the LECA data fit the pseudo first-order model better than the second-order model, indicating that each phosphate ion was sorbed onto one sorption site and formed a monodentate complex (see Fig. 6 A, D, G, J and M). These conclusions agree with the chemical compositions of the LECAs (Table 5), revealing that the proportions of poorly
crystalline Al and Fe oxides were much higher in the oxide-coated LECAs than in the regular LECAs (*Article I*).
Figure 6 – Schematic representation of different inner-sphere complexes (I – V) and outer-sphere complexes (VI) that phosphorus or arsenic (L) form on the surface of aluminum or iron (M) oxide surfaces with a neutral charge (I and VI), positive charge (II and III) and negative charge (IV and V). Monodentate complex: A, D, G, J and M; bidentate complex: B, E, H, K and N; and bidentate binuclear complex: C, F, I, L and O. Note that an oxo-group (red color) is present in phosphate (H$_3$PO$_4$) and arsenate (H$_3$AsO$_4$) but absent in arsenite (H$_3$AsO$_3$).

6.3 Degree of phosphorus saturation (DPS) and phosphorus desorption

The degree of P saturation (DPS), referring to the mineral surface covered by phosphate anions, is usually calculated for soils in agro-ecosystems to estimate the risk of P desorption from soil particles to runoff water. Moreover, DPS is also used to determine the potential P loss from suspended sediments. As expected, the oxide coatings increased the amount of poorly crystalline Al and Fe fractions (Table 5) and, thus, the number of P sorption sites
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition (Article I). This was reflected in the much lower DPS values in the coated LECAs than the regular LECAs for pH levels of 3 – 8 (Fig. 7). The Al-LECAs had a higher amount of total poorly crystalline oxides than the Fe-LECAs (Article I), whereas the DPS of the Fe-LECAs was higher than that of the Al-LECAs over the whole pH range of 3 – 8 (Fig. 7).

![Figure 7 – Degree of P saturation (DPS) (Eq. 11) obtained in the LECAs, Al-LECAs, and Fe-LECAs at varying pH at the P addition level of 200 µg L⁻¹. The error bars represent the RSD.](image)

It can be concluded that the high DPS of the LECAs favored the formation of monodentate P bonding (see Fig. 6 A, D, G, J and M). Correspondingly, a low P to metal ratio in the Al-LECAs and Fe-LECAs can be taken to favor bidentate complex (see Fig. 6 B, E, H, K and N) and / or bidentate binuclear complex (see Fig. 6 C, F, I, L and O) bonding between P and metal oxides. These conclusions agree with the results of the kinetics study, indicating that each phosphate ion was sorbed onto one surface site on the LECAs by monodentate binding, whereas each phosphate ion was sorbed onto two surface sites on the Al-LECAs and Fe-LECAs as a more stable bidentate binuclear complex (Article I). Thus, the binding of P to oxide-coated materials can be concluded to be stronger than that to LECAs. The results obtained in the subsequent desorption test support this conclusion (Article I), revealing that the desorption was largest for the LECAs with the highest DPS.

Because there is an equilibrium between the P sorbed and that in the equilibrium solution, the desorption of P from LECAs increased with decreasing sorbent to solution (water) ratios (Fig. 8). Furthermore, the surface charge of Al and Fe oxides is pH dependent and affects the sorption tendencies of anions. A high pH renders the surface charge more negative and, consequently, enhances the desorption of sorbed anions. Interestingly, the
competition of OH$^-$ ions for sorption sites favored P desorption from Fe-LECAs more compared to Al-LECAs. Because the coated LECAs did not decisively differ in their DPS values (Article I), this reaction pattern is attributable to the higher acidity of Fe$^{3+}$. This means that Fe$^{3+}$ is surrounded by a higher number of OH$^-$ groups than Al$^{3+}$ at a pH of 8, rendering the surface of Fe-LECAs more negative and, thus, enhancing the desorption tendency of phosphate groups. This reaction pattern demonstrates that sorption by Al-LECAs is less reversible than that by Fe-LECAs at elevated pH.

![Figure 8](image_url)  
**Figure 8** – Phosphorus desorbed (µg g$^{-1}$) from the LECAs, Al-LECAs and Fe-LECAs as a function of water added at a pH of 4 and 8.

### 6.4 Arsenic sorption envelopes

Similar to P, the sorption of As onto oxide surfaces also depends on pH, which affects the surface charges of oxides. However, the dependence of As sorption on pH is more complicated than that of P because As species differ decisively in their pK$_a$ values and, thus, anion speciation (Table 1).

As expected, the sorption of different As species onto LECA sorbents differed noticeably in terms of the optimal pH (Article IV). The peak sorption of As$^V$ by LECAs occurred at a pH of 2, whereas that of As$^{III}$ occurred at a pH of 10 – 11 (Fig. 9). Because As$^V$ acid was mainly in a dissociated form at pH > 2.3, the continuous decrease in the sorption with increasing pH can be attributed to the increasing dissociation degree of the As$^V$ species and increasing negative charge of the LECA surfaces. The sorption was rather constant at the pH range of 2 – 5 but decreased at higher pH (Fig. 9). Thus, As$^V$ was sorbed onto LECAs...
mainly as an outer-sphere complex at pH lower than 5, where the water molecules form a bridge between the As\textsuperscript{V} and the sorption sites (Fig. 6). However, some inner-sphere complexes may be formed at a pH of 2 but to a lower degree than the outer-sphere complexes. The sorption of As\textsuperscript{III} slightly increased with elevated pH until a pH of 8, whereafter it seemed to remain rather constant (Fig. 9). Because As\textsuperscript{III} exists mainly as the neutral molecule H\textsubscript{3}AsO\textsubscript{3} at pH < 9.1, As\textsuperscript{III} sorption at a pH of 5 – 7 can be attributed to diffusion through surface micro- or meso-pores into the inner part of LECAs and, at higher pH levels, by the formation of outer- and inner-sphere complexes (Fig. 6).

The sorption envelopes of the oxide-coated LECAs decisively differed from those of the uncoated ones (Article IV). In Al-LECAs, the sorption of As\textsuperscript{V} increased sharply at a pH of 2 – 4. The sorption peak was obtained at a pH of 4, whereafter it gradually diminished, being lower at a pH of 9 than at a pH of 2 (Fig. 9). At a pH of 2, the retention of As\textsuperscript{V} was the same in both oxide-coated LECAs but increased more slowly in Fe-LECAs than in Al-LECAs at elevated pH. Thus, the peak sorption was not reached until a pH of 6 (Fig. 9). This finding agrees with the results obtained by Wilkie and Hering (1996) and Haque et al. (2008). However, the sorption gradually decreased at pH > 6, similar to the study of Haque et al. (2008). It is noteworthy, however, that at pH levels higher than those at the peak sorption, the Fe-LECAs maintained their sorption ability better than the Al-LECAs, with the same sorption at pH levels of 9 and 2. In Al-LECAs, the sorption was 50% lower (Fig. 9).

The sorption of As\textsuperscript{III} onto Al-LECAs gradually increased until a pH of 9 and tended to diminish thereafter, but no clear sorption peak was obtained (Article IV). Because of the high pK\textsubscript{a1} value of H\textsubscript{3}AsO\textsubscript{3} (pK\textsubscript{a1} = 9.2), the sorption of As\textsuperscript{III} at a pH of 11 was higher than that at a pH of 5 (Fig. 9). The peak sorption by Fe-LECAs was obtained at a pH of 9 – 10, whereafter it dropped sharply. This result agrees with the previous finding of Masue et al. (2007). It is noteworthy that the sorption of As\textsuperscript{III} onto Fe-LECAs was higher at a pH of 11 than that at a pH of 5 (Fig. 9) and was only about half that of As\textsuperscript{V} at a pH of 6. However, after reaching the peak sorption, the Al-LECAs maintained their sorption ability better than the Fe-LECAs. The sorption envelopes of As\textsuperscript{V} and As\textsuperscript{III} onto Al-LECAs and Fe-LECAs intersected at a pH of 6 and 8, respectively. Interestingly, the sorption of As at this intersection was about the same irrespective of oxide type. This outcome indicates the synergetic effect of pH on As speciation and the surface charges of oxides.

At pH < 9, As\textsuperscript{III} is present as undissociated molecules (pK\textsubscript{a1} = 9.2). Thus, the sorption of As\textsuperscript{III} onto Al-LECAs and Fe-LECAs is lower than that of As\textsuperscript{V} at pH ranges of 2 – 6 and 2 – 8,
respectively (Fig. 9). However, at pH > 9.2, the monovalent anion $\text{H}_2\text{AsO}_3^-$ starts to predominate. Obviously, elevated pH leads to the dissociation of the aqua groups on the oxide’s surface to OH$^-$ groups and, consequently, higher negative charge on the surfaces of LECA materials (Fig. 4). The increasing electrostatic repulsion between the more negative surfaces of oxide-coated LECAs and As$^V$ anions, in turn, will weaken the sorption of As$^V$. However, arsenous acid is very weak ($\text{pK}_{a1} = 9.2$ and $\text{pK}_{a2} = 10.6$) and its deprotonation of As$^{\text{III}}$ to monovalent $\text{H}_2\text{AsO}_3^-$ and divalent $\text{HAsO}_3^{2-}$ will not take place until the pH reaches 9.2 (Table 1). $\text{H}_3\text{AsO}_3$ ($\text{pK}_{a1} = 9.2$) will be deprotonated to monovalent $\text{H}_2\text{AsO}_3^-$, which enhances the protonation of OH$^-$ groups to H$_2$O groups on the oxide surfaces of LECA materials, rendering them more favorable for the formation of inner-sphere complexes (Fig. 6 M, N and O).
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

Figure 9 – Arsenate (As\textsuperscript{V}) and arsenite (As\textsuperscript{III}) sorption onto the LECAs, Al-LECAs and Fe-LECAs as a function of pH. Initial addition concentration: 100 µg L\textsuperscript{-1}; sorbent dose: 1-1.5 g L\textsuperscript{-1}; stirring speed: 130 rpm; contact time: 24 hours; performed at room temperature. The error bars correspond to confidence intervals of 95%.
6.5 Sorption isotherms

As expected, the oxide coatings increased the apparent sorption maximum \(X_m\) of all of the LECA materials. The sorption of P and As species onto LECA materials was highly pH dependent. At a pH of 3, the oxide coatings increased the \(X_m\) of P more than twofold \((\text{Article I})\) and that of As\(^V\) and As\(^{III}\) approximately 1.5- to 1.6-fold \((\text{Article III and IV})\) \((\text{Table 6})\). The sorption of P and As\(^V\) by LECA materials was highly pH dependent. At a pH of 3, the oxide coatings increased the \(X_m\) of P more than twofold \((\text{Article I})\) and that of As\(^V\) and As\(^{III}\) approximately 1.5- to 1.6-fold \((\text{Article III and IV})\) \((\text{Table 6})\). The sorption of P and As\(^V\) by LECA materials seemed to be more sensitive to increases in pH than that by the oxide-coated LECA materials. When the pH was elevated from 3 to 8, the \(X_m\) of P onto LECA materials diminished 7.4-fold but that onto Al-LECA and Fe-LECA decreased only 2.7-fold and 3.7-fold, respectively \((\text{Table 6})\). The relative impact of the oxide coatings on the \(X_m\) of As\(^V\) was less drastic. When the pH increased from 3 to 8, the \(X_m\) of As\(^V\) decreased 4.2-fold in the LECA, 4.2-fold in the Al-LECA and 4.3-fold in the Fe-LECA. On the contrary, the \(X_m\) values of As\(^{III}\) decisively increased 9.4- to 10.9-fold when the pH increased from 3 to 10 \((\text{Table 6})\).

The results in \(\text{Table 6}\) demonstrate that As\(^V\) sorption by oxide-coated LECA is more sensitive to changes in pH than that for P. This conclusion agrees with the previous findings of Antelo et al. \((2005)\). Moreover, As\(^V\) shows a similar sorption pattern on the oxide-coated LECA but with a lower affinity than phosphate \((\text{Article I and IV})\). Hingston et al. \((1971)\) found that phosphate is more strongly sorbed than As\(^V\) onto Al oxides and have about the same sorption tendencies on Fe oxides. Manning and Goldberg \((1996)\) concluded that Al oxides tend to retain phosphate preferentially over As\(^V\). However, Gao and Mucci \((2001)\) and Hongshao and Stanforth \((2001)\) found that As\(^V\) is more strongly sorbed than phosphate onto Fe oxides (goethite). Interestingly, both P and As\(^V\) showed very similar \(X_m\) onto Al-LECA at a pH of 4 and 6, respectively. For Fe-LECA, P and As\(^V\) had the same \(X_m\) only at a pH of 6 \((\text{Table 6})\).
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

Table 6 – Apparent sorption maximum obtained for P, As\textsuperscript{V} and As\textsuperscript{III} onto the LECAs, Al-LECAs and Fe-LECAs at different pH values (n =3).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>pH</th>
<th>X\textsubscript{P,SD} (\mu g \text{ g}^{-1})</th>
<th>X\textsubscript{As\textsuperscript{V},SD} (\mu g \text{ g}^{-1})</th>
<th>X\textsubscript{As\textsuperscript{III},SD} (\mu g \text{ g}^{-1})</th>
<th>K\textsubscript{L,SD} (L \text{ mg}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LECAs</td>
<td>3</td>
<td>157.9±7.9</td>
<td>187.9±12.0</td>
<td>16.9±1.4</td>
<td>9.5±3.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>117.5±4.5</td>
<td>145.9±9.7</td>
<td>16.1±1.2</td>
<td>8.0±0.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>105.3±4.8</td>
<td>30.8±2.3</td>
<td>8.0±0.7</td>
<td>4.1±0.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>64.0±2.6</td>
<td>128.8±15.5</td>
<td>3.6±0.3</td>
<td>3.0±0.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>25.1±1.5</td>
<td>97.8±14.0</td>
<td>1.5±0.1</td>
<td>3.3±0.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>21.4±2.1</td>
<td>54.9±22.2</td>
<td>1.4±0.1</td>
<td>3.4±0.2</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>155.3±7.3</td>
<td>7.0±0.6</td>
<td>5.1±0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>183.8±8.8</td>
<td>10.8±0.5</td>
<td>4.7±0.3</td>
<td></td>
</tr>
<tr>
<td>Al-LECAs</td>
<td>3</td>
<td>373.5±20.9</td>
<td>324.6±18.2</td>
<td>25.2±7.4</td>
<td>8.0±0.4</td>
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<tr>
<td></td>
<td>4</td>
<td>341.5±10.1</td>
<td>342.6±16.7</td>
<td>46.4±0.6</td>
<td>7.9±0.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>269.8±16.7</td>
<td>64.4±1.4</td>
<td>56.8±0.7</td>
<td>7.9±0.4</td>
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<tr>
<td></td>
<td>6</td>
<td>244.2±6.1</td>
<td>244.2±5.8</td>
<td>22.9±0.1</td>
<td>5.2±0.1</td>
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<tr>
<td></td>
<td>7</td>
<td>220.4±12.8</td>
<td>167.8±16.3</td>
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<td>5.2±0.7</td>
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<td></td>
<td>8</td>
<td>136.3±18.0</td>
<td>77.7±11.0</td>
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<td></td>
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<td>265.8±6.3</td>
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<tr>
<td></td>
<td>10</td>
<td>238.5±6.6</td>
<td>15.5±0.7</td>
<td>7.0±0.5</td>
<td></td>
</tr>
<tr>
<td>Fe-LECAs</td>
<td>3</td>
<td>380.6±12.5</td>
<td>300.8±11.2</td>
<td>26.2±1.8</td>
<td>9.5±0.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>358.4±12.3</td>
<td>327.1±12.5</td>
<td>21.8±1.2</td>
<td>8.3±0.4</td>
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<tr>
<td></td>
<td>5</td>
<td>283.4±7.0</td>
<td>70.0±2.8</td>
<td>37.2±0.2</td>
<td>7.6±0.3</td>
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<tr>
<td></td>
<td>6</td>
<td>284.5±14.6</td>
<td>382.2±20.8</td>
<td>20.4±0.1</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>227.6±6.0</td>
<td>212.2±10.2</td>
<td>20.0±0.2</td>
<td>4.8±0.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>103.6±4.9</td>
<td>69.4±1.8</td>
<td>10.1±1.5</td>
<td>5.3±0.7</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>203.7±15.1</td>
<td>12.0±0.1</td>
<td>6.4±0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>278.2±7.5</td>
<td>27.5±0.9</td>
<td>13.9±0.2</td>
<td></td>
</tr>
</tbody>
</table>

LECAs that were much lower in amorphous Al and Fe than the coated LECAs (Table 5) also had a lower reactivity and sorption capacity. However, the Al-LECAs and Fe-LECAs did not decisively differ in the sum of their poorly crystalline oxides (Table 5). In all of the LECAs, the sorption of P diminished as a response to elevated pH. The same trend was also observed for As\textsuperscript{V} except for Fe-LECAs, where the peak sorption was obtained at a pH of 6 (Table 6). A low pH favors the formation of aqua ligands on the poorly crystalline oxides.

\(^{1}\) Apparent maximum P sorption (µg sorbate g\textsuperscript{-1} sorbent)

\(^{ii}\) Standard error

\(^{iii}\) The sorption of P at the equilibrium concentration of 20 µg P L\textsuperscript{-1}

\(^{iv}\) The sorption of As at the equilibrium concentration of 10 µg As L\textsuperscript{-1}

\(^{v}\) Coefficient related to bonding energy (L µg\textsuperscript{-1})

\(^{vi}\) ±SD was less than 0.01
which are more easily replaced by phosphate and As\(^{V}\) anions by ligand exchange than OH\(^{-}\) groups. Correspondingly, higher pH increases the proportion of OH\(^{-}\) ions along the surface, rendering the oxide’s surface more negative and, thus, hampering the retention of phosphate and As\(^{V}\). On the contrary, the retention of As\(^{III}\) increased with higher pH in all the LECAsorbents. The only exception was Al-LECAs, where the sorption peak was found at pH 9 (Table 6). The deprotonation of H\(_3\)AsO\(_3\) acid (pK\(_{a1}\) 9.2) to an anionic form seemed to be the critical factor controlling the sorption of As\(^{III}\). At a pH below its pK\(_{a1}\) values, the surfaces of oxide-coated LECAs will be rather saturated with OH\(^{-}\) groups (Fig. 4), whereas H\(_3\)AsO\(_3\) molecules tend to donate a proton to these groups. This step, in turn, will expedite the dissociation of H\(_3\)AsO\(_3\) to H\(_2\)AsO\(_3\)\(^{-}\). This reaction pattern increases the number of aqua groups on the oxide’s surface, which are more easily replaced than OH\(^{-}\) groups during ligand exchange (Fig. 6 M, N and O).

It is noteworthy that the oxide-coated LECAs differed in their responsiveness to pH. The X\(_m\) values for P retained by the oxide-coated LECAs intersected at a pH of approximately 6.7 (Fig. 10 A). Below this pH, the Fe-LECAs retained more P than Al-LECAs did, while the opposite trend occurred at a pH higher than 6.7. The drop in X\(_m\) in the Al- and Fe-oxide-coated LECAs was most pronounced within the pH range of 7 – 8. The X\(_m\) graphs for As\(^{V}\) sorbed onto Al-LECAs and Fe-LECAs first intersected at a pH of 4.2 (Fig. 10 B). After this point, the sorption onto Fe-LECAs continued to increase, whereas that onto Al-LECAs decreased. The graphs intersected a second time at a pH of 7.9. In the pH range of 6 – 8, sorption onto Fe-LECAs dropped drastically, whereas that onto Al-LECAs decreased rather smoothly (Fig. 10 B). However, the X\(_m\) values for As\(^{III}\) sorbed onto Al-LECAs and Fe-LECAs first intersected at a pH of 5.7 (Fig. 10 C), whereafter sorption onto both oxide-coated LECAs continued to increase. The Al-LECAs retained more As\(^{III}\) than the Fe-LECAs did up to the second intersection point at a pH of 9.7, where an opposite trend was observed (Fig. 10 C). In terms of chemistry, Al\(^{3+}\) (pK\(_{1}\)= 5.0) is a weaker acid than Fe\(^{3+}\) (pK\(_{1}\)= 2.2). Thus, at a pH range of 5.7 – 9.7, Al\(^{3+}\) will have more aqua groups in its coordination sphere than Fe\(^{3+}\), which renders Al-LECAs superior as a sorbent for As\(^{III}\). The PZCs for Al and Fe oxides are usually within the range of 5 – 10 (Parks, 1965; Goldberg et al., 1996; Cornell and Schwertmann, 2003), which means that their surfaces gradually become negatively charged until a pH of 9.7. This is consistent with the finding that the sorption of As\(^{III}\) onto Al oxides diminished after a pH of 9.7, when the surface was highly negatively charged. Consequently, the surface repelled mono- and divalent As\(^{III}\) anions. Although the surfaces of the Fe oxides were also negatively charged, As\(^{III}\) anion sorption continued. This result suggests that the
repelling effect of negatively charged Fe oxides on As$^{\text{III}}$ anions is lower than that of Al oxides. It can be hypothesized that this outcome is attributable to the magnetic properties of Fe-oxide.

Figure 10 – The apparent maximum sorption ($X_m$) of P (A), AsV (B) and (C) onto the Al-LECAs and Fe-LECAs as a function of pH. The error bars stand for SD (full data are presented in Table 6).
6.6 Effect of oxidizing agents on the sorption of arsinite

Because $\text{As}^{\text{III}}$ has a low sorption tendency onto Al and Fe oxide surfaces, its oxidation to $\text{As}^{\text{V}}$ can be taken to improve As removal from water. When $\text{MnO}_2$ was used as an oxidant, the retention of As onto LECA sorbents was significantly enhanced. The $X_m$ of $\text{MnO}_2$ increased four-fold in the LECAs, approximately three-fold in the Al-LECAs and four-fold in the Fe-LECAs. It is noteworthy that the $\text{MnO}_2$ treatment rendered Fe-LECAs a superior As sorbent compared to Al-LECAs (Article II). Moreover, it has been assumed that $\text{MnO}_2$ not only oxidizes $\text{As}^{\text{III}}$ to $\text{As}^{\text{V}}$ but also acts as a sorbent material and prevents the transformation of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$.

The reactions responsible for the oxidation of $\text{As}^{\text{III}}$ to $\text{As}^{\text{V}}$ by $\text{MnO}_2$ involve the reduction of $\text{Mn}^{\text{IV}}$ to $\text{Mn}^{\text{II}}$. This reaction is expected to occur in stages through several mechanisms. The $\text{As}^{\text{III}}$ possibly forms an inner-sphere complex with $\text{MnO}_2$, followed by electron transfer from $\text{As}^{\text{III}}$ to $\text{Mn}^{\text{IV}}$ and the release of $\text{As}^{\text{V}}$ and $\text{Mn}^{\text{II}}$ (Scott and Morgan, 1995; Nesbitt et al., 1998):

\[
2 \text{MnO}_2(s) + H_3\text{AsO}_3 \leftrightarrow 2\text{MnOOH}^+_3 + H_2\text{AsO}_4^- + H^+ \quad (1)
\]

\[
2\text{MnOOH}^+_3 + H_3\text{AsO}_3 + H^+ \leftrightarrow \text{Mn}^{2+} + H_2\text{AsO}_4^- + H_2\text{O} \quad (2)
\]

\[
2\text{MnO}_2(s) + 2H_3\text{AsO}_3 \leftrightarrow \text{Mn}^{2+} + 2H_2\text{AsO}_4^- + H_2\text{O} \quad (3)
\]

It is noteworthy, however, that the chemical reactions (1 – 3) given in the literature do not show any charge or oxygen balance. Therefore, this reaction (reaction 3) is modified to a balanced form given as reaction 4:

\[
\text{MnO}_2(s) + H_3\text{AsO}_3 + H^+ \leftrightarrow \text{Mn}^{2+} + H_2\text{AsO}_4^- + H_2\text{O} \quad (4)
\]

According to Wang et al. (2008), the reaction between $\text{As}^{\text{III}}$ and $\text{MnO}_2$ occurs both in solution and on the surface of the oxidant. Manning et al. (2002) and Lafferty et al. (2011) assumed that $\text{As}^{\text{V}}$ produced in oxidation is sorbed onto $\text{MnO}_2$. However, the sorption tendency of $\text{As}^{\text{V}}$ onto $\text{MnO}_2$ was markedly lower than that of $\text{As}^{\text{III}}$ in our study (Fig. 11). Furthermore, $\text{MnO}_2$ seemed to be decisively more efficient as a sorbent for $\text{As}^{\text{III}}$ than any of the LECA materials (Article II). Actually, this can be attributed to the sorption of produced $\text{As}^{\text{V}}$ onto the surface of $\text{Mn}^{2+}$ minerals (in reaction 4) and the precipitation of some $\text{As}^{\text{V}}$ with $\text{Mn}^{2+}$.

It is possible that some $\text{As}^{\text{V}}$ and $\text{As}^{\text{III}}$ might form As-complexes, e.g., polyarsenates that cannot be reduced to arsine in the analysis method by HG-ICP-OES, during the oxidation.
process. This, in turn, decreases the As concentration measured in the sample. This reaction pattern may partly explain why the sorption of As$^{\text{III}}$ onto MnO$_2$ was much higher than that of As$^{\text{V}}$. A further study should be conducted to assess the possible artifacts involved in sorption studies with MnO$_2$.

![Figure 11](image)

**Figure 11** – Arsenite and arsenate sorption isotherms onto MnO$_2$ at a pH of 6. $Q = \text{As sorbed (µg g}^{-1})$, $E\text{AsC} = \text{Equilibrium Arsenic Concentration (µg L}^{-1})$.

### 6.7 Effect of phosphorus on the sorption of arsenate and arsenite

The results of this study revealed that the presence of phosphate in solution diminished the As$^{\text{V}}$ and As$^{\text{III}}$ sorption in all LECA materials. In the oxide-coated LECAs, the added phosphate lowered the As$^{\text{V}}$ and As$^{\text{III}}$ sorption more than in the LECAs (*Article II and IV*). This could be attributed to the selectivity of Al and Fe oxides in the sorption of these oxyanion species. The competition between As$^{\text{III}}$ (*Article III*) and phosphate for the sorption sites was highly pH dependent and most pronounced in acidic conditions, where As$^{\text{III}}$ is weakly dissociated. At low pH (3 – 5), phosphate concentrations above 20 µg L$^{-1}$ decreased the removal of As$^{\text{III}}$ by Fe-LECAs to a higher degree than that by Al-LECAs and LECAs. When present in concentrations equal to or above 50 µg L$^{-1}$, P inhibited As$^{\text{III}}$ sorption onto oxide-coated LECAs. However, the differences between the coated sorbents became less distinct and even reversed at neutral pH. Elevated pH tended to lessen the impact of phosphate on As$^{\text{III}}$ sorption onto Fe-LECAs more than that onto Al-LECAs and LECAs. This result may be attributable to fact that Al-LECAs retain phosphate to a higher degree than Fe-LECAs at pH $\geq$ 6 (*Article I*). Elevated pH up to 10 will eliminate the effect of phosphate addition on As$^{\text{III}}$ sorption by all LECA materials.

When phosphate was present at a concentration below 20 µg L$^{-1}$, it decreased As$^{\text{V}}$ sorption onto Al-LECAs and Fe-LECAs to the same extent (*Article IV*). However, when the
concentration was equal to or above 20 µg L$^{-1}$, P lowered the As$^V$ removal by Al-LECAs more than that by Fe-LECAs (Article IV). This result agrees with the previous findings of Youngran et al. (2007). In other words, Al oxides will favor phosphate over As$^V$ during sorption. This conclusion agrees with the findings of Hingston et al. (1971), who found the sorption of phosphate to be higher than that of As$^V$ at different pH levels. However, opposite results have been reported, e.g., by Gao and Mucci (2001), who considered the affinity of As$^V$ for oxide surfaces to be higher than that of phosphate. According to Lumsdon et al. (1984), As$^V$ interacts more strongly with solid surfaces than phosphate due to its large size. As for the sorption mechanisms, Tejedor-Tejedor and Anderson (1990) concluded that phosphate forms three inner-sphere surface complexes (monodentate non-protonated, bidentate non-protonated, and bidentate protonated) on Fe oxide surfaces (see Fig. 6), and Waychunas et al. (1993) and Antelo et al. (2005) assumed that As$^V$ mainly forms bidentate complexes with Fe oxides (see Fig. 6). Generally, the competition with phosphate for sorption sites on LECA materials decreases the retention of As$^{III}$ more than that of As$^V$, which has a higher sorption tendency. Moreover, LECAs seemed to be the best option to remove As$^{III}$ from groundwater rich in phosphate (Article III and IV).
7.0 THE APPLICABILITY OF LECA MATERIALS

Because LECAs are produced from natural clay, this material can be taken as an environmentally sound sorbent for use in CWs and groundwater purification. It is light and “harvestable”, which renders it easy to replace when the sorption capacity is used up. Moreover, its efficiency can be improved by coating it with Al or Fe oxides. However, CWs and groundwater are complicated systems; the pH, redox potential, and concentrations of organic matter and competing anions may markedly fluctuate and affect the sorption process. Therefore, further studies in natural conditions are needed to test the applicability of Al- and Fe-oxide-coated LECAs as sorbents in the removal of detrimental elements in CWs and groundwater.

7.1 The applicability of sorption in risk assessment

In terms of the bioavailability and ecotoxicity of sorbate, the maximum sorption capacity of any sorbent material used to remove P and As from water is not a relevant parameter to describe its efficiency. Consideration should be given to the sorbate concentration left in the effluent solutions at given sorption levels. Thus, the actual sorption capacity is that calculated at the reference P or As concentration in equilibrium solution. For example, the sorption efficiency of P could be assessed at a concentration level of 20 µg L\(^{-1}\) (\(X_{20}\)), close to the maximum P concentration in surface water that may cause eutrophication (25 µg L\(^{-1}\)) given by the United State Environmental Protection Agency (US EPA, 1976). The critical sorption capacity of As should be assessed at the maximum standard level of 10 µg L\(^{-1}\) (\(X_{10}\)) given by the WHO (World Health Organization, 2011).

The corresponding critical sorption capacities of LECA materials estimated for P at pH levels of 3 – 8 ranged from 1.4 to 60.8 µg g\(^{-1}\) and from 5.6 to 40.5 µg g\(^{-1}\) for As\(^{V}\) (pH 3 – 8) (Table 6). The critical sorption capacity of As\(^{III}\) (pH range 3 – 10) was much lower and varied from 0.64 to 27.5 µg g\(^{-1}\) (Table 6). All of these values were much lower than the \(X_m\) capacities reported in this study (Article I, III and IV) and previous studies (see Appendix II).

Figures 12, 13 and 14 show the concentrations of P, As\(^{V}\) and As\(^{III}\) in effluent water as a function of their concentration in influent water after reaction with various sorbents at different pH levels. These figures allow one to evaluate the suitability of different sorbents to remove these anions from water to reach the quality standard. For example, at low pH (pH ~3), it is possible to use LECAs to purify wastewater from P at concentrations up to 50 µg L\(^{-1}\). However, at a pH of 5, LECAs are no longer efficient (Fig. 12). However, at pH equal to or
smaller than 5 (pH ≤ 5), oxide-coated LECAs are more efficient sorbents to treat wastewater containing P up to 120 – 150 µg L⁻¹, with Al-LECAs being a slightly better sorbent than Fe-LECAs. On the other hand, the capacity of LECAs under the same conditions is sufficient only for water containing a maximum of 35 – 50 µg P L⁻¹. However, at and above a pH of 6, the oxide-coated LECAs gradually lost their sorption ability. At a pH of 7, the Al-LECAs were still slightly superior to the Fe-LECAs and sufficiently removed the P in the water until its concentration was 65 µg L⁻¹.

Similar to P, the LECAs were a decisively weaker sorbent for As⁵ than oxide-coated LECAs at a pH of 3 – 6 (Fig. 13). In addition, the oxide-coated LECAs showed similar trends as those observed for P, but the Fe-LECAs were more efficient than the Al-LECAs at pH ≥ 4. However, at pH ≥ 7, the difference between the LECAs and oxide-coated LECAs became small, and all of the materials sufficiently purified the wastewater as the As⁵ concentration did not exceed 10 – 15 µg L⁻¹ (Fig. 13). As expected based on the high pKₐ value of H₃AsO₃, all of the LECA materials removed As³⁺ similarly from the water at a pH of 3 – 7 (Fig. 14). Actually, at a pH of 7, all of the LECAs were equal as sorbents. Upon elevating the pH to 9, the Al-LECAs showed to be superior to Fe-LECAs, but Fe-LECAs became more efficient at a pH of 10. It can be concluded that Al-LECAs could be used to treat wastewater containing ~28 µg As³⁺ L⁻¹ at a pH of 9, while Fe-LECAs are suitable only for water containing ~ 15 µg As³⁺ L⁻¹ under the same conditions (Fig. 14).
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

Figure 12 – The relationship between the P concentrations in influent and effluent water when 0.1 g of LECAs, Al-LECAs and Fe-LECAs has reacted at different pH levels with 50 mL of P-containing influent water. The horizontal line $X_{20}$ refers to the maximum allowable P level in water (20 µg L$^{-1}$).
Figure 13 – The relationship between the $\text{As}^{V}$ concentrations in influent and effluent water when 0.1 g of LECAs, Al-LECAs and Fe-LECAs has reacted at different pH levels with 100 mL of $\text{As}^{V}$-containing influent water. The horizontal line $X_{10}$ refers to the maximum allowable As level in water (10 µg L$^{-1}$).
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

Figure 14 – The relationship between the As\textsuperscript{V} concentrations in influent and effluent water when 0.1 g of LECAs, Al-LECAs and Fe-LECAs has reacted at different pH levels with 100 mL of As\textsuperscript{III}-containing influent water. The horizontal line $X_{10}$ refers to the maximum allowable As level in water (10 µg L$^{-1}$).
8.0 CONCLUDING REMARKS

The removal of P from runoff water is of great importance to counteract the eutrophication of surface water. Moreover, the purification of groundwater from As can improve the health of millions of people who live in arseniferous areas and depend on groundwater in their daily life. Well-designed sorption processes could be utilized to enhance P and As removal from contaminated water. Several factors should be taken into account to obtain efficient results. These factors include the type of sorbent, pH, redox potential and presence of other oxyanions. The efficiency of LECAs as a sorbent is improved by coating it with Al or Fe oxides. The highlights of this study are as follows:

1. The sorption of P, As\textsuperscript{V} and As\textsuperscript{III} onto LECA sorbents highly depends on the pH, which affects both the surface charge and anion speciation. For P and As\textsuperscript{V}, the sorption increased with decreasing pH, whereas for As\textsuperscript{III}, the sorption increased with increasing pH.

2. pH has a dual impact on the sorption of P and As species onto oxide-coated LECAs. It affects both the net surface charges of the Al and Fe oxides and the dissociation of corresponding acid. For P and As\textsuperscript{V}, the sorption is mainly controlled by the net surface charge of the Al and Fe oxides. However, the sorption of As\textsuperscript{III} is controlled by the dissociation of its corresponding acid.

3. The oxyanions of P and As are sorbed onto sorption sites along the surface of oxide-coated LECAs via a ligand exchange mechanism by forming inner-sphere complexes and are attached predominantly by monodentate or bidentate binuclear complexes. However, the sorption of the oxyanions of P and As by LECAs forms a mixture of inner- and outer-sphere complexes.

4. The maximum sorption of As\textsuperscript{V} by LECAs, AL-LECAs and Fe-LECAs occurred at pH levels of 2, 4 and 6, respectively, whereas that of As\textsuperscript{III} was not reached until pH levels of 10, 9 and 10, respectively.

5. Fe-LECAs are more efficient than Al-LECAs in the removal of P from solution at pH levels less than 6. However, at pH levels equal to or greater than 6, the reaction pattern is the opposite. However, sorption by Al-LECAs was less reversible than that by Fe-LECAs.
6. Al-LECAs seemed to be the best option among the materials for removing P from constructed wetlands (CWs), where high primary production elevates the pH. Moreover, their bottom deposits are at the risk of oxygen deficiency, leading to the reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$, which results in the desorption of P bound by Fe oxides.

7. The presence of competing phosphate anions significantly interferes with the removal of As species by LECA materials. This interference is higher in oxide-coated LECAs than in uncoated LECAs. The sorption of As species by Al-LECAs is more affected by competitive P than that by Fe-LECAs.

8. LECAs seemed to be the best option among the materials for removing $\text{As}^{\text{III}}$ from groundwater rich in phosphate.

9. $\text{MnO}_2$ in the sorption process enhances the sorption of $\text{As}^{\text{III}}$ onto LECAs by oxidizing it to $\text{As}^{\text{V}}$.

10. Further studies on $\text{MnO}_2$ as a sorbent and oxidizing agent for As species is required, and coating LECAs with $\text{MnO}_2$ should be studied for As removal from groundwater. Further studies are also needed to assess the purification capacity of LECA sorbents in percolation tests, where the solid to solution ratio is different from that in the batch experiments.
9.0 REFERENCES


Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECA) a study of sorption mechanisms and anion competition


Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition


Lindsay, W.L., 1979. Chemical equilibria in soils. John Wiley and Sons Ltd.


Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition


Appendix I – Chemical structures with names, abbreviations for most common As species in nature. Modified from Francesconi and Kuehnelt (2004) with permission of Royal Society of Chemistry.

\[
\begin{align*}
\text{As (V)} & \quad \text{monomethylarsonic acid (MMA)}^V \\
\text{2-Trimethylarsoniumylacetate} & \quad \text{Tetramethylarsonium ion (TMA)}^V \\
\text{arsenic acid} & \quad \text{arsenobetaine (As\textsuperscript{II})} \\
\text{As (III)} & \quad \text{monomethylarsenous acid (MMA)}^III \\
\text{trimethylarsine} & \quad \text{2-Hydroxyethyl(trimethyl)arsanium (As\textsuperscript{III}Chol)} \\
\text{As (-III)} & \quad \text{Dimethylarsine (As\textsuperscript{-III})} \\
\text{5-dimethylarsinoyl-5-deoxyribo-} & \quad \text{5-dimethylarsinoyl-5-deoxyribo-} \\
\text{osylglycerol-3-O-sulfate} & \quad \text{osylglycerol} \\
\text{Arsenoriboside-O\textsubscript{5}SO\textsubscript{3}H (As\textsuperscript{V})} & \quad \text{Trimethylarsenoriboside-OH (As\textsuperscript{V})}
\end{align*}
\]
**APPENDIX II**

**Appendix II – Results of most common sorbent used for removing phosphate, arsenate, and arsenite species from the aqueous phase.** Note that all of the experiments were carried out in batch and that the Langmuir model was used to calculate the sorption capacity.

<table>
<thead>
<tr>
<th>Sorbent Description</th>
<th>Sorbate</th>
<th>Experimental conditions</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Natural sorbents</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Activated alumina (AA)</td>
<td>As\textsuperscript{V} and As\textsuperscript{III}</td>
<td>Sorption capacity and sorption kinetics for As\textsuperscript{V} and As\textsuperscript{III} to AA were determined.</td>
<td>The sorption of As\textsuperscript{III} is much less than that of As\textsuperscript{V} for AA in most pH conditions. The maximum sorption for As\textsuperscript{V} was 15.9 mg g(^{-1}), attained at pH 5.2, and that for As\textsuperscript{III} was 3.48 mg g(^{-1}), attained at pH 6.9.</td>
<td>(Lin and Wu, 2001)</td>
</tr>
<tr>
<td>Aluminum hydroxide (prepared from aluminum sulfate)</td>
<td>P</td>
<td>Three types of phosphate were used: orthophosphate, condensed phosphate, and organic phosphate. Phosphate conc.: 2 – 15 mg L(^{-1}), sorbent conc.: 1:20 (sorbent: P solution), contact time: 60 min.</td>
<td>It was found that aluminum hydroxide has a significant removal capacity for all the phosphates. At a molar dose of 8 mol Al mol(^{-1}) P, the P removals were greater than 95% for orthophosphate and condensed phosphate, and 40% removal was achieved for the organic phosphate solution.</td>
<td>(Galarneau and Gehr, 1997)</td>
</tr>
<tr>
<td>Aluminum hydroxide</td>
<td>P</td>
<td>The effect of pH was studied at different pH from 2.9. The initial concentration of phosphate was 1.0 mM. The rate of phosphate sorption onto Al oxides was determined and the selectivity of phosphate sorption onto Al oxides was estimated in an anion complex solution at a pH of 6.9.</td>
<td>The amount of P sorbed onto Al oxides increased with increasing equilibrium concentration and sorption time. The kinetic constant was 1.26 h(^{-1}). The amount of P sorbed at pH 4 was the greatest and then decreased with increasing pH. The results indicate that Al oxides could selectively sorb P ions and were suitable for the removal of P in rivers, lakes, and the sea.</td>
<td>(Tanada et al., 2003)</td>
</tr>
<tr>
<td>Amorphous Al and Fe oxides, kaolinite, montmorillonite, and illite</td>
<td>As\textsuperscript{V} and As\textsuperscript{III}</td>
<td>0.5 g L(^{-1}) Fe oxides, 1.0 g L(^{-1}) Al oxides, and 40 g L(^{-1}) clay minerals were added to 20 µM As\textsuperscript{V} or As\textsuperscript{III} solution</td>
<td>As\textsuperscript{V} sorption onto oxides and clays decreased with increasing pH above pH 9 for Al oxides, pH 7 for Fe oxides and pH 5 for clays. The As\textsuperscript{III} sorption maximum was at approximately pH 8.5 for all materials. Amorphous Fe oxides had a greater affinity for the sorption of As\textsuperscript{III} than amorphous Al oxides.</td>
<td>(Goldberg, 2002)</td>
</tr>
<tr>
<td>Apatite (different types) and limestone</td>
<td>P</td>
<td>35 g of sorbent placed in 700 mL of solution (5–150 mg P L(^{-1})).</td>
<td>Phosphate retention in g kg(^{-1}): Limestone (sedimentary rock): 1.09 Apatite (igneous rock): 0.41</td>
<td>(Bellier et al., 2006)</td>
</tr>
</tbody>
</table>
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Initial Conc.</th>
<th>Contact Time</th>
<th>pH</th>
<th>Maximum Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotite (untreated) P</td>
<td>0-4 mg L(^{-1})</td>
<td>7 days, pH: 9.6</td>
<td>8</td>
<td>4.5 mg kg(^{-1}) (particle size &gt; 0.2 mm)</td>
</tr>
<tr>
<td>Biotite (partly neutralized) P</td>
<td>0-600 mg L(^{-1})</td>
<td>7 days, pH: 4.6</td>
<td>8</td>
<td>15400 mg kg(^{-1}) (particle size &gt; 0.2 mm)</td>
</tr>
<tr>
<td>Biotite (acid-treated) P</td>
<td>0-500 mg L(^{-1})</td>
<td>7 days, pH: 3.2</td>
<td>8</td>
<td>10900 mg kg(^{-1}) (particle size &gt; 0.2 mm)</td>
</tr>
</tbody>
</table>

Sorption isotherm for ferrihydrite, boehmite, and mixed ferrihydrite-boehmite (1:1 mass ratio) suspensions were conducted at pH 6.0 for 16 h. Freundlich isotherm models were used to determine P sorption. The maximum sorption levels observed were approximately 1860, 1420, and 850 mmol kg\(^{-1}\) for ferrihydrite, the mixed mineral, and boehmite. (Khare et al., 2004)

Friedel’s salt (prepared from CaCl\(_2\) and NaAlO\(_2\)) As\(^{V}\) Initial As\(^{V}\) concentration: 0.4-4.1 mg L\(^{-1}\), sorbent conc.: 0.2 g L\(^{-1}\), pH: 4 and 7, contact time: 48 h. Equilibrium was achieved within 48 h; the sorption capacities at a pH of 4 and 7 were 11.85 and 7.80 mg g\(^{-1}\), respectively. (Zhang et al., 2011)

Ferrihydrite (prepared from Fe(NO\(_3\))\(_3\)·9H\(_2\)O) As\(^{III}\) and As\(^{V}\) The sorption kinetics, sorption isotherms, and influence of pH on the sorption of As\(^{V}\) and As\(^{III}\) were studied by ferrihydrite. At low As concentrations and low pH, As\(^{V}\) reacted faster than As\(^{III}\) with ferrihydrite, but As\(^{III}\) sorption was faster at high As conc. Sorption maxima of 0.60 (0.58) and 0.25 (0.16) mol\(_{As}\) mol\(_{Fe}\)^{-1} were achieved for As\(^{III}\) and As\(^{V}\), respectively, at pH 4.6 (pH 9.2 in parentheses). The sorbed As\(^{V}\) was relatively greater than sorbed As\(^{III}\) at lower pH values, whereas sorbed As\(^{III}\) was greater at higher pH. (Raven et al., 1998)

Ferric hydroxide and aluminum oxide. P Different quantities of sorbent (10–1000 mg) added to P solution at an initial conc. of 4 mg L\(^{-1}\), pH 5.5 and 8.2, and contact time of 96 h at 20 °C. GFH performed approximately 1.4 times better than AA in terms of the maximum loading at a pH of 8.2 and 1.7 times better at pH 5.5. A decrease in pH led to higher loadings for both sorbents. The pH dependence was stronger for GFH than for AA. The achieved loadings for 0.1 and 0.3 mg L\(^{-1}\) P at pH 8.2 were 7.9 and 12.3 mg g\(^{-1}\) for GFH and 4.6 and 7.9 mg g\(^{-1}\) for AA. (Genz et al., 2004)

Goethite (prepared from P Sorption isotherms of P and P-enriched The sorption of P decreased with increasing pH. At pH > 3, the sorption (Chitrakar et al., 2006)
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECAs): a study of sorption mechanisms and anion competition

| Iron sulfate, akaganeite (prepared from iron chloride) | seawater on goethite: sorbent dose of 0.04-0.30 g and P conc. of 2 mg L\(^{-1}\); for akaganeite: dose of 0.02-0.20 g and P conc. of 0.33 mg L\(^{-1}\); contact time: 1 day. of P onto goethite was larger than that onto akaganeite. The max P sorption at pH 2 was 28 and 24 mg g\(^{-1}\) for akaganeite and goethite, respectively. In seawater, the uptake of phosphate increased with increasing pH up to approximately 7. |
| Sorption isotherms: initial As\(^{V}\) and As\(^{III}\) conc. of 10\(^{-6}\) - 10\(^{-3}\) mol dm\(^{-3}\) and sorbent dose of 0.1 g. The effect of pH was studied at an As conc. of 2 × 10\(^{-5}\) mol dm\(^{-3}\) and pH 3-12. The sorption kinetics were studied at an As conc. of 2 × 10\(^{-5}\) mol dm\(^{-3}\) with varying times. | Equilibrium for the three iron oxides was reached in less than 2 days, and the kinetics of the sorption seemed to be faster for goethite and magnetite than for hematite. Both As\(^{V}\) and As\(^{III}\) were more efficiently sorbed onto hematite than goethite or magnetite. The main trend observed in the variation in the arsenic sorbed with pH is a decrease in the sorption onto the three sorbents at alkaline pH values. |
| HFO, goethite, and magnetite prepared from Fe(NO\(_3\))\(_3\)·9H\(_2\)O | As\(^{V}\) and As\(^{III}\) sorption onto HFO, goethite, and magnetite at various solution compositions were studied. | The sorption of As\(^{V}\) onto HFO and goethite was more favorable than that of As\(^{III}\) below pH 5–6; above pH 7–8, As\(^{III}\) has a higher affinity for solids. The presence of P decreased the sorption of both As species onto the three oxides. The reduction of As\(^{V}\) in the presence of HFO or goethite would only slightly effect or even decrease its mobility in the environment at near-neutral pH conditions. |
| Iron oxide-coated sand | As\(^{V}\) conc.: 0.5–3.5 mg L\(^{-1}\); pH: 4-10, temp.: 27 °C, contact time: 8 h, sorbent conc.: 20 g L\(^{-1}\) | Maximum sorption capacity for As\(^{V}\): 0.128 g kg\(^{-1}\) at pH 4 0.12 g kg\(^{-1}\) at pH 7 0.08 g kg\(^{-1}\) at pH 10 (Vaishya and Gupta, 2005) |
| Muscovite and biotite | Arsenite and arsenate sorption was studied as a function of pH; the pH range was 3–8 for muscovite and 3–11 for biotite; the initial As concentration was 13 μM. | Max As retention for muscovite: 3.13 mol As\(^{V}\) g\(^{-1}\) and 3.08 mol As\(^{III}\) g\(^{-1}\) at pH 4.2–5.5. Max As retention for biotite: 3.22 mol As\(^{V}\) g\(^{-1}\) at pH 4.6–5.6 and 2.86 mol As\(^{III}\) g\(^{-1}\) at pH 4.1–6.2. (Chakraborty et al., 2007) |
| Pine wood char | As\(^{III}\) conc.: 10–100 μg L\(^{-1}\); pH: 3-4, temp.: 25 °C, contact time: 24 h, sorbent conc.: 10 g L\(^{-1}\) | Maximum sorption capacity: Pine wood char: 1.2 g kg\(^{-1}\) (Mohan et al., 2007) |
| Pine bark char | As\(^{III}\) conc.: 50-2500 | As\(^{III}\) removal capacity: 128.1 g kg\(^{-1}\) (Kamala et al., 2007) |
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**II. Man-made products**

<table>
<thead>
<tr>
<th>Iron oxide-coated LECAs</th>
<th>As(^v) conc.: 0.1–100 mg L(^{-1}), pH: 6, temp.: 25 °C, contact time: 5 h, sorbent conc.: 10 g L(^{-1})</th>
<th>The maximum sorption capacity for As(^v) was 3.12 g kg(^{-1}). (Haque et al., 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LECAs</td>
<td>P Sorption was carried out with artificial P solution; 2.5 – 40 mg L(^{-1}) was equilibrated with 20 g of substrate for 24 h. The sorption capacity was determined according to the Langmuir Equation.</td>
<td>The maximum sorption was 0.42 g kg(^{-1}). (Drizo et al., 1999)</td>
</tr>
<tr>
<td>LWAs, USA</td>
<td>P Sorption isotherms were used to study the sorption capacity. The P concentration was 0 - 320 mg L(^{-1}), with 8 g of material in 200 mL of P solution.</td>
<td>P sorption: 3465 mg kg(^{-1}) (LWAs) P sorption: 46 – 565 mg kg(^{-1}) (LECAs) (Zhu et al., 1997)</td>
</tr>
<tr>
<td>LECAs, Sweden</td>
<td>The P concentration of P was 0 - 320 mg L(^{-1}).</td>
<td>The P removed by LECAs was very low. (Brix et al., 2001)</td>
</tr>
<tr>
<td>LECAs, Denmark</td>
<td>The P conc. was 5-1000 mg L(^{-1}), with 3 g of LECAs in 75 mL of P solution.</td>
<td>The P sorption was 7.98 g kg(^{-1}). (Vohla et al., 2005)</td>
</tr>
<tr>
<td>LECAs, Estonia</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**III. Industrial by-products**

<table>
<thead>
<tr>
<th>Blast furnace slag</th>
<th>P Eight grams of sorbent was placed in 250 mL of P solution with different P concentrations (0 - 320 mg L(^{-1})).</th>
<th>The P sorption capacity ranged from 0 to 9150 mg kg(^{-1}). (Asuman Korkusuz et al., 2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash and precipitator fly ash</td>
<td>P Five grams of sorbent was placed in 25 mL of solution with different P concentrations and shaken for 24 h.</td>
<td>The P sorption to fly ash and precipitator fly ash was 3.08 and 13.77 g kg(^{-1}), respectively. (Cheung and Venkitachalam, 2000)</td>
</tr>
<tr>
<td>Fly ash, blast furnace slag and Portland cement</td>
<td>P Various masses of sorbent were shaken continuously with 200 mL of a solution of 100 mg P L(^{-1}) at pH 9.0 for 16 h.</td>
<td>The P sorption capacity of fly ash, blast furnace slag and Portland cement was 32, 60 and 83 g kg(^{-1}), respectively. (Agyei et al., 2002)</td>
</tr>
</tbody>
</table>

mg L\(^{-1}\), pH: 6, contact time: 8 h for As\(^{III}\) and 15 h for As\(^{V}\).
<table>
<thead>
<tr>
<th>Material Type</th>
<th>sorption conditions</th>
<th>sorption capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burnt oil shale</td>
<td>out with artificial P solution; 2.5 – 40 mg L(^{-1}) were equilibrated with 20 g of substrate for 24 h. The sorption capacity was determined according to the Langmuir Equation. and burnt oil shale was 0.86 and 0.58 g Kg(^{-1}), respectively.</td>
<td>1999)</td>
</tr>
<tr>
<td>Fly ash, bauxite mining residual and flue gas desulfurization</td>
<td>Two grams of each material was reacted with 30 mL of P solution with different P conc. (0 – 103.23 mM L(^{-1})) and shaken for 16 h. The maximum sorption onto fly ash, bauxite mining residual, and flue gas desulfurization was 29, 25, and 14 g Kg(^{-1}), respectively.</td>
<td>(Penn et al., 2011)</td>
</tr>
<tr>
<td>Iron oxide tailings</td>
<td>Sorption isotherm: initial P conc.: 5 – 150 mg L(^{-1}), sorbent: 20 mg L(^{-1}), pH: 6.6 - 6.8 and contact time: 24 h. The effect of pH was carried out at a P conc. of 20 mg L(^{-1}), pH of 3-10, sorbent conc. of 20 mg L(^{-1}) and contact time of 24 h.</td>
<td>The P sorption capacity considerably increased with increasing P equilibrium concentration. This capacity was approximately 7 mg P g(^{-1}) tailings at a P equilibrium concentration of 20 mg P L(^{-1}) and pH of 6.7. The maximum P sorption was 8.21 and 12.65 mg P g(^{-1}) from the Langmuir and Langmuir–Freundlich Equations, respectively. The sorption of P tends to decrease with increasing pH, from 8.6 mg P g(^{-1}) at a pH of 3.2 to 4.6 mg P g(^{-1}) at a pH of 9.5.</td>
</tr>
<tr>
<td>Iron oxide-coated cement</td>
<td>The sorption isotherms were studied by varying the initial concentrations of As(^{\text{III}}) (0.7-13.5 mg L(^{-1})) or As(^{\text{V}}) (0.5-10); the sorbent dose was 1.5 g for As(^{\text{III}}) and 0.15 g for As(^{\text{V}}) and was shaken for 2 h.</td>
<td>The maximum sorption capacity for As(^{\text{V}}) and As(^{\text{III}}) was 6.43 and 0.67 g Kg(^{-1}), respectively.</td>
</tr>
<tr>
<td>Melted slag loaded with Fe oxide</td>
<td>The arsenic conc. ranged from 20 to 300 mg L(^{-1}); the contact time was 8 h for As(^{\text{III}}) and 15 h for As(^{\text{V}}).</td>
<td>The As(^{\text{III}}) and As(^{\text{III}}) removal capacities were 2.9–30.1 g kg(^{-1}) and 18.8–78.5 g kg(^{-1}), respectively.</td>
</tr>
<tr>
<td>Portland cement</td>
<td>Different amounts of sorbent (2-25 mg L(^{-1})) were placed into 100 mL of solution containing 0.2 PPM As(^{\text{V}}) shaken for 8 h.</td>
<td>The optimal conditions included a sorbent dose of 15 g L(^{-1}) and pH 4.5. Maximum sorption capacity: 3.98 g Kg(^{-1})</td>
</tr>
</tbody>
</table>
Retention of orthophosphate, arsenate and arsenite onto the surface of aluminum or iron oxide-coated light expanded clay aggregates (LECA): a study of sorption mechanisms and anion competition

Approximately 0.1 g of sorbent was placed into 20 mL solutions with different P conc. (0.31-3100 mg L⁻¹) and shaken for 4 h at different temperatures. The effect of pH was studied at an initial P conc. of 155 mg L⁻¹.

The P sorption to red mud was 113.9 g kg⁻¹. The P sorption to red mud at 700 ºC for 2 h was 345.5 g kg⁻¹. The P sorption to treated red mud with 0.25 M HCl for 2 h was 161.6 g kg⁻¹. Phosphate removal from the samples reached a maximum at a pH of 7; afterwards, the removal of phosphate decreased with increasing pH. (Li et al., 2006)
Appendix III - The five types of sorption isotherms (reprint from Brunauer, et al. (1940) with permission from American chemical society, ACS publication).
**Appendix IV**

*Appendix IV – List of chemicals used in the present study*

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Supplier</th>
<th>Assay</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (III) nitrate nonahydrate</td>
<td>Al(NO$_3$)$_3$·9H$_2$O</td>
<td>Fluka®</td>
<td>98%</td>
<td>Source of Al oxide in Al-LECA</td>
</tr>
<tr>
<td>Ammonium molydate tetrahydrate</td>
<td>(NH$_4$)$_6$Mo$<em>7$O$</em>{24}$</td>
<td>Riedel-de Haën®</td>
<td>99%</td>
<td>P analysis</td>
</tr>
<tr>
<td>Ammonium oxalate</td>
<td>C$_2$H$_8$N$_2$O$_4$</td>
<td>Sigma-Aldrich®</td>
<td>99%</td>
<td>Determined of Al and Fe poorly crystalline oxide</td>
</tr>
<tr>
<td>Arsenate dibasic heptahydrate</td>
<td>Na$_2$HAsO$_4$·7H$_2$O</td>
<td>Sigma-Aldrich®</td>
<td>99%</td>
<td>Source of As$^V$ in article II and III</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>C$_6$H$_8$O$_6$</td>
<td>Fluka®</td>
<td>99.5%</td>
<td>P analysis, As analysis by HG-ICP-OES</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid</td>
<td>C$<em>{10}$H$</em>{16}$N$_2$O$_8$</td>
<td>Fluka®</td>
<td>98%</td>
<td>P analysis</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl super purity</td>
<td>Romil LTD</td>
<td>37%</td>
<td>As analysis by HG-ICP-OES,</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>ProLabo®</td>
<td>40%</td>
<td>Digested LECA materials, adjusted pH, As analysis by HG-ICP-OES, wash of lab equipment</td>
</tr>
<tr>
<td>Iron(III) nitrate nonahydrate</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>Fluka®</td>
<td>&gt; 99%</td>
<td>Source of Fe oxide in Fe-LECA</td>
</tr>
<tr>
<td>Manganese dioxide</td>
<td>MnO$_2$</td>
<td>Sigma-Aldrich®</td>
<td>&gt; 99%</td>
<td>Oxidizing agent</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>HNO$_3$ (super purity)</td>
<td>Romil LTD</td>
<td>67-69%</td>
<td>Digested LECA materials, adjusted pH, oxide coated LECA preparation, wash of lab equipment</td>
</tr>
</tbody>
</table>
### Retention of Orthophosphate, Arsenate and Arsenite onto the Surface of Aluminum or Iron Oxide-Coated Light Expanded Clay Aggregates (LECA’s): A Study of Sorption Mechanisms and Anion Competition

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Supplier</th>
<th>Purity</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium antimony tartrate</td>
<td>K$_2$Sb$_2$(C$_4$H$_6$O$_6$)$_2$</td>
<td>Sigma-Aldrich®</td>
<td>99%</td>
<td>P analysis</td>
</tr>
<tr>
<td>Potassium iodide</td>
<td>KI</td>
<td>Sigma-Aldrich®</td>
<td>99 %</td>
<td>As analysis by HG-ICP-OES</td>
</tr>
<tr>
<td>Potassium phosphate monobasic</td>
<td>KH$_2$PO$_4$</td>
<td>Merck®</td>
<td>99.5%</td>
<td>Source of P in article I, II and III</td>
</tr>
<tr>
<td>Sodium borohydride</td>
<td>NaBH$_4$</td>
<td>Merck®</td>
<td>98%</td>
<td>As analysis by HG-ICP-OES</td>
</tr>
<tr>
<td>Sodium dodecyl sulphate</td>
<td>NaC$<em>{12}$H$</em>{25}$SO$_4$</td>
<td>Fluka®</td>
<td>98%</td>
<td>P analysis</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>ProLabo®</td>
<td>99%</td>
<td>Adjusted pH, P analysis, As analysis by HG-ICP-OES</td>
</tr>
<tr>
<td>Sodium (meta) arsenite</td>
<td>NaAsO$_2$</td>
<td>Fluka®</td>
<td>98%</td>
<td>Source of As$^{III}$ in article II and III</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H$_2$SO$_4$</td>
<td>J.T.Baker®</td>
<td>95-97%</td>
<td>Digested LECA materials</td>
</tr>
</tbody>
</table>