

Masters Degree in Chemical Engineering

The effect of Phosphates and Silicates on Selective Sorption of Arsenic from Acid Mine Drainage and Waste Waters

Master Thesis

Foreign Institution Development Project

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Abstract

The aim of this project was to evaluate an iron oxide sorbent, the *Lewatit* FO 36, on the sorption process of arsenic in the As(V) form, on the acid mine drainage and in waste waters.

This work includes small scale column experiments at pH 5, in order to achieve the breakthrough concentrations of arsenic in presence or in absence of competing ions such as silicates and phosphates which influence the arsenic removal. The regeneration and re-use of *Lewatit* FO 36 sorbent was evaluated both in the presence and absence of phosphates.

Another iron oxide sorbent, the GEH[®], and an ion exchanger, the *Lewatit* MP 500, were studied as well. Column experiments were conducted to evaluate the phosphates influence on arsenic removal.

Preliminary tests of Langmuir were conducted to evaluate the total sorption capacity of the arsenic, both for the sorbents GEH[®] and *Lewatit* FO 36.

Different analytical techniques were used during this project: The analyses of phosphates and silicates were performed through spectrometry, the detection of arsenic by means of ICP and the determination of samples content Fe by AAS.

Finally, several conclusions were obtained: the *Lewatit* FO 36 was selective towards arsenic in the As(V) form, even though the presence of silicates and phosphates influenced the arsenic sorption capacity. The GEH[®] sorbent and the ion exchanger, demonstrated to be effective on arsenic removal in presence of phosphates. Regarding the silicates and phosphates analysis method it was not successful on its determination.

Keywords: Arsenic, Phosphates, Silicates, Selective Sorption, Breakthrough Capacity, Langmuir Isotherms.

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Notation and Glossary

C_0 – Initial concentration	g/L
C_e – Equilibrium concentration	mol/L
M – Molecular weight	g/mol
q - Concentration of As(V) sorbed by the sorbents	mol/L
q_{\max} – Maximum sorption capacity	mol/L

List of Abbreviations

AAS – Atomic Absorption Spectrometer

AMD – Acid Mine Drainage

BC – Breakthrough Capacity

BV – Bed Volumes

ICP – Inductively Coupled Plasma

MCL – Maximum Drinking Level

VR – Volumes of Resins

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1 Introduction

Arsenic has become a major concern all over the world it is a metalloid that naturally occurs in the surface and ground water and can be found in the soil and water in a variety of concentration ranges.

Humans are widely exposed to these sources of contamination, long term exposure to even low concentrations of arsenic can cause acute poisoning and can also cause skin, lungs, blood and kidney diseases such as hyperkeratosis and hyper pigmentation of skin.^[1]

The United States Environment Protection Agency (EPA) has set the arsenic standard for drinking water at 0.010 parts per million (10 parts per billion) to protect consumers served by public water systems from the effects of long-term and chronic exposure to arsenic. ^[2]

Arsenic contamination is a result of its mobilization under natural conditions as well as anthropogenic activities such as fossil combustion, mining, land filling and other industrial activities that release arsenic into the waters. Agricultural applications of pesticides and herbicides contribute to arsenic contamination as well.

Geological processes such as oxidation of arsenic-bearing sulfides, reductive dissolution of arsenic-bearing iron (hydro) oxides are also factors that contribute to release arsenic into the waters.^[3] The **Figure 1** shows the different concentrations of arsenic found in the environment.

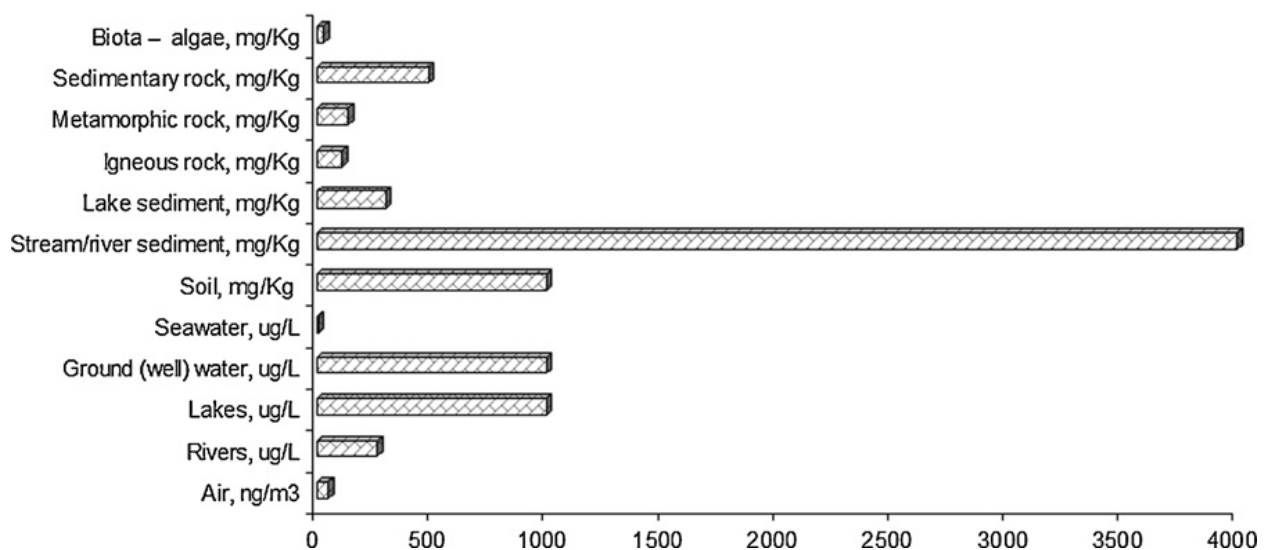
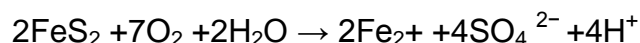


Figure 1: Concentration range of arsenic in environment. ^[4]

Beyond the above-mentioned human activities and natural processes, mining is also greatly responsible for arsenic contamination by means of waste water drainage. All over the world acidic waters from abandoned mines are discharged from drainage tunnels and tailing piles which causes a threat to aquatic life as well as contaminating ground waters; those waters resulting from mine drainage are characterized by elevated concentrations of iron, aluminum and sulfuric acid.

The principal cause of acid mine drainage is the physical and chemical weathering of a mineral called pyrite (FeS_2), which can be accelerated by mining activities. The geochemical process responsible for the formation in mine drainages can be at times initiated by the biological oxidation of pyrite which can be described by the following equation:



As a result the amount of Pyrite in waste waters from mines such as gold mines undergoing weathering is directly related to the concentration of Arsenic, one of the most toxic of heavy metals found in acid mines drainage.

Arsenic has a high affinity to sulfide mineral ores, especially pyrite, and can exist in sulfide minerals either as an important mineral-forming element or as an impurity. Although the release of Arsenic can occur due natural changes in physical/chemical conditions it is greatly increased by grinding, crushing and pulverizing operations associated with mining activities that go beyond just the exposure of large quantities of Arsenic-bearing minerals to weathering. [4]

Arsenic can be found in inorganic and organic form. The organic forms in water are methyl and dimethylarsenic under favorable conditions through biomethylation by microorganism, methylated arsenic species such as monomethylarsonous acid (MMA(III)), monomethylarsonic acid (MMA(V)), methylarsonous acid (DMA(III)), dimethylarsonic acid (DMA(V)) can be formed. Organic arsenic compounds are generally less toxic than inorganic ones. Inorganic compounds of arsenic consist of hydrides (e.g., arsine), halides, oxides, acids such as the arsenous acids (H_3AsO_3) and the arsenic acids (H_3AsO_4), and sulphides. [5, 6]

Arsenic can occur in natural waters with different valence states such as -III, 0, +III and +V. Valences -III and 0 are very rare but valences +III and +V are more common which correspond to arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) respectively. Arsenic in trivalent state is described as $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}_2^-$ and AsO_3^{3-} while that in the pentavalent state is described as AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- . Arsenic

(III) compounds are more toxic than arsenic (V) and tends to occur more in anaerobic ground waters, while Arsenic(V) is more common in surface waters.^[6]

There are two factors which controls the arsenic speciation, they are redox potential (Eh) and pH. In an oxidizing environment with pH lower than 6.9 the most dominant species is H_2AsO_4^- while at a pH higher than 6.9 the prevailing form is HAsO_4^{2-} . In strong acid or base conditions the H_3AsO_4 and AsO_4^{3-} are the dominant species. **Figure 2** shows the different species of arsenious and arsenic acids under different conditions.^[5]

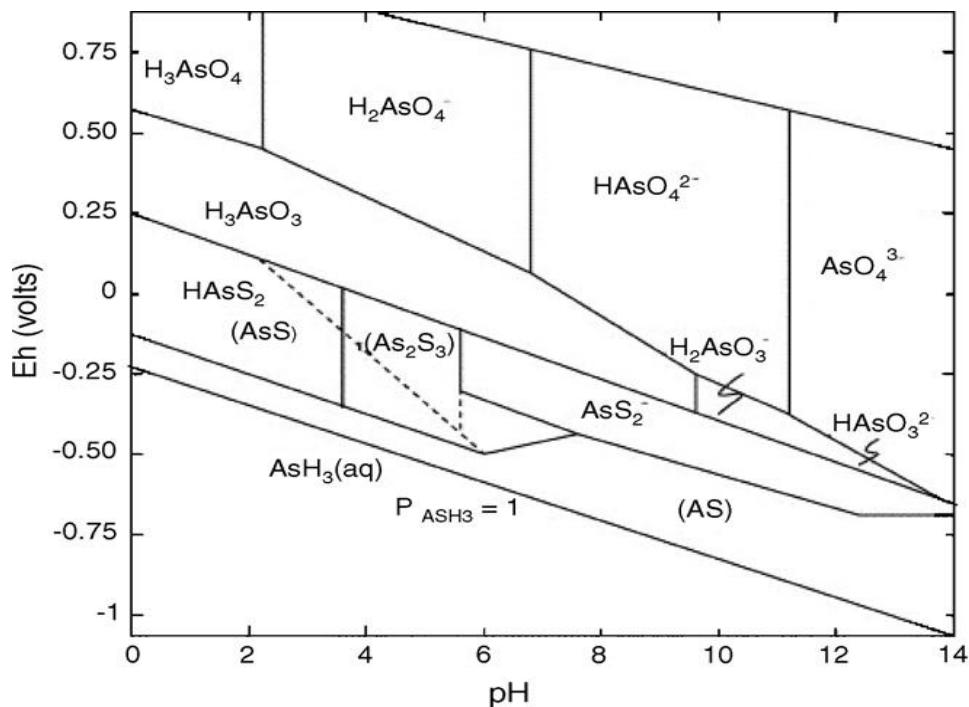


Figure 2: Eh-pH diagram for arsenic species.^[5]

Besides arsenic there are other compounds such as phosphate and silica which are present in waters in high concentrations.

Silica is usually present in groundwater at a concentration range of 5-50mg/l in the form of SiO_2 .^[7] Research proved that in a pH range of natural water silica can be found as polymeric species such as dimers, trimers, tetramers, hexamers, octamers and oligomer containing 32 atoms of silica, the most common polymer present in water is the dimeric anion $(\text{OH}_3)\text{-Si-O-SiO}(\text{OH})_2^-$.^[8] Concentration of silica in water directly depend on its pH, for instance if the pH increases, the amount of polymeric silica increases as well.^[7]

One major source of phosphates in water is due to increased use of fertilizers containing solid phosphate; concentrations in ground waters can exceed those of arsenic. Both phosphate and silica exercise a negative impact on arsenic removal.

A large number of arsenic removal technologies include several processes such as precipitation/coagulation, membrane separation, ion exchange and sorption all will be briefly described in the next chapter.

The aim of this project was studying the influence of competitive ions such as phosphates and silicates on selective sorption of arsenic into two selective sorbents based on hydrated iron oxide, from model solutions. Sorption performance will be evaluated based on the comparison of breakthrough capacities. The total sorption capacity of arsenic will be measured by Langmuir isotherms.

2 State of Art

The severe contamination of ground and drinking waters has prompted the need to develop simple, rapid and low-cost techniques for lowering arsenic concentrations.

There are several techniques for arsenic removal which are directly related arsenic valence and are most effective when the arsenic is present in the pentavalent form. [1] A large number of the removal technologies have the added benefit of removing along with arsenic other undesirable compounds.

All technologies for arsenic removal rely on a few basic chemical processes, which are summarized below.

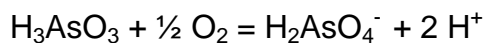
2.1 Technologies for arsenic removal

2.1.1 Major oxidation/precipitation technologies

A large number of treatment processes has an oxidation step to convert arsenic (III) to arsenic (V), this process does not remove arsenic from solutions and must be followed by another removal process such as coagulation, adsorption or ion exchange. The two principal oxidation processes are:

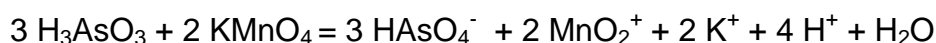
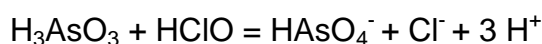
- **Air oxidation**

Atmospheric oxygen is the oxidizing agent used in air oxidation, which can be described by the following equation^[9]:



- **Chemical oxidation**

Many chemicals such as gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) can be used as oxidizing agents, but the oxidizing agent commonly used to convert arsenic(III) to arsenic(V) are hypochlorite and permanganate^[5, 9, 10]:



The principal advantages and disadvantages of using air or chemical process in the arsenic removal are the following:

Air oxidation is a slow but it is a low-cost and simple process. The chemical oxidation is a comom and simple process which besides oxidizing arsenic(III) destroys other impurities and microbes.^[5]

2.1.2 Major coagulation-flocculation/coprecipitation technologies

Coagulation-flocculation is an effective process for removal As(V), it is a kind of precipitation process which can be applied to waters in order to aid the removal of dissolved inorganic As(V). Arsenic removed from water comes out in a sludge produced by this process. Its effectiveness is affected by the dosage used and the type of coagulants which are described below:

- **Alum and iron coagulation**

The most used salts are alum and ferric salts such as ferric chloride or ferric sulfate. Both salts give an excellent arsenic removal, with laboratory studies reporting over 99% removal under optimal conditions, thus leaving residual arsenic concentrations of less than 1 µg/L, however alum performance is slightly lower than ferric sulfate.^[11]

In the coagulation process arsenic is removed by three main mechanisms^[10]:

- Precipitation: occur the formation of insoluble compounds as $Al(AsO_4)$ or $Fe(AsO_4)$, depending on used coagulant;
- Coprecipitation: soluble arsenic species are incorporated into a metal hydroxide phase;
- Adsorption: the soluble arsenic is attracted to the external surface of the insoluble metal hydroxide.

After coagulation process by these two salts some suspended particles in colloidal form can remain so it is necessary an additional filtration process to ensure an efficient arsenic removal.

An advantage of using alum and iron coagulation process the fact of it being of low capital investment and simple to operate, it is also effective in wider range of pH levels. However, it is a slow arsenic removal process and produces toxic sludge, a pre-oxidation process is required for the iron to coagulate.^[5]

- **Lime softening**

This coagulation process using lime softening it is slightly affected by the pH and therefore arsenic removal by lime softening is pH dependent. In order to achieve an effective arsenic extraction rate a large dosage of chemicals is necessary along with the readjustment of the pH in the solution. Removed arsenic comes out in the sludge produced by this process. [12]

2.1.3 Major Adsorption and ion-exchange technologies

The adsorption and ion-exchange technologies represent attractive and economic advance to arsenic removal. They use natural and synthetic exchangers whose polymeric structures are saturated by various adsorbents in order to increase their efficiency and are more effective treatment methods adopted by many researchers. A good adsorbent should have a high surface area, fast adsorption kinetics, a good physical and/or chemical stability as well as uniformly accessible pores.

- **Synthetic activated carbons**

The production of synthetically activated carbons consists of the carbonization process, a chemical or physical activation and is completed with a treatment using oxidizing agents or chemical activators. A large number of activated carbons are used in the arsenic removal from water and wastewater.

Iron containing granular activated carbon was one of the activated carbon based adsorbents synthesized for arsenic removal from drinking water; the ferric ions were impregnated into a granular activated carbon using ferrous chloride followed by a chemical oxidation with NaClO. Several experiments were conducted with different iron contents however the iron content most efficient for arsenic removal was round 6% level. The adsorption capacity obtained for arsenic with iron-containing granular activated carbon was 2.96×10^3 g As/g and the removal of arsenate occurred in a pH range between 4.4-11 while a pH above 9 the adsorption of arsenate decrease.

Another iron-containing mesoporous carbon is also used on arsenic removal. The mesoporous carbon is prepared from silica followed by a carbonization in an inert atmosphere. The maximum adsorption capacities for As(V) was 5.15 mgAs/g. [5]

- **Red Mud**

Red mud has been studied as an alternative arsenic adsorbent and it is formed during the production of alumina when bauxite ore is leaching with caustic. The As(V) removal is more favorable in acidic medium in a pH range between 1.1-3.2. The maximum adsorption capacity for As(V) is 5.07 mol/g at pH 3.2. Arsenic removal with red mud is also pH dependent with an optimum pH range of 1.3-3.5 for As(V).^[5]

- **Fly ash**

Fly ash is produced by the coal combustion as a by-product and can be applied in As(V) removal as well to restrict the As(V) migration. Several experiments of As(V) removal in dynamic columns have been conducted and it was concluded that more than 80% of arsenic was removed its concentration was reduced from 500 to 5ppm or even less. A pH of 4 was the most effective in arsenic removal.^[5]

- **Clay minerals**

Clay minerals can be found in aquatic and terrestrial environments; they have a large surface area and can adsorb cationic, anionic and neutral species of arsenic. Many studies of arsenic removal using clay minerals and oxides have been done. The typical clay minerals are kaolinite, montmorillonite and illite and it has been found that the adsorption capacity for those three clay minerals are in the range between 0.15-0.22 mmol As(V)/kg at the pH 5, 6 and 6,5 respectively.^[5]

- **Activated alumina**

Activated alumina was considered the best available technology for As(V) removal, it can be obtained by thermal dehydration of aluminum hydroxide. Activated alumina has a high surface area and a great distribution of macro and micropores, the pH range of As(V) occurs is between 6 and 8 where the activated alumina is positively charged.^[5]

The impregnation of manganese on activated alumina was found to be more effective on arsenic removal than with activated alumina alone. Fixed-bed testes where the down flow contact time was 20 minutes and the As(V) concentration studied was 0.4 mg/l reached the breakthrough concentration of 0.01 mg/L in a 825 bed volumes compared to the 580 bed volumes for only activated alumina.^[13]

The precipitation of $\text{Fe}(\text{OH})_3$ on activated alumina can reach a breakthrough capacity of 0.1 mg of As/g of adsorbent at 0.05 mg As/L. Hlavay and Polyak tried this procedure where the Fe content was 56.1 mmol/g. In this condition the total capacity of adsorbent was the 0.12 mmol/g.^[14, 15]

- **Ferrihydrite/iron hydroxide/iron oxides.**

Different kinds of ferrihydrite, iron hydroxide and iron oxides can be applied in As(V) removal from waters. Iron oxides, oxyhydroxides and hydroxides such as amorphous hydrous ferric oxide ($\text{FeO}\cdot\text{OH}$), goethite ($\alpha\text{-FeO}\cdot\text{OH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are capable adsorbents for removing As(V), amorphous ferric oxide is the most adsorption capable since it has the highest surface area.

In naturally occurring porous diatomite iron oxide was immobilized, the iron oxide could be described as an amorphous hydrous ferric oxide, sorption of As(V) with 25 % of Fe contents diatomite was similar to the amorphous hydrous ferric oxide.^[16]

Granular ferric hydroxide is used in arsenic removal, this sorbent has a great treatment capacity before arsenic exceeded the 10 g/L in the adsorber effluent with a sorption capacity of 8.5 g/kg. One of the studies with granular ferric hydroxide shows an adsorption capacity of 8 gAs/mg at pH 7 for a initial concentration of As(V) of 10 gAs/L.^[17] In a concentration range between 100 to 750 g/L with a pH range of 4-9 the adsorption of As(V) onto ferric hydroxide was investigated and the adsorption of phosphate onto ferric hydroxide was evaluated as well. Arsenic has a higher affinity to ferric hydroxide than phosphate and as the pH increases the adsorption of arsenic tends to decrease. The optimal adsorption pH for arsenic removal was 4.^[18]

The adsorption of As(V) onto ferrihydrite [$\text{Fe}^{3+}\text{O}_3\cdot 0.5(\text{H}_2\text{O})$] was studied by Raven et al, low arsenic concentrations and low pH the As(V) were compared to high arsenic concentrations and it was found that maximum adsorption capacity occurred at pH 4.6 was 0.25 molAs/mol Fe.^[19]

The oxidizing of Fe(II) to iron(III) (hydr)oxides by aeration was studied by Robert et al. It is very advantageous the use of Fe(II) instead Fe(III) because the oxidation of Fe(II) causes partial oxidation of As(III) present in water. As the As(V) has more affinity with iron oxide than As(III), the oxidation of As(III) increases the arsenic removal by iron(III) (hydr)oxide.^[20]

Goethite is an α -iron(III) hydroxide, $\text{FeO}(\text{OH})$ and it can be used in arsenic removal. This sorbent is effective on arsenic removal and can remove over more than

95% of arsenic from the water at a pH 6 since in the range of 4 to 9 the particles of goethite are stable. Outside that range the particles became unstable and begin realizing ferric ions to solution.^[21]

Studies on goethite, amorphous iron hydroxide and clay pillared with titanium (IV), and iron(III) were conducted to evaluate the arsenic removal and it was found the amorphous iron oxide has the highest removal capacity for As(V). Goethite and iron- and titanium-pillared clays the As(V) adsorption capacity were similar.

A new fibrous polymeric/inorganic sorbent was also evaluated in Arsenic remediation. This sorbent has polymer filaments impregnated with hydrated Fe(III) oxides nanoparticles, functional groups of this weak-base anion exchanger allowed high (1.0–1.4 mmol/g) and fairly uniform Fe(III) loading. While hydrous ferric oxide (HFO) microparticles provide a high sorption affinity toward dissolved arsenic species, the fibrous polymeric matrix guarantees excellent hydraulic and kinetic characteristics in fixed beds. This hybrid sorbent, FIBAN-As, was selective to arsenates and exhibited excellent arsenic removal efficiency without any pH adjustment or pre-oxidation of the influent.^[22]

Another hybrid sorbent reported as ArsenXnp has also been applied in the arsenic removal process. This anion exchanger consists of nanoparticles of hydrous iron oxide through a porous polymeric bead.^[23] The principal factor for the arsenic removal it is caused by the interaction with the nanoscale hydrous oxide surface.

- **Zero valent iron**

In the recent years the use of Zero valent iron on arsenic removal has been investigated. There are several mechanisms for arsenic removal by the use of zero valent iron, one of most successful experiments was by the use of zero valent iron filings which removed 99.8% of As(V) present in waters at pH 6.^[24]

- **Fe(III) resins**

Iron(III) loaded chelating resin containing lysine- lysine-*N,N*-diacetic acid functional groups adsorbs strongly the As(V). The maximum capacity for As(V) was 0.74 mmol/g at pH 3.5. The recovery of As(V) from the resin is done by a solution of sodium hydroxide and less than 0.1% of ferric ions ions leached into the alkaline solution.

The removal of anionic metal species such as arsenic was investigated by the using of biopolymer alginic acid pretreated with Ca^{2+} and Fe(III) . 94% of As(V) at initial concentration of 400 g/L was efficiently removed by these Ca-Fe containing beads at pH 4.^[25]

Researchers Katsoyiannis and Zouboulis investigated the arsenic removal in two media sorbents. One was the alginate biopolymer impregnated with Ca ion and coated/doped with hydrous ferric oxide, the other was the modified polystyrene and polyHIPE (PHP) coated with iron hydroxide. Both sorbents are efficient in arsenic removal but the Ca-Fe-doped alginate was found to be most efficient.^[26, 27]

- **Anion exchangers**

The As(V) adsorption by the use of titanium dioxide loaded onto an Amberlite XAD-7 resin was also studied. This anion exchanger strongly adsorb As(V) in a pH range between 1 and 5. The maximum of adsorption capacity achieved by this resin was 0.063 mmol/g for As(V) at pH 4.

Another anion exchanger adsorbent obtained from the coconut coir pith and carried with a weak basic dimethylamino hydroxypropyl groups was evaluated in arsenic removal. With this anion exchanger 99.2% of As(V) was removed at pH 7.^[5]

3 Experimental

3.1 Chemicals and Solutions

All experiments with phosphate and As(V) were conducted with the same concentration of As(V), 5 mg/L, while the phosphate concentration present in the mixture varied. The As(V) and phosphate were obtained from solid sodium arsenate and sodium phosphate which were purchased from *Wytwórnia Odczynników Chemicznych* and *Lachema N.P.*, respectively .

The silicates and As(V) mixtures were used with the same As(V) concentration as in the case of phosphates mixtures. The process of dissolving silicates in water is complicated. Silicates tend to form polymers in water and so it is necessary to separate silicates as monomers, for this matter the solid silicates were heated in presence of sodium carbonate at 1000 °C in a platinum disc. Once the silicates and sodium carbonate were melt, the molten salts were dissolved in hot water. The silicates concentrations varied as well. The silicates were purchased from *Toscano* and the sodium carbonate was purchased from *Wytwórnia Odczynników Chemicz.*

The pH (InoLab Level I, WTW Germany) solutions were adjusted using either sodium hydroxide 1M or hydrochloric acid 1M as appropriate to yield the desired final pH of 5 or 8 for the mixture of 500 mg/L of phosphates and 5 mg/L of As(V).

3.2 sorbents

Iron oxide based sorbents have been used in arsenic removal from waters, due to its effectiveness. The arsenic removal experiments were conducted with two different iron oxide sorbents, the GEH[®] and the FO 36, and with an ion exchanger, MP 500. The GEH[®] was obtained from *Wasserchemie & Co. KG*, and the FO 36 and MP 500 from *Lewatit* respectively.

Table 1 summarizes the data supplied by the manufacture on the principal characteristics of the iron oxide sorbents and the ion exchanger used in this work. ^[28-31]

Table 1: Principal characteristics of GEH[®], Lewatit FO 36 and Lewatit MP 500

Sorbents	GEH[®]	FO 36	MP 500
Structure	-	Macroporous	Macroporous
Matrix	-	Crosslinked polystyrene	Crosslinked polystyrene
Functional Group	-	FeO(OH)	Quaternary amine
Diameter (mm)	0.35 - 2	0.35	0.61
Superficial area (m²/g)	250 - 300	-	1.87
Density (kg/m³)	1500	1250	1060

3.3 Arsenic removal

3.3.1 Preparation of sorbents for arsenic removal

Before using GEH[®], a backwash was required to remove fine particles and impurities. So, water was pumped upflow through the column. As the grain size of GEH[®] obtained from the manufacturer ranged between 0.32 and 2 mm, the GEH[®] was sieved to a size of 0.5 to 0.8 mm.

The MP 500 was obtained from the manufacturer in the ionic form Cl⁻. So to convert the sorbent into the desired form, which was the OH⁻ form, the sorbent had to be washed with a NaOH 1M solution. The solution was pumped through the column at 10 BV/h.

The *Lewatit* FO 36 was directly used as it was obtained from the manufacturer.

3.3.2 Fixed bed columns for arsenic removal

Fixed bed columns were carried out using glass columns (10 mm in diameter and 50 mm of length) and the packed volume of each column was 15 mL. The solutions were pumped downflow through the column at 6 BV/h with a peristaltic pump PCD 31.2 (Kouril, Czech Rep.) to ensure a constant flow rate.

Several cycles, lasting a period of 20 hours each, were conducted until the effluent arsenic level reached the 10 $\mu\text{g/L}$. The samples were collected by a fraction collector FCC 61 (Laboratorní Pstroje, Prague) at regular intervals, each 20 minutes. Every sample used during this experiment contained 30 mL of effluent which corresponds to 2 BV. **Figure 3** shows the column tests experiments.



Figure 3: Colum testes experiments.

3.3.3 Regeneration of Sorbents

The GEH[®] sorbent couldn't be regenerated because of its 100% Fe content. [32] The physical attrition granules caused by the regeneration process would cause further particles degradation and as a consequence the GEH[®] would be only viable for single use applications.

The *Lewatit* FO 36 was regenerated using an alkaline-brine solution (2% NaOH and 2% NaCl) at 4 BV/h during three hours. Posteriorly, water at 10 BV/h was passed through the column during 15 minutes. Finally, the column was rinsed with CO₂ sparked- distilled water for about 4 BV/h. This regeneration process was recommended by the manufacturer's manual.

Even though the latter was recommended, yet another way to regenerate the *Lewatit* FO 36 was used. In this case the column was regenerated using only an alkaline solution of 1M of NaOH at 13 BV/h.

The regeneration procedure used on *Lewatit* MP 500 consisted in passing an alkaline solution of 1M NaOH at 13 BV/h through the column.

3.4 Arsenic Analysis by ICP

The As(V) provinient from fixed bed columns and regeneration processes was analyzed by the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-EOS) Optima 2000 DV (Perkin- Elmer Instruments, USA). All samples were acidified with 0.3% of HNO₃. Detection limit for arsenic was 0,001 mg/L. The samples which exceeded the maximum concentration limit, 10 mg/L, had to be diluted.

3.5 Phosphates Analysis by Spectrophotometry UV-Visible

Phosphates were analyzed by colorimetric assessment using potassium phosphate (were obtained through Wytwórnia Odczynników Chemicz) as a standard.

The colorimetric assessment is based on a color reagent that is added to the solutions and which contains ammonium molybdate, antimony potassium tartrate, ascorbic acid and sulfuric acid. The solutions of ascorbic acid, ammonium molybdate and antimony potassium were first mixtured. Sulfuric acid must be added immediately

after the addition of antimony tartrate to avoid the generation of turbidity in the color. The color reagent solution must be prepared daily.

Phosphates react in acidic medium with ammonium molybdate and antimony potassium tartrate to form an antimony-phospho-molybdate complex which is reduced to a blue-colored complex by ascorbic acid. The blue-colored is proportional to the phosphates concentration.^[33]

The spectrophotometer analysis consisted of preparing thirteen standard solutions. Each standard solution had a known phosphate concentration (0.05, 0.1, 0.25, 0.75, 1, 2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20 mg/L) which was used for the calibration.

Moreover, 10 mL of each phosphate samples and standard solutions were retrieved and transferred to a plastic bottle. In a further step, 1 mL of colored reagent was added to each one of the plastic bottles in order to form a blue complex. Fifteen minutes later the phosphate analysis was initiated.

Absorbance analyses of the solutions (phosphates concentration) were measured at 690 nm against a blank sample and executed by a spectrophotometer (CECIL CE 2041).^[33]

3.6 Silicates Analysis by Spectrophotometry UV-Visible

One of the most successful colorimetric procedures for silicates analysis consists in a method where a yellow silico-molybdate complex is formed in a sulfuric acid solution. In the silicates colorimetric assessment the same procedure used by the phosphates analyzes was followed.

At first, the standard solutions were prepared by dilution of a 1000 g/l Si solution. After that, standard solutions with 0.5, 1, 2.5, 5, 6.25, 10, 12.5, 20 mg/L of Si were prepared from 1000 g/L of Si solution and used for calibration.

Furthermore, 15 milliliters of each sample were taken to a plastic bottle and 1 mL of sulfuric acid and 2.5 mL of ammonium molybdate were added. After one minute and then four minutes were passed, 1 mL of ammonium persulphate and lemon acid, were respectively added as well.

The absorbance of each solution (silicates concentration) was measured at 430 nm against a blank sample and executed by a spectrophotometer (CECIL CE 2041).

3.7 Fe analysis by Atomic Absorption Spectrometer

The Fe content of the collected samples was determined by an Atomic Absorption Spectrometer (Spectrometer AA 220 Varian). The limit detection on AAS is 0.05 mg/L for Fe.

3.8 Preliminary tests of Langmuir (Isotherms)

In order to determine the Langmuir isotherms constants, batch sorption experiments were conducted at pH 5 with different concentrations of As(V) (0.1, 0.5, 1, 5, 10, 12.5, 25 and 50 mM).

Initially solutions of As(V) and 0.05M of HEPES buffer (Merk) were prepared and stored. Then 0.3 mL of each sorbent were added in 100 mL bottles containing different concentrations of A(V). The next step was to add 10 mL of HEPES buffer solution to each bottle. The HEPES buffer solution was used to maintain the pH solution at 5.

The following step was to adjust the pH with 1M of NaOH and 1M of HCl. Plastic bottles were used as batch reactors which were mixed on a platform shaker Unimax 1010 (Heidolph Instruments, Germany) for 72 hours. After this, samples were collected and analyzed on ICP.

The pH of the batch sorption was measured at the end of the experiment. **Figure 4** shows the batch sorption experiment.



Figure 4: Batch sorption experiment.

4 Results and Discussion

4.1 Column test with *Lewatit* FO 36

Many iron oxide based sorbents have shown a great sorption capacity for arsenic, particularly in the As(V) form which has been investigated by many researchers. However, there is no consensus in the literature about the type of mechanism leading this kind of sorption. [20, 29, 31, 34, 35]

Column tests were performed to evaluate the arsenic sorption and the influence of competing ions such as silicates and phosphates on arsenic sorption onto *Lewatit* FO 36.

4.1.1 Influence of Phosphates in As(V) removal

To understand the real impact of phosphates in As(V) removal on *Lewatit* FO 36 several column tests with different concentrations of phosphates and 5 mg/L of As(V) were conducted. A sorption with 5 mg/L of As(V) was made to evaluate the influence of competitive ions, such as phosphates, on As(V) sorption.

All columns were filled with 15 mL of *Lewatit* FO 36 and the solution was pumped through the column at 6 BV/h at pH 5. In these conditions and considering the speciation of both compounds in water, which can be observed in **Figures 5** and **6** the principal species of arsenic and phosphate present in solution were H_2AsO_4^- and H_2PO_4^- [18]

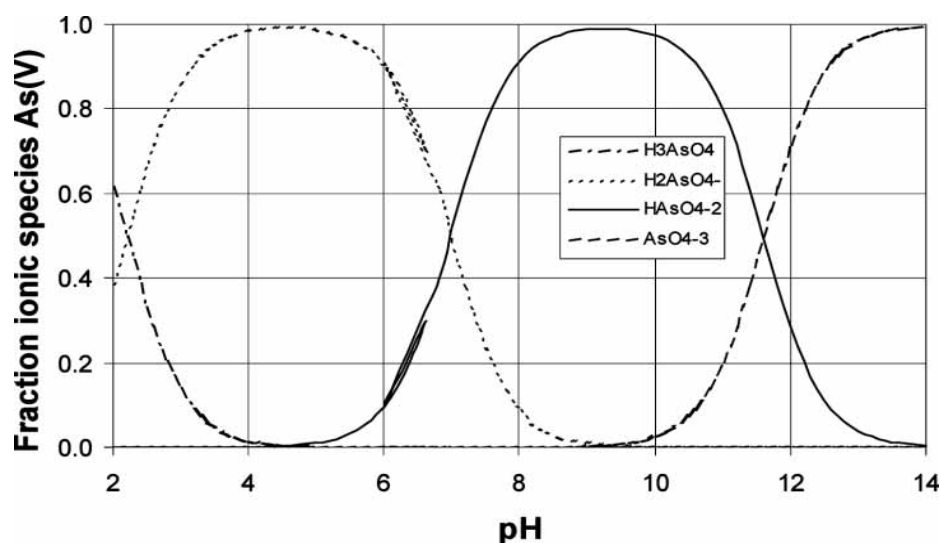


Figure 5: Arsenic speciation diagram. [18]

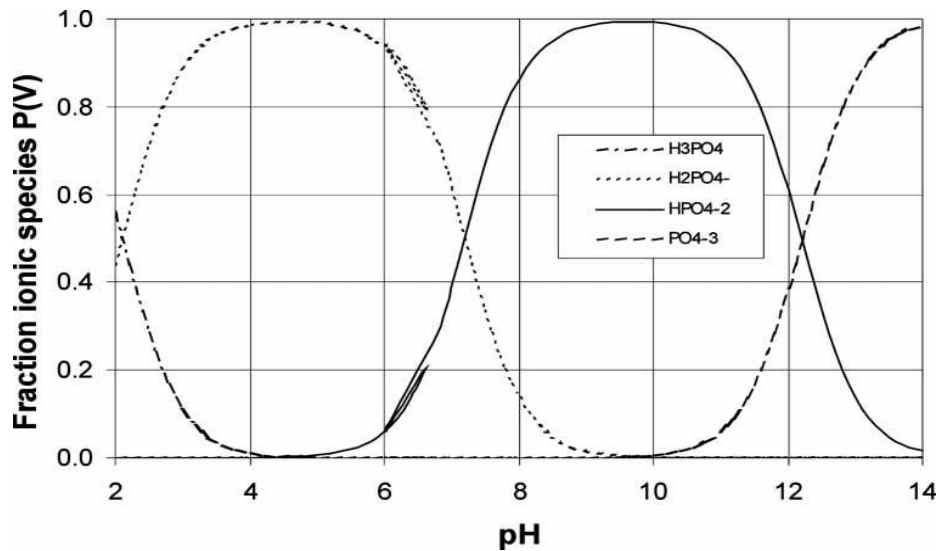


Figure 6: Phosphate speciation diagram.^[18]

First of all a sorption with 5 mg/L of As(V) was performed, this sorption is represented in **Figure 7**.

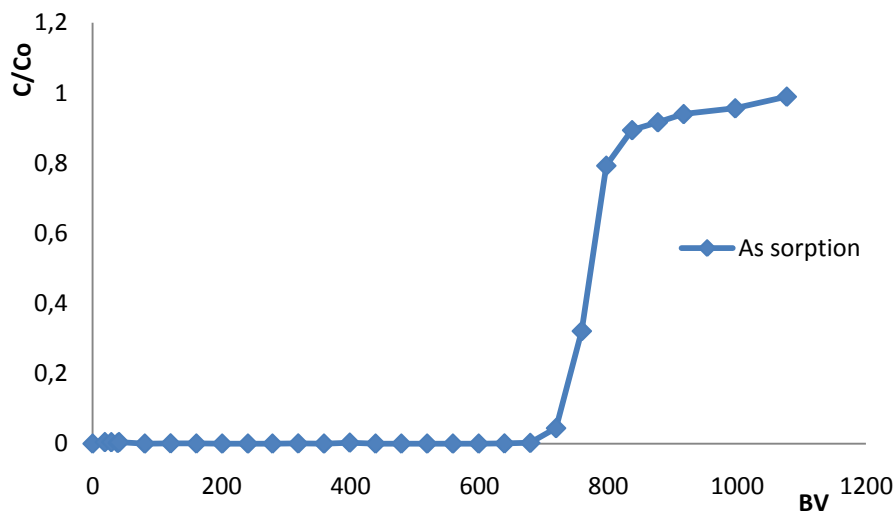


Figure 7: Sorption behavior of 5 mg/L of As(V)

After 679 BV no As(V) was uptaken by the column. The BC reached for As(V) was 0.047 mol As(V)/L of sorbent which was calculated by the followed equation:^[36]

$$BC \left(\frac{\text{mol}}{\text{L}} \right) = \frac{C_i \left(\frac{\text{g}}{\text{L}} \right) \times BV(\text{L})}{VR(\text{L}) \times M \left(\frac{\text{g}}{\text{mol}} \right)} \quad (1)$$

where BC corresponds to the breakthrough capacity of sorbent, C_i is the initial concentration, VR is the sorbent volume and M the molar weight of As(V).

The breakthrough capacity is the total amount that the resin can capture until it reaches the breakthrough concentration, in other words it happens when the sorbent is saturated. The breakthrough concentration is based on the MCL in potable water which is $10\mu\text{g/L}$. [2]

The sorption of As(V) in presence of different concentrations of phosphates is represented in the **Figure 8**.

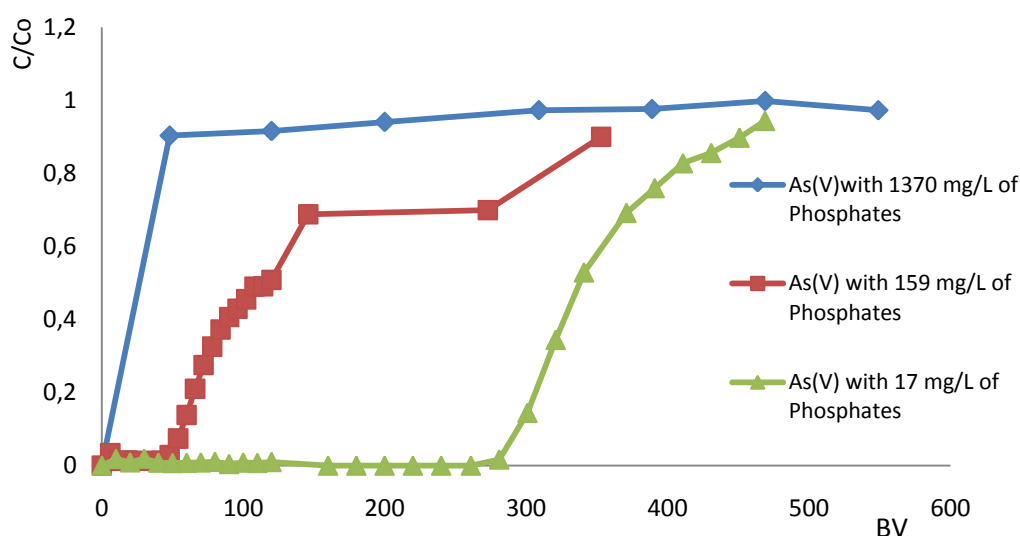


Figure 8: As(V) sorption with different concentrations of phosphates.

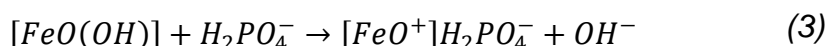
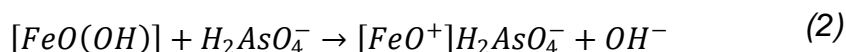
By analyzing **Figure 8**, it is visible that the sorption of As(V) in presence of 1370 mg/L of phosphates is diminute, and so hardly any As(V) is sorbed in the column. However, the As(V) sorption in presence of 159 mg/L of phosphates lasted until 12 BV. Besides, some As(V) lingered on the column, and thus the BC was not possible to calculate (since the concentration in which the column BC was higher than MCL).

The sorption of As(V) in presence of 17 mg/L of phosphates lasted until 281BV. The BC reached by the *Lewatit* FO 36 was 0.016 mol As(V)/L of sorbent.

Comparing the BC obtained for the sorption of As(V) in presence of 17 mg/L of phosphates with the sorption of only As(V) it is notorious that in presence of phosphates the As(V) sorption decreases.

As mentioned previously, there is no consensus in the type of mechanism which leads the sorption process of As(V) onto *Lewatit* FO 36. It is nonetheless believed that

As(V) forms complexes on iron oxide surface, even though there are many discussions about the exact structure of the surface complexes. The following equations exemplify the main mechanisms of As(V) and phosphates sorption on iron oxide surface of *Lewatit* FO 36.



The process of arsenic removal by *Lewatit* FO 36 could be assumed as an sorption process accompanied by an ion exchange process. If the undissociated acid donates a proton to the surface hydroxyl group to form water that one can be displaced. The proton produced is used to remove the hydroxyl group from the coordinating layer of the surface and provide a site for the anion to attach.

Sorption of As(V) species is known to take place via coulombic as well as Lewis acid-base interactions (ligand exchange reaction) to form monodentate and bidentate inner sphere complexes.

The presence of phosphates decrease the BC of arsenic as was referred above. As phosphates and As(V) are chemically similar it was expected that phosphates will compete for similar sites, reducing As(V) uptake as it was demonstrated by the experimental results. As the concentrations of phosphates in waters increase the As(V) sorption decrease.

4.1.2 Influence of silicates in As(V) removal

Besides phosphates there are other species which influence the As(V) removal from waters.

Silicates, apart from phosphates are the species which have a great impact in As(V) removal due to its great affinity to the iron oxide surface through ligand exchange with the hydroxyl functional group. [20, 35]

Several studies about competitive sorption in arsenic removal reveal that silicates are the main inhibitor of As(V) sorption. This could be related to its elevated water concentrations (~ 10 ppm) and its ability to form polymeric species both in solution and at iron oxide surface. [7, 8]

Similarly to the case of phosphates, several column tests were conducted to evaluate the impact of silicates on As(V) removal using *Lewatit* FO 36 sorbent.

The procedure used in the sorption of phosphates was replicated for the silicates sorptions. Two different concentrations of silicates in solutions were used with 5 mg/L of As(V). The next figure, **Figure 9**, shows the As(V) profile concentrations during the two sorptions.

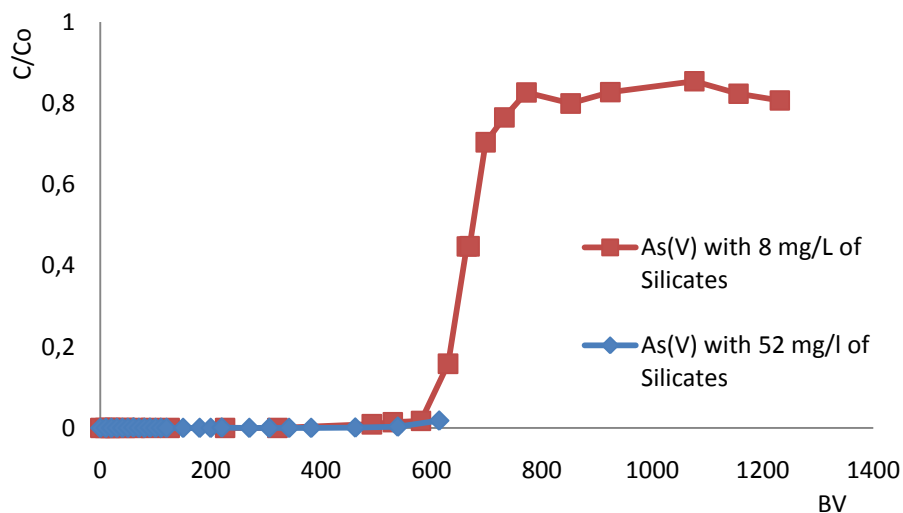


Figure 9: As(V) sorption with 52 and 8 mg/L of Silicates and without Silicates

The presence of silicates in solutions influences the As(V) sorption, as it can be observed in **Figure 9**.

The BC in these two columns was reached with 0.036 and 0.034 mol As(V)/L of sorbent at 539 and 492 BV respectively. By comparing the BC of each sorption, it can be concluded that as long as the concentration of silicates increases, the As(V) sorption increases as well. Nevertheless, this is the opposite of what should happen since the silicates have a negative influence on the As(V) sorption. According to the previously stated, As(V) should have been mostly captured in sorption of 8 mg/L of silicates other than for 52 mg/L of silicates. These results could be connected to some experimental errors related to the analytic method chosen to determine silicates or to the analytic method which is not the most accurate.

Comparing the BC from As(V) in presence of silicates with BC from As(V) sorption onto *Lewatit* FO 36, 0.047 mol As(V)/L of sorbent, the sorption of As(V) decreases in presence of silicates. This could be explained by the increase of electrostatic repulsions of arsenic anions which reduce the number of available sorption sites for the arsenic species caused by the sorption of silicates on iron oxide surface.

However, as the silicates concentrations in solutions increase the As(V) sorption slightly increases based on the BC reached by the sorptions of 52 and 8 mg/L of silicates.

4.1.3 Sorption pH for As(V) removal

The *Lewatit* FO 36 is an iron oxide based sorbent with Fe content around 23%.^[32] This sorbent must work at pH higher than 4. If not, the iron oxide will be released into the solution and thus losing its functionality. In addition to that, the As(V) sorption to iron oxide surfaces tends to decrease as pH values increase, at least between the range of pH 6 to pH 9.^[37] According to the mentioned facts a pH of 5 was chosen as the optimal pH for As(V) removal onto *Lewatit* FO 36.

Another important matter is that the pH varied during the sorption process. **Table 2** shows the sorption pH of As(V) by itself and in presence of phosphates and silicates.

Table 2: Values of pH for As(V) removal

Sorptions	pH
As(V)	3.84
As(V) and 16 mg/L of Phosphate	3.40
As(V) and 8 mg/L of Silicates	3.78
As(V) and 52 mg/L of Silicates	3.98

The interaction mode between As(V) species and iron oxide sorption sites is lead by the speciation of As oxy-compounds in aqueous solution as function of pH, along with the type of sorption sites. At pH 5 the iron oxide sorptive sites are FeOOH_2^+ and the predominant species of As(V) is H_2AsO_4^- .

The pH variation during the sorption process, more precisely, at the initial part of the column runs could be explained by the decrease of the initial sphere complexes stability with the covering degree ($\text{FeOOH}/\text{FeOOH}_2^+$). The deprotonation or dehydration reaction of the inner sphere complexes, caused by the hydroxyl group or H^+ losses, initiates a series of consecutive reactions between the superficial complexes and the predominant species from the aqueous solution on the adjacent sorptive sites, which explains the experimental results.

4.1.4 Regeneration of *Lewatit* FO 36

To evaluate the reuse of *Lewatit* FO 36, the columns related to the 17 mg/L of phosphates with 5mg/L of As(V) and the one containing only 5 mg/l of As(V) sorptions were regenerated. Based on fact that at $\text{pH} > 10$ the net surface charge is negative, and produces repulsive electrostatic forces between As(V) oxyanions and the sorbent, the *Lewatit* FO 36 can be regenerated using an alkaline solution. At alkaline pH, sorption sites are deprotonated and negatively charged.

The *Lewatit* FO 36 columns were regenerated in two different ways as was explained in the experimental part. The regeneration process used in the column of 17 mg/L of phosphates with 5 mg/L of As(V) sorption was the recommended by the manufacturer. Concentrations profiles of As(V) and phosphates during the regeneration process are provided in **Figure 10**.

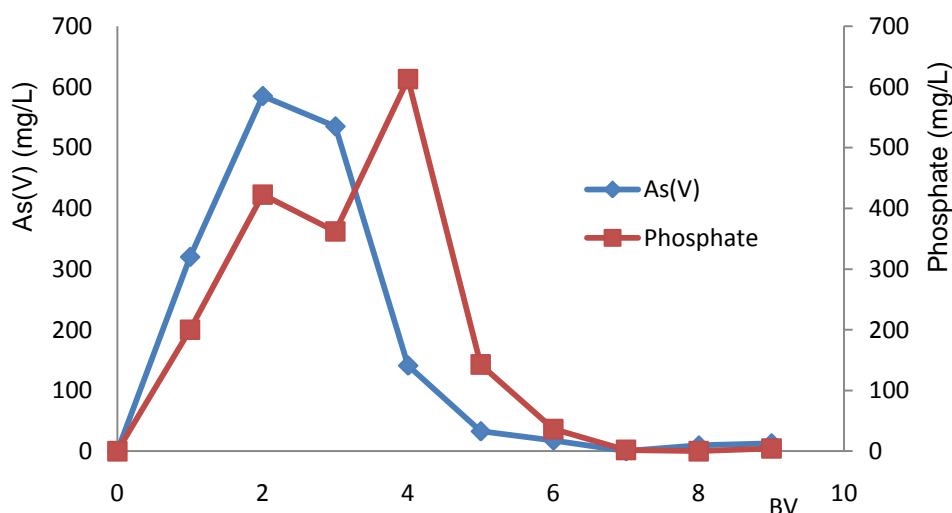


Figure 10 : As(V) and Phosphate concentrations during the regeneration.

In less than 6 BV most of the As(V) was completely desorbed from the *Lewatit* FO 36. 100 % of As(V) was recovered during the regeneration process. The phosphates were also measured during the regeneration step. Only 42 % of phosphates were recovered from the sorbent. The low phosphate concentration obtained can be explained by the method chosen to analyze the presence of phosphates.

The column related to the As(V) sorption (as the only compound) was regenerated as well. **Figure 11** shows the As(V) concentrations during the regeneration process. The regeneration procedure was, again, the recommended by the manufacturer.

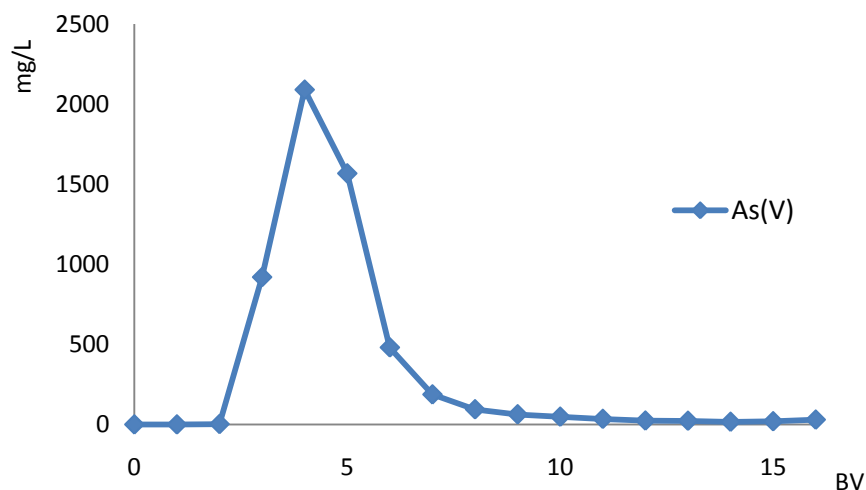


Figure 11: As(V) concentrations during the regeneration

At 10 BV nearly all the As(V) was desorbed from the column. The regeneration of As(V) from *Lewatit* FO 36 was 100 % successful.

The 8 mg/L of silicates and 5 mg/L of As(V) column was regenerated with 1M of NaOH solution. In **Figure 12** are represented the concentrations profiles of As(V) and silicates desorbed from the *Lewatit* FO 36.

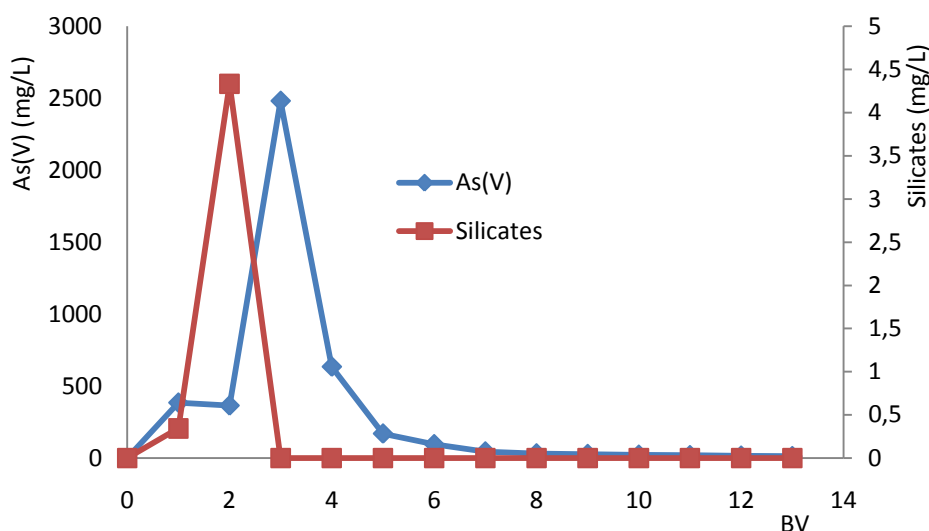


Figure 12: As(V) and Silicates concentrations profile during the regeneration process.

While only 1.17% of silicates were recovered, the recovery for As(V) was 91.48%. Once again, the analytical method chosen to analyze silicates can explain these results.

In order to verify if the *Lewatit* FO 36 was able to be reused after the regeneration process the 17 mg/L of phosphate and 5 mg/L of As(V) was performed with the regenerated sorbent. **Figure 13** shows the sorption behavior of As(V) and phosphates before and after the regeneration process.

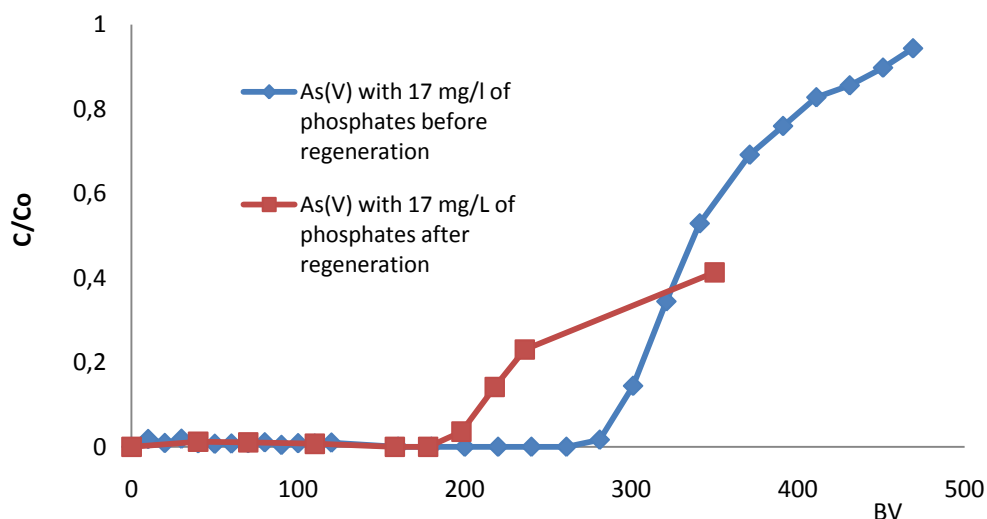


Figure 13: Comparison of As(V) with 17 mg/L of Phosphates sorption before and after the regeneration process.

The BC of As(V) in the regenerated sorbent was 0.015 As(V) mol/ L of sorbent at 198 BV. Comparing the BC of As(V) obtained in the pure sorbent sorption (0.016 mol As(V)/L of sorbent) with the BC reached with the regenerated sorbent (0.015 mol As(V)/L of sorbent), it can be noticed that the ones relative to the pure sorbent are slightly higher than the BC achieved from regenerated sorbent. Therefore separation of As(V) from phosphates is better when the sorbent used is pure.

Posteriorly, sorption of solely As(V) in the regenerated sorbent was conducted. The **Figure 14** demonstrates a comparison of As(V) sorptions before and after the regeneration process.

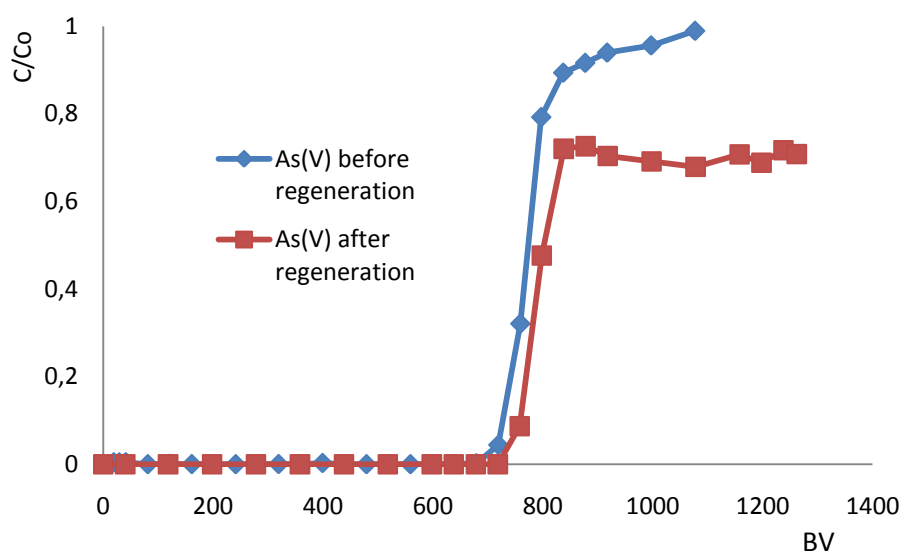


Figure 14: Comparison of As(V) sorption before and after regeneration process

After the regeneration process the As(V) sorption capacity achieved by the regenerated sorbent was 0.0559 As(V) mol/L of sorbent at 758 BV. The BC obtained was higher than the BC of the pure sorbent. So, the regenerated sorbent can retain much more As(V) than the new *Lewatit* FO 36.

4.1.5 Fe release during As(V) sorption and regeneration

As the *Lewatit* FO 36 is an iron oxide based sorbent, the iron released during the sorption of 5 mg/L of As(V) and during the regeneration process was measured by the

AAS. No Fe concentration was detected in the samples from sorption since the Fe concentrations were below of the detection limit, 0.05 mg/L. In the regeneration only after 9 BV it was possible to measure the Fe concentration. The total amount of iron released into the samples was 1.495 mg/L.

4.2 Column test with GEH[®]

GEH[®] sorbent has great affinity to arsenic. The further results were conducted in order to evaluate the sorption capacity of arsenic using the GEH[®] sorbent.

4.2.1 Influence of Phosphates in As(V) removal

The influence of phosphates in As(V) removal from waters was also tested with another sorbent, the GEH[®]. Phosphates have a great affinity to the surface of GEH[®], so phosphates will compete with As(V) for sorption sites onto GEH[®]. The procedure used in the GEH[®] sorption columns was analog to the one used in the *Lewatit* FO 36. Two different concentrations of phosphates were tested to evaluate the behavior of As(V) in presence of this competitive ion. In **Table 3** are represented the As(V) BC reached in presence of 145 mg/L and 17 mg/L of phosphates.

Table 3: As(V) BC reached in presence of phosphates

Sorption	BC (mol As(V)/L of sorbent)
5 mg/L of As(V) and 145 mg/L of phosphate	0.011
5 mg/L of As(V) and 17 mg/L of phosphate	0.079

As can be verified, as long as the phosphate concentration increases, the As(V) captured by the GEH[®] decreases.

The high interference of phosphates on the arsenic removal sorption was already observed in this work. This fact, is due to the competition of phosphates and As(V) for the sorption sites on GEH[®] because of the close affinity of phosphate and As(V) for iron oxide.

Besides these two sorptions, the 5 mg/L of As(V) sorption was performed as well. However, even after 2113 BV, it was not possible to reach the As(V) BC. This fact shows the high treatment capacity of GEH[®] which was demonstrated in other studies. [29] The high treatment capacity of GEH[®] can be explained by the structure of GEH[®]; its loose hydrated structure is permeable to hydrated ions allowing sorption to easily occur which shows the great treatment capacity of GEH[®] in waters for arsenic removal.

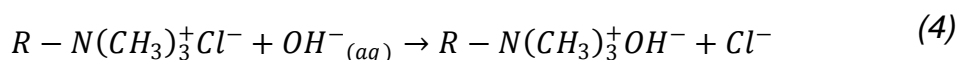
4.2.2 Fe release during As(V) sorption

During the GEH[®] sorption the Fe released into the aqueous solutions was measured by AAS. As far as *Lewatit* FO 36 is concerned, no Fe was found in the samples because its concentration was below of the detection limit, 0.05 mg/L, of AAS.

4.3 Column test with *Lewatit* MP 500 resin

Apart from the previously stated sorbents, there were studies performed using the *Lewatit* MP 500 resin.

The experiments were conducted with a solution containing 5 mg/L of As(V) and 810 mg/L of phosphates at pH 8. The column was filled with 15 mL of *Lewatit* MP 500 resin and the solution was pumped at 6 BV/h. As the *Lewatit* MP 500 was purchased on ionic form of Cl⁻, it was necessary to pass through the resin 10 BV of 1 M NaOH to transform the resin into the hydroxyl form. The following equation briefly describes the process:



The ion exchange process is strongly dependent on the charge of the ions and on the pH of the solution. However the speciation of arsenic and phosphates is directly dependent of the pH solution as well. At pH 8 the principal species of arsenic and phosphates present in solution are HAsO₄²⁻ and HPO₄²⁻ which can be observed in the speciation diagrams, **Figures 5** and **6**.

The arsenic and phosphates will exchange with the hydroxyl group during the ion exchange process and compete for the functional groups. The ion exchange process of phosphates and arsenic through the resin can be described as:

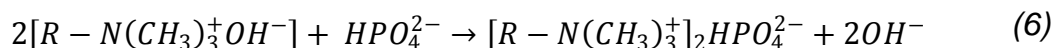
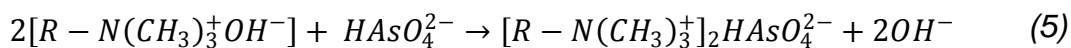


Figure 15 shows the concentrations profile of As(V) and phosphates during ion exchange process using the Lewatit MP 500 resin.

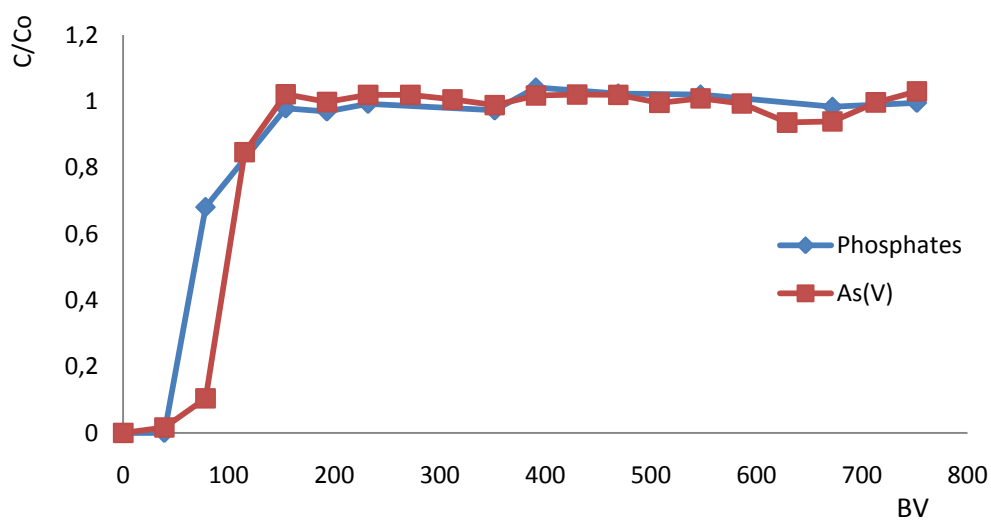


Figure 15: Sorption of As(V) in presence of 810 mg/L of phosphates.

The As(V) and the phosphates were rapidly captured into the column once the As(V) reached the BC after 39 BV. The BC for As(V) was 0.0029 mol/L of resin at pH 7.88.

The BC of As(V) obtained by the *Lewatit* MP 500 was much lower comparing with the BC obtained by *Lewatit* FO 36 and GEH[®] to high concentration of phosphates. It is mainly due to the high excess of phosphates and also the higher affinity of strong basic functional groups (quaternary ammonium) towards HPO_4^{2-} . The diameter of hydrated ions is higher for As(V) than for HPO_4^{2-} , therefore HPO_4^{2-} are preferred over $HAsO_4^{2-}$. As a result of higher concentration and affinity, phosphates are preferably taken up by the MP 500 resin than the As(V).

After the sorption, the column was regenerated with 1M of NaOH. The results concerning the regeneration process are shown in **Figure 16**.

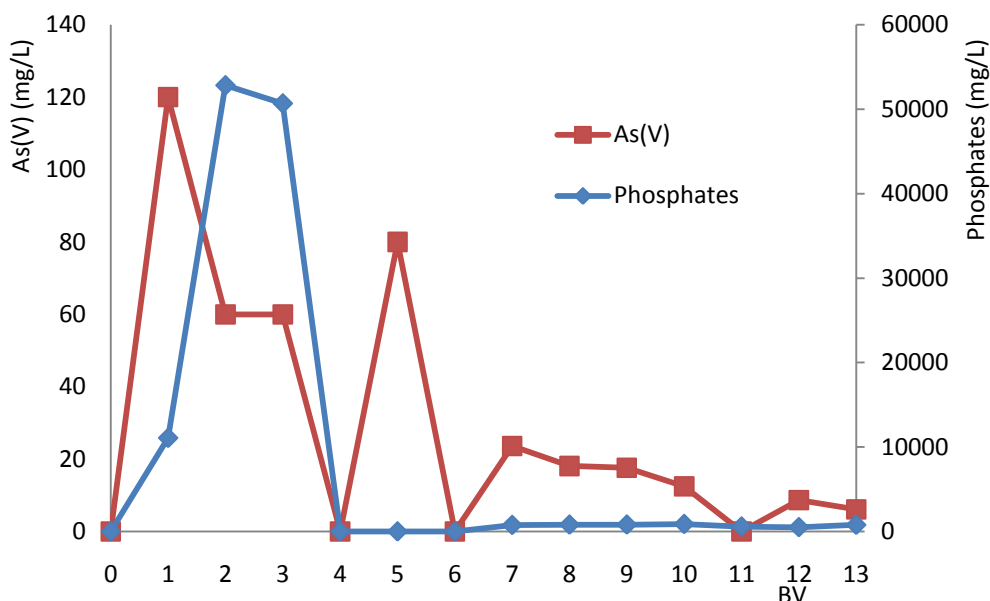


Figure 16: Profile concentrations of As(V) and Phosphates during the regeneration process.

Phosphates were almost regenerated until 4 BV while As(V) was removed as long as the regeneration process occurs.

Phosphates were 100% removed from the column while As(V) was only 84 % removed.

4.4 Langmuir Isotherms

The description of the equilibrium during the ion exchange or chemisorption is normally performed using the Langmuir isotherms. Unlike other models, it takes into account only certain given number of sorption sites (functional groups) that can be occupied by the sorbed species. Thus, the selective sorption of As(V) onto iron oxide based sorbents was described with Langmuir isotherms represented by the following equation:

$$q = \frac{q_{max} C_e}{K_l + C_e} \quad (7)$$

Where C_e is the equilibrium concentration of the As(V) in solution in mol/L, q is the concentration of as(V) sorbed by the sorbents in mol/L, q_{max} is the calculated sorption maximum in mol/l and K_l is the Langmuir parameter.

The Langmuir isotherm is derived assuming: there is a limited area available for sorption, arsenic is sorbed in a monomolecular layer, the sorption process is reversible and equilibrium is achieved. **Figure 17** and **18** shows the plot of C_{eq} (mol/L) vs q (mol/L) for As(V) sorption onto *Lewatit* FO 36 and GEH[®].

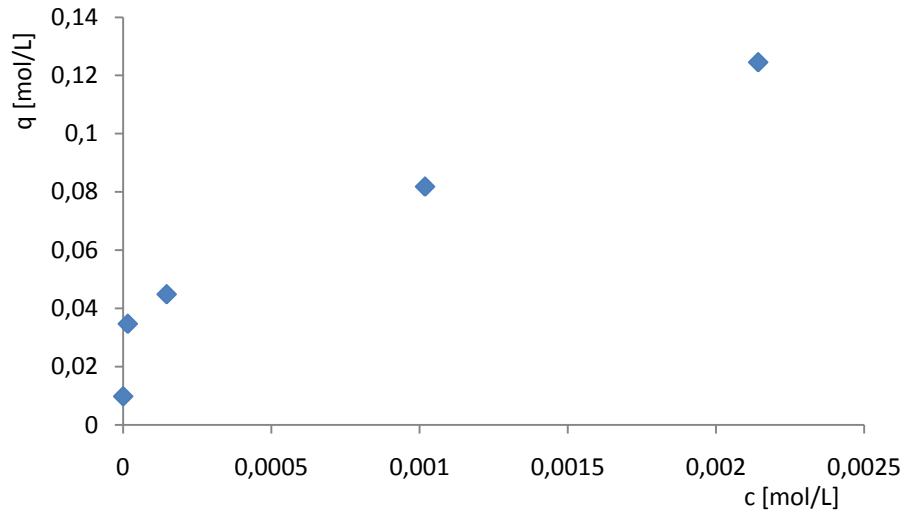


Figure 17: Sorption isotherm for *Lewatit* FO 36 at pH 5.

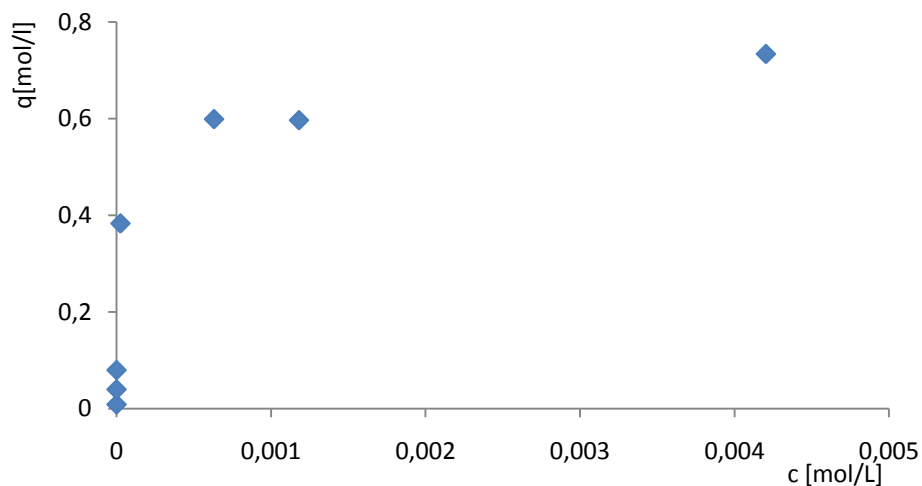


Figure 18: Sorption isotherm for GEH[®] at pH 5.

By a non linear regression of the equation it was possible to calculate the Langmuir isotherms parameters. The non linear regression used was:

$$\frac{C_{eq}}{q} = \frac{K_l}{q_{max}} + \frac{C_{eq}}{q_{max}} \quad (8)$$

Table 4 lists the constants obtained by non linear regression analysis of the sorption isotherm data collected for As(V) in this study.

Table 4: Correlation coefficients (r^2), sorption maximum (q_{\max}), and Langmuir parameter (K_l) by Langmuir equation for As(V) on *Lewatit* FO 36 and GEH[®].

	pH	R^2	q_{\max} (mol/L)	K_l
<i>Lewatit</i> FO 36	5	0.9425	0.124	1,61E-04
GEH [®]	5	0.9953	0.732	5,86E-05

Both sorbents exhibited a good coefficient of correlation, besides GEH got a better correlation coefficient than *Lewatit* FO 36. The non linear Langmuir function results, indicate that GEH has higher sorption maximum than *Lewatit* FO 36, while the Langmuir parameter, K_l , was higher for *Lewatit* FO 36 than GEH[®].

A high K_l value represents a relatively high retention capacity of arsenic at low dissolved arsenic concentrations, which was achieved for *Lewatit* FO 36 sorbent.

As a result of great treatment capacity of GEH it was not possible to obtain the BC of As(V). However the the BC of As(V) sorption onto GEH[®] can still be estimated by the Langmuir parameters. The BC obtained by the Langmuir parameters was 0.31 mol As(V)/L of sorbent. (**Annexe B**)

5 Conclusions

This work point towards a connection between the concentration of phosphates and silicates, and the As(V) sorption capacity.

In the case of *Lewatit* FO 36 sorbent, as long as the phosphate concentration increases the As(V) sorption decreases. As opposite to the phosphates, silicate concentration increases leads to an increase of As(V) utptaken by the sorbent.

As far as the regeneration processes used on *Lewatit* FO 36 are concerned, it was noticeable that this process was not as effective when comparing the phosphates and silicates removal from the sorbent compared to the As(V).

The reuse of *Lewatit* FO 36 demonstrated to be a viable process, since the amounts of arsenic removed using this reused sorbent were similar to the ones using the pure form.

The GEH[®] sorbent revealed a great treatment capacity for As(V) removal from water. Both GEH[®] and *Lewatit* MP 500 showed that in presence of phosphates the As(V) sorption capacity decreases.

The preliminary testes of Langmuir demonstrated that GEH[®] has the maximum sorption capacity comparative to *Lewatit* FO 36.

6 Work Assessments

6.1 Aims Achieved

The proposal of this project was study the effect of phosphates and silicates on arsenic removal by selective sorption on two iron oxide based sorbents, *Lewatit* FO 36 and GEH, and in an ion exchanger, *Lewatit* MP 500.

The silicates effect using the GEH could not be studied but the remaining objectives were accomplished during these five months.

6.2 Limitations and further work

The principal limitation during the development of this project was the availability of laboratory material. Consequently I only finished the laboratory part one week before deliver this report.

Moreover, the lack of support and the limited information related to the elaboration of this project given by the supervisor prejudiced the performance of this work.

At last but least important, only the supervisor spoke correctly in English damaging the communication with the other co-workers.

As a suggestion for further works, it would be interesting to try other analytical methods to measure silicates and phosphates concentration in aqueous solutions.

6.3 Final appreciation

It was an enriching experience for me as a person and after that I fell more capable to adapt to new situations.

Nevertheless, and even though i put all my effort into this project, I think could have done a better work and would have felt more satisfied if the above mentioned limitations had not happened.

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Annexe A – Langmuir Parameters

In **Table A1** and **A2** are represented the As(V) inlet and outlet concentrations measured by ICP and the respective concentration sorbed in each sorbent.

Table A1: As(V) inlet and As(V) outlet concentrations measured by ICP and the concentration sorbed into Lewatit FO 36.

FO36				
As (mM)	As _{inlet} (mg/L)	As _{outlet} (mg/L)	q (mol/l)	C _e /q
0,10	2,21	0,00	0,010	0,000
0,50	8,97	1,16	0,035	0,000
1,00	21,08	10,99	0,045	0,003
5,00	94,70	76,30	0,082	0,012
10,00	188,50	160,50	0,125	0,017
12,50	226,00	209,50	0,073	0,038
25,00	487,00	465,00	0,098	0,063
50,00	855,00	803,00	0,231	0,046

Table A2: As(V) inlet and As(V) outlet concentrations measured by ICP and the concentration sorbed into GEH®.

GEH				
As (mM)	As _{inlet} (mg/L)	As _{outlet} (mg/L)	q (mol/l)	C _e /q
0,10	2,02	0,000	0,009	0,000
0,50	9,02	0,000	0,040	0,000
1,00	17,99	0,000	0,080	0,000
5,00	88,10	0,000	0,384	0,000
10,00	182,00	0,001	0,599	0,001
12,50	222,70	0,001	0,597	0,002
25,00	480,00	0,004	0,734	0,006
50,00	1560,00	0,008	4,160	0,002

To calculate the concentration of As(V) sorbed in each sorbent the following equation was used:

$$q = \frac{C_{inlet} \left(\frac{g}{L}\right) - C_{outlet} \left(\frac{g}{L}\right)}{V_{Solution} (L) \times V_{Resin} (L) \times M \left(\frac{g}{mol}\right)} \quad (1)$$

Figure A1 and **A2** shows the plot of C (mol/L) vs C/q for As(V) sorption onto Lewatit FO 36 and GEH[®].

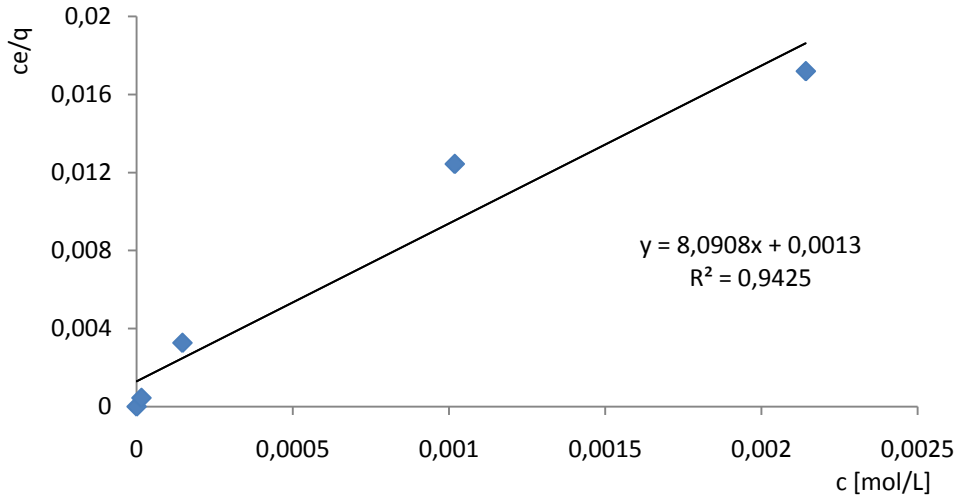


Figure A1: Non linear regression of Lewatit FO 36.

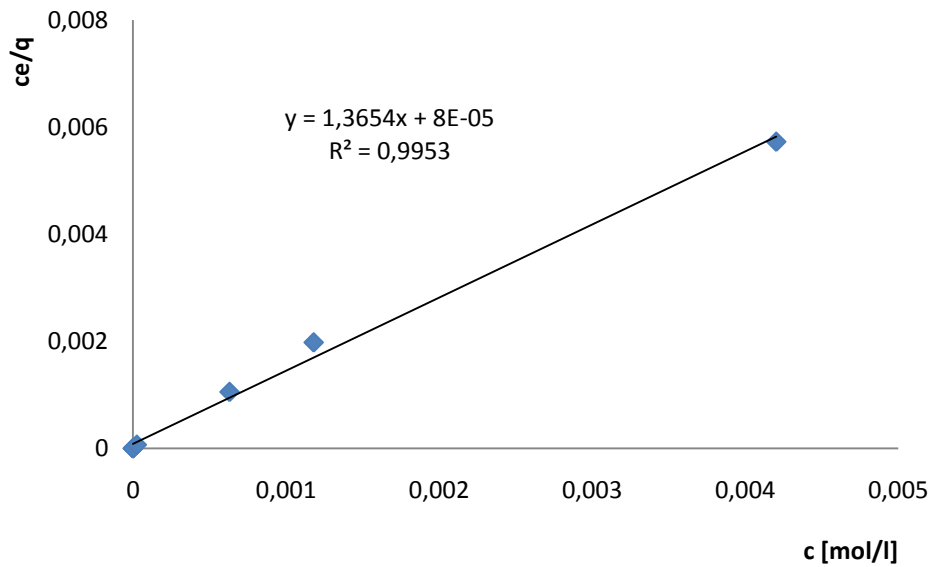


Figure A2: Non linear regression of GEH[®].

By the non linear regression equation the Langmuir parameters were obtained:

- **Lewatit FO 36:**

$$\frac{1}{q_{max}} = 8.0908 \leftrightarrow q_{max} = 0.124 \text{ mol/L}$$

$$\frac{K_l}{q_{max}} = 0.0013 \leftrightarrow K_l = 1.61 \times 10^{-4}$$

- **GEH:**

$$\frac{1}{q_{max}} = 1.365 \leftrightarrow q_{max} = 0.732 \text{ mol/L}$$

$$\frac{K_l}{q_{max}} = 8.0 \times 10^{-5} \leftrightarrow K_l = 5.86 \times 10^{-5}$$

Annexe B - Estimation of Breakthrough capacity of As(V) on GEH[®]

Through the non linear regression obtained for GEH[®] it was possible to estimate the BC concentration of As(V) for the initial concentration of 6.81×10^{-5} mol/L:

$$\frac{C_{eq}}{q} = \frac{K_l}{q_{max}} + \frac{C_{eq}}{q_{max}}$$

↓

$$y = 1.3654x + 8 \times 10^{-5} \leftrightarrow y = \frac{C_{eq}}{q} = 0.00017$$

$$\frac{C_{eq}}{q} = 0.00017 \leftrightarrow q = 0.393 \text{ mol/L}$$

As the point was knowing the breakthrough capacity of As(V) sorption onto GEH[®], which correspond to the concentration when the sorbent starts to be exhausted. This corresponds approximately to 80 % of total As(V) sorbed (represented by the yellow area in the **Figure B1** into the sorbent. Can be calculated by the following equation:

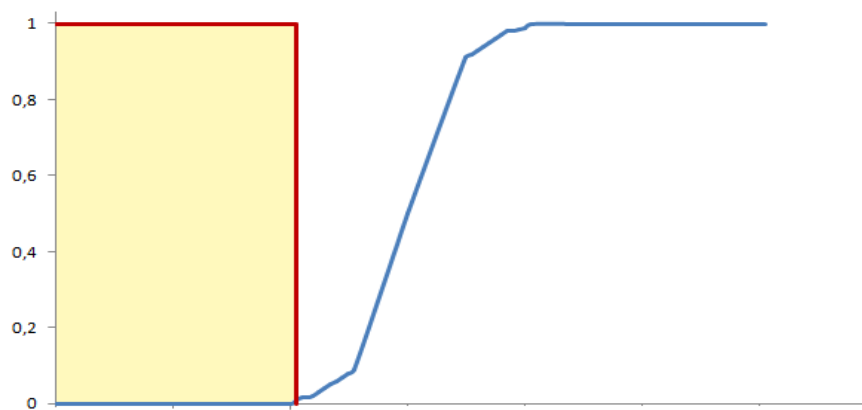


Figure B1: Schematic representation of the area corresponding to the breakthrough capacity.

$$BC = q(C_i) \times 0.8 \leftrightarrow BC = 0.031 \text{ mol/L} \quad (2)$$