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Phosphate recovery from phosphate conversion coatings waste liquid at Volvo Trucks Tuve

Bachelor's thesis in the Chemical Engineering program

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Abstract

Volvo trucks at Tuve factory accumulate waste water from the phosphate conversion coating process and the current recycling involves a filter press and also collecting the waste water in tanks which Stena Recycling empties several times a week.

The aim of the work described in this report was to see if solvent extraction of phosphorous with a tricaprylmethylammonium chloride ligand (in short TCMA) can be used on the wastewater from the conversion coating process at Volvo Group Trucks Tuve to recover the phosphate and reduce the need for replenishing phosphorous in the process.

The conclusion was that TCMA could work but to determine the possible success of using TCMAs in a solvent extraction of phosphate further thorough testing is needed. But first the question that needs to be answered is what the purpose of recycling the phosphorous from the waste water is. Is it to reduce the amount of phosphorous needed for the process by reusing it or should the phosphorous be extracted and sold for other use?

Acknowledgement

I dedicate this thesis to my father, who unfortunately never got to see it finished, but always was a big supporter of me finishing my degree.

I want to thank all people who helped me and supported me through this.

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And the rest of my friends who have listened to me during this process, you are my heroes,

Content

1. Introduction

At Volvo Group trucks operations, cab and vehicle assembly at Tuve, the main focus is to assemble the cabins (known as cabs) and trucks. The only parts manufactured on site are the frame members, which consists of steel and is the center frame, to which all parts for the cabs are assembled. Therefore it is essential to protect these from corrosion as well as other wear and tear. A usual way to protect the frame member is by phosphate conversion coating. In the automotive industry, phosphate conversion coatings have many functions, it is used for corrosion resistance (Wang et al. 2004), appearance enhancement, but also as adhesive promotion (Finishing 1999).

The conversion coating process produces wastewater, which contains high concentrations of both metals and other inorganic substances. The waste water must be treated before being released to the final wastewater treatment plant. The wastewater have high amounts of e.g. phosphate, sodium and potassium (Chemetall AB n.d.). Since the conversion process is a phosphate-based conversion, it would be preferable for Volvo Trucks to retrieve some of the phosphate in this stream for reuse.

There have been reports of eutrophication in water that may be linked to the vehicle industry and specifically emissions from surface treatments including the use of zinc phosphate. Therefore there is an interest to reduce the phosphate content in waste water (Kobya et al. 2010).

The aim of the work described in this report was to investigate if solvent extraction of phosphate with tricaprylmethylammonium chloride ligand (in short TCMA) can be used on the wastewater from the conversion coating process at Volvo Group Trucks Tuve, to recover phosphate in order to reduce the need for replenishing phosphorous in the process.

The use of solvent extraction with TCMA to separate phosphate from the other substances in this type of wastewater has not been investigated before. Solvent extraction has been used in other fields, such as the nuclear chemistry industry, and could therefore also be interesting to try on phosphate conversion coating wastewater. To separate phosphate a ligand known as TCMA was tested. If it works successfully it will separate phosphate from other substances and after stripping i.e. released from the TCM it would be possible to reuse the phosphate.

2. Theory

2.1 Phosphate conversion coating

Phosphate conversion coating is a method where a metal surface is covered by a chemical converted into a non-metal crystalline coated surface in an acidic solution, therefore the method is used to enhance different traits (Finishing 1999).

The process can be divided into four steps based on the chemistry involved:

- Cleaning/Degreasing
- Activation/Conditioning
- Phosphating
- Posttreatment

2.1.1 Cleaning/degreasing

Degreasing is a pretreatment for the steel, mainly to clean and prepare the steel. Two methods are commonly used for degreasing and dependent on which solvents are chosen, it can be separated into aqueous cleaning or organic degreasing.

Chlorinated degreasing is a process where grease and oil is removed with chlorinated hydrocarbons. This is a less environmental friendly choice than organic degreasing. Alkaline degreasing is a form of organic degreasing, which involves NaOH and KOH and causing a pH of 12-14 (Ogle et al. 1999). Often many additives are added with alkaline degreasing, such as silicates, phosphates, borates, carbonates and complexing agents (Ogle et al. 1999). The choice of cleaning is dependent on the type of dirt needed to be removed and also the substrate (Quitmeyer 2006).

2.1.2 Activation

The activation step consists of a titanium oxide colloid solution treatment that forms growth places for the phosphate crystals. This results in shorter reaction times as well as smaller crystals of the phosphate (Ogle et al. 1999). This process is known to be sensitive to changes in pH, temperature and water hardness.

2.1.3 Phosphating

The phosphating process involves treating the metal pieces with an acidic phosphate solution. A surface layer of phosphates of iron and the alloying metals present in the steel is formed through a chemical process that proceeds under hydrogen evolution, with the whole process controlled by the acidity. The process self-inhibits when the surface is covered by phosphate crystals (Ogle et al. 1999). The phosphating step can be designed in two different ways: spray or immersion. Spraying is fast and guarantees a good size on the crystals. It is recommended for high volume production. One disadvantage is possible drag-over of contaminants (Ogle et al. 1999).

Immersion means that the product is being dipped/immersed in a bath. The advantage is less drag-over of contamination, lower cost and maintenance needed (Ogle et al. 1999), but this method is not as suitable for high volume production (Quitmeyer 2006).

From the phosphating process a byproduct in the form of a sludge is common. It consists of oxidized iron that has formed insoluble phosphates. Other byproducts are phosphate precipitations with other metals, that forms a scale on the equipment due to heating, since metal phosphates are less soluble at higher temperatures(Ogle et al. 1999). Often a lot of valuable metals are found in the sludge, e.g. zinc and iron (Kuo 2012).

2.1.4 Posttreatment
Posttreatment consist of sealing the surface by forming oxides, hydroxides and phosphates on the metal surface, thereby interlocking the conversion coating (Ogle et al. 1999). The sealing can be done as a normal water rinse or a chromic acid sealing, finishing with another rinse and optional drying (Quitmeyer 2006).

2.1.5 Phosphate conversion process at Volvo Group Trucks Tuve
The surface treatment process at Tuve consist of 13 steps, where the phosphating process is performed in step 5, seen in Figure 1.

Wastewater is formed at several stages in the process, see the schematic layout of Tuve site Figure 1. Therefore, the composition of the wastewaters varies at different stages of the process. The final wastewater consists of streams from step 3, 6, 7, 8 and 9 and they are combined into two tanks.

Surface treatment Volvo Tuve

0	1	2	3	4	5	6	7	8	9	10
Steel blaster	Pre degrease	Degrease	Rinse	Rinse/Activation	Phosphating	Rinse	Rinse	Rinse	DI rinse	Drying

13	12	11
Cooling	Oven	Paint

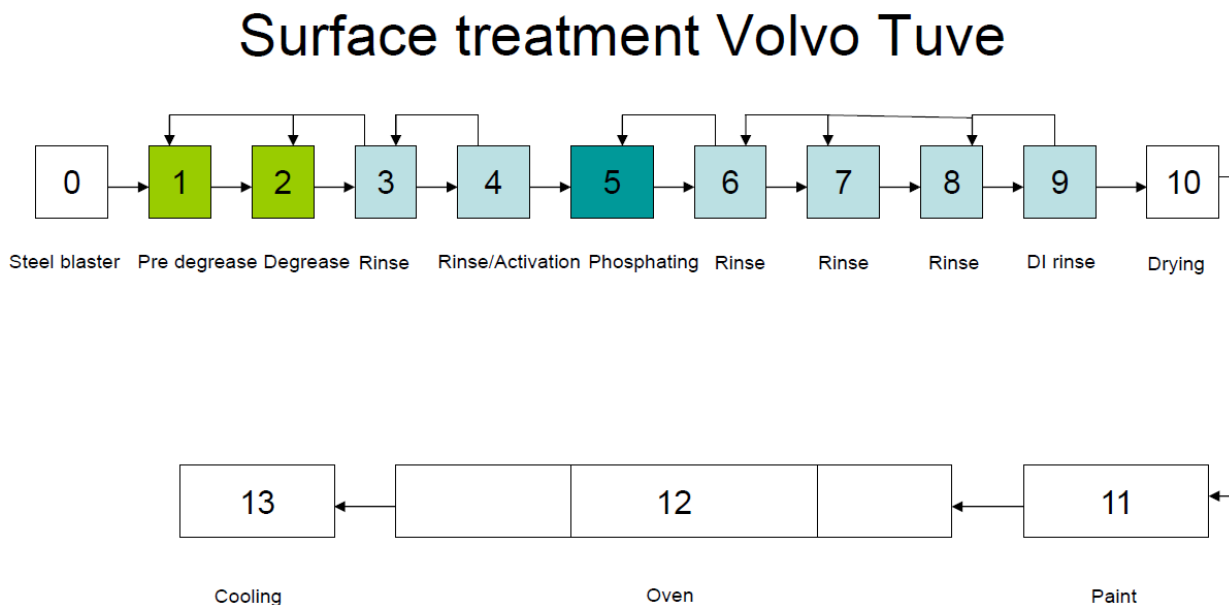**FIGURE 1: LAYOUT OF PHOSPHATE CONVERSION COATING PROCESS AT VOLVO GROUP TRUCKS TUVE** (The chemquest group 2000)

Gardobond 26 (The ChemQuest Group 2000) is added at the start of conversion coating in step 5. It is a solution of water soluble inorganic salts e.g. zink diphosphate, other metal phosphates, nickel nitrate, manganese dinitrate and manganese phosphate (ChemetallAB 2010), mixed with the drag over from previous step.

To monitor the processes, samples of process water from the outflow from step 5 are analyzed with ICP by Chemetall AB. The results from some test dates are presented in Table 1.

TABLE 1: ICP RESULTS FROM CHEMETALL AB

Content	Concentration 14/04/01 (Chemetall AB n.d.)	Concentration 14/05/27 (Chemetall AB n.d.)	Concentration 14/06/27 (Chemetall AB n.d.)
Aluminum	2 mg/l	4 mg/l	3 mg/l
Boron	-	1 mg/l	1 mg/l
Calcium	6 mg/l	3 mg/l	4 mg/l
Cobalt		-	1 mg/l
Iron	4 mg/l	3 mg/l	2 mg/l
Potassium	68 mg/l	72 mg/l	0.11 mg/l
Magnesium	2 mg/l	1 mg/l	2 mg/l
Manganese	0.34 g/l	0.74 g/l	0.59 g/l
Sodium	7.6 g/l	5.3 g/l	7.4 g/l
Nickel	0.58 g/l	1 g/l	0.91 g/l
Phosphorous	5.4 g/l	7.6 g/l	5.0 g/l
Sulfur	97mg/l	0.12g/l	0.21g/l
Silicon	0.38 g/l	0.33 g/l	0.42 g/l
Zinc	0.41 g/l	0.57 g/l	0.83 g/l

The drag-over from activation baths is an interesting aspect in the calculations of the flows of phosphate, in some cases it is calculated to 5 liters/cab body (Swera IVF 2009). Chemicals that must be kept track of are phosphate, sodium, fluoride and titanium (Swera IVF 2009) also known as pollutants, due to their effect on the phosphating conversion. There is also a drag-over of chemicals from the phosphating step (number 5) to the rinse step (number 6-8) (Swera IVF 2009).

From earlier studies it has been concluded that reducing the wastewater volume is the most effective aspect in cost-saving for the phosphating conversion process (Swera IVF 2009). Due to the fact that fresh water is up to ten times cheaper than the cost for wastewater and that 80 % of the fresh water can be saved, also less fresh water will reduce the production of waste water and sludge(Swera IVF 2009). One economic incentive for recovery of phosphate is that the treatment of wastewater can cost as much as 100 SEK/m^3 and freshwater cost over 10 SEK/m^3 (Swera IVF 2009).
In the Volvo Group Trucks Umeå facility the reduction of wastewater volume and sludge production has been a priority for years and improvements have been done since 1996 (Lindskog 2008).

2.2 Phosphate recovery

The most common phosphate recovery from wastewater in Sweden is a combination of biological and chemical removal, also known as conventional three-step purification. This method is used by over 60 % of the municipal wastewater plants. The first step is mechanical cleaning by gratings, sand bed and pre-sedimentation to remove large objects such as stones, woodchips, paper, hair etc. (Naturvårdsverket 2008).

The second step is the biological step and consist of microorganisms feeding on the organic material and here most of the nitrogen is removed. The microorganisms forms flocs and sediments in sedimentations tanks (Naturvårdsverket 2008).

The third step is known as the chemical step, were the phosphate is removed from the water by adding precipitation agents. These contains aluminum or iron ions, which precipitates the phosphates aluminum or iron phosphates. Then the wastewater settles in sedimentations tanks before being returned to the natural waters. In this step up to 90 % of the phosphate is removed (Naturvårdsverket 2008).

Another method, tried in full scale in the United States and Canada, is called Ostara Pearl. With this method phosphate is precipitated from waste water with the help of magnesium chloride. The crystals formed are known as Struvite ($MgNH_4PO_4 \cdot 6H_2O$). After adding i.e. ammonia, the substance can be turned into pellets and reused as fertilizers on farms(Tideström 2012).

2.3 Different methods for phosphate recovery from conversion coating process

When working with metal finishing the wastewater will contain metals bounds to complexing agents, consisting of both organic and inorganic substances. These complexing agents will interfere in the recovery process. The reason for using a complexing agent is that otherwise the metals can precipitate on unwanted areas (Wang et al. 2004).

The separation methods of the metal complex can be divided into three groups (Wang et al. 2004).

- Pretreatment and hydroxide precipitation
- Modified hydroxide precipitation
- Other treatment: electrocoagulation (Kobya et al. 2010), adsorption and ion exchange (Wang et al. 2004).

2.3.1 Hydroxide precipitation with pretreatment

Here the process consist of a pretreatment that aims to destroy the complexing agents or transform them into a compound that cannot compete in the precipitation(Wang et al. 2004). A complex breaker is dimethyldithiocarbamate (DTC)(Wang et al. 2004). Another pretreatment is oxidation with chlorine and ozone.

2.3.2 Modified hydroxide precipitation

Here the treatment consists of modifying with other agents that the complex can bind to instead of the metals. It will induce higher pH and is also known as high pH precipitation (Wang et al. 2004).

2.3.3 Other treatment

Over the years many different treatments have been developed. Some of these treatments will be presented below.

Chemical precipitation is mostly used for removing phosphorous and not recover it for reuse, it is also the leading technique used today. It includes an addition of salts, mainly divalent metal salts that causes the precipitation, then after sedimentation separation, the sludge containing metal phosphates is separated from the water (Morse et al. 1998).

In electrocoagulation, charged particles agglomerate with an added chemical, coagulate and then subsequently sediment to the bottom. It will take place in a separation reactor, which is often in the form of a electrolytic cell, comprising sacrificial electrodes which removes the metals from wastewater(Mollah et al. 2001). The sacrificial electrodes are made of conductive metals and they can be placed in both monopolar and bipolar cells. In a bipolar cell the sacrificial anodes are not connected to any current (Mollah et al. 2001).

The process can be described in three steps(Mollah et al. 2001) :
1) Coagulants formed from the sacrificial electrodes by electrolytic oxidation.
2) Contaminants destabilized, suspension particulate and emulsion breaking
3) Flocculation of destabilized phases

Adsorption of phosphate can be done using a calcined double layer hydroxide, in which trivalent ions forms positively charged layers, that adsorbs the phosphate(Lv et al. 2008). The adsorption process is deemed easy and gives a lesser sludge production, it is not often used on solid waste (Kuzawa et al. 2006) and is easy to operate (Lv et al. 2008).

2.4 Phosphate recovery at Volvo Group Trucks Tuve

Most of the phosphate recovery methods only concentrate on removing phosphorous from the solution, but in the phosphate conversion process it could possibly be an advantage if the drag-over compounds were removed and the phosphorus solution recirculated back in the process.

In earlier studies done at Volvo Group Trucks Umeå, a combination of nanofiltration and reversed osmosis membrane filtration with evaporation, was tested in a phosphate conversion process on galvanized steel (Swera IVF 2009). At this study 77 % of the chemicals were retrieved, and the water consumption was reduced by 80 % (Lindskog 2008), but these two factories are not identical and the focus in the study was to reduce water consumption.

2.5 Solvent extraction

Solvent extraction is also known as liquid-liquid extraction and the process is driven by chemical reaction equilibrium (Rydberg n.d.). In solvent extraction there are two phases, usually one organic phase and one aqueous phase, also known as the feed phase (Kreider-Mueller 2014). The organic phase is usually the extractor and contains ligands that are designed to bind to the ions that are to be extracted from the aqueous phase and a diluent. The organic phase may also contain a modifier and synergistic agent (Kreider-Mueller 2014). The separation force in solvent extraction is the difference in chemical potential for the given substance between the organic and aqueous phases (Watarai 2008). During the separation process these two immiscible liquids interact through mixing. After mixing they are allowed to settle and thereby separating back into two phases due to the density difference. It is important that the two liquids have a low mutual solubility, but it cannot be zero since then the wanted substance cannot be extracted (Seader & Henley 2006). For a successful extraction to occur the phases in the mixture must interact and important is therefore the droplet size, smaller droplet size gives a larger interaction area and thereby an larger dispersion(Jan Rydberg 2004) .

The purpose of the feed phase is to dissolve acids and contaminations in the water (Kreider-Mueller 2014), hence an important aspect of this separation method is the properties of the liquids, such as viscosity, surface tension, density and polarity (Kreider-Mueller 2014).

The main focus of this work was to see if the chosen ligand will connect to the phosphate and thereby be able to separate it from the wastewater. The chosen ligand is tri-capryl-methyl-ammonium chloride (in short TCMA). Its chemical structure can be seen in Figure 2. It is an ionic liquid with a quaternary ammonium ion with three octyl groups, a methyl group and a chloride ion, to balance the charge of the ammonium (Rikard Ylmén, personal communication).
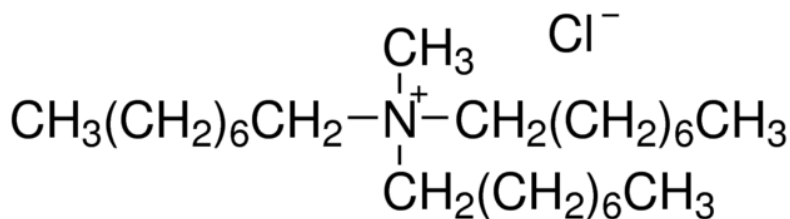
FIGURE 2: TCMA MODEL(SIGMA ALDRICH.)

One of the solvents chosen as diluent for the ligand was 1-octanol, due to its polar properties and that it is environmentally friendly. The other organic solvent that was chosen was kerosene, due to its non-polar properties(Atkins & Jones 2004) and because it is cheap.

2.6 Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES also known as inductively coupled plasma atomic emission spectrometry (ICP-AES)(Leclercq et al. 2015) consist of aerosol generation, aerosol transportation, excitation/ionization and detection of metals and other elements (Leclercq et al. 2015). The generation and transportation of aerosol can also be called the sample preparation system.

The carrier gas used was argon, due to its properties as an inert gas, that gives a useful plasma for analyzes. Argon also has a minimal reactivity with samples and therefore minimizes unwanted interference (Chabert 2011). The aerosol generation is where the liquid sample is transformed to an aerosol through a nebulizer(Arai 2001). The aerosol transportation step is when the sample passes the spray chamber(Leclercq et al. 2015) that separates the big droplets from the smaller(Arai 2001). The small droplets then goes to the plasma and the big droplets goes to waste(Leclercq et al. 2015).

The torch is made out of three quartz tubes(Arai 2001) to withstand the temperatures occurring with argon use (Chabert 2011). The sample is applied in the center tube (Chabert 2011), and the other two shape the plasma torch but also protects the sample from melting (Chabert 2011). Surrounding the torch is a Radio-frequency generator (RF generator)(Chabert 2011). It supplies an oscillating magnetic field(Arai 2001), and a coil connects it to the plasma (Chabert 2011).

The magnetic field will speed up the electrons that crashes with the argon gas, and the suspended elements which causes ionization(Arai 2001). The ionized sample will emit photons of light, the energy of these photons can be expressed in wavelength, and are specific for each elements (Arai 2001)and thereby forms an optical emission spectra(OES). The resulting data are presented in counts and can after that be used to calculate concentrations for each element.

3. Experimental

The focus of the experiments was solvent extraction of phosphate from the wastewater from step 6 of the phosphate conversion process (see Figure 1). Another part was aimed at the filtered sludge where different acids were tested to see if the sludge could be dissolved.

3.1 Analysis of elements in aqueous solutions

First the content of the waste water was analyzed with ICP-OES, the waste water was tested for 28 elements. For calibration a stock solution consisting of HNO_3, containing 0.4 g of each of the elements listed in Table 2:

TABLE 2: CONTENT OF INTERNAL STANDARD FOR THE ICP-OES

Al	Ca	Fe	Mn	P	Si	Zn
As	Cd	K	Mo	Pb	Sn	Zr
B	Cr	Li	Na	S	Sr	
Ba	Cu	Mg	Ni	Sb	Ti	

To be able to analyze the process water it had to be diluted 1:10 and 1:100, since there was no knowledge on the concentration of the samples. A too high concentration is not recommended in the ICP-OES, since high concentration is not measurable with ICP and it can also interfere in the measuring. Each test was done in a triplet.

3.1.1 Solvent extraction

Solvent extractions experiment for phosphate recovery were done in the following way:
For solvent extraction of the phosphate, two different solvents were used: 1-octanol and kerosene (Solvent 70). To both solvents a TCMA was added in three different concentrations: low (3 volume-%), medium (10 volume-%) and high (30 volume-%). Since the TCMA is a very viscous liquid, it is hard to mix a 3 % concentration from pure solution, due to the fact that it is difficult to get an accurate small amount of TCMA in the micropipette. Therefore it was reasonable to dilute a part of the 30 % solution into 3 % instead.

For the 30 % TCMA sample 7.5 ml TCMA was added to 17.5 ml 1-octanol.
From the 30 % TCMA sample, the 10 % TCMA was constructed through diluting 2 ml 30 % TCMA with 18 ml 1-octanol.
For the 1-octanol solvent extraction two different temperatures was tried,25°C and 40 °C. The later temperature is the temperature at which the wastewater at Volvo Group Trucks Tuve is retrieved.

Since the ligand contains chloride as a counter ion, it was foreseen that this ion could interact unfavorably with the phosphate ion extraction. Therefore the chloride ions needed to be replaced before the solvent extraction to improve extraction. The 25 °C 1-octanol samples were done both with and without an ion exchange with KOH. The ion exchange was constructed so that 5 ml of the wastewater sample and TCMA was added to a 12 ml vial. Subsequently 7 ml of 3M KOH was added, and the vials was hand shaken for 2 minutes. The vials were left for settling for one hour, allowing separation of the phases to be done.

Each sample for solvent extraction was prepared in the same way, i.e. each vial was prepared with equal amount of wastewater and the solvent phase and all sample vials were agitated in a water-heated shaker for 10 minutes as a part of the solvent extraction.

Since some of the samples show a precipitation after the solvent extraction, it was decided to use a centrifuge on all the samples to increase separation of the two phases. The centrifuge was set at 5000 rpm for 5 minutes.

To analyze the samples in the ICP-OES the samples were diluted, so a sample of 0.1 ml was added to 9.9 ml HNO_3, with the concentration 0.1 M.

3.2 Sludge

At Volvo Tuve the sludge goes through a filter press that removes a lot of water and then collected as a sludge cake which was a hard substance. Three different acids (HCl, H_2SO_4 and HNO_3), in three different concentrations (concentrated, 6M and 3M) were used to try to dissolve the solid sludge. To maximize the interaction between acid and sludge, the sludge cake was ground into a fine powder, as seen in Figure 3.

The first test was to see if sludge cake could be dissolved, so 1 g of sludge cake powder was put in a beaker, and then covered with equal amount of 3M solutions of either HCl, H_2SO_4 or HNO_3. The same procedure was done with 6M acid solution and concentrated acids. All the samples were allowed to react overnight.

The following test was to take 1 g sludge cake powder and cover it with concentrated HCl, and 2 ml of H_2O_2, to assure that all solid particles dissolved before ICP-OES. Then the samples were diluted 1:10 and 1:100 since the concentration of elements in the sludge were unknown.

FIGURE 3: GROUND PHOSPHATE SLUDGE CAKE

4. Results

For the process water the elemental analysis was done only for K, Na, Ni, Mn, P, Si, and Zn. After studying the results from Chemetall AB, these elements were considered the most likely to appear in process water in higher amounts. Therefore, the analyses of the samples were done on only these eight and not for all 28 elements. For the dissolved sludge, the analyses were the same as for the waste water but included Fe as well.

4.1 Analysis of untreated waste water

The results of the analyzed process water are presented in detail in table 4, and in entirety in appendix A. For a simpler overview the average value of the triplets will be used, some triplets of data contained outliers. The outliers were removed from the average and the revised average were marked with *. The first row in Table 4 are the ICP-OES analysis results for the untreated waste water. These were used as the reference point for the ICP results from the extraction. The reference point chosen is the 100 times diluted sample, since the 10 times diluted samples showed incoherent results, which are believed to be the results of the high concentrations in the samples.

TABLE 4: CONCENTRATION OF ELEMENTS IN THE AQUEOS PHASE AFTER SOLVENT EXTRACTION (AVERAGE OF THREE RESULTS. ALL ORGANIC PHASES WERE BASED ON OCTANOL

Set	Fe [mg/dm³]	K [mg/dm³]	Mn [mg/dm³]	Na [mg/dm³]	Ni [mg/dm³]	P [mg/dm³]	Si [mg/dm³]	Conc Zn [mg/dm³]
Original waste water sample	25,6	30,1	85,3	1180	139,1	559	57,2	82,1
3 % TCMA-Cl 25 °C	11,9	32,5	85,5	911	139	643	54,9	804
10 % TCMA-Cl 25 °C	13,1	31,0	84,6*	903	137	552	48,5	790
30 % TCMA-Cl 25 °C	18,8	31,9	83,9	883	139	539	46,7	792
3 % TCMA-OH 25 °C	19,6	114	4,33	922	13,8	278	47,7	53,8
10 % TCMA-OH 25 °C	10,7	139	1,07	896	8,71	92,6	44,9	28,5
30 % TCMA-OH 25 °C	10,5	86,7*	0,96	949	8,84	20,5*	40,9	29,8
3 % TCMA-OH 40 °C	10,8	169	1,44	913	9,95	280	47,0	29,1
10 % TCMA-OH 40 °C	10,6	135*	0,88	919	8,47	71,0*	48,3	11,7
30 % TCMA-OH 40 °C	10,5	542*	0,93	955	8,74	32,0*	41,1	6,1

4.2 Solvent extraction results

4.2.1 Extraction with TCMA-Cl in 1-octanol at 25 °C

First set (sample 10, 11 and 12) consisted of an organic phase with 3 % TCMA in 1-octanol and the liquid phase process water at 25 °C. There was no change in color or consistency, from before or after centrifuging and all three samples were clear fluids (as seen in Appendix B Figure B1).

After the calculations of the ICP-OES results (seen in Table 4) the concentration was almost the same, therefore there seems to be no extraction and it seems to be a measurement error or contamination in case of the phosphor, since it has increased in the sample instead of been removed.

Second set (sample 4, 5 and 6) consisted of an organic phase 10 % TCMA in 1-octanol and the liquid phase process water at 25 °C. The samples were all containing a homogeneous clear fluid, and no change in color or consistency, before or after centrifugation (as seen in Appendix B Figure B2). The calculations of the ICP-OES results (seen in table 4) show an increase of zinc but no extraction, supported by nearly no change of the amounts left in the sample after extraction.

The third set (sample 7, 8 and 9) consists of an organic phase 30 % TCMA and 1-octanol and the liquid phase process water at 25 °C. Clear fluids both before and after centrifugation (as seen in Appendix B Figure B3). After the calculations of the ICP-OES results it is clear that the wanted extractions has not occurred.

4.2.2 Extraction with TCMA with KOH ion exchange in 1-octanol at 25 °C

The next batch of samples were a combination of process water with 1-octanol as solvent, at 25 °C and a variation of the concentration of TCMA. But in these samples a KOH ion exchange was added to see its effect on TCMA.

Fourth set (sample 1, 2 and 3) consists of an organic phase 3 % TCMA in 1-octanol the liquid phase process water at 25 °C and were treated with a KOH ion exchange, before the solvent extraction was executed at 25 °C. The first obvious results were that one sample had some residue occurring in form of a top partition, which do not occur in the other two. As also seen in Appendix B Figure B4, after the centrifuge the samples were coherent except for sample 1 and 2 where some sediment occurred after the centrifuge. After the calculations of the ICP-OES results it was clear that half of the phosphorous had been extracted but manganese and nickel had also been extracted, unfortunately it seems a lot of zinc had been extracted as well.

Fifth set (sample 13, 14 and 15) consists of an organic phase 10 % TCMA in 1-octanol, the liquid phase process water at 25 °C and a KOH ion exchange, before a solvent extraction was performed at 25 °C. All three samples had a residue top phase after solvent extraction. After centrifugation, a two-layer boundary phase of residue, the first a white coloured and the second a brown coloured, as can be seen in Appendix B Figure B5. After the calculations of the ICP-OES results these show a success since most of the phosphorous has been extracted, but also manganese, some sodium, nickel, and zinc have been extracted.

Sixth set (sample 16, 17 and 18) consists of an organic phase 30 % TCMA in 1-octanol and the liquid phase process water at 25 °C and a KOH ion exchange, before a solvent extraction was performed at 25 °C. A clear difference between one sample and the others was seen, both after solvent extraction and after centrifugation, seen in Appendix B Figure B6. After the calculations of the ICP-OES results it seems to be the best extraction of phosphorous in theses series but sample 18 is inconclusive for potassium, phosphorous and zinc extraction. The brown top partition is a residue phase, that do not occur in sample 18 and therefore the results for sample 18 is discarded from the average value for potassium, phosphorous and zinc, the reviewed values are marked with *.

4.2.3 Extraction with TCMA with a KOH ion exchange in 1-octanol at 40 °C

The last 1-octanol samples was a combination of process water with 1-octanol as solvent, with a variation of the concentration of TCMA, these also had a KOH ion exchange. But instead the temperature was changed to 40 °C since the process water has this temperature in the factory.

Seventh set (sample 19, 20 and 21) consist of an organic phase 3 % TCMA in 1-octanol and the liquid phase process was water at 25 °C with KOH ion exchange, before a solvent extraction was performed at 40 °C. All samples show residue after solvent extraction but more residue in 20 and 21 after the centrifuge, seen in Appendix B Figure B7.
After the calculations of the ICP-OES results, sample 20 was deemed unfit in regard for nickel and therefore excluded from the average value for nickel, and the reviewed value is marked with *. The revised results show a good extraction of phosphorous since more than half of it is removed.

Eighth set (sample 22, 23 and 24) consist of an organic phase with 10 % TCMA in 1-octanol and the liquid phase was process water at 25 °C with a KOH ion exchange, before a solvent extraction was performed at 40 °C. Sample 22 and 23 both have a milk-like yellow residue and a clear bottom phase, were sample 24 has a clear phase and yellow brown residue bottom phase, (seen in Appendix B Figure B8). After centrifuge both 22 and 23 has a three-phased system with top and bottom phase which are clear and the phase boundary which has a white and brown residue. Sample 24 is a two-phase system after centrifuge and a brown sediment.
After the calculations of the ICP-OES results, it was clear that sample 24 have been compromised therefore its result for phosphorous was excluded from the average results, and the revised average value marked with *. The new average results show a good extraction of phosphorous but seems to have also extracted manganese, nickel and zinc.

Ninth set (sample 25, 26 and 27) consists of an organic phase with 30 % TCMA in 1-octanol and the liquid phase was process water at 25 °C with a KOH ion exchange, before a solvent extraction was performed at 40 °C. Sample 25 and 27 show the same response to solvent extraction, a two-phase system with a brown milk-like residue top phases and white milk-like bottom phases, (seen in Appendix B Figure B9). Sample 26 has a milk-like white top phase and a more residue yellow brown bottom phase.

After the calculations of the ICP-OES results sample 26 differs for potassium, phosphorous and zinc, it was excluded from the average and the new average value is marked with * in Table 4. This set has one of the highest extraction of phosphorous but also a very high extraction of manganese, nickel and zinc, and something is off with the reading on potassium.

4.2.4 Extraction with TCMA with a KOH ion exchange in kerosene at 25 °C
The following samples were supposed to reflect on the importance of solvents, so therefore a combination of process water at 25 °C and a variation of the concentration of TCMA was used. But in these samples the solvent was kerosene.

Tenth set (sample 28, 29 and 30) consist of an organic phase with 3 % TCMA in kerosene the liquid phase was process water at 25 °C with a KOH ion exchange, before a solvent extraction was performed at 25 °C. All three samples have two clear phases, as seen in Appendix B Figure B10.

Eleventh set (sample 31, 32 and 33) consist of an organic phase with 10 % TCMA in kerosene and the liquid phase was process water at 25 °C with KOH ion exchange, before a solvent extraction was performed at 25 °C. All three sample show different phases seen in Appendix B Figure B11, 31 has two clear phases, 32 has form one white milk-like phase and 33 has three phases top and bottom phases are white milk-like and middle phases is a brown milk-like phases.
After centrifuge sample 31 is still two clear phases, 32 is now at least three phases: top phase is clear, next brownish and a white milk-like boundary phase and sample 33 is two clear phases, a brown boundary layer and a bottom white milk-like phase.

The test with kerosene showed many different results but none indicated complete mixing and separation so after conferring with other results using kerosene and TCMA, therefore samples 28 to 33 were excluded and not analysed with ICP-OES. The reason kerosene did not work as solvent is perhaps that kerosene is nonpolar and therefore harder to solve in water (Atkins & Jones 2004) and therefore the TCMA have not interact with the waste water sample.

4.3 Dissolving sludge

At first it seemed that only the concentrated HCl, managed to dissolve the sample, turning the sample yellow brown. The 6M HCl had the same effect but with some residue left in the bottom of the cup. To be sure that all residue was dissolved some drops of H_2O_2 was added to the solution, results are seen in figure 4. It seems that the concentrated acid work best.

FIGURE 4: RESULTS OF DISSOLVING SLUDGE CAKE
LEFT: CONCENTRATED HCL AND SLUDGE CAKE   MIDDLE: 6M HCL AND SLUDGE CAKE   RIGHT: 3M HCL AND SLUDGE CAKE

The concentrated H_2SO_4 had a reaction with the sample but instead of dissolving it, a new precipitate was formed. The precipitation was a milk-like grey/black nature, seen in figure 5. Some of the residue remained after two weeks.
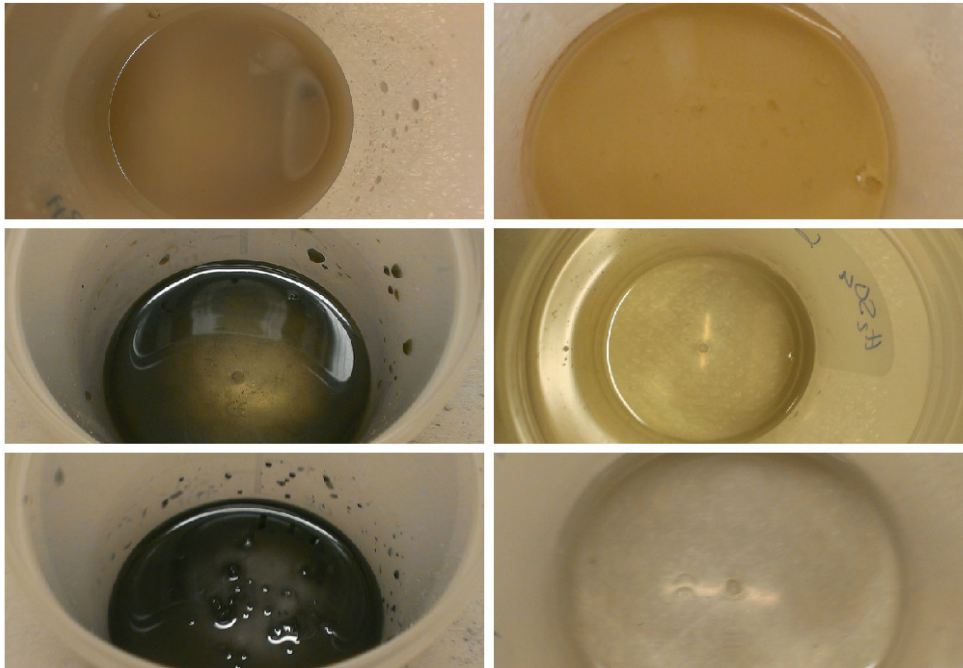

FIGURE 5: RESULTS OF DISSOLVING SLUDGE CAKE
TOP LEFT: CONC. H_2SO_4 AND SLUDGE CAKE   TOP RIGHT: TWO WEEKS LATER
MIDDLE LEFT: 6M H_2SO_4 AND SLUDGE CAKE   MIDDLE RIGHT: TWO WEEKS LATER
BOTTOM LEFT: 3M H_2SO_4 AND SLUDGE CAKE   BOTTOM RIGHT: TWO WEEKS LATER

The least dissolution could be seen with HNO_3 in any concentration, where even after two weeks the residue from the sludge remain in some of the cups, both seen in figure 6.

FIGURE 6: RESULTS OF DISSOLVING SLUDGE CAKE
TOP LEFT: CONC. HNO_3 AND SLUDGE CAKE   **TOP RIGHT: TWO WEEKS LATER**
MIDDLE LEFT: 6M HNO_3 AND SLUDGE CAKE   **MIDDLE RIGHT: TWO WEEKS LATER**
BOTTOM LEFT: 3M HNO_3 AND SLUDGE CAKE   **BOTTOM RIGHT: TWO WEEKS LATER**

5. Discussion

The first results were that this separation process was sensitive, which are seen from all the samples with residue fallout. Many samples show this result directly after the water-heated shaker and they could had been discarded and excluded from the rest of the experiments but were included now to affirm the results. However, these samples were also the ones with the best phosphorous extraction results. A residue phase is not preferable in industrial extraction, since it would need another separations step, and in this experiment, we used a centrifuge. The formation of a residue or third phase usually accounts to a wrong choice of solvent, this was foreseen and therefore the KOH ion exchange introduced. Perhaps another solvent can reduce the brown precipitation in some of the samples, also lead to better extraction. Hence, there is a need to proceed with further tests.

After studying the set of samples with KOH ion exchange, it was concluded that the chlorine ions do interfere in the extraction, therefore the KOH ion exchange is necessary for a good extraction. In the samples with KOH ion exchange the ICP-OES readings has an increase of potassium in the aqueous phase from the KOH. This should be future studied and perhaps a smaller amount of KOH ion exchange will give the same or a better separation result.

Since there probably is a surplus of potassium from the KOH ion exchange, there could also be a change of the pH from the OH ions, this could be the explanation for the brown precipitation seen in some samples, since it could be $Mn(OH)_2$ precipitation that easily oxidizes to brown MnO_2. The effect on pH was not considered during these experiments and this could be furthered tested and perhaps another wash can be considered.

The amount of TCMA can be studied further to find the optimal amount of TCMA. The 3 % TCMA samples show the less phosphorous extraction and in further experiment be excluded.
For the samples with 10 % TCMA it seems that there is a correlation with the amount of phosphorous extraction and pollutants also being extracted. It seems that the amount of TCMA should be between 10 and 30 %, but the right amount of TCMA is hard to determine from so few tests. Especially since the best results is found in 30 % TCMA and 25 °C but the 30 % TCMA in 40 °C set also had good results but had the most interfering results on the manganese, nickel and zinc, and had been discarded.

Sodium, is known as one of the phosphating bath pollutants and must be checked to stay under a certain level for the process to provide the wanted outcome, it is also known to accumulate in the system. The increase of sodium in the extraction, could be an effect of the KOH ion exchange used and this need to be examined, if recycling of this feed is considered. Since the successful phosphor extraction with 10% TCMA did not coincide with sodium extraction, this a positive outcome and should be studied further. In addition, bath pollutants should be studied further, perhaps an ion exchange that removes unwanted substances could be added. Or another ion exchange added with another ligand removing substances. Since no test was made with stripping some of the substances can be left in raffinate phase.

Seen in the results is a high extraction of nickel and zinc, these two elements might not influence the phosphating conversion process but could cause other problem at high concentrations. High zinc concentrations are not preferable, since it is an environmental hazard. The nickel is affected by the suspected change in pH and could accumulate in the waste water and are therefore necessary to remove. The question raised is the intent of the waste water. Is the purpose to recycle the waste water

with phosphorous in it, to reduce the amount of phosphorous needed in the process or should the phosphorous be extracted and sold for other use. If the choice is to recycle the waste water with phosphor, then this extraction should instead be focused on removing other substances than the phosphor. If the purpose is to extract the phosphorous to sell it for further use, then the concentration of zinc and nickel is a problem. Since most phosphorous is used as fertilizer and zinc is a substance not wanted in fertilizers. Also, the supposable raise of pH could lead to a $Ni(OH)_2$ precipitation also not wanted in any products. The effect of nickel and zinc should be studied since these substances have shown to be strongly extracted in this process, perhaps this can be altered in a stripping process. Another aspect is multiple stage extraction to remove unwanted substances, which is not uncommon in this field.

Since the temperature on the waste water does not seem to affect the results, the most sensible action would be to continue doing the testing at 40 °C, to reduce cost if this would be implemented at site. The point of recycling phosphorous was to reduce wastewater cost, but if there instead creates a cost in form of wastewater of KOH ion exchange and perhaps also further waste from the stripping process to retrieve the phosphor the suggested process is not economically viable. A comparison of the cost of phosphorous recycling and the waste production from recycling should also be done.

Another aspect of the extraction is to test if the centrifugation after extraction affects the results or not, it depends on the density of the liquids and some solvent extractions are performed with a centrifugal extractor to reduce another time-consuming step and energy consumption.

Today's filtration of process water produces sludge, which has to be dissolved to make it possible to recover the phosphorous in it. The filtration step is perhaps a redundant process that only hinder the recycling process. Since it is both time consuming and not user-friendly to use strong acids in industry, if filtration is still wanted, perhaps further testing on different combinations of acids or other dissolving agents should be tested. Another interesting study is to see if the large amount of iron could be extracted from the sludge or even the waste water before filtration. The choice also here depends on the purpose of the extraction, reuse in process or extraction for trade.

In multiple sets there seems to be something interfering with the potassium, whether it is just in the ICP readings or an unwanted reaction in the sample, is hard to say without more experiment. As seen in Appendix B Figure B4 only sample 1 has formed an emulsion phase, this could explain some of the irregularity of the samples, since the origin of the emulsion phase is unclear.

Another question would be how to recycle the KOH ion exchange if implemented at site, seems a setback if reducing the phosphorous amount in wastewater would create another waste water in the form of a KOH ion exchange instead. Also, the stripping can lead to further waste that also need to be considered.

The best results for phosphorous extraction is found in the samples with KOH ion exchange and with 10 % TCMA and were independent on temperature. Also, a more comprehensive series of samples should be performed to confirm this result, since many of the results came from sets that had at least one sample that had to be revised. As discussed at the presentation another testing could be done with another set up in the ratio of solvent and extractor, since this ratio has been shown to have an effect on the results.

6. Conclusion

Due to many questions still pending there is no clear conclusion that can be drawn from these results and therefore more experiments are needed before it could be determined if the solvent extraction process using TCMA could work or not. It was clear from the results from the present work that the process managed to remove a significant part the phosphate from the waste water but it is unclear if this phosphorous ended up in the organic phase or in the third phase that was formed. However, before continuing the first question to consider, is regarding the purpose of recycling the phosphor; is the phosphorous supposed to be recycled, as recycle feed in the phosphating process, or is the phosphorous supposed to be retrieved and used for other purposes, for example as fertilizer?

If continuing the development of the solvent extraction process for extraction of phosphate from the waste water by TCMA the amount of TCMA should be between 10 % and 30 %, since lower concentration did not give any sufficient results. To reassure less interaction with Cl-ions the KOH ion exchange is needed but given all the residue production noticed after the KOH ion exchange, perhaps another ion exchange should be tested. The temperature seems to be a non-issue so therefore it would be energy efficient for the industry to continue the experiments with 40 °C.

One question raised is if this process will provide more wastewater than it reduces, this should also be taken into consideration. Another question is the sludge production, perhaps it would be better to reduce the metals before the filtration and therefore reducing one waste component.

None of the results for the sludge is suitable for industrial design since highly concentrated acid are not to recommended for industrial use, but if there were more time it could be explored if any other combination of acids or dissolving agent can dissolve the sludge.

If continuing with this method I suggest the following:

- Continue testing with other solvents to reduce brown residue.
- Study the source of potassium surplus
- The effect of pH change
- Testing out suitable amount of TMCA, starting at 10 %
- Test the ratio of solvent and extraction for better results
- Test other ion exchange combination
- Study if centrifugation affect the results?
- Try if another separation method could be chosen instead of water-heated shaker?
- Decide if the purpose is to recycle the waste water with phosphorous in it, to reduce the amount of phosphorous needed in the process or should the phosphor be extracted and sold for other use.

Appendix A. Results of ICP-OES

Set	Sample	Conc Fe [mg/dm³]	Conc K [mg/dm³]	Conc Mn [mg/dm³]	Conc Na [mg/dm³]	Conc Ni [mg/dm³]	Conc P [mg/dm³]	Conc Si [mg/dm³]	Conc Zn [mg/dm³]
Original waste water sample		0,25	0,30	0,85	11,8	1,39	5,66	0,56	0,82
		0,25	0,30	0,84	11,7	1,37	5,54	0,56	0,80
		0,27	0,31	0,86	11,9	1,41	5,58	0,59	0,84
3 % TCMA and Cl in octanol at 25 °C	10	0,12	32,9	88,3	942	144	657	56,2	829
	11	0,12	33,2	85,6	899	139	647	54,8	808
	12	0,12	31,2	82,6	891	134	625	53,6	773
10 % TCMA and Cl in octanol at 25 °C	4	0,13	30,7	3,38	918	136	546	48,2	786
	5	0,13	31,9	83,1	873	141	567	49,6	816
	6	0,13	30,2	86,0	913	133	542	47,5	768
30 % TCMA and Cl in octanol at 25 °C	7	0,19	32,5	81,7	862	142	544	47,0	808
	8	0,19	30,8	87,5	918	134	526	45,8	764
	9	0,19	32,4	82,4	869	141	546	47,3	803
3 % TCMA and OH in octanol at 25 °C	1	0,36	125	6,09	924	15,7	272	48,0	72,5
	2	0,12	127	3,51	924	12,7	272	45,2	47,9
	3	0,11	90,7	3,38	918	13,2	290	50,0	41,1
10 % TCMA and OH in octanol at 25 °C	13	0,11	147	1,65	919	9,78	76,5	46,3	33,5
	14	0,11	129	0,71	834	7,62	115	42,3	24,6
	15	0,11	139	0,86	936	8,74	85,7	46,0	27,3
30 % TCMA and OH in octanol at 25 °C	16	0,11	185	1,37	1020	10,1	24,5	32,4	33,6
	17	0,11	75,4	0,85	958	8,64	16,5	28,0	26,1
	18	0,10	0,00*	0,65	868	7,74	495	62,4	378*
3 % TCMA and OH in octanol at 40 °C	19	0,11	179	1,40	919	9,54	276	47,5	27,6
	20	0,11	164	1,11	899	90,6*	281	47,2	24,5
	21	0,11	164	1,82	920	10,4	282	46,4	35,2
10 % TCMA and OH in octanol at 40 °C	22	0,11	146	1,02	915	8,78	76,6	45,7	28,1
	23	0,11	124	0,92	923	8,44	65,3	44,9	2,58
	24	0,11	2146	0,70	917	8,19	399	54,2	4,26
30 % TCMA and OH in octanol at 40 °C	25	0,10	162	0,78	967	8,76	17,3	29,3	2,53
	26	0,11	4450*	1,03	952	8,71	238*	56,8	12,0*
	27	0,11	922	0,98	945	8,76	46,6	37,3	3,79

Appendix B. Sample pictures
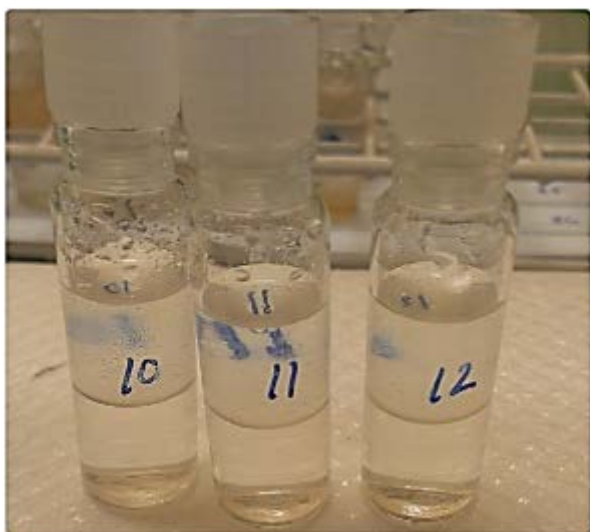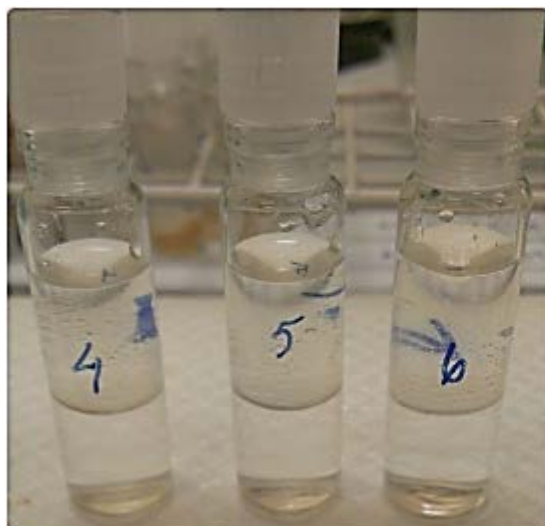

B1: SAMPLE 10, 11, 12
LEFT: AFTER SOLVENT EXTRACTION   **RIGHT: AFTER CENTRIFUGE**
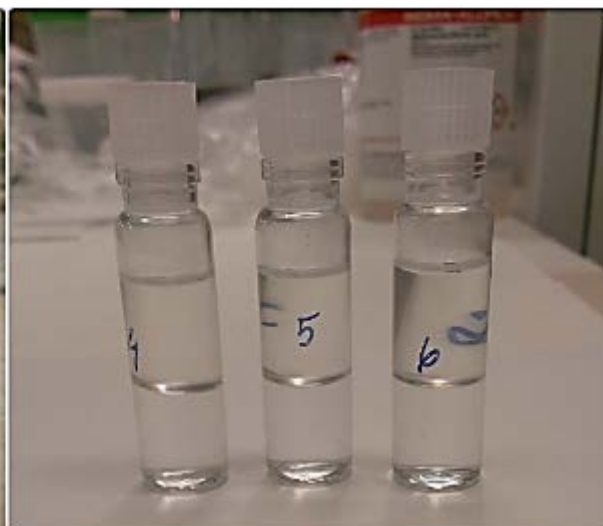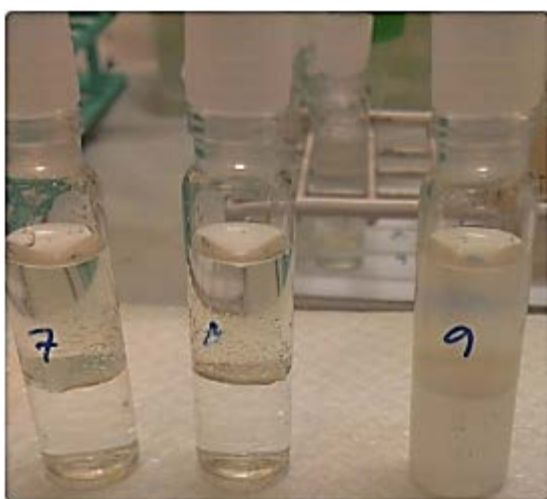

B2: SAMPLE 4, 5, 6
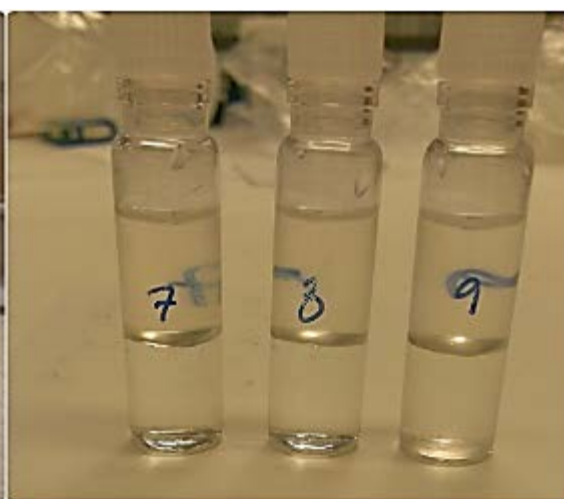**LEFT: AFTER SOLVENT EXTRACTION**   **RIGHT: AFTER CENTRIFUGE**
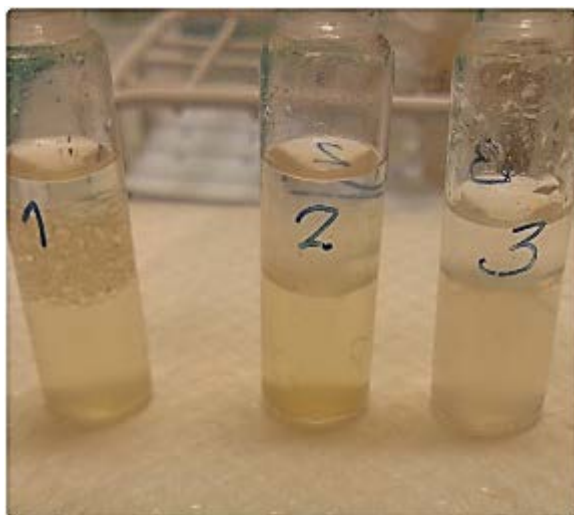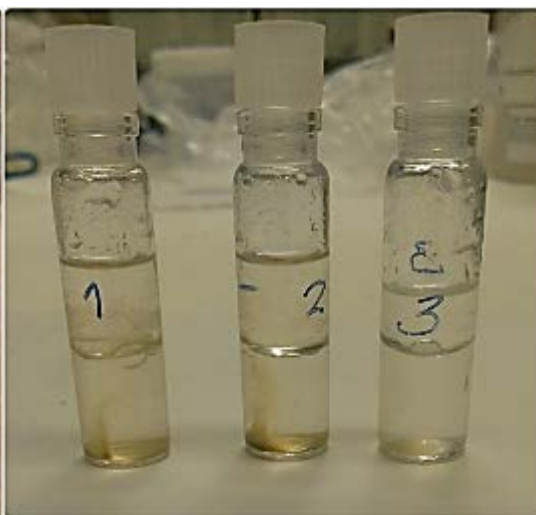

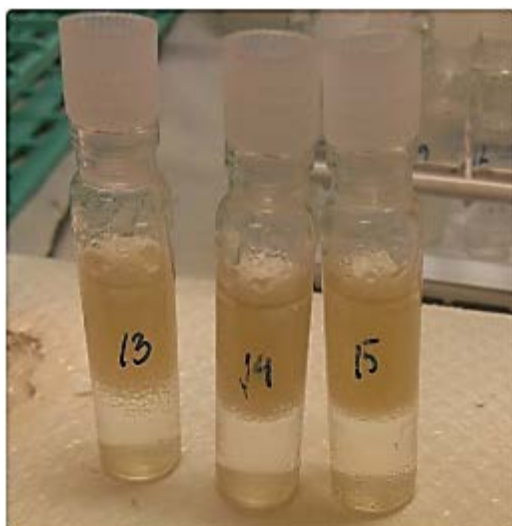**B3: SAMPLE 7, 8, 9**
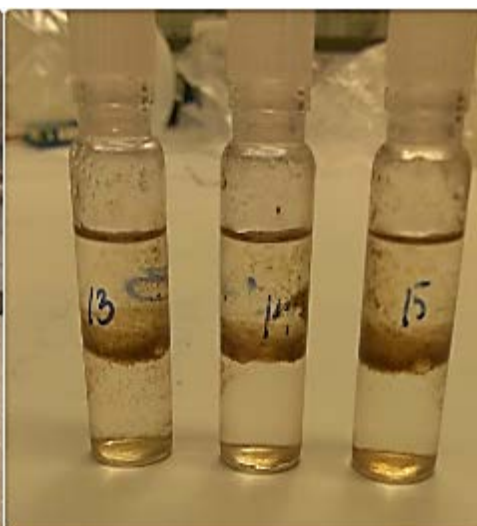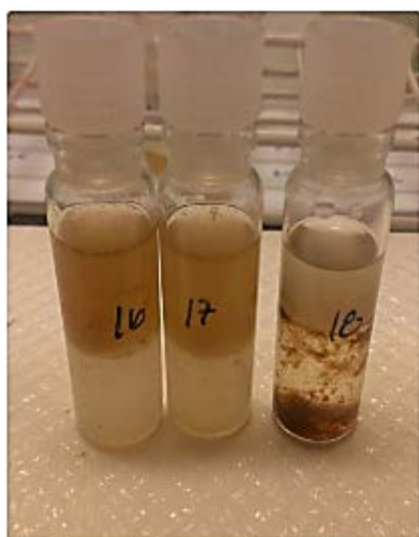**LEFT: AFTER SOLVENT EXTRACTION**   **RIGHT: AFTER CENTRIFUGE**

B4: SAMPLE 1, 2, 3
LEFT: AFTER SOLVENT EXTRACTION   **RIGHT: AFTER CENTRIFUGE.**

B5: SAMPLE 13, 14, 15
LEFT: AFTER SOLVENT EXTRACTION   **RIGHT: AFTER CENTRIFUGE**
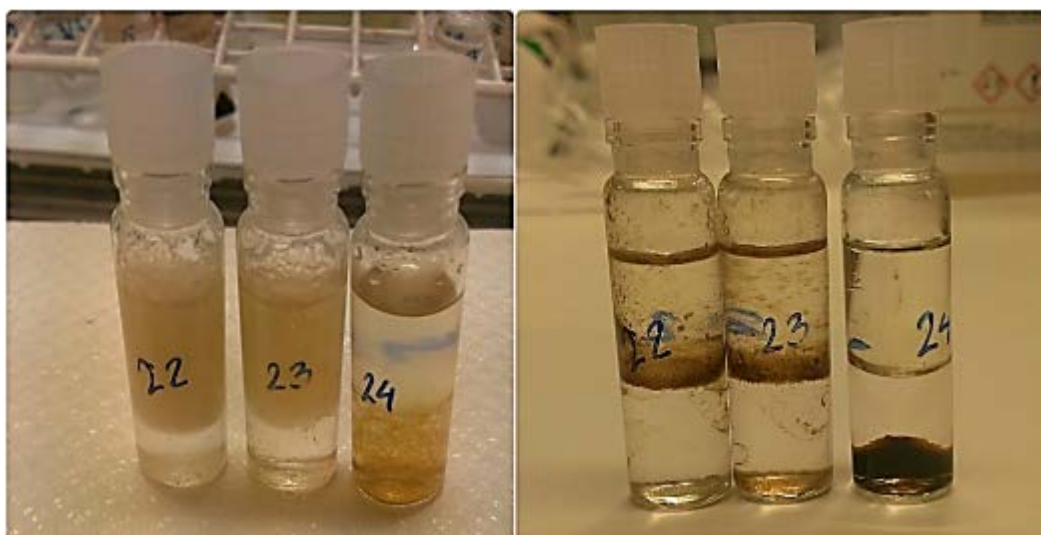

B6: SAMPLE 16, 17, 18
LEFT: AFTER SOLVENT EXTRACTION   **RIGHT: AFTER CENTRIFUGE**
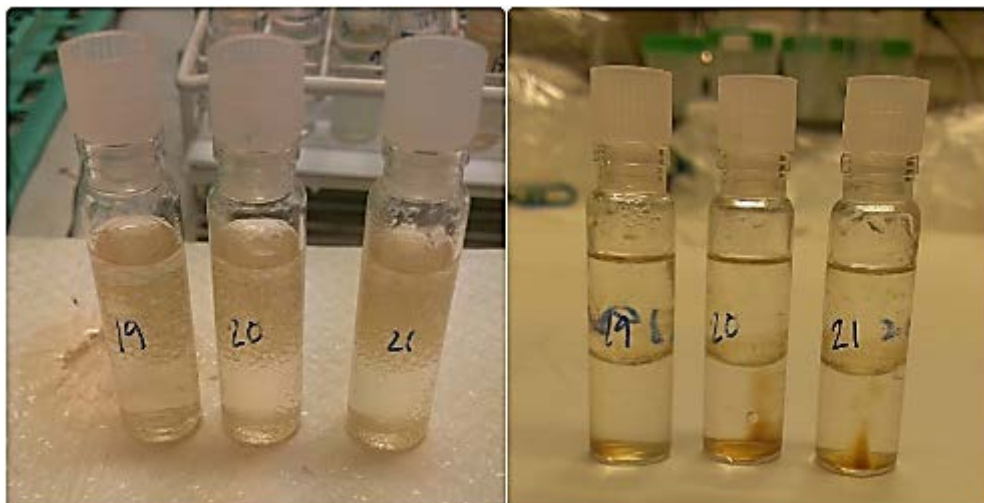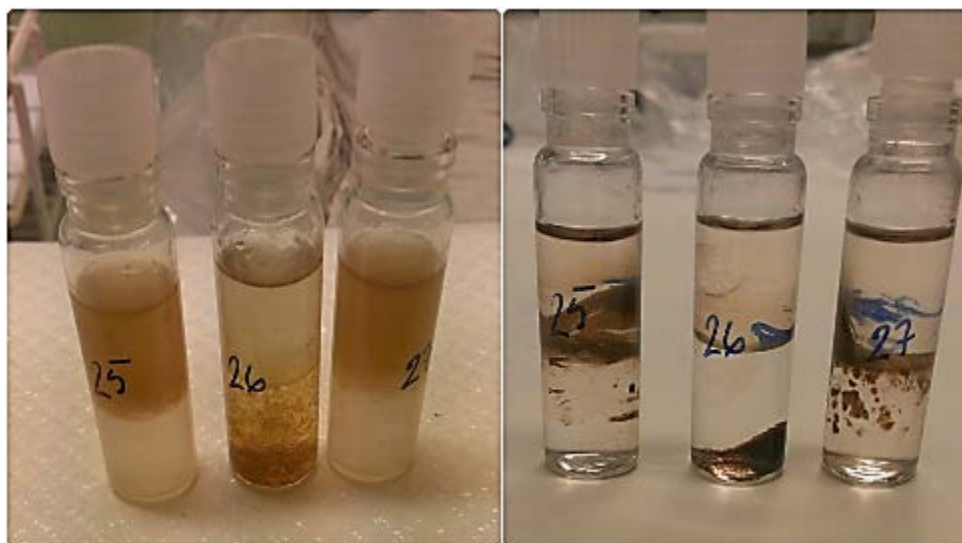
B7: SAMPLE 19, 20, 21
LEFT: AFTER SOLVENT EXTRACTION   **RIGHT: AFTER CENTRIFUGE**

B8: SAMPLE 22, 23, 24
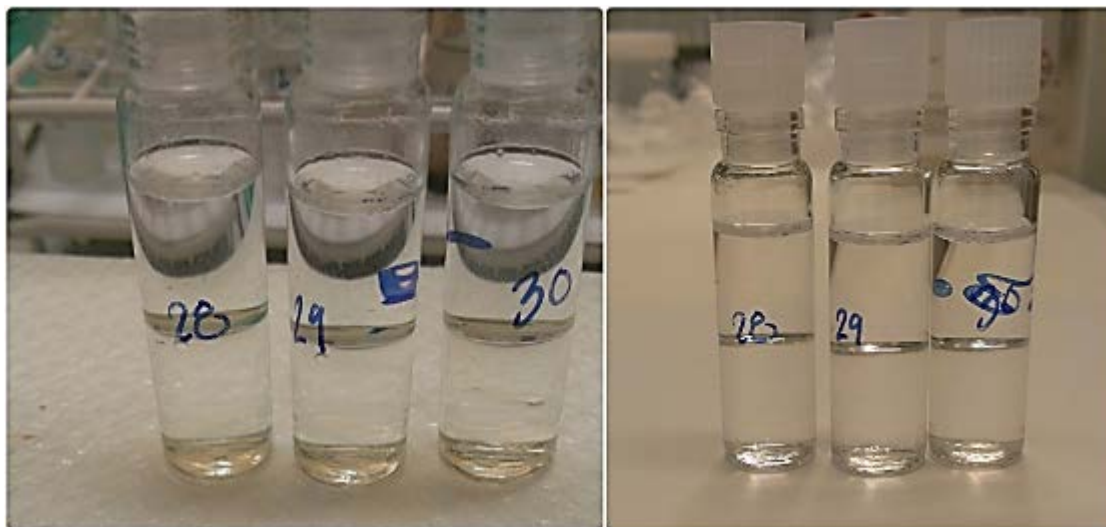**LEFT: AFTER SOLVENT EXTRACTION**   **RIGHT: AFTER CENTRIFUGE**

B9: SAMPLE 25, 26, 27
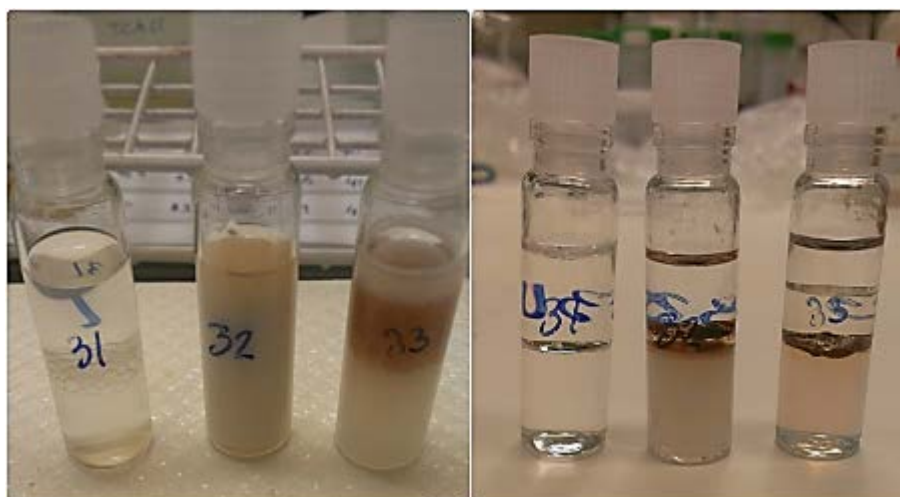 **LEFT: AFTER SOLVENT EXTRACTION**   **RIGHT: AFTER CENTRIFUGE**

B10: SAMPLE 28, 29, 30
LEFT: AFTER SOLVENT EXTRACTION   RIGHT: AFTER CENTRIFUGE

B11: SAMPLE 31, 32, 33
LEFT: AFTER SOLVENT EXTRACTION   RIGHT: AFTER CENTRIFUGE

References

Anon, Tricaprylylmethylammonium chloride mixture of C8-C10 C8 is dominant | Sigma-Aldrich. Available at: http://www.sigmaaldrich.com/catalog/product/aldrich/91042?lang=en&region=SE [Accessed May 27, 2015].

Arai, Y., 2001. Chapter 4. , pp.29–51. Available at: http://kar.kent.ac.uk/1841/.

Atkins, P. & Jones, L., 2004. *Chemical principles: The quest for insight (3.th ed.)* (3.th ed.)., New York: Freeman.

Chabert, P., 2011. Inductively coupled plasmas. , pp.219–259.

Chemetall AB, 9600 Volvo Tuve fosf bad.

Chemetall AB, 9667 Volvo Tuve fosf bad.

Chemetall AB, 9712 Volvo Tuve fosf bad.

ChemetallAB, 2010. Gardobond 26 se 10/2. , (1907), pp.1–26.

Finishing, C.P., 1999. Phosphate Conversion Coatings. *Metal Finishing*, 97, p.572.

Jan Rydberg, 2004. *Solvent Extraction Principles and Practice, Revised and Expanded* 2nd ed., CRC Press.

Kobya, M. et al., 2010. Treatment of rinse water from zinc phosphate coating by batch and continuous electrocoagulation processes. *Journal of Hazardous Materials*, 173, pp.326–334.

Kreider-Mueller, A., 2014. *Solvent Extraction*,

Kuo, Y.M., 2012. An alternative approach to recovering valuable metals from zinc phosphating sludge. *Journal of Hazardous Materials*, 201–202, pp.265–272. Available at: http://dx.doi.org/10.1016/j.jhazmat.2011.11.081.

Kuzawa, K. et al., 2006. Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent. *Chemosphere*, 62, pp.45–52.

Leclercq, A. et al., 2015. Introduction of organic/hydro-organic matrices in inductively coupled plasma optical emission spectrometry and mass spectrometry: A tutorial review. Part I. Theoretical considerations. *Analytica Chimica Acta*. Available at: http://linkinghub.elsevier.com/retrieve/pii/S0003267015004407.

Lindskog, N., 2008. *Volvo Technology AB*,

Lv, L. et al., 2008. Phosphate Removal and Recovery with Calcined Layered Double Hydroxides as an Adsorbent. *Phosphorus, Sulfur, and Silicon and the Related Elements*, 183(February 2015), pp.519–526.

Mollah, M.Y. et al., 2001. Electrocoagulation (EC)--science and applications. *Journal of hazardous materials*, 84, pp.29–41.

Morse, G.K. et al., 1998. Review: Phosphorus removal and recovery technologies. *Science of the Total Environment*, 212, pp.69–81.

Naturvårdsverket, 2008. Rening av avloppsvatten i Sverige 2008. , pp.1–24.

Ogle, K., Arcelor, R. & Maizie, D., 1999. Phosphate Conversion Coatings. *Metal Finishing*, 97(5), p.572.

Quitmeyer, J., 2006. Grasping the phosphate coating process. *Metal Finishing*, 104(9), pp.47–50. Available at: http://linkinghub.elsevier.com/retrieve/pii/S002605760680303X.

Rydberg, J., *Solvent-extraction princples and practice*,

Seader, J.. & Henley, E.J., 2006. *Separation process principles* second., John Wiley & Sons, Inc.

Swera IVF, 2009. *Closed Loop Zinc phosphate*,

The ChemQuest Group, 2000. Surface treatment. *Metal Finishing*, 98, p.73.

Tideström, H., 2012. *Teknik för fosforåtervinning ur avlopp*,

Wang, L.K. et al., 2004. Treatment of Metal Finishing Wastes. *Handbook of Industrial and Hazardous Wastes Treatment*, pp.203–274.

Watarai, H., 2008. Fundamentals in Solvent Extraction Processes.