PHOSPHORUS RELEASE FROM SEWAGE SLUDGE BY USE OF ACIDS AND BASES

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Abstract
Introductory laboratory experiments with sludge fractionation using acid and base have been carried out at the division of Water Resources Engineering, Royal Institute of Technology (KTH) in Stockholm, Sweden. The release of total phosphorus at different pH-values was analysed and the amount of chemicals needed was measured to reach a wanted pH-value. The decrease of suspended solids was analysed.

The results indicate a high release of phosphorus at low pH-values with only use of acid, without heat or pressure. Digested sludge contains a lot of phosphorus, which is released with chemicals. Acid addition seems to be more useful for total phosphorus release in digested sludge than use of base. The introductory studies show that the amount of total phosphorus release is doubled for each unit drop in pH-value. There is a connection between the amount of chemicals needed to reach a wanted pH-value. The higher or lower pH-value, the more chemicals are needed. The decrease in suspended solids did not show any significant results in short-time experiments.

Keywords
Chemical precipitation, phosphorus removal, product recovery, sludge

INTRODUCTION

In conventional wastewater treatment works sewage is treated for removal of nutrients and pollutants by help of chemical and biological methods. Most of the sewage content of phosphorus, metals and micropollutants finally end up in the sludge. Harremoës (1996) means that sludge should be seen both as a resource, which can be recycled and as a threat to the environment.

Recently a national goal in Sweden has been proposed that phosphorus in sewage sludge shall be recycled by 75% before 2010 (Wallgren, 2001). This goal is going to be investigated by the Swedish Environmental Protection Agency (SEPA). Recovery of phosphorus is also important for the phosphate industry and the Western European phosphate industry has set up a goal to reuse 25% of the recovered phosphate as raw material within a decade (Fielding, 2000).

The demand of phosphorus recovery both from SEPA and the phosphate industry has led to an increase of interest to find other solutions to recover phosphorus than in agricultural use. Especially the way to produce phosphorus products from sludge is an interesting alternative where the sludge may be seen as a raw material to produce a suitable phosphorus product with properties for marketing.

Difficulties at present to find a sustainable sludge handling technology is the base to find new alternatives. Product recovery by use of sludge fractionation is such a method. There exist several different technics for sludge fractionation to recover products. The fractionation may be built on physical, mechanical, biological and/or chemical methods. Physical methods use heat and pressure while chemical methods use for instance acid and base. Sludge fractionation may be performed at different steps in the sludge process system (Hultman and Levlin, 1997).

Phosphorus is a finite resource, which will not last more than 200 years (Enskog and Johansson, 1999). By recovery of phosphorus a recycling is created of a finite resource. Leakage of phosphorus from landfills to groundwater and nearby recipient will also decrease.

Phosphorus recovery from wastewater treatment plant sludges follows generally three steps:
1) Transfer of soluble phosphorus compounds into biomass (enhanced biological phosphorus removal, algae) or as a chemically bound phosphorus compound by adding a precipitation agent.
2) Solubilisation of sludge bound compounds (including phosphorus compounds) by different methods as the use of physical, mechanical, biological or chemical means. During this step for instance phosphorus is transferred into a relatively small stream compared with the influent flow and the phosphate concentration in this stream may be 10-50 times higher compared with the influent phosphate concentration.
3) The phosphate enriched stream may also contain a lot of other components as precipitation agents, organic materials and heavy metals and separation technologies as chemical precipitation, crystallisation, ion exchange or membrane technology must be used to obtain a reasonably clean phosphorus product.

Earlier phosphorus in wastewater was mainly considered as a removal problem and much focus has been laid on the first step. Removal of phosphorus in combination with phosphorus recovery poses a challenge for new operational strategies to combine the three steps above.

In the Scandinavian countries phosphorus is mainly removed by chemical precipitation. In this case phosphorus is bound strongly to metal ions and for phosphorus release technologies there may be necessary to use acids combined with high temperature and pressure. The commercial system KREPRO uses this concept and has near full-scale experiences in Helsingborg and plans for a modified plant in the city of Malmö. The system BioCon uses heat drying and incineration followed by sulphuric acid leaching of the produced ash and product recovery through a system of ion exchangers. The system is planned to be installed in the city of Falun in Sweden.

METHODS

Sludge
Sludge samples were obtained from wastewater treatment plants in Stockholm operating with biological and chemical treatment. Ferrous sulphate is used as chemical precipitation agent. In the two first experimental series sludge from Henriksdal treatment plant (630 000 p.e.) was used, and in the third experiment sludge from Loudden (about 30 000 p.e.).

Experimental design

1. The aim of the first experiment was to study how much chemicals were needed to be added into the sludge to reach a wanted pH-value. Three different types of sludge were used (primary sludge mixed with excess sludge, digested sludge and post-precipitated iron sludge from the deep-bed filters). The first sludge type represents sludge entering the digester. Chemical was added to a given amount (250 ml) of sludge and was stirred in a beaker by a mini-flocculator for mixing. Hydrochloric acid (HCl) was added to the sludge samples to reach low pH-values (down to pH-value 1.5) and sodium hydroxide (NaOH) was used to reach high pH-values (up to pH-value 12.5).

2. In the second experiment the release of phosphorus and the change of suspended solids were analysed. Three different types of sludge were used (primary sludge mixed with excess sludge, digested sludge and post-precipitated iron sludge from the deep-bed filters). Hydrochloric (HCl) was used as acid while sodium hydroxide (NaOH) was used as base. The chemicals were added to a given amount (200 ml) of sludge and were stirred in a beaker by a mini-flocculator for 2 h. The sludge was mixed at different pH-values (2, 4, 10 and 12, respectively). The sludge was centrifuged for 15 min at 3500 rpm and the liquid phase was filtrated through 0.45 μm filter. The samples were stored frozen before analyses.

3. In the third experiment hydrochloric acid (HCl) was added to digested sludge at different pH-values (2, 3, 4 and 5) and a mixing time of 2 h was used. The release of total phosphorus, the chemical demand and the change in suspended solids were studied. The sludge was centrifuged after the mixing for 15 min at 3500 rpm and the liquid phase was filtrated through 0.45 μm filter. The samples were stored frozen before analyses. Experiments were performed in triplicate.

Analyses

The total phosphorus content was analysed by using the equipment Aquatec® from the company Tecator. This equipment works with flow injection analysis (FIA), which means that the samples run as a type of drop through a very thin hose. By passing special chemicals the total soluble phosphorus content in samples is determined spectrophotometrically.

The suspended solids were determined by using the standard method SS-EN 872, which is a method based on filtration through glasfiber filter. The time between sampling and analysis exceeded 4 h in the experimental serie 1 and 2. Meanwhile the samples were stored in a dark cooling room.

Theory

If an acid is added to a sludge suspension different sludge components will be dissolved. Important inorganic sludge components that might be dissolved are shown in Table 1.

Table 1. Dissolution of inorganic sludge components

Component	Dissolution reaction	g HCl/g component
$Fe(OH)_2$	$Fe(OH)_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O$	0.813
$Fe_3(PO_4)_2$	$Fe_3(PO_4)_2 + 4H^+ \rightarrow 3Fe^{2+} + 2H_2PO_4^-$	0.409
$Fe(OH)_3$	$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$	1.025
$FePO_4$	$FePO_4 + 2H^+ \rightarrow Fe^{3+} + H_2PO_4^-$	0.726
$Al(OH)_3$	$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$	0.936
$Al\,PO_4$	$Al\,PO_4 + 2H^+ \rightarrow Al^{3+} + H_2PO_4^-$	0.598
$CaCO_3$	$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$	0.730
$MgCO_3$	$MgCO_3 + 2H^+ \rightarrow Mg^{2+} + CO_2 + H_2O$	0.869

Depending on sludge composition 0.4 – 1.0 g HCl is needed to dissolve 1 g of inorganic sludge. A sludge with the composition of dissolved inorganic material equal to $Fe(OH)_2$ 28.2%, $Fe_3(PO_4)_2$ 33.7%, $Al(OH)_3$ 17.4 %, $CaCO_3$ 15.0 % and $MgCO_3$ 5.7 % would need 0.69 g HCl/g dissolved inorganic material based on data in Table 1. The chosen example corresponds approximately to the ash composition of inorganic material that may be dissolved by acids (Hultman et al., 2001).

Acids also reacts with alkalinity consuming soluble substances as hydrogen carbonate and organic acids. Acid, which does not react with sludge components or soluble alkalinity consuming substances will decrease the pH-value.

Bases, as sodium hydroxide will react with different sludge components and soluble substances as hydrogen carbonate and ammonium and remaining hydroxide ions will increase the pH-value.

RESULTS AND DISCUSSION

Sludge concentration
The sludge concentration in the experiments is shown Table 2.

Table 2. Sludge concentration as suspended solids (SS), volatile suspended solids (VSS) and fixed suspended solids (FSS)

Sludge type	Experiment Serie No	Initial sludge conc. SS (g/l)	Initial sludge conc. VSS (g/l)	Initial sludge conc. FSS (g/l)
Sludge before digester (BD)	1	23	18.5	4.5
Digested sludge (DS)	1	42.8	22.4	20.4
Sludge from filters (FS)	1	0.76	0.41	0.35
Sludge before digester (BD)	2	27.8	22.2	5.7
Digested sludge (DS)	2	40.8	22.3	18.5
Sludge from filters (FS)	2	0.74	0.42	0.32
Digested sludge (DS)	3	22	14	8

The sludge phosphorus content is about 3.2 % for digested sludge from Henriksdal wastewater treatment plant and 2.9 % from Loudden wastewater treatment plant (Stockholm Vatten, 2000).

Needs of chemicals

To release phosphorus at different pH-values it is important to know how much chemicals are needed to reach a wanted pH-value. The lower or higher pH-value wanted the higher addition of chemicals is needed, which is shown in Figure 1-2. The sludge from the deep-bed filter shows highest chemical need. The filter sludge contained the smallest amount of released total phosphorus compared to the other sludge types.

The experiments indicate a connection between chemical amount and wanted pH-value. The average value of chemical addition needed in experimental serie 3 is shown in figure 2 and the acid addition to reach lower pH-value forms a line. The amount of chemicals needed to reach a certain pH-value is shown in Table 3.
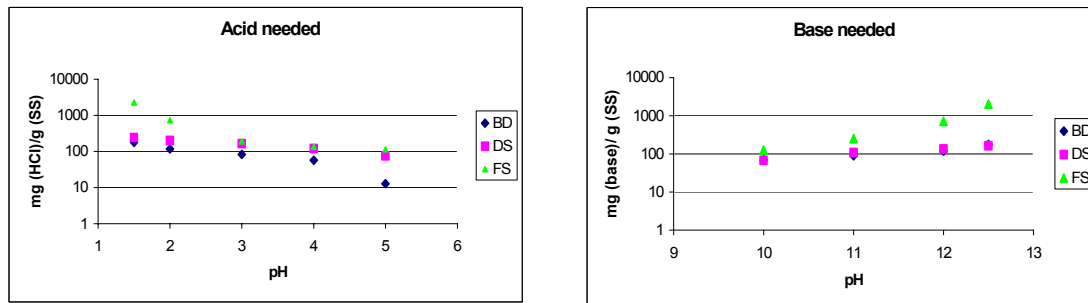

Figure 1: Acid and base needed to reach wanted pH-values in experiment 1.
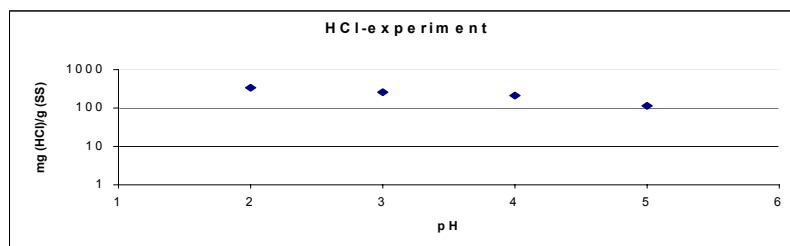

Figure 2: Acid needed to reach wanted pH-values in experiment 3. (log-scale)

The results show that main addition of chemicals to reach a certain pH-value is due to the H^+ or OH^- concentration for filter sludge. This depends on the low sludge concentration (0.76 g/l). For pH-values below 4–5 or above 10–11 reactions mainly occur with sludge components as most alkalinity has been removed below pH 4–5 and most ammonium and hydrogen carbonate is transferred to ammonia and carbonate, respectively, above pH-value 10–11. To reach low pH-values (as 1.5) or high pH-values (as 12.5) sludge reactions dominated the dosage of hydrochloric acid and sodium hydroxide, respectively, for the digested sludge and the sludge before the digester.

Table 3. Need of acid (HCl) or base (NaOH) to reach a certain pH-value

Experiment serie No	Type of sludge	pH	mol/l H^+ or OH^-	Dosage of	mol/l	mg/g (SS)
1	BD	1.5	0.032	HCl	0.113	179
	BD	2	0.01		0.074	117
	BD	3	0.001		0.052	83
	BD	4	0.0001		0.036	57
	BD	5	0.00001		0.008	13
	DS	1.5	0.032		0.282	240
	DS	2	0.01		0.236	201
	DS	3	0.001		0.193	165
	DS	4	0.0001		0.141	120
	DS	5	0.00001		0.089	76
	FS	1.5	0.032		0.047	2257
	FS	2	0.01		0.015	720
	FS	3	0.001		0.004	192
	FS	4	0.0001		0.003	144
	FS	5	0.00001		0.002	96
1	BD	10	0.0001	NaOH	0.040	70
	BD	11	0.001		0.051	89
	BD	12	0.01		0.069	120
	BD	12.5	0.032		0.101	176
	DS	10	0.0001		0.072	67
	DS	11	0.001		0.116	108
	DS	12	0.01		0.143	134
	DS	12.5	0.032		0.175	163
	FS	10	0.0001		0.002	105
	FS	11	0.001		0.005	263
	FS	12	0.01		0.014	736
	FS	12.5	0.032		0.038	1999
3	DS	2	0.01	HCl	0.170	282
	DS	3	0.001		0.13	216
	DS	4	0.0001		0.11	183
	DS	5	0.00001		0.07	116

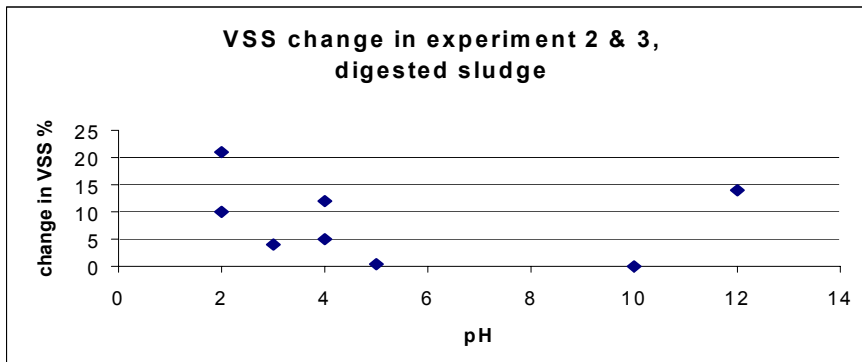**Decrease in suspended solids**

The changes in suspended solids (SS), volatile suspended solids (VSS) and fixed suspended solids (FSS) in experiment 2 and 3 are shown in table 4. The decrease is largest in the inorganic material at low pH-values. Sludge entering the digester (BD) shows approximately a decrease of 30% for VSS at high pH-values (pH 12). The increase of solids may be a result of precipitation of soluble metal ions to carbonate or hydroxide. The change in VSS is shown in figure 3 and the change in FSS is shown in figure 4. The change in VSS shows a decrease both at acid and basic conditions, while the FSS does not change above pH-value 5.

Table 4. Changes in suspended solids (SS), volatile suspended solids (VSS) and fixed suspended solids (FSS) in experiment 2 and 3

Experimental serie No	Type of sludge	pH	Percentage decrease (-) or increase (+)			Dosage of HCl or NaOH				
			SS	VSS	FSS	mg/g SS	mg/g VSS	mg/g FSS	mg/g removed VSS	mg/g removed FSS
2	BD									
		2	-18	-7	-58	131	164	640	2349	1104
		4	-10	-4	-30	59	74	288	1850	961
		10	-11	-16	6	65	82	319	512	*
		12	-20	-27	-1	100	125	487	464	48748
	DS									
		2	-39	-21	-60	224	409	493	1949	822
		4	-21	-12	-32	134	246	296	2046	925
		10	5	1	11	55	100	121	*	*
		12	-8	-14	1	137	251	303	1793	*
	FS									
		2	-5	1	-14	740	1304	1711	*	12221
		4	0	-8	10	148	261	342	3259	*
		10	12	-5	35	108	190	250	3808	*
		12	8	-14	38	756	1333	1749	9519	*
3	DS									
		2	-30	-10	-63	282	443	776	4432	1232
		3	-17	-4	-52	216	339	593	8473	1141
		4	-13	-5	-40	183	287	502	5736	1255
		5	-4	-0.4	-0.9	116	183	319	45625	35486

BD=sludge before the digester, DS=digested sludge, FS=filter-bed sludge
* the value increased

Figure 3. Percentage change of volatile suspended solids (VSS) as a function of pH value.
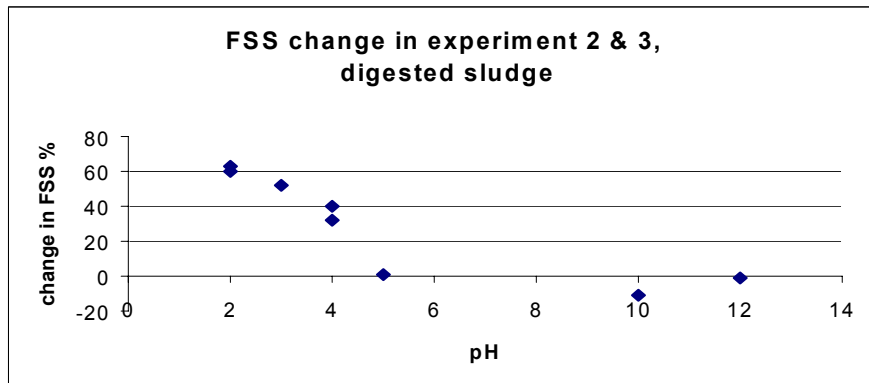
Figure 4. Percentage change of fixed suspended solids (FSS) as a function of pH value.

Release of phosphorus
The total phosphorus content in the liquid phase in the first "phosphorus experiment" is shown in Figure 5. The higher release of phosphorus from digested sludge compared with sludge before the digester is depending on a higher concentration of the sludge and content of phosphorus of the digested sludge. The variation of the values of total phosphorus was not investigated in this experiment rather the trend of which type of sludge contained most phosphorus and where the largest total phosphorus release takes place.
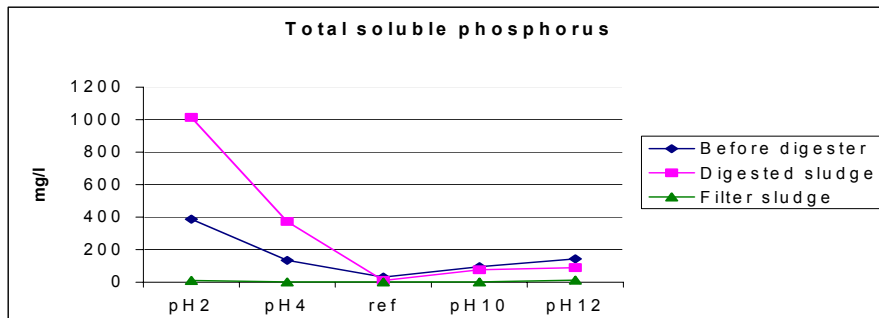
Figure 5: Total soluble phosphorus (mg/l) in experiment 2 with the sludge types before digester, digested sludge and filter sludge.

The phosphorus amount is depending on the content of the sludge and its particles. Taking the initial suspended solids (SS) into account for the total phosphorus, the following figure is created (see figure 6). Similar result is shown as the preceding figure, that digested sludge has a high release of phosphorus at low pH-values. The filter sludge does not release much phosphorus (for detailed total phosphorus values, see table 5).
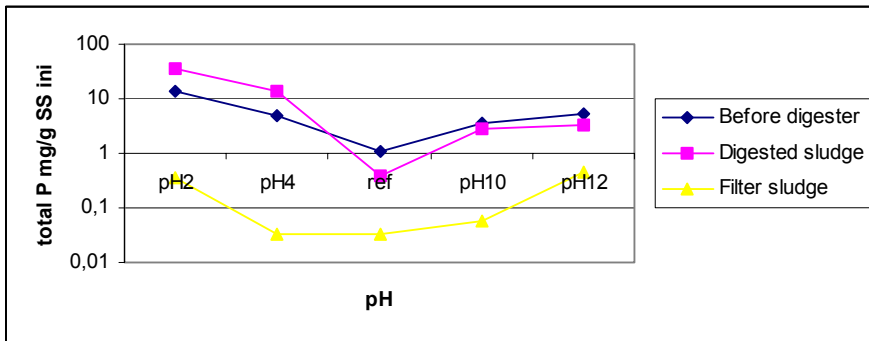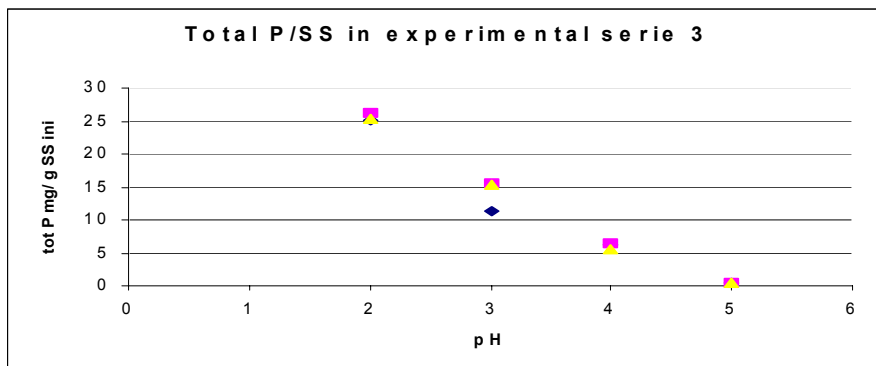
Figure 6. Total soluble phosphorus/ SS initial in experiment 2 with the sludge types before digester, digested sludge and filter sludge (log-scale).

In the second phosphorus experiment the variation of the total phosphorus was tested with three different runs. The small variation of the released amount of total phosphorus in the second experiment is shown in Figure 7. The released total phosphorus seems to be doubled in value when the pH-value is dropped one unit. The amount of total phosphorus divided by the initial suspended solids (SS) is shown in Figure 8.
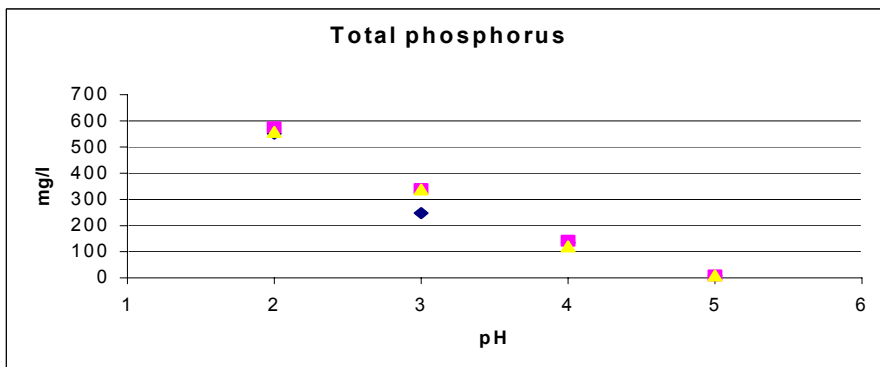
Figure 7: Total soluble phosphorus in experiment 3 at different pH-values and at three different runs.

Figure 8: Total phosphorus/ SS initial in experiment 3 at different pH-values and at three different runs.

Summarised in Table 5 is the amount of released phosphorus expressed as (mg P/l) and (mg P/g SS) from experimental series 2 and 3. Digested sludge contains most phosphorus compared to the other sludge types. The filter sludge gives approximately the same amount of total phosphorus at low pH-values as high ones.

Table 5. Release of phosphorus from different sludge in experiment 2 and 3

Experiment No	Type of sludge	pH	Release of phosphorus	
			mg/l	mg P/g SS
2	BD	2	388	14
	BD	4	134	5
	BD	6	31	1
	BD	10	95	3
	BD	12	143	5
	DS	2	1014	36
	DS	4	373	13
	DS	6	10	0.3
	DS	10	75	2.7
	DS	12	89	3.2
	FS	2	10	0.4
	FS	4	1	0.03
	FS	6	0.9	0.03
	FS	10	1.6	0.06
	FS	12	12	0.4
3	DS	2	561	25
	DS	3	308	14
	DS	4	132	6
	DS	5	9.1	0.4

BD=sludge before the digester, DS=digested sludge, FS=filter-bed sludge

The different types of sludge differ by the sludge concentration in the experiments, the phosphorus content in the sludge and how the phosphorus is bound. For example the primary sludge consists of solid particles from incoming wastewater. These are separated by mechanical treatment in the pre-sedimentation basins. Before entering the pre-sedimentation basin into the activated sludge process iron sulphate is added for the first phosphorus flocculation. The excess sludge is biological sludge, which has been removed from the activated sludge process, i.e. the phosphorus is to largest part bound biologically. In the digester chamber a large part of the organic material disappears, which releases a part of the phosphorus. Ferrous sulphate is added before the sand filter which makes the deep-bed filter sludge containing phosphorus bound to iron. The sand filter is the last step in the treatment process, which makes the content of particles very low in the deep-bed filter sludge obtained from back-washing.

Similar as Zoppoth (1998) found in her master thesis work addition of sodium hydroxide to the post-precipitated iron sludge to pH-values between 9 and 12 did not cause any significant release of phosphates.

The experiment did not show a large decrease in volatile suspended solids (VSS) after the mixing time 2h. Fujii (1997) found a VSS decrease of 30% after treating activated sludge 24h with sodium hydroxide at pH 12 and Zoppoth (1998) received the result of nearly total dissolution of the inorganic substances by pH-values down to 1.6 after treated post-precipitated iron sludge 24h with HCl. Dissolution of filter sludge is much depending if the precipitated iron is in ferrous or ferric form.

Adding NaOH in different doses might be a possibility to decrease the organic material. The phosphorus recovery is facilitated by a decreasing amount of organic material.

CONCLUSIONS

Fractionation of sludges by use of acids or bases is an important step to release different components from the sludge including phosphorus. At addition of acids a large fraction of the inorganic material can be dissolved and thereby also sludge bound phosphorus compounds. Part of the organic material is also dissolved. The total soluble phosphorus concentration increased by about a factor two if the pH-value was lowered one pH unit. Addition of bases up to pH-value 12.5 caused only minor changes of the sludge content of inorganic material and no significant release of soluble total phosphorus compounds. However, a release was obtained of organic compounds in the sludge.

ACKNOWLEDGEMENT

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