PHYSICO-CHEMICAL P REMOVAL FROM THE LIQUID FRACTION OF PIG MANURE AS AN INTERMEDIARY STEP IN MANURE PROCESSING

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Abstract. Intensive animal farming has resulted in overproduction of manure in parts of the industrialized world. The localized excessive nutrient emission has detrimental effects on both ecology and economy. In response to European guidelines, Flanders (Belgium) has imposed obligations on the agricultural sector to process a portion of the produced animal manure. To achieve the stringent criteria for discharge of processed waste water, overly expensive engineering techniques are currently required (mostly membrane technology). This paper examines the potential of more economic physico-chemical techniques for P-removal from pre-treated liquid animal manure. Two techniques for dephosphatation were performed sequentially: (i) the use of flocculants ($FeCl_3$, $FeCl_2$, $FeClSO_4$, Poly Aluminium Chloride (PAC), Na Aluminate) and subsequently, (ii) the use of substrates to further reduce P-levels by adsorption or precipitation (expanded clay (argex), Fe-oxide powder, clay, calcinated clay, alganite, sand). The P-removal efficiencies obtained in this research are promising to consider implementation of physico-chemical P-removal as an intermediary step in animal manure processing after secondary pre-treatment in an activated sludge reactor and before tertiary treatment.

Keywords: adsorption, dephosphatation, flocculation, phosphorus, pig manure, waste water treatment

1. Introduction

Intensification of livestock production in parts of Western Europe, in combination with a decline in arable land, has resulted in local overproduction of manure. In Flanders (Belgium), the estimated excess mass of nutrients amounts to 170×10^6 kg N and 20×10^6 kg P per year (Lauwers *et al.*, 2002). Excessive fertilization of arable land, above crop requirements, results in nutrient enrichment of both groundwater and surface water. This in turn leads to detrimental effects on water quality, typically associated with eutrophication, such as algal blooms and disrupted oxygen household. Excessive emission of nutrients to the environment can therefore result in detrimental ecological, economic and social effects (Hill and Sobsey, 2001; Hunt and Poach, 2001). To reduce effects of industrial agriculture on the environment, the Flemish agricultural sector has since 2003 been forced to process a portion of

the produced nutrient surplus. A total of about 2 400 000 tons of pig manure need to be processed on an annual basis (VCM, 2004). Average cost of manure processing in Flanders is currently estimated at €30–36 per m^3 (Feyaerts *et al.*, 2002).

Manure processing in Flanders generally occurs in three steps: (i) separation of the manure into liquid and solid fractions, (ii) conversion of the solid fraction into an exportable product, mostly by composting and (iii) reduction of the nutrient content in the liquid fraction (Feyaerts *et al.*, 2002). To achieve reduction down to the discharge criteria of 2 mg l^{-1} P, expensive techniques are required, e.g. ultrafiltration, reversed osmosis, activated coal and/or ion exchange. As an alternative approach after separation, the liquid fraction can be spread over arable land with or without additional reduction of the nutrient content by biotreatment (Feyaerts *et al.*, 2002). However, a number of drawbacks related to the composition and characteristics of the liquid fraction restrict the sustainability of spreading, either with or without additional nutrient content reduction: (i) the high salt content may deteriorate soil quality, (ii) higher volumes of waste water are required to achieve fertilizer effects, (iii) elevated risks for nutrient leaching at higher hydraulic loads (up to 250 m^3 ha^{-1} for processed liquid fraction), (iv) a high degree of nitrification during secondary treatment adds to these risks by the elevated content of mobile NO$_3^-$ in the processed waste water. In addition, shortage in arable land may also limit this approach.

In a previous study, the feasibility of achieving discharge criteria by constructed wetlands (*Phragmites australis*), following secondary treatment (activated sludge reactor), was evaluated (Meers *et al.*, 2004). The high P-levels in the secondary treated effluent (265 ± 56 mg l^{-1}), in comparison to the stringent discharge threshold levels (2 mg l^{-1}), limited the feasibility of this approach. Likewise, Stone *et al.* (2004) could only reduce TP-levels to 34–62 mg l^{-1} in a marsh–pond–marsh system (8% mean reduction) and therefore recommend pre- or post-treatment for efficient P-removal. A 3-stage vertical-flow constructed wetland with internal recirculation was also incapable of lowering P-concentrations below 18 mg P l^{-1} (Sun *et al.*, 2003).

This paper therefore examines inexpensive physico-chemical methods for P removal from the secondary treated liquid fraction of pig manure as an intermediary step between (a) the activated sludge reactor and (b) tertiary treatment using constructed wetlands. To this end, flocculation by Fe- and Al-based flocculants was assessed. In addition, the adsorption capacity of a number of potential filter bed materials for additional polishing of the remaining P levels in the pre-treated waste water will be discussed as well.

2. Material and Methods

2.1. WASTE WATER CHARACTERISTICS

The pig manure used in this experiment was pre-processed on the farm by (i) separation into liquid and solid fractions and (ii) subsequent passage through an

TABLE I

General properties and composition of secondary treated liquid fraction of pig manure used in our experiments; intervals depict standard deviation ($n = 3$)

pH	8.3 ± 0.2	Cl ($mg\,l^{-1}$)	2355 ± 176
Conductivity ($mS\,cm^{-1}$)	17.2 ± 0.8	Cu ($mg\,l^{-1}$)	1.2 ± 0.4
Dry weight (m:m, %)	1.5 ± 0.1	Zn ($mg\,l^{-1}$)	1.6 ± 0.5
N_{total} ($mg\,l^{-1}$)	244 ± 106	Fe ($mg\,l^{-1}$)	16.2 ± 15.2
$N_{kjeldahl}$ ($mg\,l^{-1}$)	185 ± 41	Mn ($mg\,l^{-1}$)	0.6 ± 0.3
$NO_3^-–N$ ($mg\,l^{-1}$)	18 ± 16	Na ($mg\,l^{-1}$)	1142 ± 179
$NH_4^+–N$ ($mg\,l^{-1}$)	37 ± 14	K ($mg\,l^{-1}$)	4012 ± 359
P_{total} ($mg\,l^{-1}$)	322 ± 89	Ca ($mg\,l^{-1}$)	71 ± 58
COD ($mg\,l^{-1}$)	3336 ± 311	Mg ($mg\,l^{-1}$)	49 ± 36

activated sludge reactor (SBR; Trevi NV, Ghent, Belgium) with a residence time of 30 days. Characteristics of the liquid fraction after pre-processing, used in the experiments, are presented in Table I.

Conductivity and pH were determined potentiometrically using an LF 537 conductivity electrode and an Orion model 520 pH meter respectively. Dry weight content was determined as residual weight after 24 h drying at 103 °C. Metals and alkali elements (Cu, Zn, Fe, Mn, Na, K, Mg and Ca) were analysed using ICP-OES (Varian Vista MPX, Palo Alto, CA, USA) after *aqua regia* digestion of the waste water samples (25 ml sample +7.5 ml HCl and 2.5 ml HNO_3).

Total nitrogen and Kjeldahl nitrogen were determined using a Kjeltec system 1002 distilling unit after digestion of the sample in respectively a sulphuric acid salicylic acid mixture and sulphuric acid. Finally, the captured ammonia in the distillate was titrated with 0.01 M HCl in the presence of a methyl red bromocresol green mixed indicator (Van Ranst *et al.*, 1999). Nitrate was determined potentiometrically using a nitrate specific electrode (Van Ranst *et al.*, 1999). Total phosphorus content was determined using the colorimetric method of Scheel (Van Ranst *et al.*, 1999). Chloride content was determined by titration with 0.05 M $AgNO_3$ using a Methrohm 718 Stat Titrino automatic titration unit, provided with an Ag-electrode and a $Hg/HgSO_4$ reference electrode. A standard curve was made using NaCl standard solutions (Van Ranst *et al.*, 1999). Chemical Oxygen Demand (COD) was determined photometrically using Dr. Lange standardized cuvette-tests (LCK014, range 1000–10 000 mg/L COD; Dr. Bruno Lange GmbH & Co, Düsseldorf, Germany).

2.2. FLOCCULATION EXPERIMENTS

The flocculants used in the experiments were obtained as liquid solutions from Brenntag, Belgium and Kronos Ecochem, Germany. Five different products were evaluated for P-removal by means of flocculation: $FeCl_2$, $FeCl_3$, $FeClSO_4$, Na

Aluminate and PAC Sachtoklar 39 (Poly Aluminum Chloride). Of each flocculant solution, 3 different doses were tested: $1 \, ml \, l^{-1}$, $3 \, ml \, l^{-1}$ and $5 \, ml \, l^{-1}$. This corresponded with the following Fe or Al addition per L waste water: $119–594 \, mg \, l^{-1}$ for $FeCl_2$, $183–915 \, mg \, l^{-1}$ for $FeCl_3$, $187–935 \, mg \, l^{-1}$ for $FeClSO_4$, $155–775 \, mg \, l^{-1}$ for Na Aluminate and $122–610 \, mg \, l^{-1}$ for PAC Sachtoklar 39. Tests were performed in triplicate in 2 L containers on 1.5 L volumes of waste water. After application of the flocculants, the containers were shaken shortly and subsequently allowed to stand for 48 h before supernatant fluid was separated from the underlying sludge by using a separating funnel. Relative volume of sludge and supernatant were determined and the P_{Total} contents analysed.

In a second flocculation experiment, the effect of flocculant application was evaluated at a larger scale. To this end, $FeCl_3$ was administered at the intermediate dosage of $3 \, ml \, l^{-1}$ ($550 \, mg \, l^{-1}$ Fe(III)) to 1.5 L, 50 L and 1000 L of waste water respectively. As in the previous experiment, the mixture was stirred shortly after addition of the flocculant and subsequently allowed to stand for 48 h. Volumes of sludge and supernatant were determined, as well as their respective P_{Total} contents.

2.3. ADSORPTION EXPERIMENTS

P-removal by adsorption or precipitation to various substrates was evaluated. One kilogram of each substrate was placed in a 2 L container with free percolation. Subsequently, a daily load of 1 L of liquid fraction of pig manure, pre-treated with $3 \, ml \, l^{-1}$ $FeCl_3$, was applied. The purpose for this experiment was to examine whether adsorption by filter media could be employed as a mechanism for further polishing the waste water which was first treated with flocculants. At the end of the experiment, the substrates were rinsed with deionised water to remove excess waste water. The substrates tested were: (i) coarse sand, (ii) fine sand, (iii) expanded clay (Argex), (iv) coarse sand:clay (75:25), (v) coarse sand:argex (75:25), (vi) coarse sand:fine sand:clay:argex (72.5:17.5:7.5:2.5), vii) calcinated clay granules, (viii) alganite, (ix) coarse sand:Fe-oxide powder (90:10). The mixtures (iv), (v) and (vi) have been presented on mass basis. Clay was added in various mixtures with sand and argex (iv, vi) to allow for sufficient hydrological conductivity when percolating. The optimal Fe-oxide–sand mixture (ix) was selected based on previous experience. At higher Fe-oxide dosage, the percolation filters were observed to "bleed" colloidal Fe-oxides into the percolate. Materials for substrates (i)–(vi) were obtained from a local vendor in building materials. Substrates (vii) and (viii) are commercially obtained clay substrates, processed for use as adsorptive animal litter. The Fe-oxide powder used in substrate (ix) is a waste product from the ferro-metallurgic industry (Sidmar NV, Ghent, Belgium).

For analysis of total P content in the substrates, 1 g of air dry weight was digested in 7.5 ml HCl and 2.5 ml HNO_3. After standing overnight, the digest was heated on a hot plate ($150 \,^{\circ}C$) for 2 h. After filtering and diluting to 50 ml in a volumetric

flask, colorimetric determination of P_{Total} was similar to the method described above (Section 2.1). The expanded clay granules (argex) were pulverized prior to analysis.

3. Results and Discussion

3.1. FLOCCULATION EXPERIMENTS

The application of flocculants can induce a precipitation reaction, in which phosphates precipitate as Ca, Mg, Fe or Al complexes. The removal of P from dairy waste waters using flocculants has been documented by Sherman *et al.* (2000). Powers and Flatow (2002) also used flocculation in pig manure processing. As in this study, the studies by Sherman *et al.* (2000) and Powers and Flatow (2002) used short time spans for initial stirring before final sedimentation.

Table II summarizes the observed volumes of sludge and supernatant, their respective P contents and the removal efficiency of P from the supernatant, after treatment with the flocculants under investigation. The removal efficiency was calculated as the proportional fraction of total P in the system, present in the flocculation sludge. For all flocculants, increasing doses resulted in decreasing P-levels in the supernatant. The lowest removal efficiencies were observed for Na Aluminate,

TABLE II

Observed volumes of sludge and supernatant (ml) and their respective P-content ($mg\,l^{-1}$) following treatment with the flocculants under study; intervals depict standard deviation ($n = 3$)

| Flocculant | Application dose | | Sludge | | Supernatant | | Removal efficiency (%) |
	($ml\,l^{-1}$)	Fe/Al ($mg\,l^{-1}$)	Volume (ml)	P-content ($mg\,l^{-1}$)	Volume (ml)	P-content ($mg\,l^{-1}$)	
Na-aluminate	1	155	150	1013 ± 0	1350	274 ± 9	14 ± 2
	3	465	193	1208 ± 15	1307	238 ± 2	26 ± 3
	5	775	344	986 ± 12	1156	214 ± 0	34 ± 4
PAC	1	122	230	1274 ± 47	1270	249 ± 6	23 ± 3
	3	366	507	1141 ± 31	993	78 ± 1	76 ± 9
	5	610	750	806 ± 59	750	27 ± 0	91 ± 11
FeCl$_2$	1	119	479	561 ± 10	1021	298 ± 2	7 ± 1
	3	356	488	1280 ± 10	1012	135 ± 1	58 ± 7
	5	594	662	655 ± 10	838	75 ± 2	78 ± 9
FeClSO$_4$	1	187	389	693 ± 3	1111	237 ± 5	26 ± 3
	3	561	466	1006 ± 34	1034	71 ± 1	78 ± 9
	5	935	695	722 ± 8	805	31 ± 2	91 ± 12
FeCl$_3$	1	183	259	770 ± 6	1241	160 ± 3	39 ± 1
	3	550	439	824 ± 5	1061	33 ± 3	88 ± 8
	5	915	660	576 ± 5	840	13 ± 1	95 ± 8
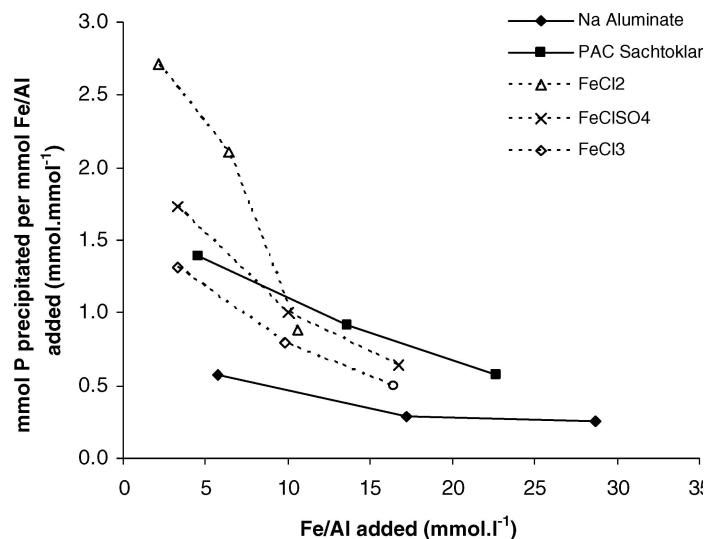
Figure 1. P removal efficiency, expressed as mmol removed per mmol Fe/Al added to the waste water ($n = 3$; S.D. $< 7.5\%$, not shown for clarity).

with the other 4 flocculants exhibiting comparable performances. At the highest applied doses of $FeClSO_4$ and $FeCl_3$, removal efficiencies achieved levels of 91–95%. This implies a high presence of reactive orthophosphates in the pre-treated waste water. Passage through the activated sludge reactor is thought to have resulted in mineralization of organic materials, and therefore also of the organophosphates, present in the pig manure.

Figure 1 compares the efficiency of the different flocculants, expressed as mmol P removed per mmol Fe/Al applied. Again, Na Aluminate was the least efficient in binding P. At the lowest doses, $FeCl_2$ demonstrated a higher P removal per mmol flocculant, while the highest dose was more in line with the results observed for PAC, $FeCl_3$ and $FeClSO_4$. Flocculant efficiency decreased as application rate increased for all flocculants. This implies that progressively more flocculant needs to be added for each additional mmol P removed. Removal in function of applied dose will therefore follow an exponential and not a linear path. Correlations for exponential regression between P levels in the supernatant and applied mmolar amounts of Fe/Al, as expressed in Equation (1), all exceeded $R^2 > 0.98$.

$$[P]_T = [P]_0 \times e^{-k[Fe/Al]} \tag{1}$$

where $[P]_T$ is the concentration of P in supernatant after treatment (mmol l^{-1}); $[P]_0$ the initial P concentration (mmol l^{-1}); k the exponential reduction coefficient and [Fe/Al] is the Fe or Al added (mmol l^{-1}).

The highest k-coefficient was observed for $FeCl_3$ ($k = 0.19$), followed by $FeCl_2$ ($k = 0.16$), $FeClSO_4$ ($k = 0.15$), PAC Sachtoklar 39 ($k = 0.12$) and Na

Aluminate ($k = 0.01$). Based on extrapolation from Equation (1), the dose of flocculants required to achieve discharge criteria can be estimated. To reduce initial levels ($[P]_0 = 322\,mg\,l^{-1}$; Table I) to the relevant criterion for discharge of treated waste water ($[P]_T = 2\,mg\,l^{-1}$ P), $26.7\,mmol\,l^{-1}$ FeCl$_3$ ($1470\,mg\,l^{-1}$ Fe), $31.8\,mmol\,l^{-1}$ FeCl$_2$ ($1746\,mg\,l^{-1}$ Fe) or $33.9\,mmol\,l^{-1}$ FeClSO$_4$ ($1863\,mg\,l^{-1}$ Fe) would be needed.

Barrow *et al.* (1997) obtained P-removal efficiencies of 88% from dairy waste waters by treatment with $807\,mg\,l^{-1}$ FeCl$_3$ ($278\,mg\,l^{-1}$ Fe). In their study FeCl$_3$ proved to be slightly more efficient in P-removal than Fe$_2$(SO$_4$)$_3$. Powers and Flatow (2002) achieved P-removal efficiencies of 30% and 83% when applying 40 and $250\,mg\,l^{-1}$ FeCl$_3$ (13–$86\,mg\,l^{-1}$ Fe) to pig manure containing 143–$234\,mg\,l^{-1}$ P$_{Total}$. No additional removal was observed at doses of $625\,mg\,l^{-1}$ FeCl$_3$. This may indicate that in their experiment, the remaining fraction above 83% consisted out of non-reactive forms of phosphates. Sherman *et al.* (2000) observed 0.17 mmol P removed per mmol Fe applied to manure at rates ranging between 188 and $376\,mg\,l^{-1}$ FeCl$_3$. This is substantially below levels observed in the current study, as presented in Figure 1. The higher flocculation efficiency achieved in the current experiment was attributed to pre-treatment in an activated sludge reactor.

As presented in Figure 2, produced sludge volumes were high for all flocculants tested, with levels up to 50% of the total volume in the highest applied doses. Furthermore, sludge volumes (%) increased linearly with increasing dose of the various flocculants. The produced volumes were comparable for FeCl$_3$, FeClSO$_4$, and PAC per mmol Fe/Al applied, while FeCl$_2$ application resulted in higher sludge volumes.
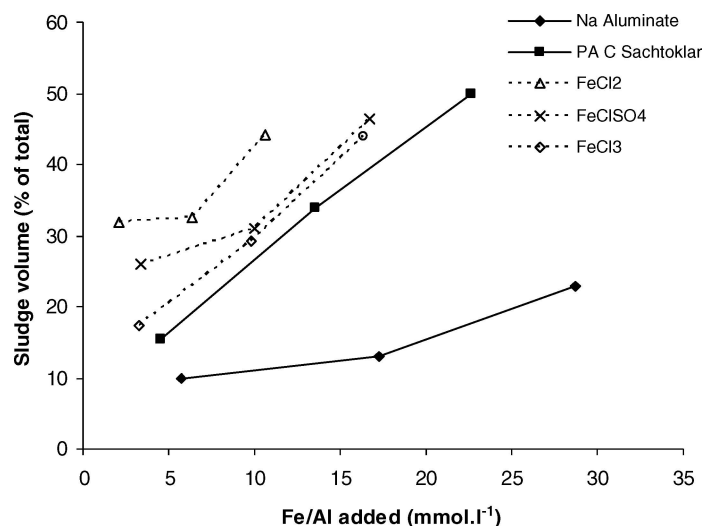

Figure 2. Sludge volume production, following treatment with the flocculants under study ($n = 3$; S.D. $< 5\%$, not shown for clarity).

If $FeCl_3$ or $FeClSO_4$ would be applied to decrease P-levels down to discharge levels ($2 \, mg \, l^{-1}$ P), as described above, then the estimated sludge production would increase up to 62% and 76% of the total volume respectively. The resulting sludge is very aqueous and the substantial waste stream offers additional dilemmas for further processing if subsequent separation of sludge and supernatant are conducted by decantation. Future studies will therefore include the evaluation of other separation techniques to reduce sludge volume as well as P content in the supernatant fluid. For example, Aguilar *et al.* (2002) proposed a number of coagulant aids to optimize reduction of the produced sludge volume after physico-chemical treatment of slaughterhouse waste water. The main action of these aids is to bring together and agglutinate the flocs formed by the coagulant, thus obtaining a considerable increase in the size of the same and a subsequent increase in the settling rate speed, as well as an improvement in the quality of the effluent. These authors obtained a reduction in produced sludge volume of up to 41.6% when anionic polyacrylamide was used in combination with ferric sulphate: at a dosage of $500 \, mg \, l^{-1}$ Fe and $50 \, mg \, l^{-1}$ polyacrylamide at pH 7, produced sludge volume reduced from 60% to 35%.

In manure processing, the resulting sedimentation sludge will ultimately be recycled as a fertilizer or soil enhancer, fit for export within or outside of the European Union. From the perspective of potential plant toxicity, Fe-based flocculants are therefore to be favoured above Al-based flocculants. In this regard, $FeCl_3$, $FeClSO_4$ and $FeCl_2$ are favoured over PAC Sachtoklar 39 for this particular use, although similar efficiencies in P-removal were observed.

Next to P-removal efficiency and desired sedimentation sludge characteristics, the economic cost will ultimately play a decisive role in the selection of the most suitable amendment. When ordered in bulk from the two manufacturers, $FeCl_3$ would approximately cost €$250 \, m^{-3}$, $FeCl_2$ €$75 \, m^{-3}$ and $FeClSO_4$ €$145 \, m^{-3}$. The lower cost for the latter 2 flocculants, is due to the fact that they are recycled from waste streams as secondary resources. Because the $FeCl_2$ solution used in our experiments contains a lower Fe content than the other two, higher volumes would be required to achieve similar results. To achieve legal discharge criteria using the flocculants under investigation according to Equation (1) would therefore cost €$1.95 \, m^{-3}$ with $FeCl_3$, €$1.49 \, m^{-3}$ with $FeClSO_4$ or €1.16 with $FeCl_2$. However, in light of the dilemmas posed by the linearly increasing proportional sludge volumes, combined with decreasing P-removal efficiency at progressively higher flocculant doses, an optimal dose, lower than the one required for total P-removal, may be preferred. At rates of $10 \, mmol \, l^{-1}$ Fe added, either in the form of $FeCl_3$ or $FeClSO_4$ ($3 \, ml \, l^{-1}$), sludge production is about 30% of the total volume while P-levels in the remaining supernatant have been reduced by 78–88%. Product cost per m^3 waste water would then range between €0.4 and €0.8. The remaining 10–20% of P in the supernatant then requires further polishing, either in a tertiary plant based system (constructed wetlands) or by substrate adsorption in a percolation filter (Section 3.2).

To evaluate P-removal efficiency when scaling the process from $1.5 \, l$ up to $50 \, l$ and $1000 \, l$, a second sedimentation experiment was performed by applying $3 \, ml \, l^{-1}$

TABLE III

Observed volumes of foam, sludge and supernatant (ml) and their respective P-content ($mg\,l^{-1}$) following treatment with $3\,ml\,l^{-1}$ $FeCl_3$ observed at different scales of operation; intervals depict standard deviation ($n = 3$)

| Test volume (L) | Foam | | Sludge | | Supernatant | | Removal efficiency (%) |
	P ($mg\,l^{-1}$)	Volume (L)	P ($mg\,l^{-1}$)	Volume (L)	P ($mg\,l^{-1}$)	Volume (L)	
1.5	–	–	824 ± 5	0.4	33 ± 3	1.1	88 ± 8
50	–	–	1859 ± 53	10	79 ± 2	40	82 ± 1
1000	2391 ± 644	7	1674 ± 884	170	115 ± 1	823	61 ± 1

$FeCl_3$ ($550\,mg\,l^{-1}$ Fe applied) to increasing volumes of waste water. Table III presents the observed volumes for sludge, supernatant and foam, their respective P content and the overall removal efficiency from the waste water. The removal efficiency decreased at increasing scale of the experiment. Further research will be required into the underlying causes. At the moment it is thought to be due to less optimal homogenization of the flocculant/waste water mixture at higher volumes. Sedimentation of flocculated P in the highest volume tested (1000 l), was thought to have been suboptimal, indicated by the formation of foam consisting out of floating P-precipitates. The foam was observed to gradually release these precipitates back into the waste water through sedimentation, resulting in a less efficient separation of waste water and flocculated P.

3.2. ADSORPTION EXPERIMENTS

Because sludge volumes linearly increased with increasing dosage of flocculants, while P-levels decreased marginally at higher doses, an optimal dose of $10\,mmol\,l^{-1}$ Fe ($550\,mg\,l^{-1}$ Fe) was proposed for physico-chemical precipitation (Section 3.1). Residual P-levels require further removal in order to obtain the discharge criterion of $2\,mg\,l^{-1}$ P. This could occur by constructed wetlands, the use of P-binding substrates, or a combination of both. The binding of P to substrates occurs by adsorption and precipitation reactions with Ca, Mg, Al and Fe (Arias et al., 2001). Substrates with reactive Al- and Fe-hydroxides or -oxides or calcareous substances are suitable for the removal of P (Arias et al., 2001). Drizo et al. (1999) assessed a number of different substrates for their potential of removing P from waste water: bauxite, shale, burnt shale oil, $CaCO_3$ as calcite, zeolite clay, expanded clay (argex) and fly ash. Depending on the substrate used, a P adsorption capacity of $420–860\,mg\,kg^{-1}$ was observed. Cameron et al. (2003) obtained good P removal from municipal sewage with a steel furnace slag filter, to remove residual P-levels after passage through a free-water constructed wetland. In the current study, a number of substrates were assessed by allowing the pre-treated liquid fraction of

pig manure to percolate over 1 kg dry weight of the various substrates under evaluation. Pre-treatment of the waste water occurred by passage through an activated sludge reactor and flocculation by $3 \, \text{ml} \, \text{l}^{-1}$ 40% $FeCl_3$ ($10 \, \text{mmol} \, \text{l}^{-1}$ Fe(III)).

Figure 3 shows influent and effluent levels of P after percolation over the substrates under evaluation. Initially, effluent levels were significantly below those in the influent. As the substrates were progressively saturated with P, the effluent levels started to increase. For the unamended sandy substrates, P_{Total} in the effluent was the same as observed in the influent, after 4 l of waste water was allowed to percolate over 1 kg of substrate. Addition of argex, clay or Fe-oxides yielded better results, with the sand:clay mixture showing the best performance. Fe-oxide amendment to sand was also evaluated at higher doses than the one described in Figure 3 (i.e. 20% and 30% Fe-oxide), but at these doses the oxides were observed to 'bleed' from the substrate, turning the effluent red. Higher doses of clay amended to the sand (>25%) were likewise evaluated, but resulted in significantly decreased hydraulic conductivity. Calcinated clay only exhibited low removal of P.

To quantify the adsorption capacity of the various substrates, two methods of calculation were adopted. Firstly, the difference was made between influent and effluent levels and integrated over the applied volumes of waste water. Secondly, the substrates themselves were analysed for P content at the end of the experiment and compared with control levels in untreated substrates. Table IV presents the estimated P-adsorption capacity, as calculated by these two methods. Differences can be observed between both means of estimation, yet the majority of these fall within the standard deviation intervals. Alganite and, to a lesser extent, coarse sand exhibited negative adsorption capacities when calculated as Δ[Treated, Untreated substrate]. This suggests leaching of P already present in these substrates. In particular alganite was found to already contain elevated levels of P in untreated controls ($9708 \pm 283 \, \text{mg} \, \text{kg}^{-1}$). In general, the unamended sand substrates as well as calcinated clay did not exhibit worthwhile P-removal capacities. Addition of Fe-oxide or argex improved the adsorption capacity. The highest P adsorption capacity, however, was observed for the sand:clay mixture (75:25).

To estimate the proportional importance of the clay, argex and Fe-oxide amendments in the various sand mixtures, calculations were conducted in accordance with Equation (2). For the values of $P_{\text{max,mixture}}$ and $P_{\text{max,sand}}$ in this equation, the estimates presented in Table IV were averaged.

$$P_{\text{max,mixture}} = X \times P_{\text{max,sand}} + Y \times P_{\text{max,amendment}} \tag{2}$$

where $P_{\text{max,mixture}}$ is the adsorption capacity of the mixture (Table IV); $P_{\text{max,sand}}$ the adsorption capacity of sand (Table IV); $P_{\text{max,amendment}}$ the adsorption capacity of the amendment and X, Y are the mass fractions of sand and the amendment respectively.

Equation (2) resulted in adsorption capacities for argex, clay and Fe-oxide of $484 \, \text{mg} \, \text{kg}^{-1} \, P$, $1146 \, \text{mg} \, \text{kg}^{-1} \, P$ and $513 \, \text{mg} \, \text{kg}^{-1} \, P$ respectively. When compared to the full argex substrate, as shown in Table IV, distinctly higher values were
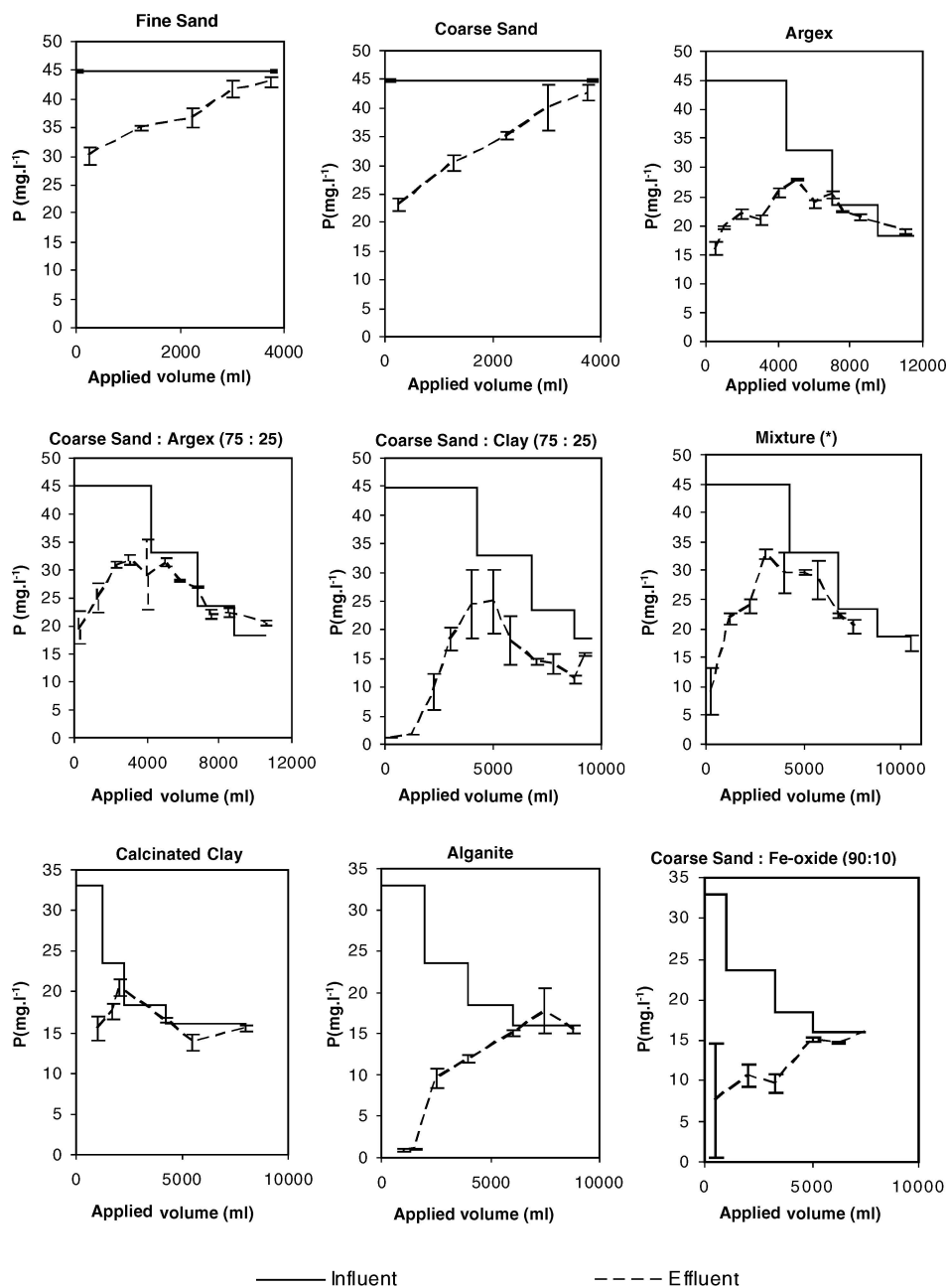
Figure 3. Influent and effluent levels of P in waste water percolated over the various substrates under investigation (1 kg substrate per column); waste water in experiment concerns the liquid fraction of pig manure after (i) separation, (ii) passage through activated sludge reactor (30 days) and (iii) treatment with $3\,ml\,l^{-1}$ 40% $FeCl_3$ ($n = 3$).

TABLE IV

Estimated P-adsorption capacity of the various substrates under evaluation (mg kg^{-1}); calculations based on integrated difference between influent and effluent levels (1st column) and on difference in P content of the susbtrate with or without application of waste water (2nd column); intervals depict standard deviation ($n = 3$)

Substrate	$\Sigma(\Delta[\text{influent, effluent}])$	$\Delta[\text{Treated, untreated substrate}]$
Coarse Sand	43 ± 4	-27 ± 73
Fine Sand	31 ± 3	8 ± 5
Expanded Clay (Argex)	190 ± 7	71 ± 37
Coarse Sand:Argex (75:25)	153 ± 36	90 ± 155
Coarse Sand:Clay (75:25)	319 ± 35	493 ± 291
Calcinated Clay	59 ± 10	21 ± 42
Alganite	139 ± 17	-895 ± 432
Mixture[a]	117 ± 9	267 ± 180
Coarse Sand:Fe-oxide (90:10)	90 ± 15	108 ± 92

[a]72.5% coarse sand, 17.5% fine sand, 7.5% clay, 2.5% argex.

observed: 71–190 mg kg^{-1} P-binding capacity. This difference was attributed to the fact that in the full argex substrate, the granules tended to float when waste water was applied to the pots, resulting in suboptimal contact between substrate and influent. This effect was observed to be far less in the argex:sand mixtures. Adsorption capacity of argex may therefore be underestimated in the pure argex treament. To validate this hypothesis 5 kg of argex granules were submerged for 48 h in 60 L of waste water with a P_{Total} of 79.3 mg l^{-1}. After exposure to argex, P_{Total} decreased to 49.1 mg l^{-1}. Assuming, P removal occurred predominantly at the level of the argex granules, this would result in a P-binding capacity of 362 mg kg^{-1}. Drizo *et al.* (1999) observed adsorption capacities for expanded clay, zeolite and bauxite of 420 mg kg^{-1} P, 460 mg kg^{-1} P and 610 mg kg^{-1} P respectively. With exception of much higher adsorption capacity observed for the clay substrate in the current experiments, our results are in general agreement with those reported by Drizo *et al.* (1999).

4. Conclusion

Physico-chemical precipitation by Fe-based flocculants can provide an efficient intermediary step to remove much of the excess phosphates. Although equally efficient in our experiments, Al-based flocculants are considered to be less suitable, considering the eventual valorisation of the sedimentation sludge in agriculture and the risk for increased phytotoxicity at elevated levels of Al. Removal down to the 2 mg l^{-1} P discharge threshold would require 27 mmol l^{-1} FeCl$_3$ or 34 mmol l^{-1} FeClSO$_4$ and cost €1.5–2.0 per m^3 waste water in product cost. The FeClSO$_4$ used

in our experiments, recycled as a secondary resource, is comparable in performance but cheaper in product cost than the industry grade $FeCl_3$ product. However, treatment down to discharge criteria would result in a voluminous aqueous sludge, which accounts for 62–76% of the total volume. Unless the sludge can be subsequently dewatered efficiently, this approach is not sustainable. Treatment with $10\,\text{mmol}\,l^{-1}$ Fe on the other hand would result in a P-removal efficiency of 78–88%, while sludge volume production is 30% of the total volume. However, further treatment by other means (e.g. substrate adsorption and/or constructed wetlands) would then still be required to reduce P-levels to below discharge criteria.

Additional physico-chemical P-removal could be achieved by using adsorbing filter bed materials. The most promising substrates, observed in our experiments were: (i) clay, with a P-adsorption capacity of $1146\,\text{mg}\,\text{kg}^{-1}$, (ii) expanded clay (argex) with a capacity of $484\,\text{mg}\,\text{kg}^{-1}$, (iii) Fe-oxide powder with a capacity of $513\,\text{mg}\,\text{kg}^{-1}$. Application of P-adsorbing substrates can occur either in a filter bed containing these substrates, by mixing them with the pre-treated waste water in a second sedimentation treatment or by using these substrates in a constructed wetland. Valorisation of P-saturated products is feasible for both clay and Fe-oxide by recycling them and co-processing them with the solid fraction of pig manure into a final exportable soil enhancer or fertilizer. The proposed waste management pathway is both more economic and sustainable than current engineering techniques (mostly membrane technology), required to achieve discharge criteria.

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