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'Active' filters: a mini-review on the use of industrial by-products for upgrading phosphorus removal from treatment wetlands.

F. Chazarenc*, M. Kacem, C. Gérente and Y. Andrès

ABSTRACT

In treatment wetlands for domestic wastewater disposal, a considerable decrease in phosphorus removal is generally observed after 3-4 years following the startup. Treatment wetlands performances have to be upgraded more and more often by directing durably discarded P according to requirements. The use of high P-capacity media was identified as a major issue over the last 10 years, and elevated P-sorption capacities of industrial by-products including steel-slag, iron-slag, oil-shale-ash and coal ash were recently highlighted. Besides updating the knowledge, this mini-review is aimed at critically evaluating the feasibility of using industrial by-products inside or downstream of treatment wetlands in terms of P-sorption capacities, mechanisms and limits. Most of the valuable available literature (46 articles in peer reviewed journals) has been incorporated. Recent advances were mainly considered as half of the articles were published over the last three years. In selected papers, investigations were mainly conducted at lab-scale in batch (49%) or columns (38%) and to date, there have been few attempts to estimate the efficiency of field-scale experiments (13%). Among the P-removal mechanisms it was mostly postulated that industrial by-products both favor Ca-P precipitation followed by crystallization and sorption on active sites onto the surface of the media (e.g. ferrous oxides). Max P-sorption capacities (from 0.01 to 50 g P/kg material) are not solely relevant, but environmental aspects such as alkalinity release and clogging were investigated. The technical and economical feasibility of field-scale filters is discussed. Despite the fact that there have been few works dealing on how to deal with industrial by-products after P-saturation, possibilities have been discussed including replacement/rejuvenation and valorisation as fertilizers.

Keywords. Phosphorus retention, industrial by-products, steel slag, fly and bottom coal ash, oil-shale ash.

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INTRODUCTION

In treatment wetlands for domestic wastewater disposal, a considerable decrease in phosphorus removal is generally observed after 3-4 years following the startup. Treatment wetlands performances have to be upgraded more and more often by directing durably discarded P according to requirements. Legislation on P discards in the surrounding environment is becoming stricter worldwide including (for) wastewater treatment plant having a capacity less than 2000 PE (People Equivalent). In average, wastewater discharge guidelines generally require TP (Total Phosphorus) concentrations to be less than 1 mg/L. Many solutions have been found to durably remove phosphorus from wastewater, in all cases P is removed by converting the phosphorus ion into a solid form either by physico-chemical or biological process. Phosphorus removal in constructed wetlands occurs from adsorption, plant uptake, complexation, and precipitation (e.g. Vymazal, 2007). Phosphorus cycling and storage involves a complex set of processes. Plant uptake is not a suitable measure of the net removal rate in a wetland because most of the stored phosphorus is returned to the water by decomposition processes. Since the plant uptake

is not a sustainable P removal mechanism, there are two other possibilities for phosphorus removal:

a) Chemical pre-precipitation which is a standard in technical wastewater treatment plants for activated sludge technology. Typically metal hydroxides are used and phosphorus is removed with the surplus sludge from the system. Only preliminary tests have been carried out for using pre-precipitation for treatment wetlands but it seems that the use of metal salts (FeCl_3 , Al_2SO_4) is not technically and economically feasible (Esser et al., 2004).

b) Use of special filter materials. A lot of research has been performed to test filter material for wetland systems to overcome poor P removal using specific materials (Westholm, 2006). Among the main reactive media used, the use of industrial by-products (IBPs) has recently followed an increase. The use of IBPs including steel and iron-slag, coal or oil-shale-ash was shown to be efficient for removing P from wastewater as it represented both a source of calcium and hydroxide for P precipitation along with a source of metal oxides for P adsorption. If the good P-sorption associated with using IBPs have been repeatedly demonstrated at the lab

scale, it remains unclear whether lab results can be applied at the field scale and how each IBP will behave when used in full scale units. In other words, besides updating the knowledge, this mini-review aimed at critically evaluating the feasibility of using IBPs inside or downstream of treatment wetlands in terms of P-sorption capacities and durability, technical feasibility and limits. We reviewed most of the valuable literature published in peer reviewed journals, and focused on the use of IBPs for P removal from all wastewater sources. Others IBPs were studied for wastewater treatment including cement clinker, cement kiln dust, calcinated cow bone, red mud, etc., but we decided to put an emphasis on the use of steel and iron slag and on power plant incineration ashes because they are available worldwide and were mostly studied.

STUDIES SELECTION

The studies were selected using the search engine of ISI Web of Knowledge with "industrial by-products" or "slag" or "ash" and "wastewater treatment" or "phosphorus removal" as keywords. The studies were selected according to the following criteria: 1) lab scale (batch, columns) and/or field scale (filter filled with reactive media) experiments were conducted using IBPs; 2) at least one of the IBPs investigated was from iron or steel industry or from power plant industry; 3) phosphorus removal from wastewater was the main goal of at least one of the investigation in the paper.

We found 46 papers matching our criteria (see Table 1 for study identification number). Recent advances were mainly considered as half of the articles were published over the last three years. In selected papers, investigations were mainly: batch/equilibrium (49%), columns/dynamic (38%) and to date, there have been few attempts to estimate the efficiency of field-scale experiments (13%). Considering the findings of the 46 selected papers it was difficult to normalize all the data. Thus we decided to form three groups:

Batch/equilibrium investigations: in which fresh or weathered reactive media were in contact with P-enriched solution for less than a week to:

- determine sorption mechanisms and to model it using mainly Freundlich and Langmuir isotherms.
- compare sorption capacities between samples before a second step of dynamic experiments (#7, #9, #1).

- models P-sorption kinetics using the pseudo second order model (#20, #21), the intra-particle diffusion model (#20) or using Mintab (#13).

Columns/dynamic investigations: in which reactors were fed for (during almost 1 month under dynamic conditions with a synthetic P solution or real effluent. Studies were mainly focused on

- P-sorption capacities of the media in process conditions;

- the effect of one or two controlled parameters on P-sorption including inlet pH, inlet P concentration, residence time distribution etc.

- the durability and reversibility of P-sorption.

Field scale: in which investigations were made on reactors of almost 1 m³ of total volume and their performance to treat real wastewater in situ conditions.

Furthermore, Scanning Electronic Microscope (SEM) investigations were conducted on the different media used in the three groups to observe surfaces nature and composition and their evolution during P-sorption. It was a powerful tool to better understand P-sorption mechanisms. The investigations were mainly conducted on by-products coming from three main industries: (Table 2): steelmaking slag (78% of the investigation), coal burning by-products (14%), oil shale burning by-product (3%). In steelmaking industry, input materials (iron ore, scrap metal, fluxing agents such as lime, etc.) are charged to a furnace, refined, and heated beyond their melting points. Two or more liquids are formed when these materials reach a state of complete fusion. The liquid with the lowest specific gravity forms a layer on the surface of the melt that is called slag (Proctor et al., 2000). In the power plant industry, coal or oil-shale combustion generates fly and bottom ash. Fly ash is generally captured from the chimneys of power generation facilities, whereas bottom ash is removed from the bottom of the furnace.

BATCH / EQUILIBRIUM ANALYSIS

Batch experiments are easily feasible and low cost, as they do not require more than few grams of IBPs, and can give interesting results shortly compared to columns or bench scale experiments. Three main investigations are conducted using batch experiments: kinetics modelling to better understand P removal mechanisms, isotherm drawings to estimate the maximum P-sorption capacity of the IBPs at a given contact time and de-sorption analysis (saturated media is placed in desorption solution and P release is measured) to estimate the bounded P potential release

Acid neutralisation capacities (ANC) were also measured in parallel with batch experiments to estimate the available CaO in the media, as CaO

release was supposed to be a major mechanism favouring P-sorption (#20).

In most batch investigations, the amount of P bounded on the media compare to the amount of precipitated P in the solution was not distinguished as many protocols were based on supernatant filtration (0.45 μm filter) followed by o-PO_4 colorimetric measurement. Thus the maximum sorption capacity of the media must have been overestimated, and this was confirmed in several studies when batch investigations were conducted along with column fixed bed scale trials.

Moreover, the maximum removal capacity was observed to be more or less proportional to the maximum P concentration used in the isotherms experiments. For example the maximum P-sorption of 46.5 or 50 g P/kg material were observed when using maximum P concentration of 8000 to 14 000 mg

P/L (#8, #18). In real wastewater conditions P content would vary between 1-10 mg P/L thus the maximum sorption capacities are not applicable to wastewater conditions (#27). Abrasion was also reported as a biased factor, especially in studies using large agitation by creating fine particulate matter possibly increasing P-sorption capacity (#14).

Considering the large amount of experimental conditions assayed in batch experiments it is difficult to compare Freundlich, Langmuir or others isotherm references (Frumkin, BET, Temkin...), sometimes even within the same study (#8). It was also difficult to rank the different IBPs tested in the selected papers as a wide range of maximum P-sorption capacities were observed along with contradictory results in ranking IBPs from a study to another.

Table 1 Details on the experiments selected

Study #	Authors	Industrial by-product studied	Type of experimental investigations				
			Batch / equilibrium	Column / bench scale	Field scale	SEM investigation	Desorption analysis
1	Yamada et al., 1986	BF	x			x	x
2	Sunahara et al., 1987	BF		x			
3	Mann and Bavor, 1993	BF	x				
4	Lee et al., 1996	BOF (dust), BF	x				
5	Lee et al., 1997	BOF (dust), BF	x				
6	Mann, 1997	BF, BOF, Fly and Bottom ash (coal)	x	x			x
7	Baker et al., 1998	BF, BOF	x	x		x	x
8	Sakadevan and Bavor, 1998	BF, BOF	x				
9	Johansson, 1999a	BF (amorphous, crystalline)	x				
10	Johansson, 1999b	BF (amorphous, crystalline)		x			x
11	Johansson and Gustafsson, 2000	BF (amorphous, crystalline)	x				
12	Grüneberg and Kern, 2001	BF (amorphous)		x			x
13	Agyei et al., 2002	BF, Fly ash (Coal)	x				
14	Drizo et al. 2002	EAF	x	x		x	
15	Smyth et al., 2002	BOF			x		
16	Cameron et al., 2003	BF			x		
17	Naylor et al., 2003	EAF		x			
18	McDowell, 2004	EAF, BOF, Fly and bottom ash (coal)	x				
19	Yim and Kim, 2004	BF, EAF, BOF		x		x	
20	Kostura et al., 2005	BF (amorphous, crystalline)	x				
21	Oguz, 2005	BF	x				
22	Shilton et al., 2005	EAF		x			
23	Vohla et al., 2005	Bottom ash (oil-shale)	x		x		
24	Calder et al., 2006	BF			x		
25	Cha et al., 2006	BOF		x			
26	Drizo et al., 2006	EAF		x			
27	Hedstrom and Rastas, 2006	BF	x	x			
28	Hylander et al., 2006	BF (amorphous, crystalline)		x			
29	Kim et al., 2006a	BOF	x	x		x	
30	Kim et al., 2006b	BOF		x		x	
31	Shilton et al., 2006	Melter slag			x		
32	Xu et al., 2006	BF, Fly ash (coal)	x				
33	Chazarenc et al., 2007	EAF		x			
34	Korkusuz et al., 2007	BF (amorphous)	x		x		
35	McDowell et al., 2007	EAF	x				
36	Mortula et al., 2007	BF	x				
37	Pratt et al., 2007a	Melter slag	x			x	x
38	Pratt et al., 2007b	Melter slag				x	
39	Weber et al., 2007	EAF		x			
40	Yan et al, 2007	Fly and bottom ash (coal)	x				x
41	Zhang et al., 2007	BF		x			
42	Chan et al., 2008	Bottom ash (Coal)	x	x	x	x	
43	Gustafsson et al., 2008	BF		x			x
44	Kaasik et al., 2008	Bottom ash (Oil-shale)	x			x	
45	Lu et al. 2008	BF, BOF	x				x
46	Xiong et al., 2008	BF, EAF	x	x		x	x

Table 2 Description of industrial by-products used to treat phosphorus from wastewater.

Industrial origin, common names	Short description	Main composition	Remarks
Nonmetallic coproduct of iron and steel production			
	<u>Crystalline Slag (CS)</u> : Air-cooled: Air-cooled slag is produced by allowing the molten slag to cool slowly in air in an open pit. When the material solidifies under slow cooling conditions, escaping gases leave behind a porous, low-density aggregate. Less foam: Hard granulated slag		
BF Slag , Blast Furnace slag is used for iron production	<u>Amorphous Slag (AS)</u> : Granulated: by quenching (rapid cooling) the molten slag into glass by using high-pressure water jets. When formed under controlled rapid cooling in air (quenching), the slag tends to be hard and dense, making it especially suitable for use in road base and similar structural applications. Contain more foam: Soft granulated slag Expanded: controlled rapid cooling of molten slag in water or in water with a combination of steam and compressed air. Steam and other gases enhance the porosity and vesicular nature of the slag, resulting in a lightweight aggregate suitable for use in concrete: Soft granulated slag	CaO ~ 40 % SiO ₂ ~ 35 % Al ₂ O ₃ ~ 10 % MgO ~ 10%	No environmental risks associated with the use of BF used for road construction.
BOF Slag , Basic Oxygen Furnace, or SF, Steel Furnace, is used for steel production	Produced in a furnace supplied with oxygen to remove carbon. Can have several degrees of foaming. Slag foaming is caused by the combustion of carbon in the metal itself and is a drawback to the process.	CaO ~ 50 % Fe ~ 15 % SiO ₂ ~ 10 % MgO ~ 5 %	Almost no risks of heavy metal release in converted slag. Can be used as fertilizer in agriculture.
EAF Slag , Electric Arc Furnace is used for steel and stainless steel production	Produced in an electric arc furnace, a furnace adapted for scrap metal recycling. Very crystalline form, hard granulated slag. Composition of EAF slag can change from a production batch to another depending on the nature and amount of scrap metal recycled.	CaO ~ 50 % SiO ₂ ~ 30 % MgO ~ 5 % Fe ~ 2.5 %	considering the quality of the steel produced, adjuvent such as Vanadium can be added .
Melter Slag is a specific production from sands rich in iron	Mainly produced in New-Zealand, melter slag are rich in TiO ₂ .	TiO ₂ ~ 35 % Al ₂ O ₃ ~ 18 % CaO ~ 15 % SiO ₂ ~ 12%	
Power station 1: Coal burning by-product			
Bottom ash (coal) or Coal slag	Bottom ash represents the waste residue from burning coal. The composition is related to the type of coal used (e.g. bituminous, lignite and sub-bituminous). In average, they consist mostly of silicon dioxide (SiO ₂), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous; aluminium oxide (Al ₂ O ₃) and iron oxide (Fe ₂ O ₃). Bottom ash is much coarser than fly ash. It is an almost sand-like material that is sluiced from the bottom of the boilers.	CaO ~ 10 % SiO ₂ ~ 40 % Al ₂ O ₃ ~ 20 % Fe ₂ O ₃ ~ 7%	It exhibits cementitious and/or pozzolanic properties, which makes it useful in concrete and geotechnical construction applications
Fly ash (coal) or Fly ash	Fly ash is a very fine powder material that is carried with the stack gases and generally collected by electrostatic precipitators or baghouse filters prior to exiting the stack.		Heterogeneous, mixture of glassy particles with various identifiable crystalline phases including quartz, mullite, iron oxides...
Power station 2: Oil-shale burning by-product			
Oil-shale ash , Oil-shale bottom ash	Oil-shale ash is an industrial waste from burning of oil-shale dust (50/50 mixture of oil-shale and limestone) in temperature of 1300-1460C. The finest part (particles < 100 microns) is called fly ash, which form ca 65-80% of whole ash.	CaO ~ 40 % SiO ₂ ~ 30 % Al ₂ O ₃ ~ 10 %	

COLUMNS / DYNAMIC EXPERIMENTS

Depending on the size of the columns, dynamic experiments can represent an alternative low cost option to batch investigations. However, in many columns a significant change in P removal was observed after at least 6 months of investigations. Thus to be effective, dynamic

experiments have to last for at least 6 months (Table 4).

The effect of loading rate, thus of residence time distribution, was studied in several columns investigation. Two or more loading rate were frequently studied, generally by modifying loading rate over time in the same units and comparing the different time series (#2, #25,

#33, #39, #41). Although 40% of the studies used synthetic solutions (P salt and tap water),

other sources were investigated as well including domestic wastewater (#6, #25, #27, #28, #41, #42, #46), waste stabilization pond or constructed wetland effluent (#22, #33) or dairy effluents (#12, #39). Large differences between P-sorption capacities were recorded according to the nature of the treated water. In one study the same experimental set-up was used both at the lab scale and at the field scale and results were better when treating a waste stabilization pond effluent rather than a synthetic solution (#22). This highlighted the limits of lab scale columns investigation as the P removal process can be greatly affected by real life conditions. Several columns investigations were stopped due to clogging. Clogging was a big issue when using IBPs and was mainly associated to the use of fine media size, to biofilm development

caused by large amount of TSS and COD in the supplied effluent, and in a minor extend, to CO₂ capture and precipitation under CaCO₃ inside media, and to the flow rate. To overcome clogging several solutions has been proposed including the use of pre-filter to remove soluble CO₂ and organic carbon (#2, #33), the use of larger sized media (more than 5 mm medium diameter) and the use of closed columns to prevent atmospheric CO₂ to be trapped (#33). One other major issue of the columns investigations was the high pH recorded at the outlet especially at the beginning of experiments. In all the studies except (#48) pH was greater than 9 and moreover, in nearly one third of the studies, a pH decrease at outlet was observed along with P removal efficiency decrease. Thus reducing outlet pH represents a major issue but can act directly on P-removal efficiency and care must be taken when solving this problem.

Table 3 Main batch results.

Study #	IBPs tested	Particle size (mm)	Ratio IBPs/water (g/mL)	Range in [P] mg (P/L)	Contact time (h)	Max sorption capacity (mg P/g mat.)	Main results
1	BF1 (porosity 5.0%) BF2 (porosity 8.8%) BF3 (porosity 23.3%) BF4 (porosity 55.6%)	0.06-2	0.02	0.85-375	1		Bets pH for P retention: 8.0 BF (the more porous one) showed better P retention. The P adsorbed was large at high T. the P adsorption decrease with increasing the concentration of co-existing salt.
3	BF (amorphous) Fly Ash	0.08-4.75 < 0.5	0.5	5-100	24	0.16 0.42 0.26	BF > BF (amorphous) > Fly ash.
4, 5	Converter slag (dust) BF	0.018 0.050	Column exp.	0-50	-	33.4 15.6	Column system but results based on equilibrium conditions Intraparticle diffusion was observed to be very slow process and represented the rate controlling step
6	BF (amorphous) BF BOF Fly Ash (coal) Bottom Ash (coal)	2 15 15 0.012 10	0.5 0.5 0.5 0.05 0.25	5-100	30	0.45 0.40 0.38 0.625 0.06	Fly ash > BF (amorphous) > BF = BOF
7	Mix with 5% wt BOF (oxide) Mix with 5% wt BOF Mix with 5% wt OG-sludge Mix with 5% wt BF-sludge	0.003-0.1 0.84 Powder Powder	0.1	10	10	-	Results gave: BOF-oxide=BOF-slag>OG-sludge>BF-sludge
8	BF BOF	N/A	0.1	0-8000 0-200	48	44.2 1.9	Very high capacity for BF were reached Chemical P adsorption is dominant and is initially fast, slower physical adsorption might take place when approaching saturation of binding sites The presenc of Ca, Al and Fe oxides in substrates may improve the removal capacity of substrates by both adsorption and precipitation
9, 11	BF-Amorphous BF-Crystalline Fly ash Powder	0-0.125 0.25-4 0-0.125 0.25-4	0.02	0-25	24	0.3 0.15 0.9 0.7	BF-Crystalline coarse>BF-Crystalline fine>BF-Amorphous P removal was associated to strongly alkaline condition (pH>9) and large amount of soluble Ca However the supersaturation was maybe too low to initiate Ca-P precipitation
13	Fly Ash BF	0.026 0.031	0.01	20-80	10	from 1.7 to 11 from 3 to 20.6	No effect of particulate size. Better removal at higher temperature and ant lower pH
14	EAF	2.5-10	0.05	0-20 0-320	24	4	Depending on the range of P concentration applied P sorption on EAF increased 13 times from 0.3 to 4 mg P/g
18	Fly ash (coal) Bottom ash (coal) (1) Bottom ash (coal) (2) Melter slag (1) Melter slag (2) BOF	- <2 2-4 0-10 0-10 0-10	0.05	0-150 0-150 0-150 0-150 0-14000	16	- 3.1 1.8 2 2 50	Both melter slags had neither toxicological nor agronomic impairment
20	BF-crystalline BF-amorphous-fine BF-amorphous BF-amorphous-coarse BF-Amorphous II	0-0.1 0-0.063 0-0.1 0.1-0.18 0-0.1	0.01	50-500	150	18.94 16.08 6.47 3.22 8.5	High correlation between slag capacities and Acid neutralization Capacities for both Amorphous and crystalline BF Kinetic: model of the pseudo-second-order reaction and by applying the intra-particle diffusion model The intra-particle diffusion only exercised its influence during the initial 60 min of the sorption process and then controls the limiting rate of this process
21	BF	0.02-0.03	0.06	150-500	1	3.56	Equilibrium after 20 minutes. Confirmation the P removal on BF slag is favored at high temperature
23	Oil shale fly ash Oil shale bottom ash	<0.063	0.04	5-1000	48	4	o-PO4 removal was achieved at an optimum pH of 4,5 In the pH range 3 – 8.5, phosphate removal probably occurs by ion-exchange mechanisms. At values higher than pH 8.5, phosphate removal take place by a precipitation mechanism It was hypothesized that phosphate removal at pH 8.5 decreased because of stronger competition with hydroxide ions on the adsorbent surface.
27	BF-crys-fresh BF-crys-Weath BF-crys-Weath++	0.5-2 0.5-2 1-5.6	0.013	0- 20	20	from 0.038 to 1.5 from 0.025 to 0.64 from 0.012 to 0.24	Weathered slag have a lower P csorption capacity. Real wastewater decrease P sorption compare to synthetic effluent.
29	BOF	<0.075	0.001	3	24		High alkalinity reduced P sorption, Mg was a P sorption limiter as well, Fluoride seemed to increase P sorption (fluorapatite). Fe had a limited effect.
32	Bottom ash (coal) Fly ash (coal)	- -	0.05	100-1000	24	>8 >8	Use of peat decreased the pH and reduced P sorption in the batch experiments. P adsorption: furnace slag-fly ash P sorption capacity for by-products was influenced by the content of Ca, Mg, Fe and Al.
34	BF (Amorphous)	< 3	0.032	0-320	24	0.01 to 9.15	Loosely-bound P was due to the high metal content and large surface area of the BF, whereas Ca-bound P was due to high Ca content and basic condition (pH>7.7)
35	mix of: Melter slag-85%; EAF-10%; BF-5%	2-4	0.05	0-50	16	4.5	pH at the end = 7,8
36	BF	1.25	0.004; 0.008; 0.012; 0.016	2.5	12 days	0.59	Under similar experiment conditions, P sorption was lower when using real wastewater (51%) compare to P spiked deionised water (88% removal)
37	Melter slag Saturated in P						Max P release (100%) at low pH and Eh (pH 4.9 and Eh -400 mV)
40	6 types of coal ash: Bituminous-Bot-fresh Bituminous-Bot-Weat Lignite-Bot-fresh Bituminous-Fly-fresh Bituminous-Fly-Weat Lignite-Fly-fresh	1.92 0.07 1.98 0.11 0.15 1.05	0.05	5-40 5-40 5-40 450-700 200-600 950-1500	72	0.01-0.08 0.02-0.10 0.09-0.79 0.90-12.50 3.90-10.00 19.4-29.5	Fly ash > Bottom ash Lignite coal > bituminous coal Precipitation of calcium phosphate was predominant mechanism
42	Bottom ash (coal)	2.4-10	0.025	0-540	24	1.37	The removal rate of total phosphorus is basically a function of the degree of adsorption of ion to the soil matrix. The high concentrations of aluminium, iron and calcium of coal slag provided an enormous potential for the system to serve as phosphorus sinks. However, phosphorus adsorption sites can be blocked by a biofilm coating on the soil particles.
44	Bottom ash (Oil-shale) weathered	1-2 < 0.01	0.001 to 0.01	1.3	1 to 216	65	Results suggest that the phosphorus removal is only governed by the chemical precipitation mechanism The good P-binding potential of hydrated oil-shale ash is due to the high ratio of reactive Ca minerals. Treatment with P-containing solution causes the partial-to-complete dissolution of Ca minerals and the precipitation of Ca-carbonates and Ca-P phases.
45	BF BOF	<0.1	0.02	50-8000	6	46.5 33.3	Ca-P precipitation was shown to be the major P retention mechanism At pH 6.93, the P desorbability was about 10% The removal of P in BF and BOF is related to the formation of phosphate calcium precipitation and the adsorption on hydroxylated oxides
46	EAF	<2	0.04	1-45	2	5.3	The phosphate adsorption percentage increased with increasing contact time and attained equilibrium at variable time according to the initial concentrations of phosphate. The removal percentage decreased with the increasing initial phosphate concentrations.

Table 4 Main Columns results.

Study #	IBPs tested	Particle size (mm)	Nb of units	Vtot/unit (L)	Flow type*	Retention time (d)	Experiment duration Pore vol. Days	Influent characteristics (TSS, COD, TN...)	Inlet P (mg P/L)	Outlet pH	Observed		Main findings
											P sorption	P retention (g/kg)	
2	BF	0.15-10	1	17.7	S V D	0.016-0.012	500	Synt. Sol.	1.1 - 7.9	11 - 9	> 95%	0.29	Wastewater decarbonation increased P removal process. Best conditions for P removal: Ca ²⁺ : 80; CO ₂ less than 15 mg/L
6	BF BOF	15	6	0.07	U V	6	115	Autoclaved 2d effluent	10	8.5-9.5	32% 28%	0.088 0.076	pH 7-9 RTD 24 min More than 80% P remained bound to gravel after P desorption
7	Mix 5% BOF with 45% limestone and 50 % silica	0.5	1	6.3	S V	0.9	1450	Synt. Sol.	3.3	9-10	>80%	0.6	One of the longer experiment, 4 years. Good efficiency of the mix
10	BF (crystalline) BF (amorphous)	0-0.125 0.25-4	7	35	U V	NA	392	Synt. Sol.	10	12 - 8 12 - 10.5	80 - 40% 80 - 60 %	1.25	Gradient was observed, P mainly retained at the surface. Amorphous slag = better potential
12	BF (amorphous)	0.3-1	6	9.1	S B L	NA	126	Dairy farm effluent (COD: 300-1199; TN: 43-213)	46 - 42	NA	>97 %	0.06	High amount of P 0.15 g/kg were stored under the form of NH ₄ Cl-P in the slag substrate
14	EAF	2.5-10	1	1.25	S V D	0.34	278	Synt. Sol.	350-400	9.9 - 10.5	NA	2.35	Regeneration assay increased slightly lifespan by emptying the column and giving a rest period of 4 weeks.
17	EAF	5-15	20	280	S H	4	210	Fish farm effluent (TSS: 187; COD: 373; TKN: 12.4)	2.7	9.4-10.7	>86%	NA	Plant encountered difficulties to develop under high pH conditions....
19	BF BOF	0.6	3	0.7	U V	0.02	34 180	Synt. Sol.	3 - 6	8 11 >10.5	74.2 % 99.3 % 99.9 %	NA	SEM analysis provides evidence that the cristallization of HAP occurs on surface of slag
22	EAF	NA	2	17.7	U V	3-48 12-72	208 183	Synt. Sol. WSP effluent			24% 64%	NA	Effect of HRT well tested. Field study gave better results than the lab effluent.
25	BOF	1-2	4	1	S V U V	NA	263	2d effluent (TN: 25)	2	11	100%	NA	High pH associated with slag gave poor nitrification. Relative redox was non-oxidative due to slag presence
26	EAF 79% EAF, 21% Limestone	2.5-10	4	8	V S	1	116 11	Synt. Sol.	20 400	11 10.6	100%	2.5 2.2	Adding limestone did not significantly improve P removal efficiency. Max retention not reached. Large differences between batch and bench-scale in terms of P sorption capacities. Sulfite release were also measured
27	BF Wheathered	1-5.6	1	8.5	S H	3.8	98	Settled domestic effluent	1.0-5.3	9 - 7	100 - 70%	0.02 - 0.005	Pot valorization in planted experiments, can be recycled as a combined fertilizer for plant production
28	BF	0.25 - 4 2-7	4	35	U V	NA	469	Settled domestic effluent	4.2	8.9-9.2	NA	0.3 - 0.05	SEM investigation showed precipitate were mainly under HAP form
29	BOF	0.5-1.2	1	1.25	S V D	NA	454	Synt. Sol.	2 - 5		90.4%	NA	A pre-treatment column was used to trap organic matter and inorganic carbon to increase lifespan of slag columns. High outlet pH however.
33	EAF	5-15	6	6.2	S V D	1.1 - 0.5	112	CW effluent (TSS: 29; COD: 35)	12	10.3	>75%	0.3	Differences between previous lab scale experiments and actual field results, field results better (probably because of the dairy wastewater composition)
39	EAF	5-14	6	55	S V D S V	12 - 24	269 180	Raw and treated dairy effluent (Raw: TSS: 900; BOD: 2800; treated TSS: 124; BOD: 800)	38 29	10.0 - 9.0 11.0 - 8.5	80 % 63%	1.5 1.8	A comparative study conducted during 6 month. Good perf off BF but few data available
41	BF	8-12	1	49	U V	NA	180	Diluted domestic effluent (BOD: 21.3. TN: 12.5)	0.9	NA	90%	NA	Possibility of quick saturation of the coal was not investigated
42	Bottom ash (coal)	2.4 - 10	3	18	S B L	1	112	Raw domestic effluent	2.5	NA	70%	NA	Biofilm was formed on the coal slag in the pilote system after 3 months of startup stage
43	BF	0-4	1	4.7	S V	NA	1590	Synt. Sol.	5	11.4 - 8.8	95- 85.6%	3.11 - 1 (outlet)	Removal mechanisms were studied and showed role of amorphous tricalcium phosphate in removal
46	BF, EAF	<2	2	6.3	NA	NA	30	2d effluent	1 - 3.4	7.5-8.0	62-79%	NA	Despite the short time the experiment lasted, confirmation of the potential of slag for P removal

Field scale studies

Study #	IBPs tested	Particle size (mm)	Nb of units	Vtot/unit (m3)	Flow type*	Retention time (d)	Experiment duration Months	Influent characteristics (TSS, COD, TN...)	Inlet P (mg P/L)	Outlet pH	Observed		Main findings
											P sorption	P retention (g/kg)	
15	BOF mixed with stone 1:1	NA	1	1.4	U V	NA	26	Domestic effluent	7	12	100%	NA	Large pb of filter clogging observed against time
16	BF	0.45-2.6	3	1.5	U V	NA	7	Filter 1: primary Filter 2: secondary Filter 3: tertiary	0.9 0.03 0.04	NA	99.4 54 59	NA	The maximum sorption was not reached. P removal efficiencies of Filter 2 and * were low due to the weak influent P concentration
23	Oil-shale ash	<0.15	1	4.75	H S	2	23	2 nd effluent	7.7	NA	62 - 88%	NA	P removal decrease probably due to snow melt conditions and biofilm development.
24	3.9% BF in gravel	NA	1	1.6	H S	NA	12	WSP and CW effluent	1.5 - 6	10.4 - 9.1	< 0.4 mgP/L	NA	Hydraulic conductivity calculated in the laboratory can be reduced by as much as ten in the field due to clogging
31	Melter slag	10 - 20	10	1440	H S	3	132	WSP effluent	8.5	NA	77 - 35%	1.5	Initial (year period during which P removal achieved was more than 77%!!! Good performances were associated with the high pH out of the WST during algae growth
34	BF (30 cm layer in a VF CW)	<3	1	17.6	U V	NA	12	Settled domestic effluent	6.6	7.67	52%	0.07	Large differences between batch and bench-scale in terms of P sorption capacities.
42	Bottom ash (coal)	2.4 - 10	3	13.6	S B L	NA	5	Domestic effluent	2.6	Na	23 - 38%	NA	Phosphorus adsorption sites can be blocked by a biofilm coating on the soil particles

* UV: Unsaturated Vertical SH: Saturated Horizontal SBL: Saturated Batch Load SVD: Saturated Vertical Downward

P REMOVAL MECHANISMS (SEM and desorption analysis)

Among the P-removal mechanisms it was generally shown by SEM investigations that industrial by-products both favour Ca-P precipitation followed by crystallization and sorption on active sites onto the surface of the media (e.g. ferrous oxides). Several studies pointed out the presence of both adsorption and crystallisation but without confirming the presence of hydroxyapatites (#1), others studies identified adsorption on metal oxides as the main mechanism (#14): 46.5% of retained P was bound to Fe, #37, #38), and finally in the remaining studies, hydroxylapatite (HAP) or complex Ca-P aggregates formation was clearly observed and hypothesized as the main removal mechanism (#7, #19, #29 with observation of competitive CaCO₃ crystallisation, #30, #44, #46).

Several investigations were conducted to estimate the bounding capacity of IBPs by putting P-saturated media in batch with a wide range of solutions (from very acid to very alkaline) and following P release. It was mainly shown that P was desorbed acid conditions (pH lower than 4) and by very negative Eh potential associated to low pH (#37). Considering the behaviour of a field scale unit the main limit associated to P-desorption was observed to be the release during hydraulic overloading (#23 during snow melt).

FROM LAB SCALE TO FULL SCALE

In several studies efforts of full scale design based on lab scale results were done to estimate amount of IBPs required (#8, #34). However, considering the variability of batch scale results and the large effect of real wastewater quality on P-retention efficiency, the use of lab results to design full scale units can lead to major design errors (over and under estimation of the amount of IBPs required, #14).

Where to place the IBPs? Studies in which IBPs has been placed directly in the constructed wetland gave controversial results, both because this new plant encountered difficulties to develop under high pH conditions (#17) or because of low P-retention observed compare to lab experiments (#34). Moreover a problem of media replacement could represent a problem as well established plants could be destroyed by this operation. Placing the filter at the head of the CWs could lead to reduced P-retention as biofilm development was observed as a limiting P-sorption factor (#42). Thus placing the active filter downstream of the CWs represents the best

solution and was successfully tested at the field scale (#31, #23, #16).

Saturated or unsaturated flow? Vertical unsaturated flow seems not adapted to P-sorption onto slag as the contact time required between media and P was observed to be optimal at more or less 1 day (Table 4). Moreover several studies comparing saturated and unsaturated flow were likely to confirm the limits of unsaturated flow.

Since a large decrease was observed in the only full scale system operating for more than 5 years (#31), after reaching about 1.2 kg P/ t material a replacement or rejuvenation has to be investigated. Despite these observations there have been few works dealing on how to handle with industrial by-products after P-saturation, possibilities have been discussed including replacement/rejuvenation (#39) and valorisation as fertilizers (#12). This kind of investigations has to be developed in future researches.

RECOMMENDATIONS

Based on this review work the following recommendations were proposed for future experiments or design using IBPs as reactive media to remove P from wastewater in CWs environment:

Batch tests should be used only as a pre-test to estimate roughly the affinity between P and IBPs and eventually to compare samples behaviour using the same protocol. Maximum sorption capacities estimated through batch tests should not be used to design full scale units as they might results to misleading data.

Substrate should be tested directly in the field conditions (eg columns fed with real wastewater in the field T° condition etc.) to avoid large differences between laboratory and field scale design.

To reduce high pH, mixing IBPs with others substrates such as gravel, limestone or others material favouring seeded crystallization of HAP (cow bone, sedimentary apatite etc.) represent a promising solution.

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